Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

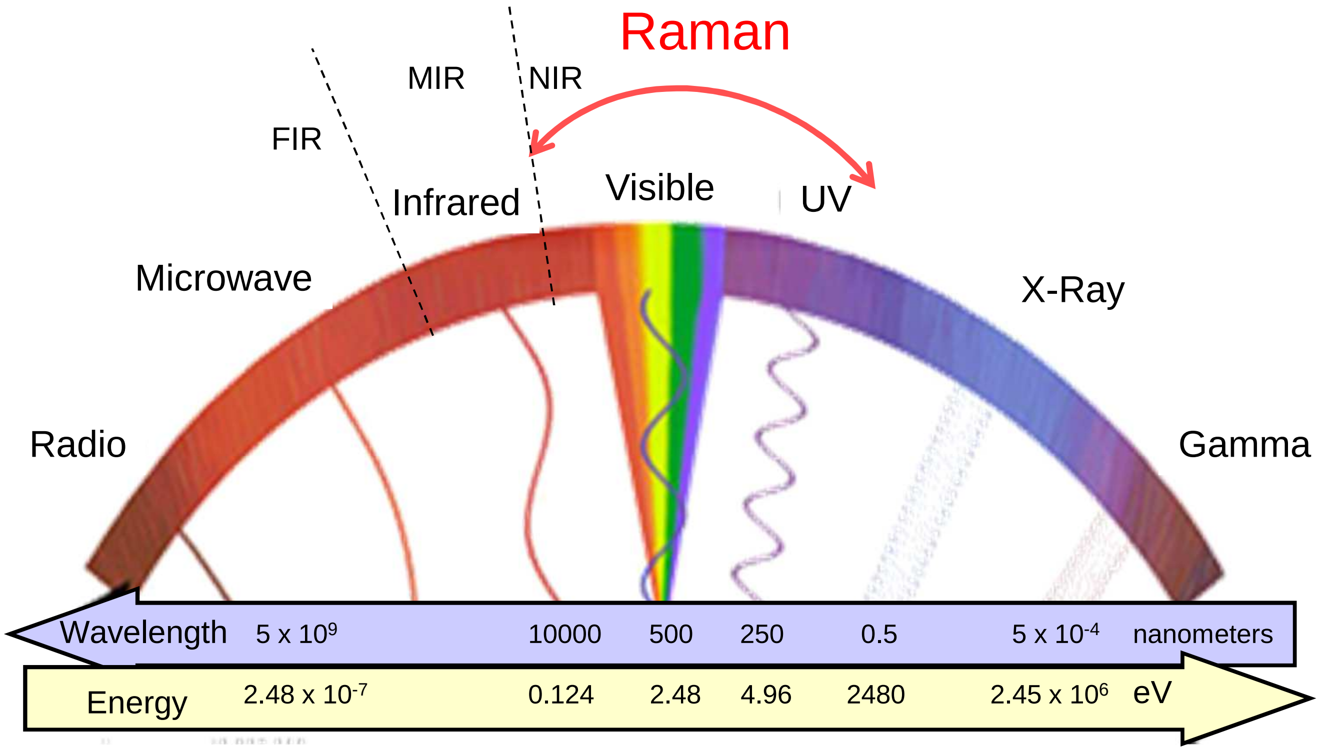
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

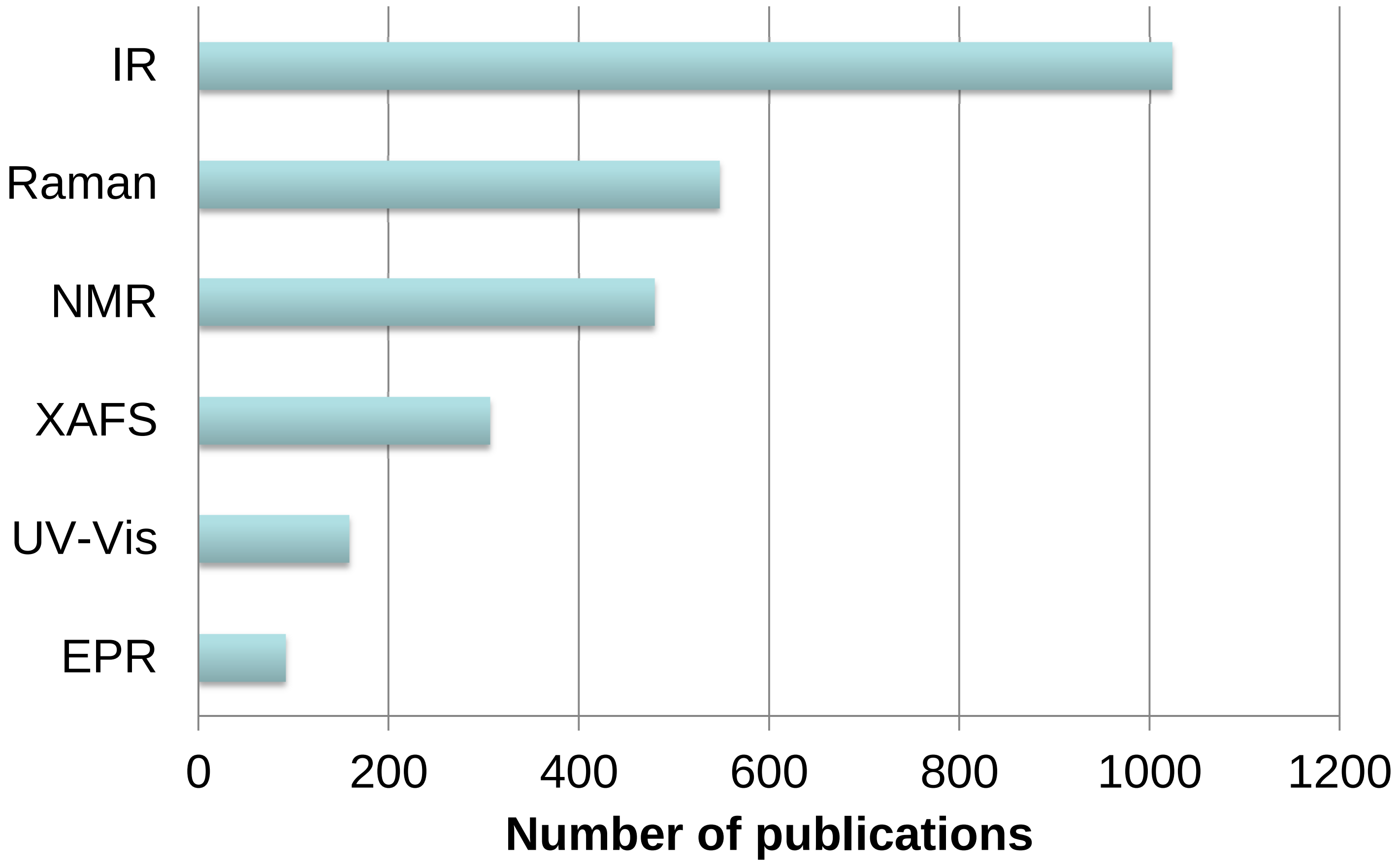
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

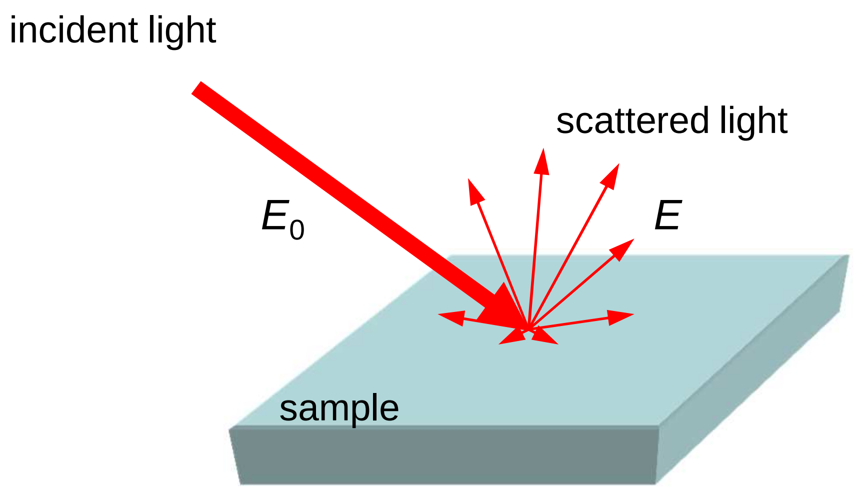


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
    - ❑ Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

- ❑ E_0 = incident beam irradiance
- ❑ α = polarizability of the particle (ease of distortion of the electron cloud)
- ❑ λ = wavelength of the incident radiation
- ❑ θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

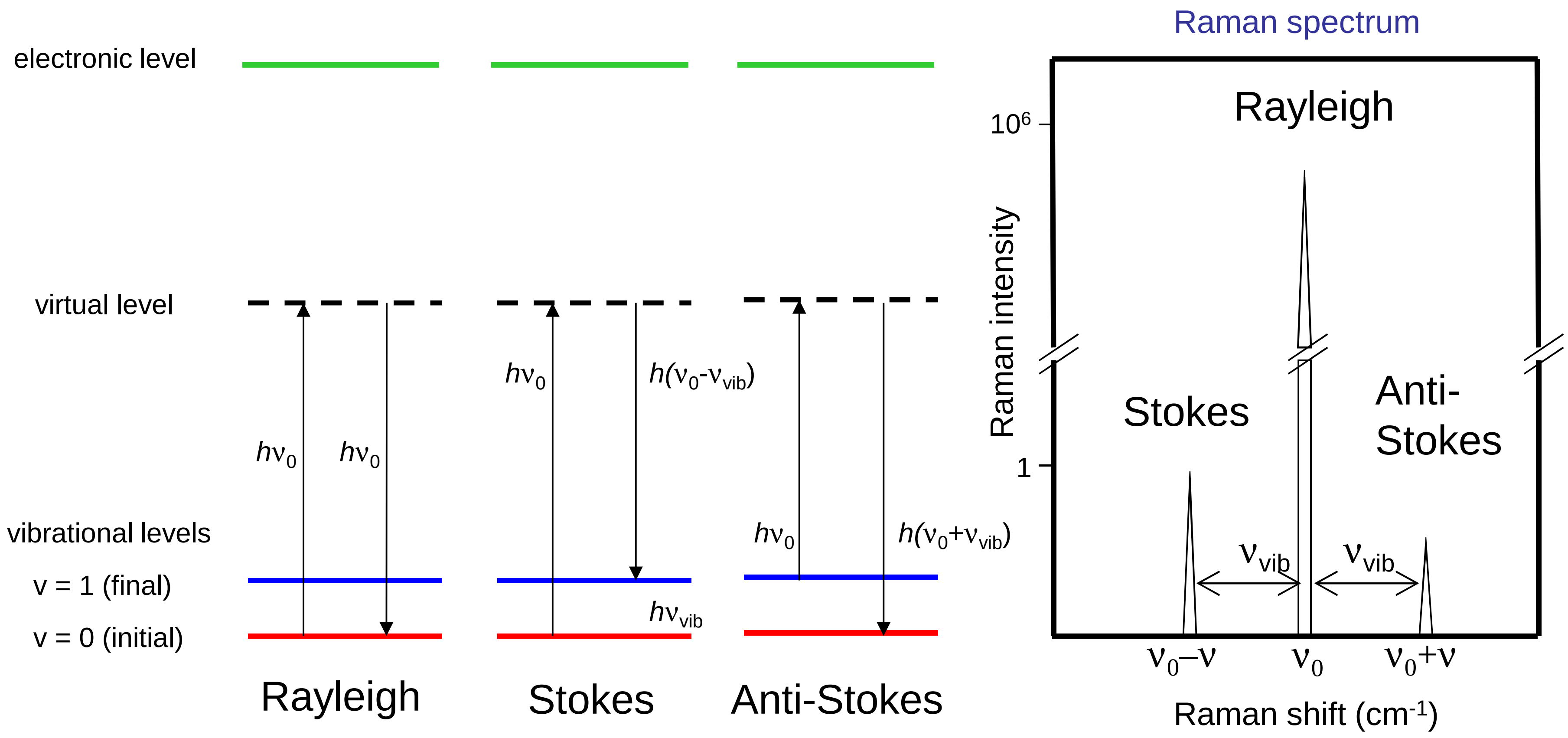
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x \cdot \cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\,(\text{Anti-Stokes})}{I\,(\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

- ❑ 4th power of ν (4th power law)
- ❑ 2nd power of $\Delta\alpha$
  - properties of molecules
  - strength of bonds

↓

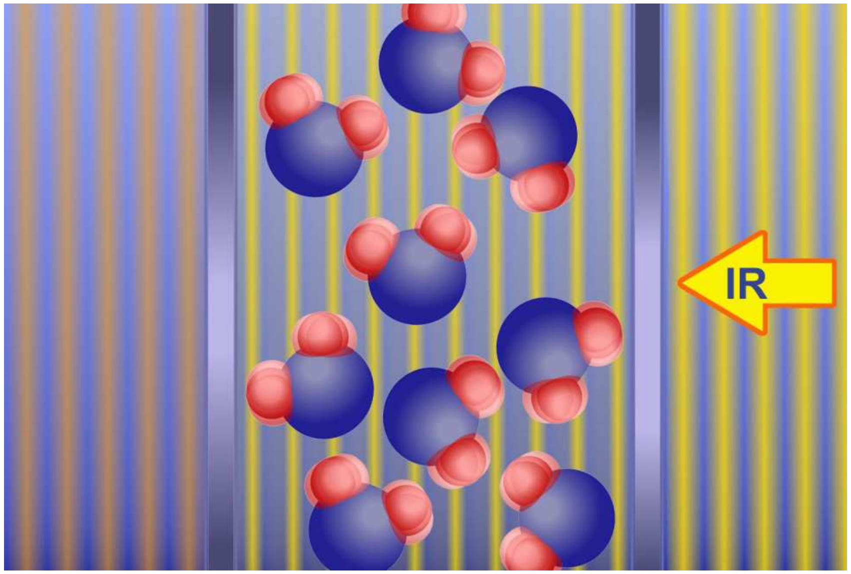
covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

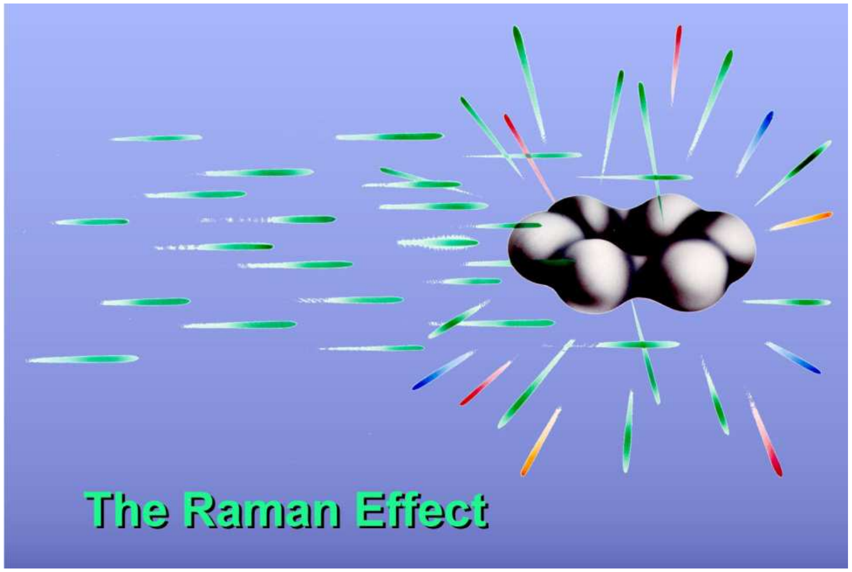
- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

Raman *vs.* Infrared

Infrared

Raman





Absorption of IR light

Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial\mu}{\partial Q}\right)^2 \neq 0$$

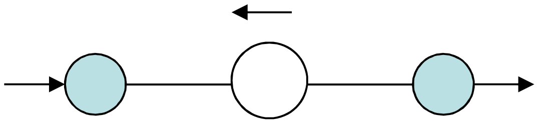
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial\alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - large electron clouds
  - not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

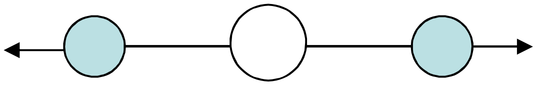
Raman *vs.* Infrared

CO_2



ν_{as}

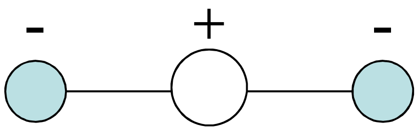
2349 cm^{-1}



ν_s

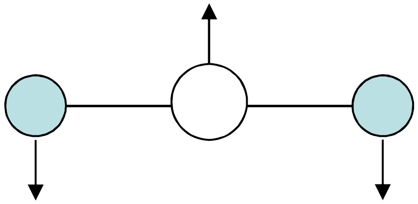
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



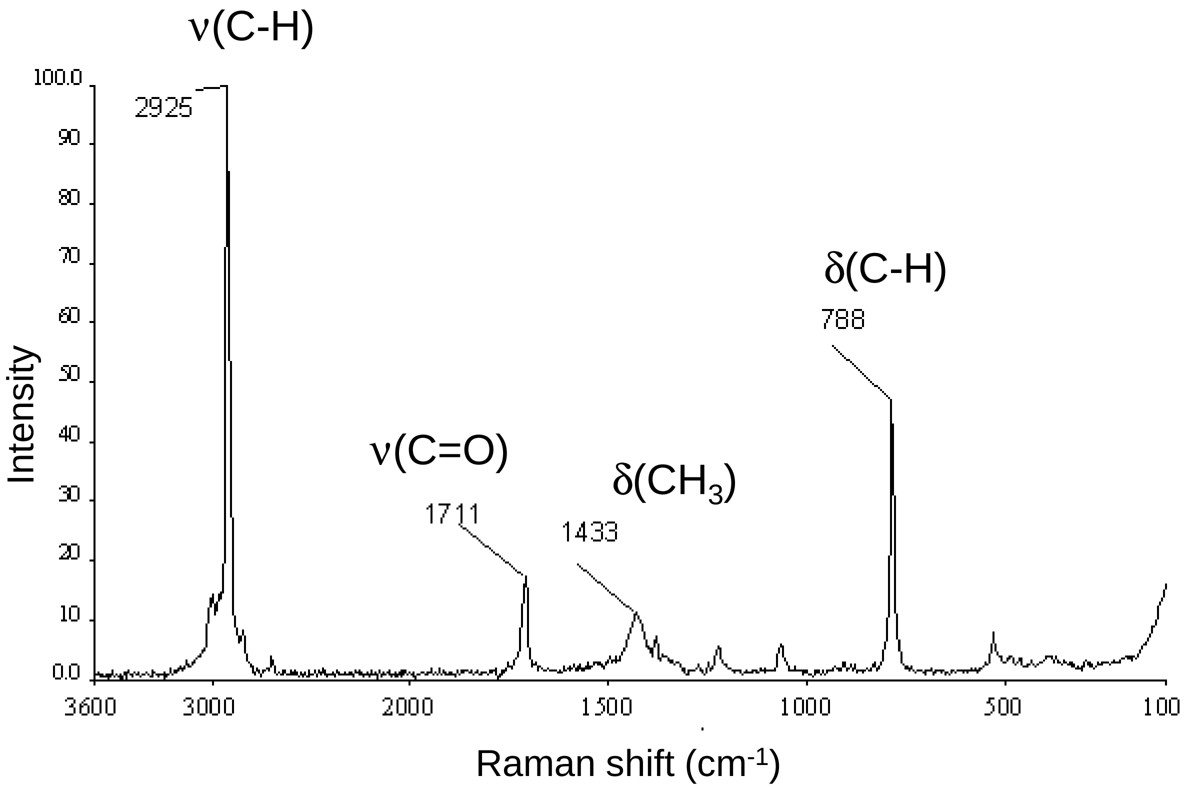
δ

667 cm^{-1}

degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared

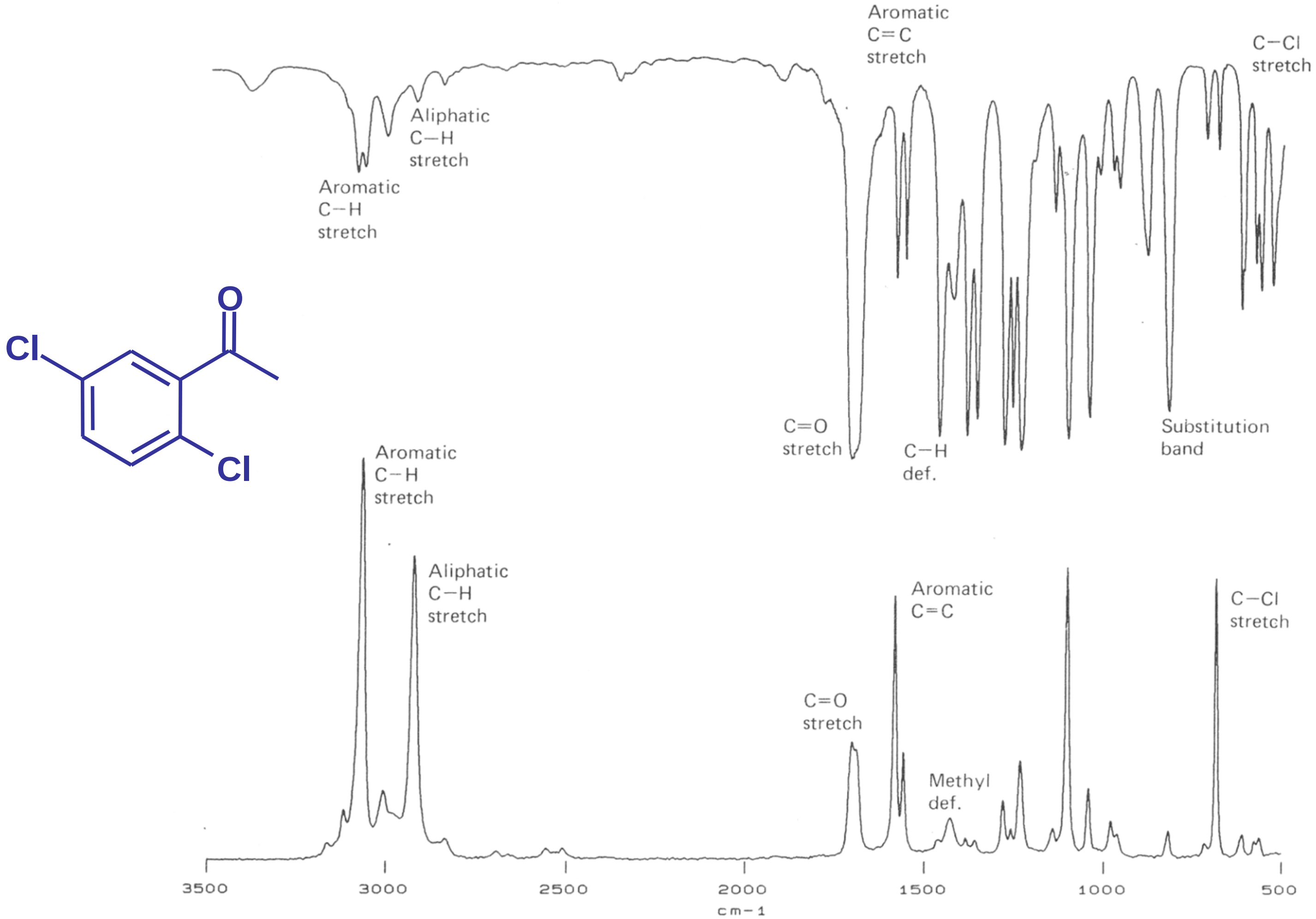


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

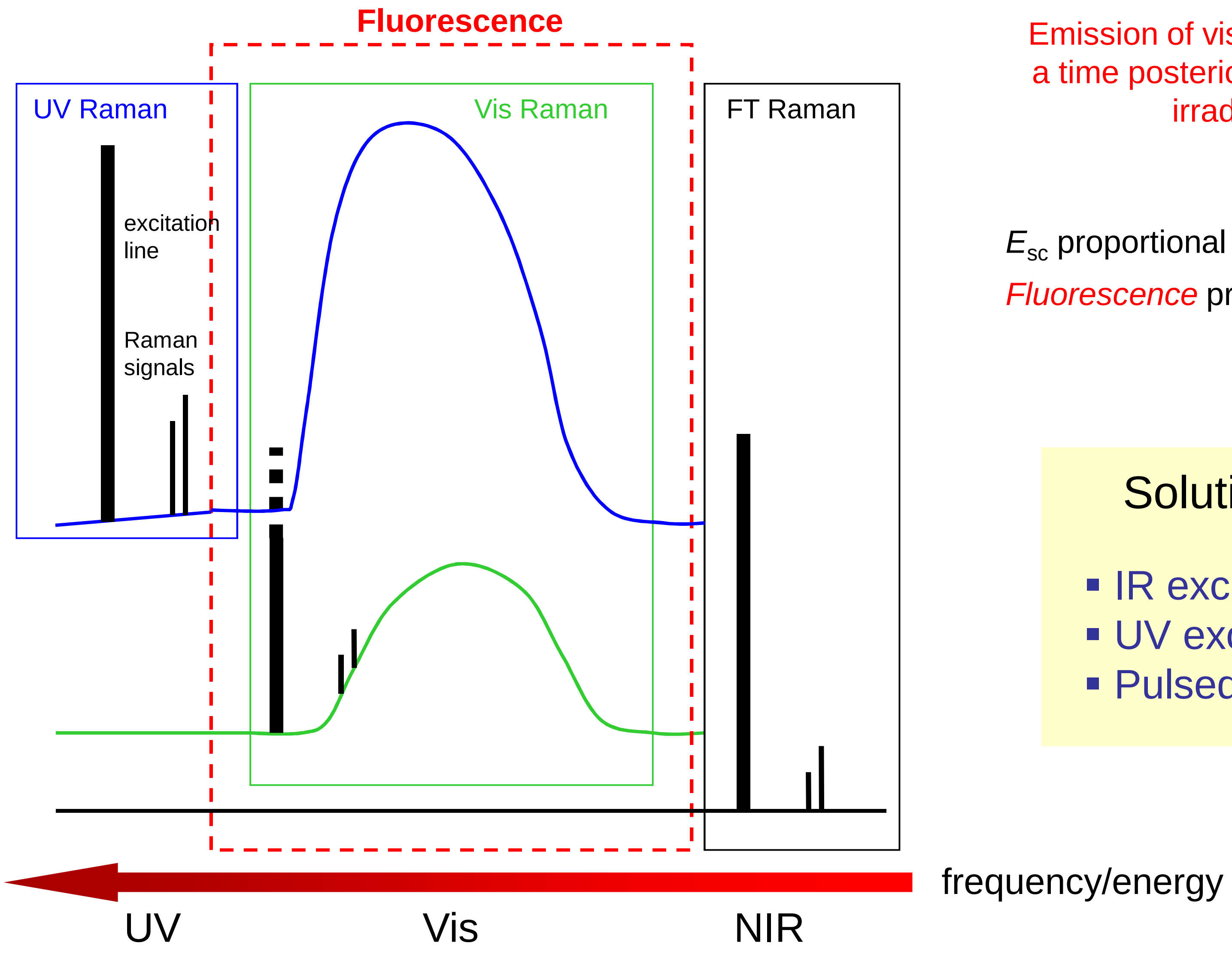
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 µm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

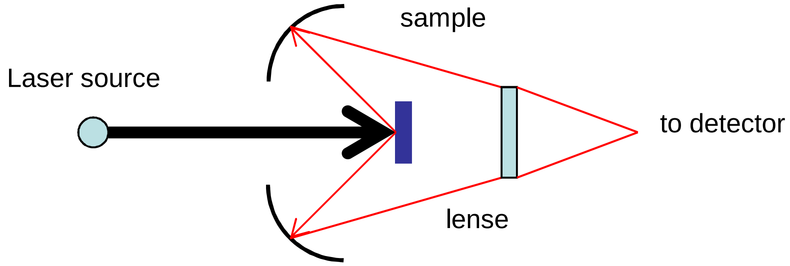
Fluorescence proportional to ν

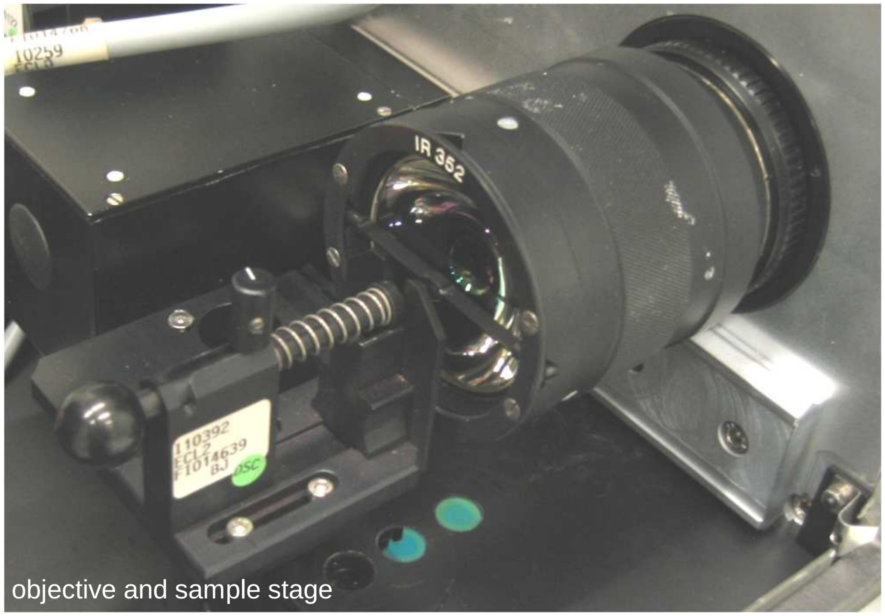
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

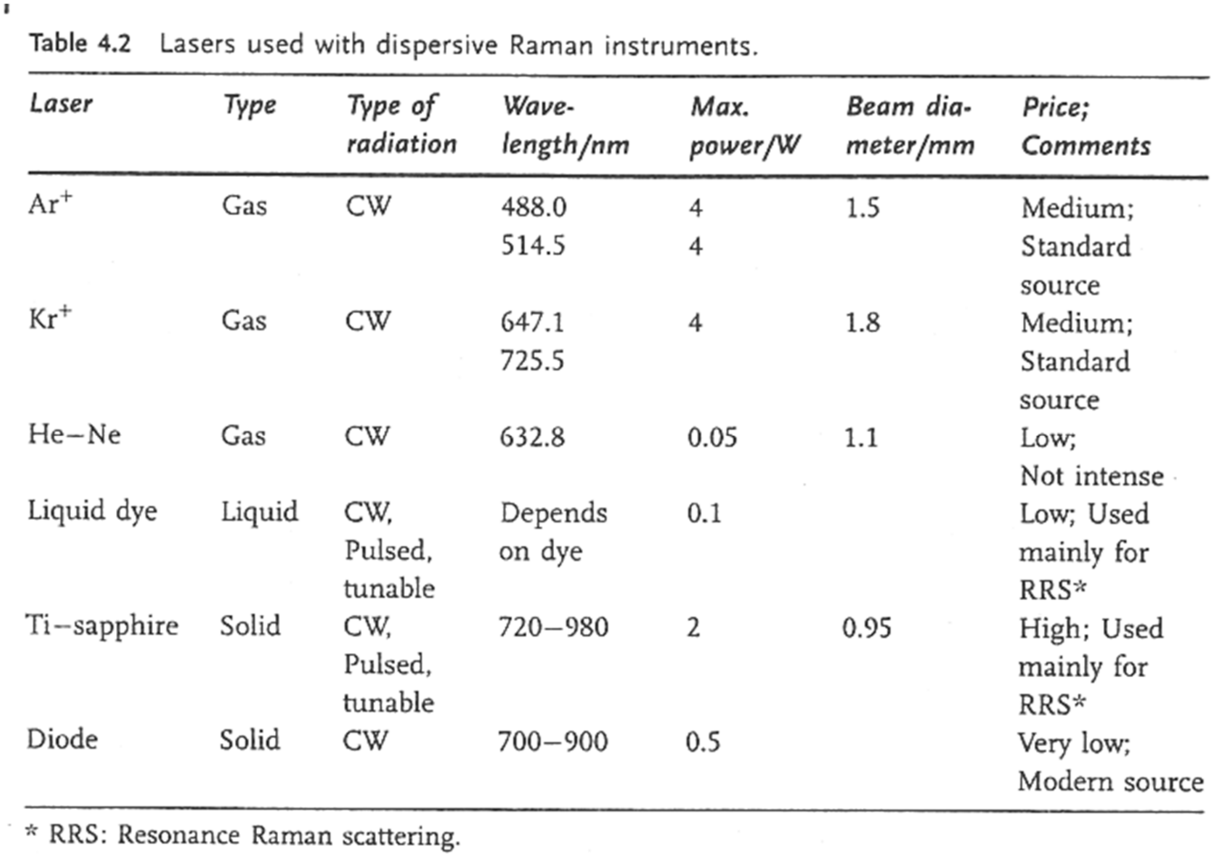


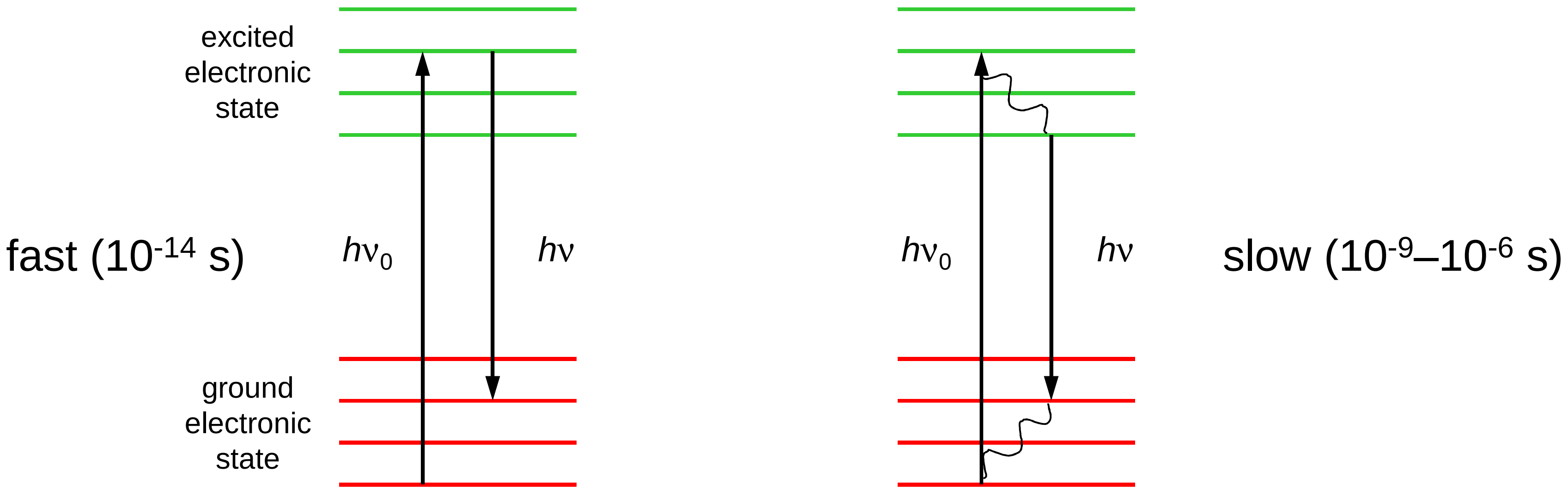
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



Resonance Raman scattering

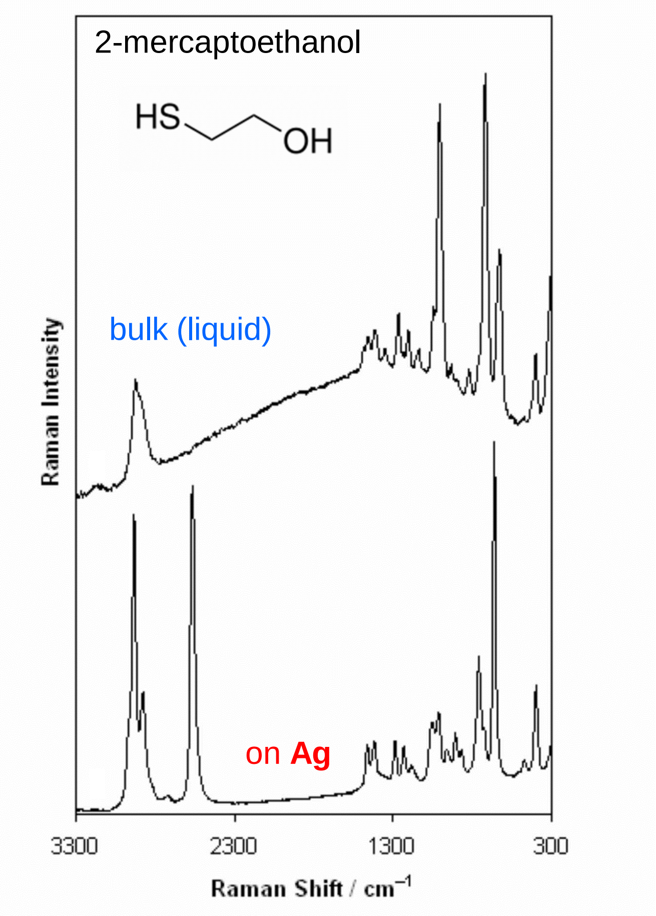
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

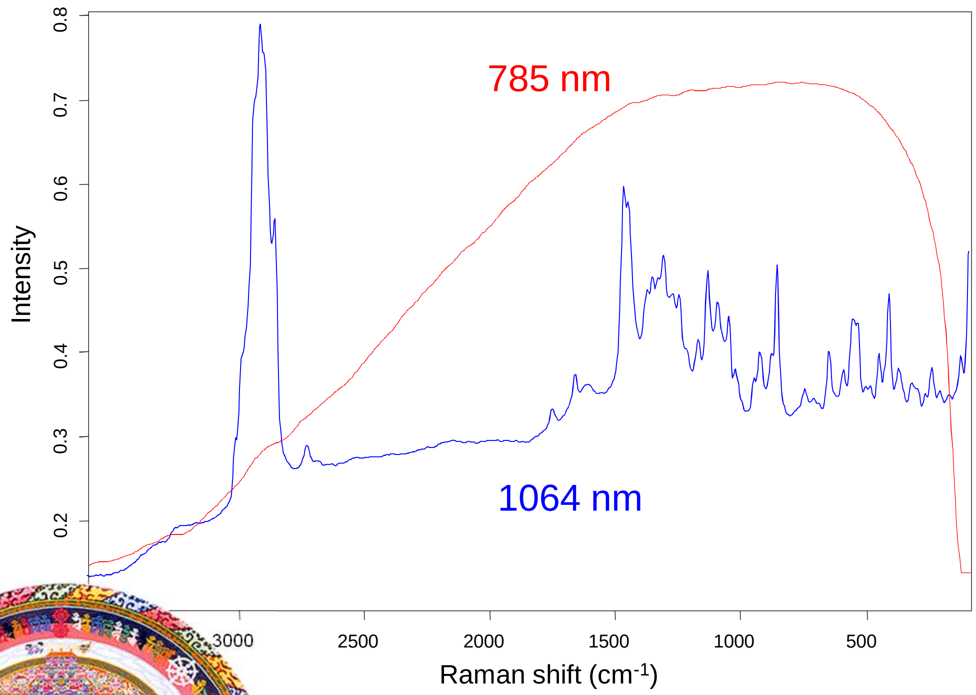
- Remarks:

❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc. (E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



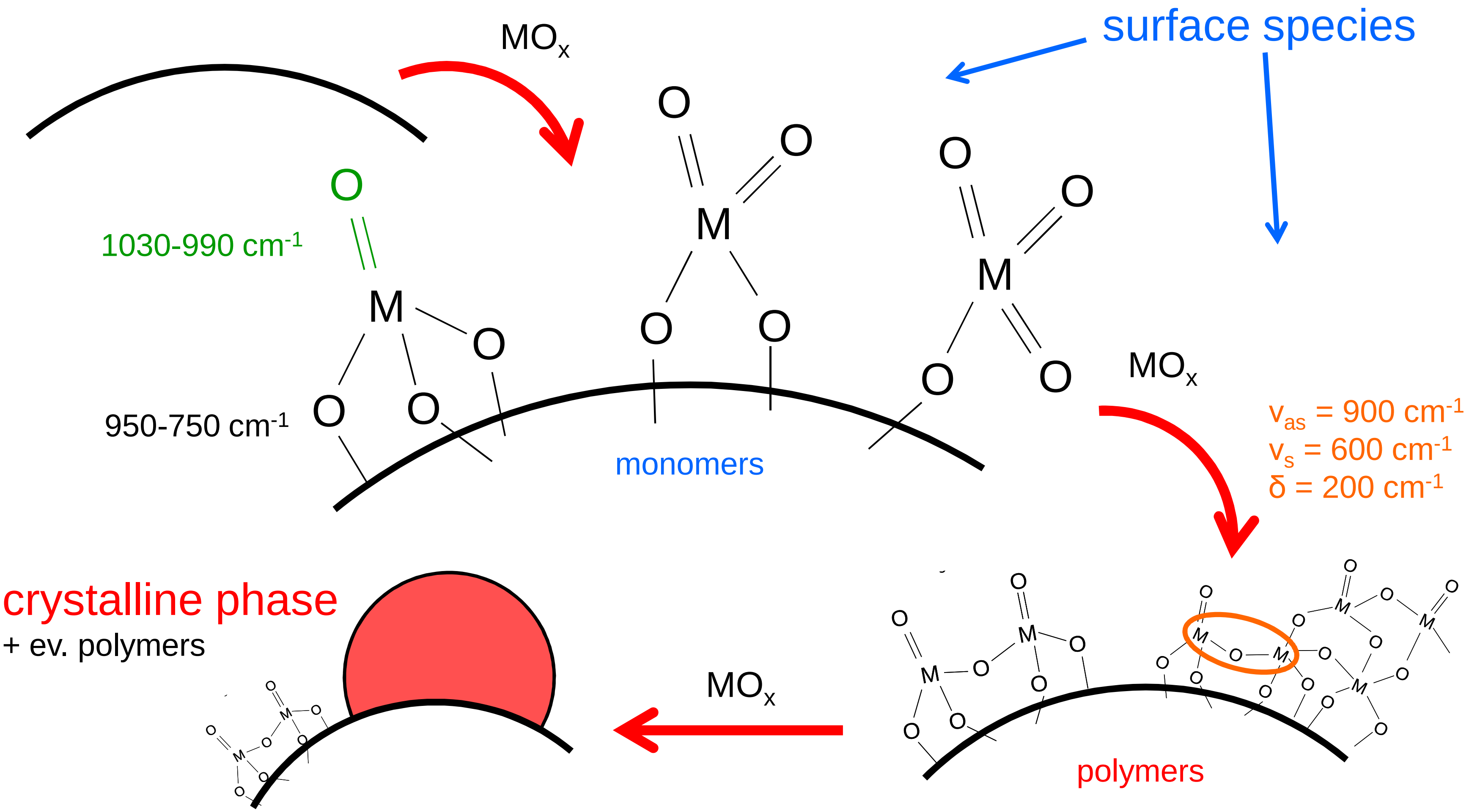
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



surface species

MO_x

1030-990 cm^{-1}

950-750 cm^{-1}

monomers

MO_x

ν_{as} = 900 cm^{-1}
ν_s = 600 cm^{-1}
δ = 200 cm^{-1}

polymers

MO_x

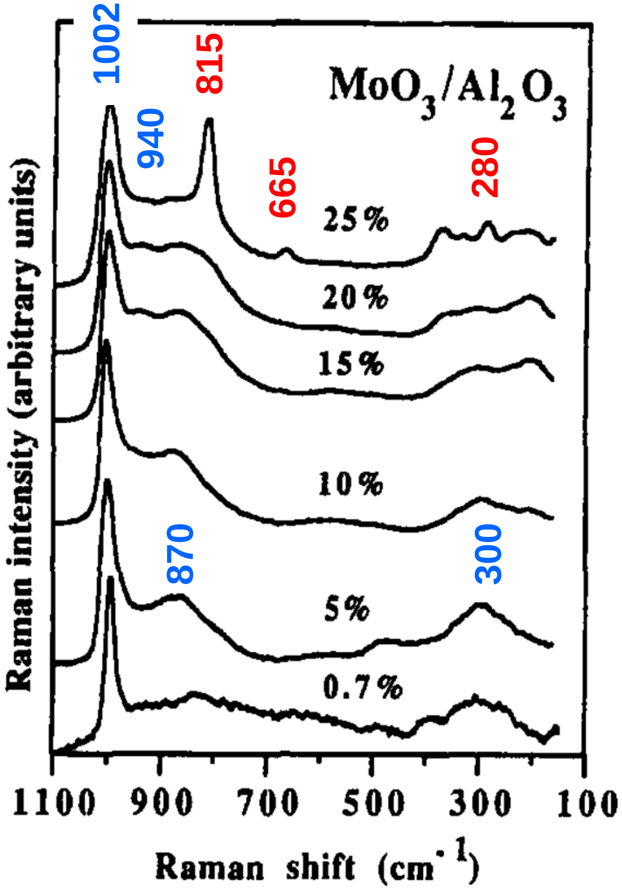
crystalline phase
+ ev. polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



surface MoO_3

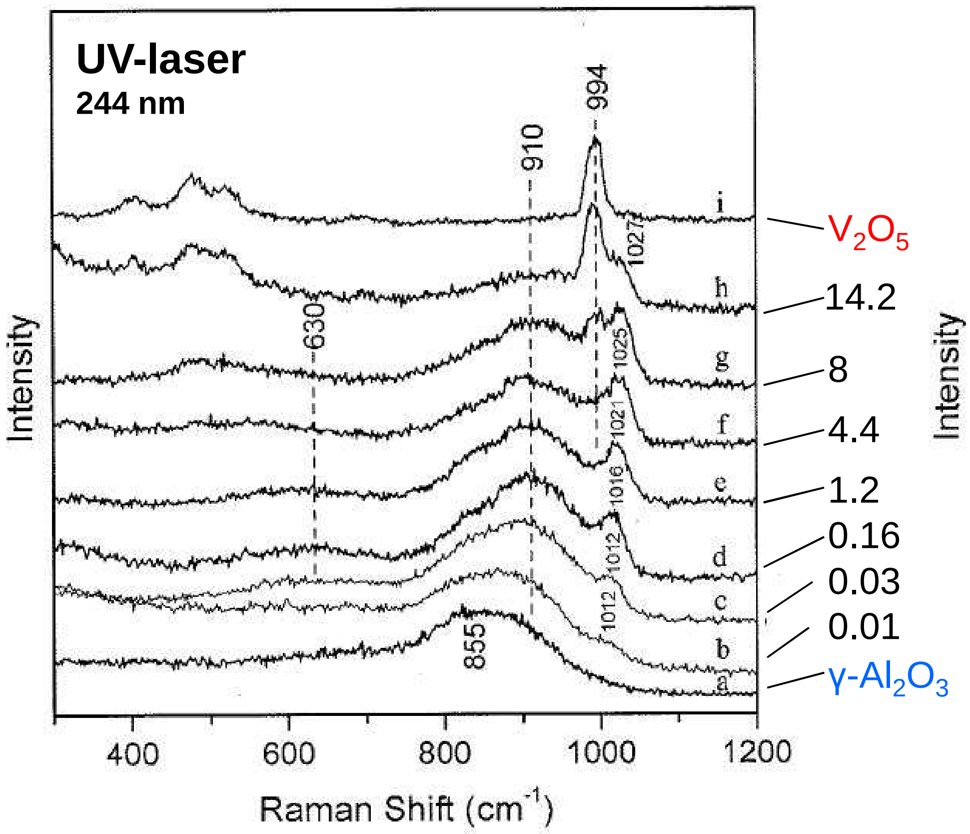
crystalline MoO_3

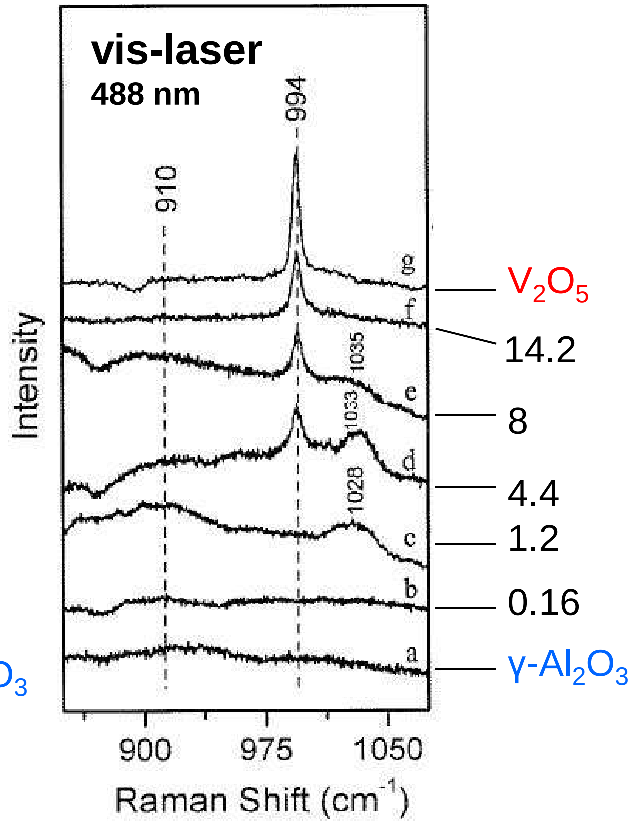
MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

- Monomeric & polymeric species

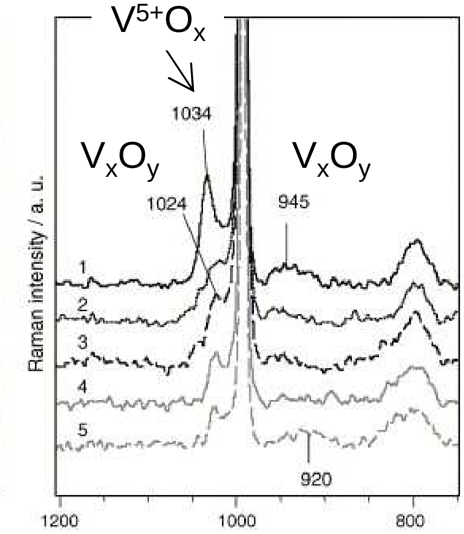




Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

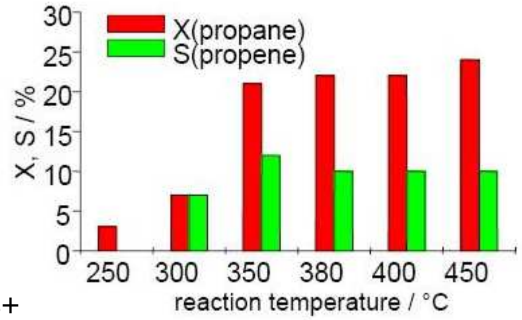
Applications

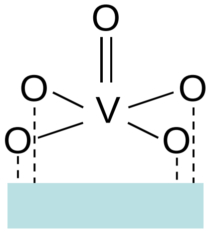
- Reactivity of V/TiO_2 after oxidative treatment

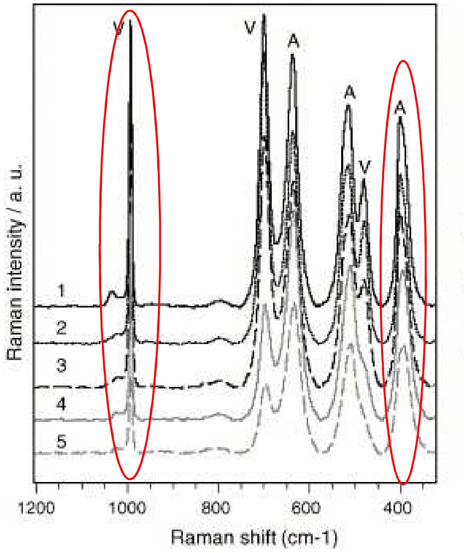


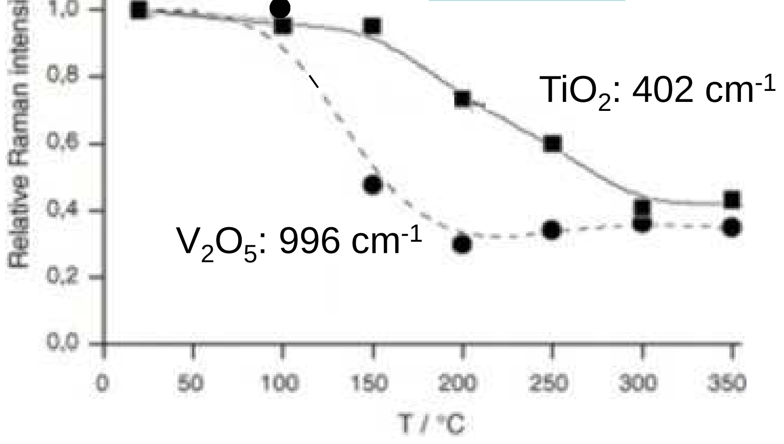
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

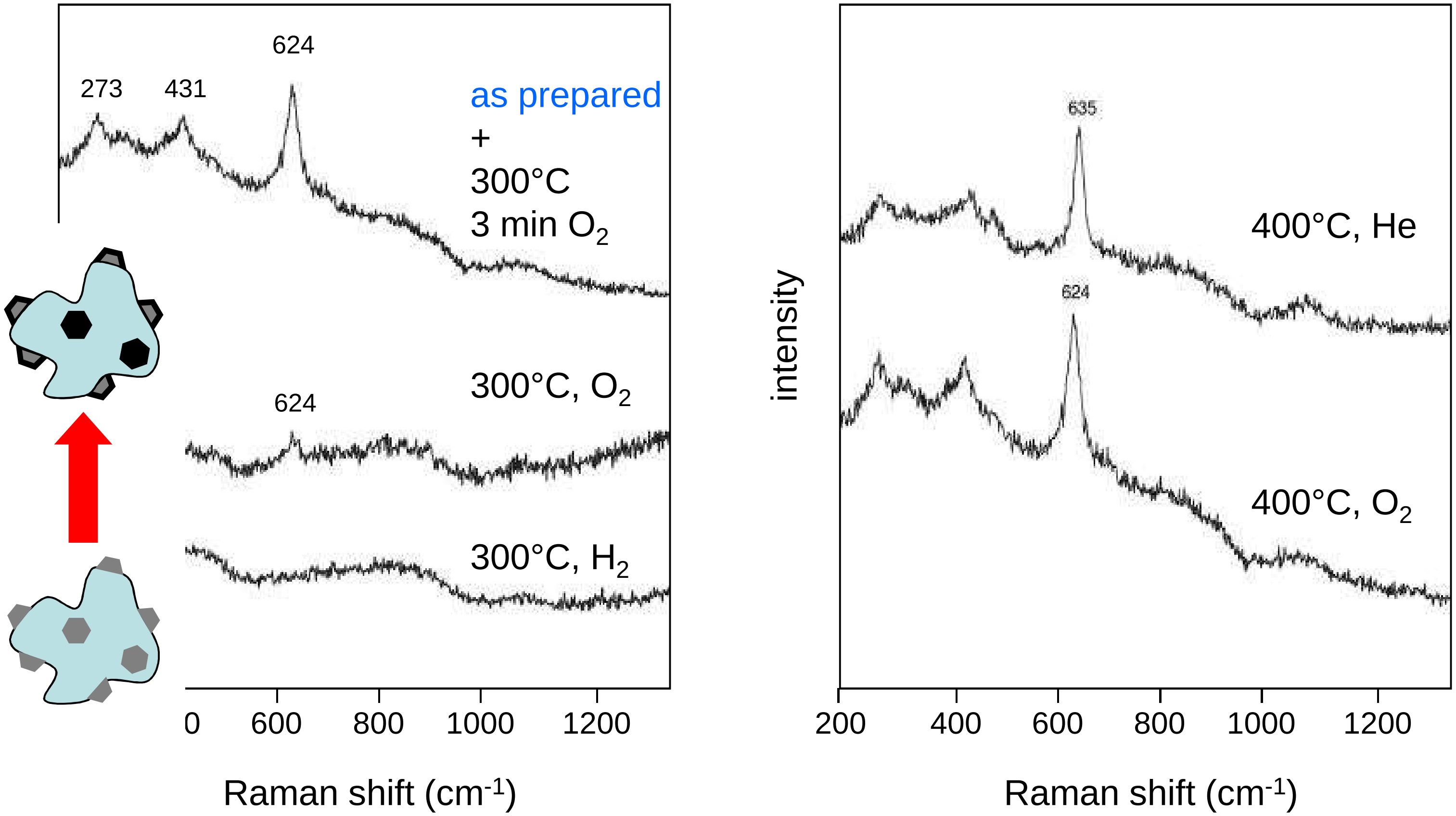
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



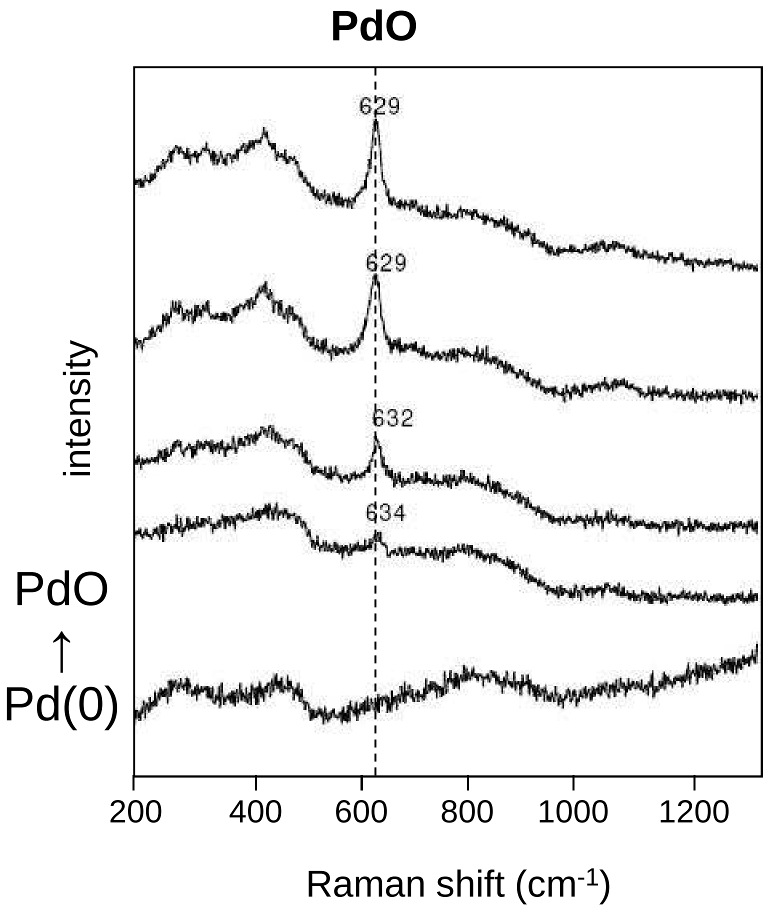
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

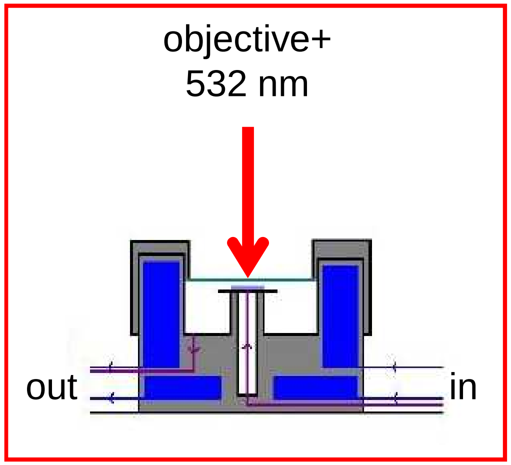
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



	CH_4 conv.
500°C	**24 %**
450°C	**15 %**
425°C	**4 %**
400°C	**2 %**
400°C, H_2 reduced Pd	

feed CH_4/O_2 (1:10)

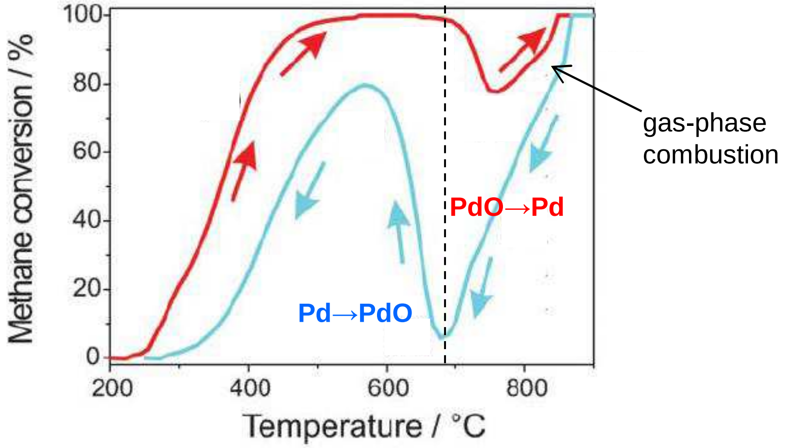
near PdO mode

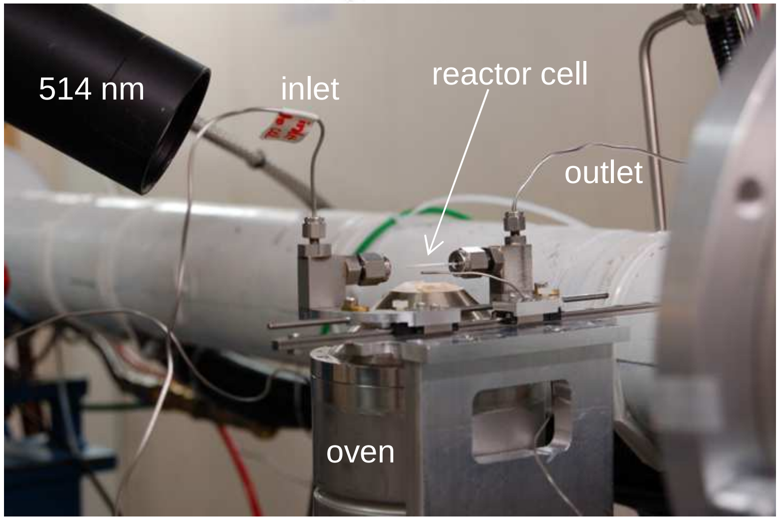


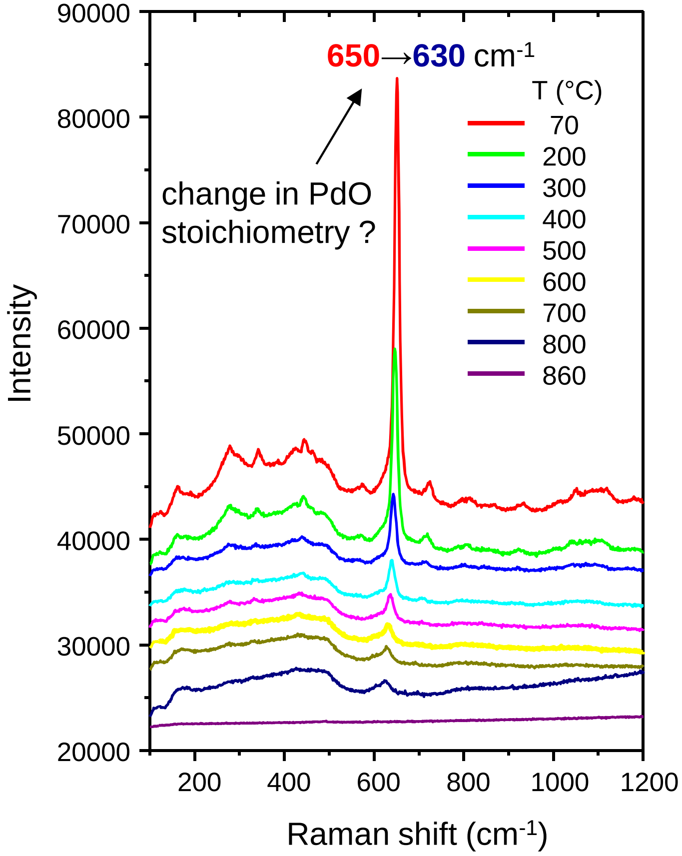
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







change in PdO stoichiometry ?

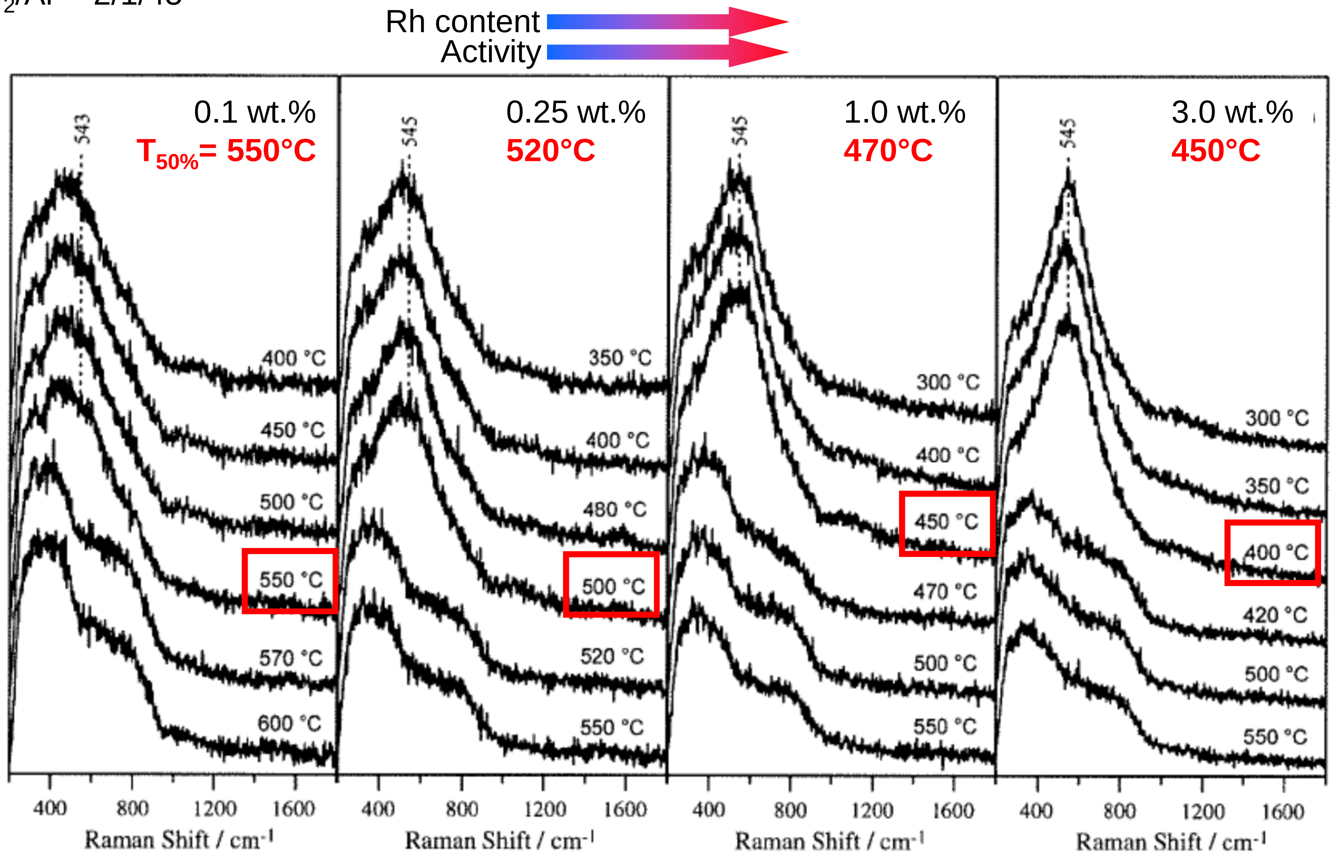
1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

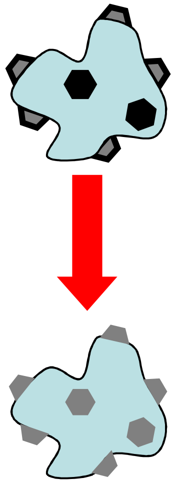
- Methane partial oxidation over Rh/Al_2O_3

3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$



RhO_x
↓
Rh(0)



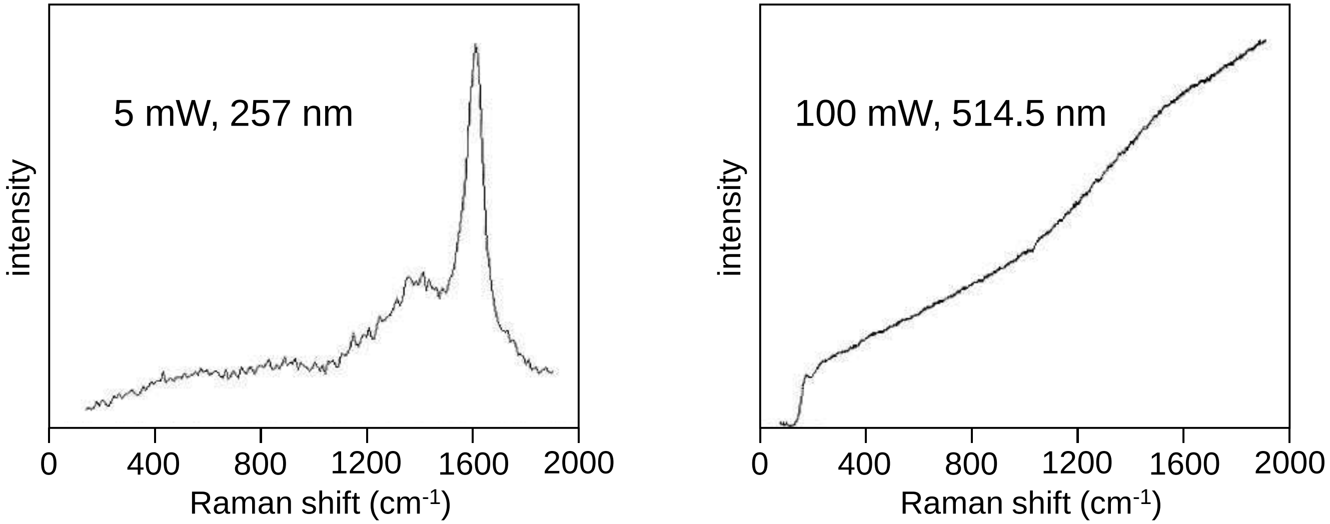
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - ☐ No fluorescence

  (only few molecules fluoresce below 260 nm)

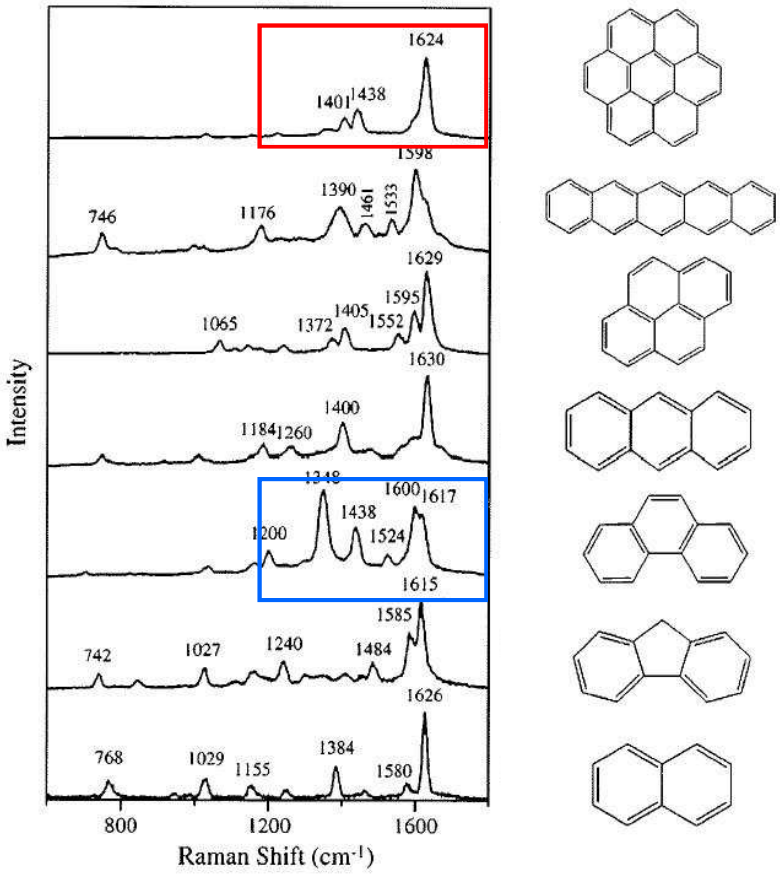
Rh/Al_2O_3, coked 500°C in naphtha

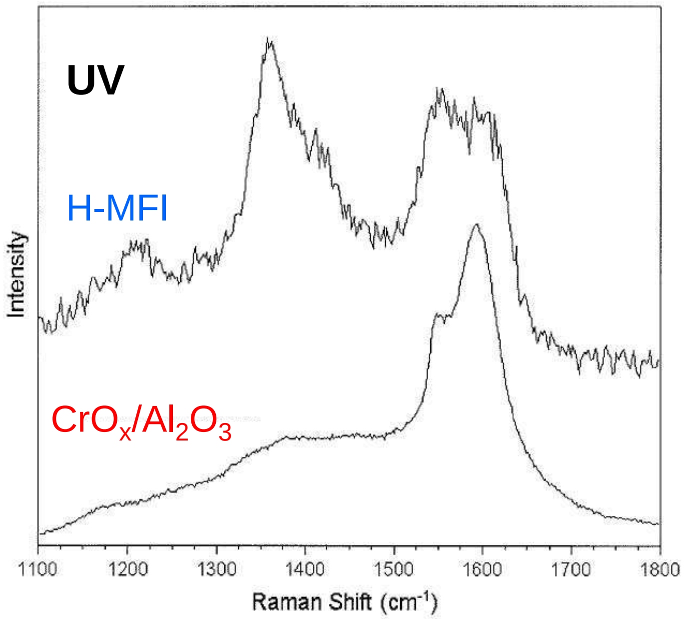


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





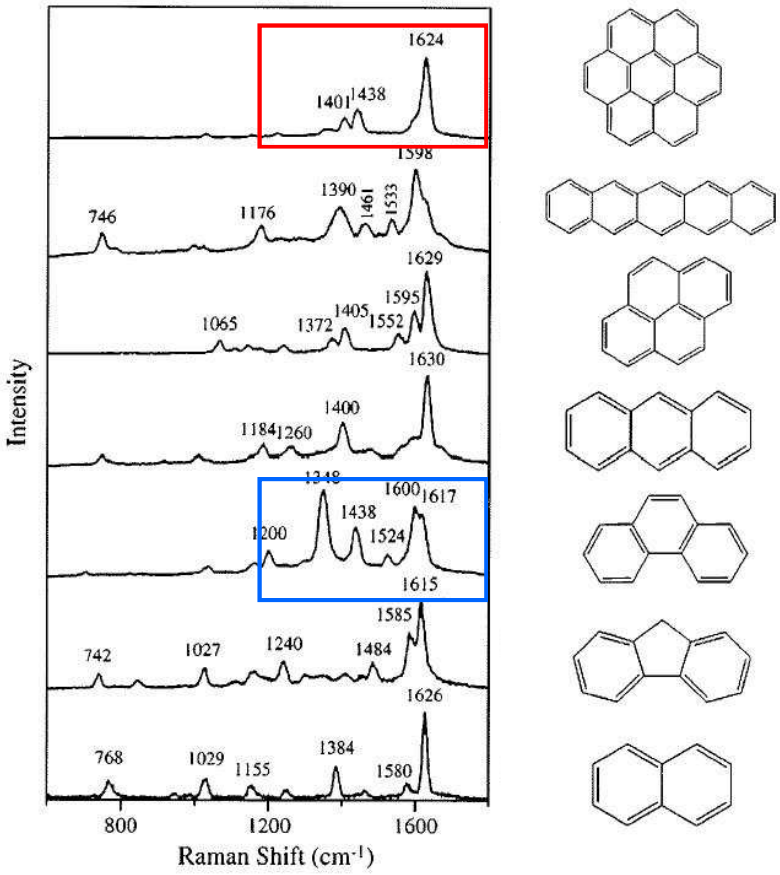
Coke classification
1D topology, chain-like
2D topology, sheet-like

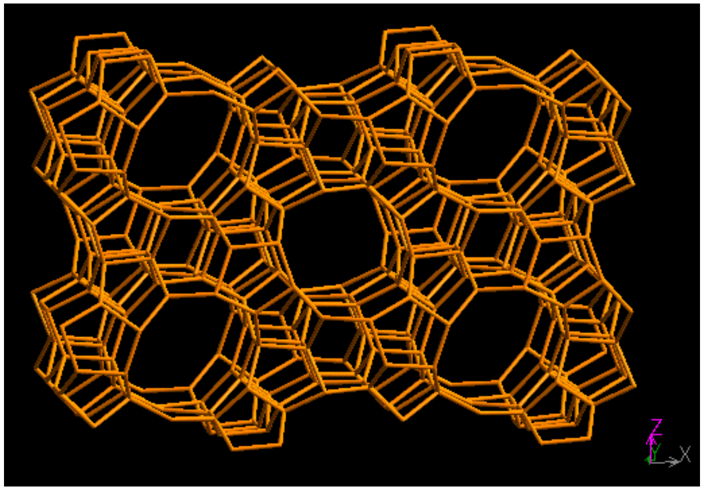
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





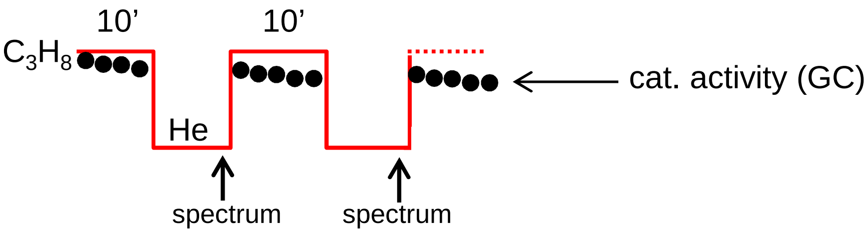
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

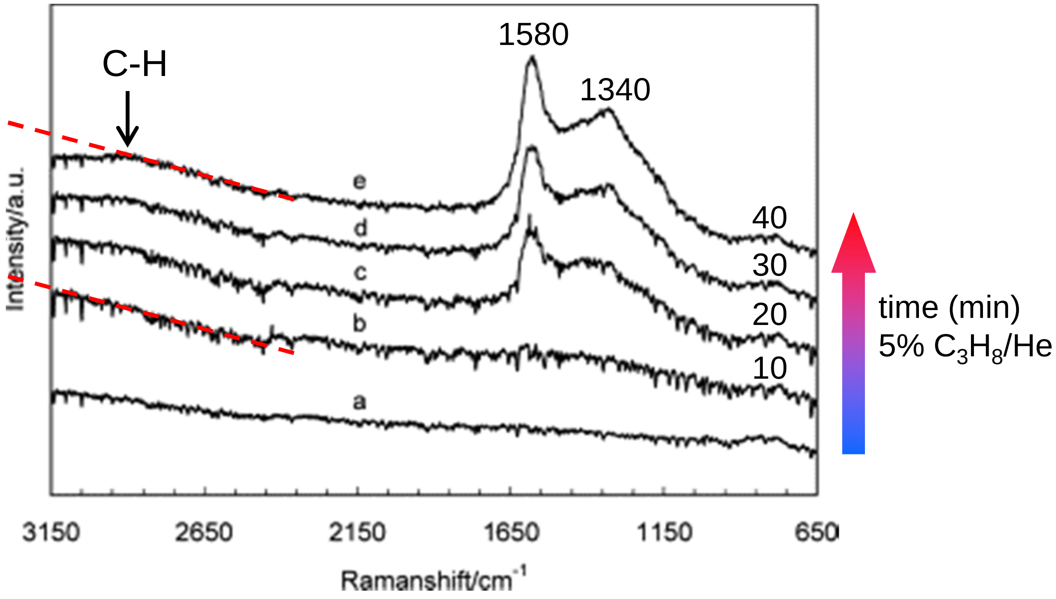
Stair, *Adv. Catal.* **51** (2007) 75

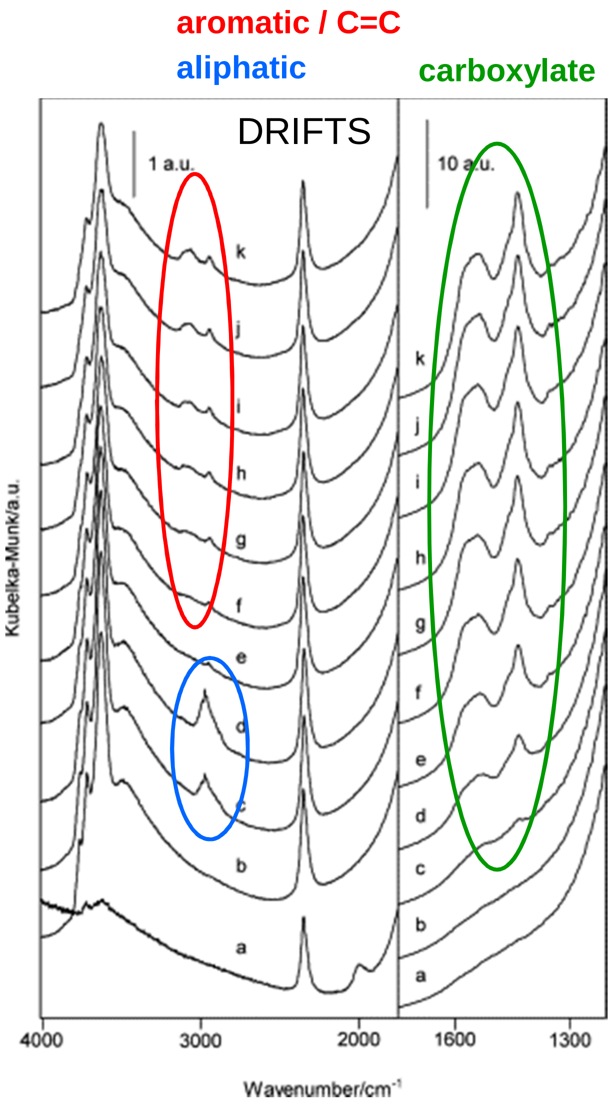
Applications

- Propane dehydrogenation



Cr$_2$O$_3$/Al$_2$O$_3$, 580°C, 514 nm

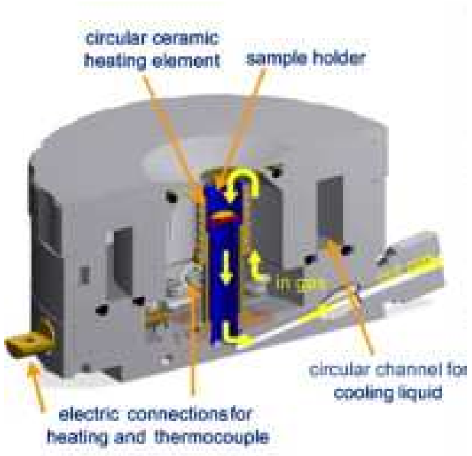


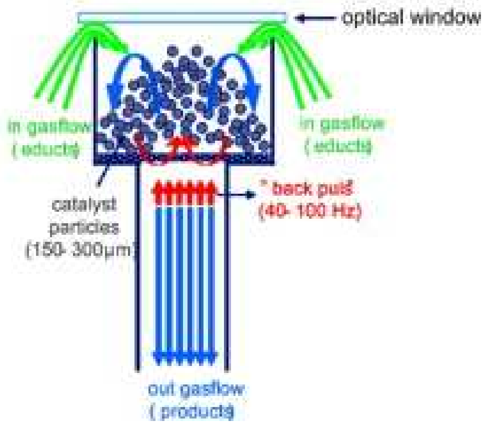


Airaksinen et al., *J. Catal.* **230** (2005) 507

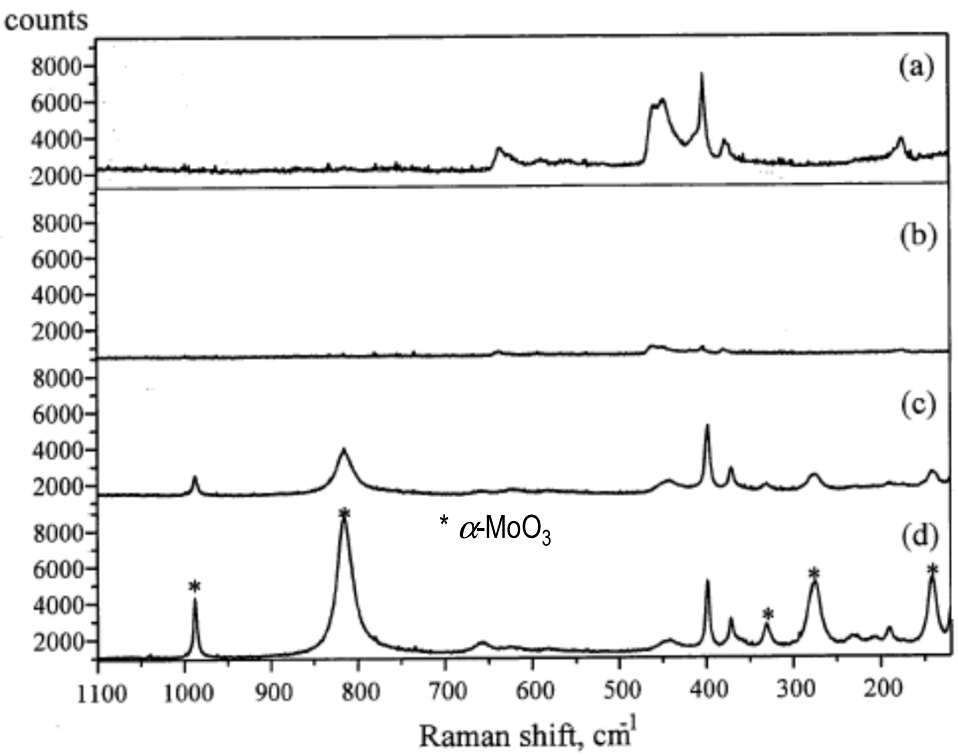
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min full power, FB

MoS_2, 6 min 1/8 power

MoS_2, 1 min full power

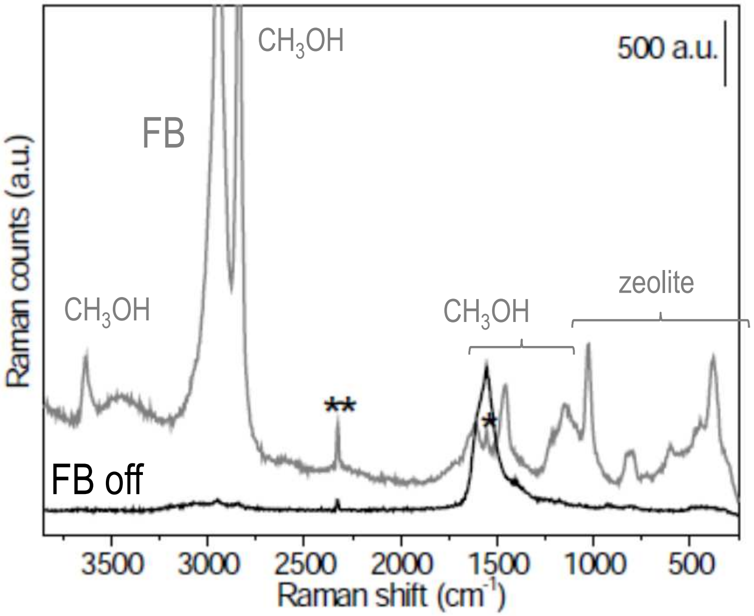
MoS_2, 6 min full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

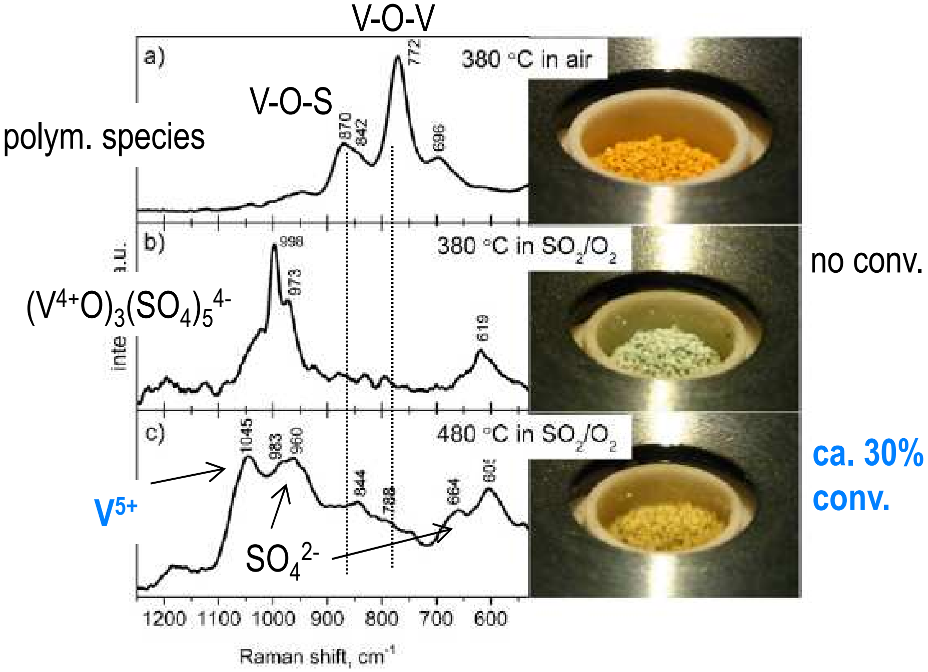
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

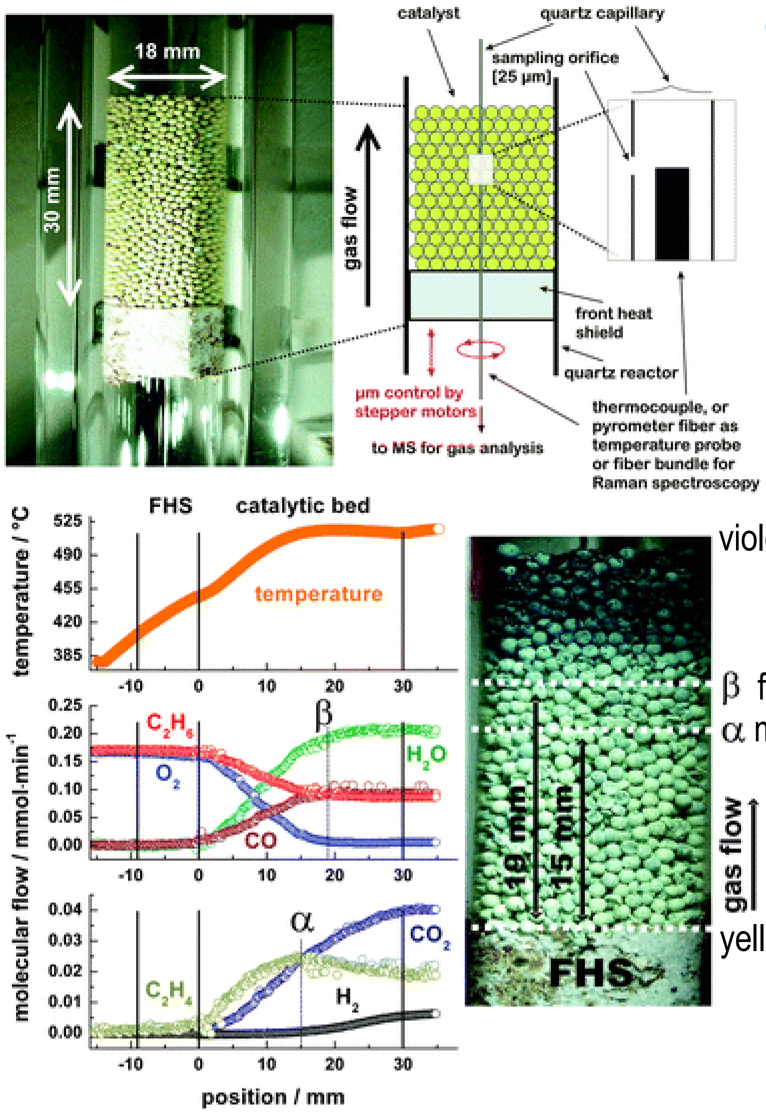


active species: mono- & dimeric V^{5+} oxosulfate species

Beato et al., *Catal. Today* 205 (2013) 128

Applications

- Fixed bed reactor



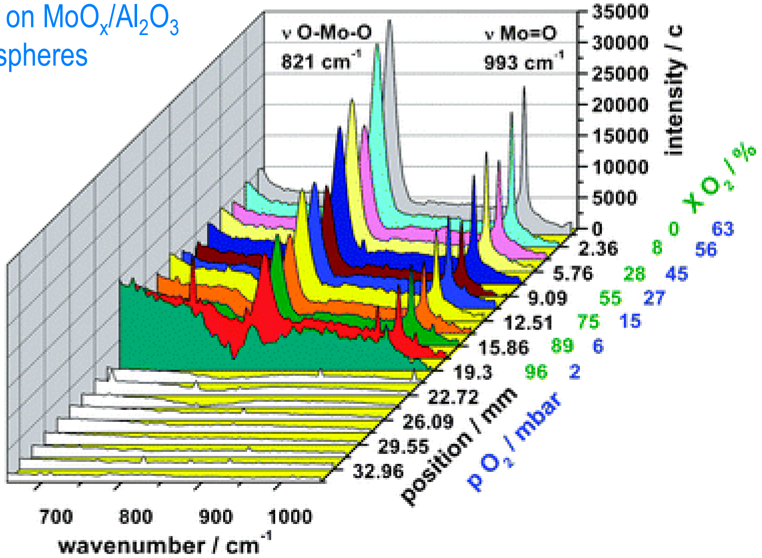
violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

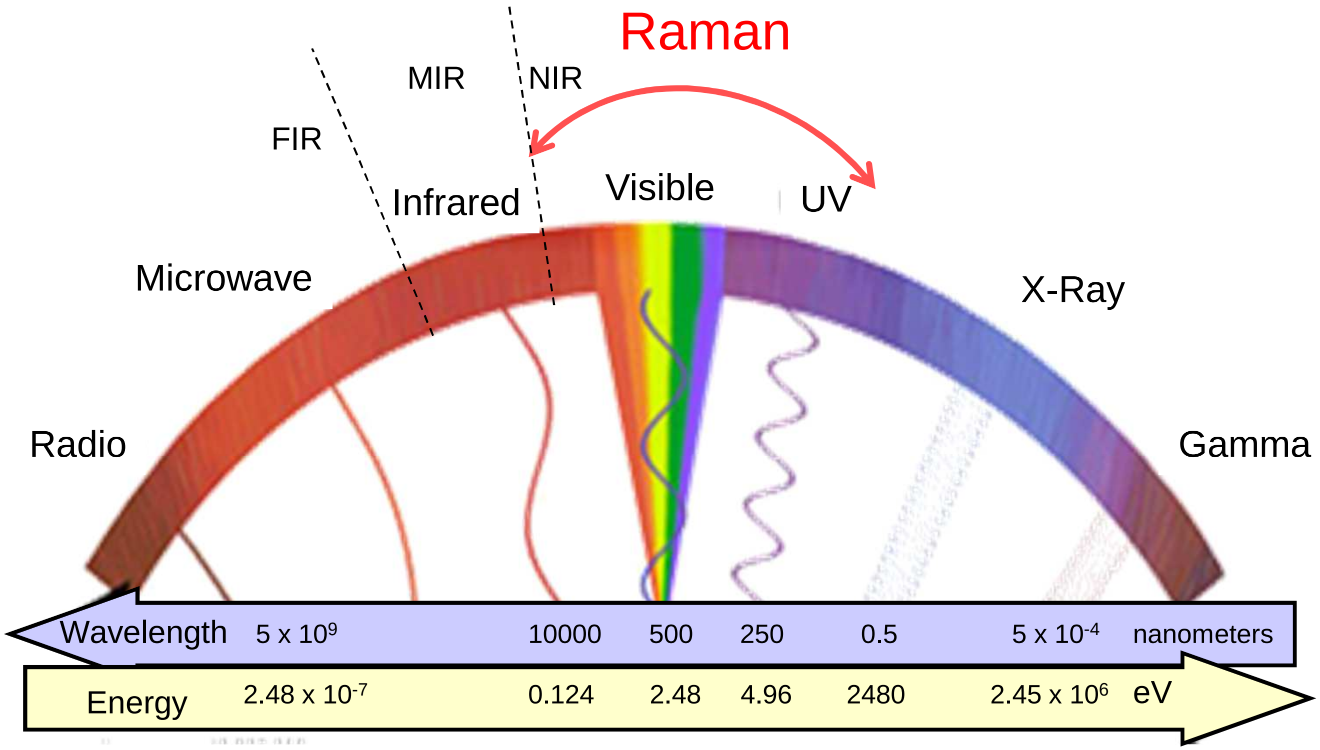
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

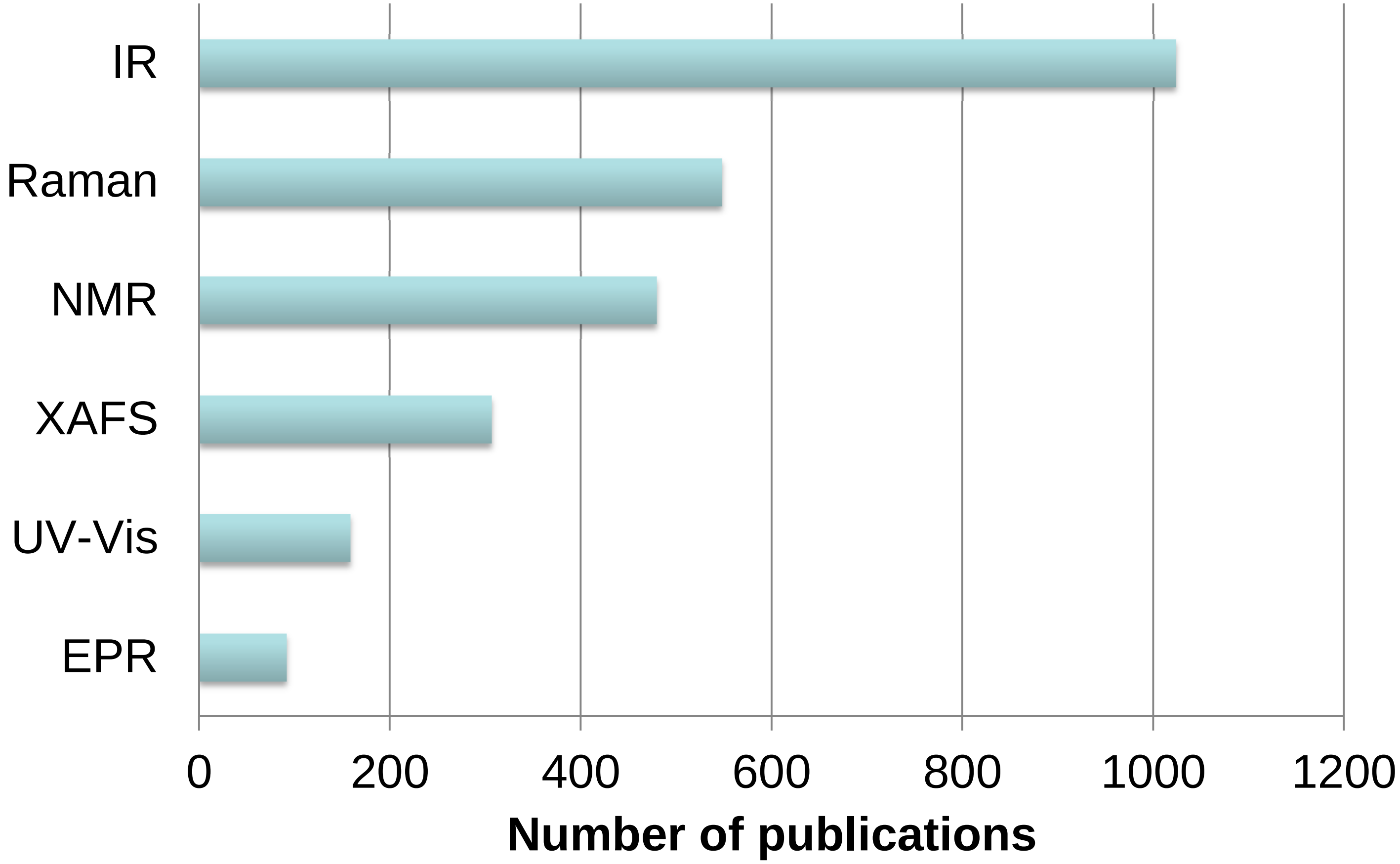
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

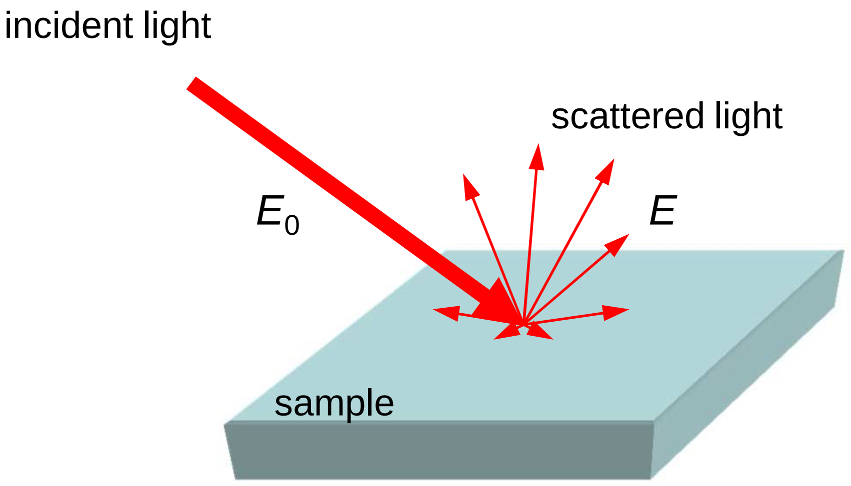


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{\mathrm{vib}} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

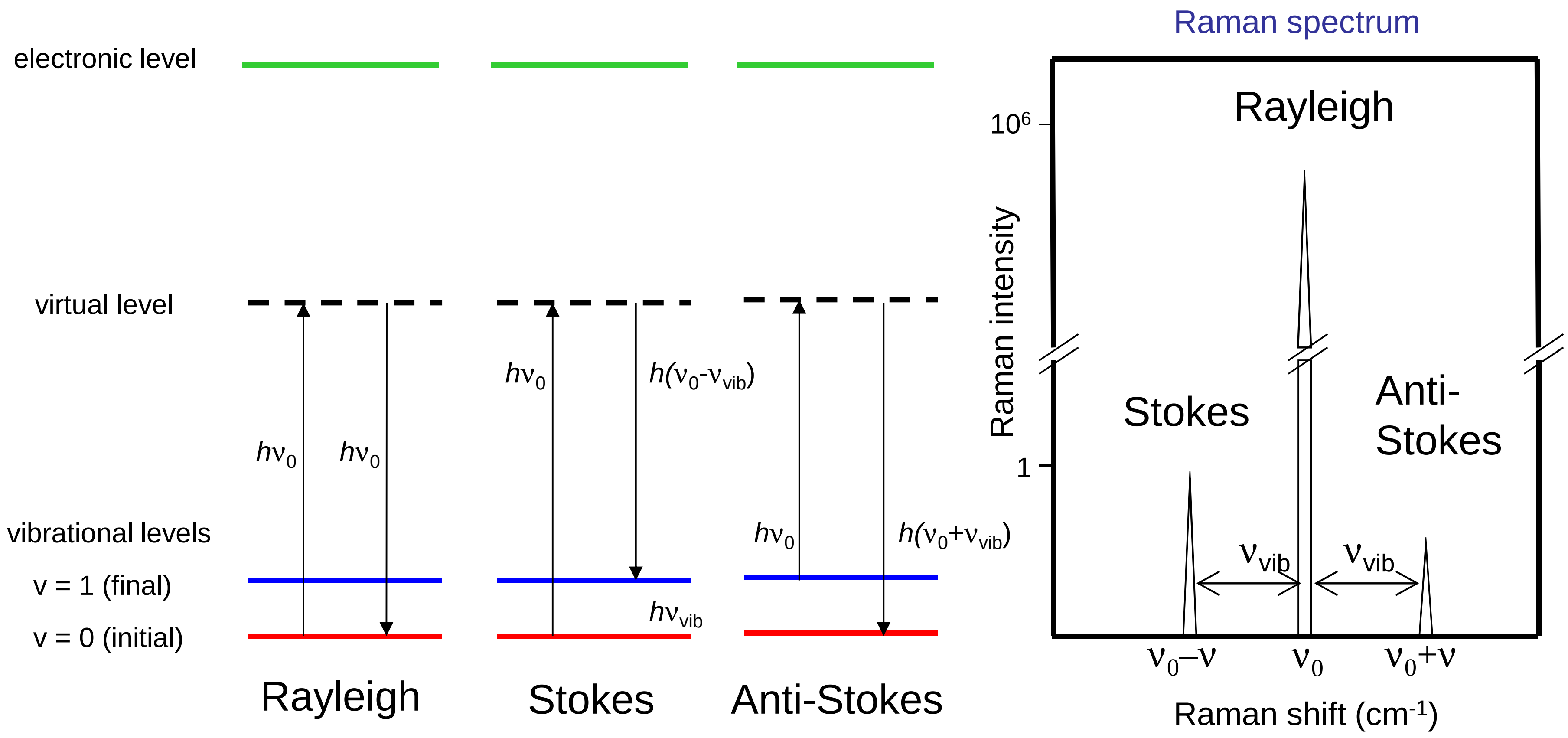
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\ (\text{Anti-Stokes})}{I\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2\,(1+\cos^2\theta)}{\lambda^4}\,E_0$$

  - ❑ 4th power of ν (4th power law)
  - ❑ 2nd power of $\Delta\alpha$
    - properties of molecules
    - strength of bonds

↓

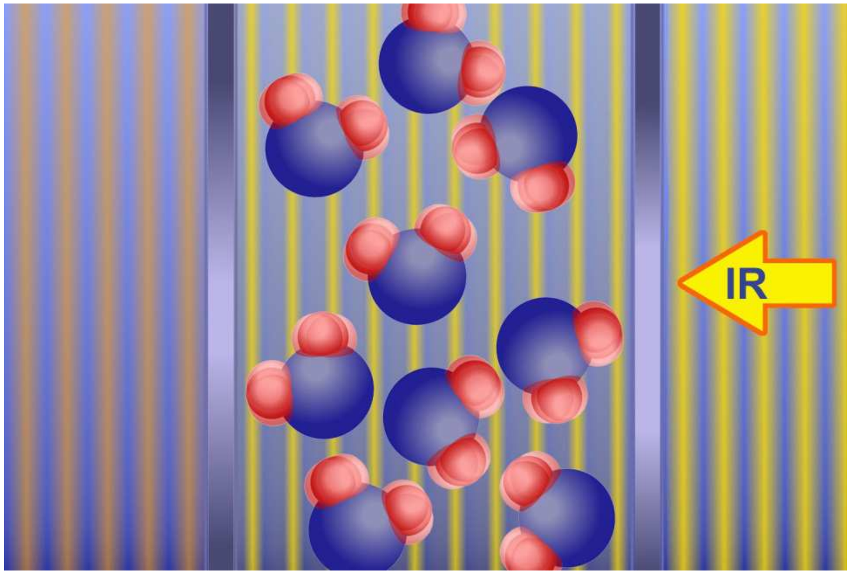
covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

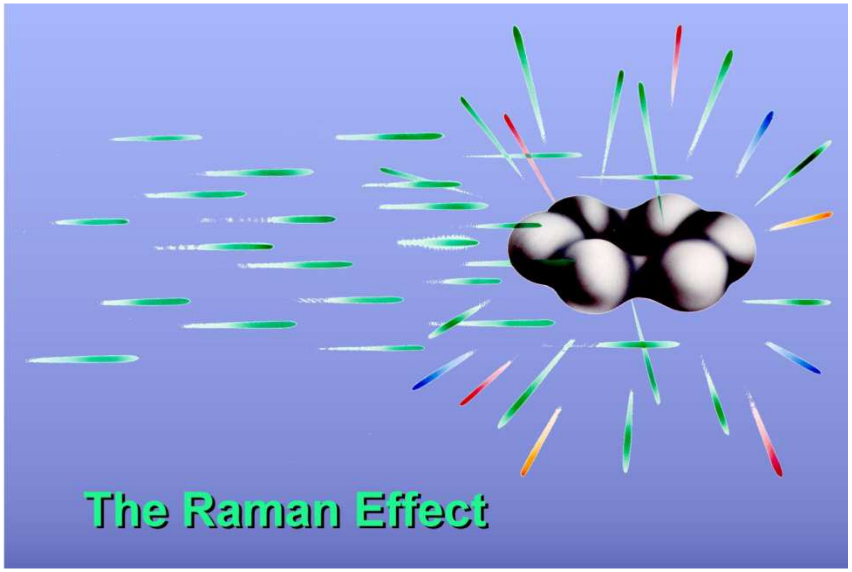
Raman *vs.* Infrared

Infrared

Raman



Absorption of IR light



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

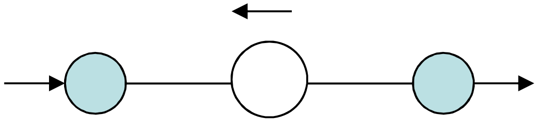
- high absorption for polar bonds ($C=O$, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - ❑ large electron clouds
  - ❑ not polar
- H_2O is a very weak Raman scatterer
- $C=C$ double bonds strong Raman scatterers

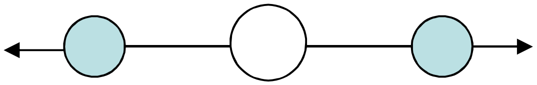
Raman *vs.* Infrared

CO_2



ν_{as}

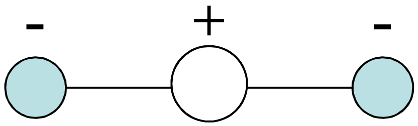
2349 cm^{-1}



ν_s

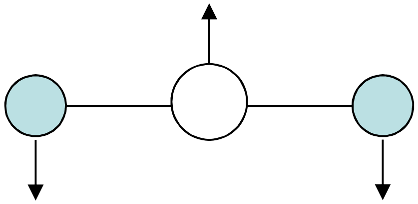
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



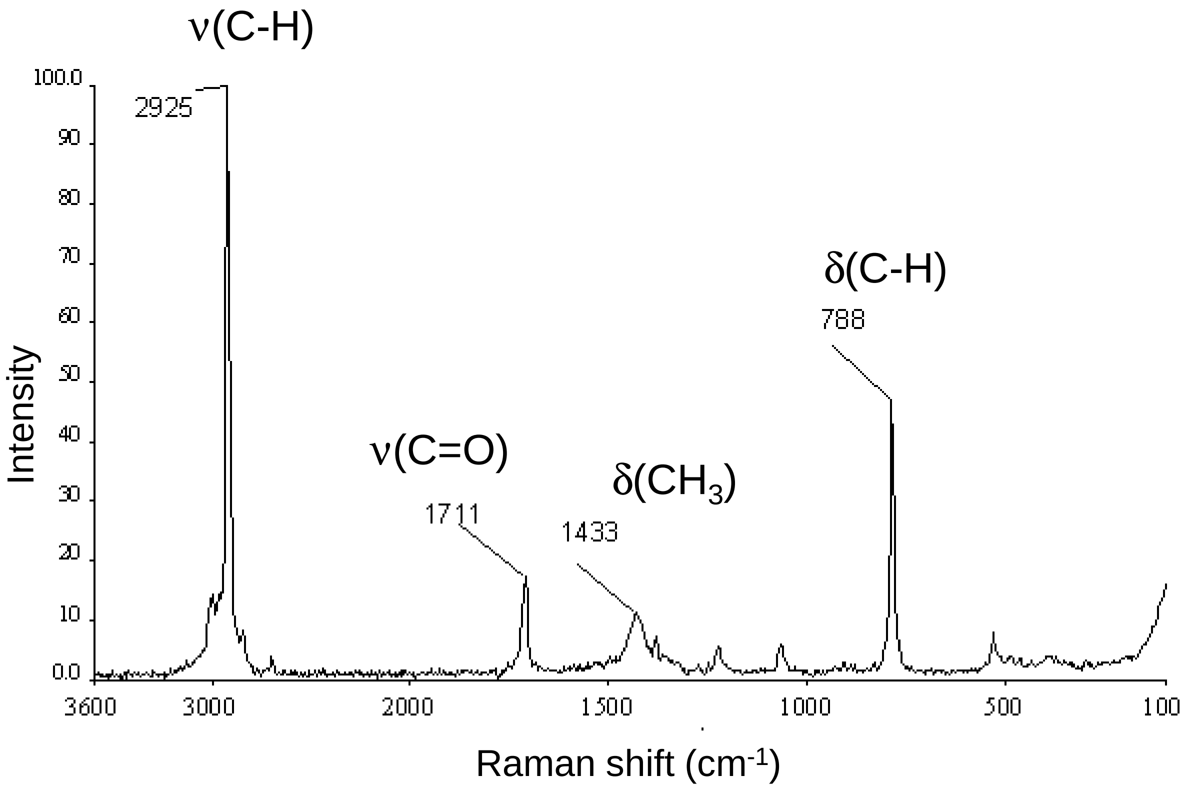
δ

667 cm^{-1}

degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared

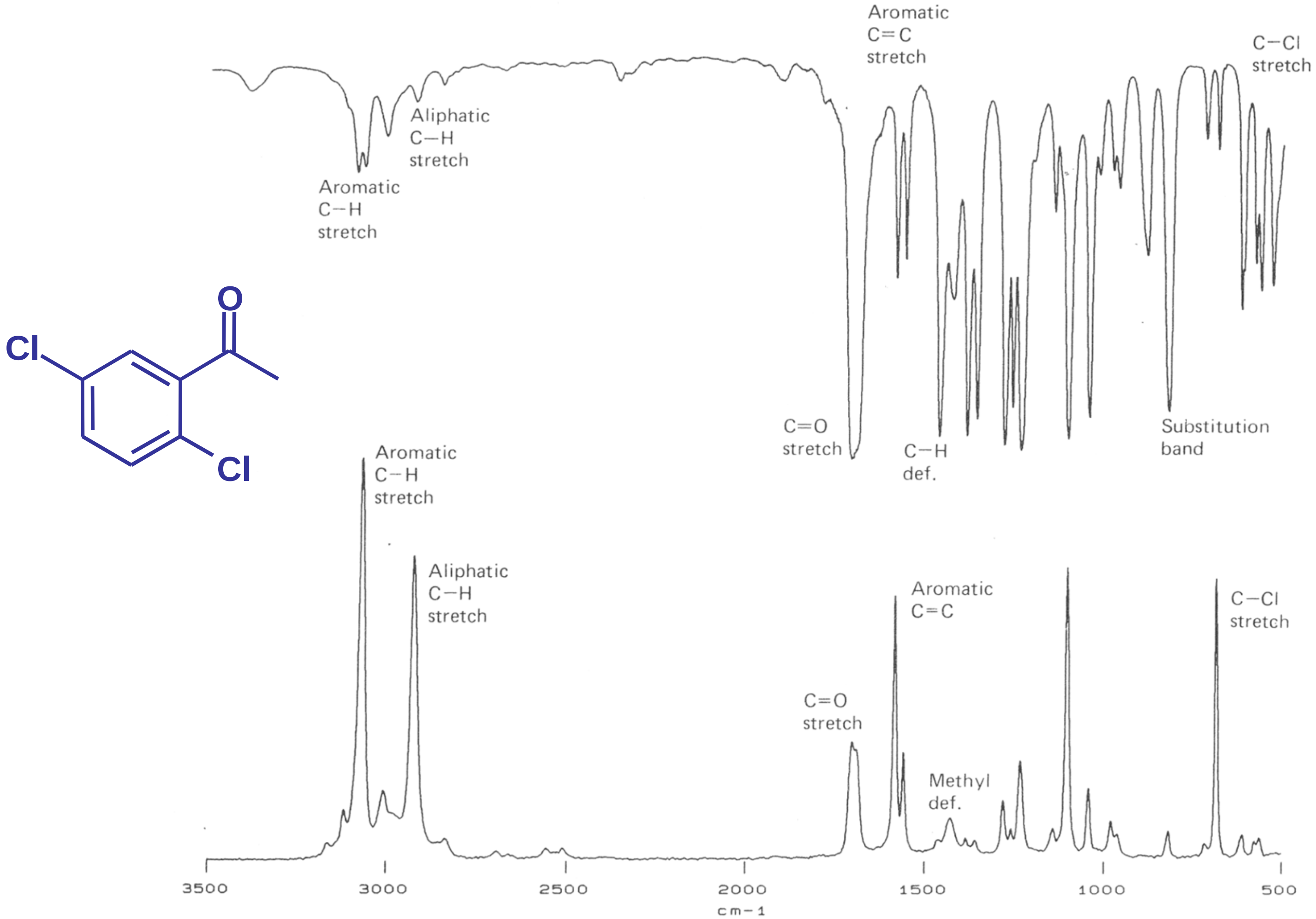


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

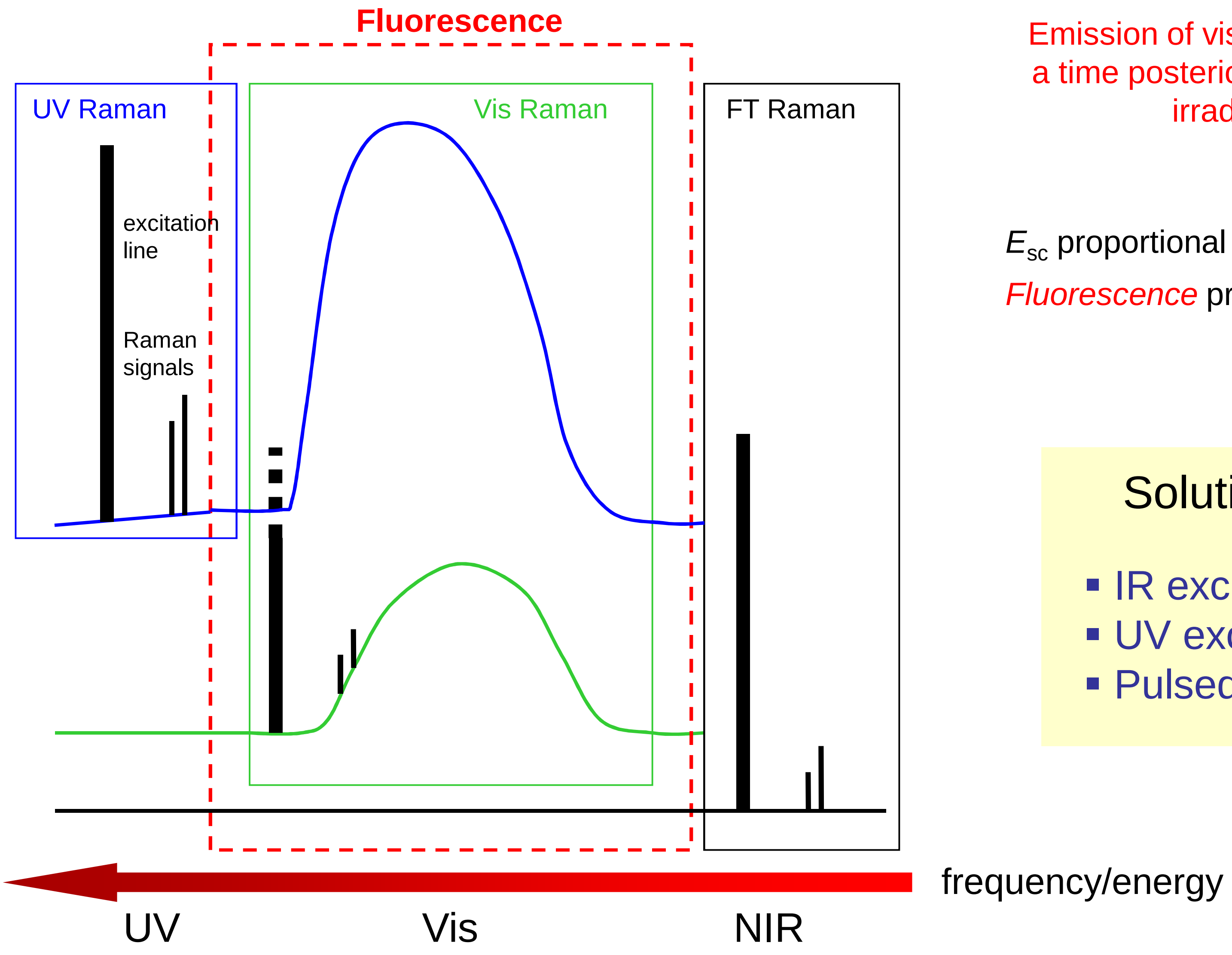
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 µm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

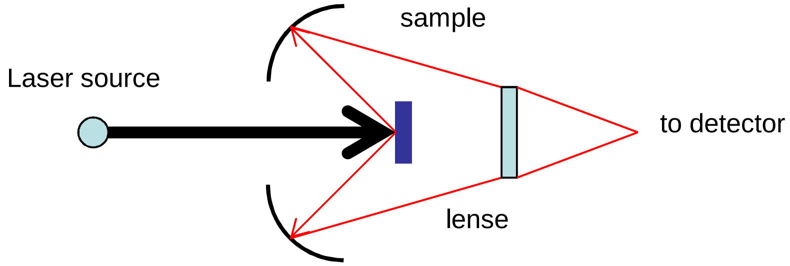
Fluorescence proportional to ν

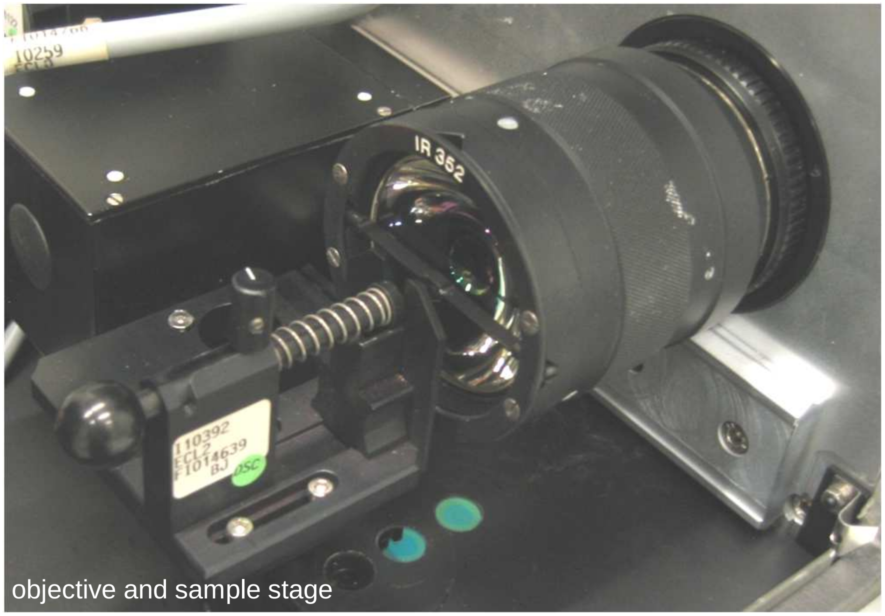
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation




objective and sample stage

Lasers

Excitation wavelengths

UV	250 nm
Vis (green)	514 nm
Vis (red)	633 nm
NIR	780 nm
IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

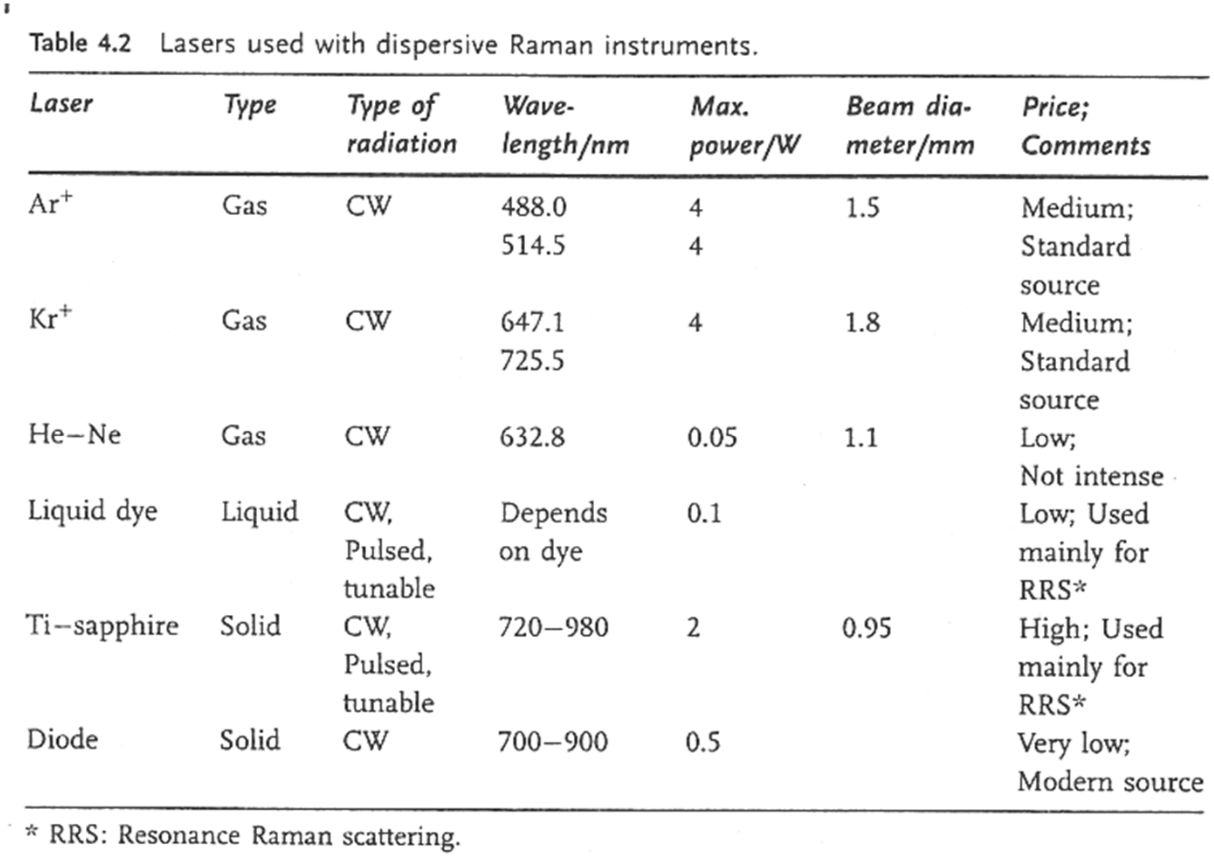


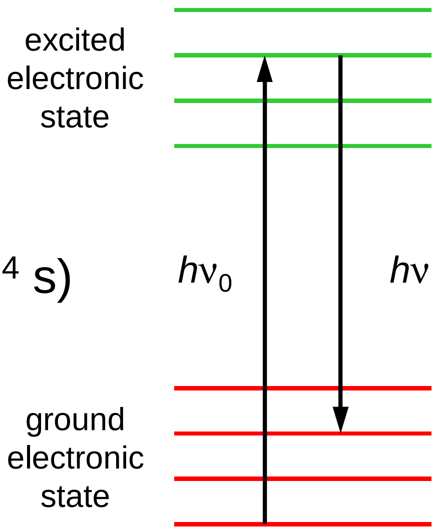
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam diameter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

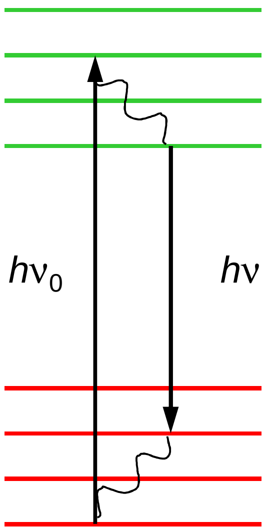
Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



fast (10^{-14} s)

Resonance Raman scattering



slow (10^{-9}–10^{-6} s)

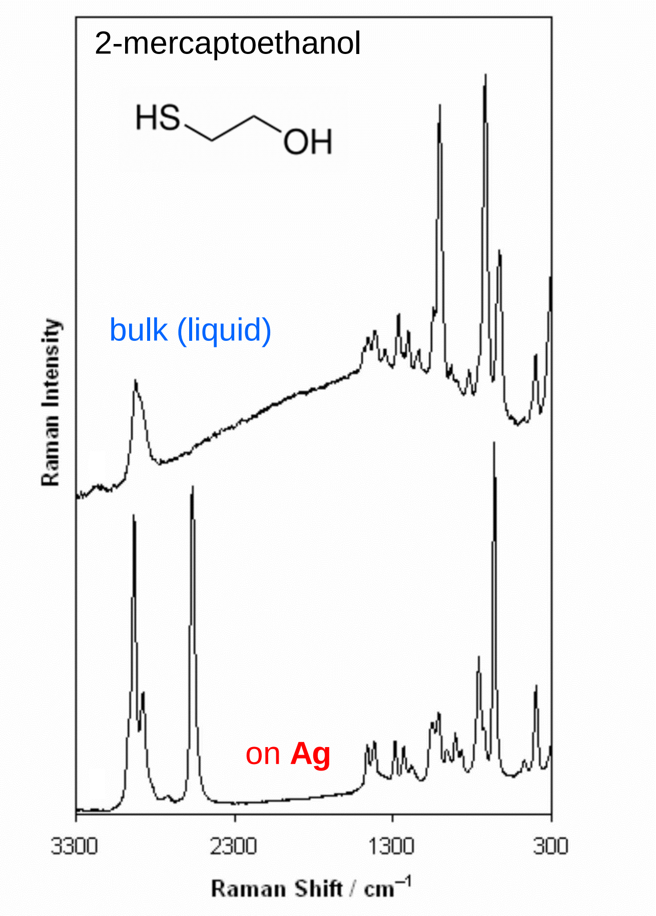
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

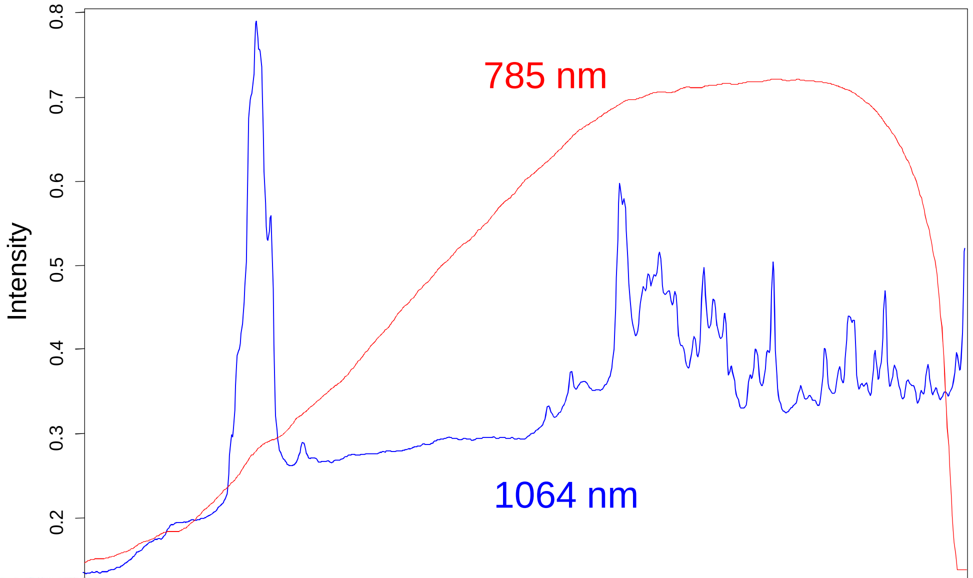
- Remarks:

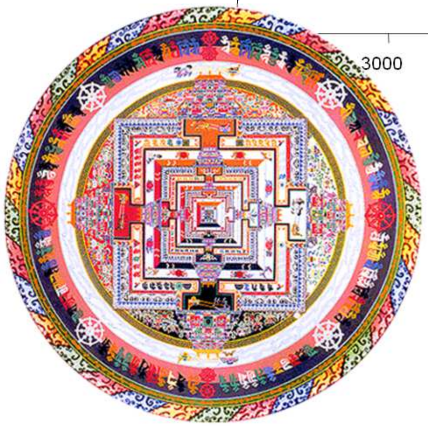
❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring





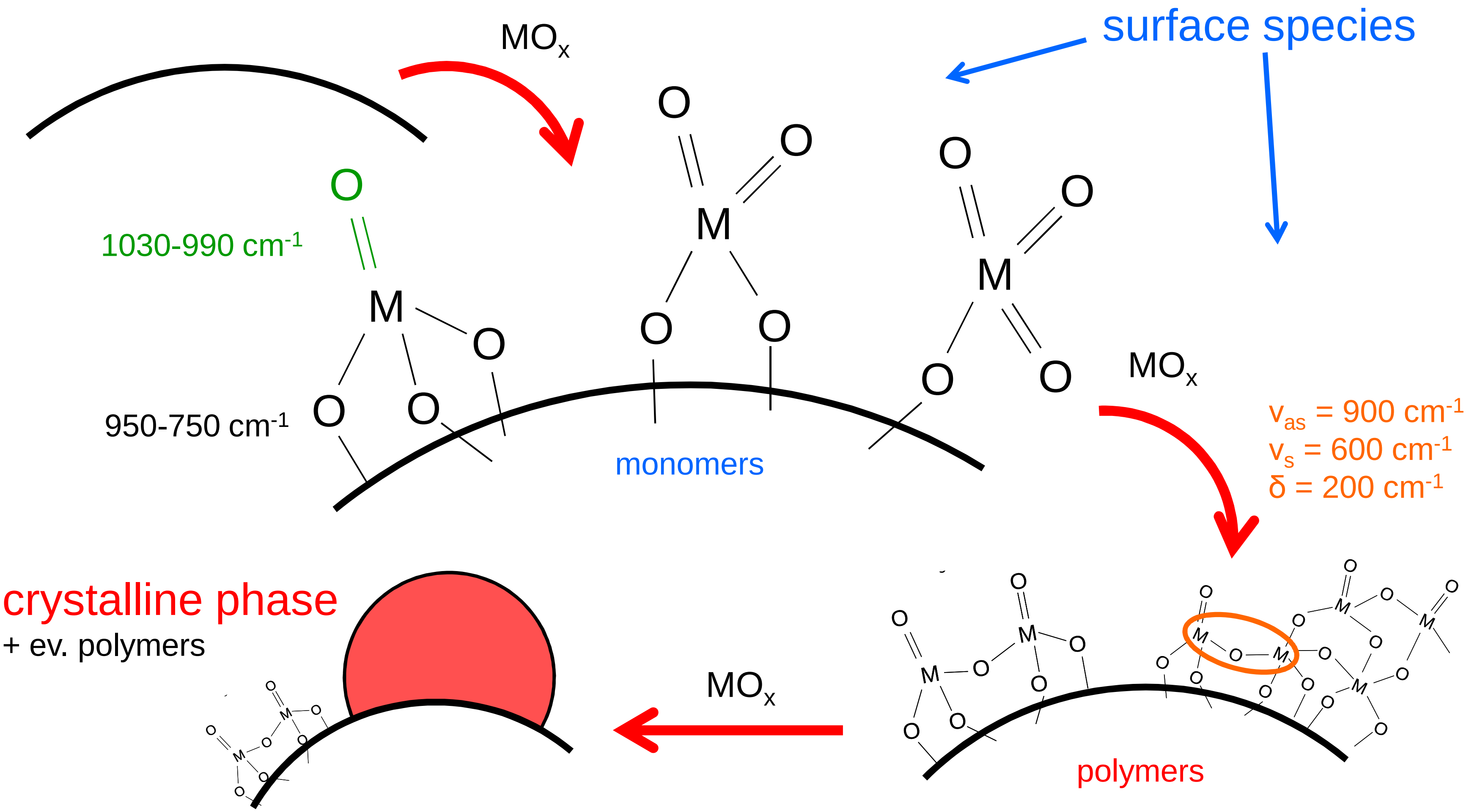
Applications

MO_x/$M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



MO_x

surface species

1030-990 cm^{-1}

950-750 cm^{-1}

monomers

MO_x

ν_{as} = 900 cm^{-1}
ν_s = 600 cm^{-1}
δ = 200 cm^{-1}

crystalline phase
+ ev. polymers

MO_x

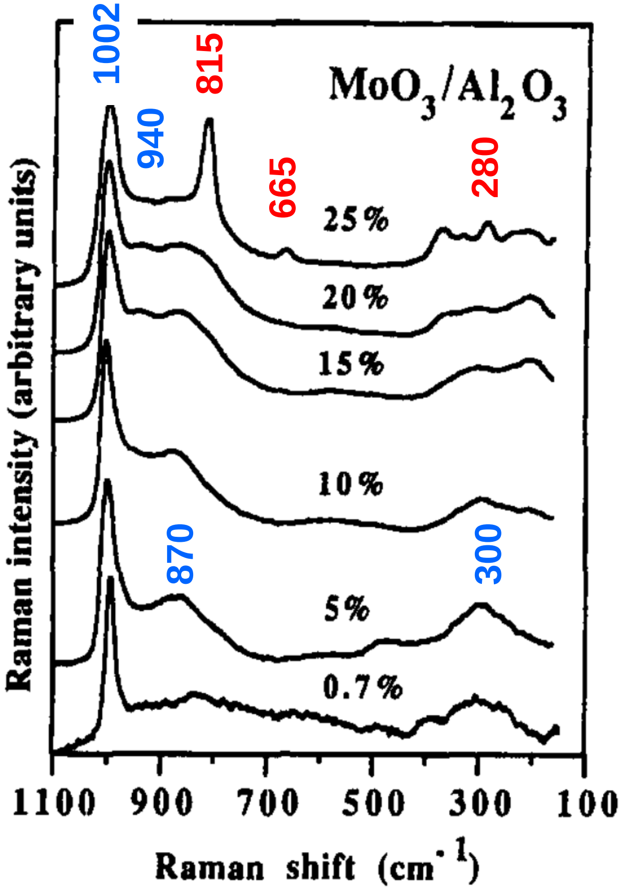
polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



surface MoO_3

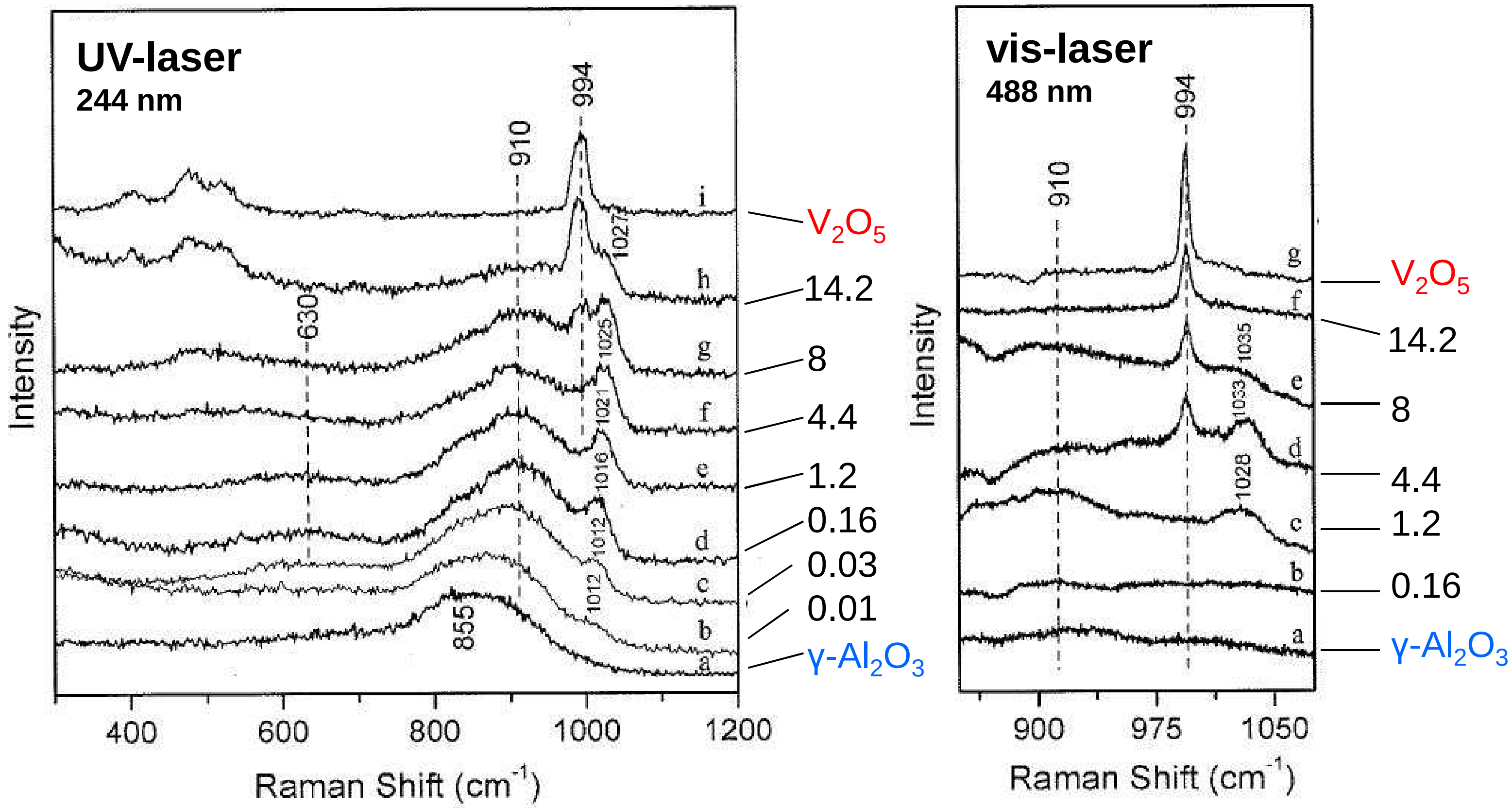
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

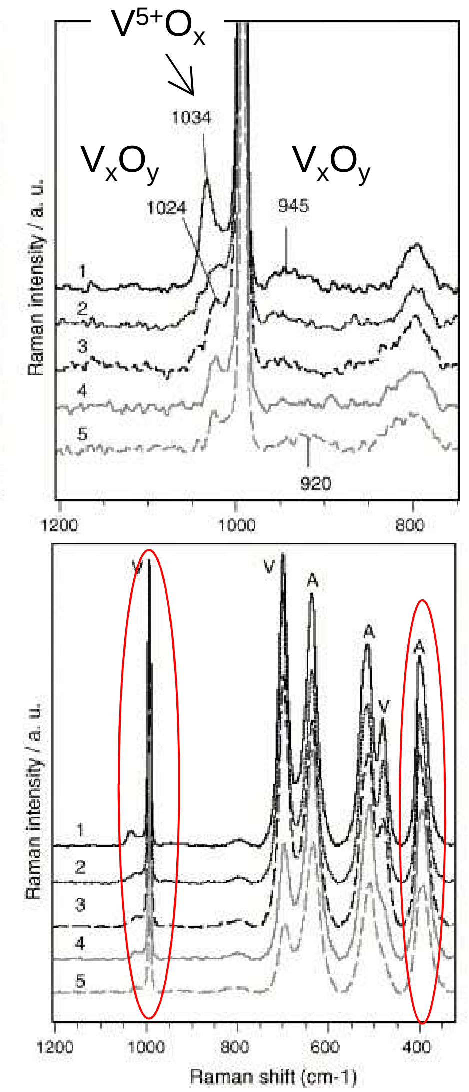
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

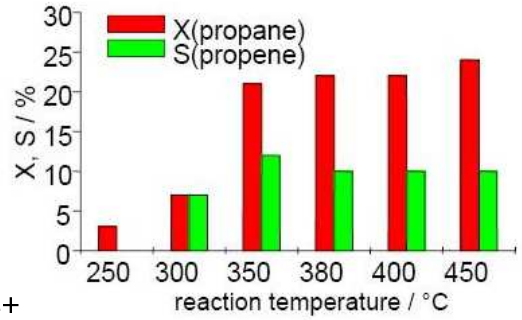
Applications

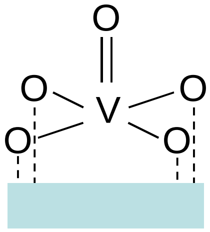
- Reactivity of V/TiO_2 after oxidative treatment

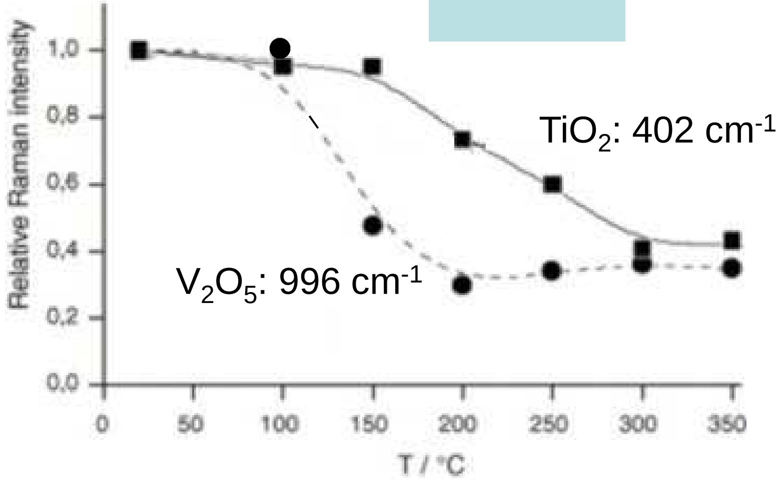


air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$







TiO_2: 402 cm^{-1}

V_2O_5: 996 cm^{-1}

Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

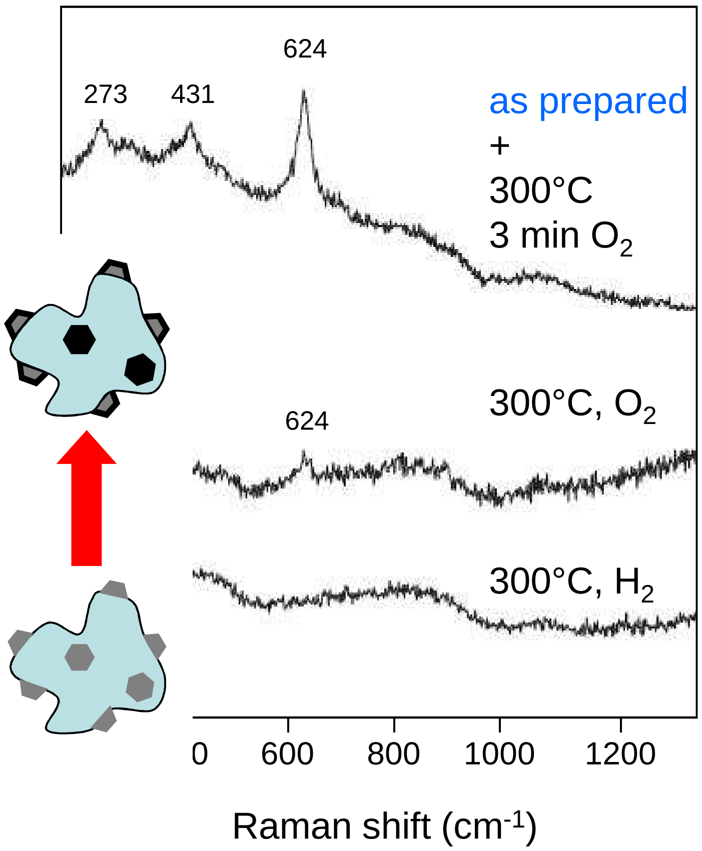
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

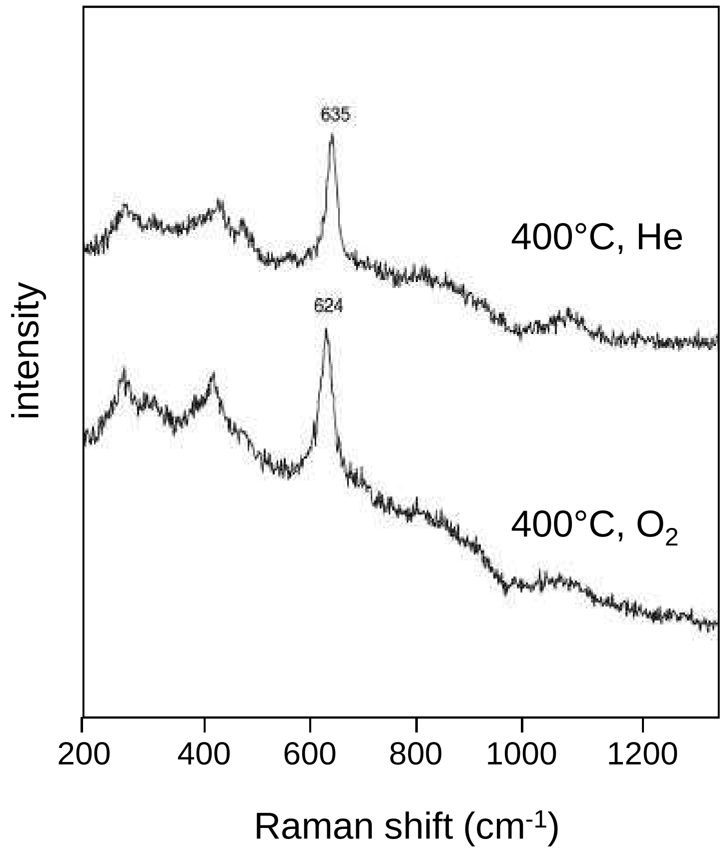
Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3





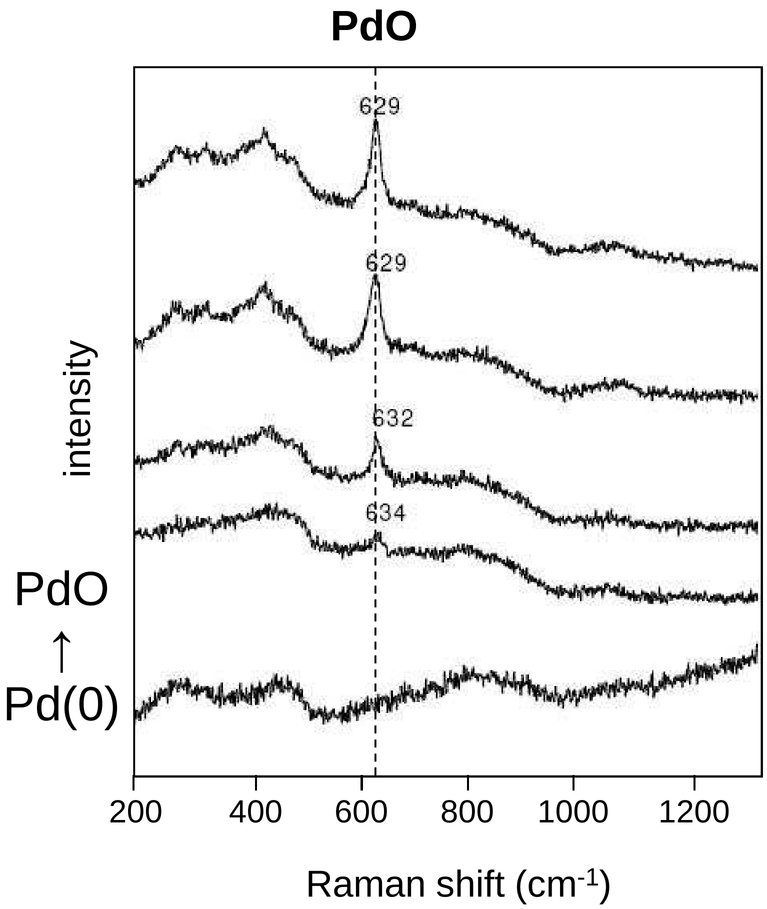
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

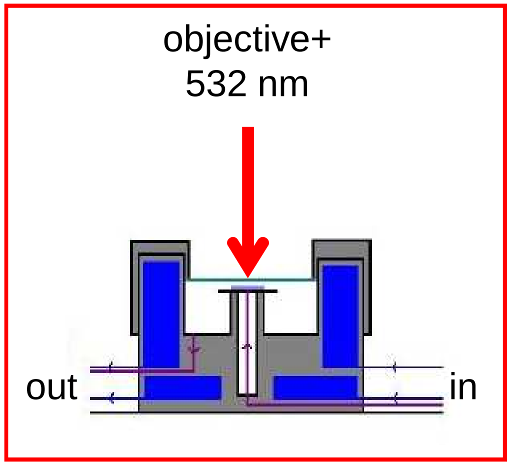
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



	CH_4 conv.
500°C	**24 %**
450°C	**15 %**
425°C	**4 %**
400°C	**2 %**
400°C, H_2 reduced Pd	

↑ feed CH_4/O_2 (1:10)

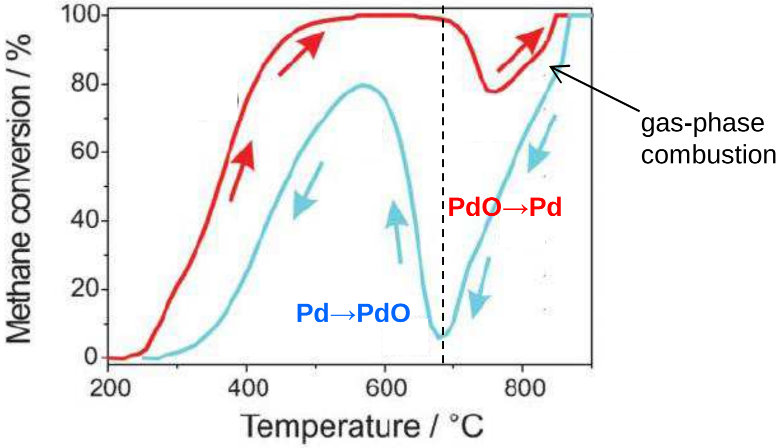
near PdO mode

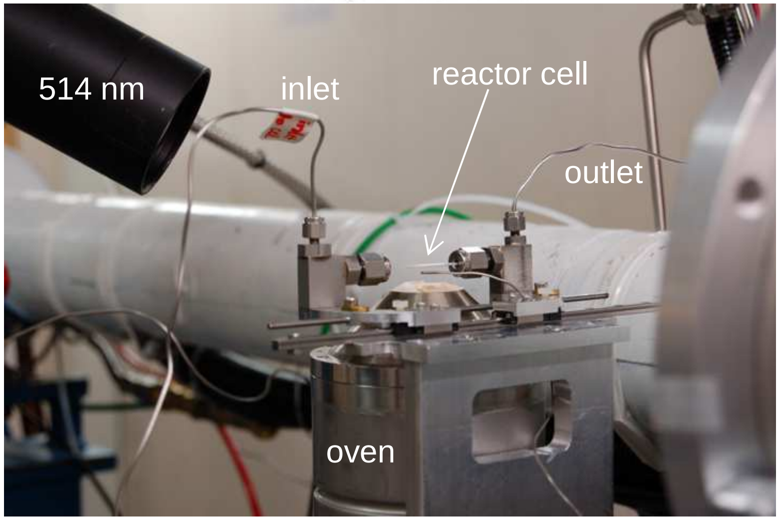


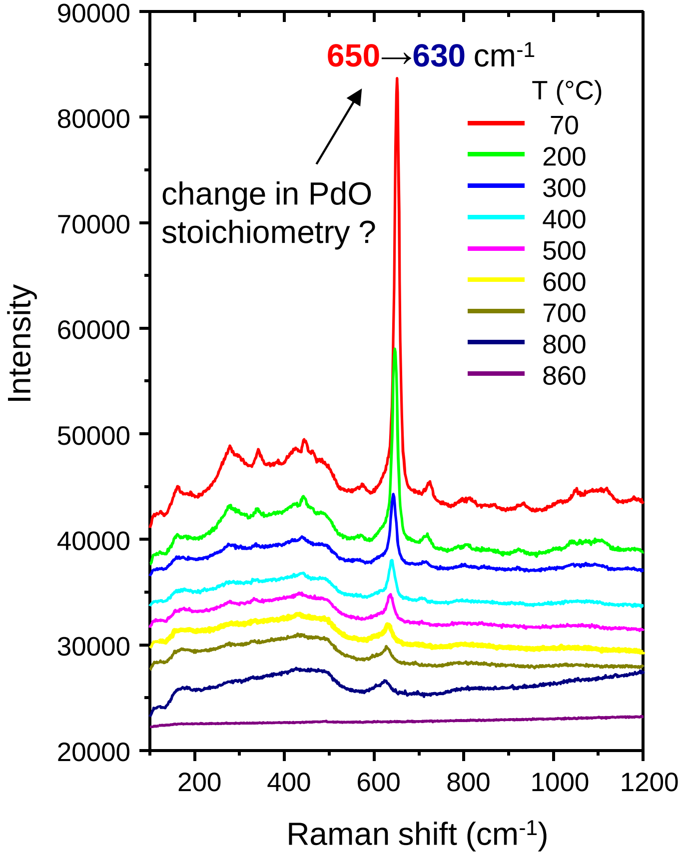
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

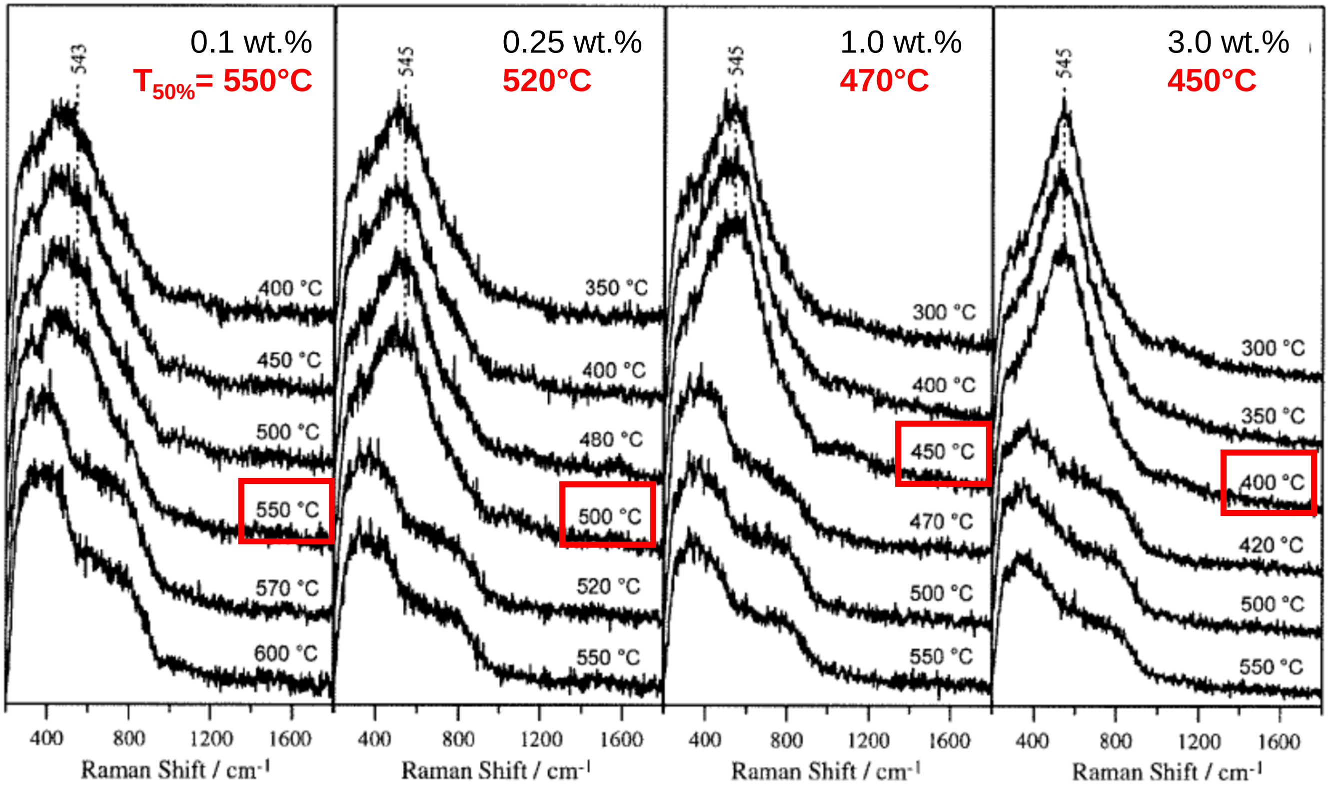
Applications

- Methane partial oxidation over Rh/Al_2O_3

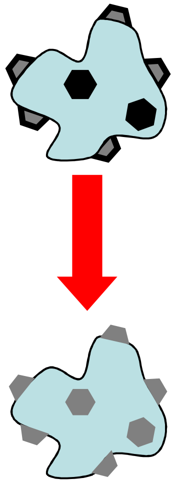
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content
Activity



RhO_x
↓
Rh(0)



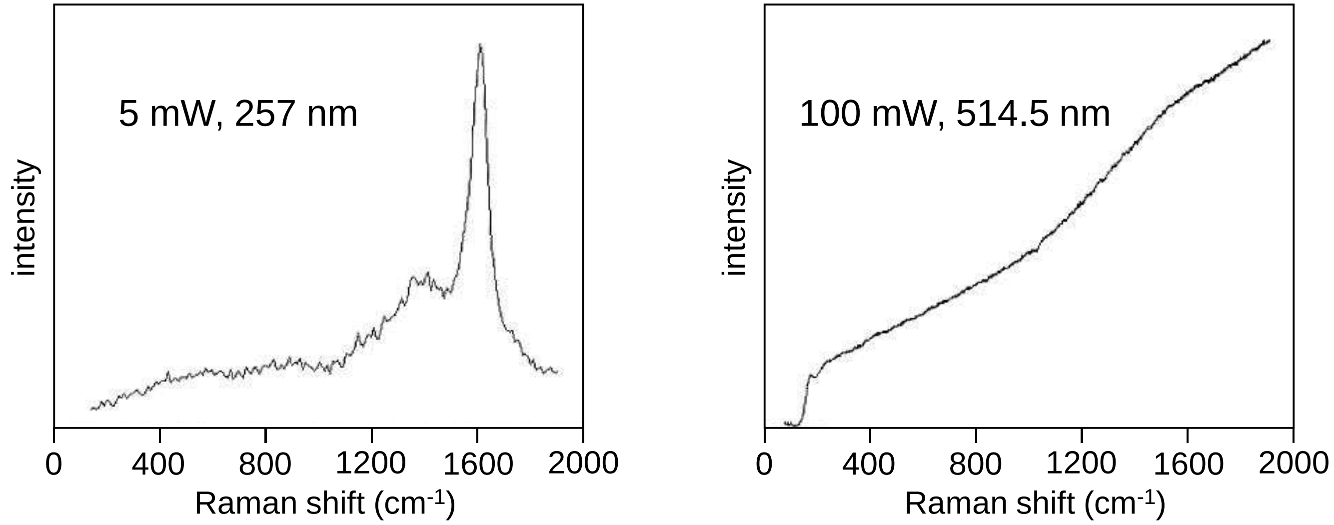
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

    (only few molecules fluoresce below 260 nm)

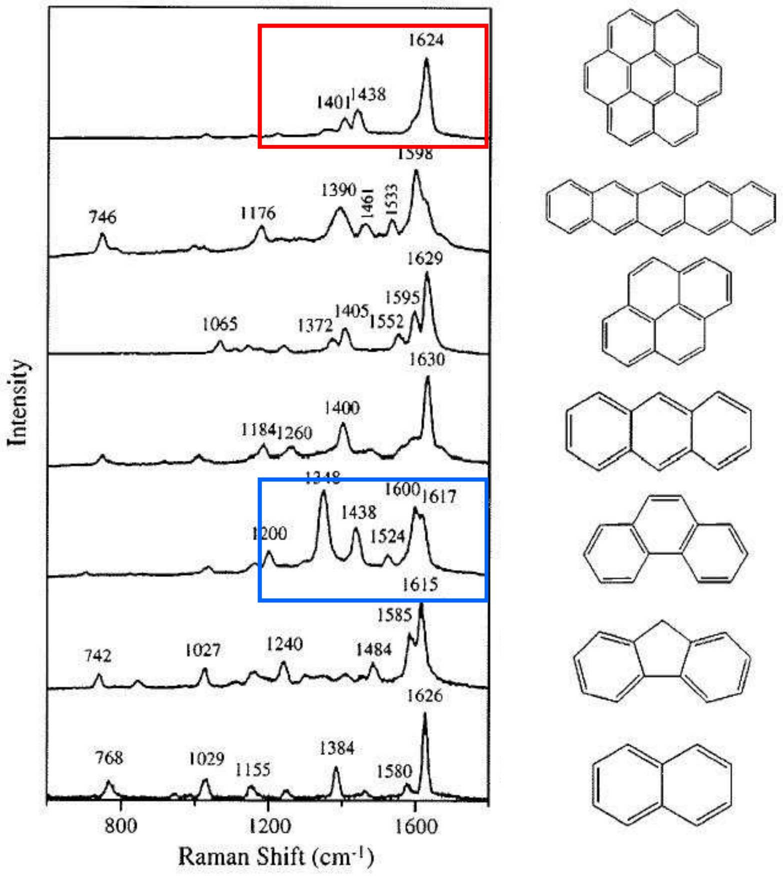
Rh/Al_2O_3, coked 500°C in naphtha

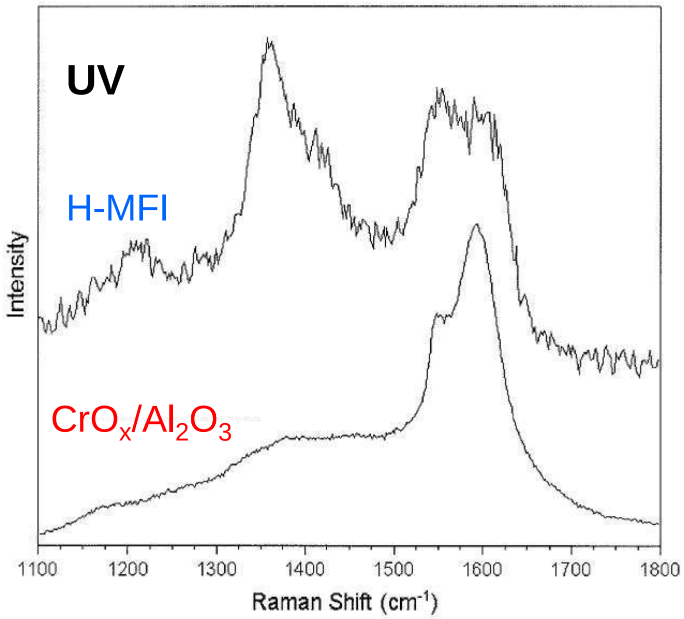


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





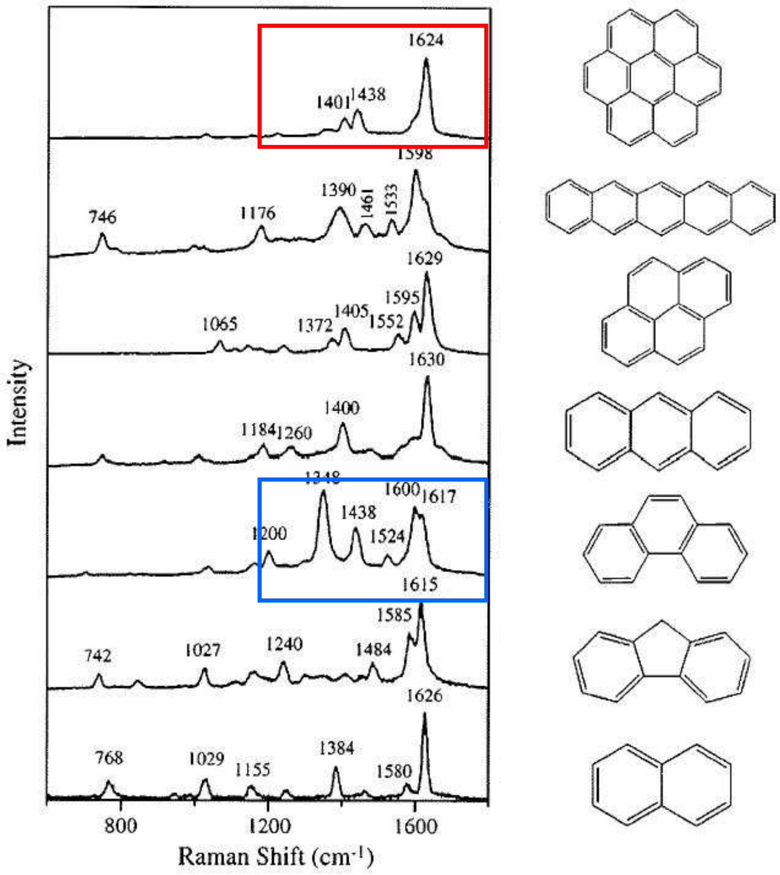
Coke classification
1D topology, chain-like
2D topology, sheet-like

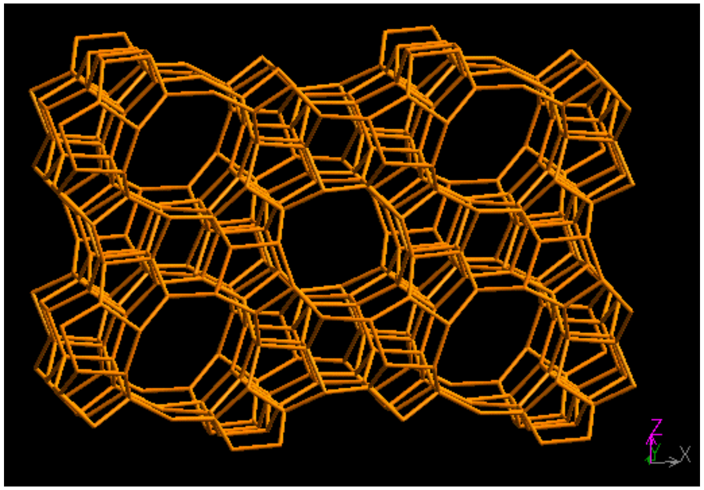
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





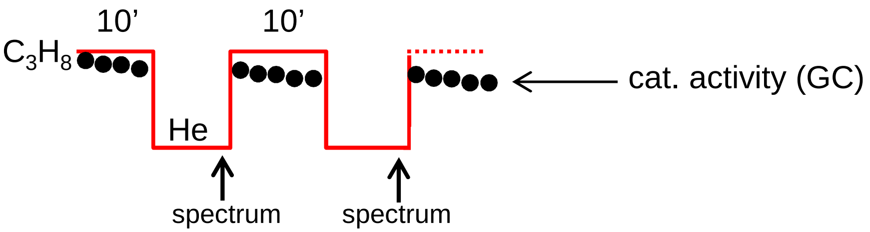
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

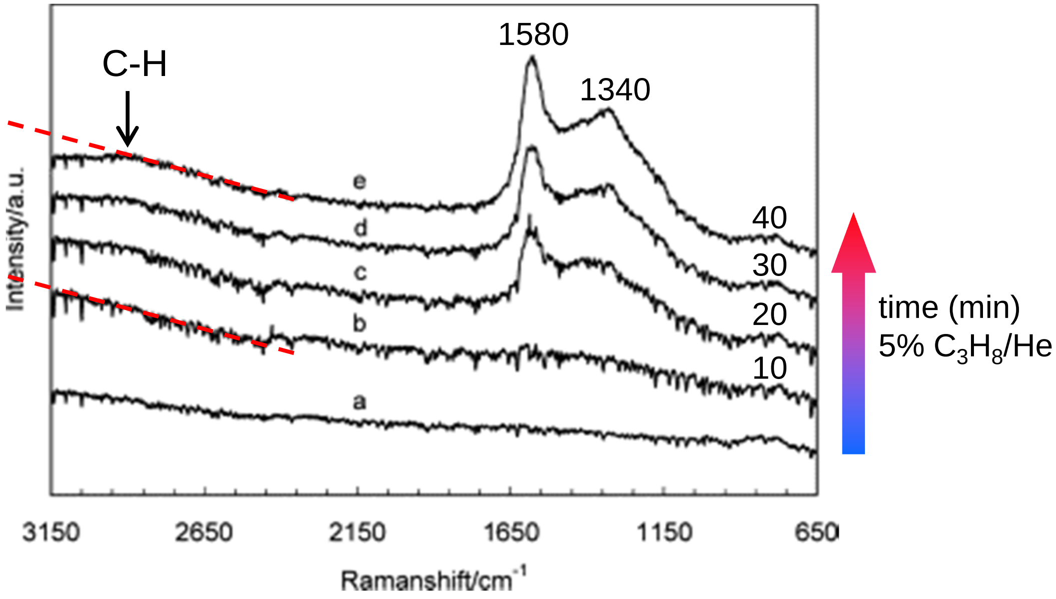
Stair, *Adv. Catal.* **51** (2007) 75

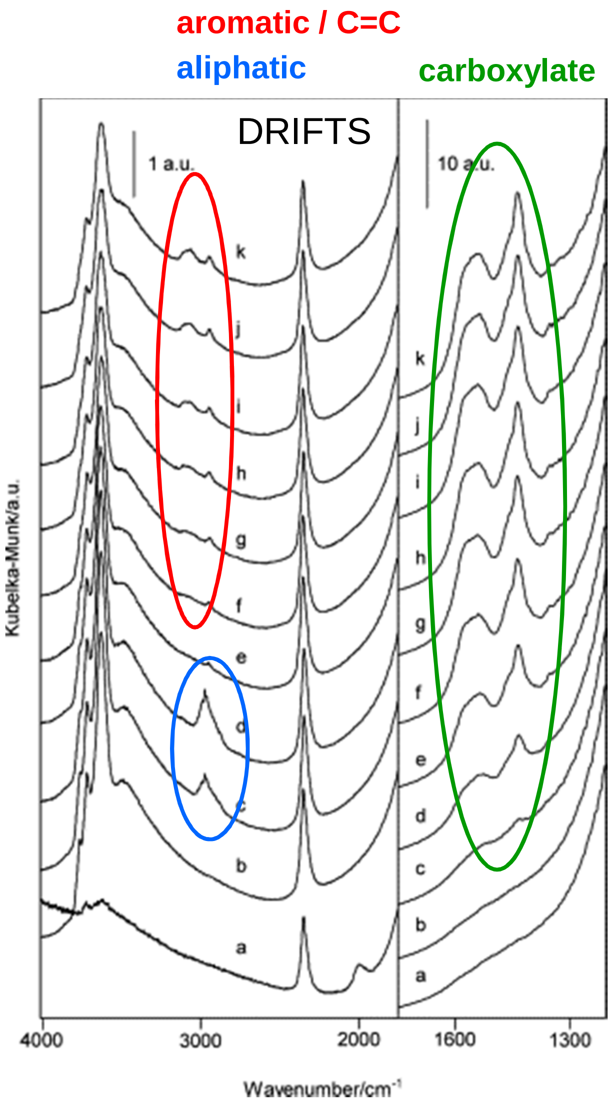
Applications

- Propane dehydrogenation


10’
10’
C_3H_8
He
spectrum
spectrum
cat. activity (GC)

Cr_2O_3/Al_2O_3, 580°C, 514 nm

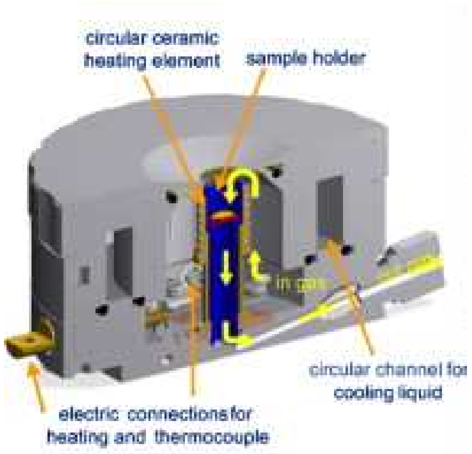


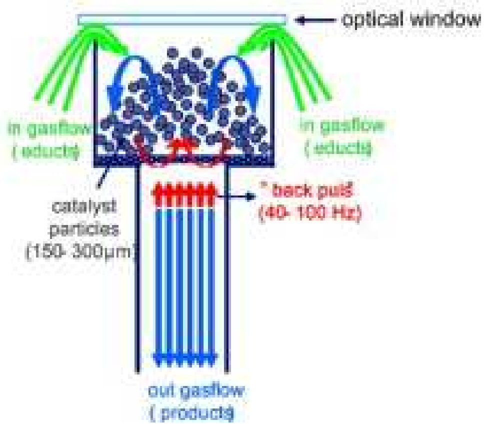


Airaksinen et al., *J. Catal.* **230** (2005) 507

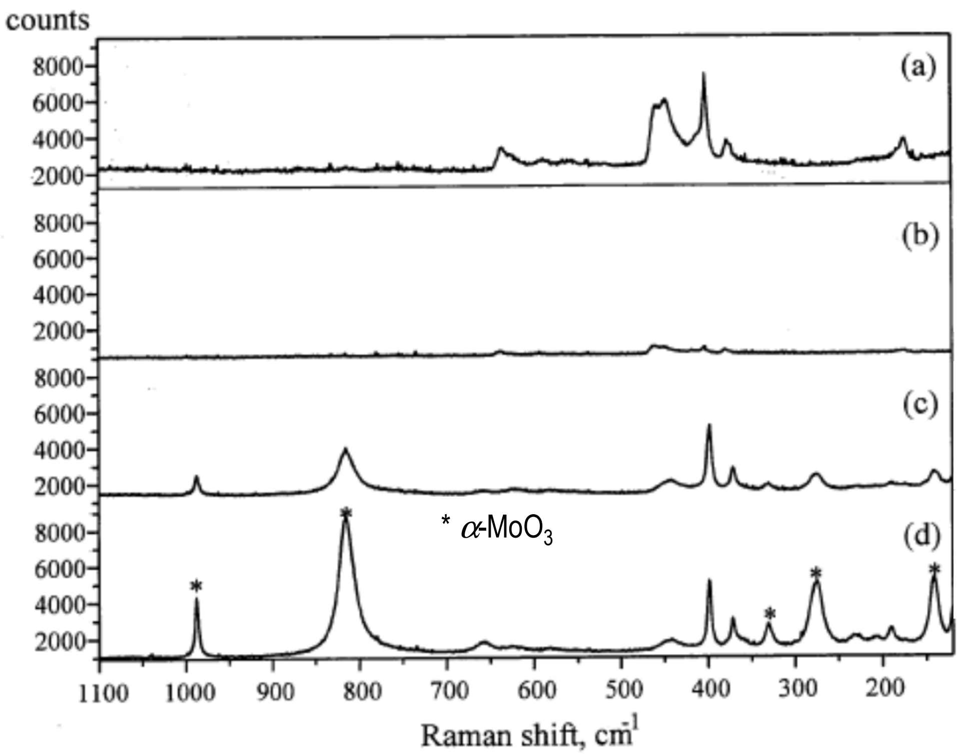
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min
full power, FB

MoS_2, 6 min
1/8 power

MoS_2, 1 min
full power

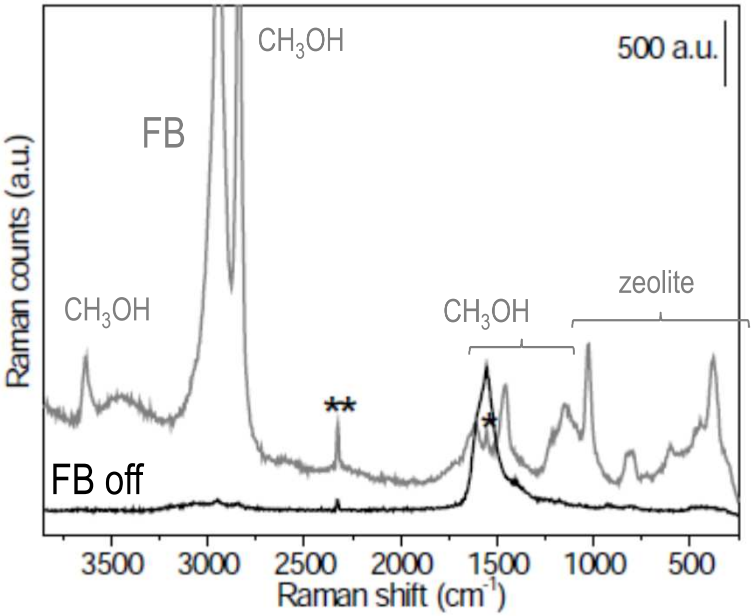
MoS_2, 6 min
full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

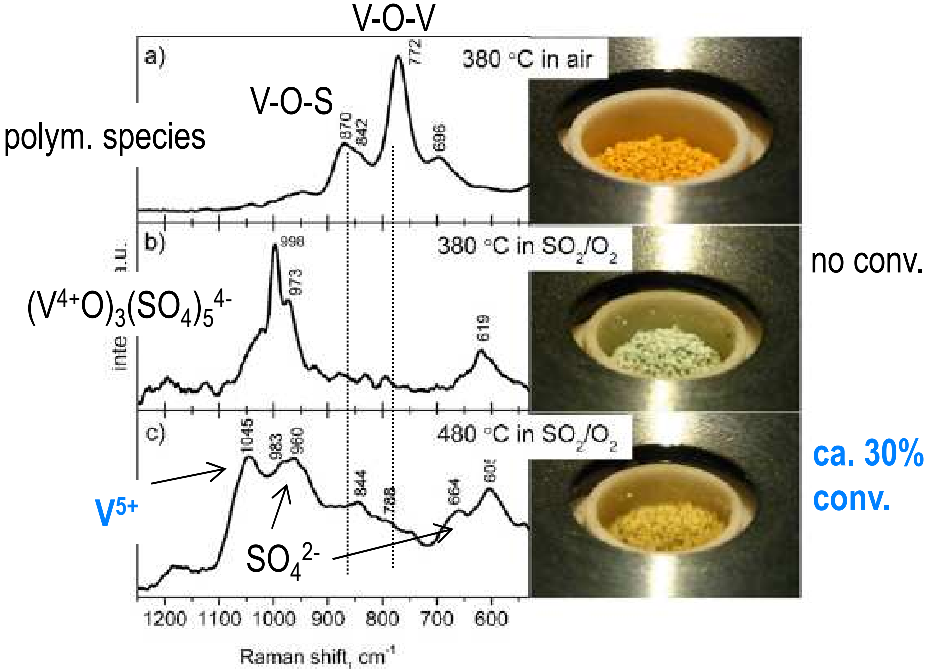
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

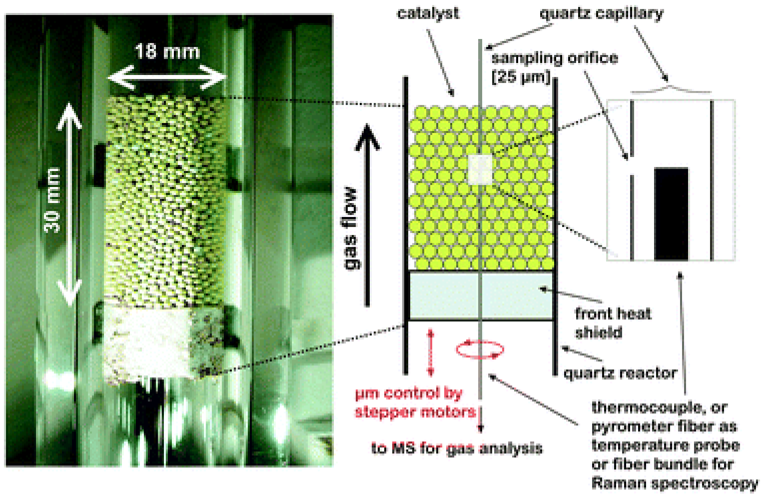


active species: mono- & dimeric V^{5+} oxosulfate species

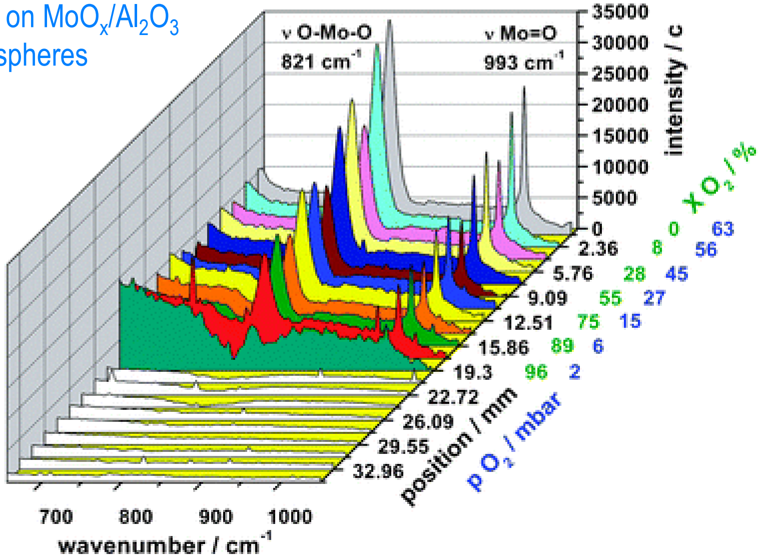
Beato et al., *Catal. Today* 205 (2013) 128

Applications

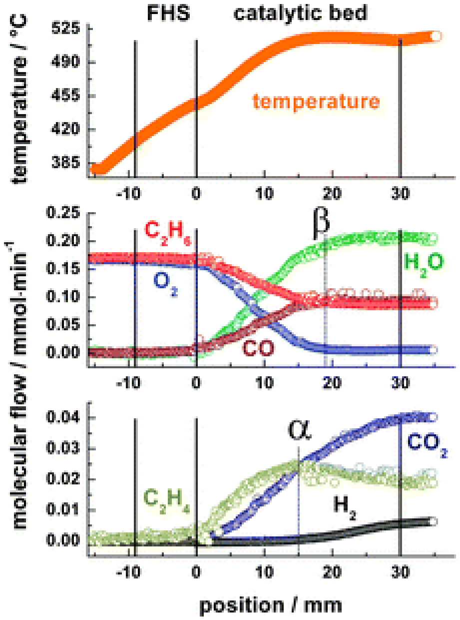
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

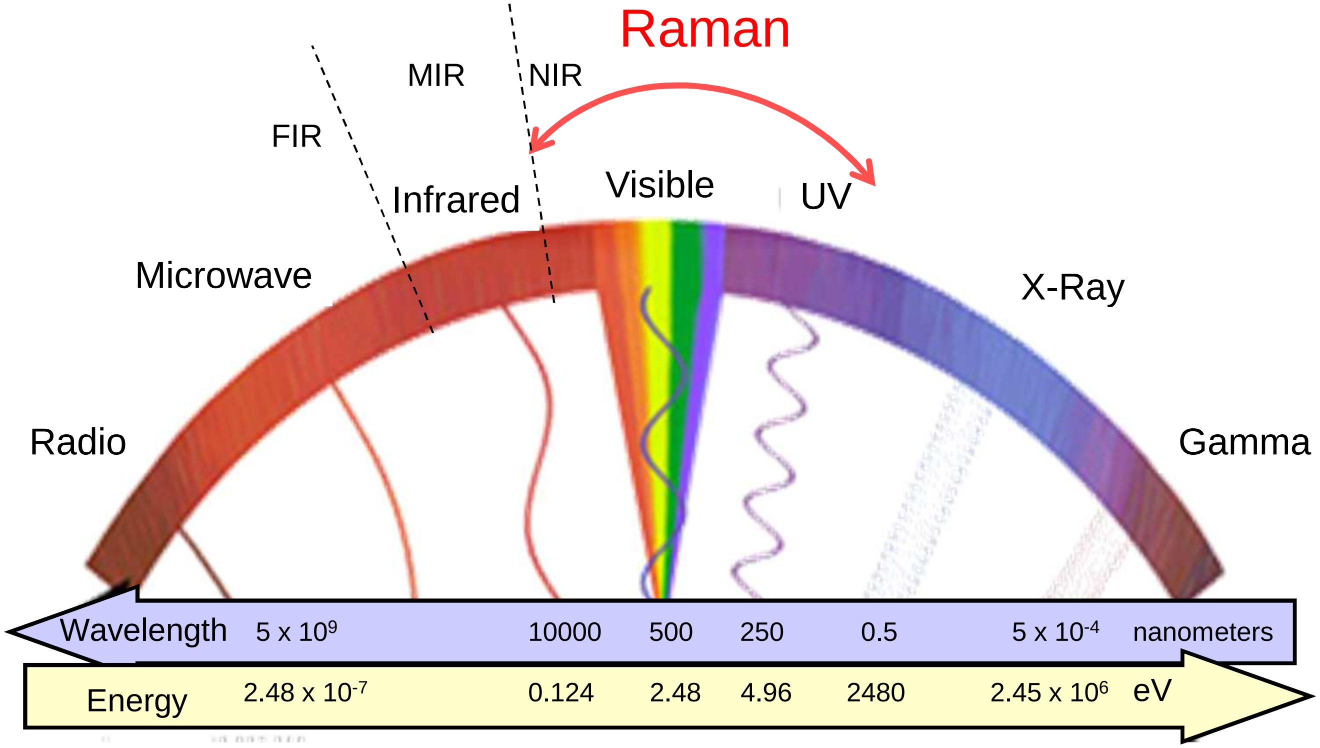
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

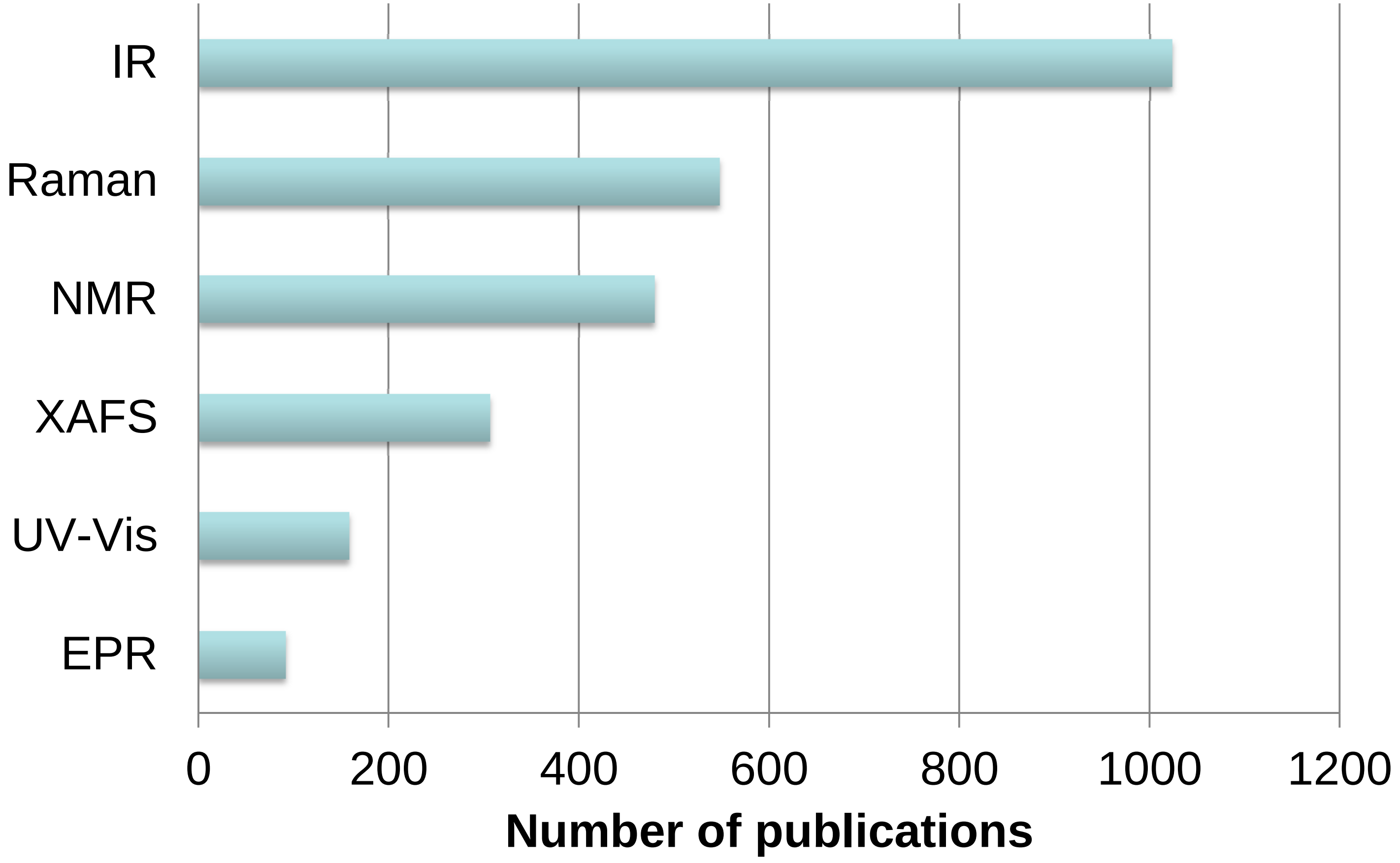
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

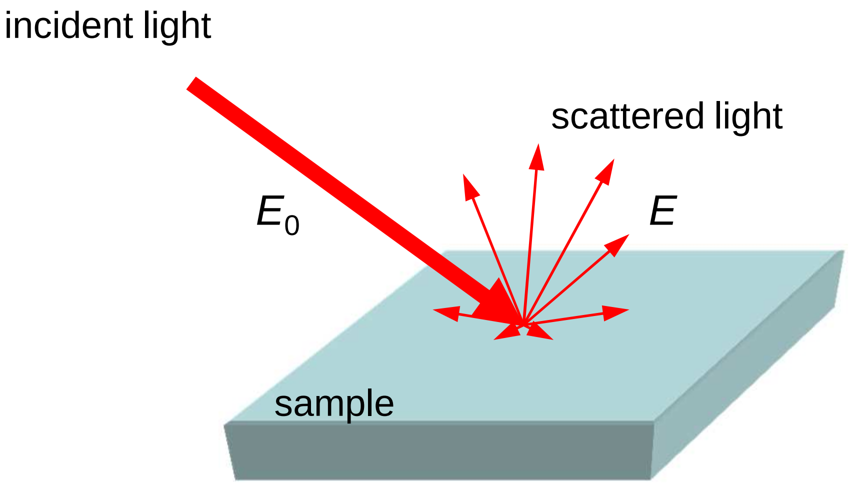


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib}t)$

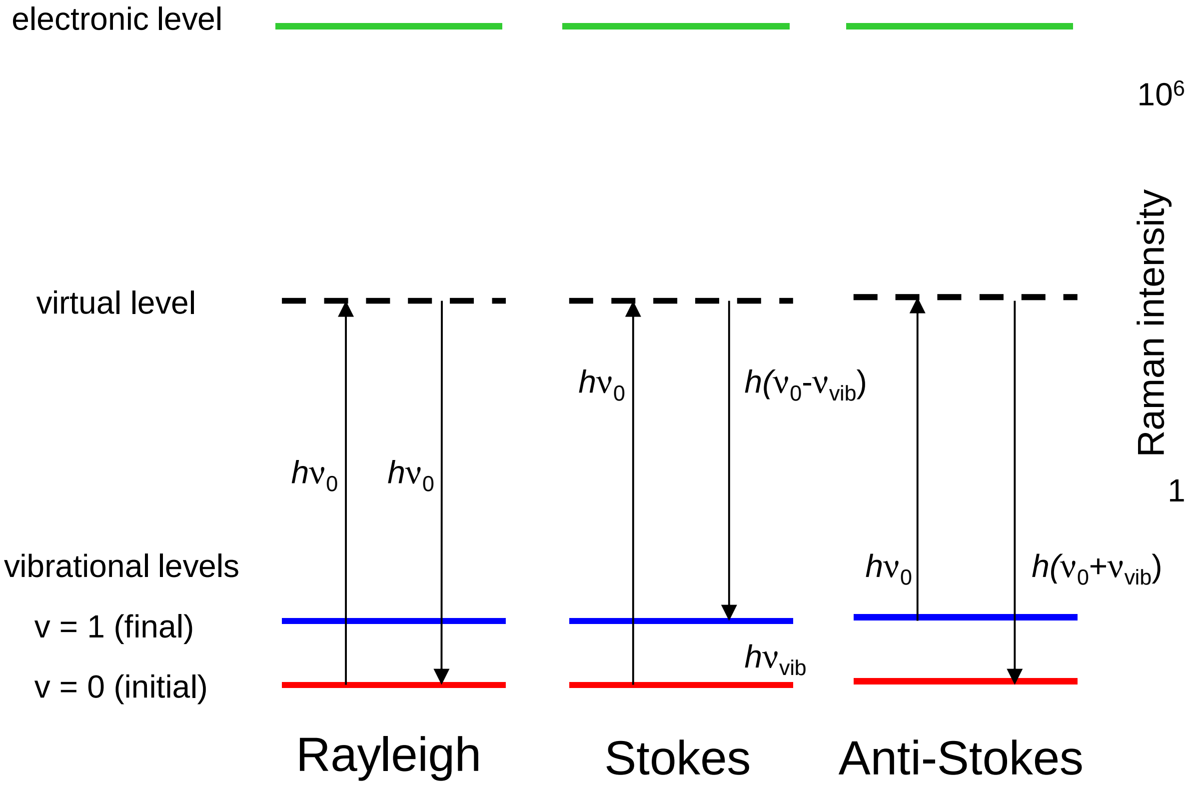
$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib}t)]E_0\cos(2\pi\nu_0 t)$$

$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib}t)\cos(2\pi\nu_0 t)$$

$$\text{and}\quad \boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



electronic level

virtual level

vibrational levels

v = 1 (final)

v = 0 (initial)

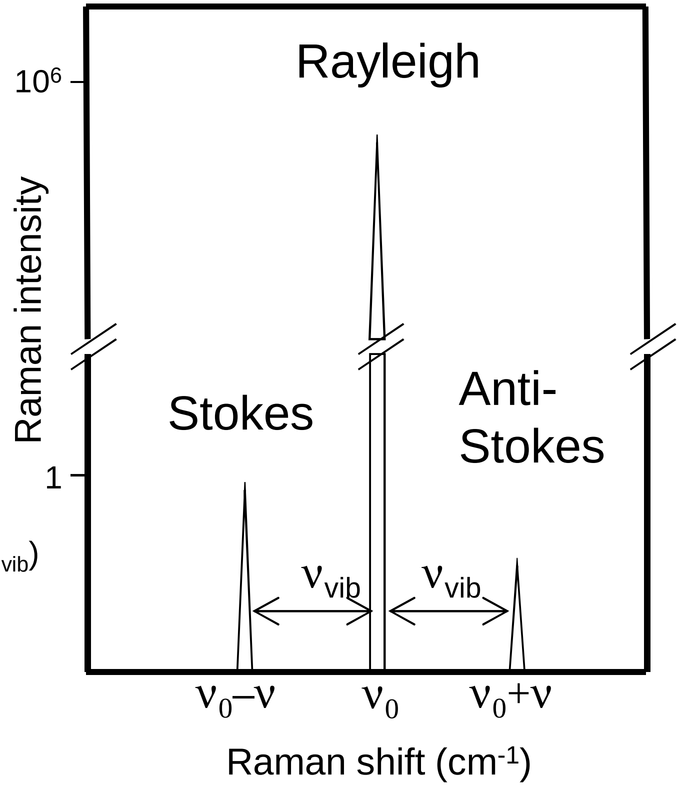
$h\nu_0$ $h\nu_0$

$h\nu_0$ $h(\nu_0\text{-}\nu_{vib})$ $h\nu_{vib}$

$h\nu_0$ $h(\nu_0+\nu_{vib})$

Rayleigh Stokes Anti-Stokes

Raman spectrum



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\ (\text{Anti-Stokes})}{I\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

- ❑ 4th power of ν (4th power law)
- ❑ 2nd power of $\Delta\alpha$
  - properties of molecules
  - strength of bonds

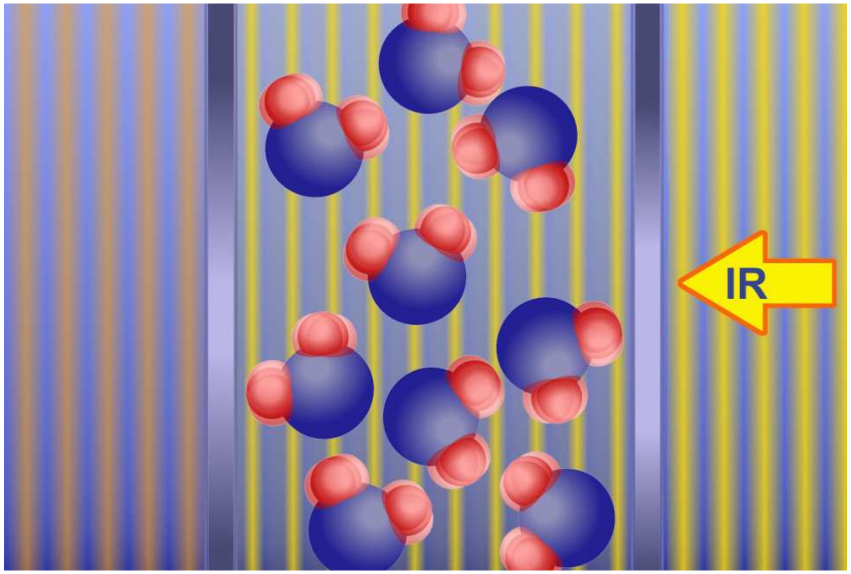
↓

covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

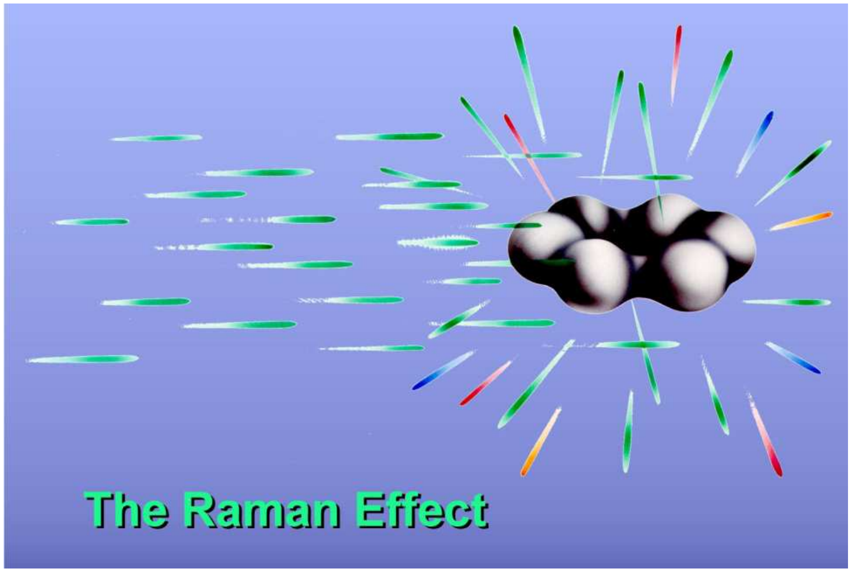
Raman *vs.* Infrared

Infrared



Absorption of IR light

Raman



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial\mu}{\partial Q}\right)^2 \neq 0$$

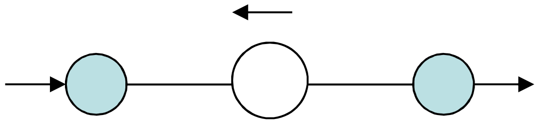
- high absorption for polar bonds ($C=O$, H_2O, NH, etc.)

$$\left(\frac{\partial\alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - ❑ large electron clouds
  - ❑ not polar
- H_2O is a very weak Raman scatterer
- $C=C$ double bonds strong Raman scatterers

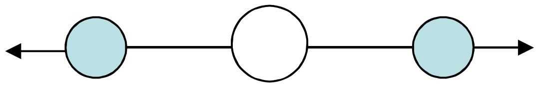
Raman *vs.* Infrared

CO_2



ν_{as}

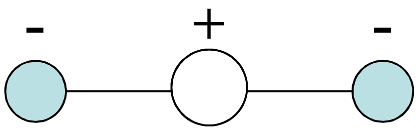
2349 cm^{-1}



ν_s

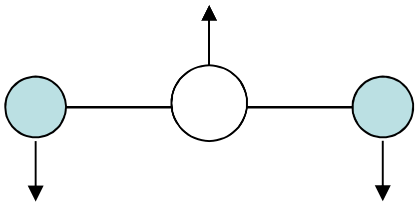
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



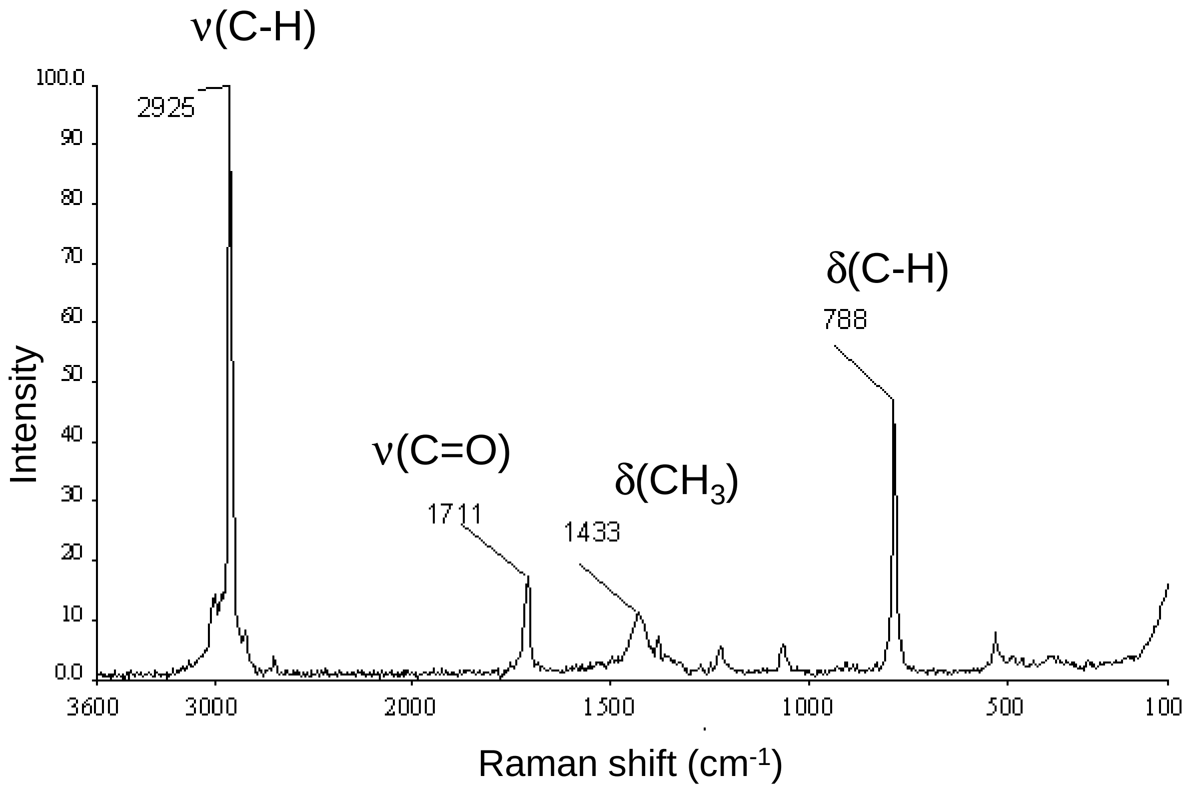
δ

667 cm^{-1}

degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared

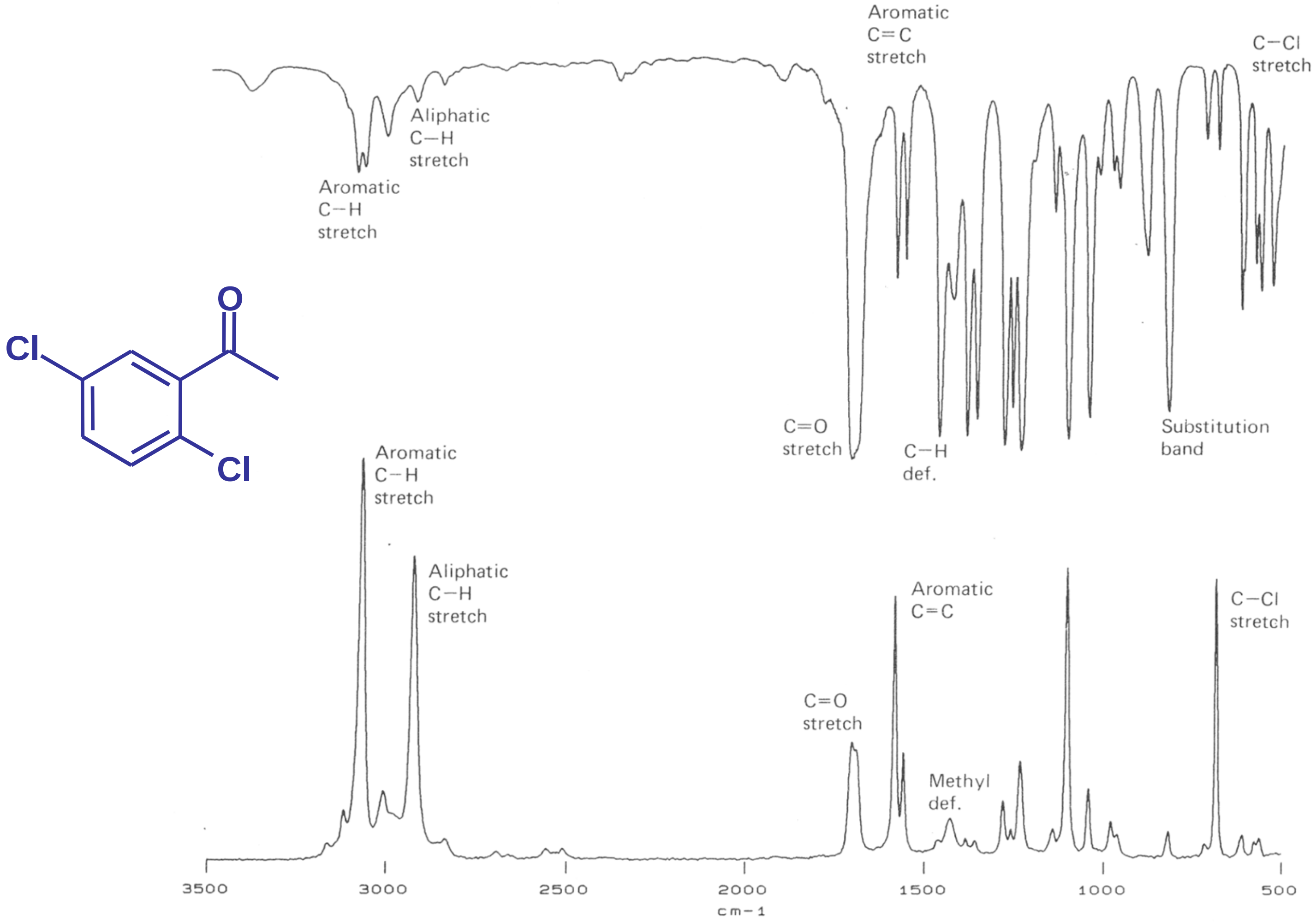


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

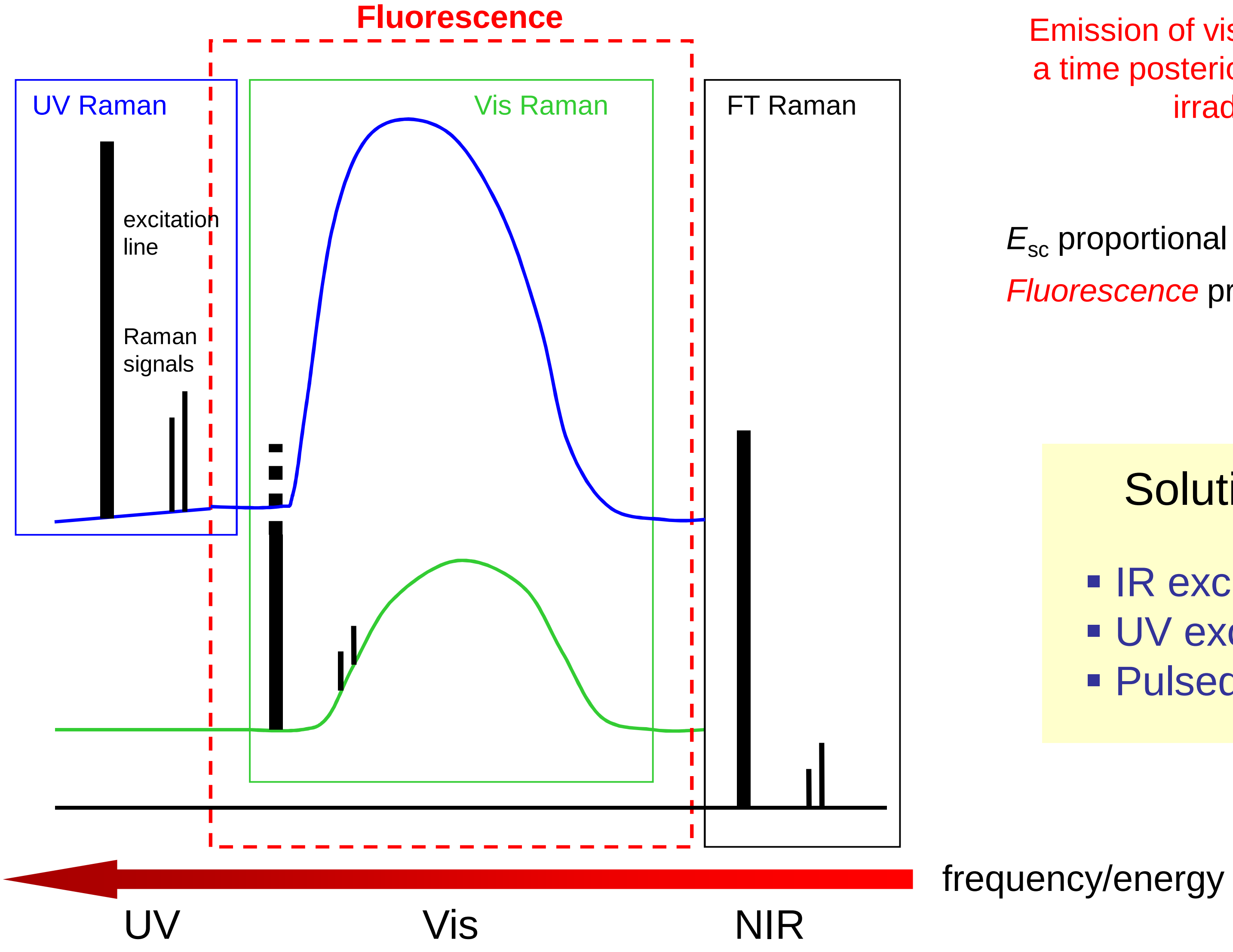
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 µm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

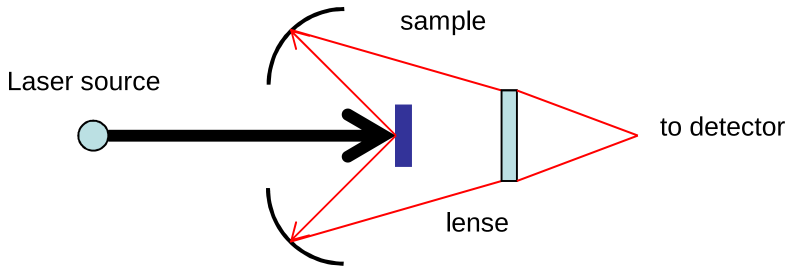
Fluorescence proportional to ν

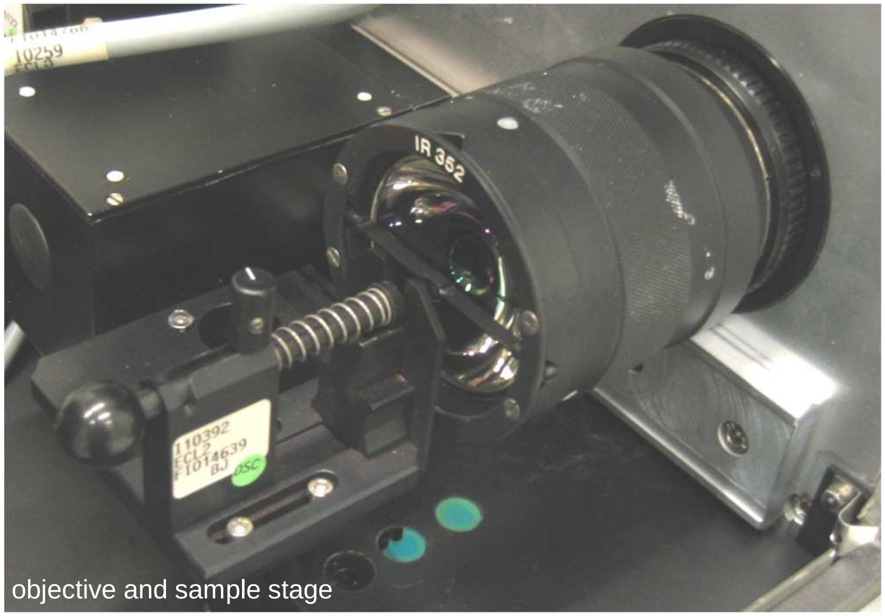
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

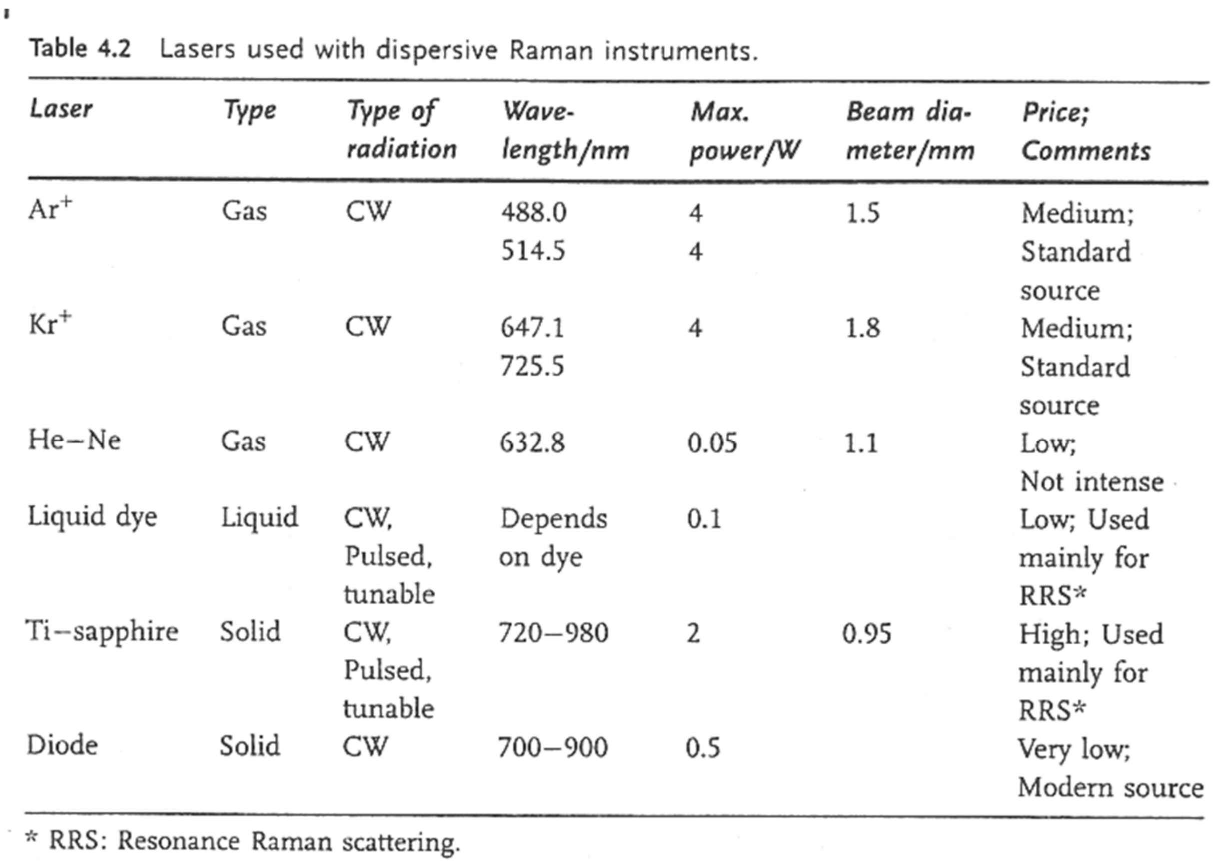


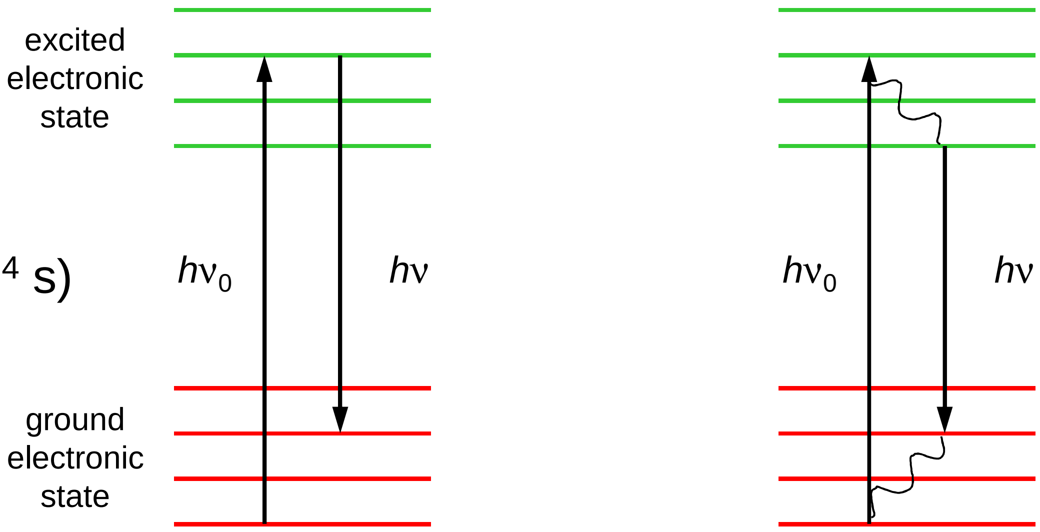
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



excited electronic state

ground electronic state

fast (10^{-14} s)

$h\nu_0$ $h\nu$

Resonance Raman scattering

$h\nu_0$ $h\nu$

slow (10^{-9}–10^{-6} s)

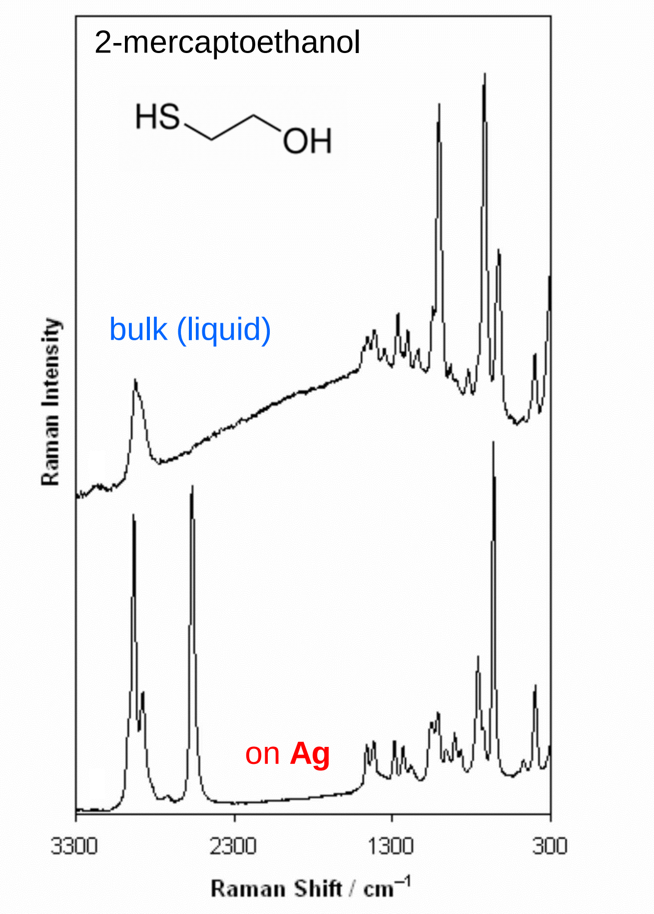
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

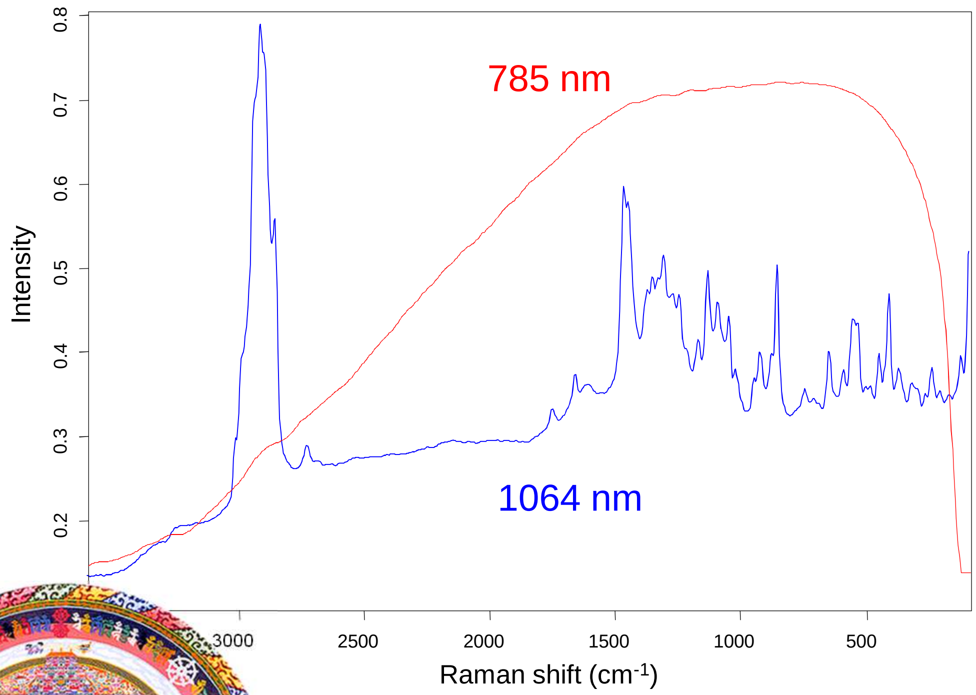
- Remarks:

❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



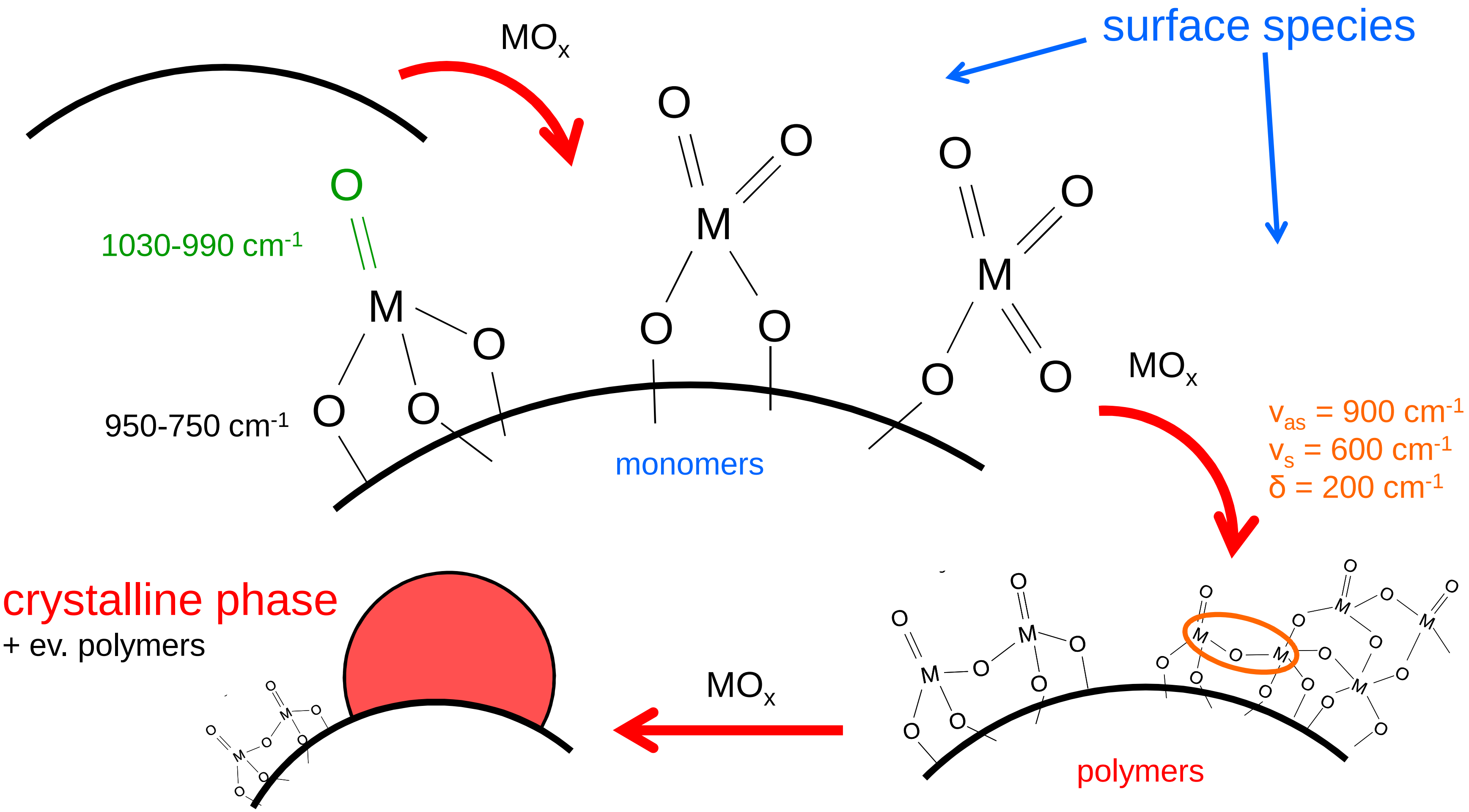
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species

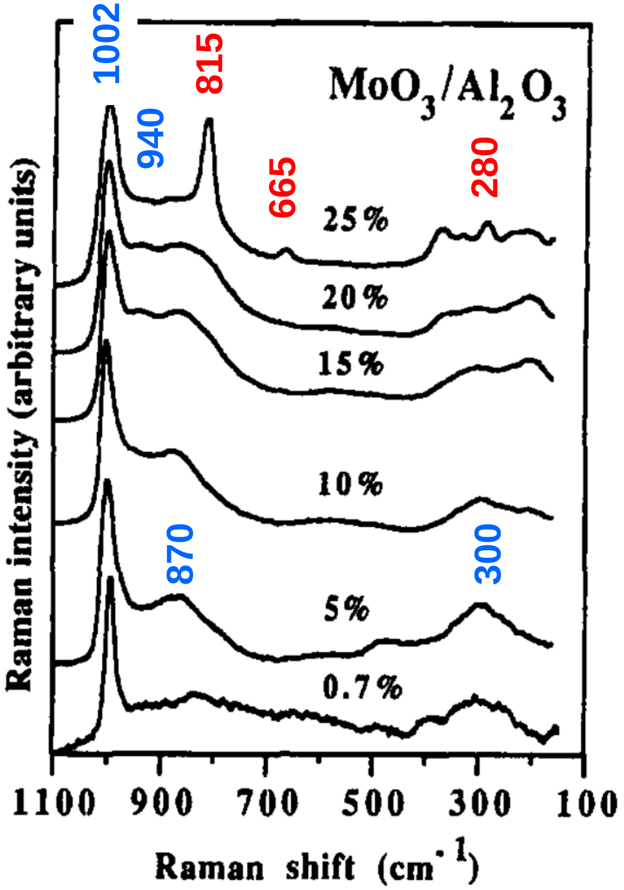


Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



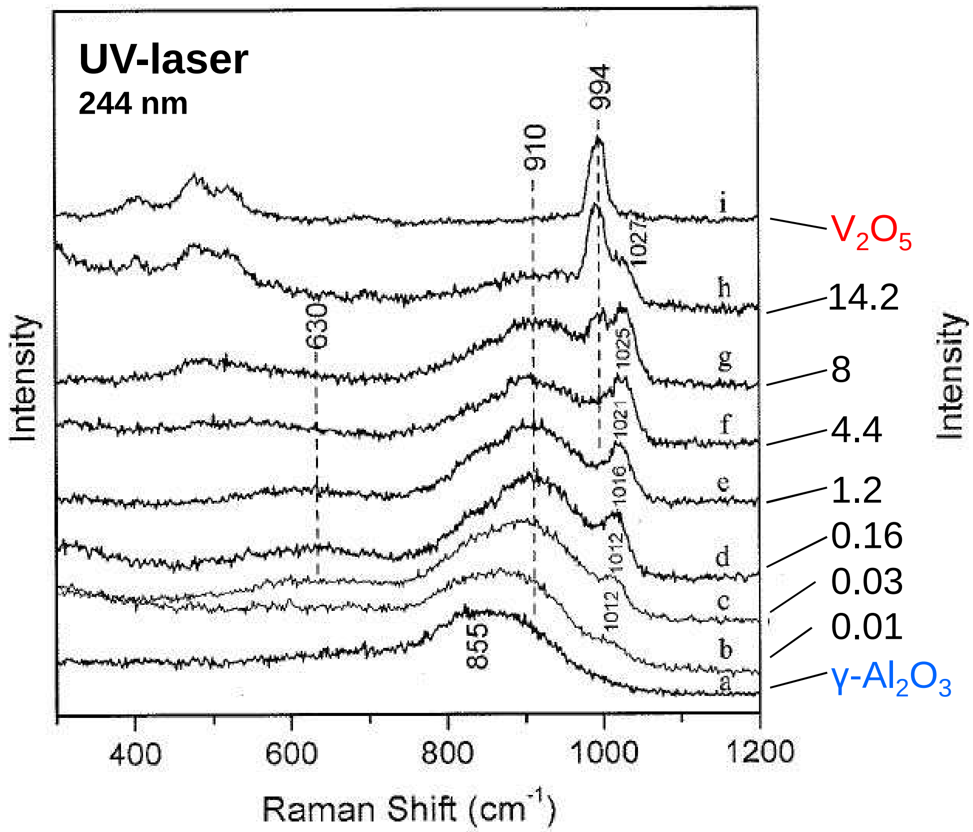
surface MoO_3
crystalline MoO_3

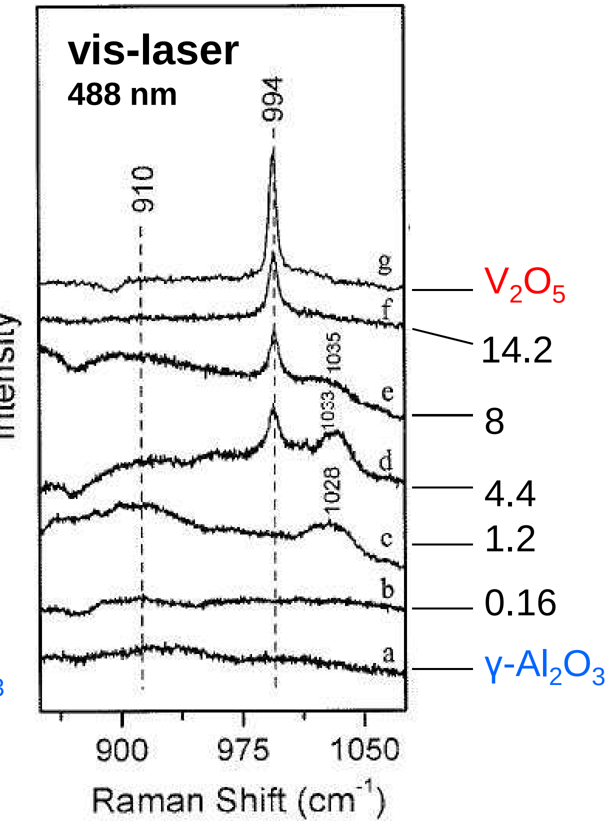
MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

- Monomeric & polymeric species

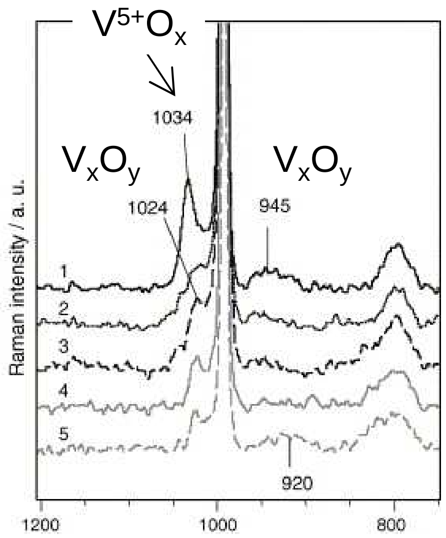




Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

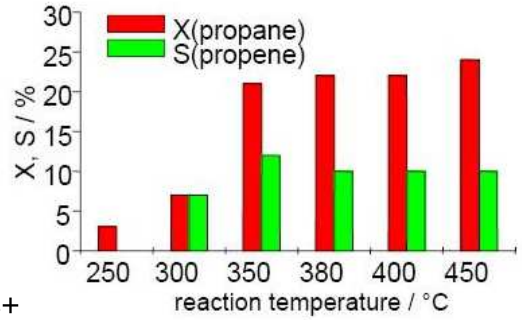
Applications

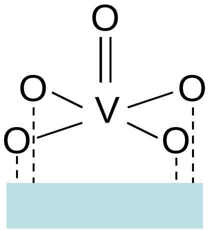
- Reactivity of V/TiO_2 after oxidative treatment

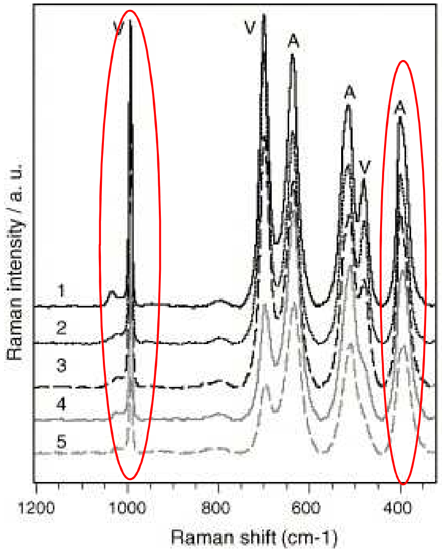


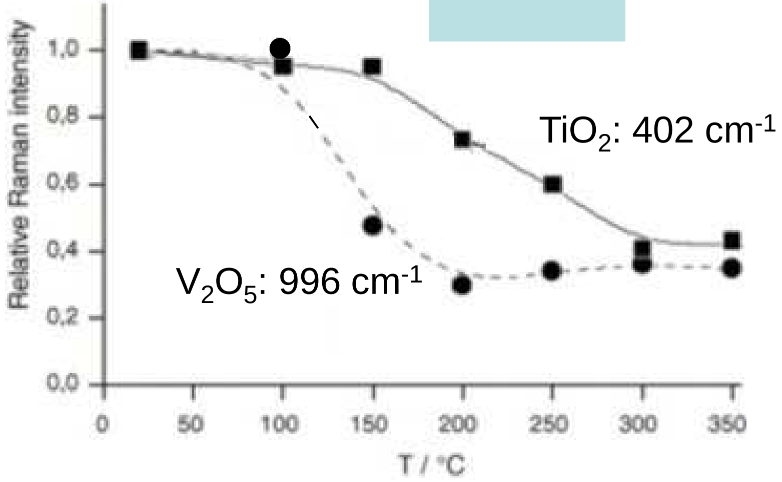
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

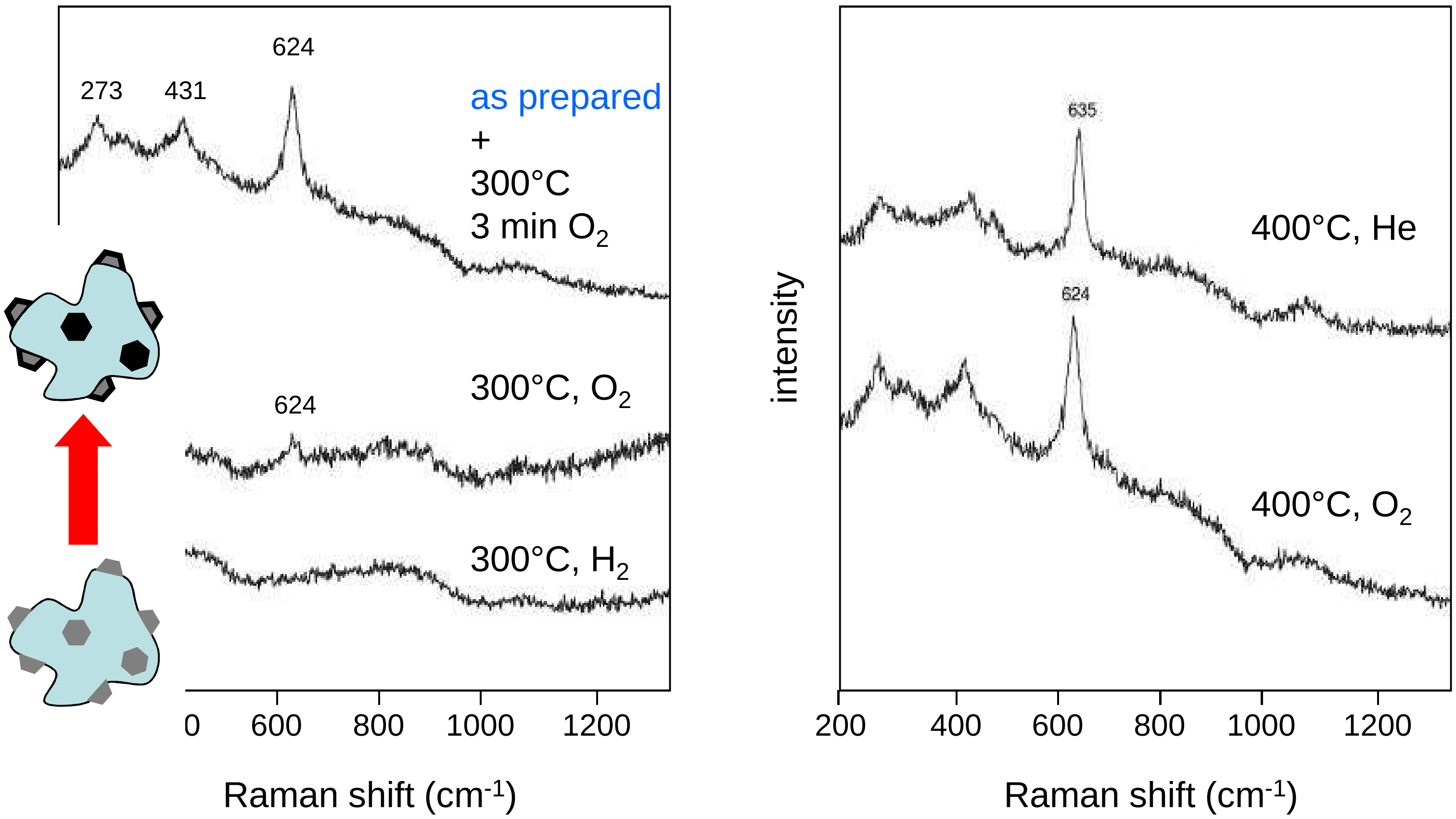
M/MO$_X$ (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



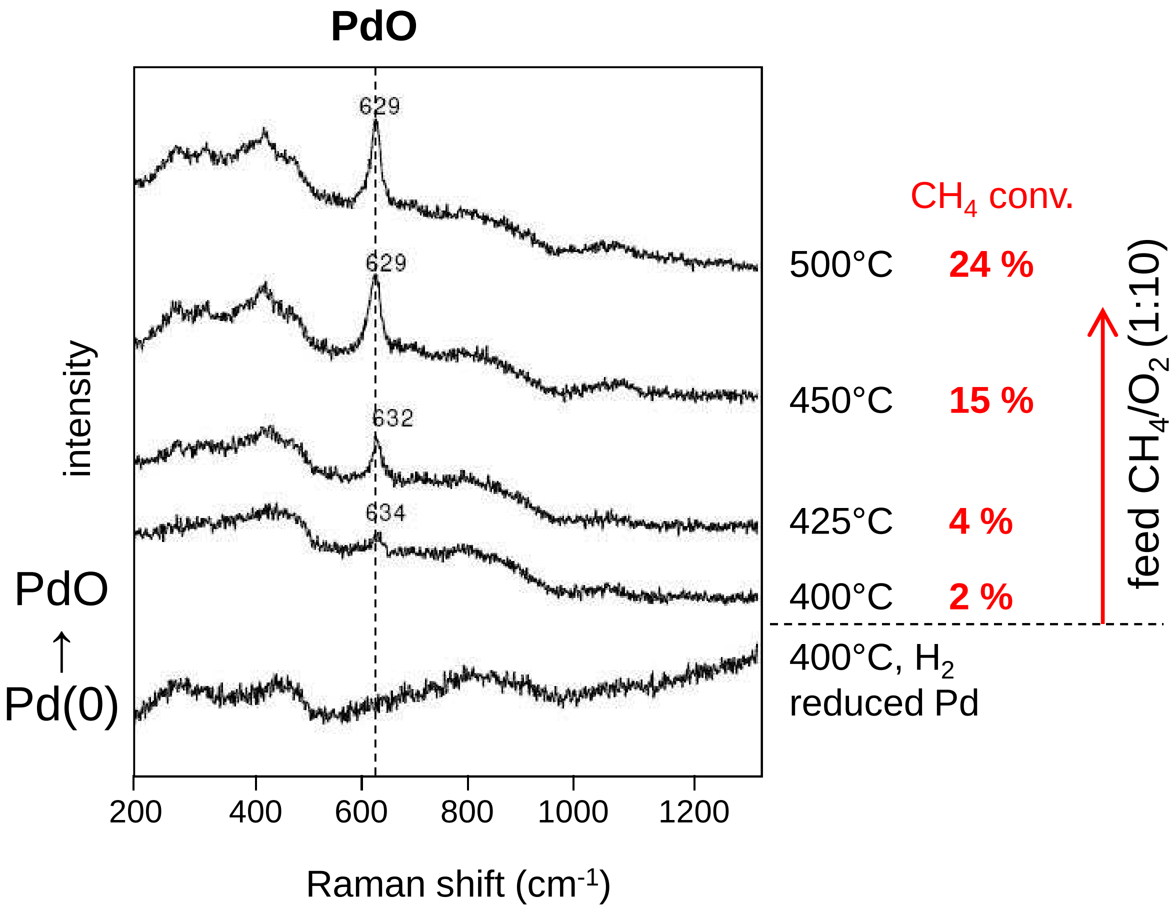
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

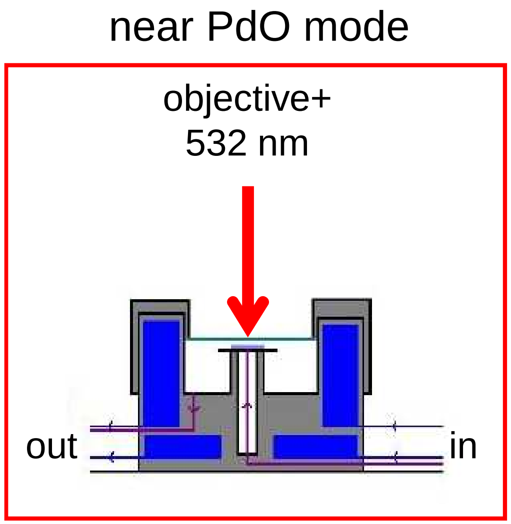
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

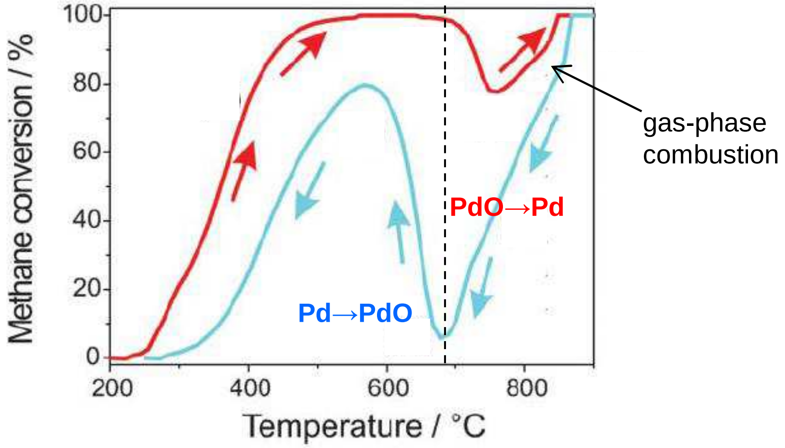


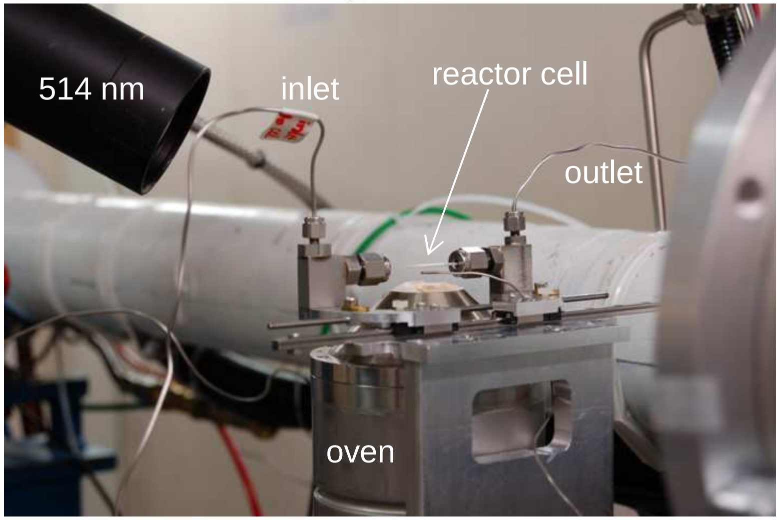


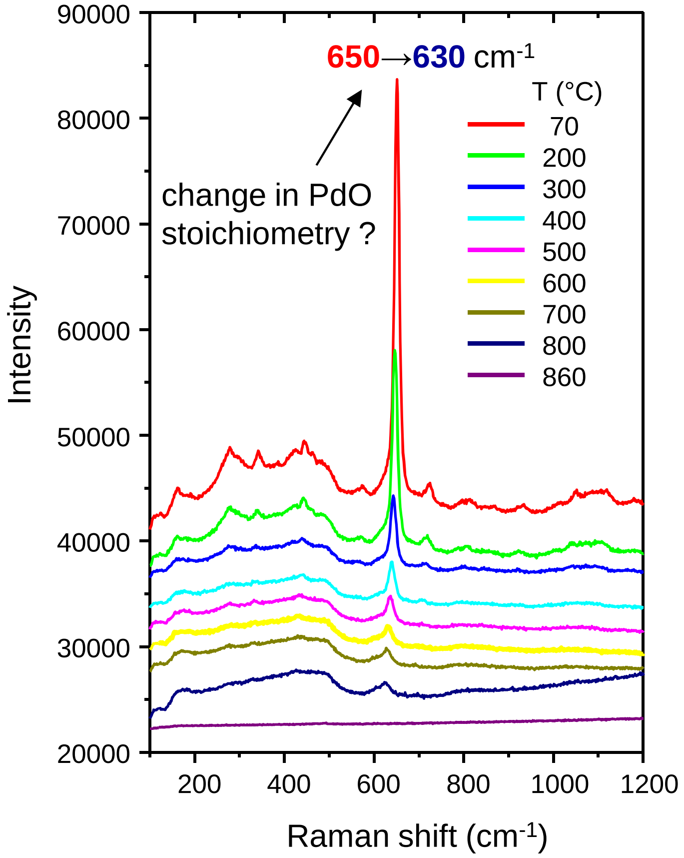
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

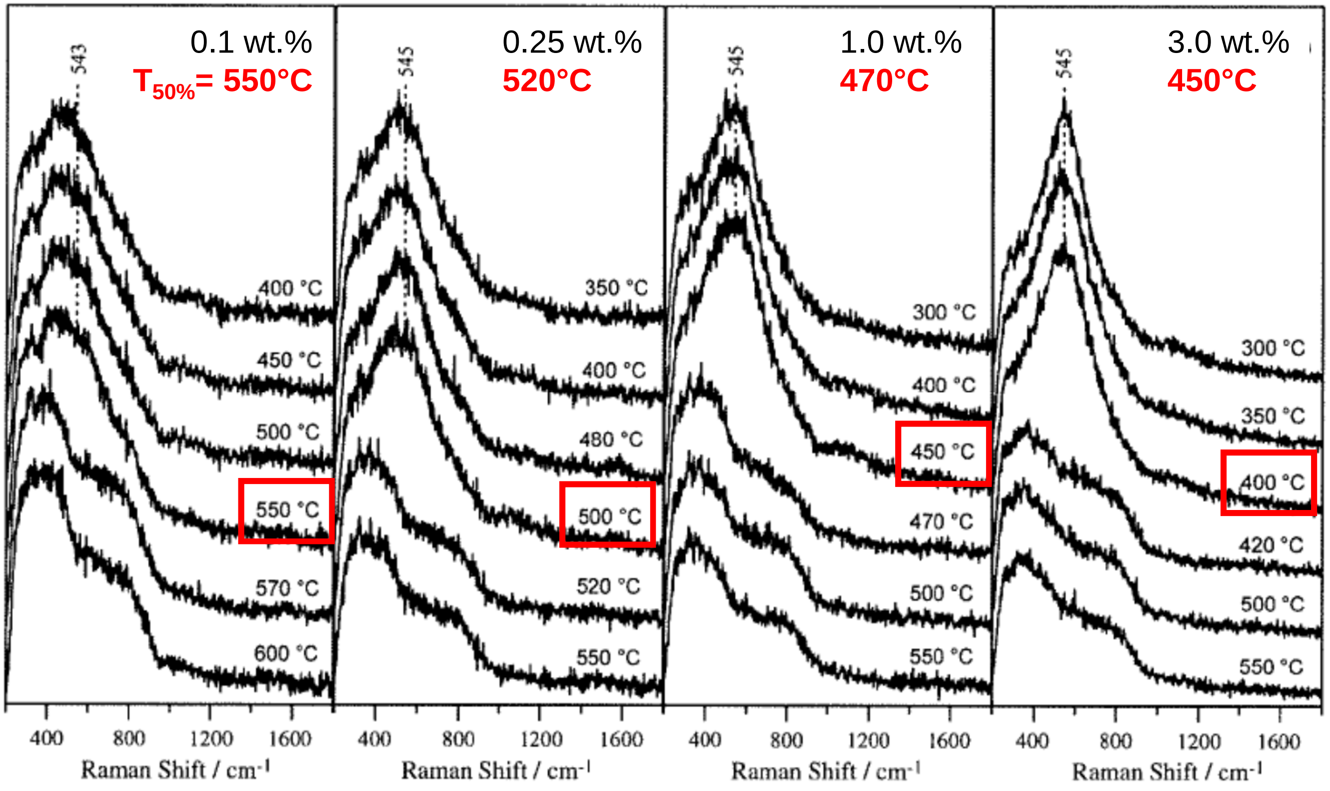
- Methane partial oxidation over Rh/Al_2O_3

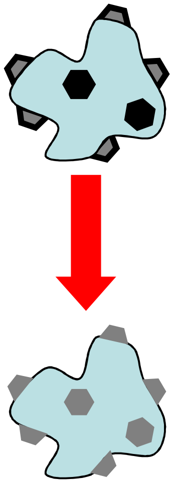
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$


Rh content
Activity

RhOx
↓
Rh(0)





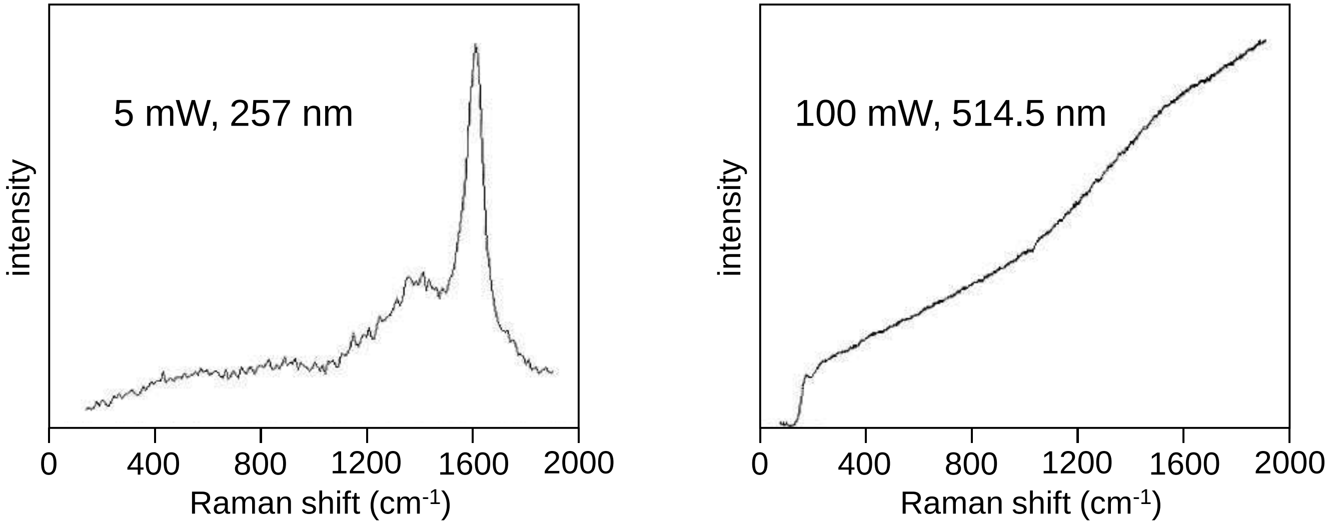
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

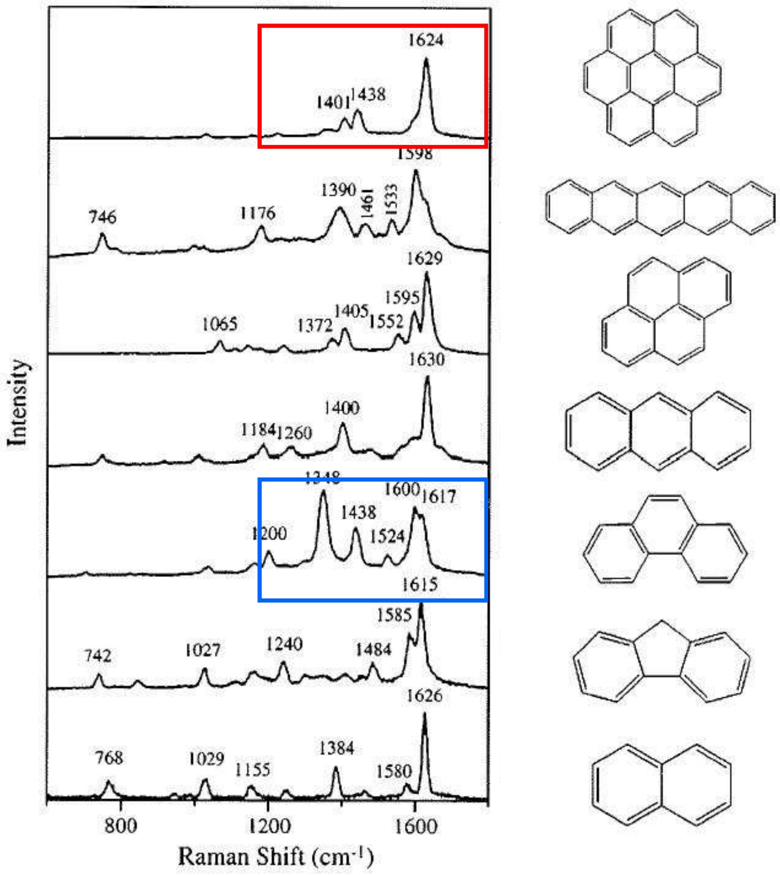
Rh/Al_2O_3, coked 500°C in naphtha

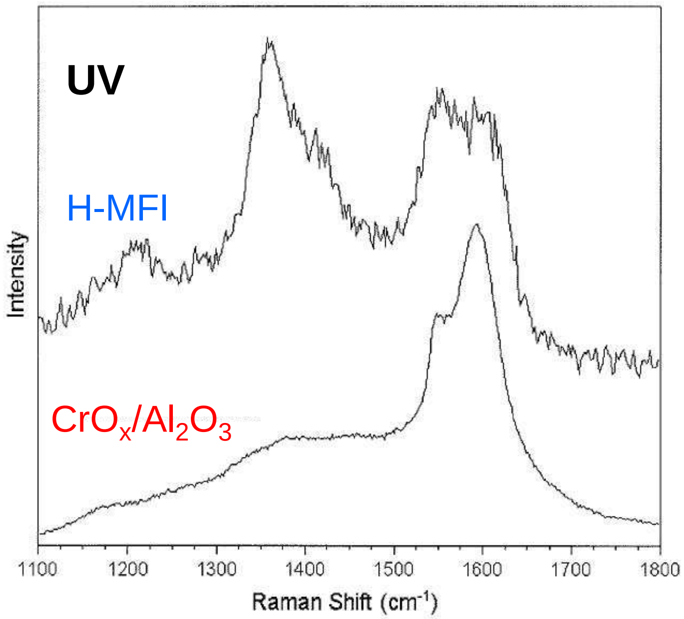


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





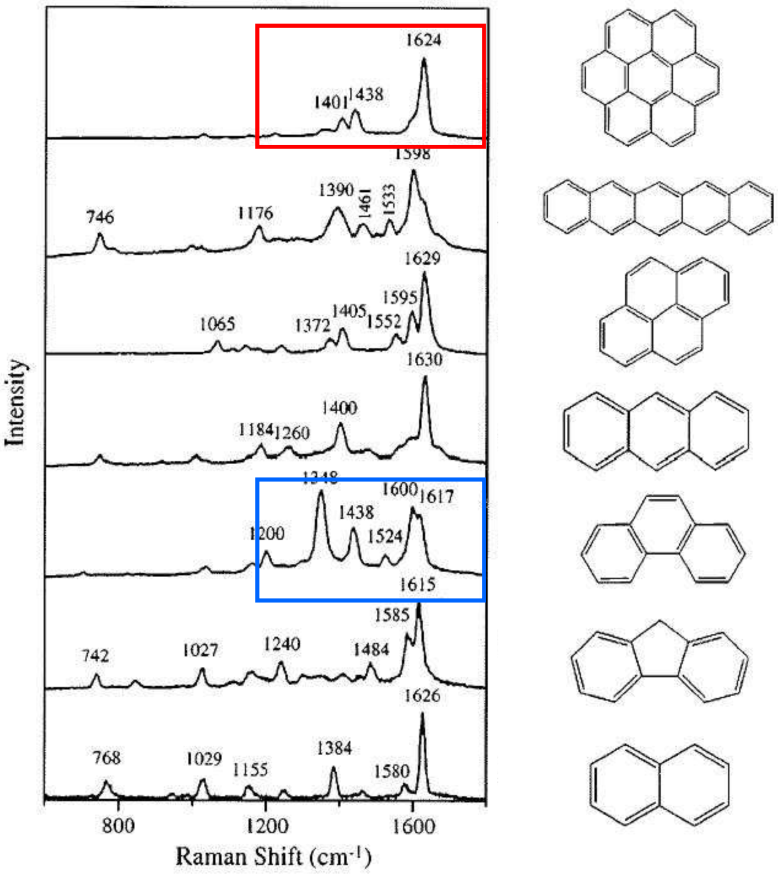
Coke classification
1D topology, chain-like
2D topology, sheet-like

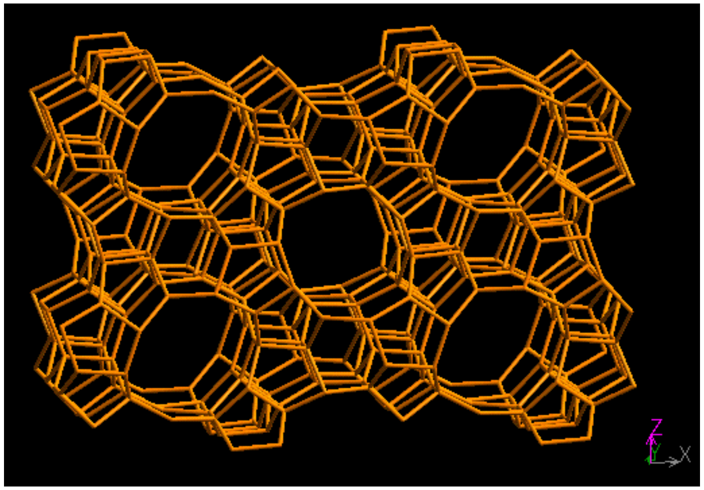
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





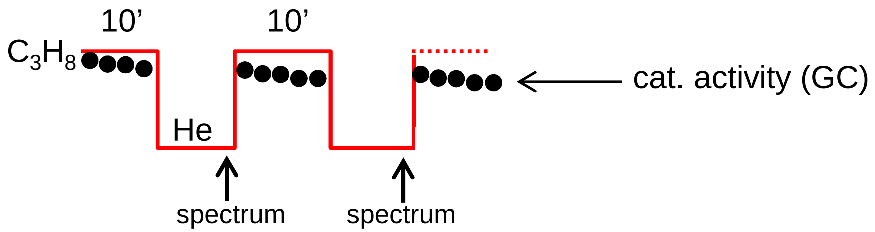
Coke classification
1D topology, chain-like
2D topology, sheet-like

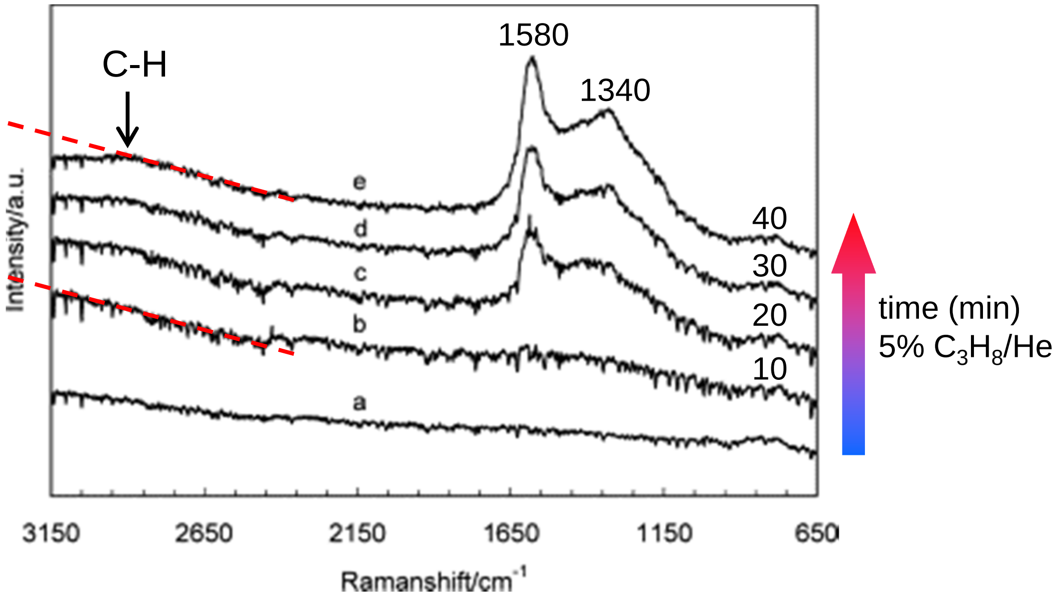
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

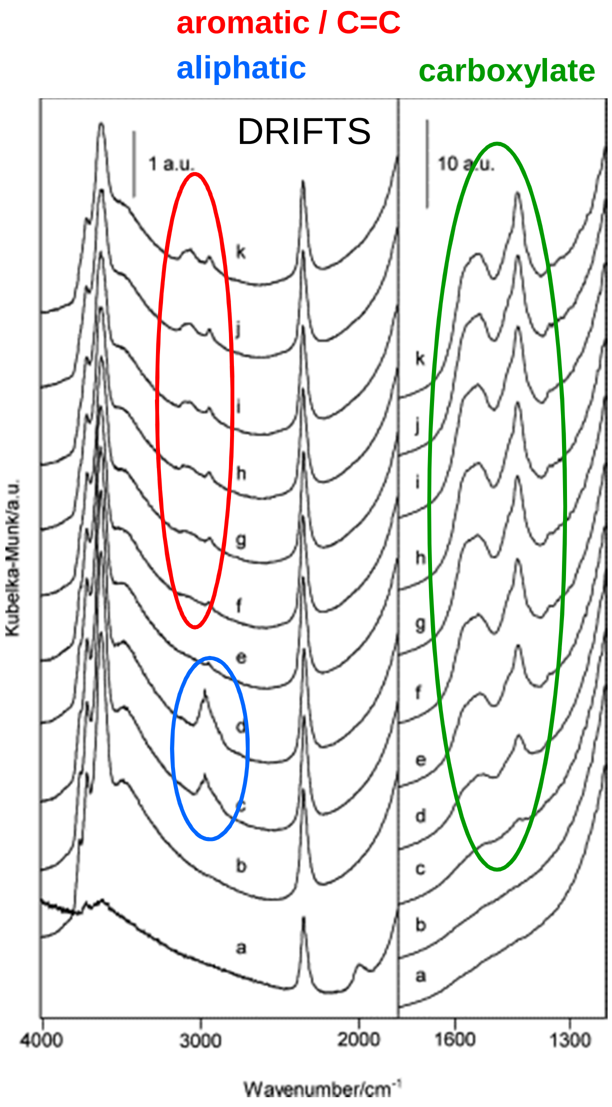
Stair, *Adv. Catal.* **51** (2007) 75

Applications

- Propane dehydrogenation



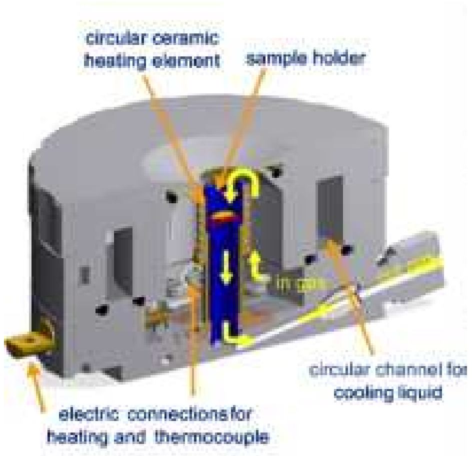

Cr$_2$O$_3$/Al$_2$O$_3$, 580°C, 514 nm

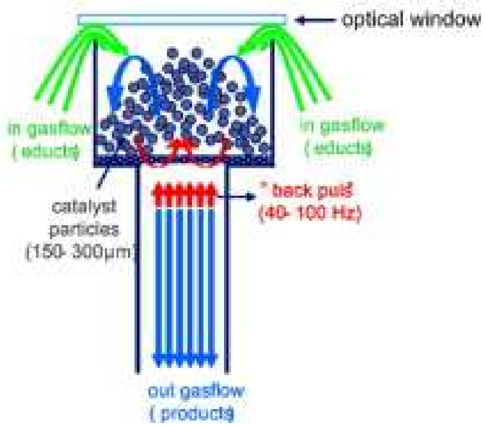


Airaksinen et al., *J. Catal.* **230** (2005) 507

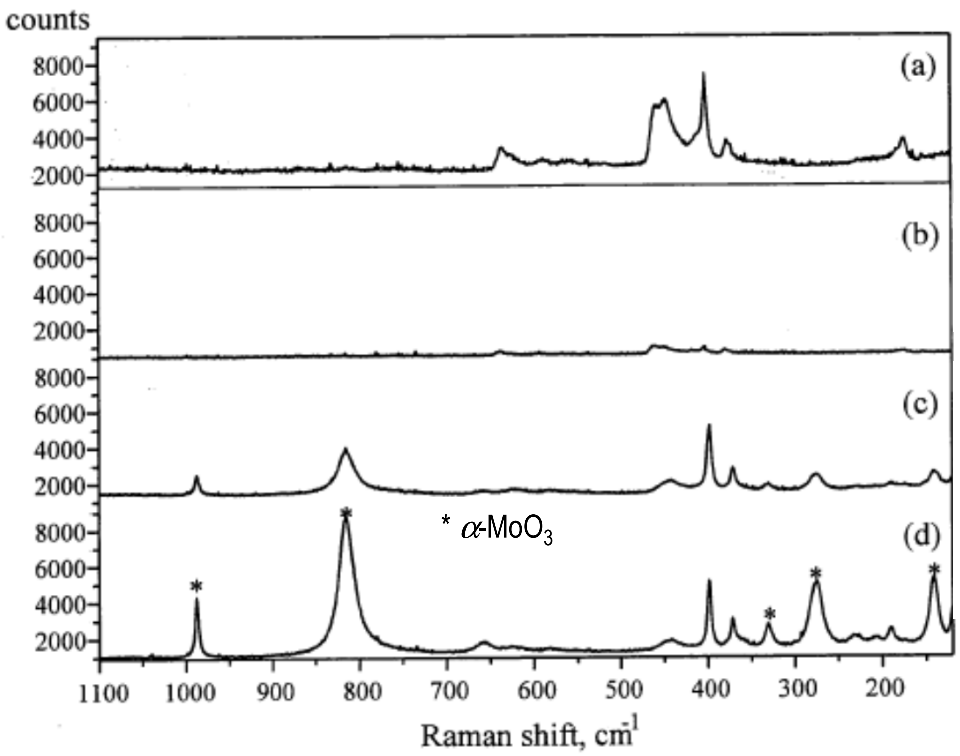
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min
full power, FB

MoS_2, 6 min
1/8 power

MoS_2, 1 min
full power

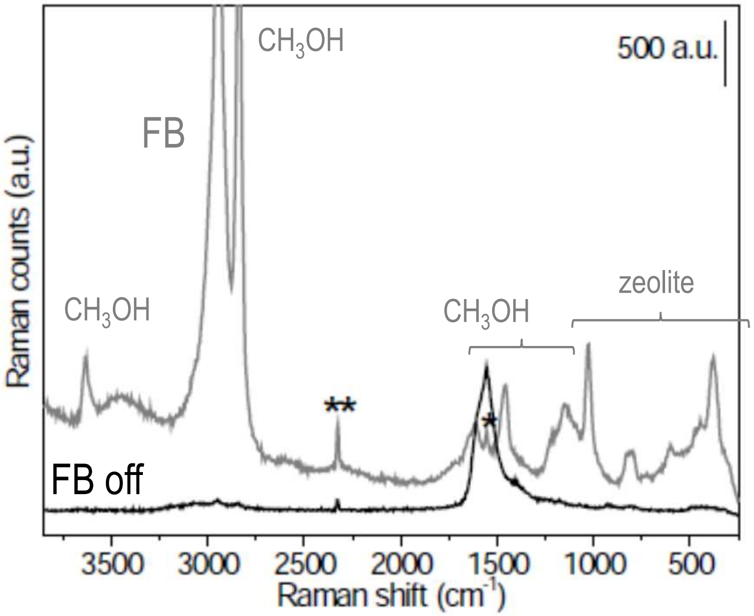
MoS_2, 6 min
full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

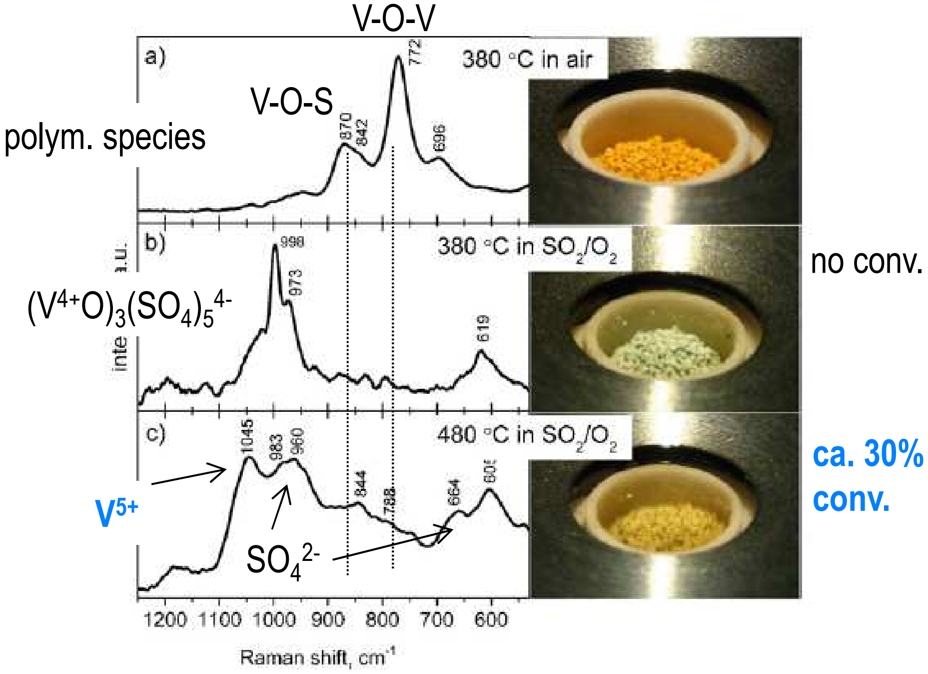
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

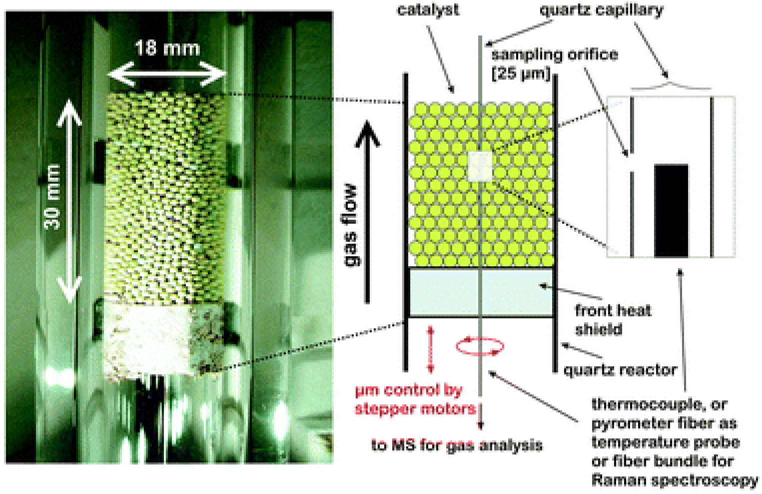


active species: mono- & dimeric V^{5+} oxosulfate species

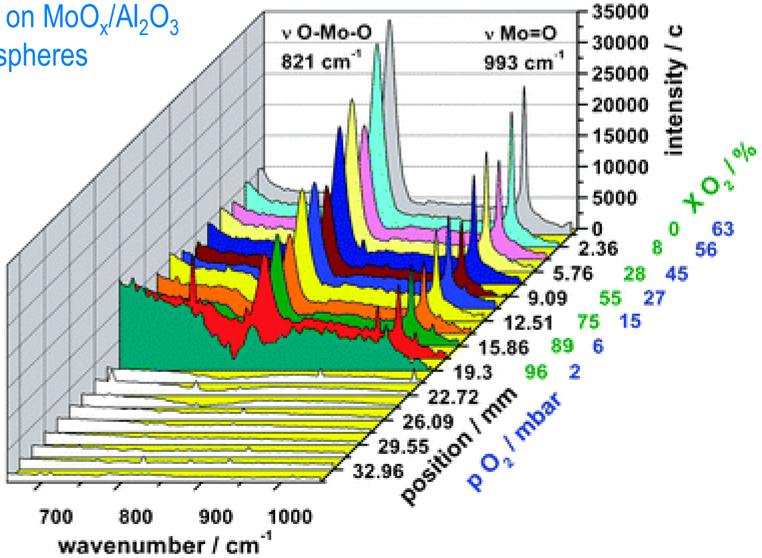
Beato et al., *Catal. Today* 205 (2013) 128

Applications

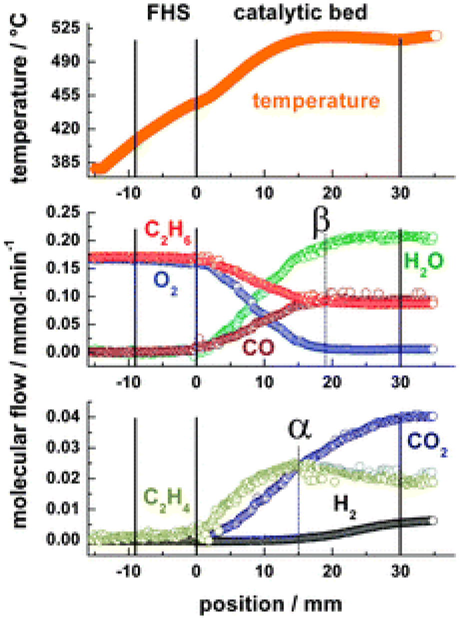
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

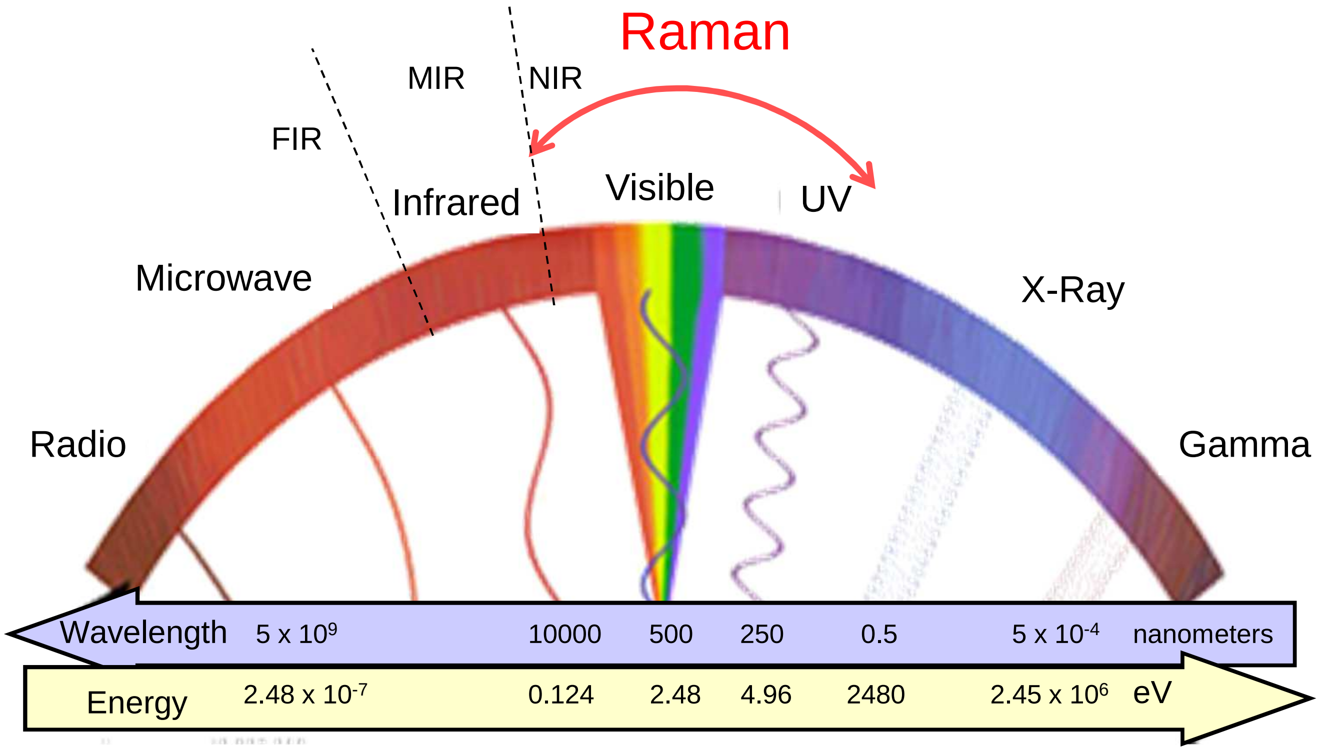
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

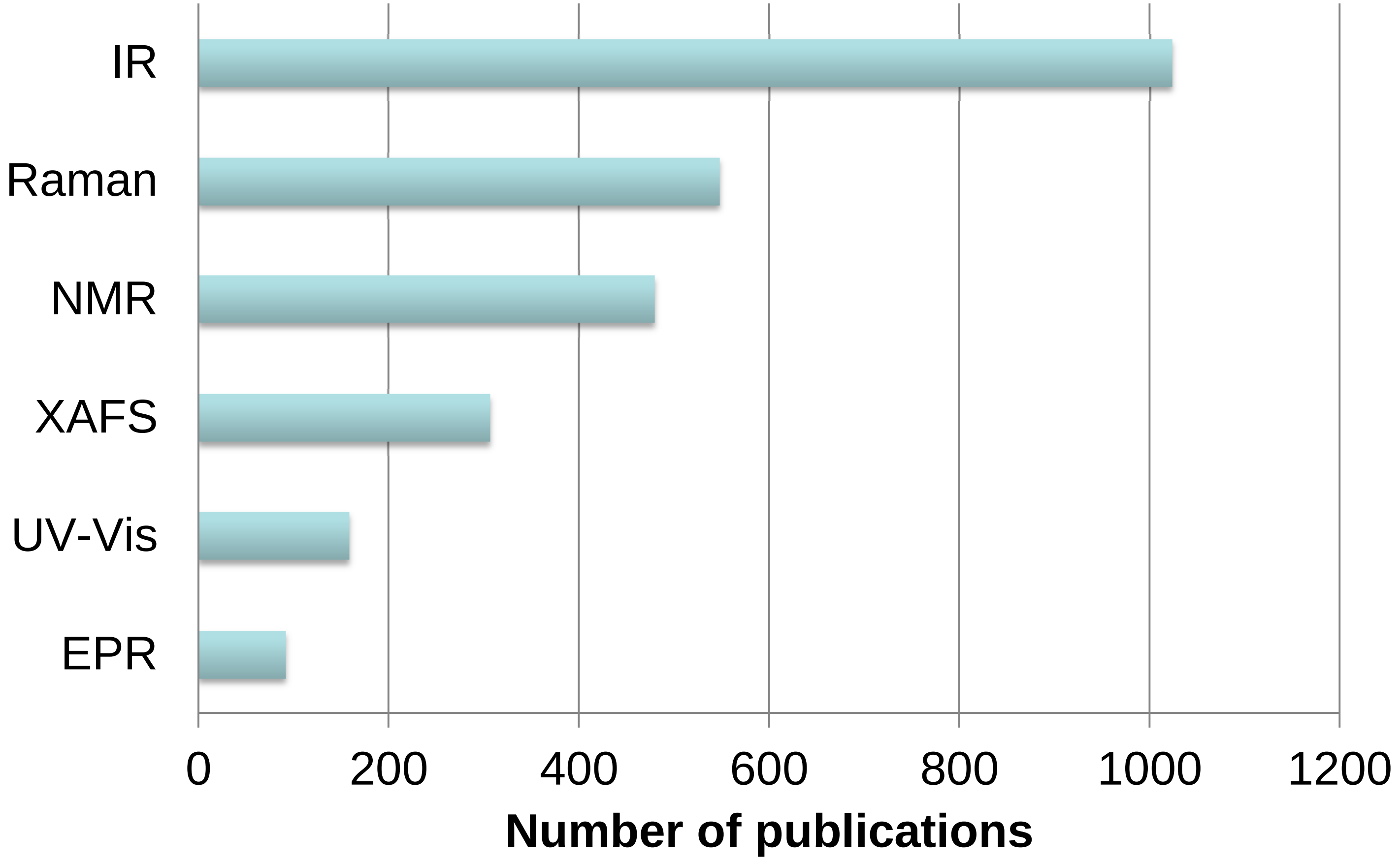
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

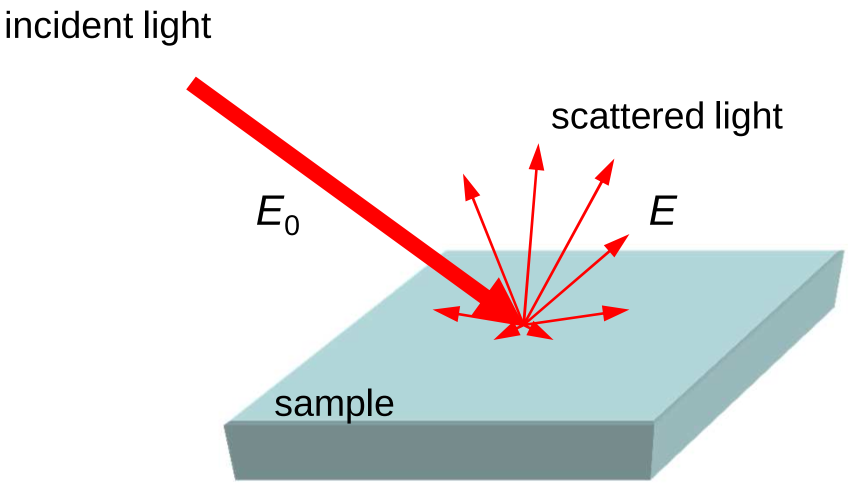


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$E_{vib} = E_0 - E$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

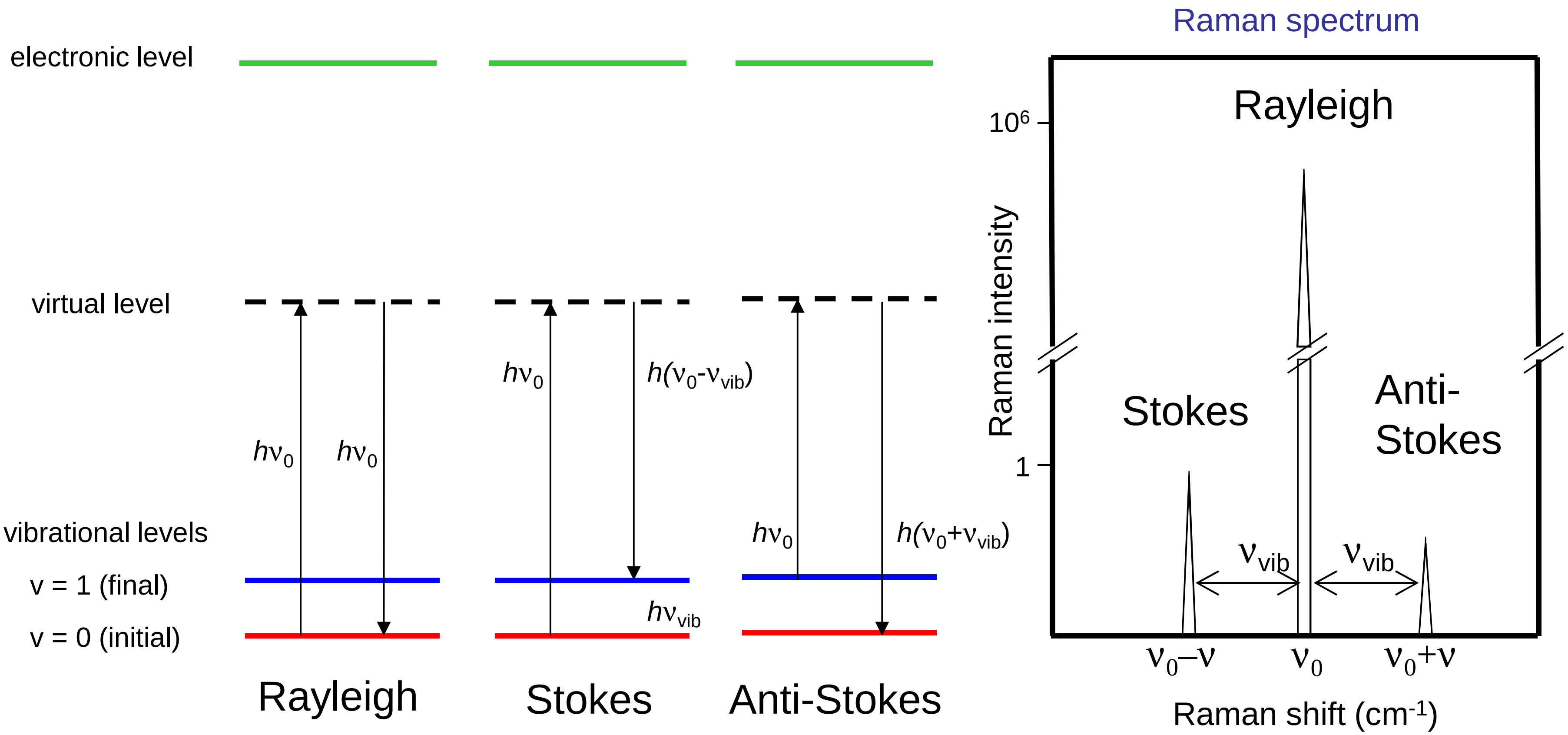
$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

$$\text{and}\quad \boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\text{ (Anti-Stokes)}}{I\text{ (Stokes)}} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:
  - 4th power of ν (4th power law)
  - 2nd power of $\Delta\alpha$

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

- properties of molecules
- strength of bonds

↓

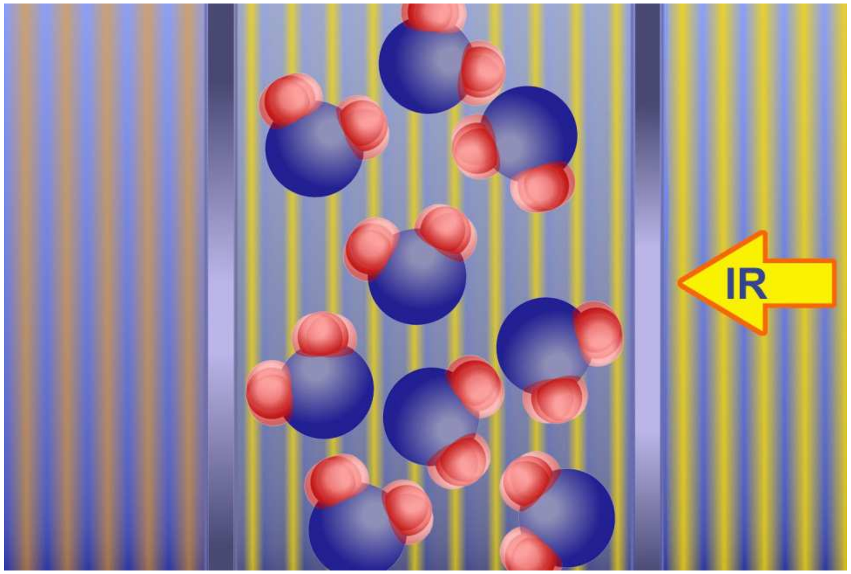
covalent bond STRONG bands (catalysis!)

ionic bond WEAK bands

- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

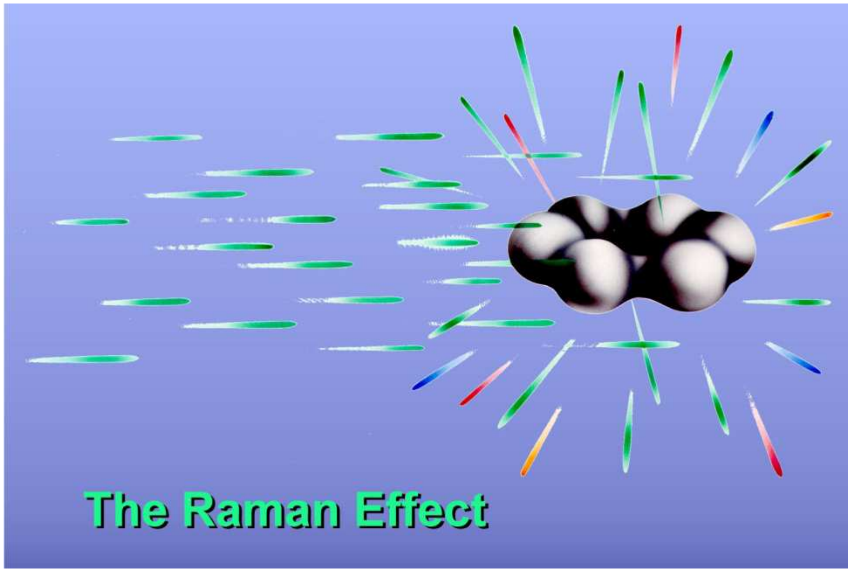
Raman *vs.* Infrared

Infrared



Absorption of IR light

Raman



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

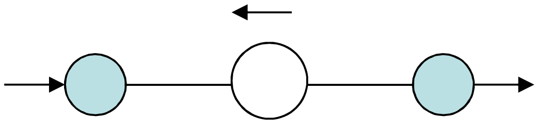
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - ❑ large electron clouds
  - ❑ not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

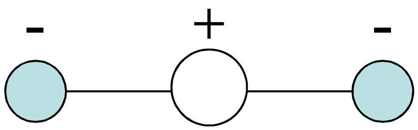
Raman *vs.* Infrared

CO_2



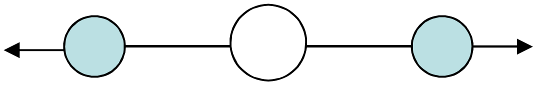
ν_{as}

2349 cm^{-1}



δ

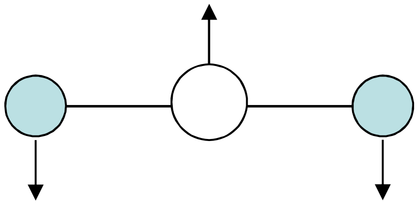
667 cm^{-1}



ν_s

1340 cm^{-1}

Raman active



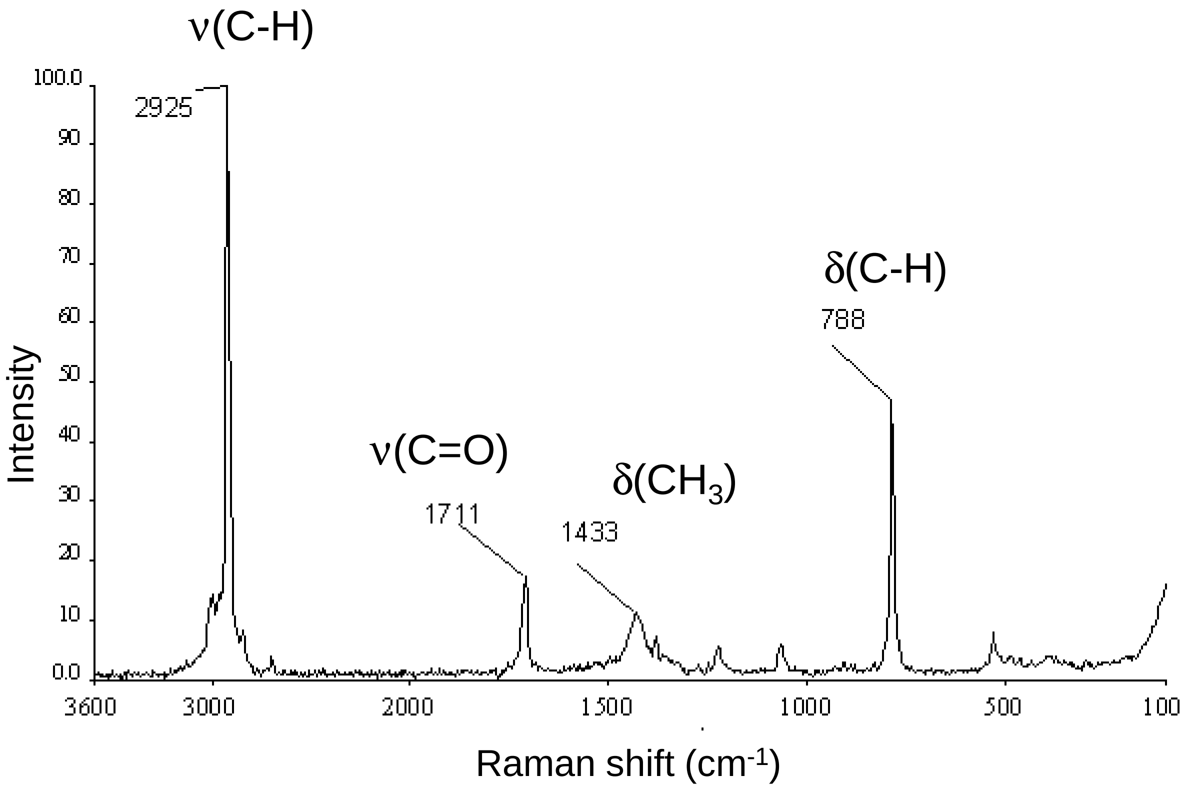
δ

667 cm^{-1}

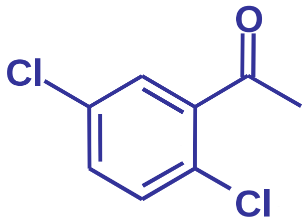
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



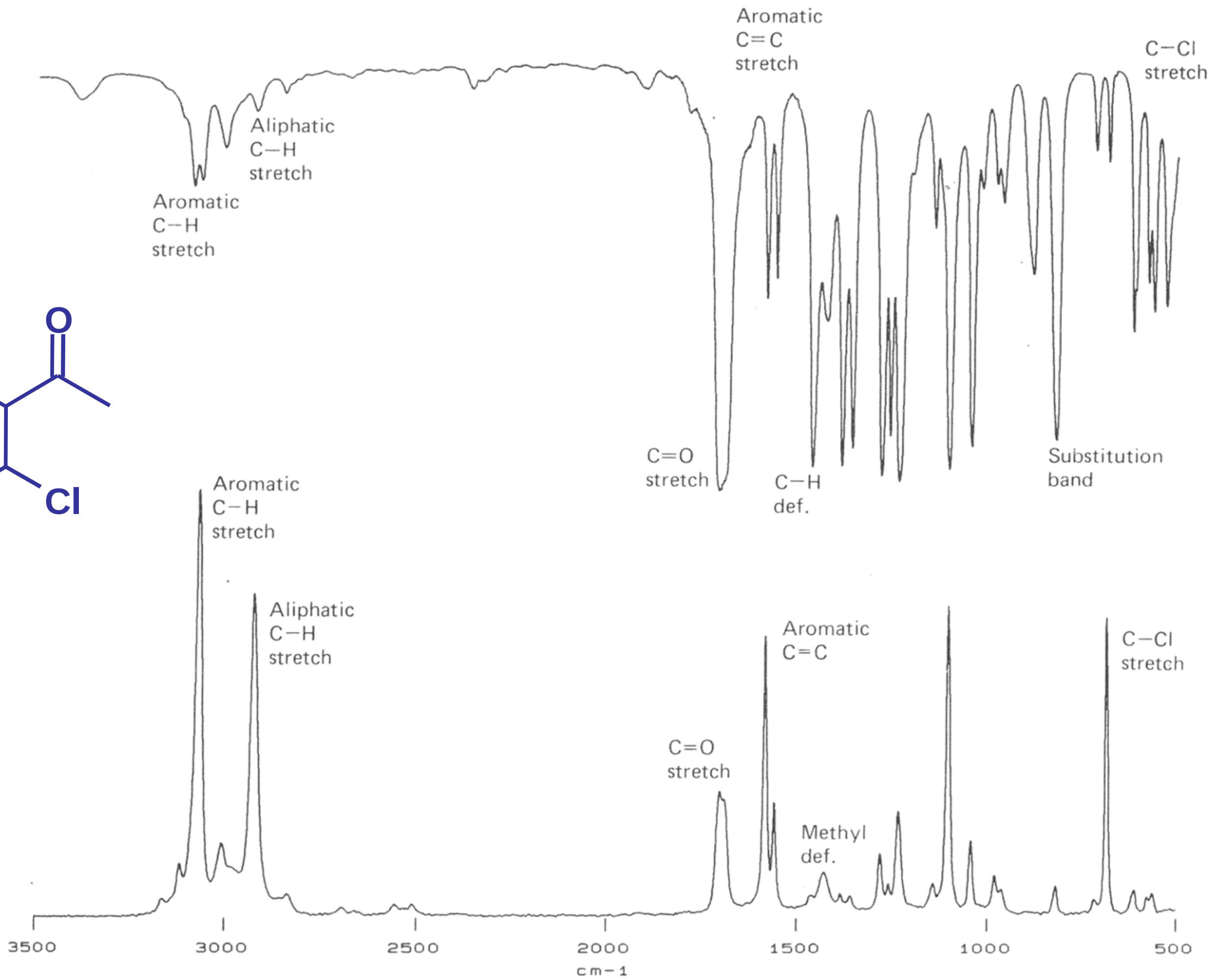


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

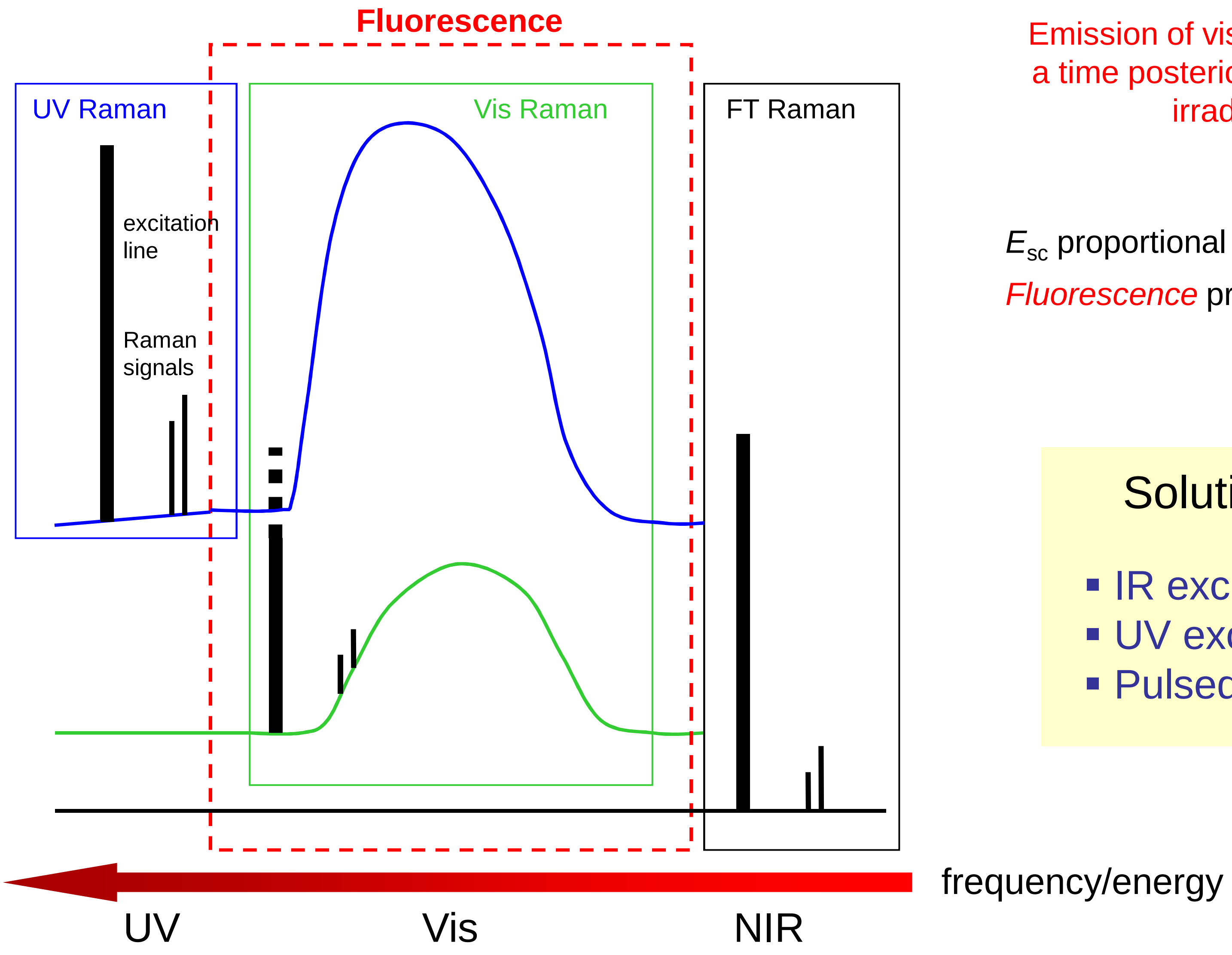
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 μm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during
a time posterior to the sample
irradiation

E_{sc} proportional to ν^4

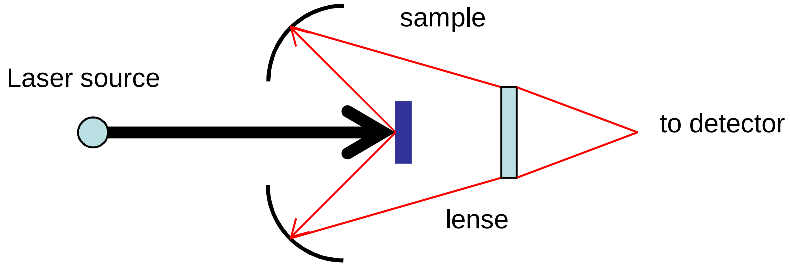
Fluorescence proportional to ν

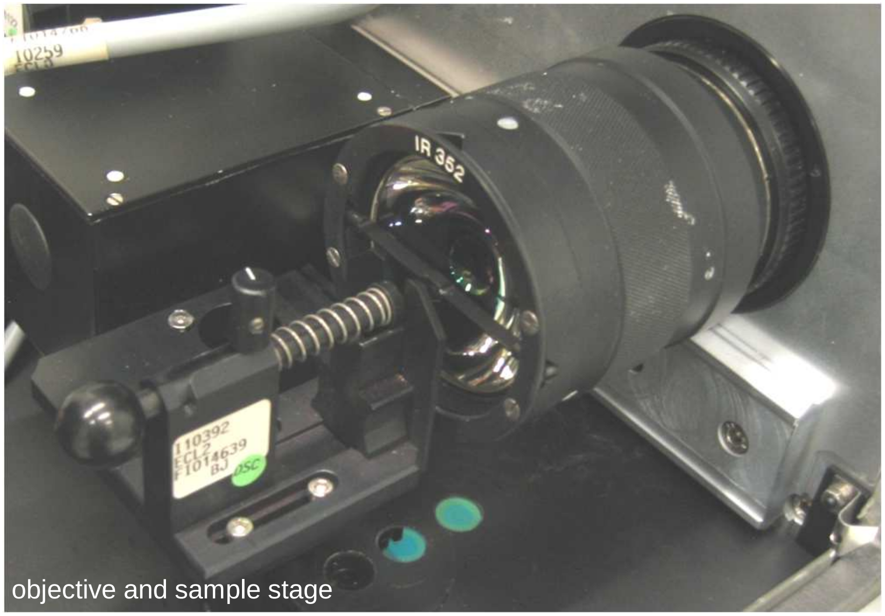
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation




objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

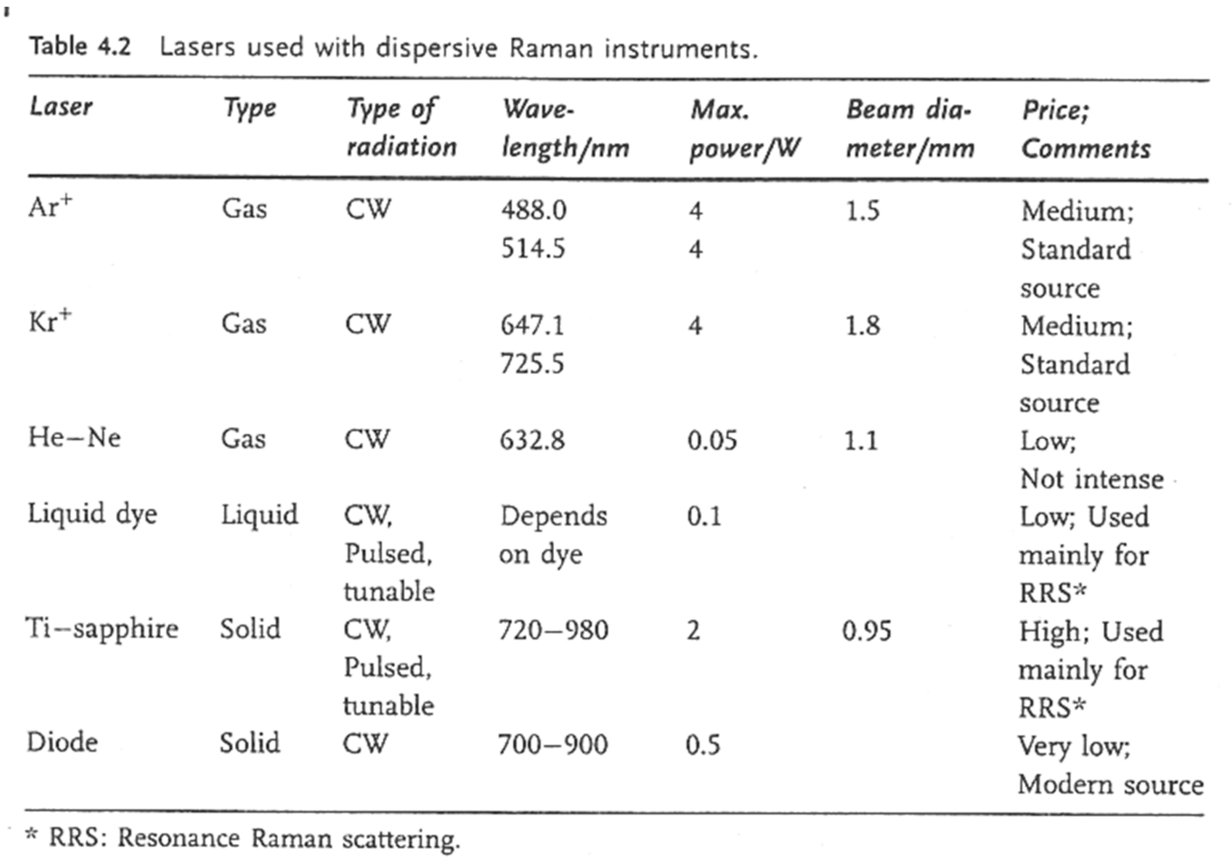


Table 4.2 Lasers used with dispersive Raman instruments.

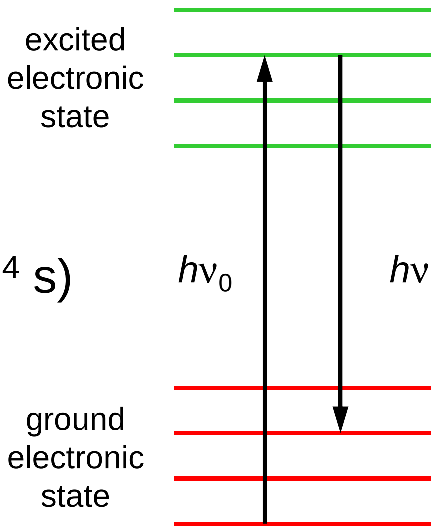
Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

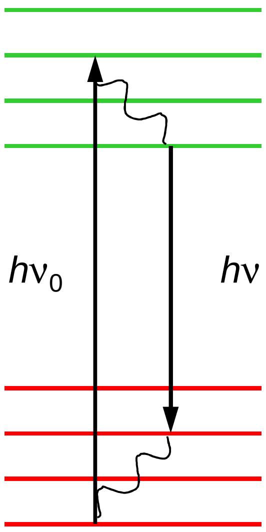
Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited

fast (10^{-14} s)



Resonance Raman scattering



Fluorescence

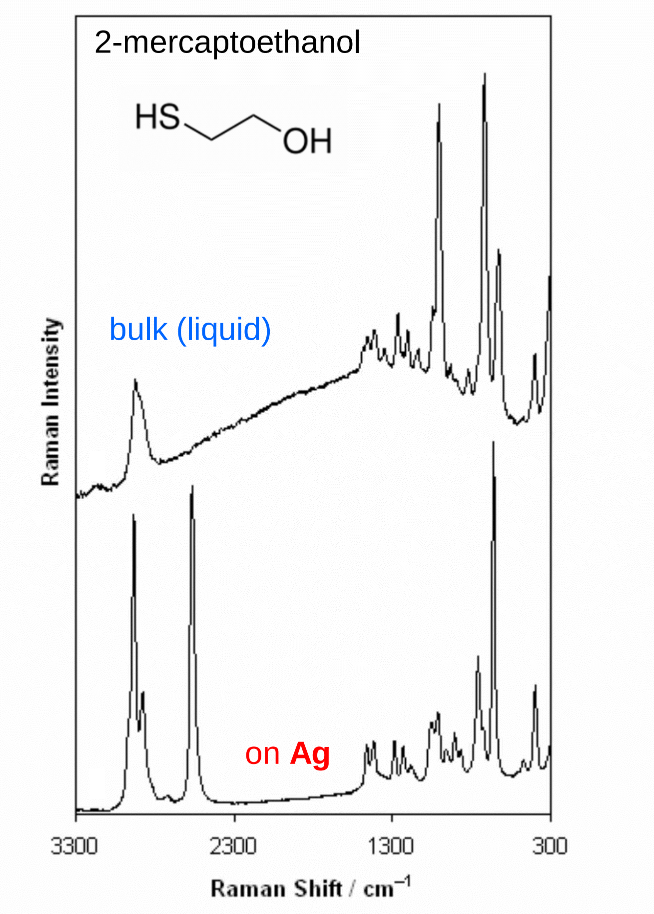
slow (10^{-9}–10^{-6} s)

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu
- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])
- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

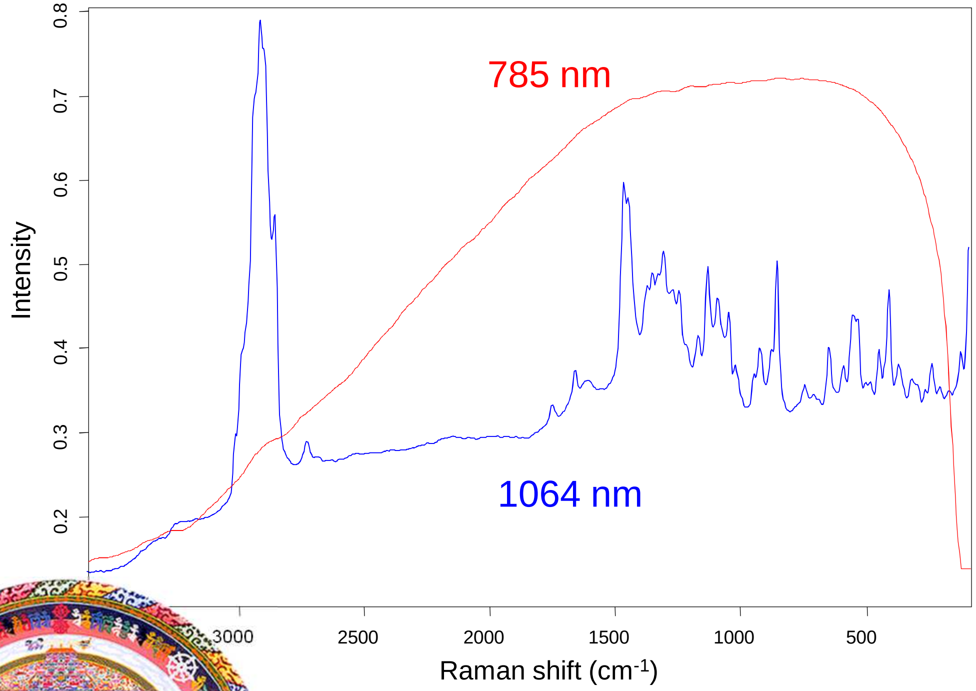
- Remarks:

❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



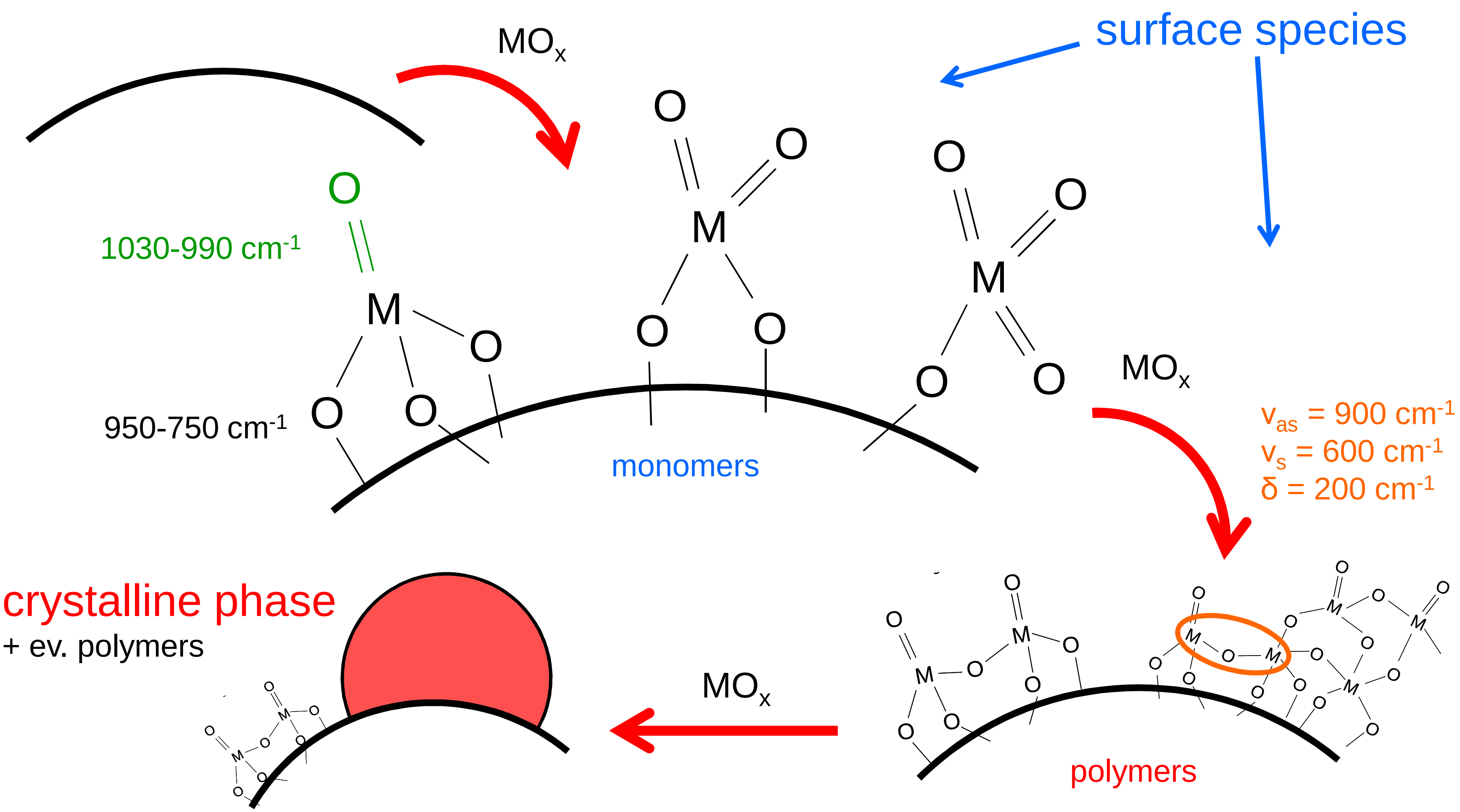
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species

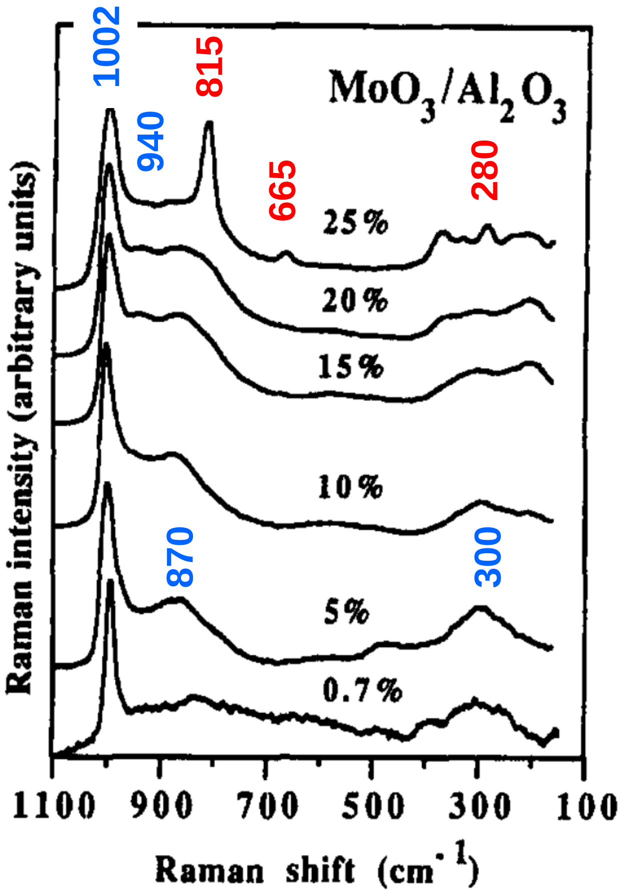


Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



surface MoO_3

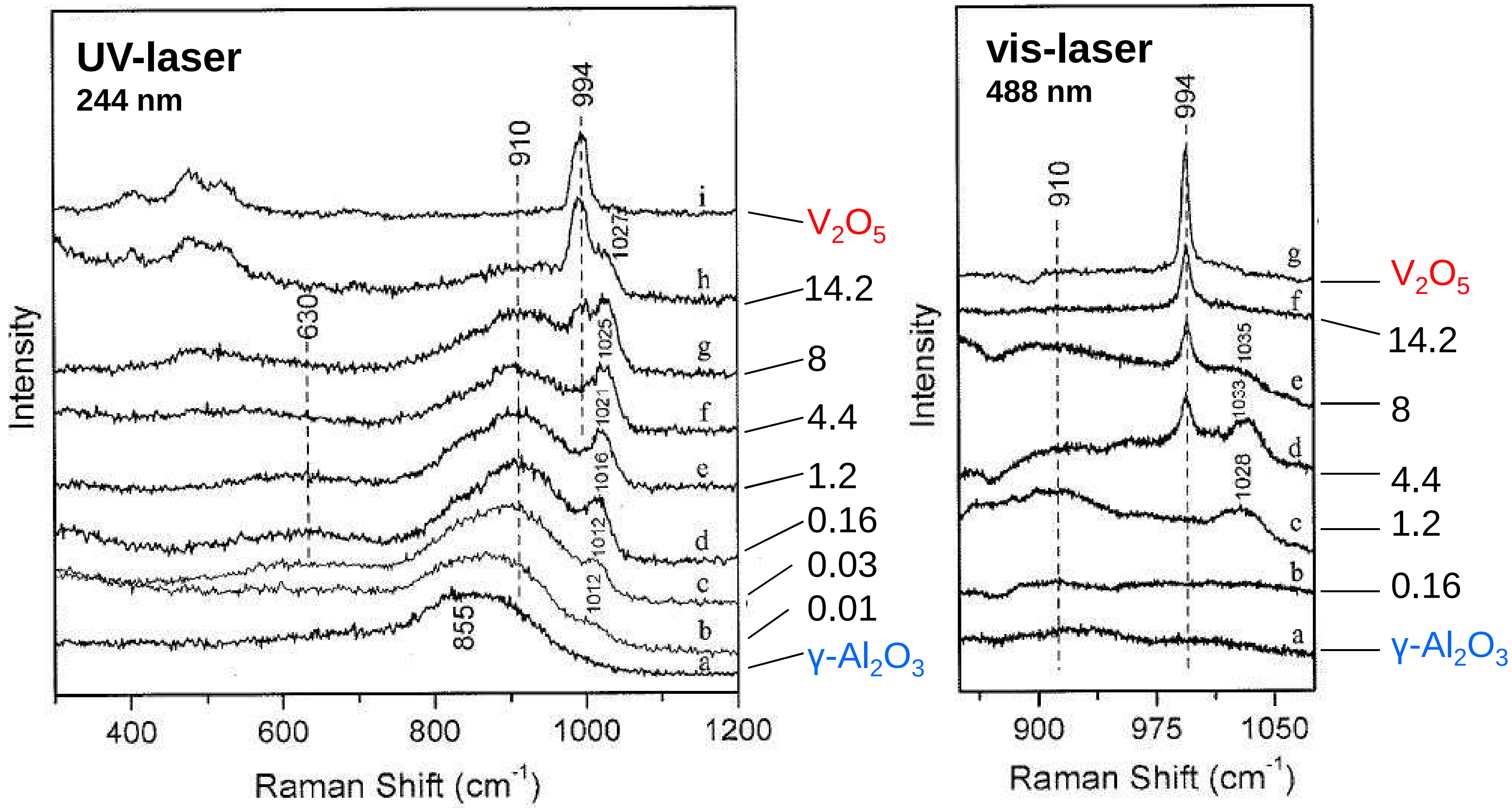
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

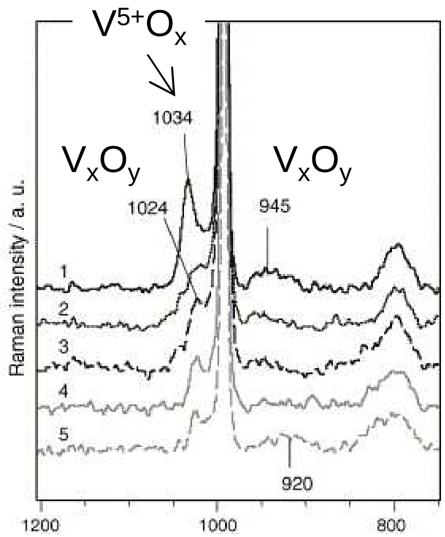
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

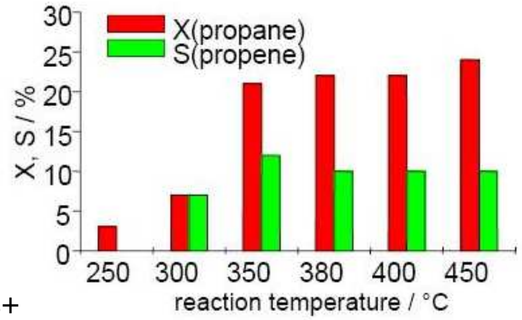
Applications

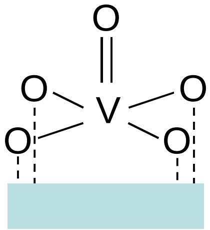
- Reactivity of V/TiO_2 after oxidative treatment

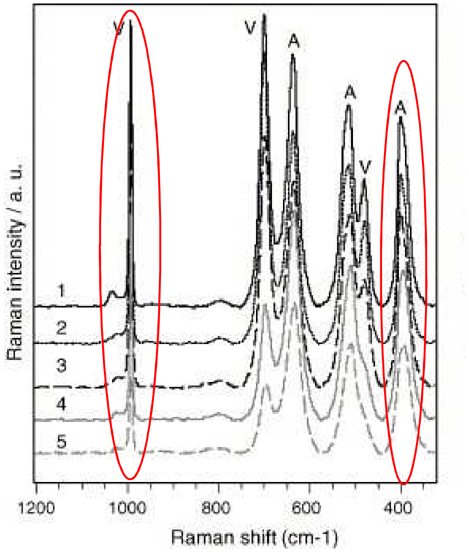


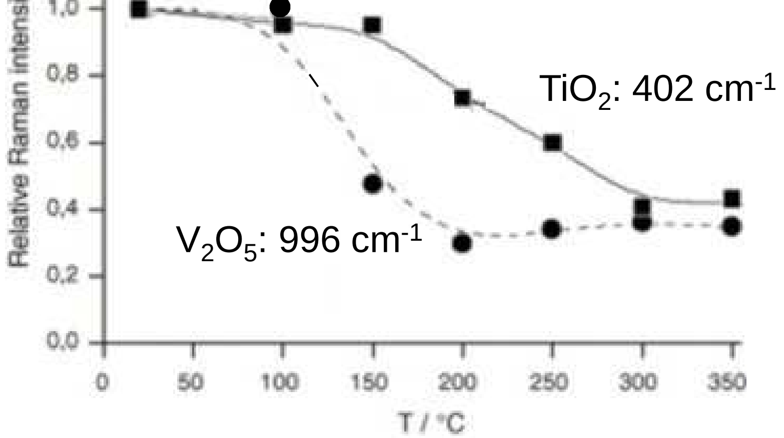
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









TiO_2: 402 cm^{-1}

V_2O_5: 996 cm^{-1}

Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

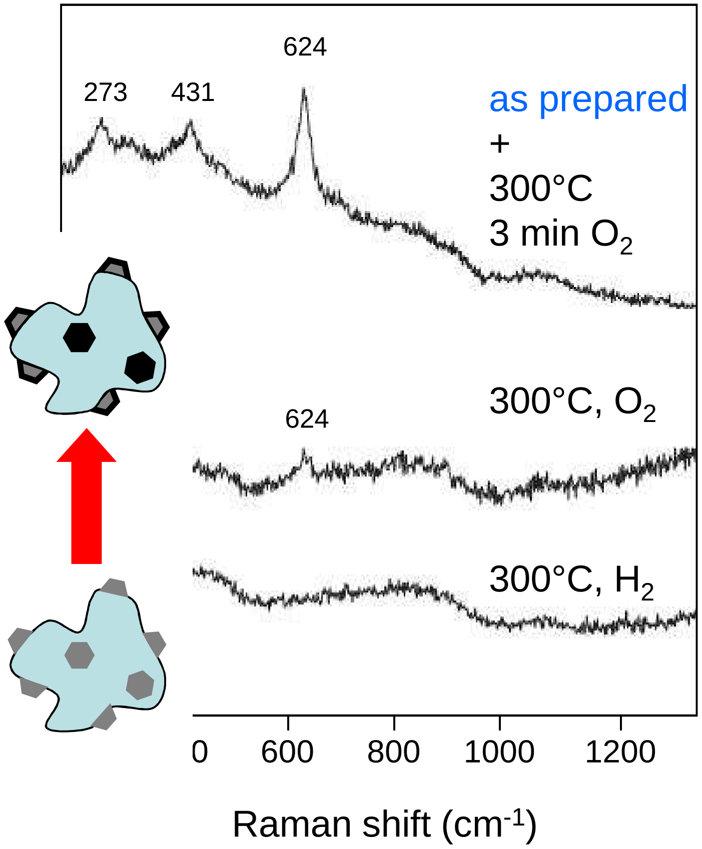
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…) used for total and partial oxidation reactions

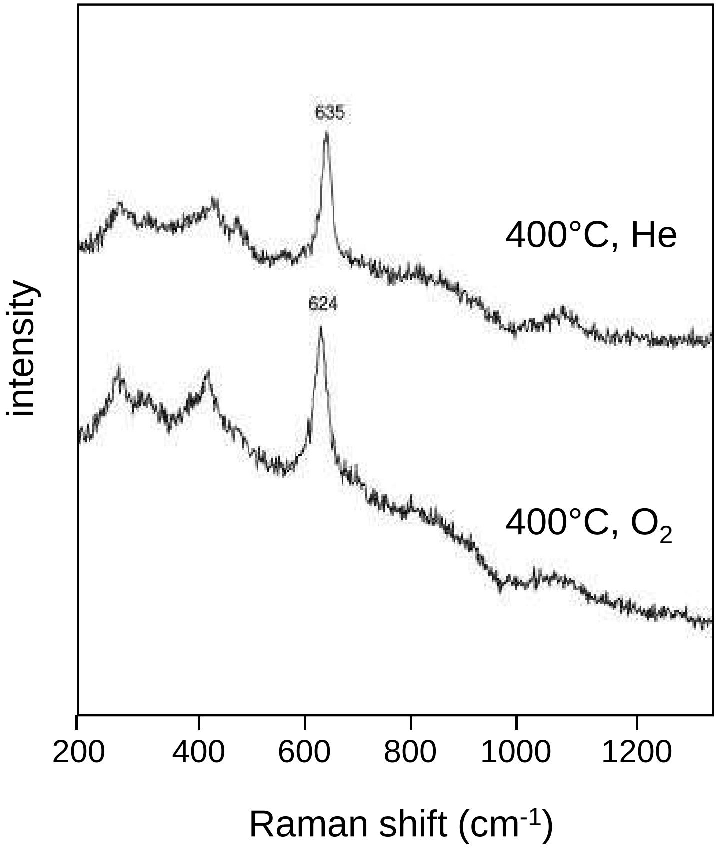
Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3





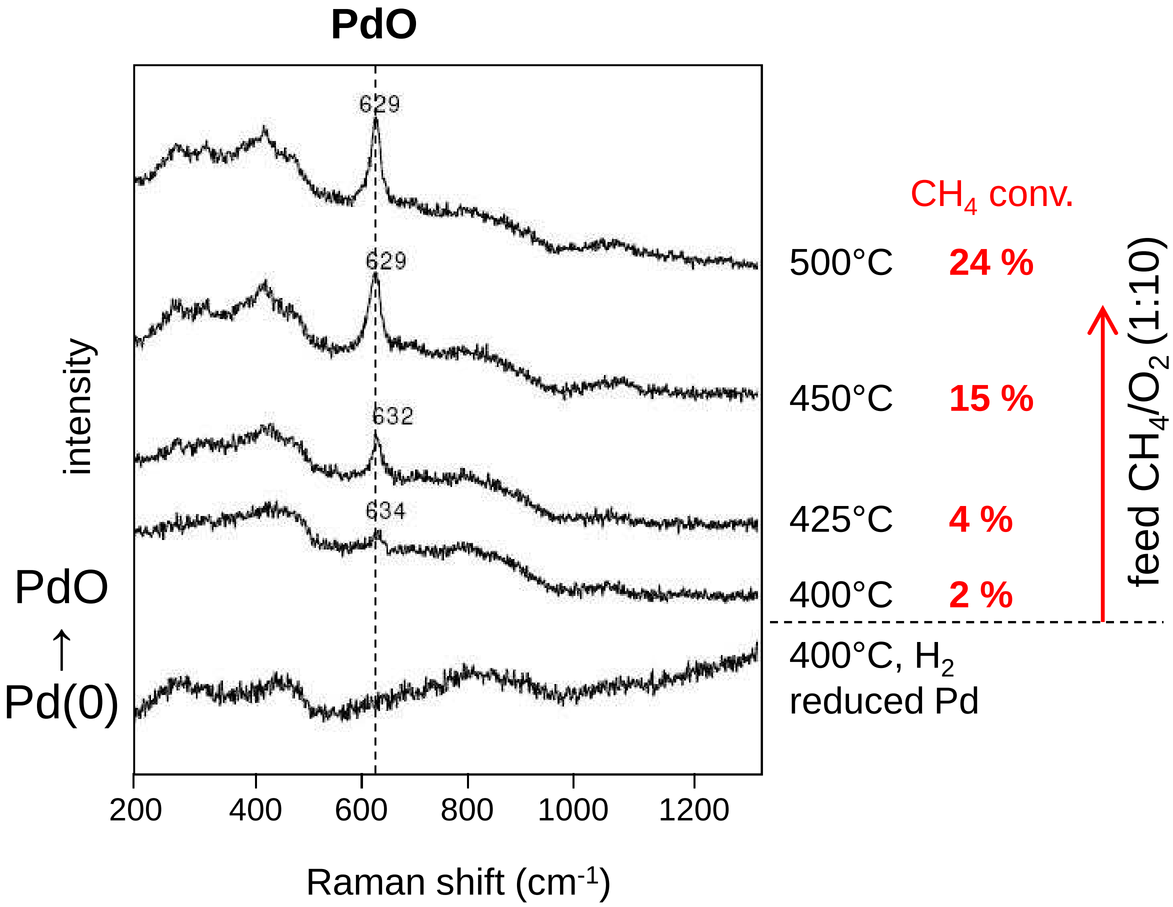
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

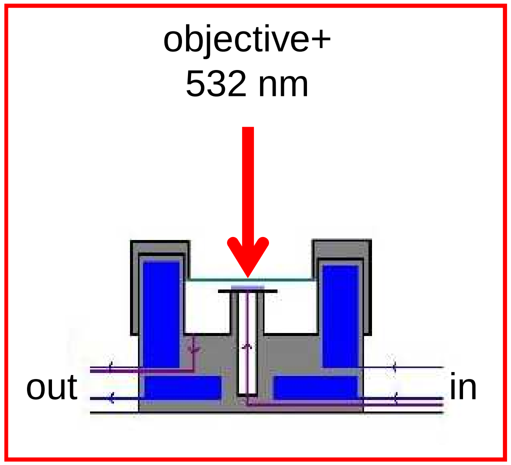
Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



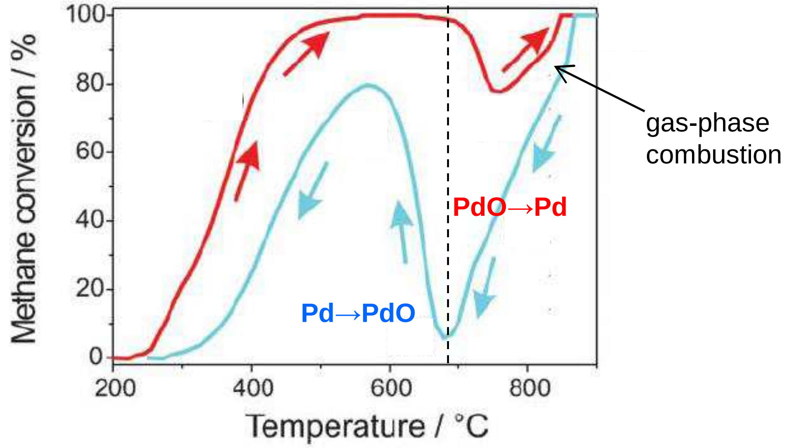
near PdO mode

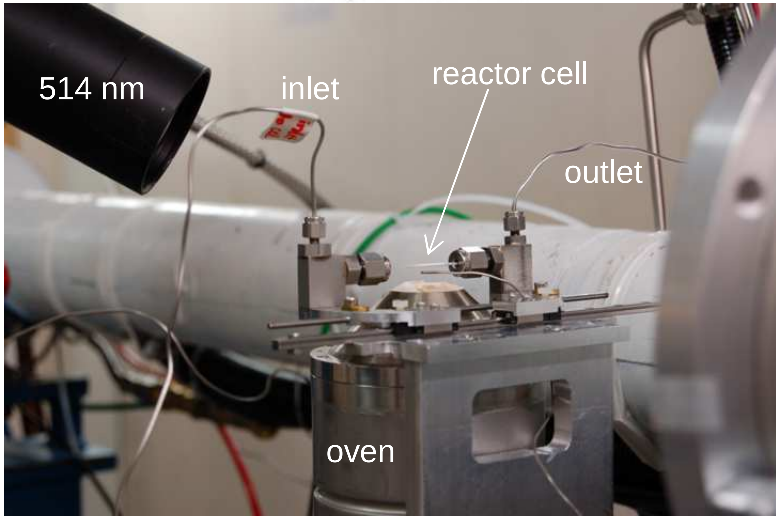


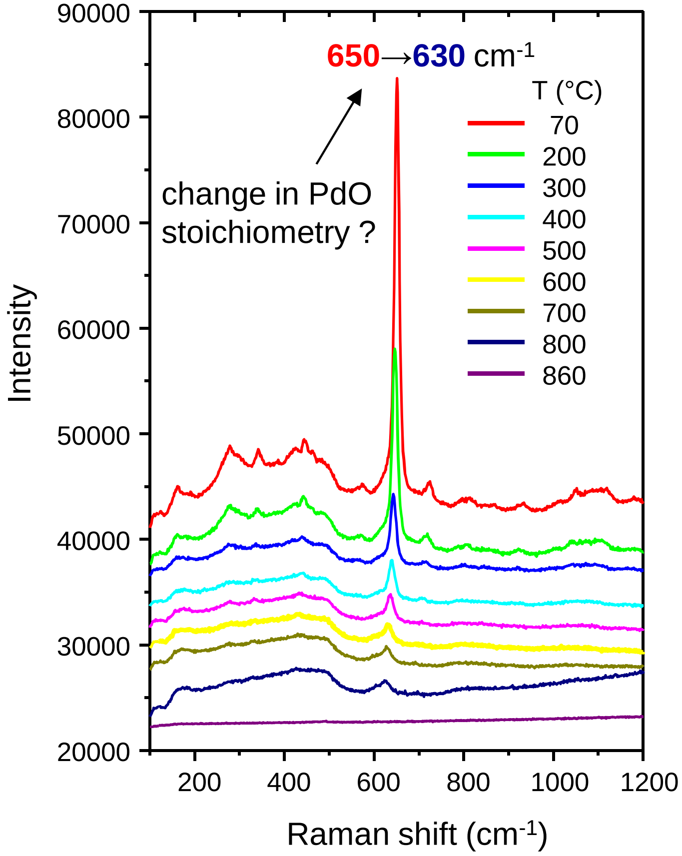
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

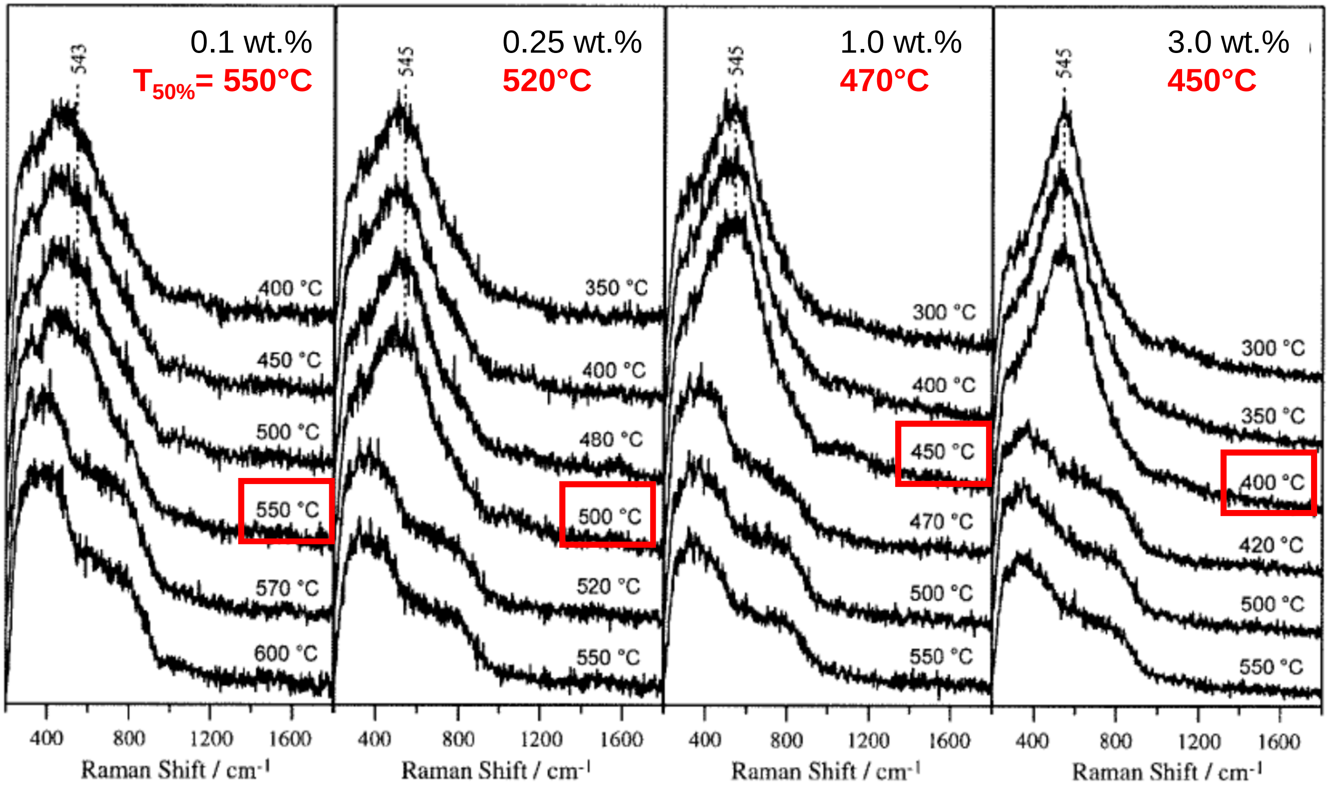
Applications

- Methane partial oxidation over Rh/Al_2O_3

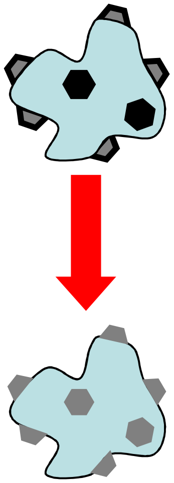
3 mW, 325 nm
$CH_4/O_2/Ar$ = 2/1/45

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content
Activity


0.1 wt.%
$T_{50\%}$= 550°C
0.25 wt.%
520°C
1.0 wt.%
470°C
3.0 wt.%
450°C

RhO_x
↓
Rh(0)



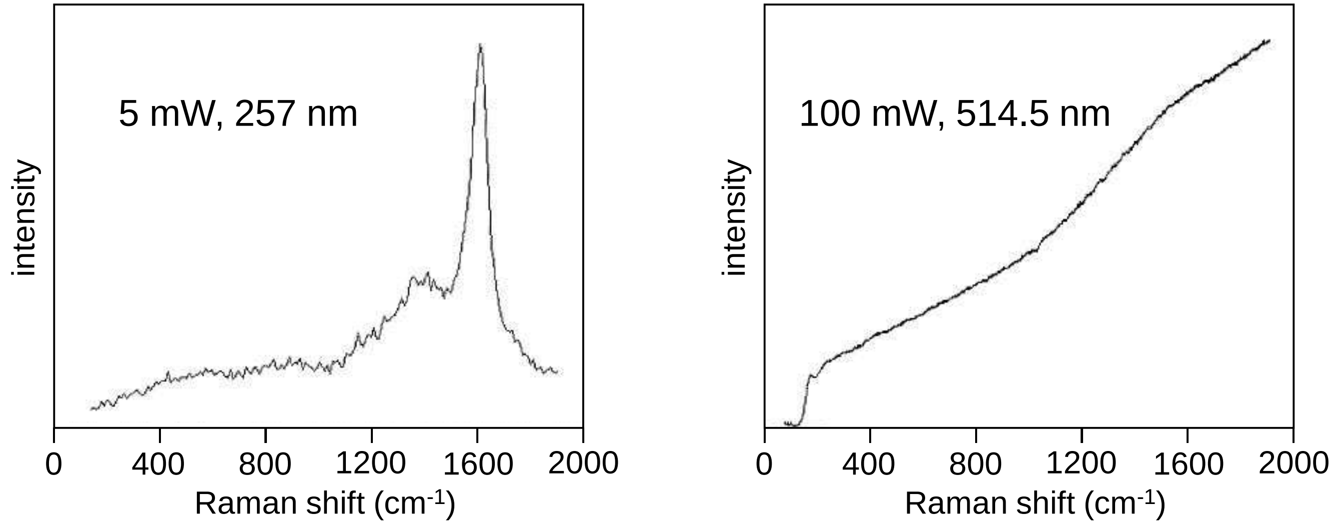
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

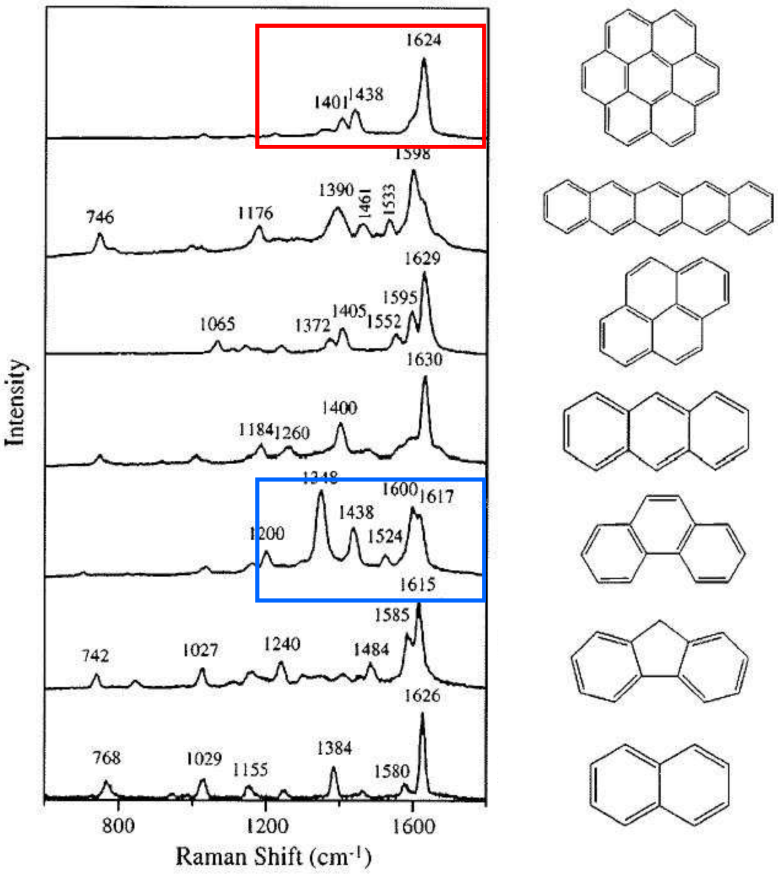
Rh/Al_2O_3, coked 500°C in naphtha

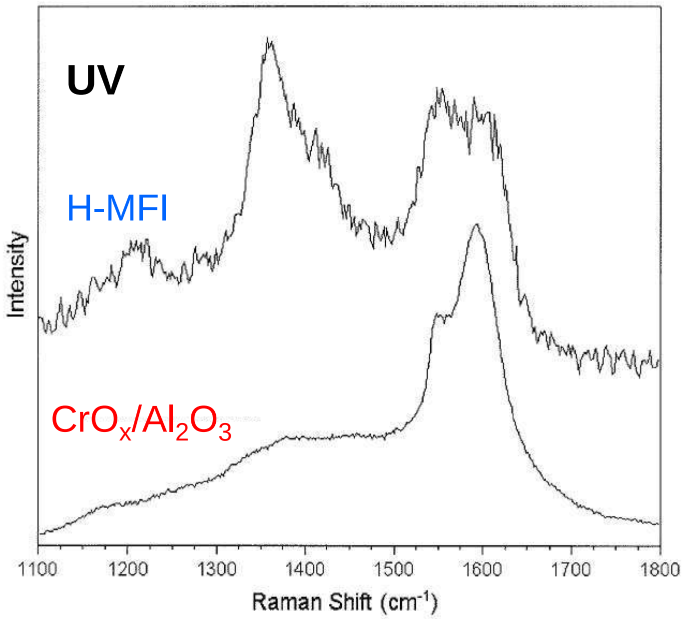


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





Coke classification

1D topology, chain-like

2D topology, sheet-like

Coke from:

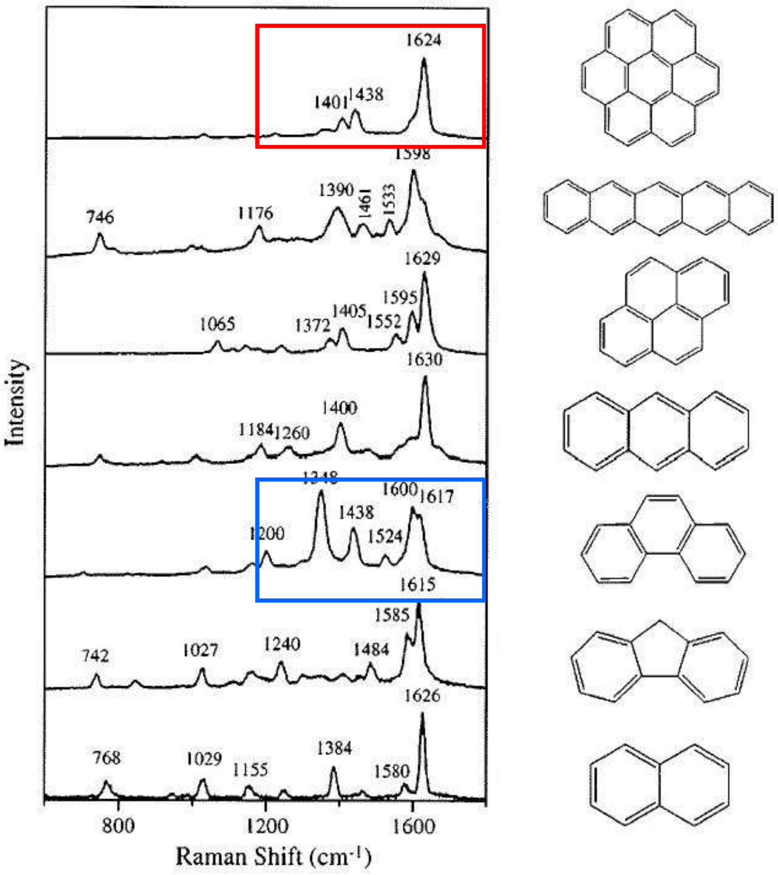
H-MFI: methanol-to-hydrocarbons (MTH)

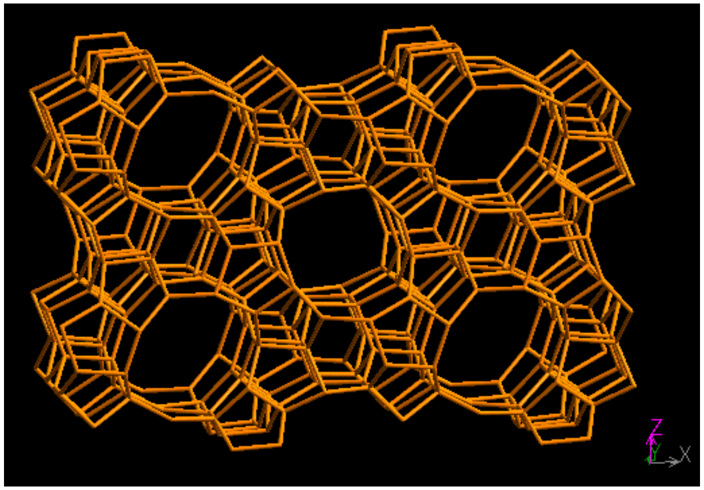
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





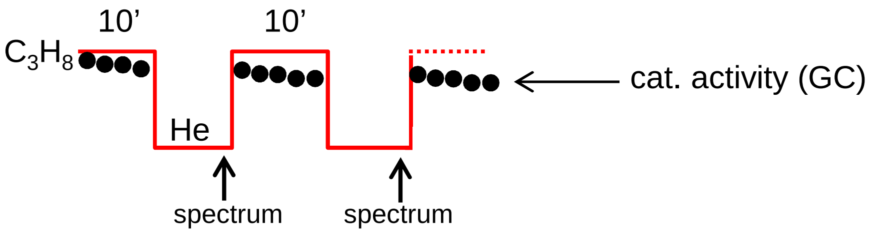
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

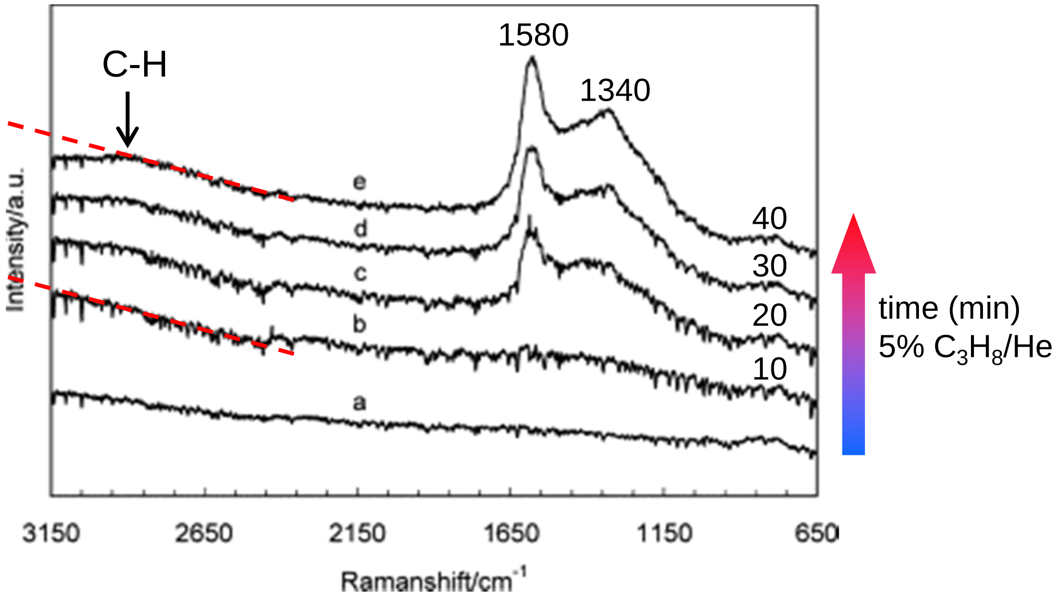
Stair, *Adv. Catal.* **51** (2007) 75

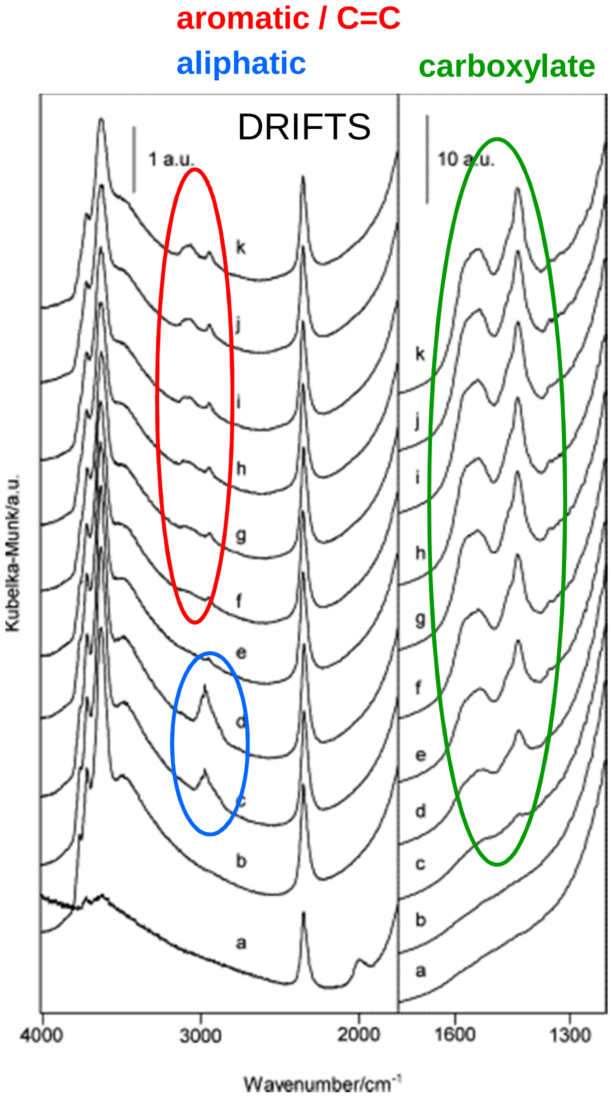
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

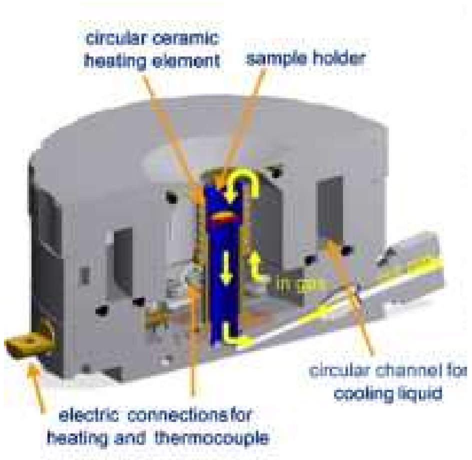


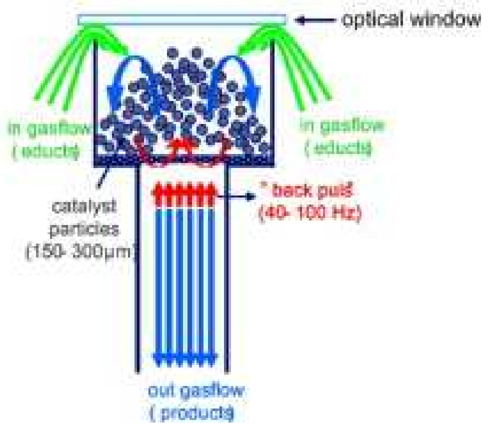


Airaksinen et al., *J. Catal.* **230** (2005) 507

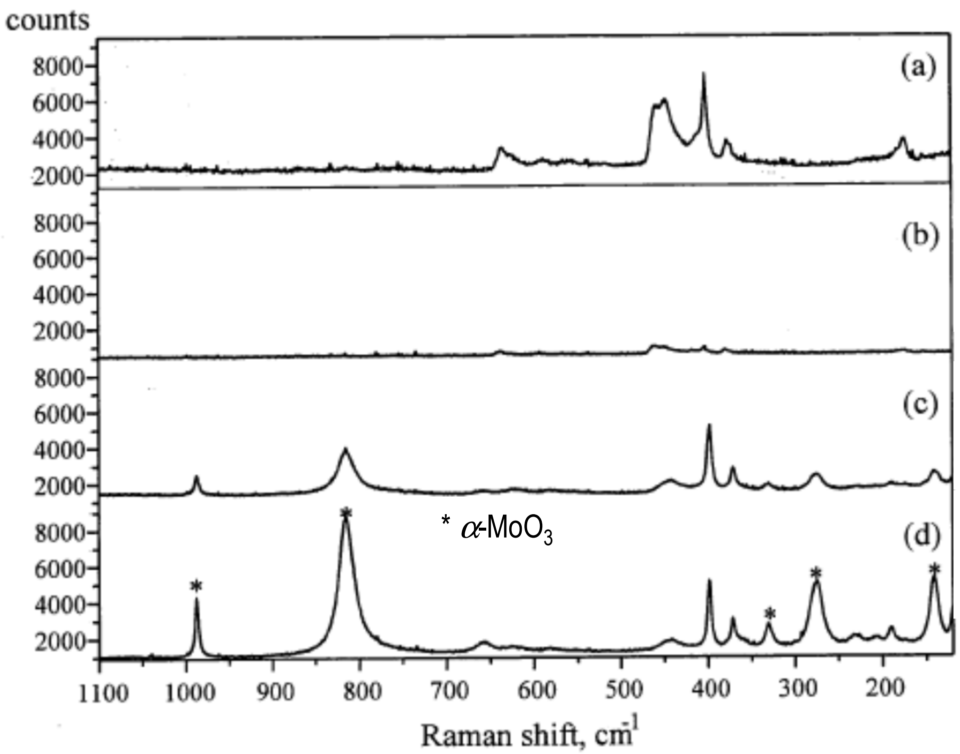
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min full power, FB

MoS_2, 6 min 1/8 power

MoS_2, 1 min full power

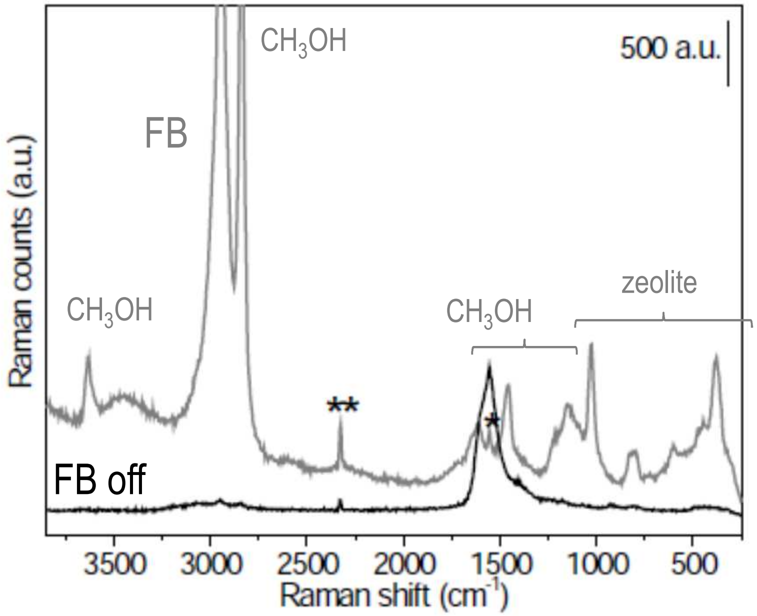
MoS_2, 6 min full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

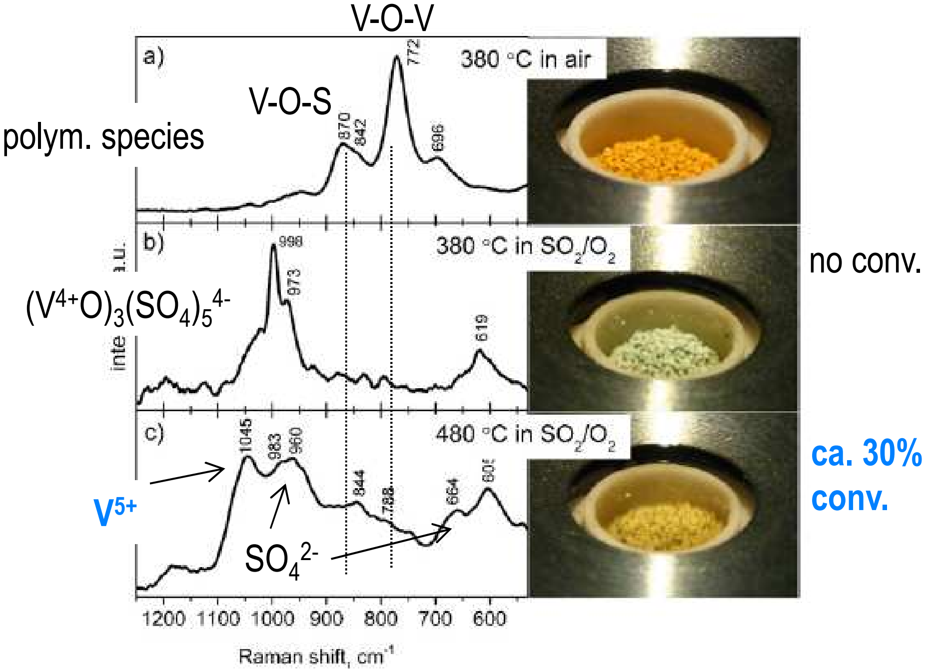
- Fluidized bed reactor cell

CH$_3$OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH$_3$OH decomposition

Sulfuric acid V$_2$O$_5$/pyrosulfate catalyst
λ= 514 nm

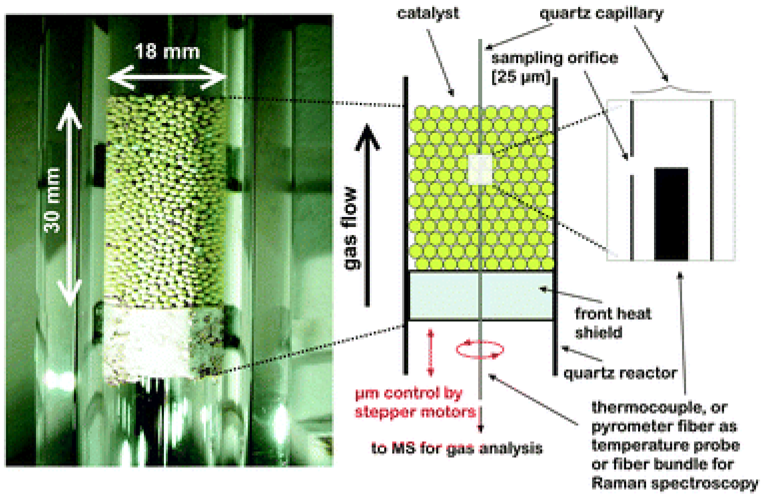


active species: mono- & dimeric V^{5+} oxosulfate species

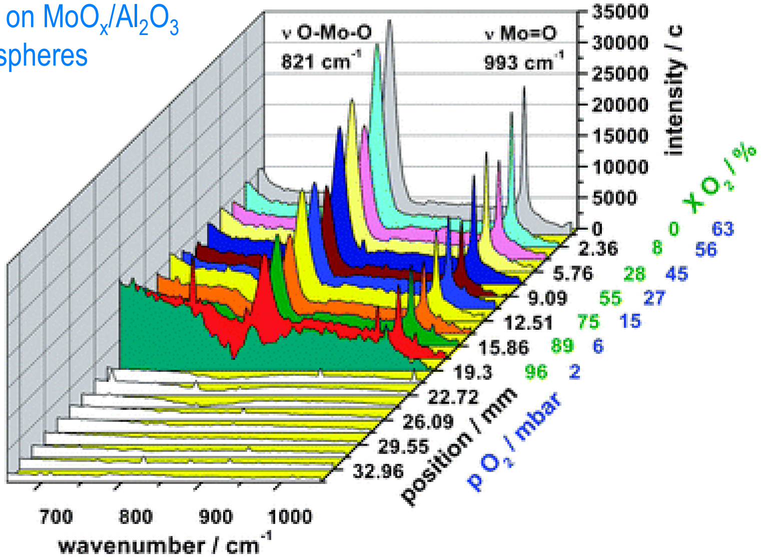
Beato et al., *Catal. Today* 205 (2013) 128

Applications

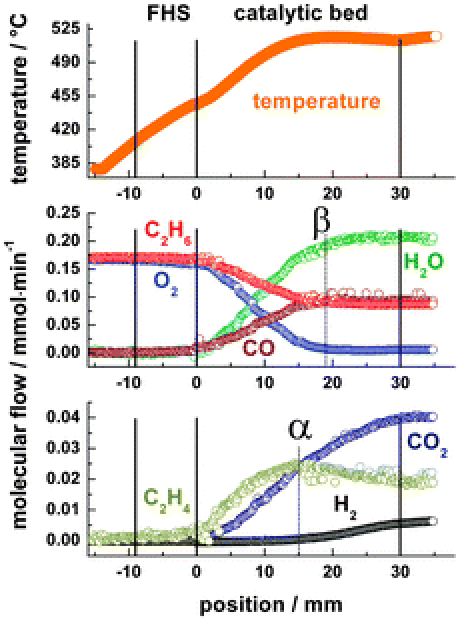
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

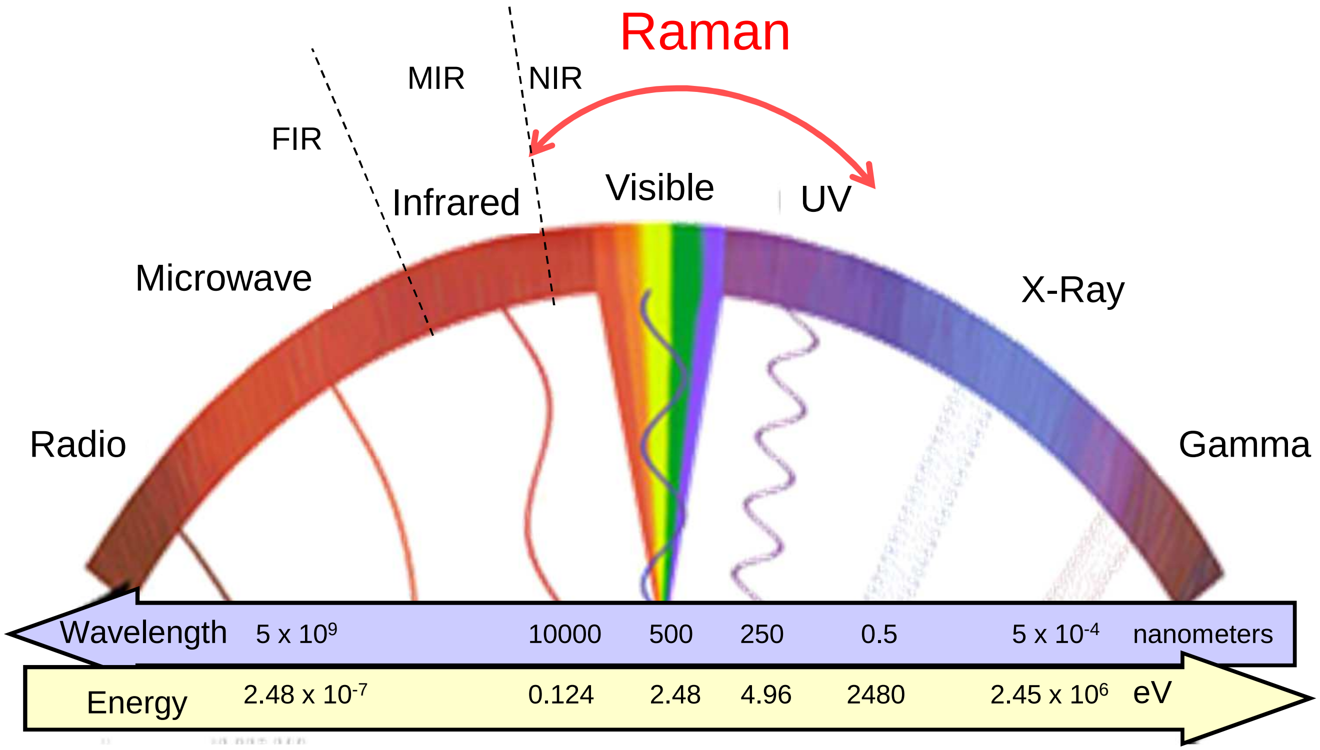
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

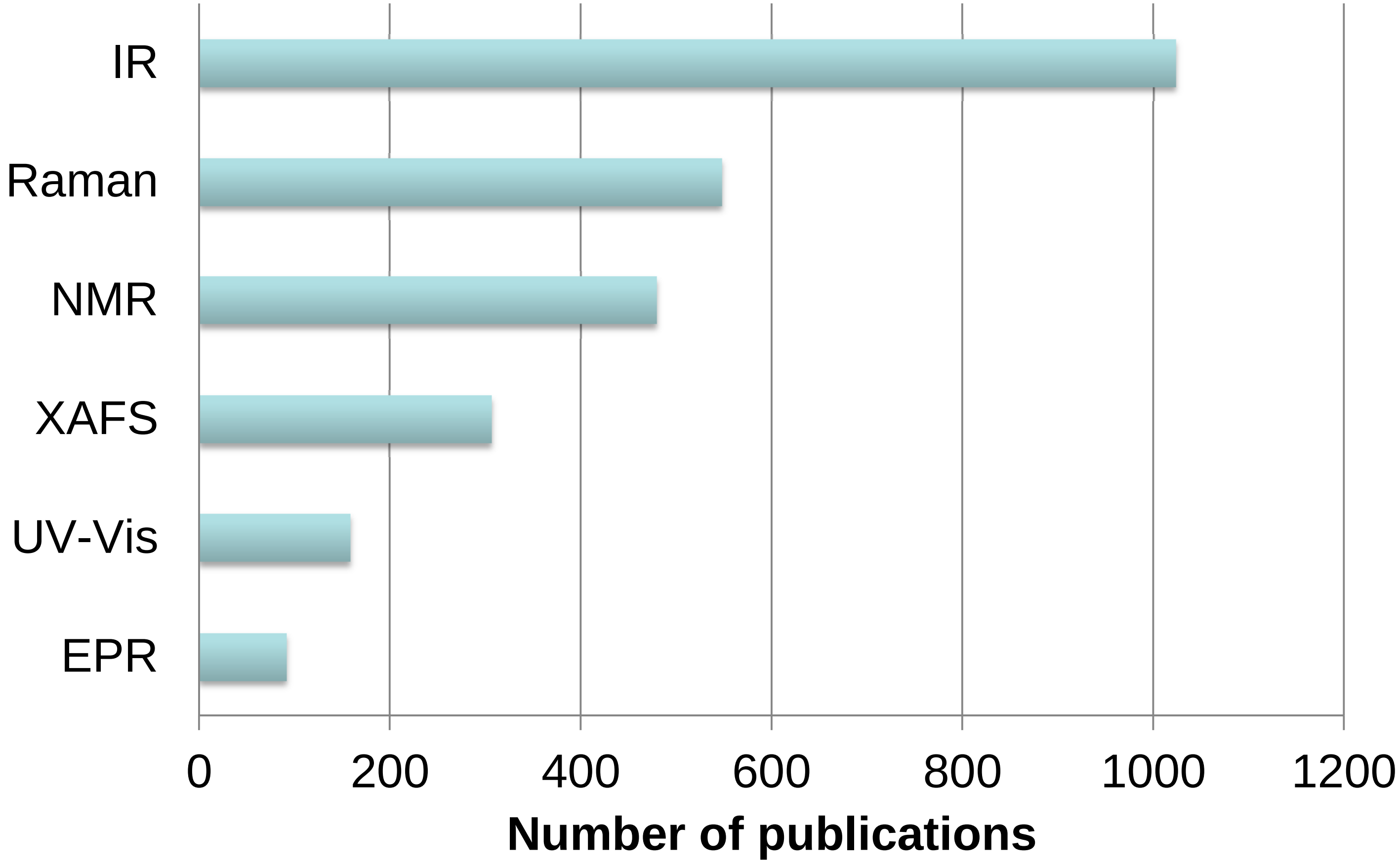
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

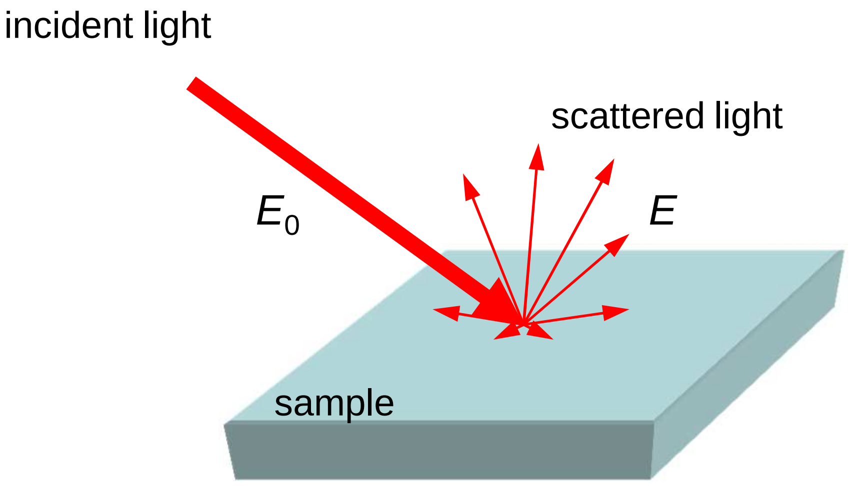


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

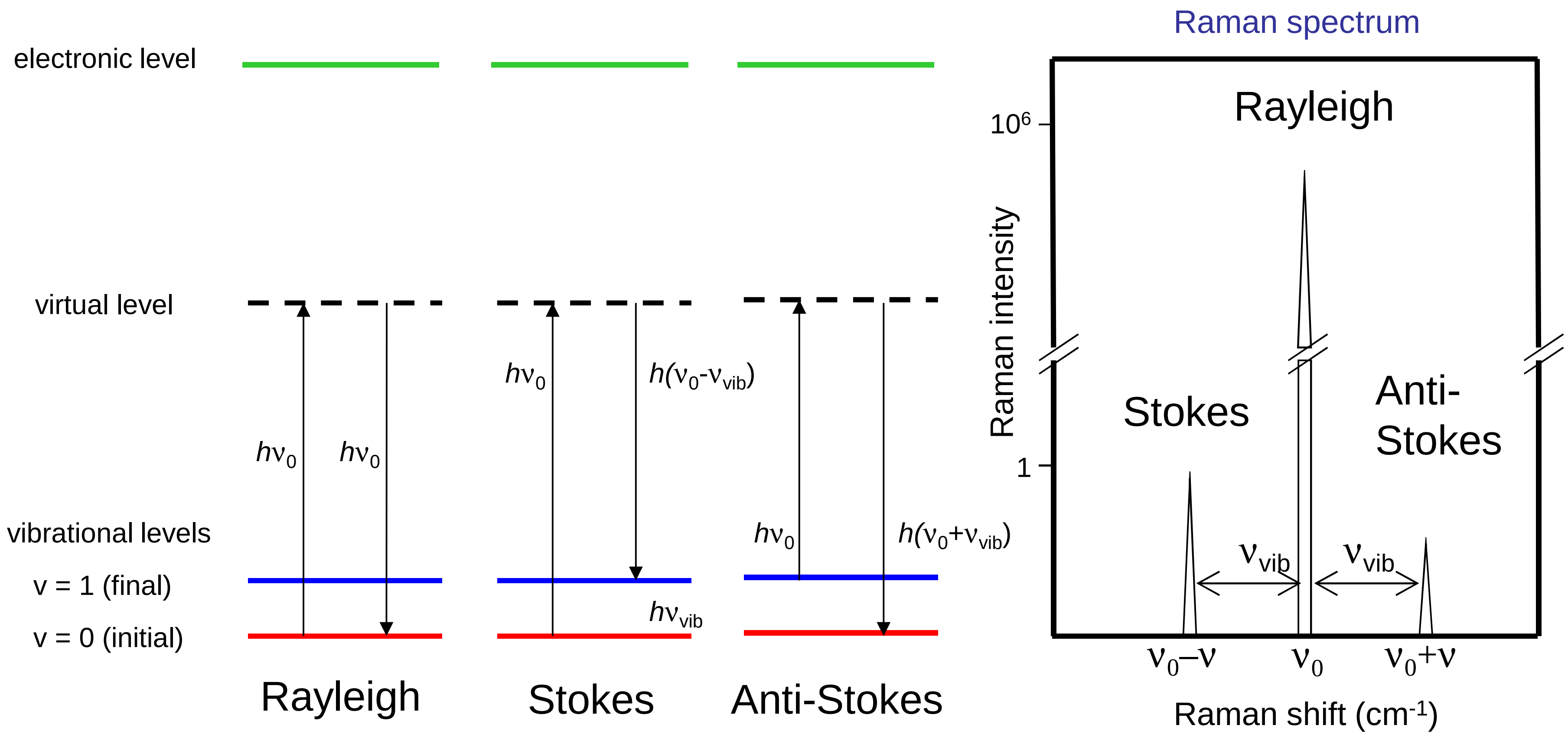
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{\mathrm{I}\ (\text{Anti-Stokes})}{\mathrm{I}\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:
  - 4th power of ν (4th power law)
  - 2nd power of $\Delta\alpha$
    - properties of molecules
    - strength of bonds

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

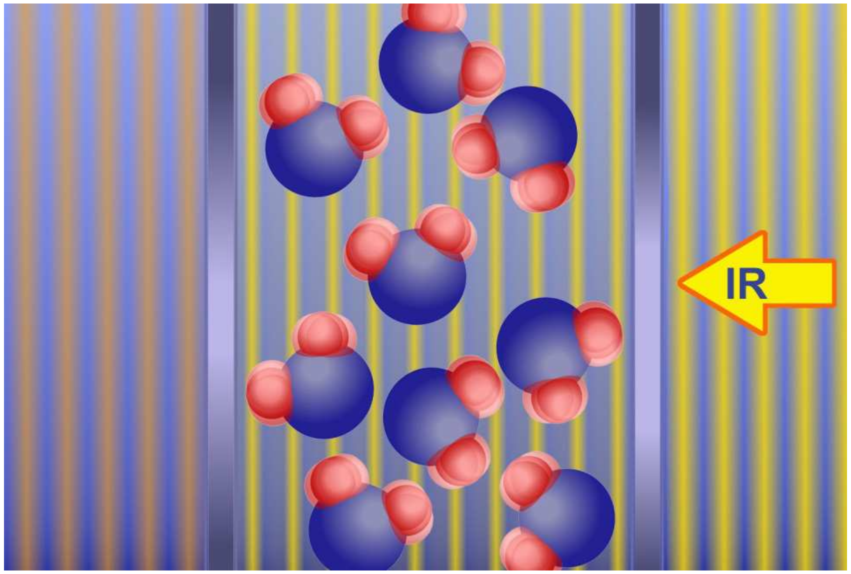
↓

covalent bond	STRONG bands	(catalysis!)
ionic bond	WEAK bands	

- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

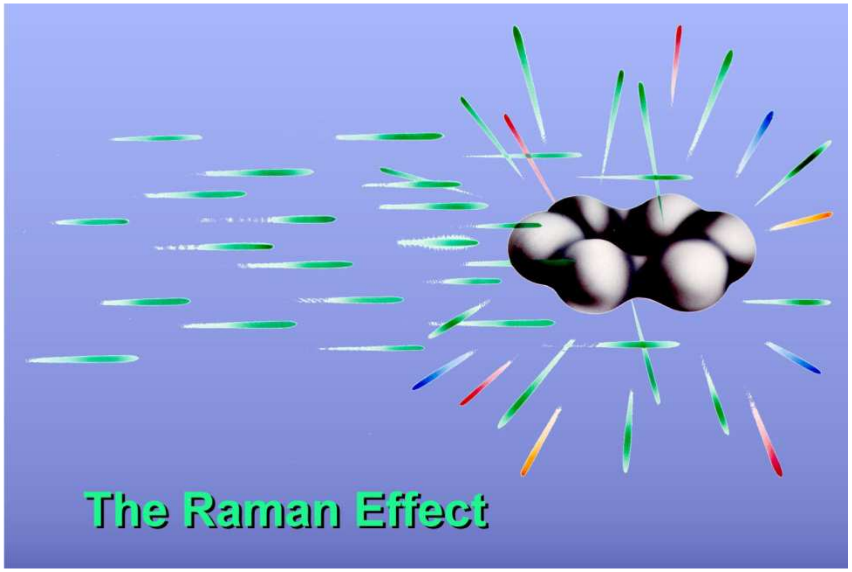
Raman *vs.* Infrared

Infrared



Absorption of IR light

Raman



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial\mu}{\partial Q}\right)^2 \neq 0$$

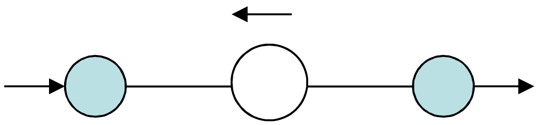
- high absorption for polar bonds ($C=O$, H_2O, NH, etc.)

$$\left(\frac{\partial\alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
    - large electron clouds
    - not polar
- H_2O is a very weak Raman scatterer
- $C=C$ double bonds strong Raman scatterers

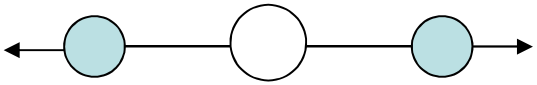
Raman *vs.* Infrared

CO_2



ν_{as}

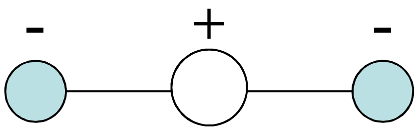
2349 cm^{-1}



ν_s

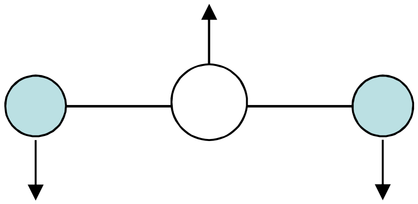
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



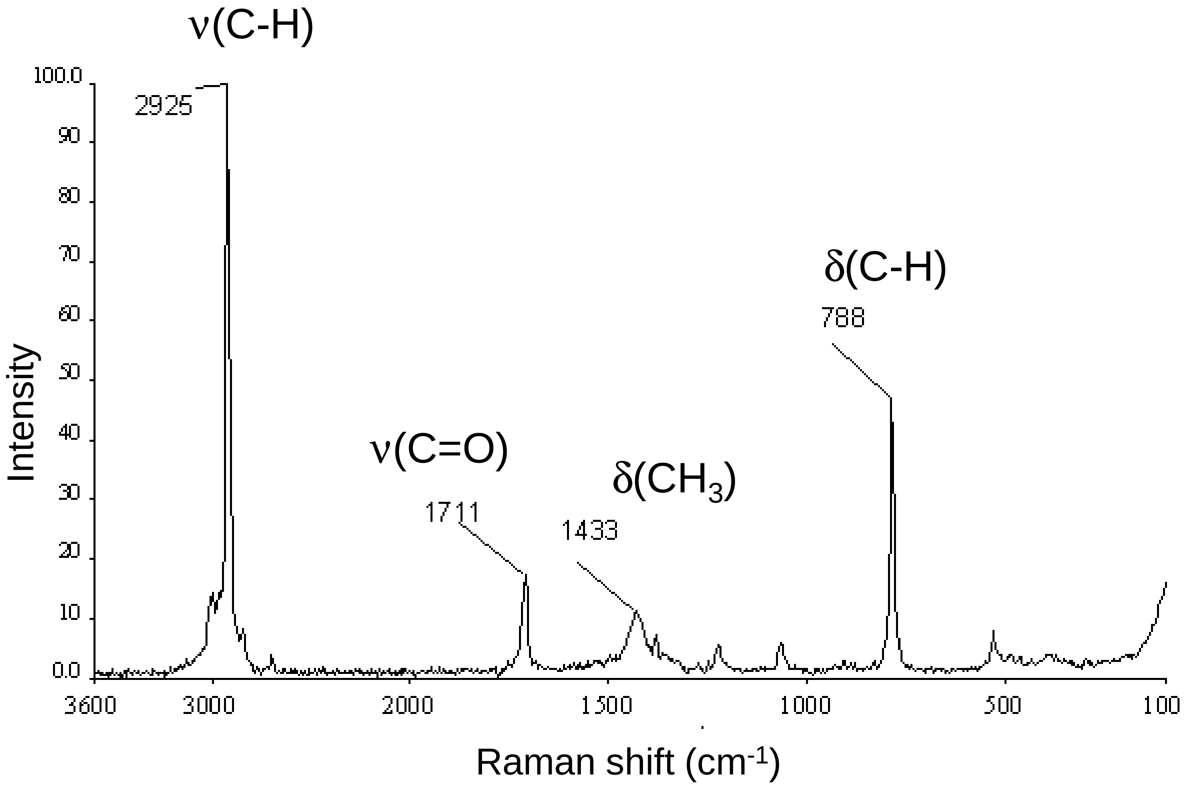
δ

667 cm^{-1}

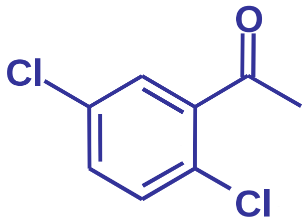
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



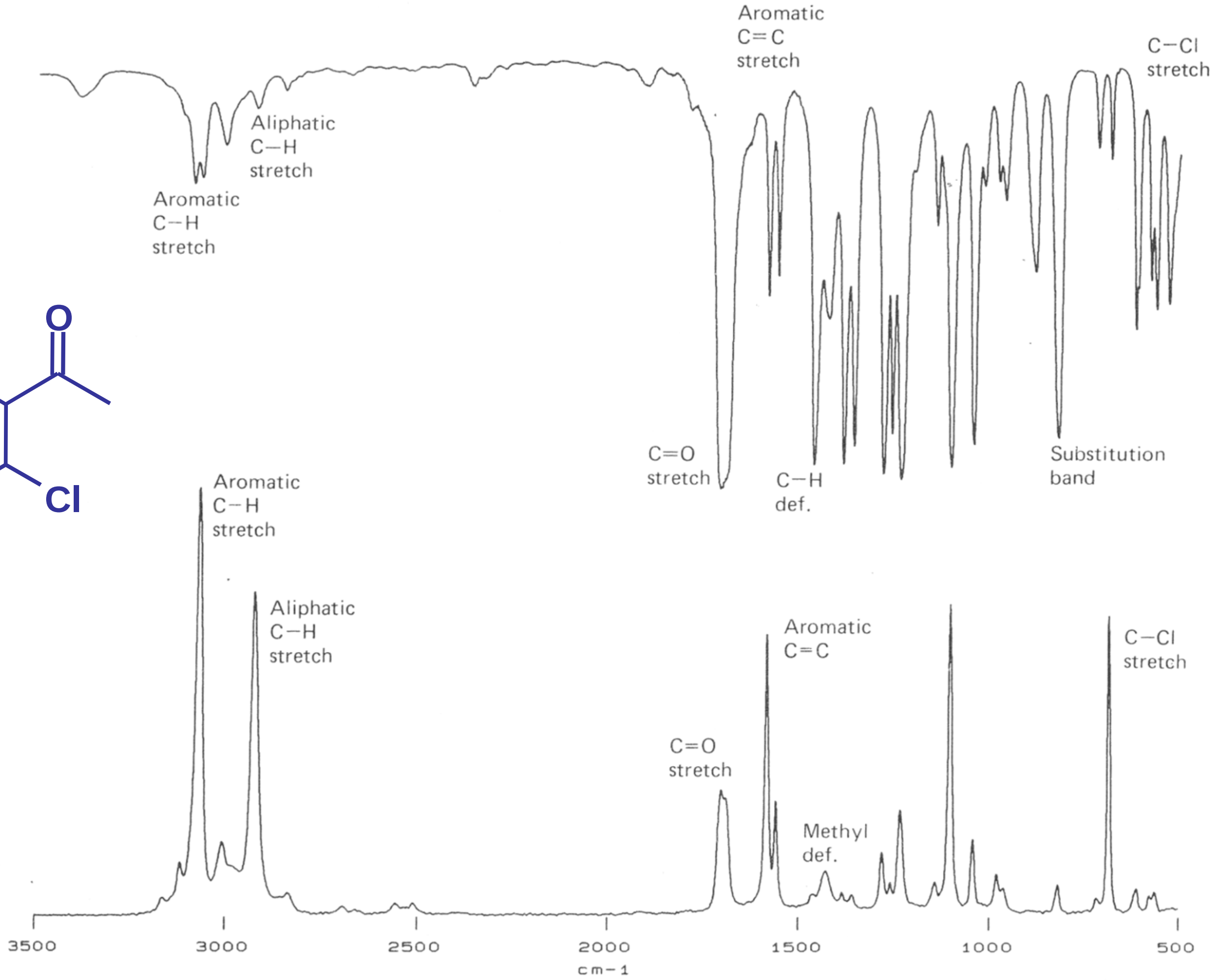


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

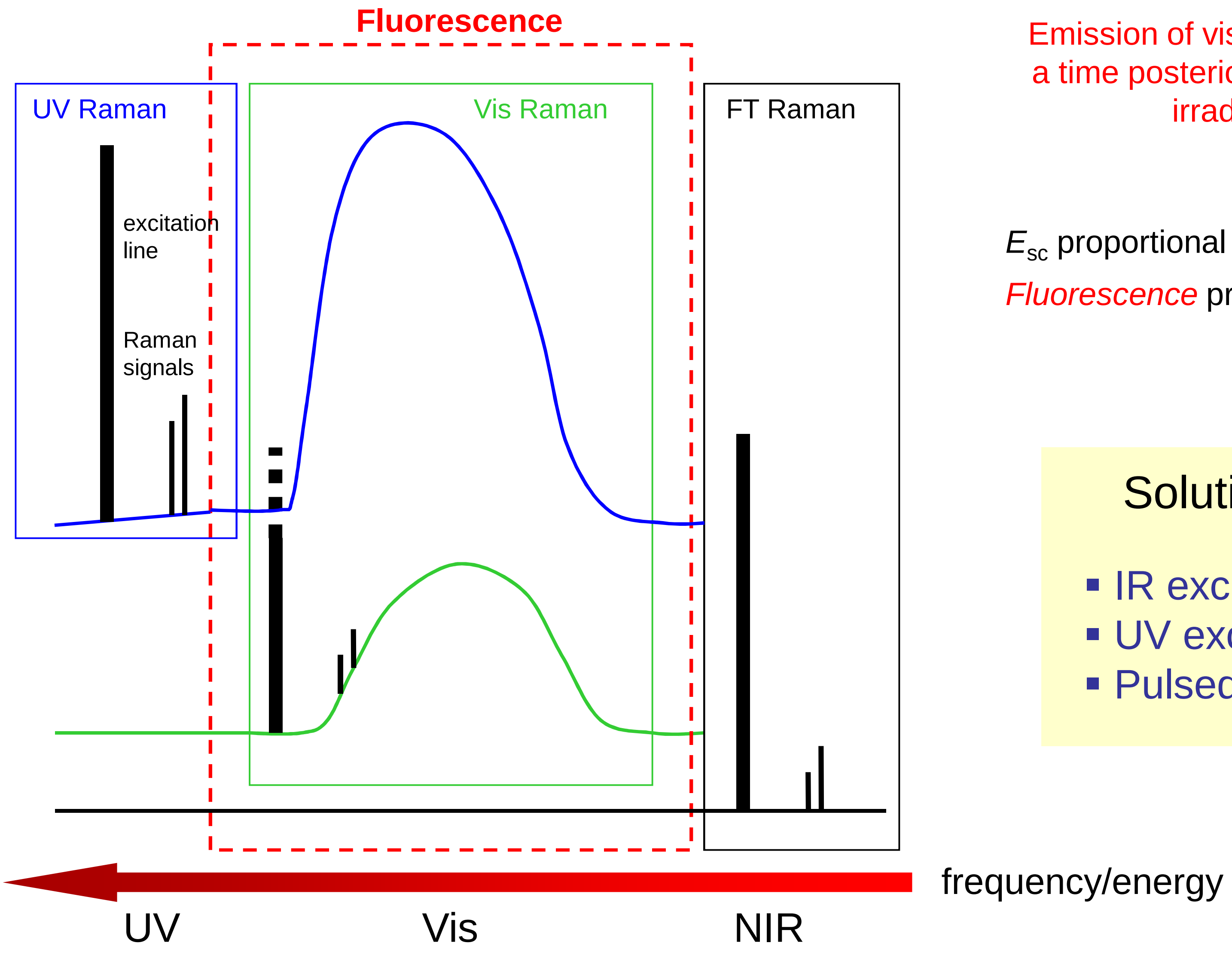
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 μm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

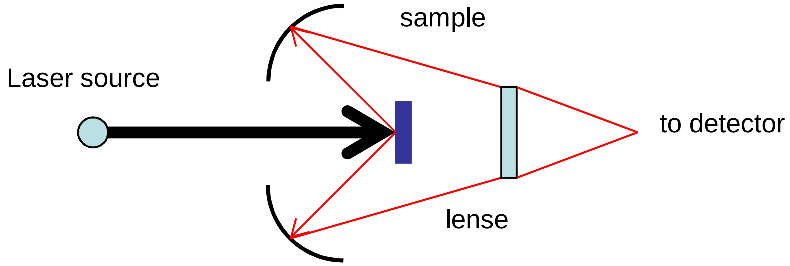
Fluorescence proportional to ν

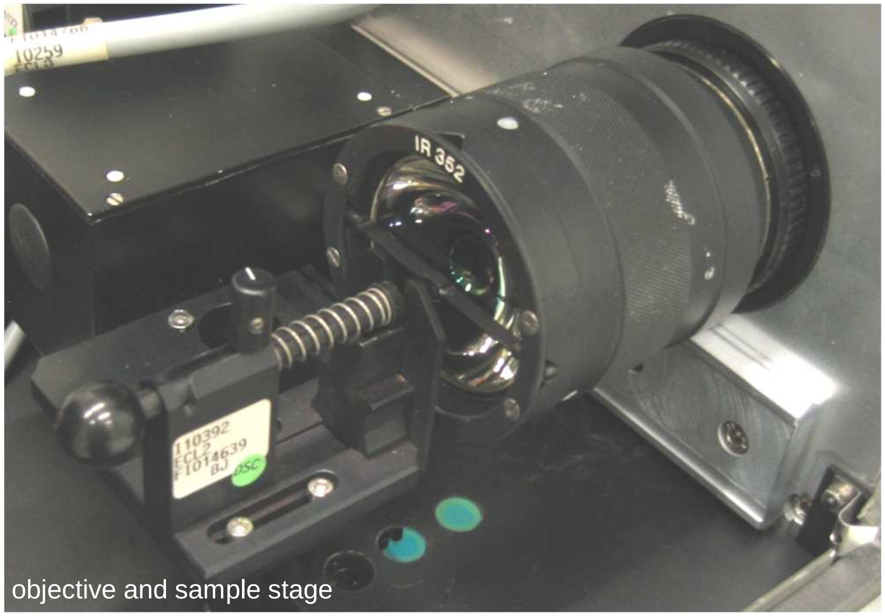
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers
Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

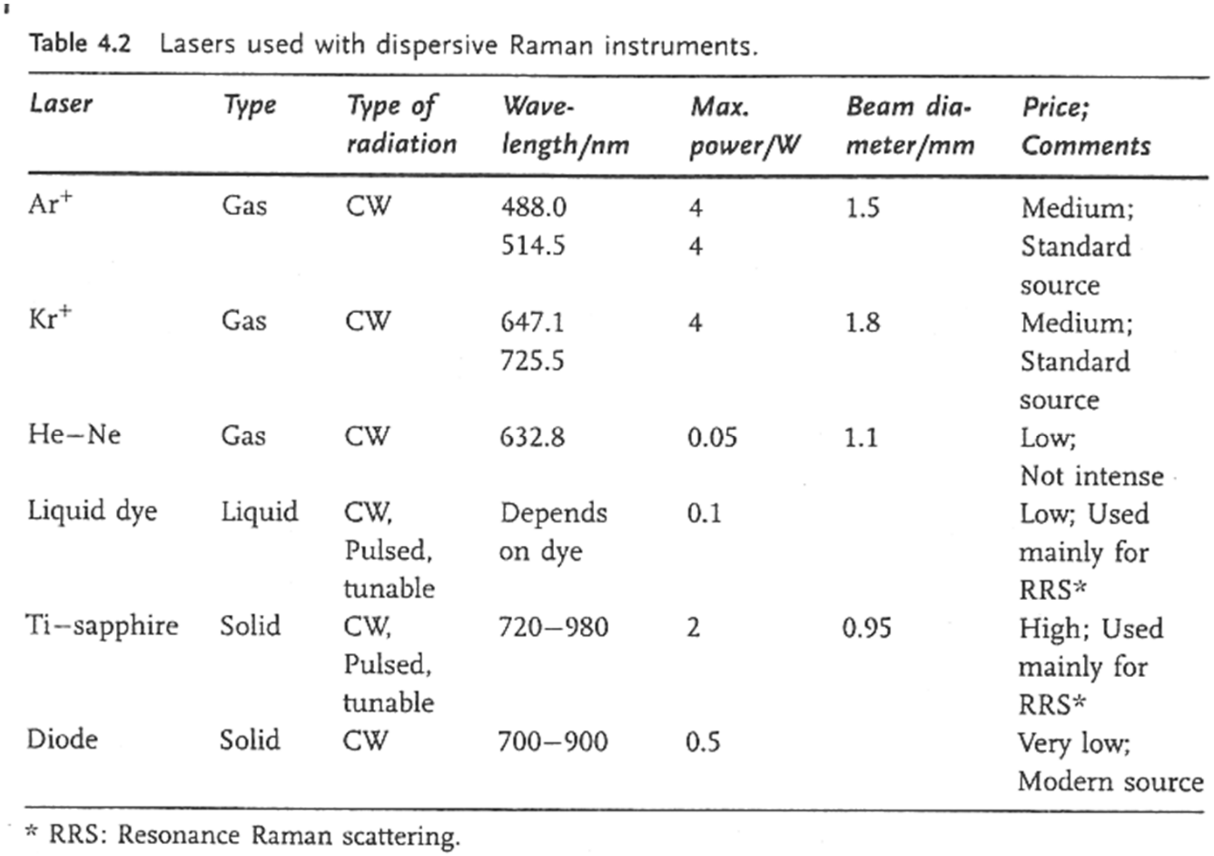


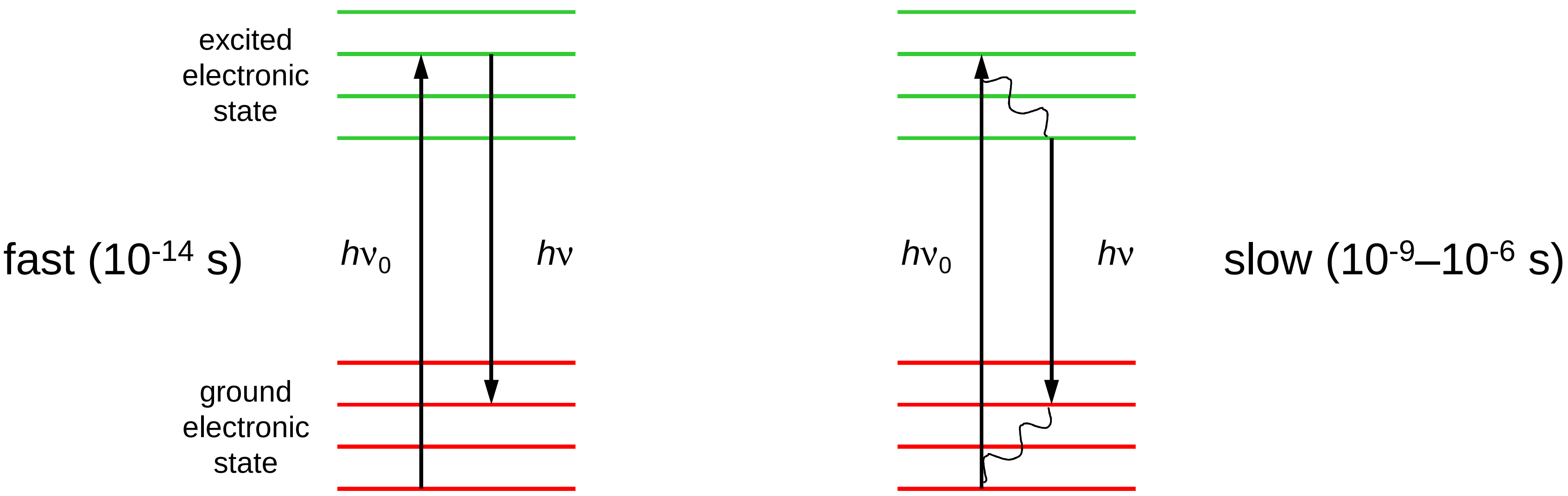
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



Resonance Raman scattering

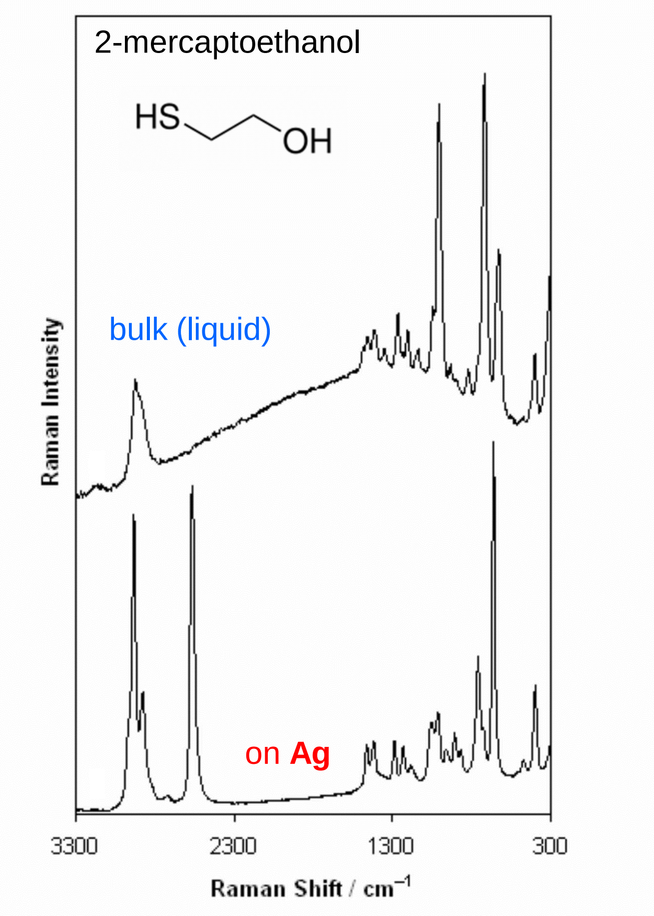
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

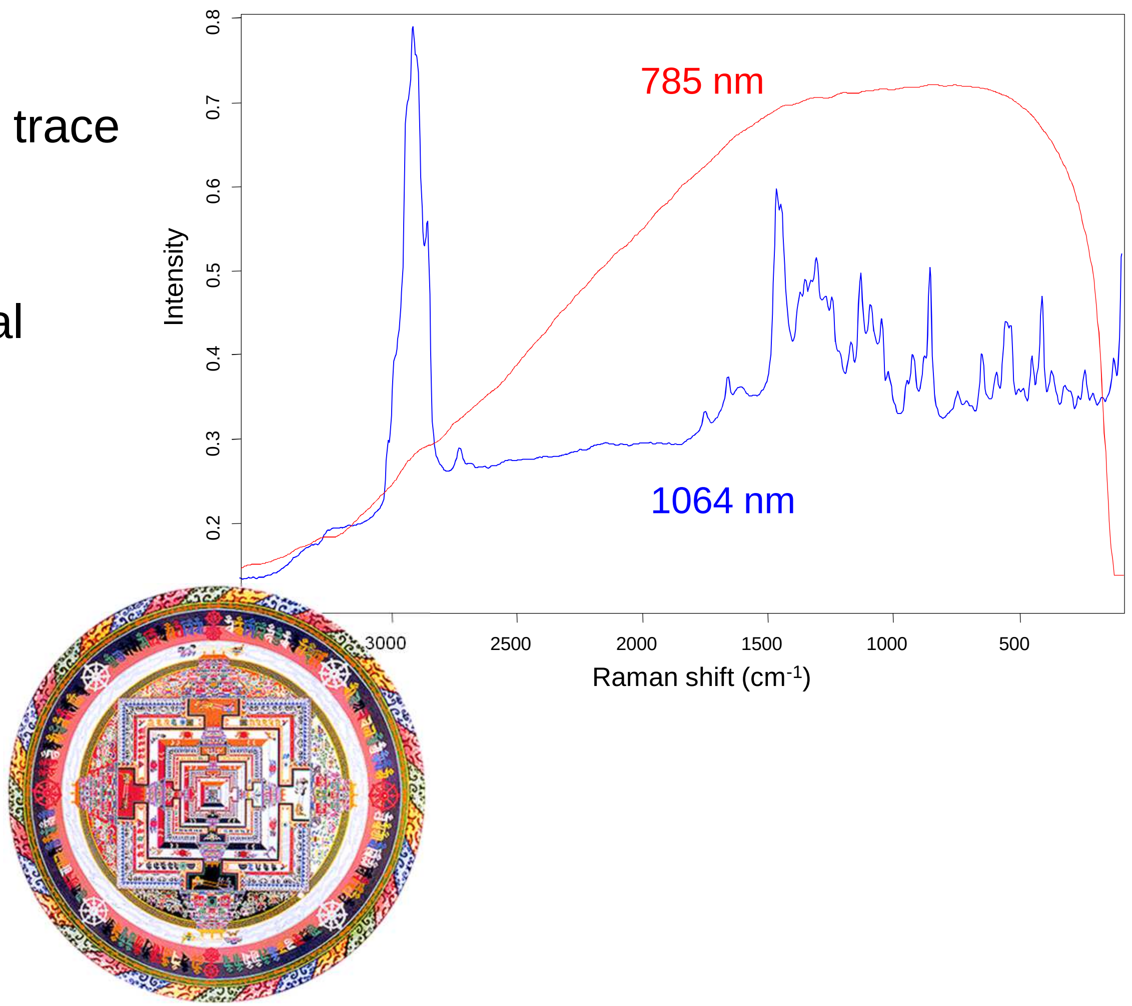
- Remarks:

❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



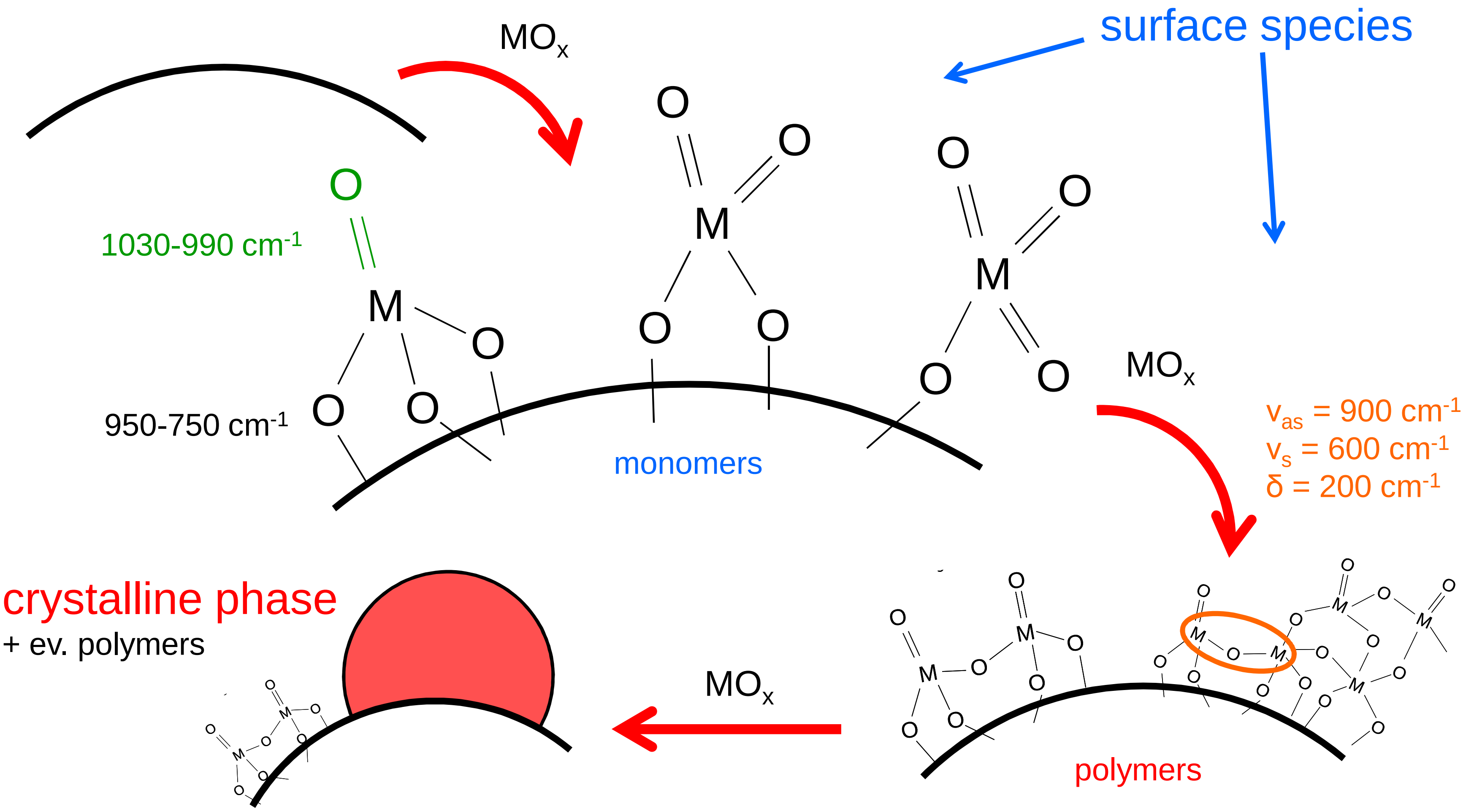
Applications

MO_x/$M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



MO_x

surface species

1030-990 cm^{-1}

950-750 cm^{-1}

monomers

MO_x

$v_{as} = 900\ cm^{-1}$
$v_s = 600\ cm^{-1}$
$\delta = 200\ cm^{-1}$

polymers

MO_x

crystalline phase

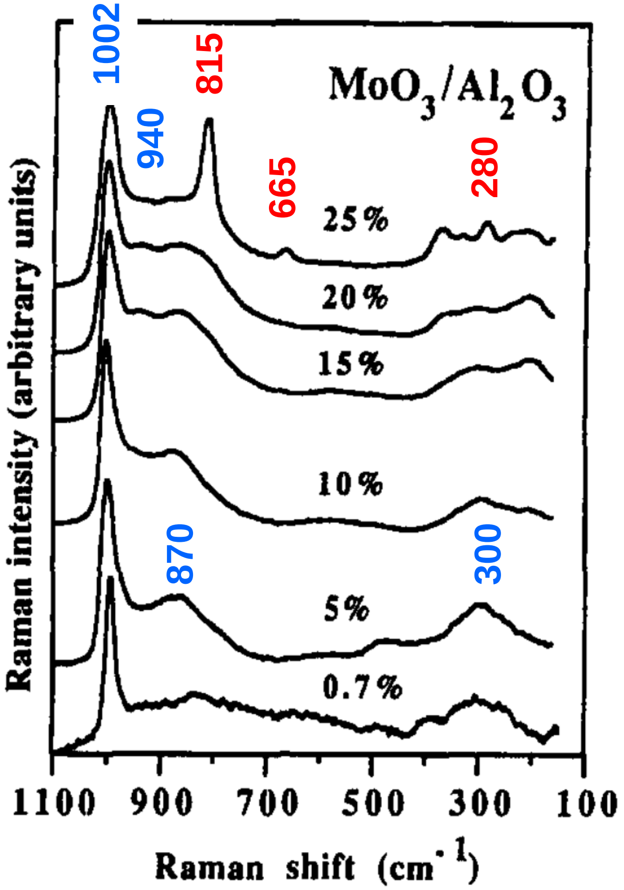
+ ev. polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



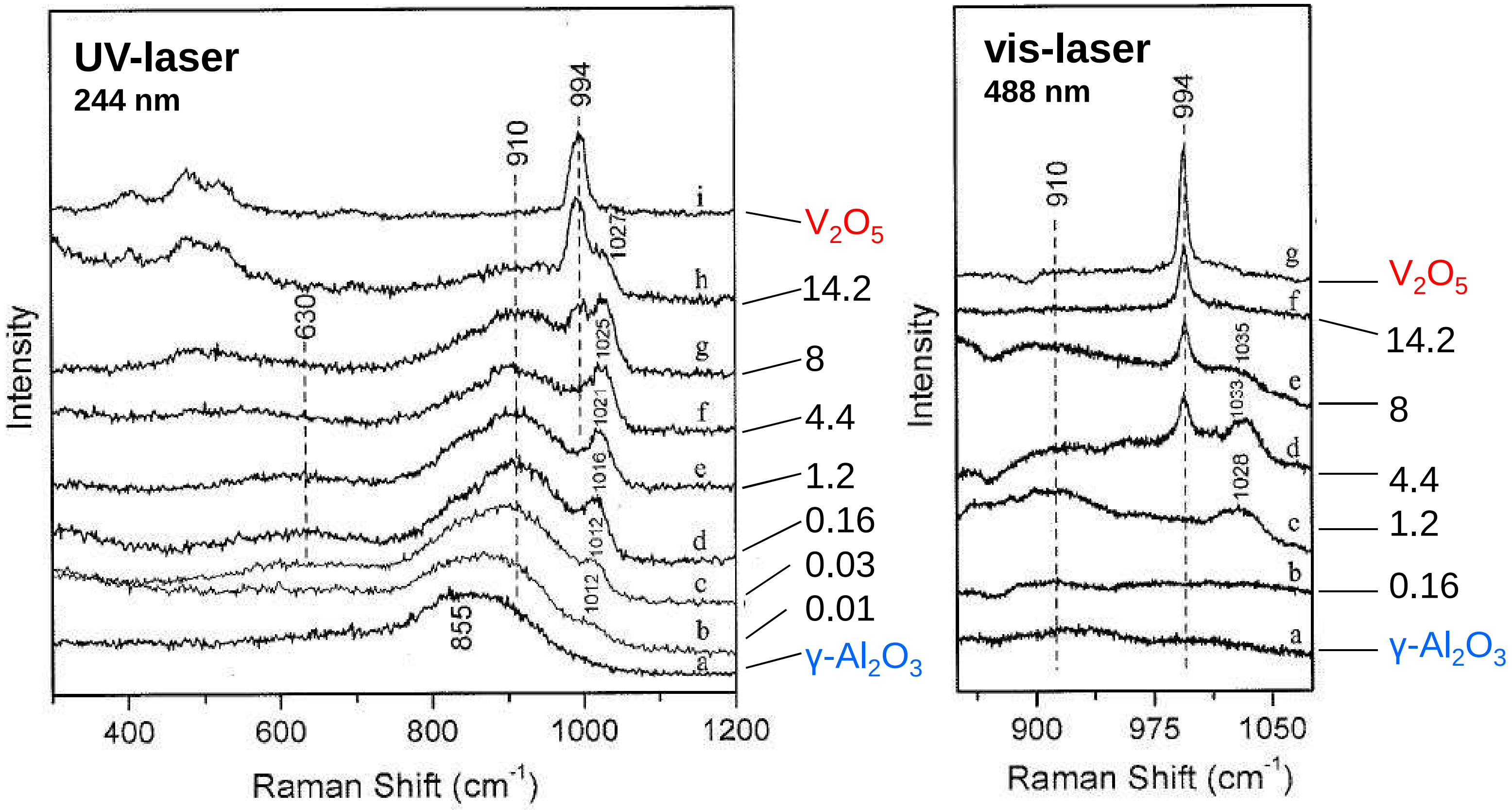
surface MoO_3
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

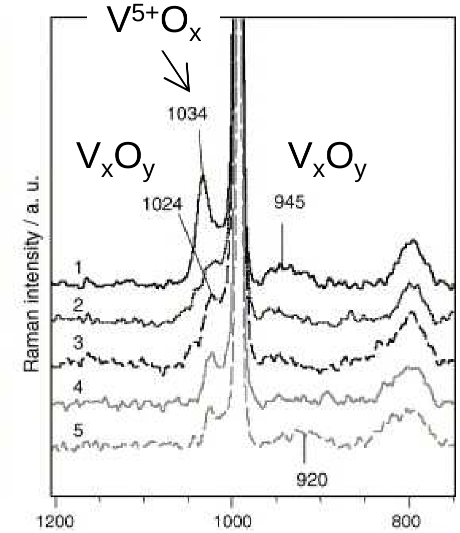
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

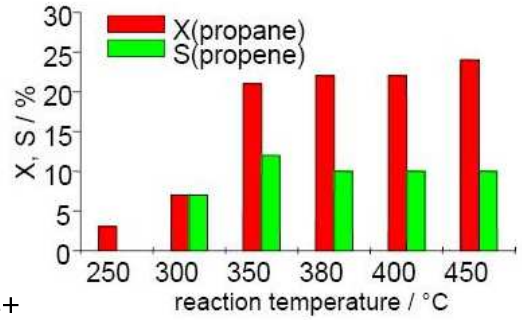
Applications

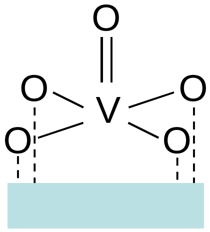
- Reactivity of V/TiO$_2$ after oxidative treatment

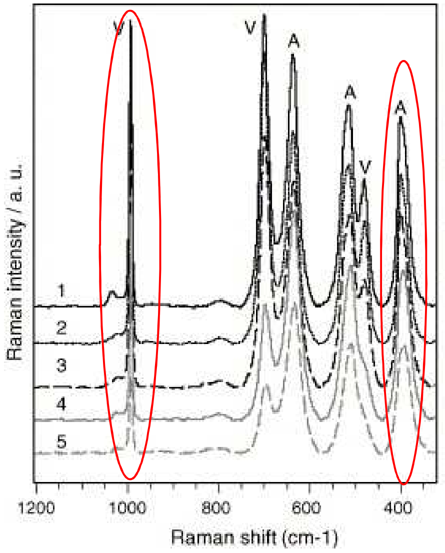


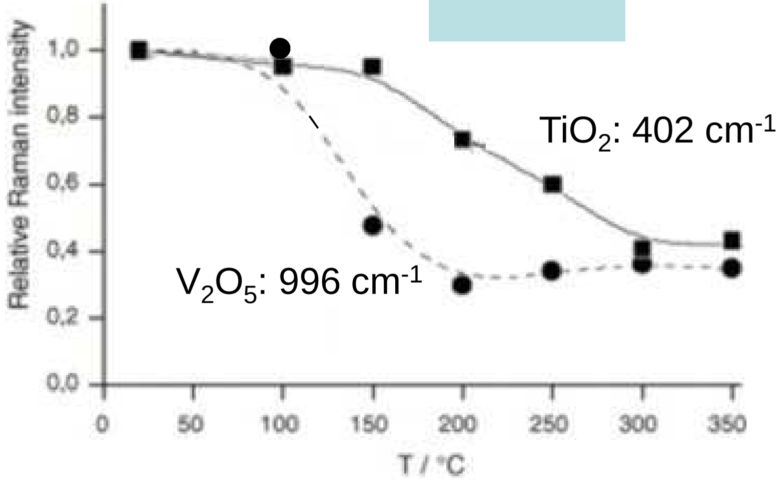
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

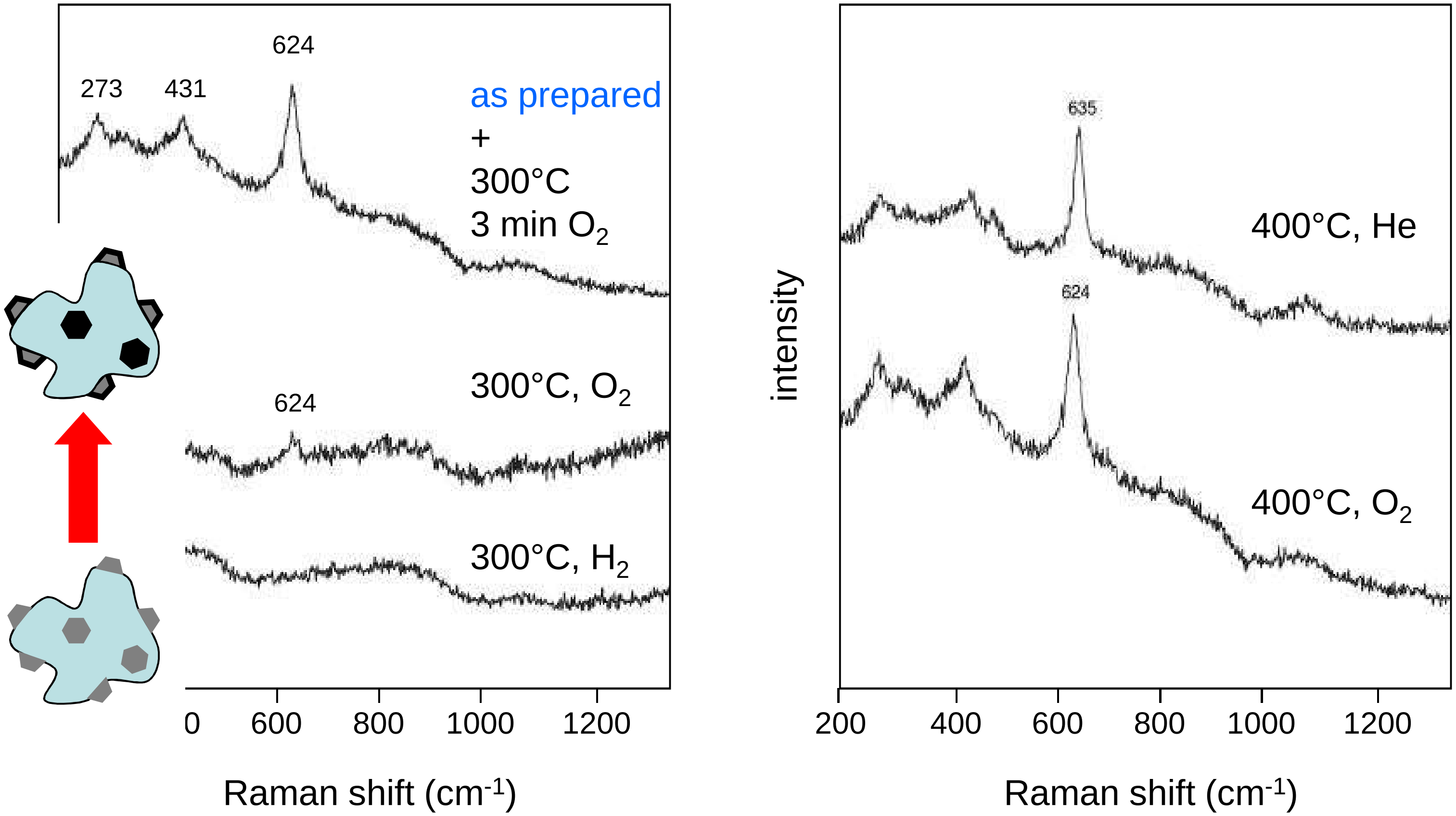
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



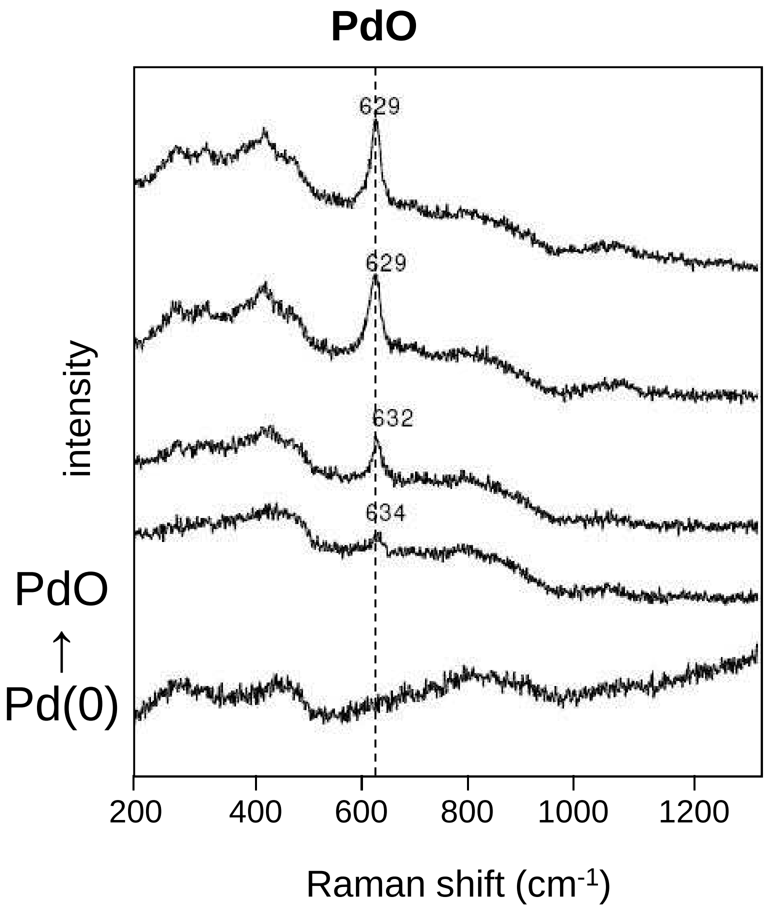
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

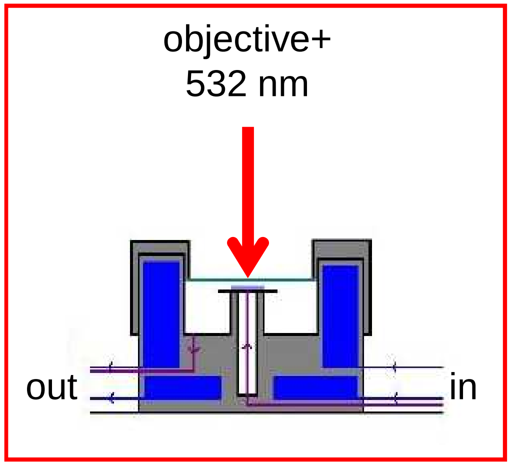
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



	CH_4 conv.
500°C	**24 %**
450°C	**15 %**
425°C	**4 %**
400°C	**2 %**
400°C, H_2 reduced Pd	

feed CH_4/O_2 (1:10)

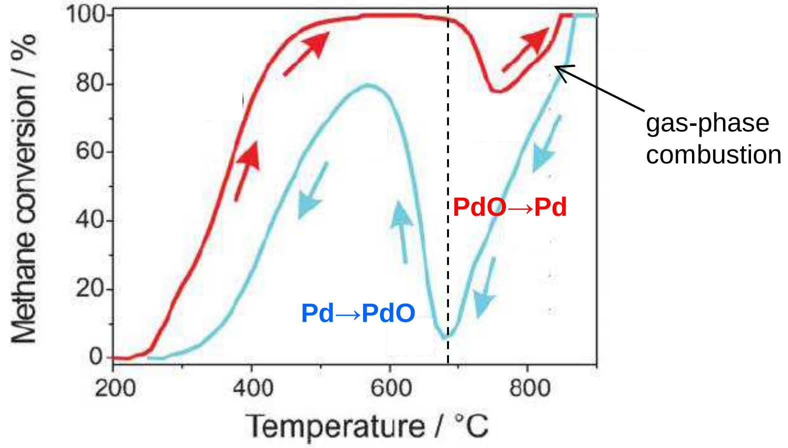
near PdO mode

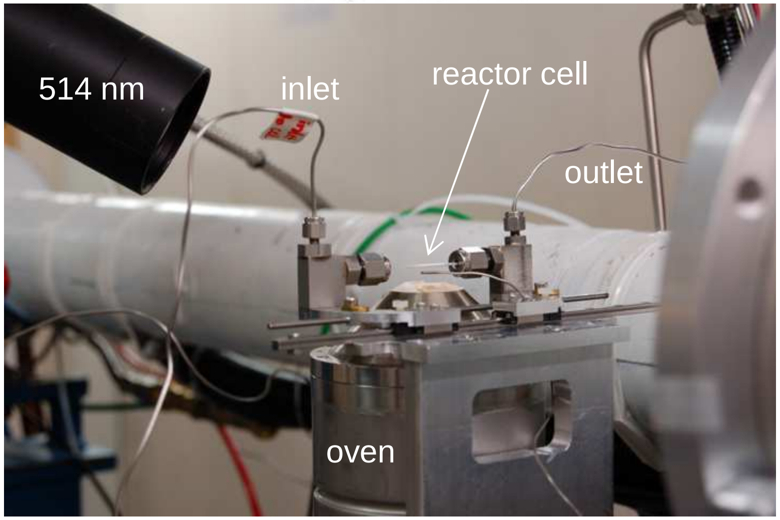


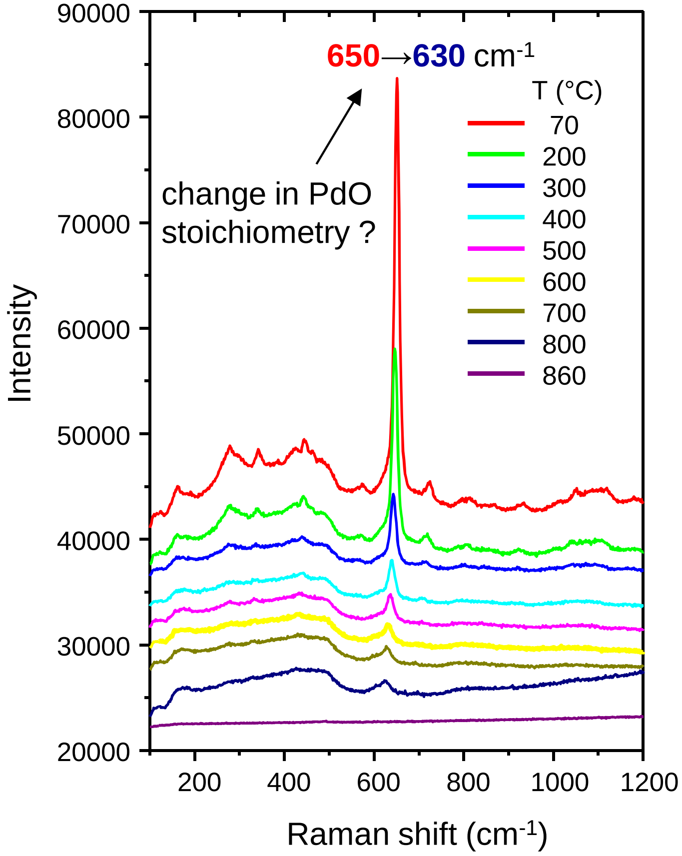
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

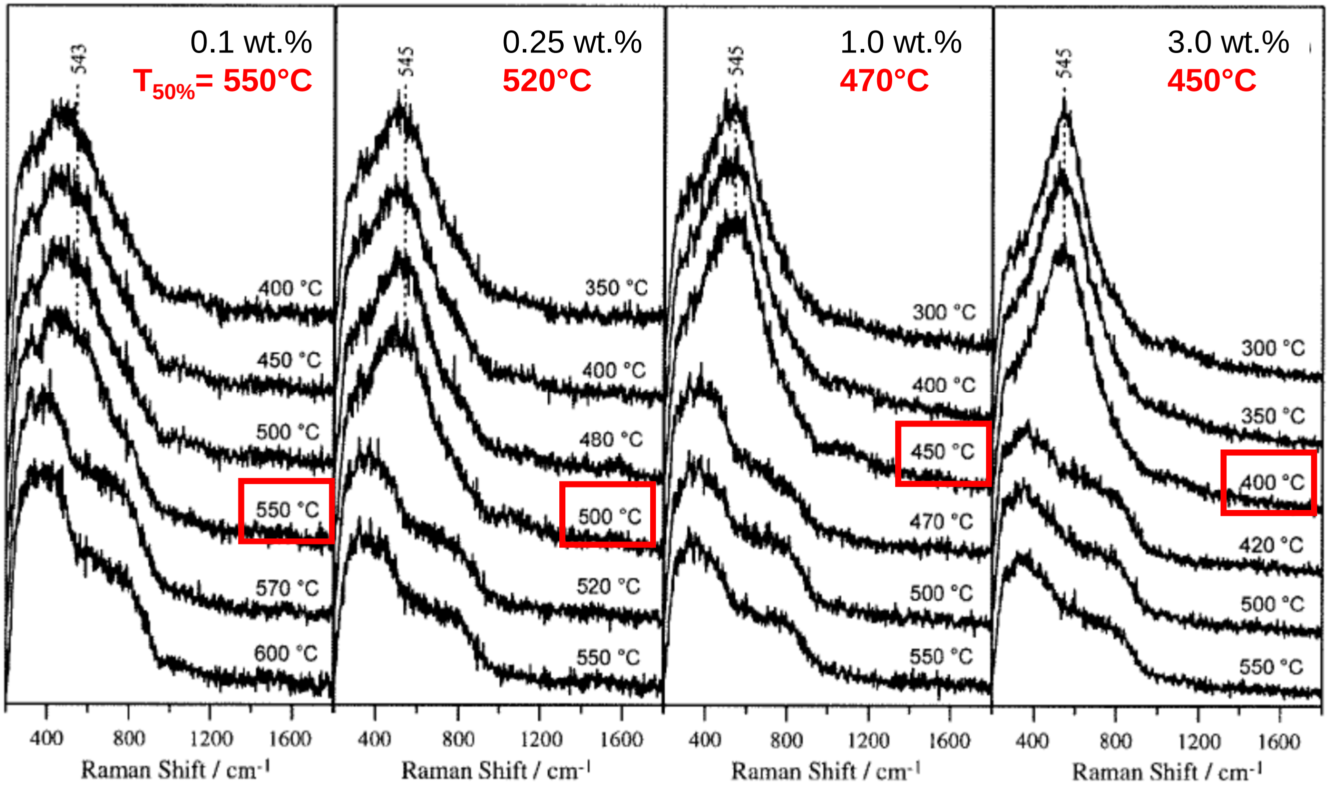
- Methane partial oxidation over Rh/Al_2O_3

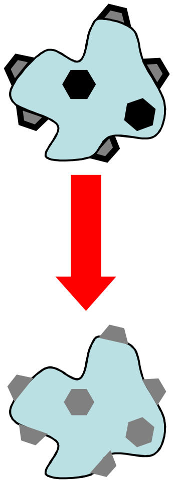
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content →
Activity →

RhOx
↓
Rh(0)





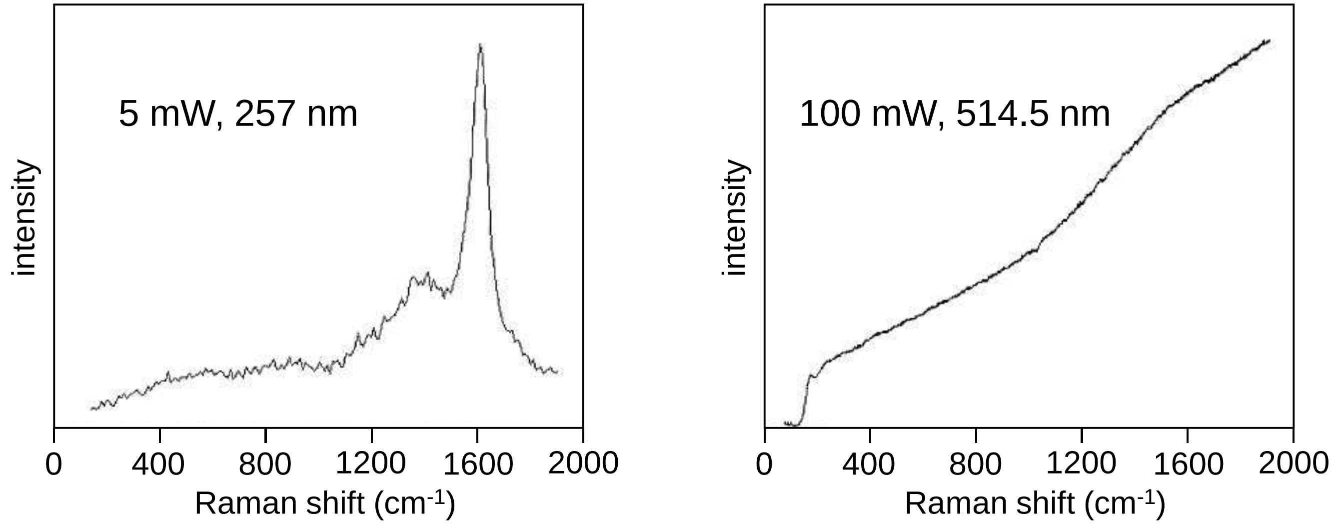
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

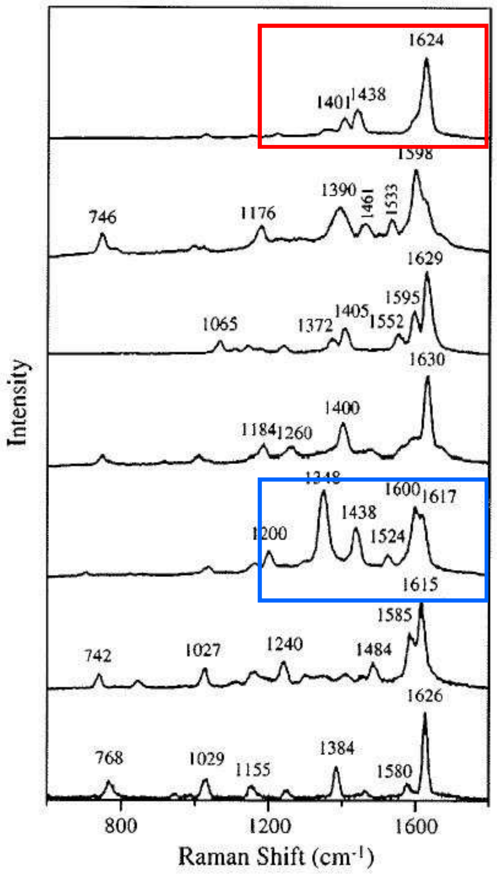
Rh/Al_2O_3, coked 500°C in naphtha

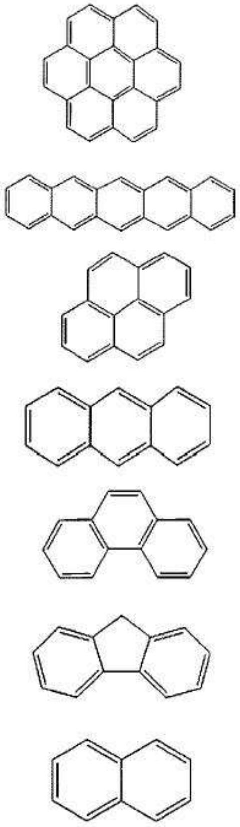


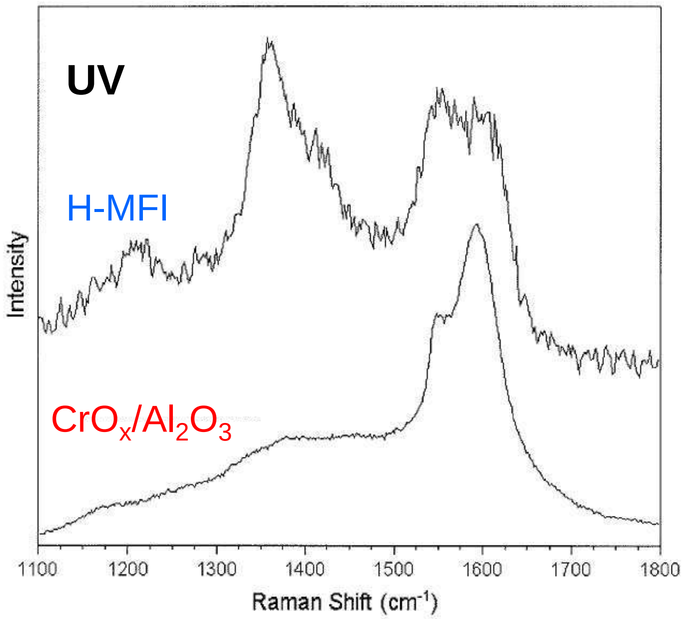
Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization







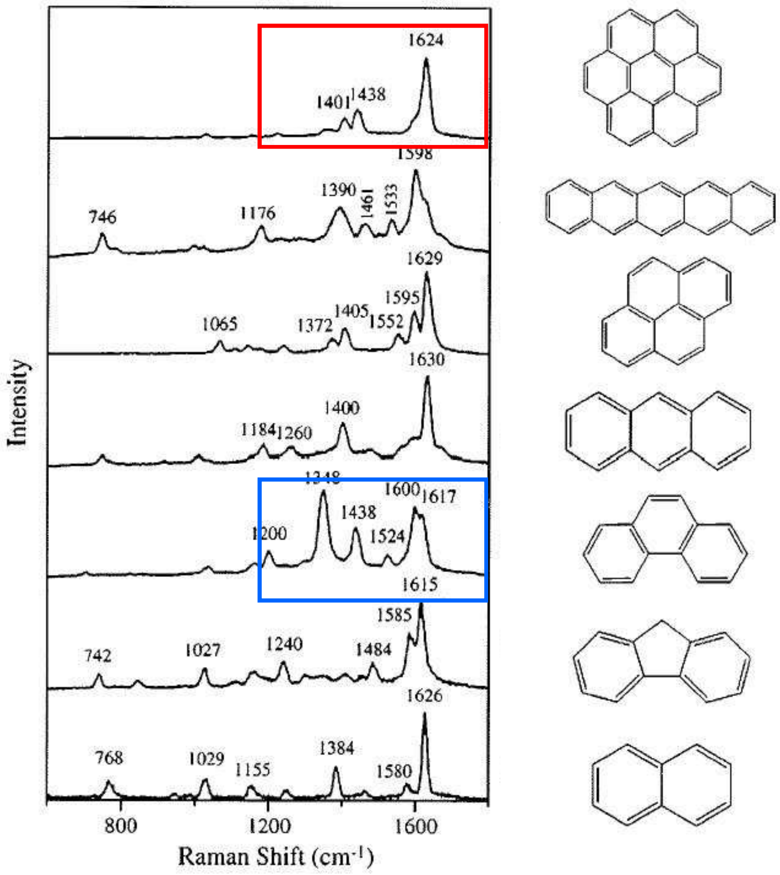
Coke classification
1D topology, chain-like
2D topology, sheet-like

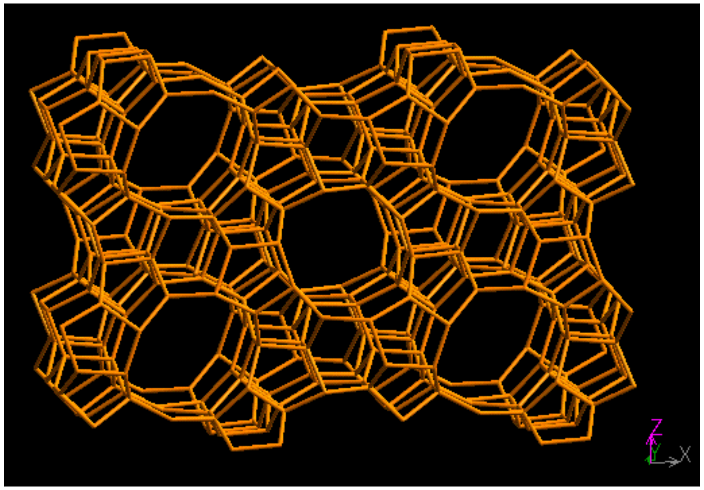
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





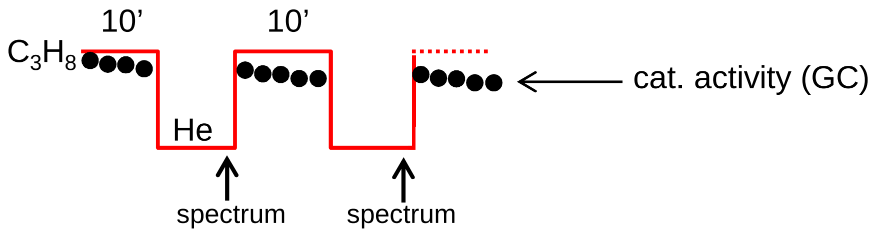
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- Propane dehydrogenation


10’

10’

C_3H_8

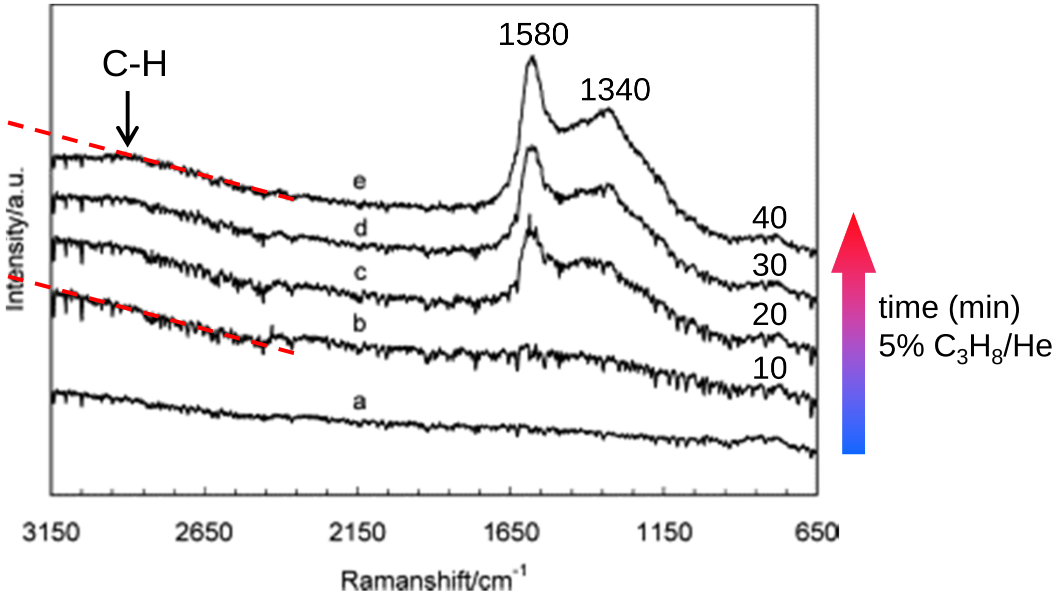
He

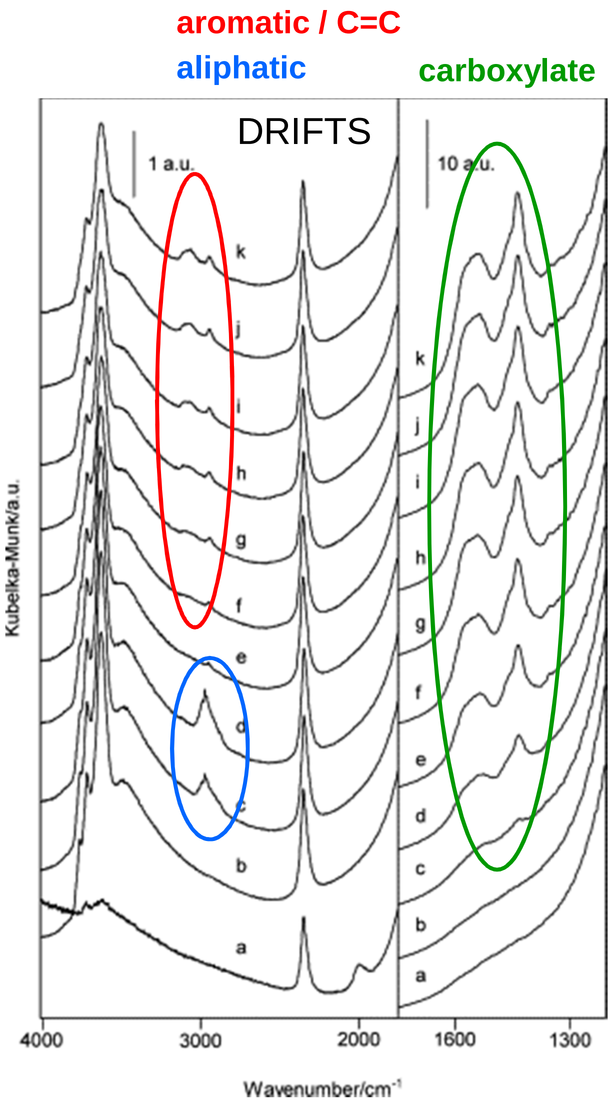
spectrum

spectrum

cat. activity (GC)

Cr_2O_3/Al_2O_3, 580°C, 514 nm

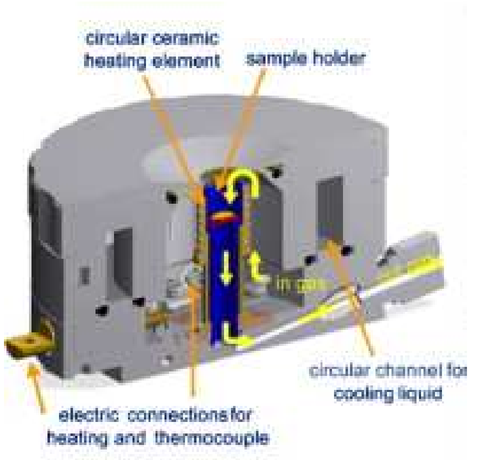


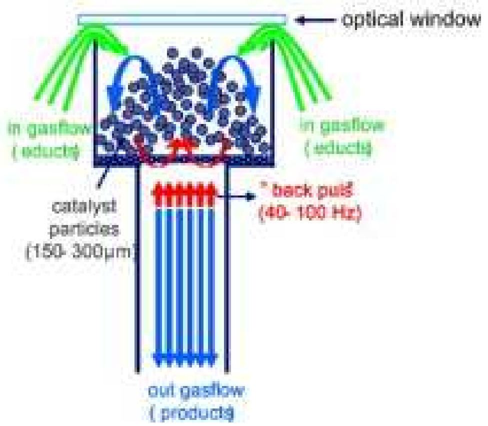


Airaksinen et al., *J. Catal.* **230** (2005) 507

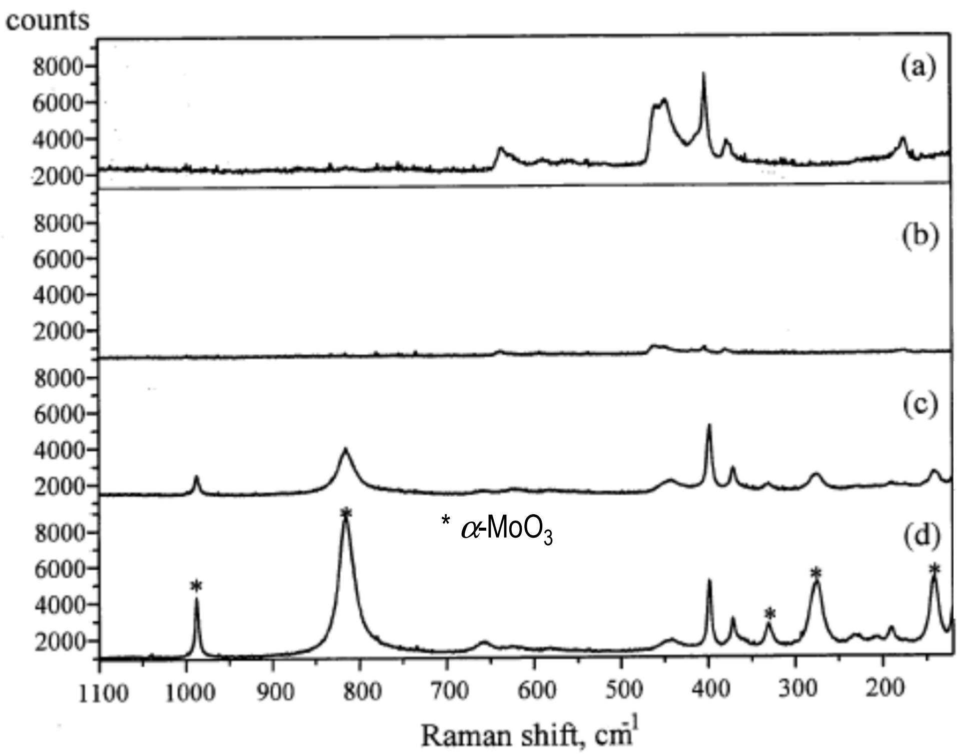
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min
full power, FB

MoS_2, 6 min
1/8 power

MoS_2, 1 min
full power

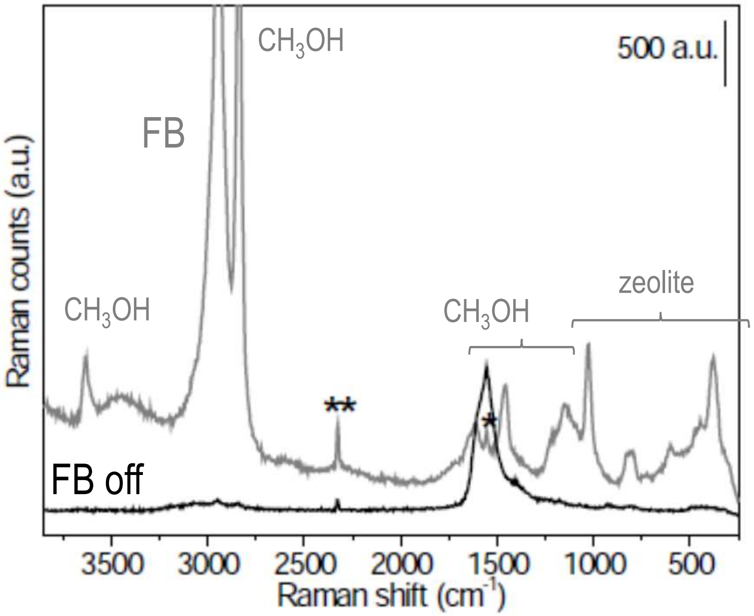
MoS_2, 6 min
full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

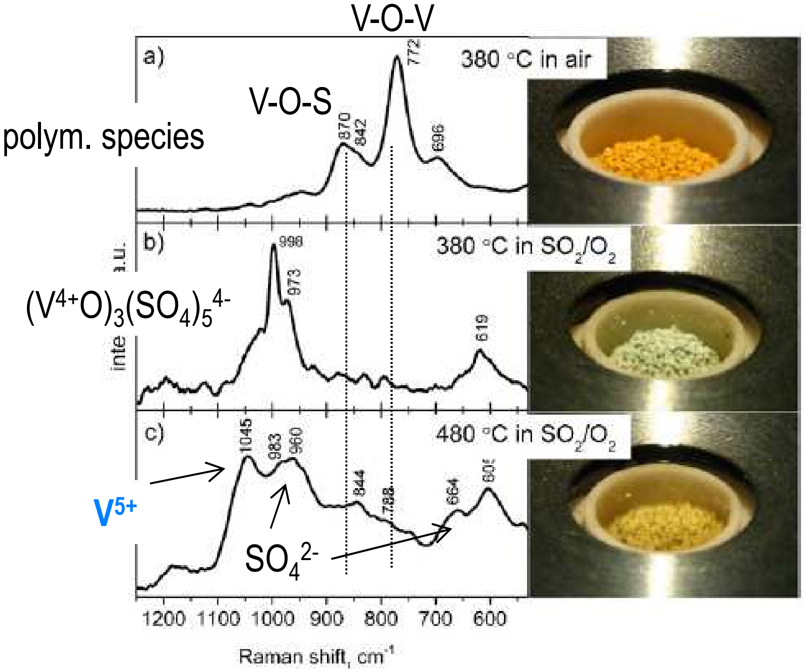
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

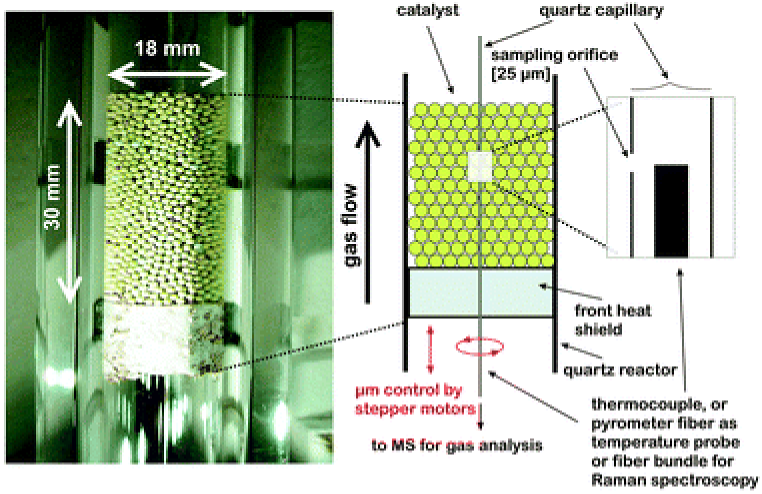


active species: mono- & dimeric V^{5+} oxosulfate species

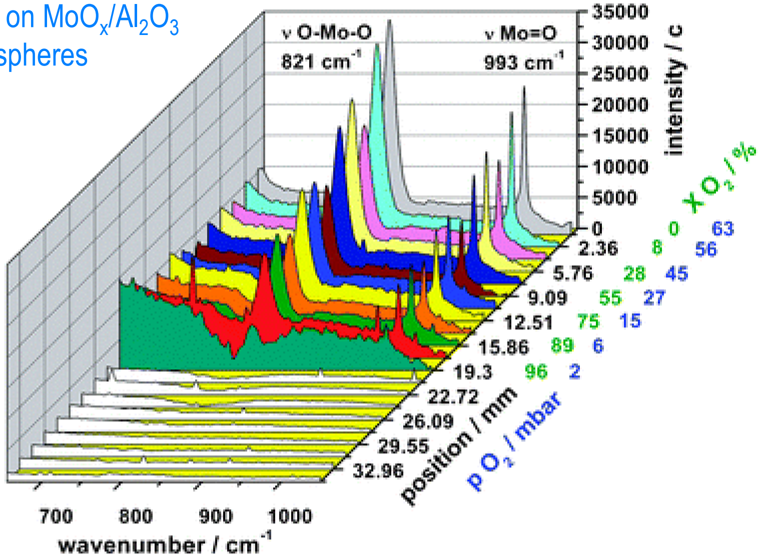
Beato et al., *Catal. Today* 205 (2013) 128

Applications

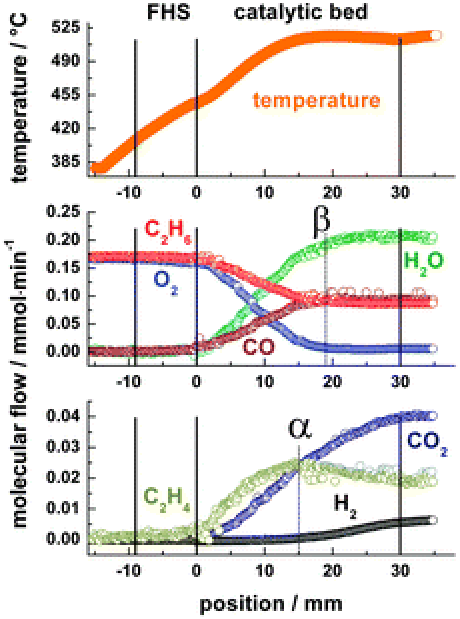
- Fixed bed reactor

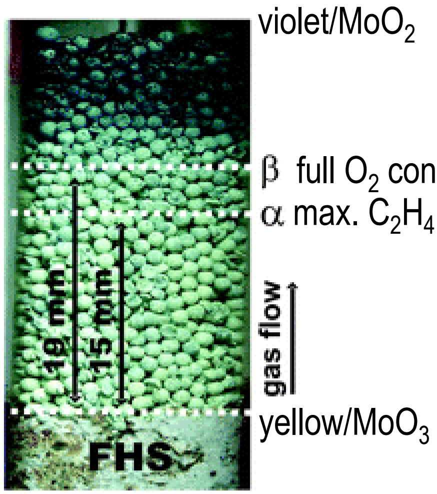


ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm





- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

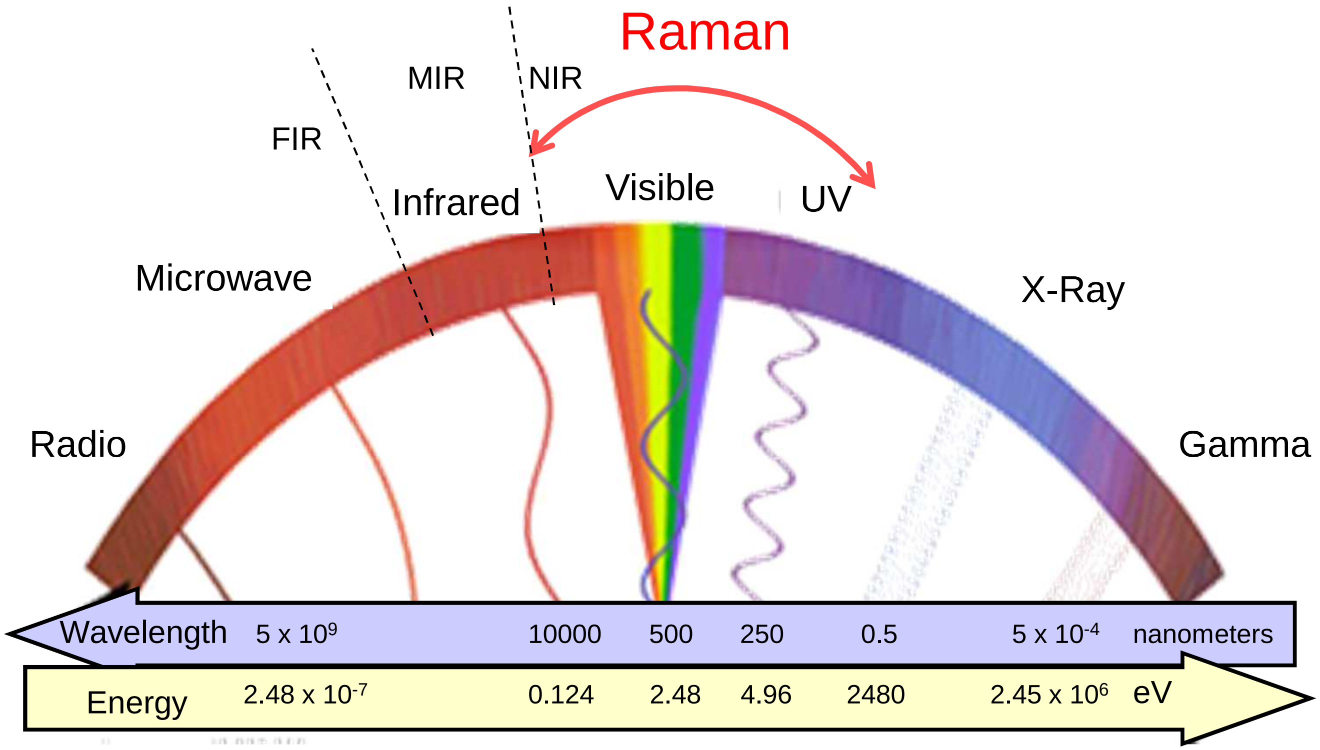
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

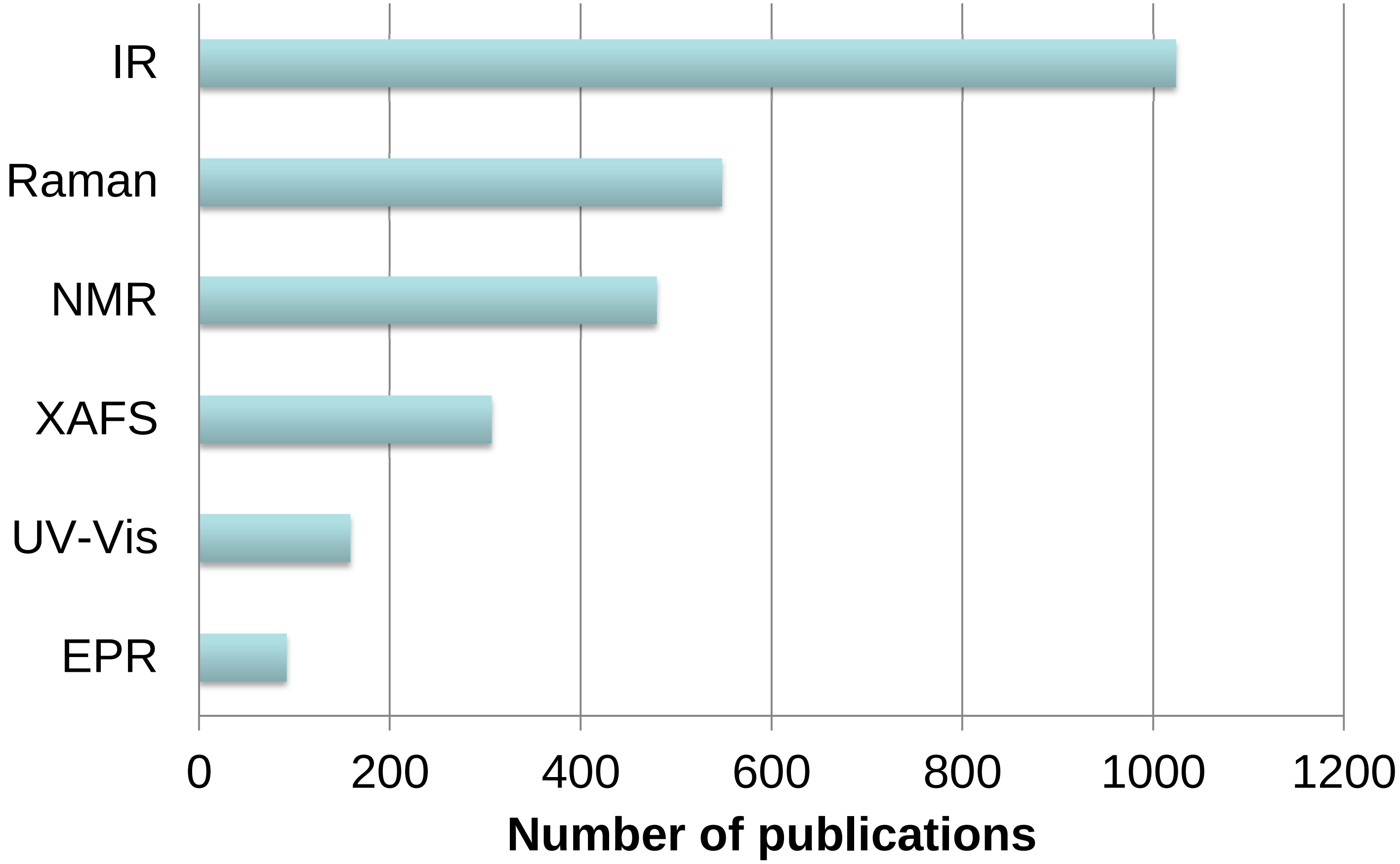
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

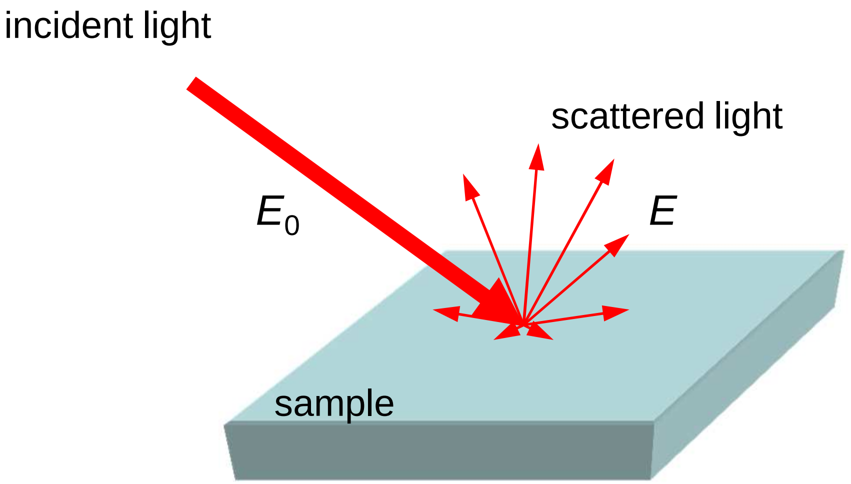


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

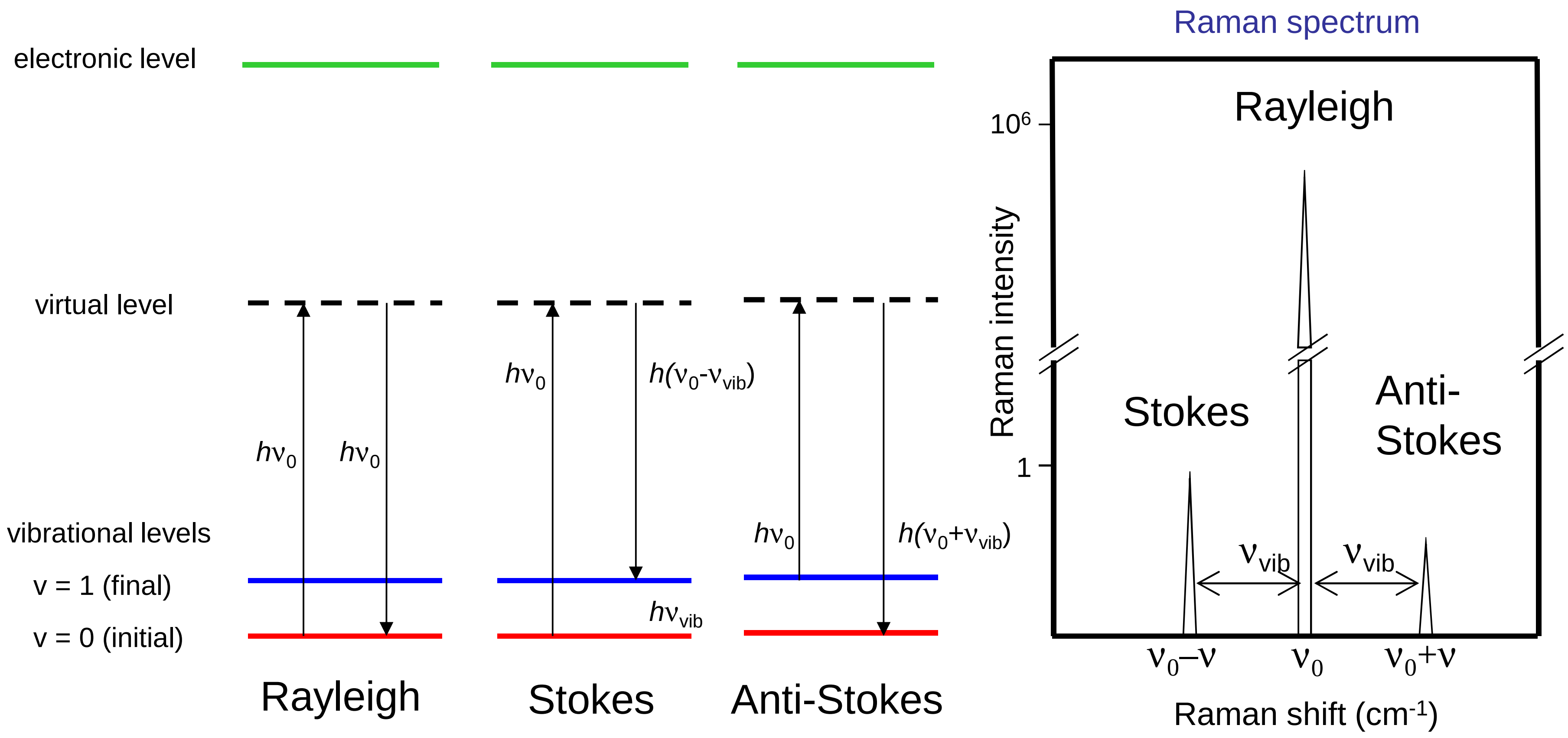
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\text{ (Anti-Stokes)}}{I\text{ (Stokes)}} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

- ☐ 4th power of ν (4th power law)
- ☐ 2nd power of $\Delta\alpha$
  - properties of molecules
  - strength of bonds

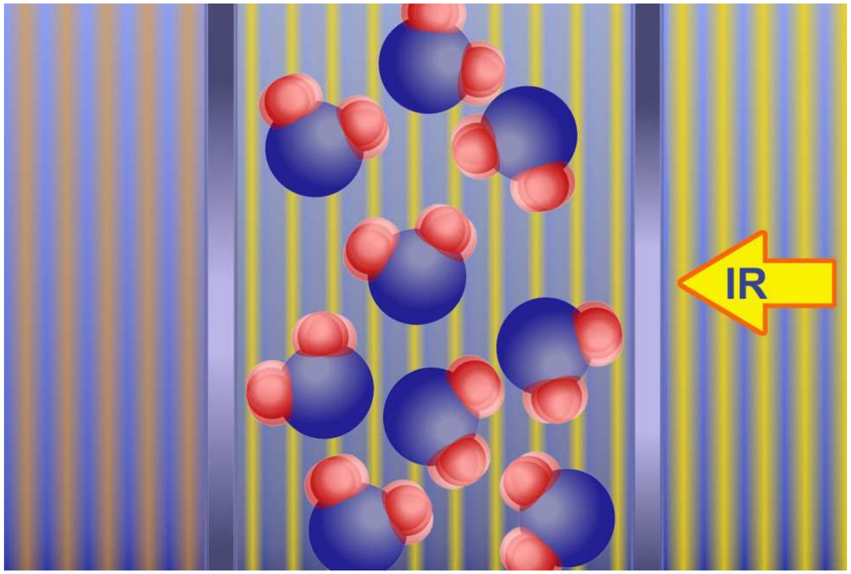
↓

covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

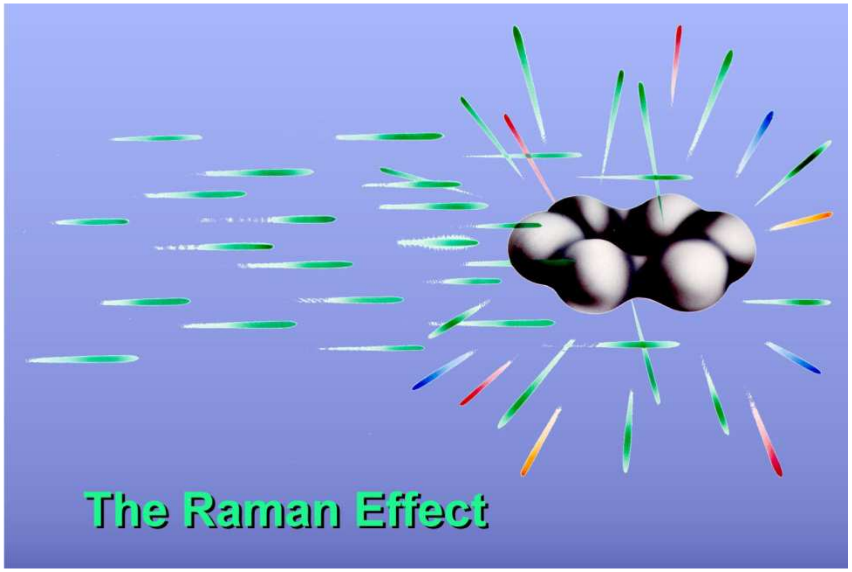
Raman *vs.* Infrared

Infrared



Absorption of IR light

Raman



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

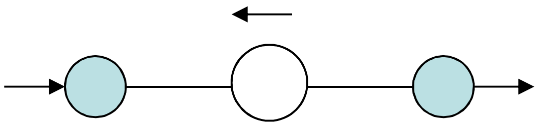
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
    - large electron clouds
    - not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

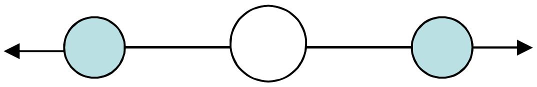
Raman *vs.* Infrared

CO_2



ν_{as}

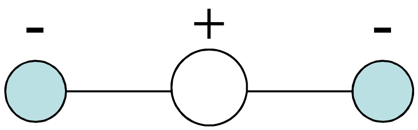
2349 cm^{-1}



ν_s

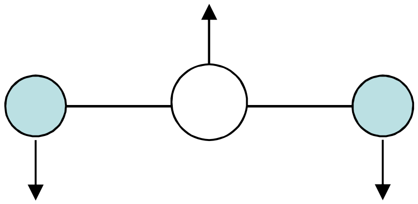
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



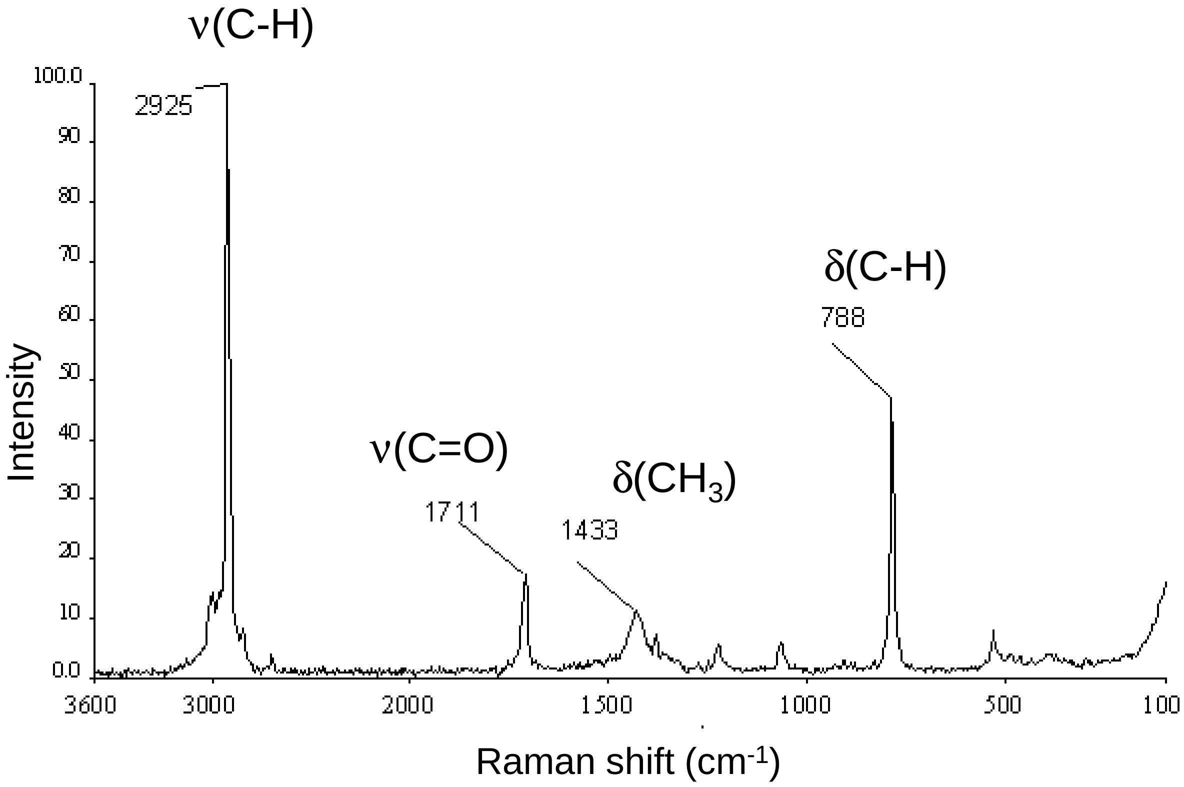
δ

667 cm^{-1}

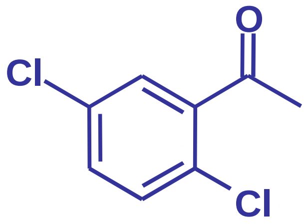
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



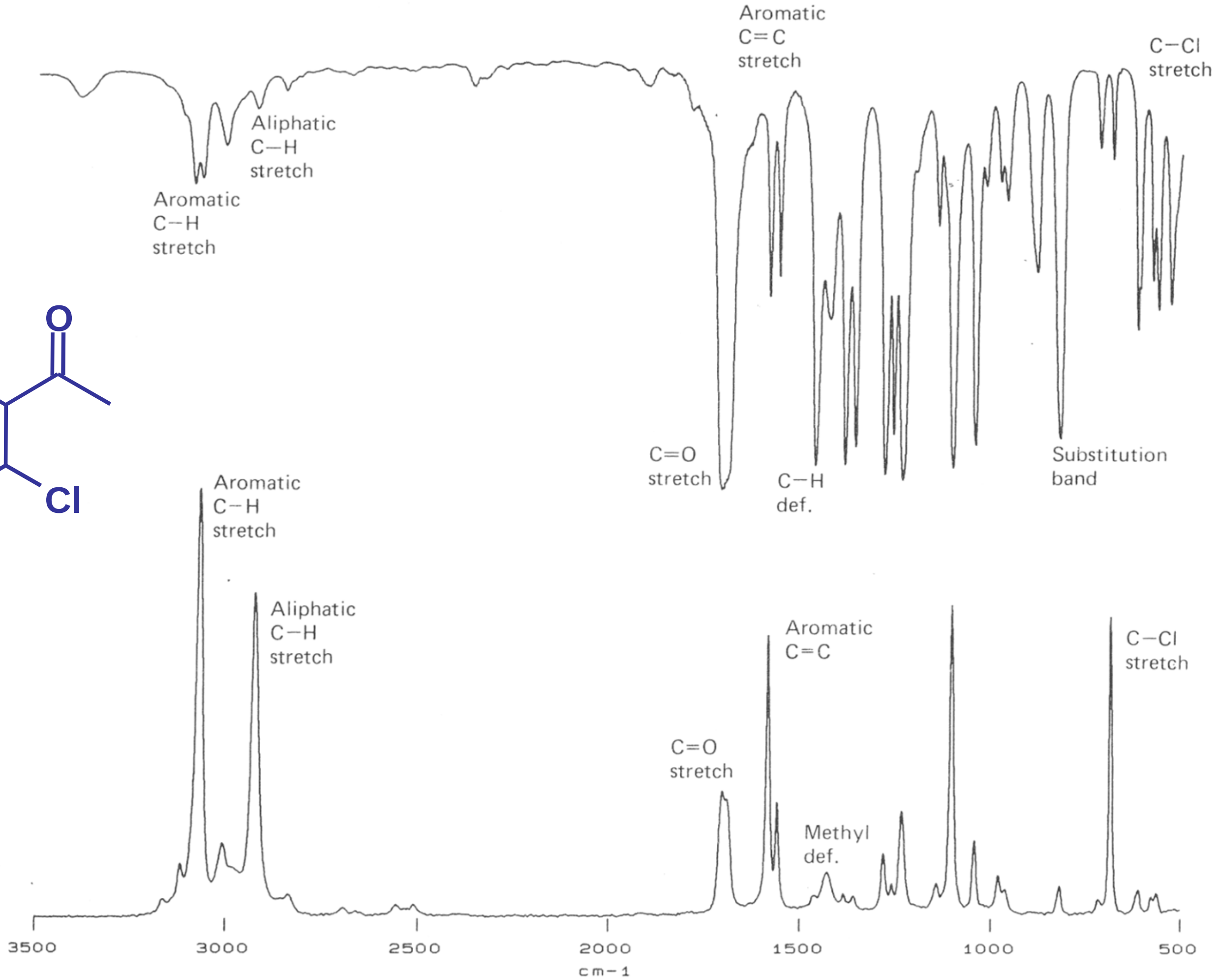


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

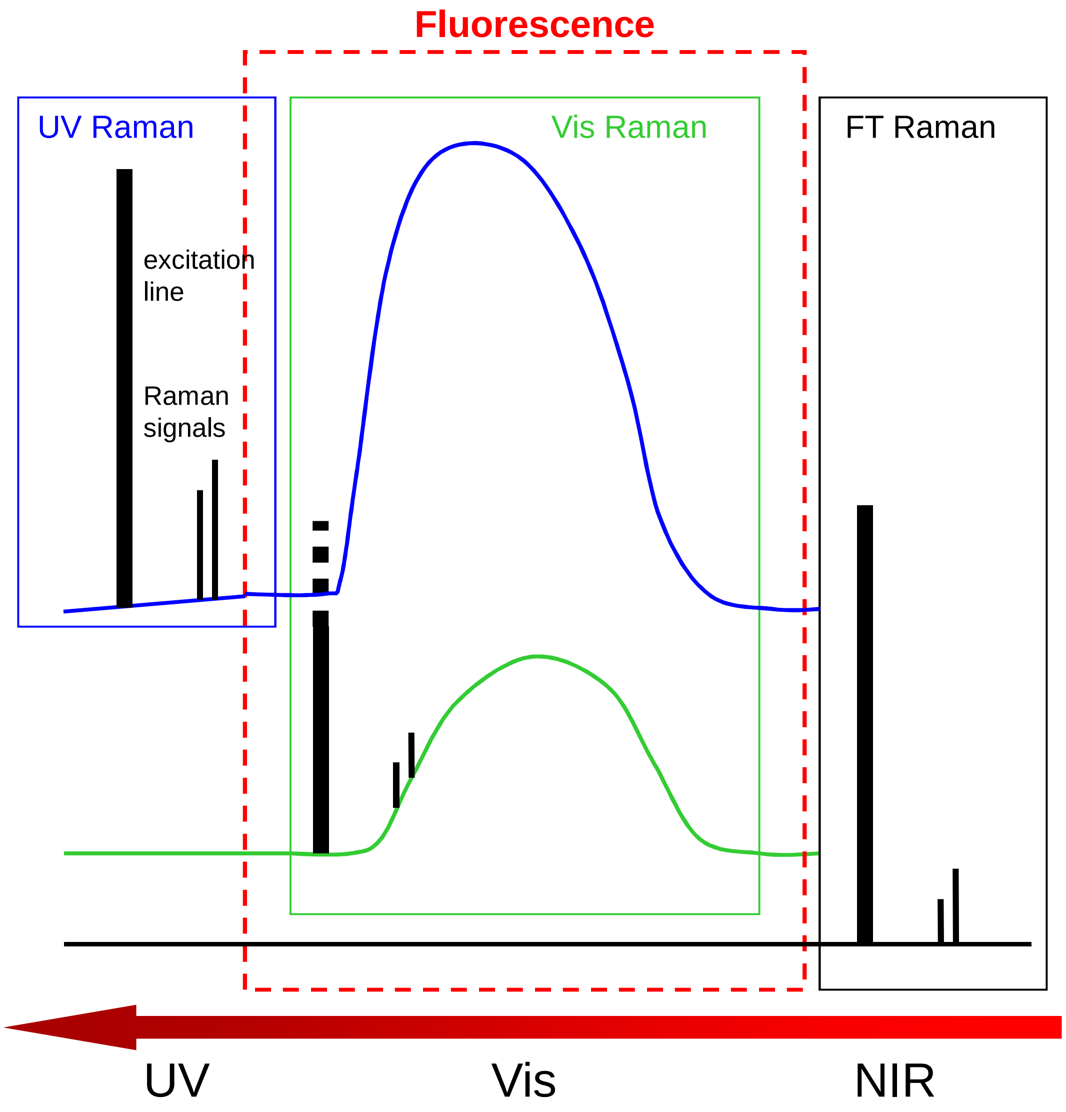
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 µm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

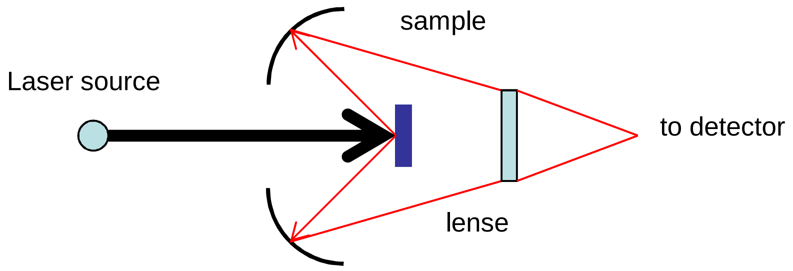
Fluorescence proportional to ν

Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation

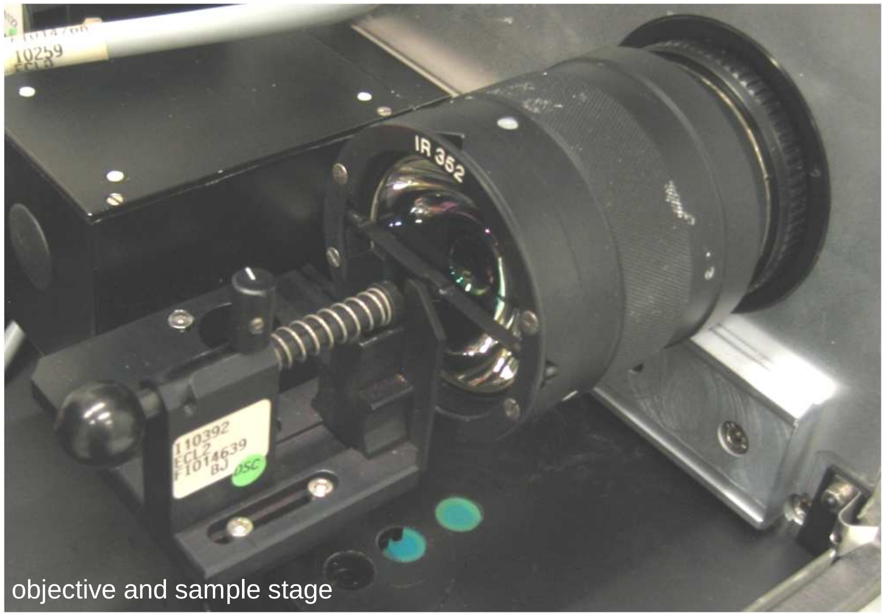


sample

Laser source

to detector

lense



objective and sample stage

Lasers
Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

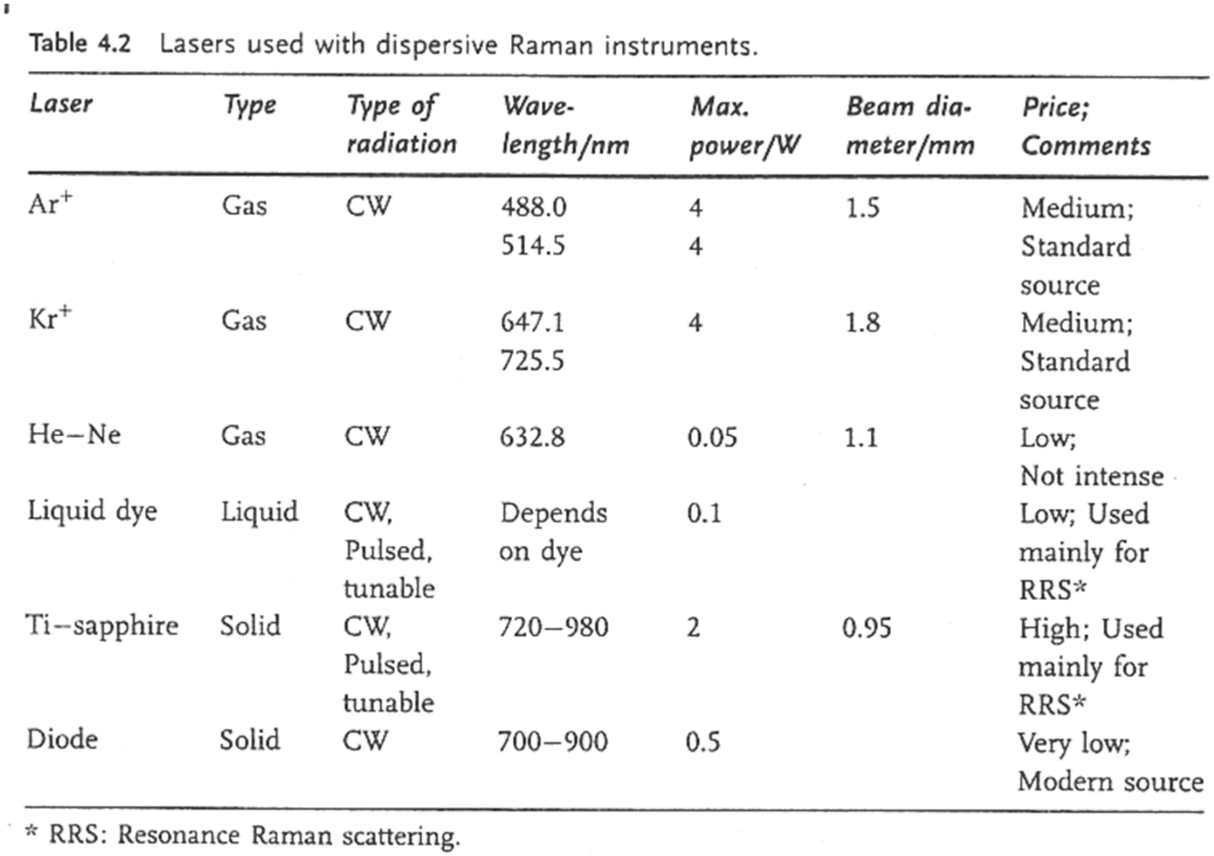


Table 4.2 Lasers used with dispersive Raman instruments.

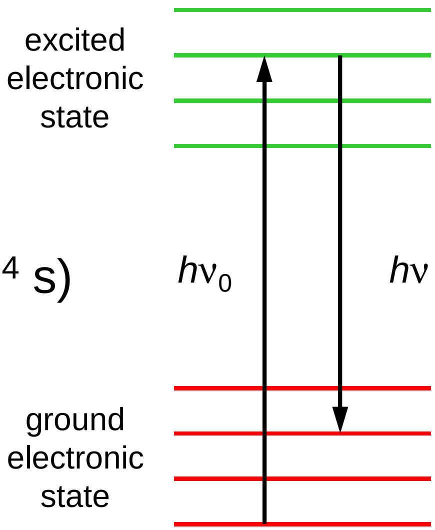
Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

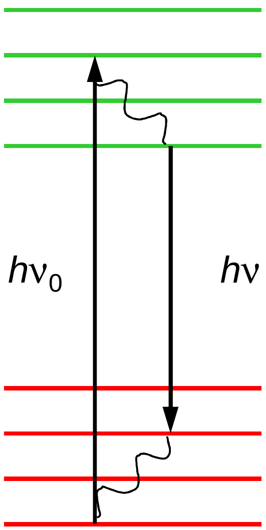
Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited

fast (10^{-14} s)



Resonance Raman scattering



Fluorescence

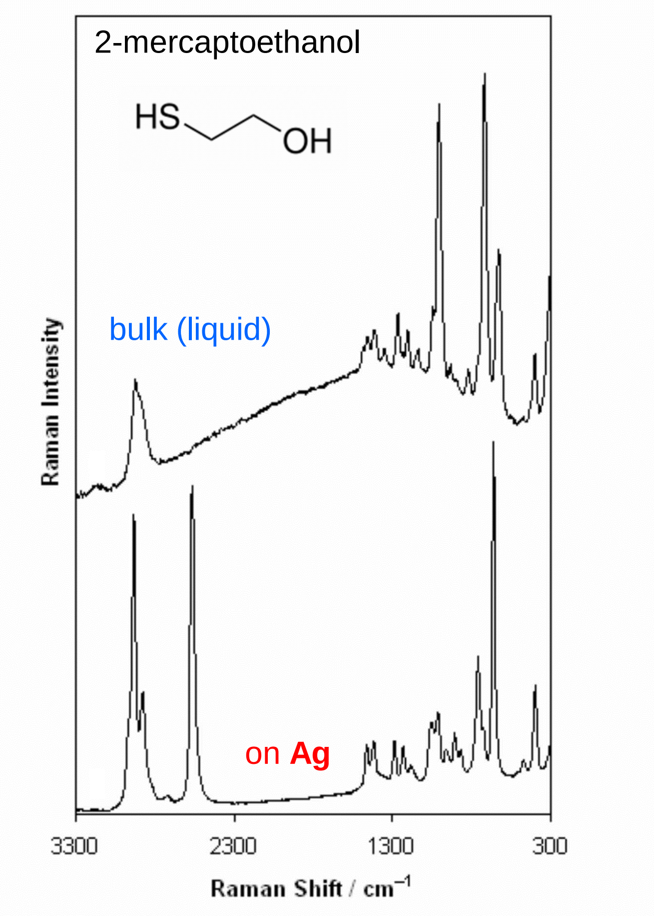
slow (10^{-9}–10^{-6} s)

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

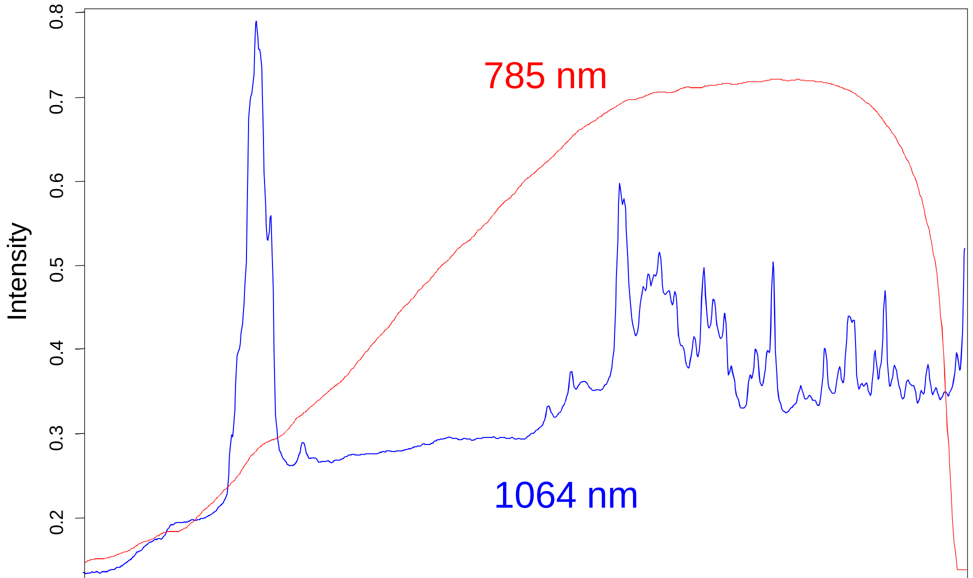
- Remarks:

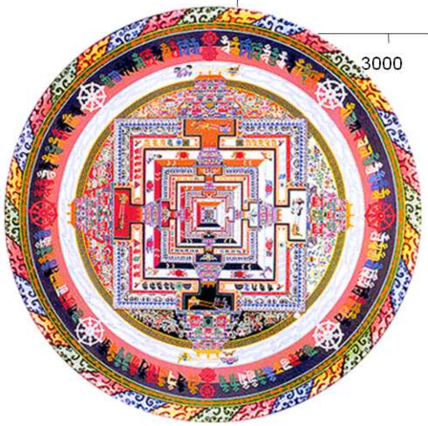
❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring





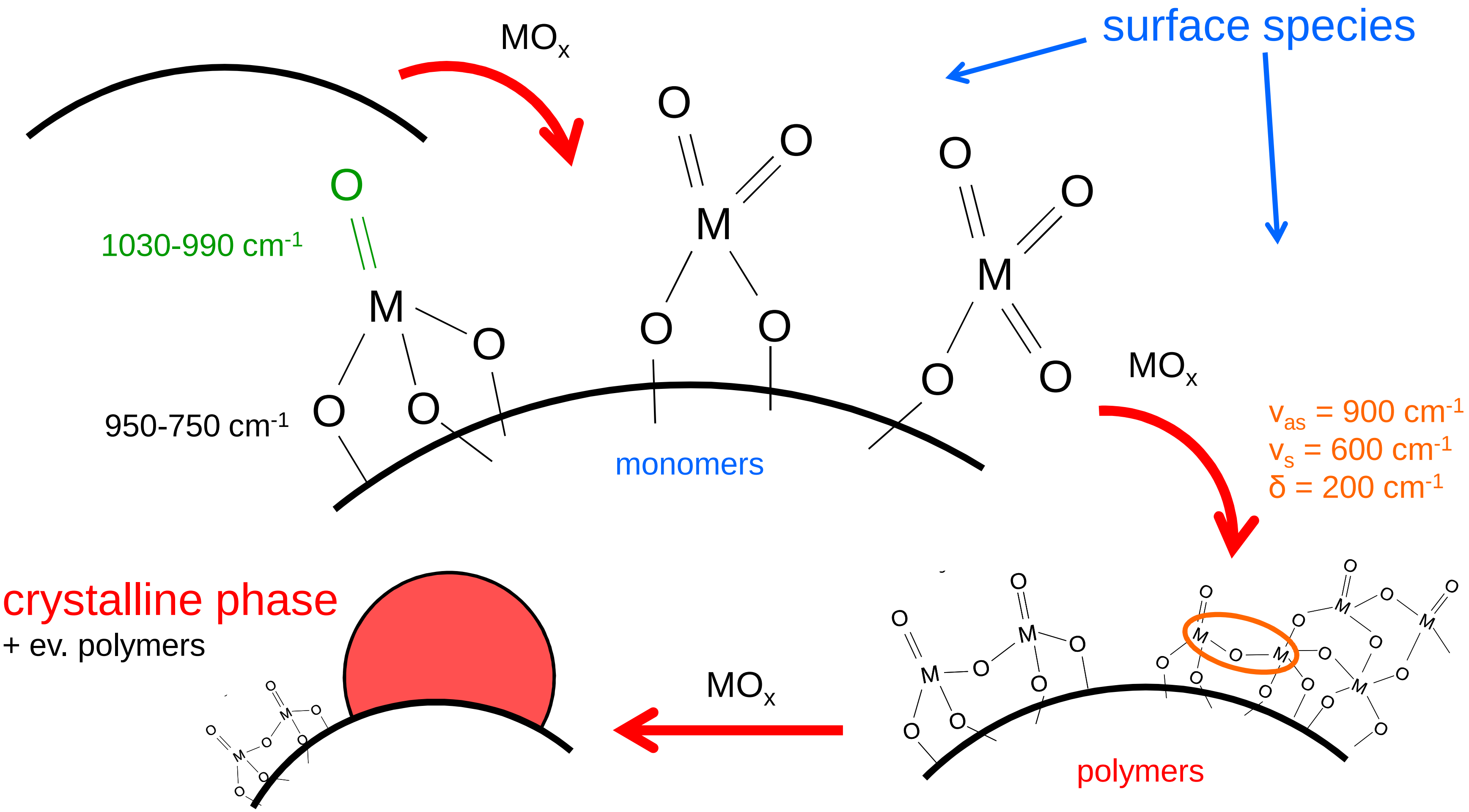
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species

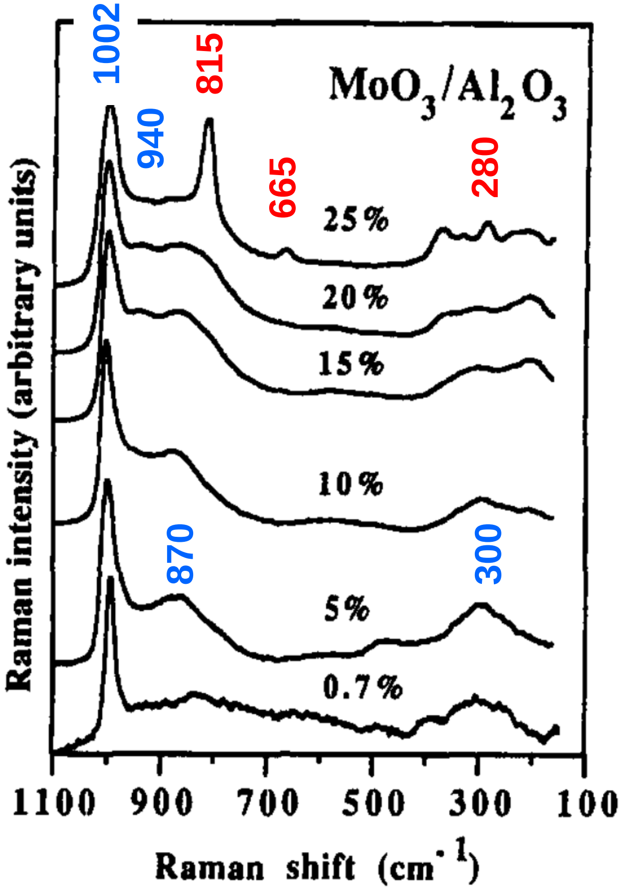


Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



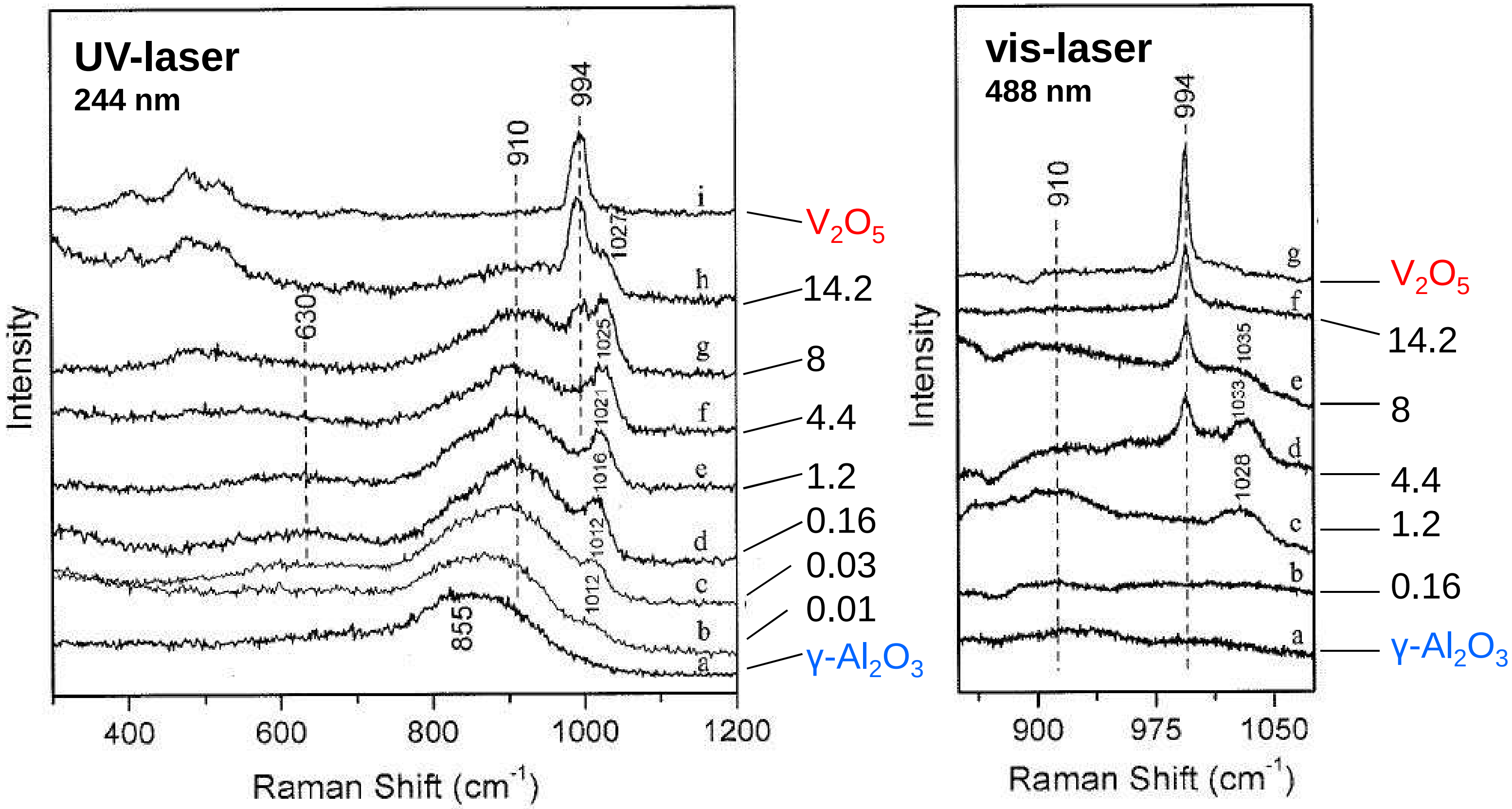
surface MoO_3
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

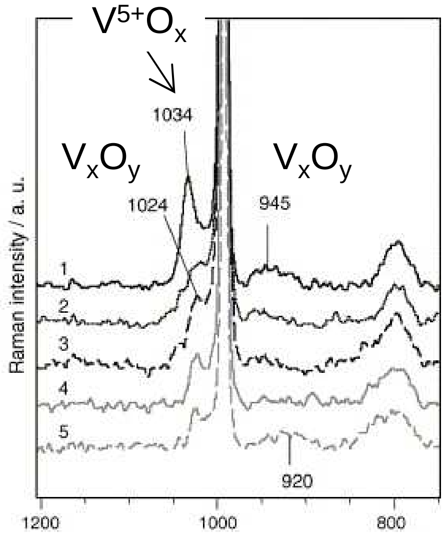
- Monomeric & polymeric species



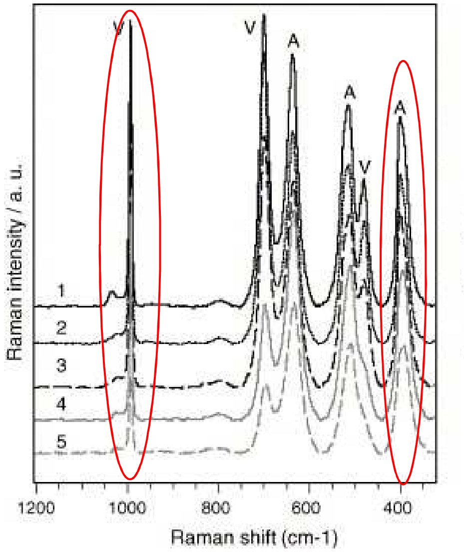
Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

Applications

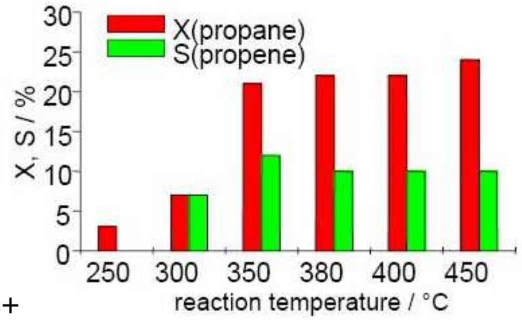
- Reactivity of V/TiO_2 after oxidative treatment

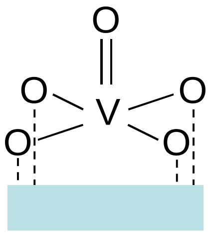


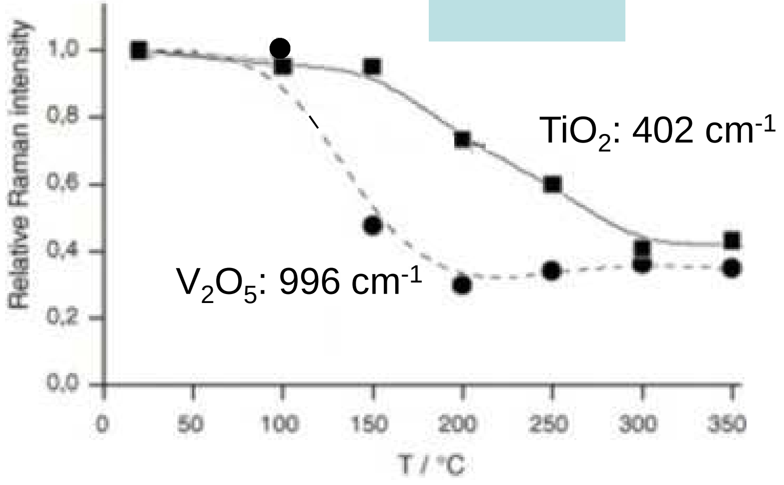
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C



$V^{5+} \longrightarrow V^{4+}$







TiO_2: 402 cm^{-1}

V_2O_5: 996 cm^{-1}

Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

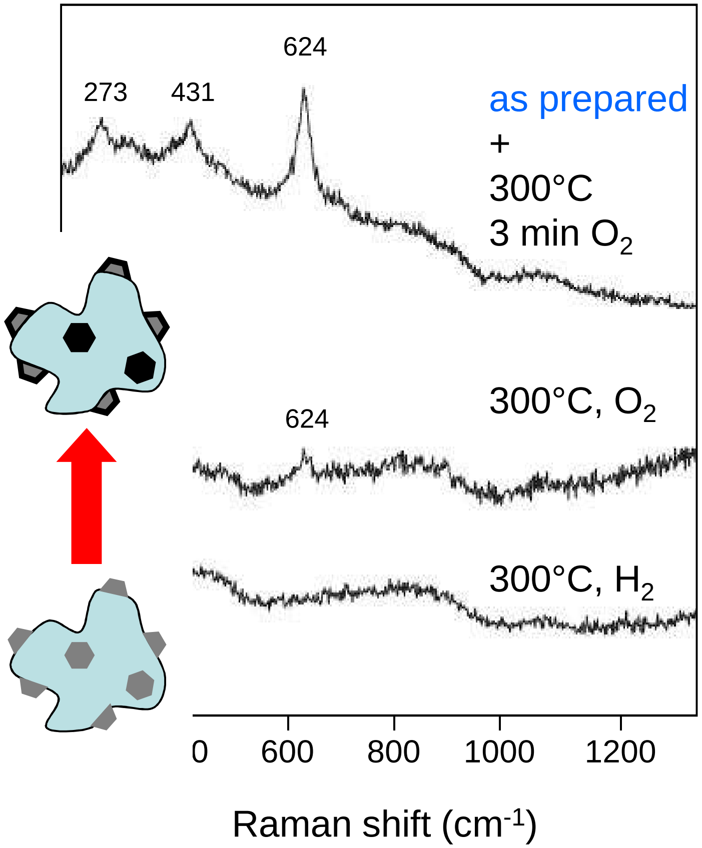
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

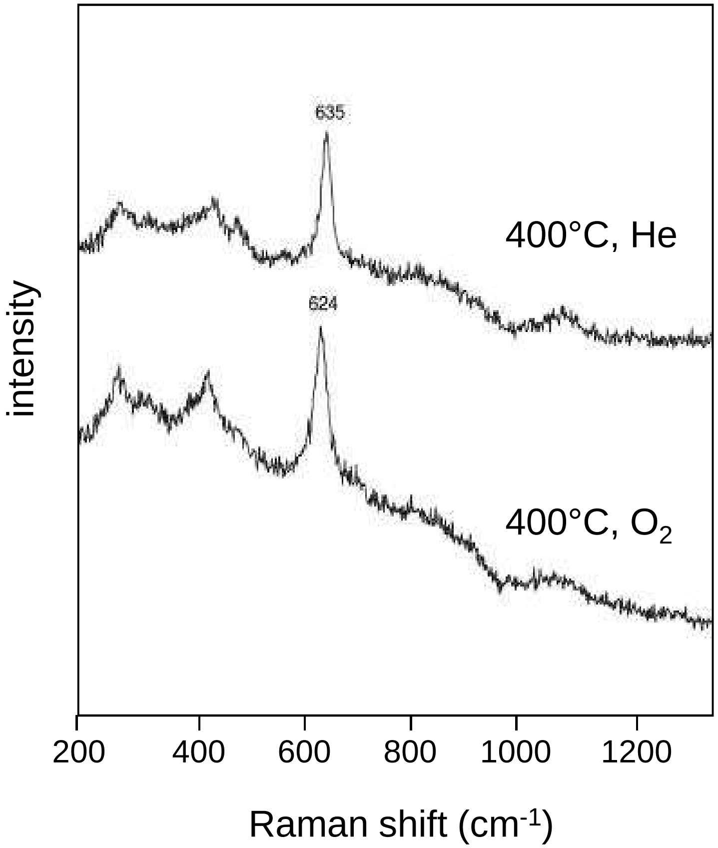
Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3





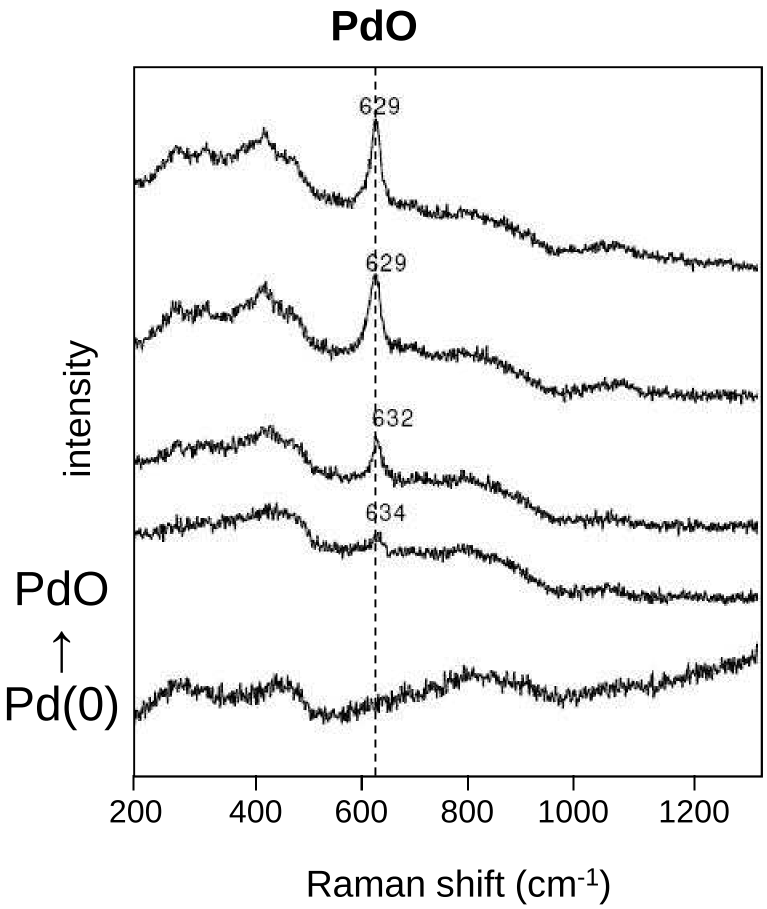
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



CH_4 conv.

500°C **24 %**

450°C **15 %**

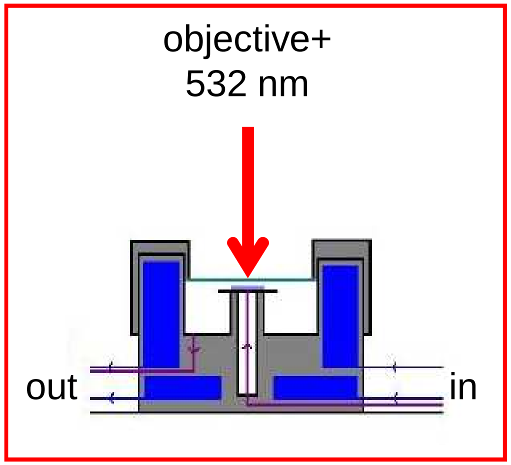
425°C **4 %**

400°C **2 %**

400°C, H_2
reduced Pd

feed CH_4/O_2 (1:10)

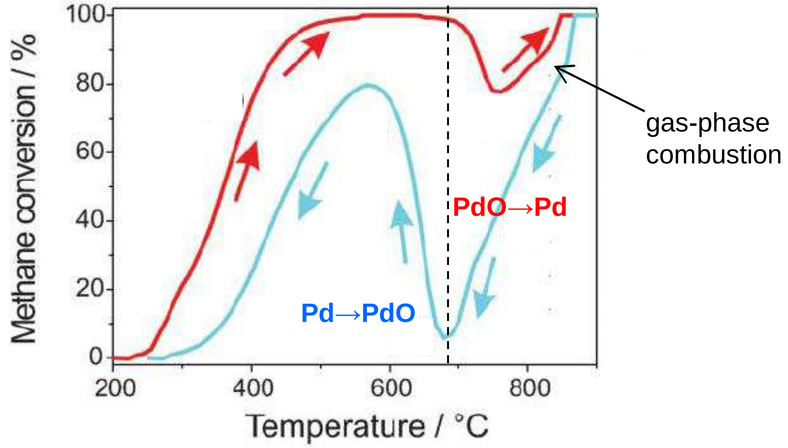
near PdO mode

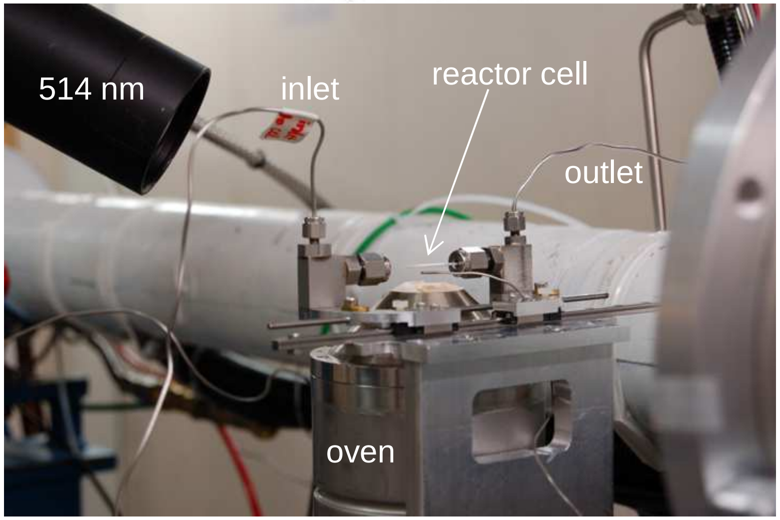


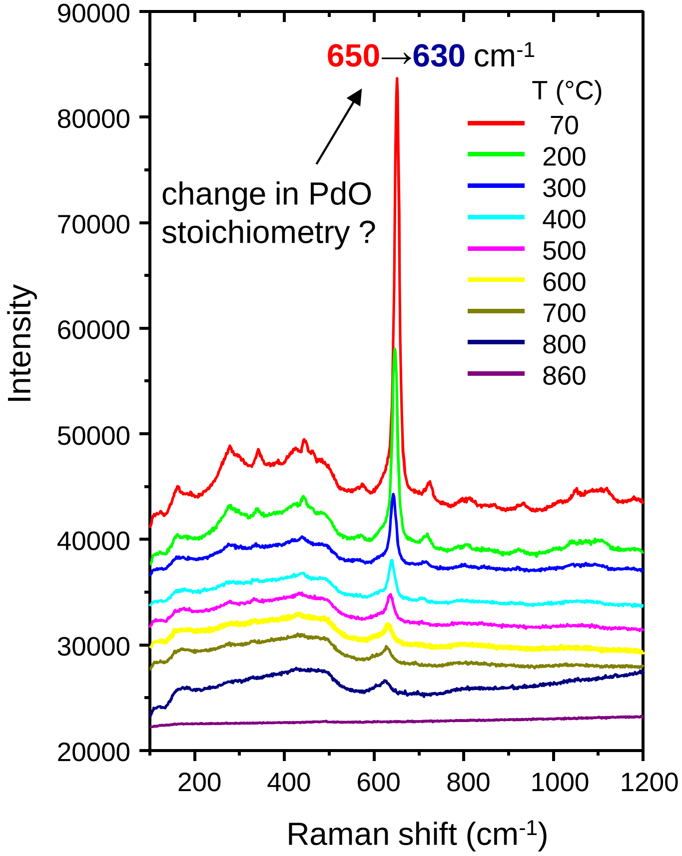
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

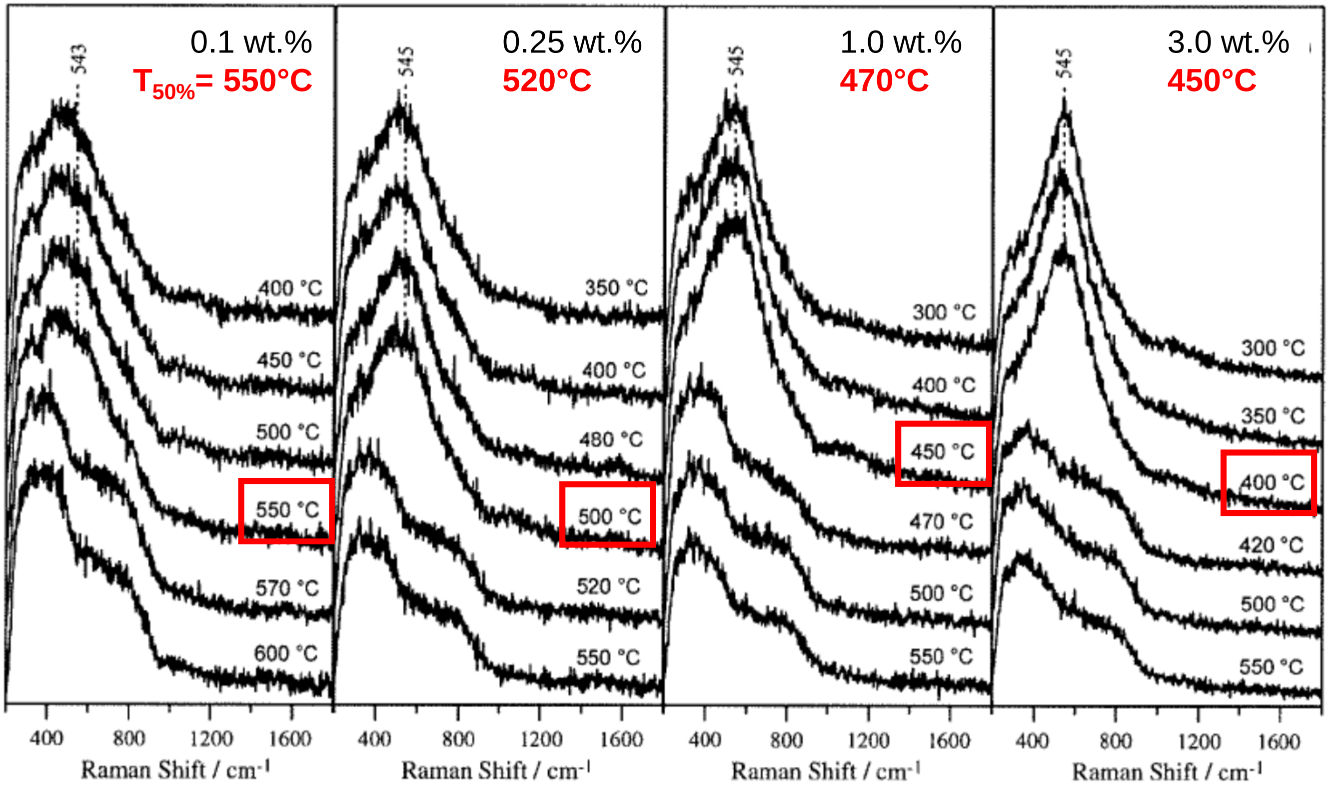
- Methane partial oxidation over Rh/Al_2O_3

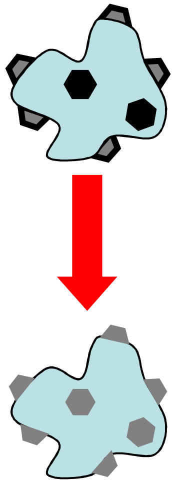
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content →
Activity →

RhOx
↓
Rh(0)





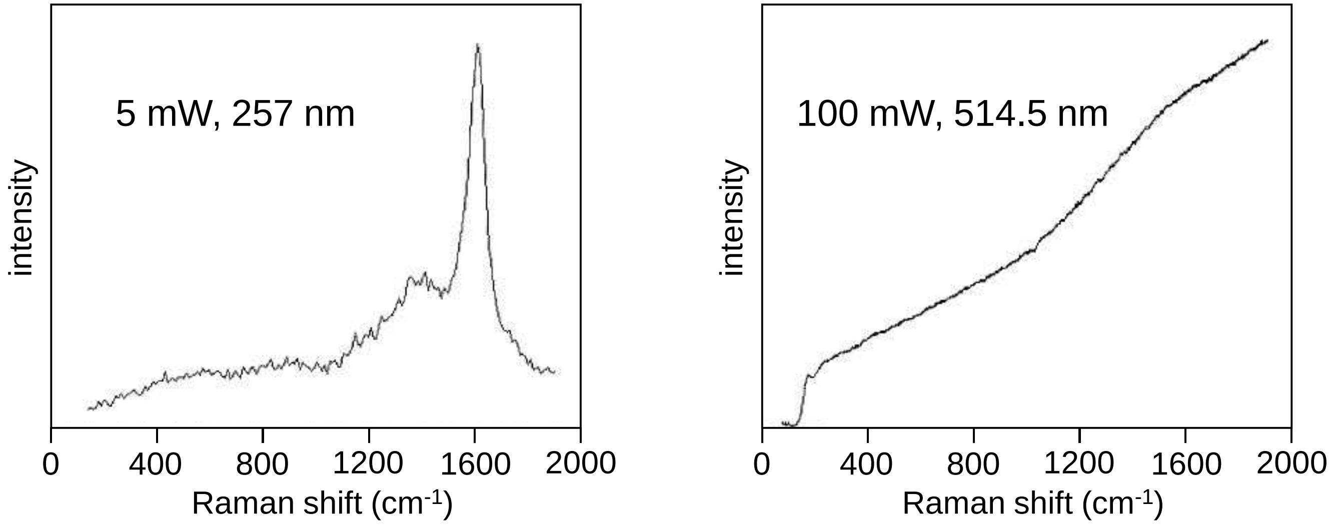
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

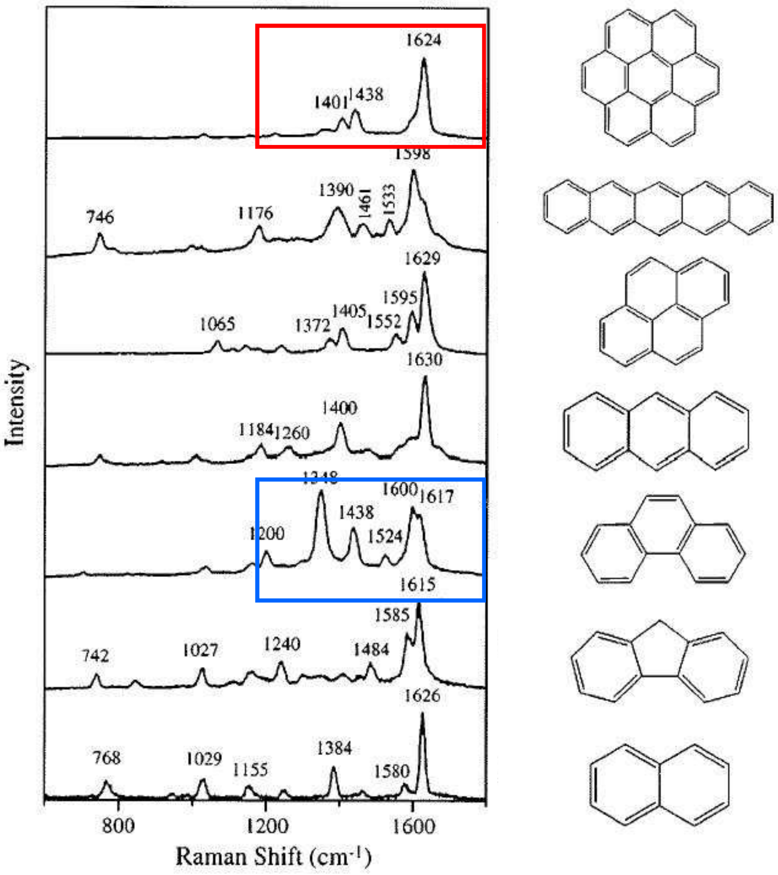
Rh/Al_2O_3, coked 500°C in naphtha

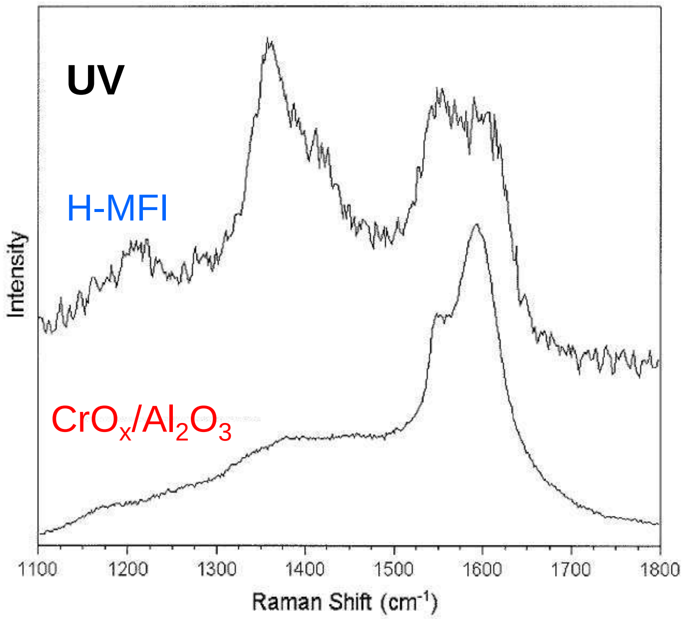


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





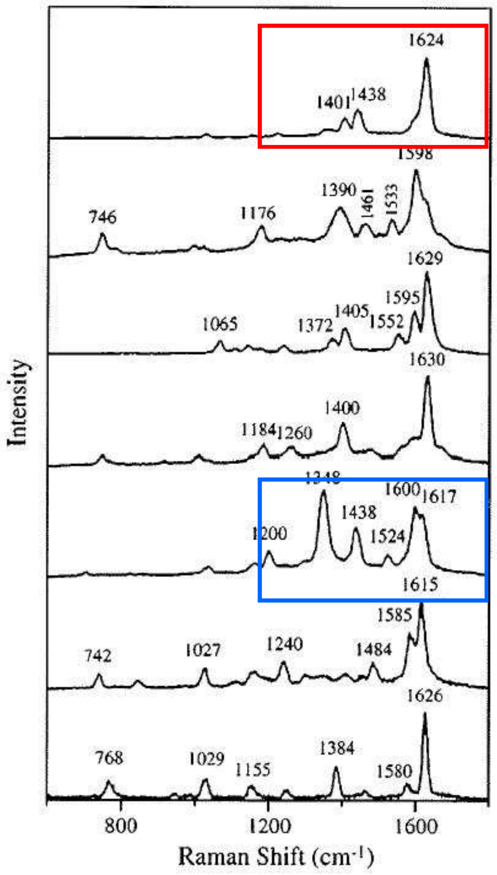
Coke classification
1D topology, chain-like
2D topology, sheet-like

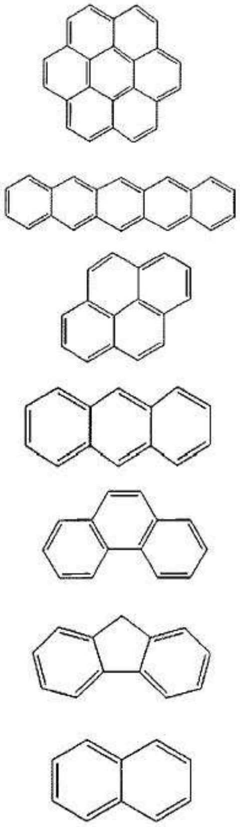
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

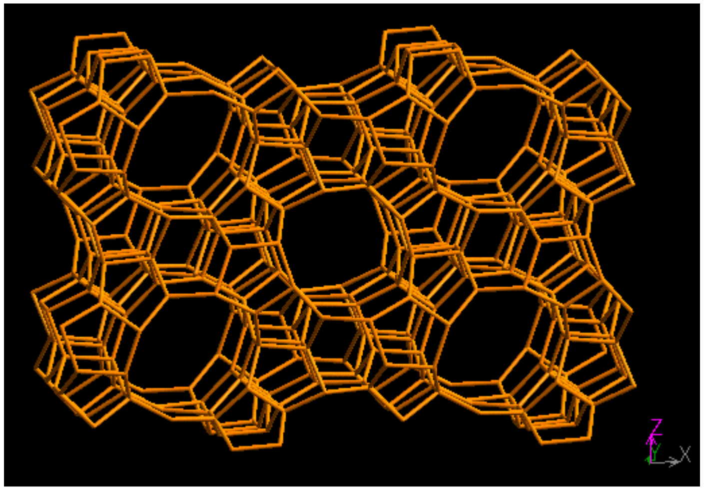
Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization







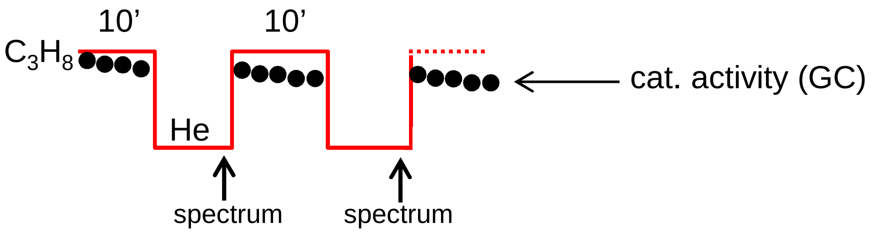
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

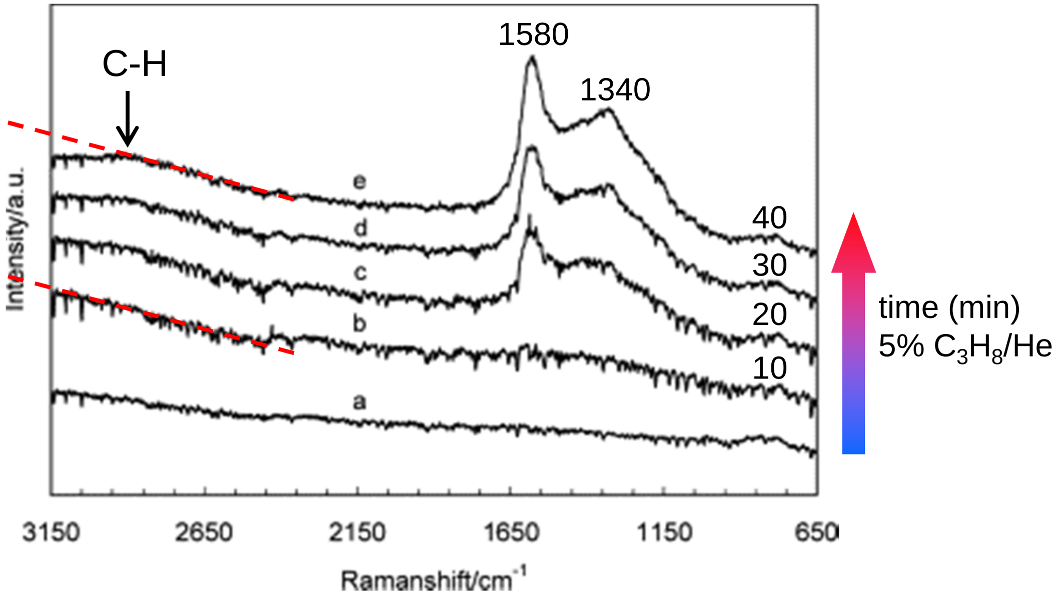
Stair, *Adv. Catal.* **51** (2007) 75

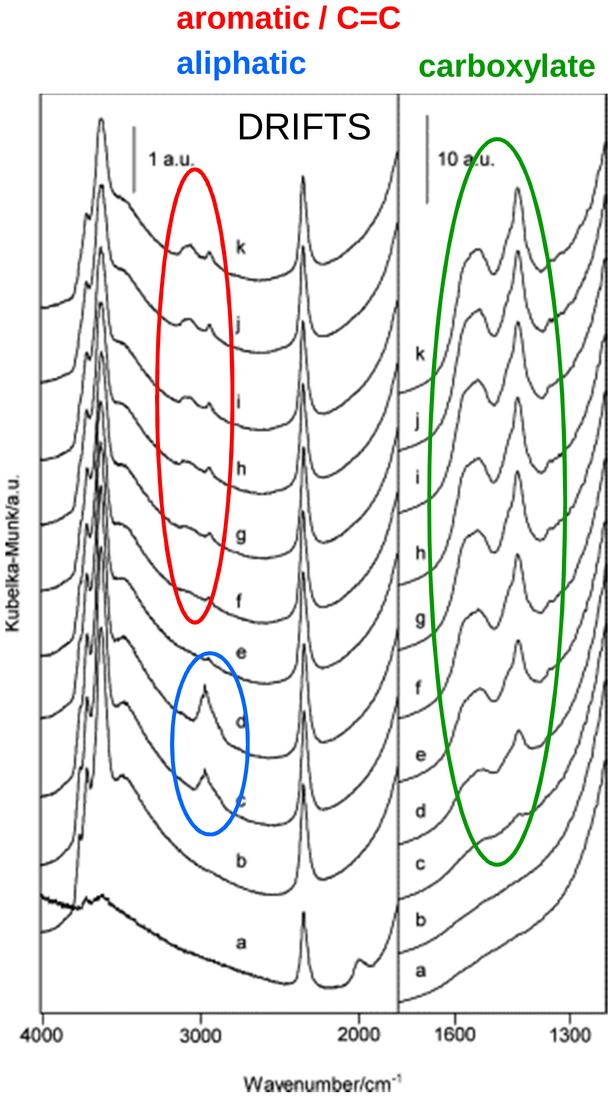
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

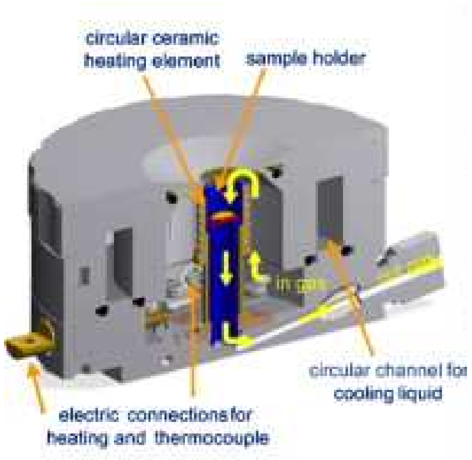


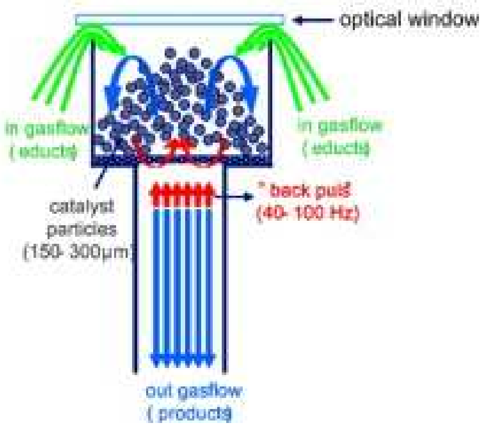


Airaksinen et al., *J. Catal.* **230** (2005) 507

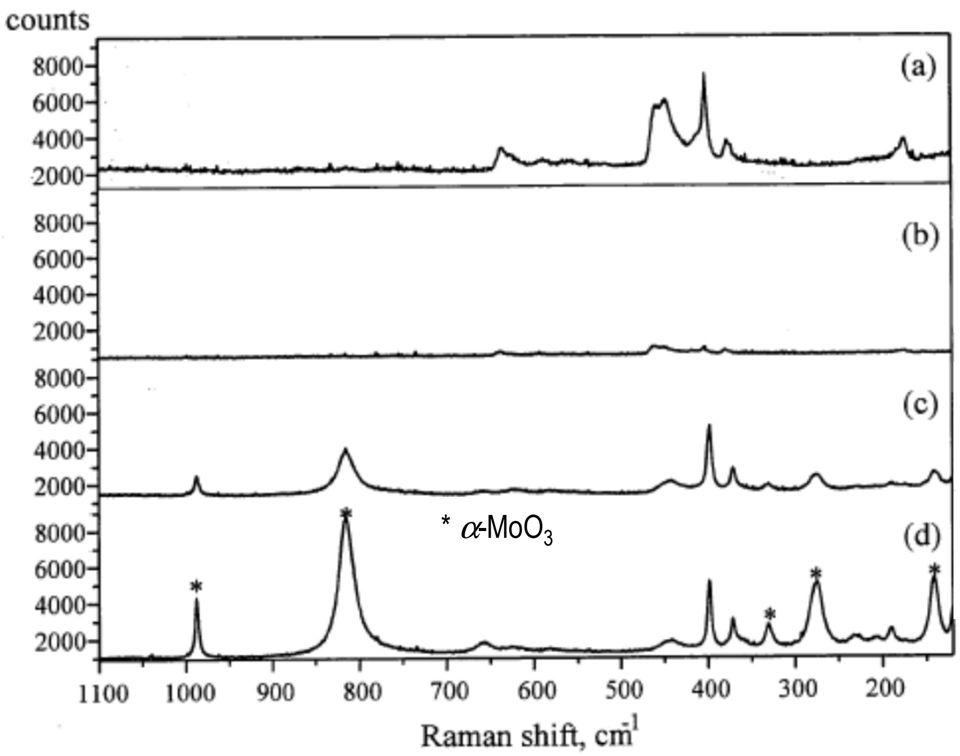
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min
full power, FB

MoS_2, 6 min
1/8 power

MoS_2, 1 min
full power

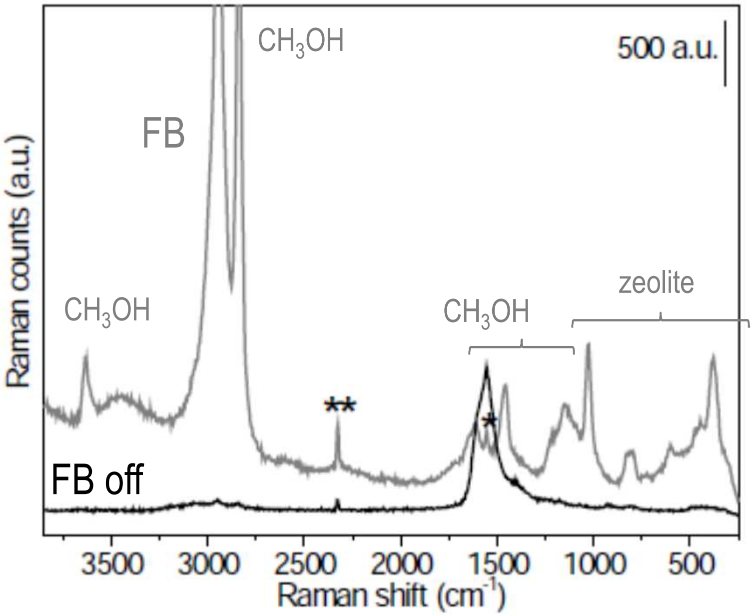
MoS_2, 6 min
full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

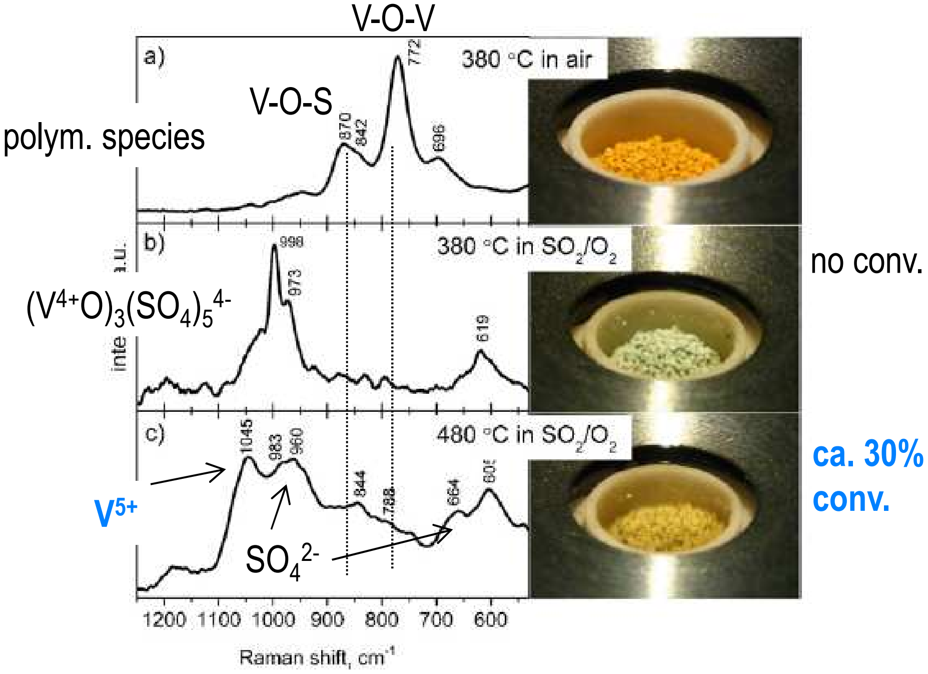
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

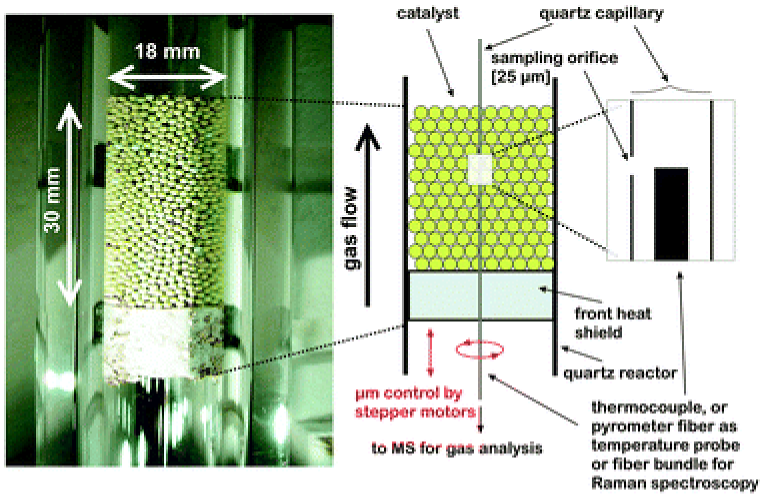


active species: mono- & dimeric V^{5+} oxosulfate species

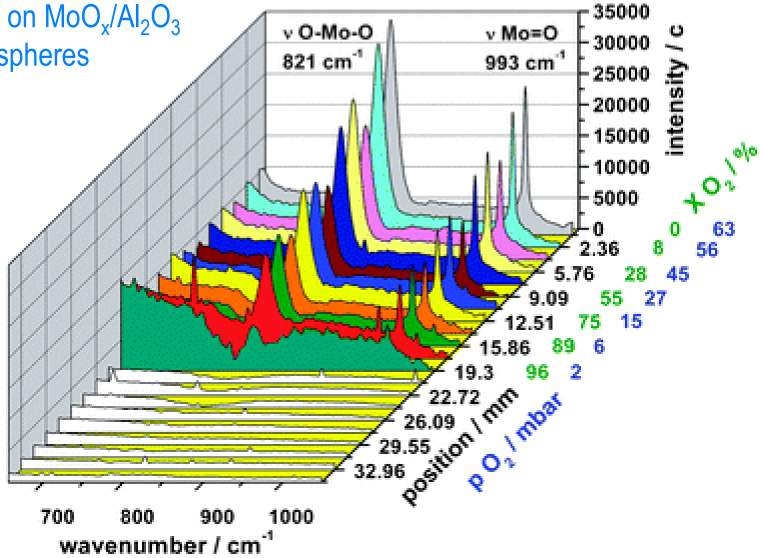
Beato et al., *Catal. Today* 205 (2013) 128

Applications

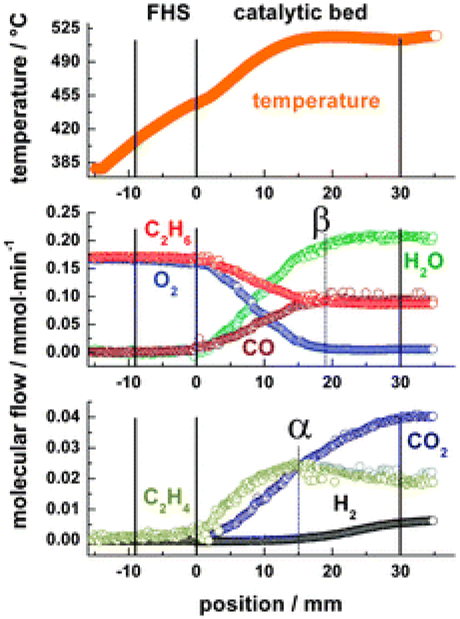
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

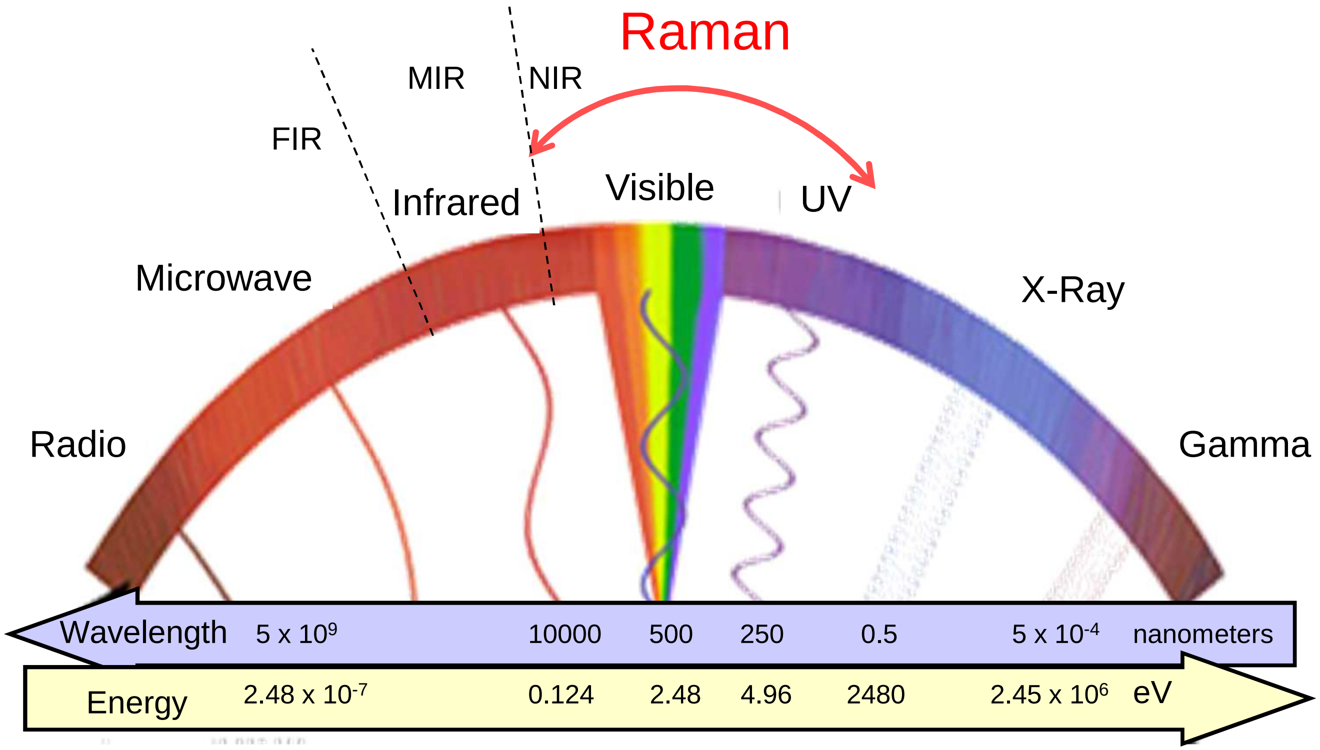
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

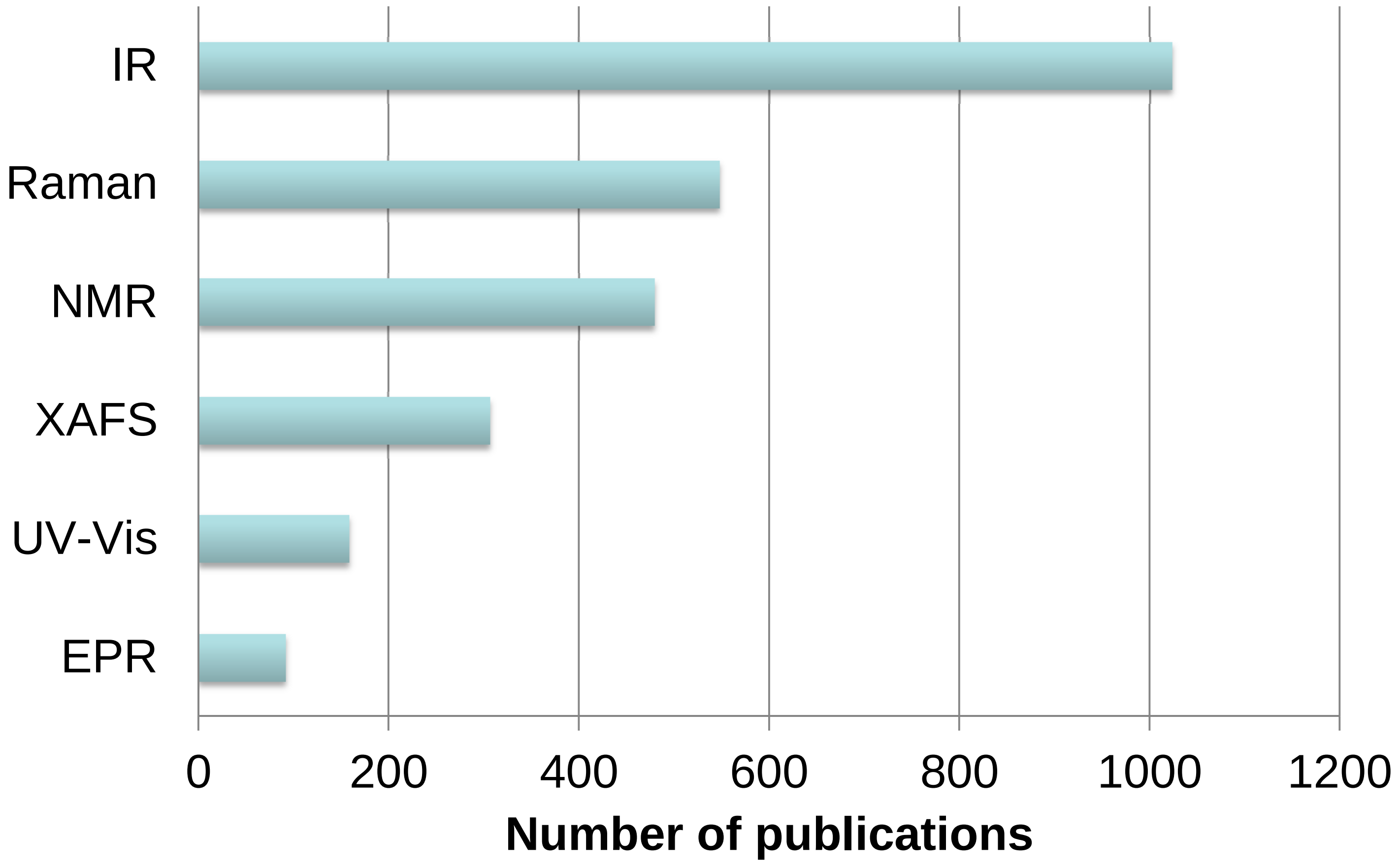
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

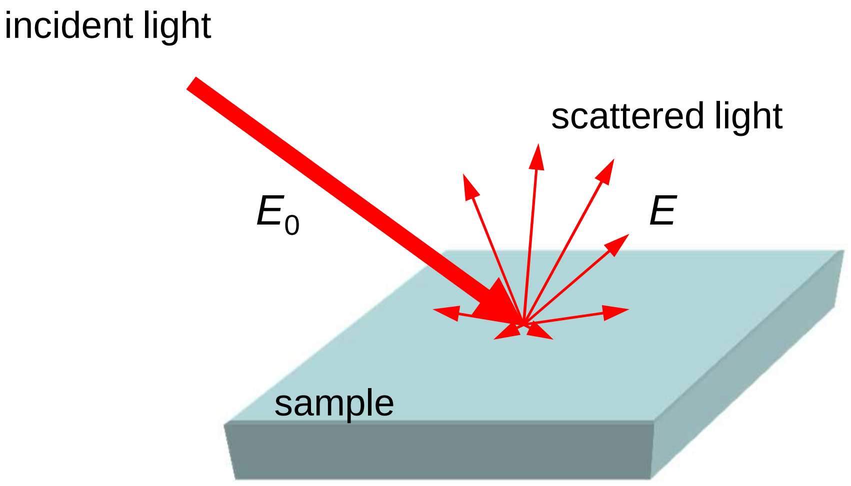


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

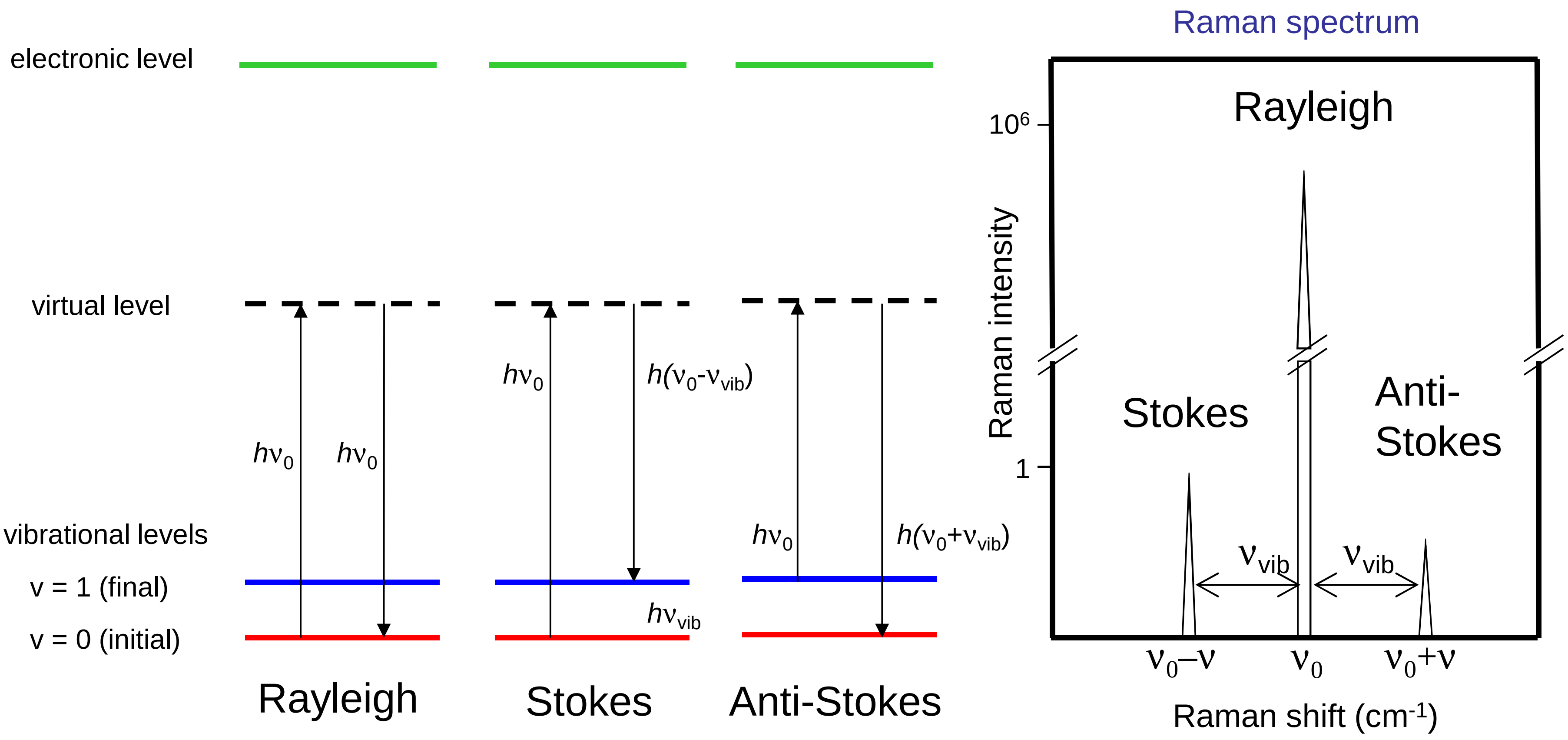
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\ [\cos(x+y)+\cos(x–y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\ (\text{Anti-Stokes})}{I\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:
  - 4th power of ν (4th power law)
  - 2nd power of $\Delta\alpha$

    - properties of molecules
    - strength of bonds

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

↓

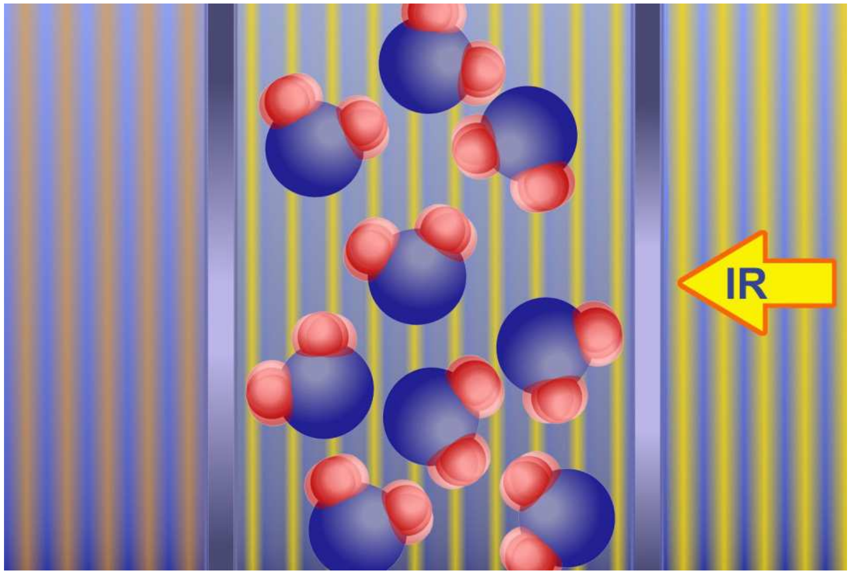
covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

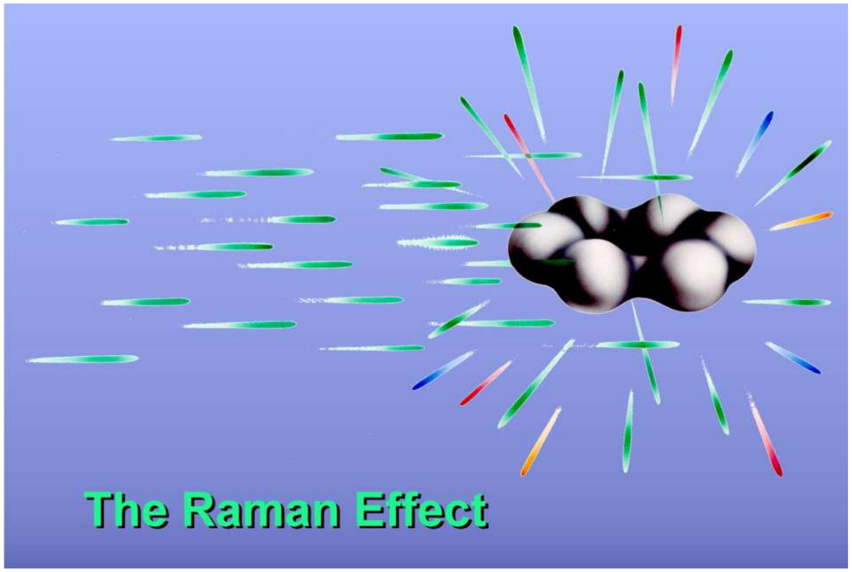
- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

Raman *vs.* Infrared

Infrared

Raman





Absorption of IR light

Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

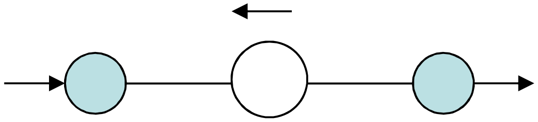
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - ❑ large electron clouds
  - ❑ not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

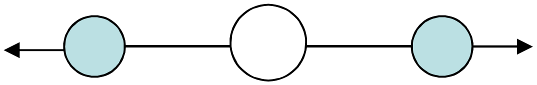
Raman *vs.* Infrared

CO_2



ν_{as}

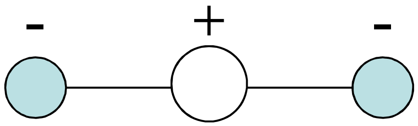
2349 cm^{-1}



ν_s

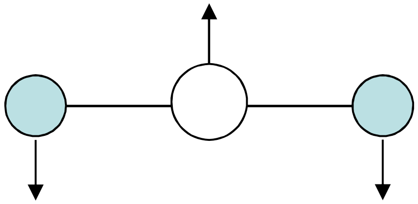
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



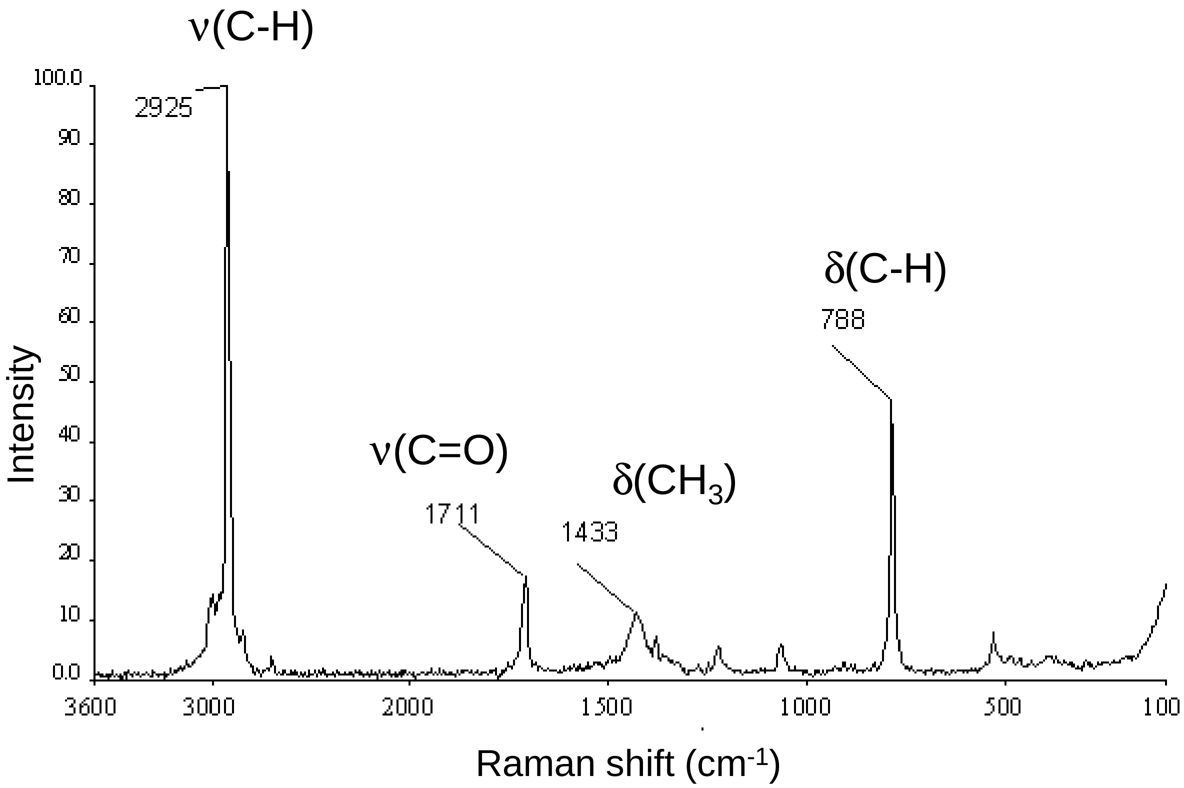
δ

667 cm^{-1}

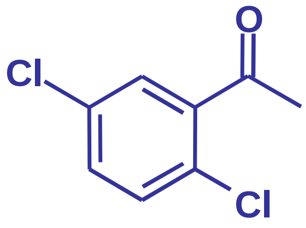
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



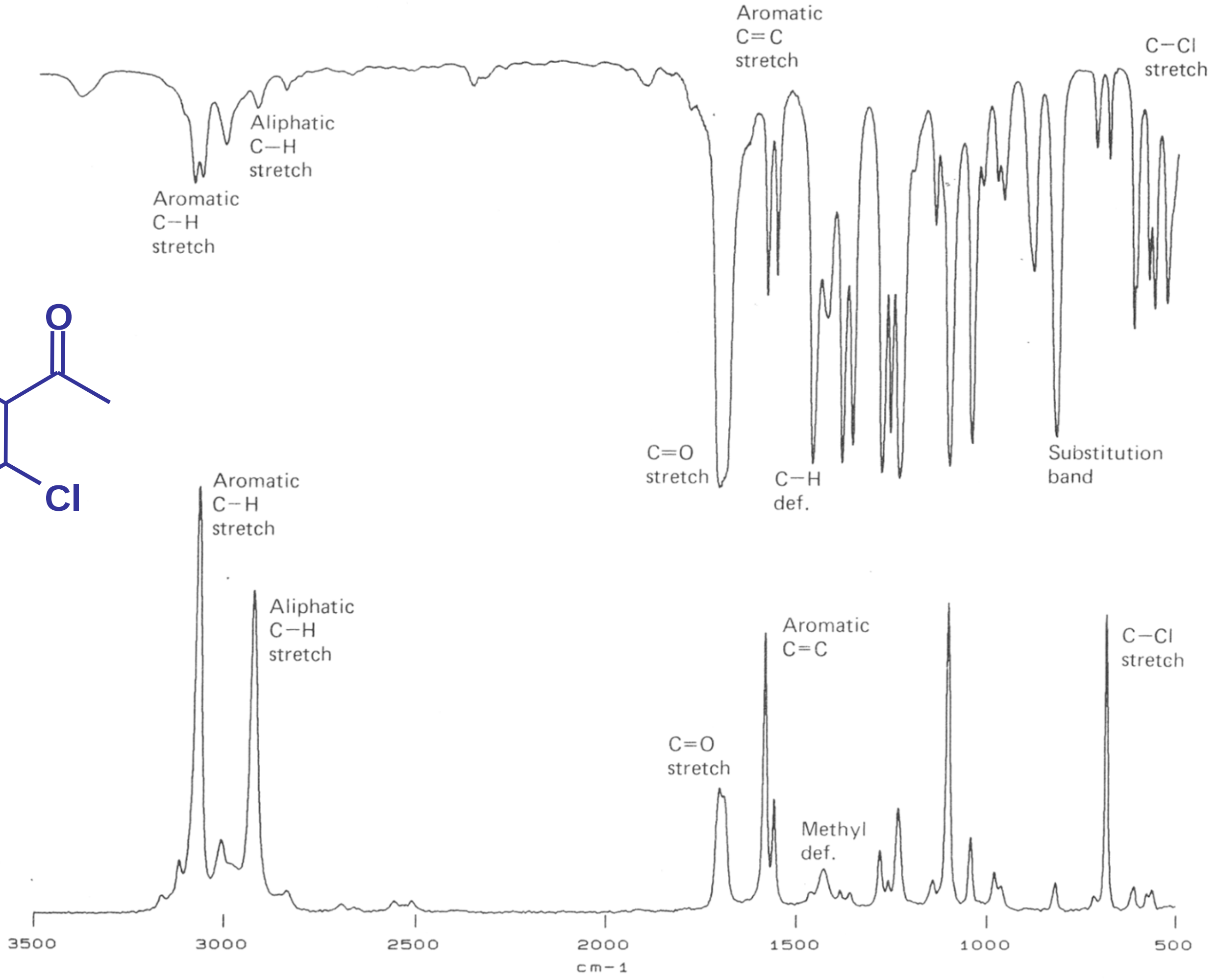


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

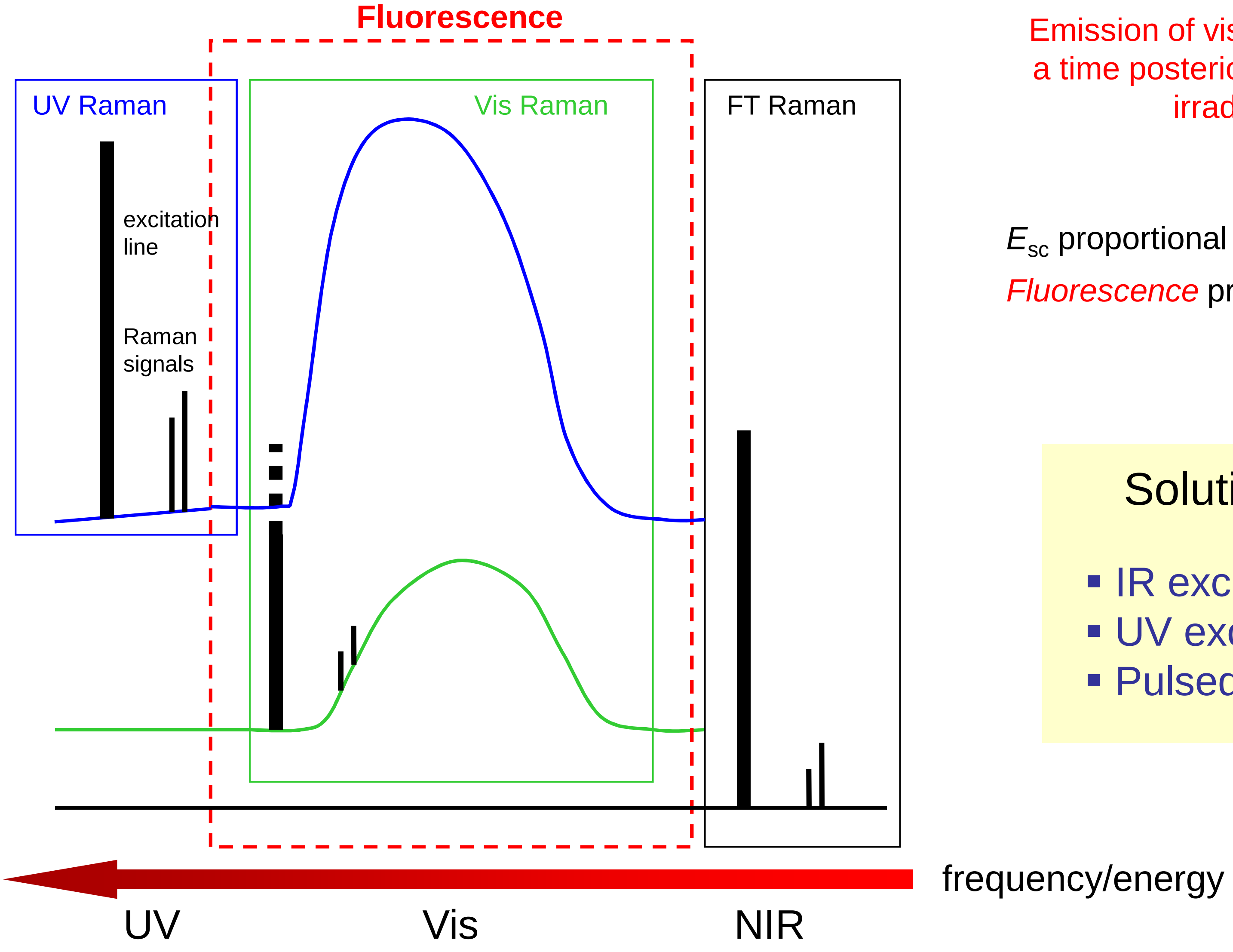
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 µm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

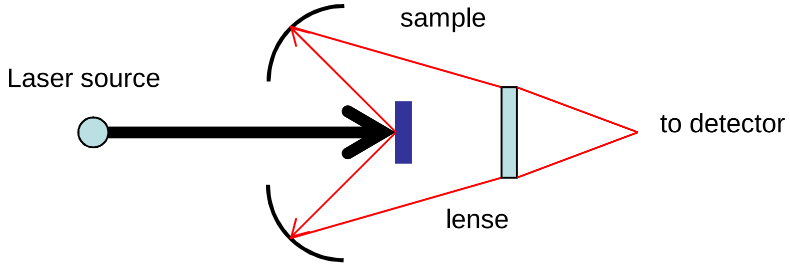
Fluorescence proportional to ν

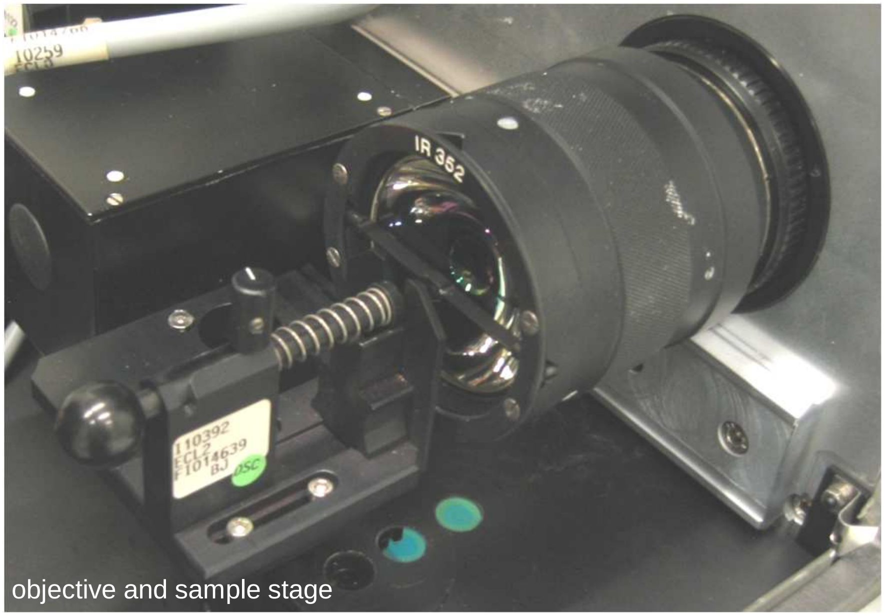
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers

Excitation wavelengths

UV	250 nm
Vis (green)	514 nm
Vis (red)	633 nm
NIR	780 nm
IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

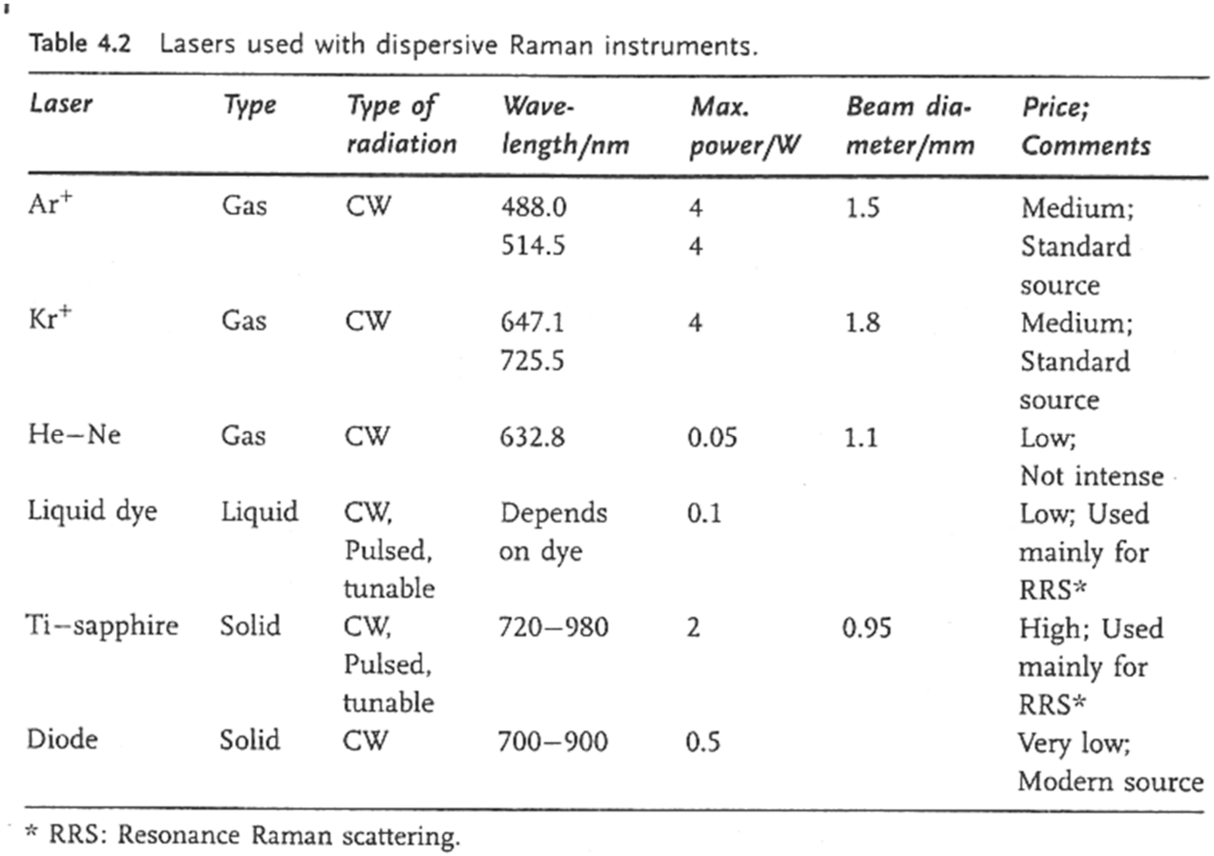


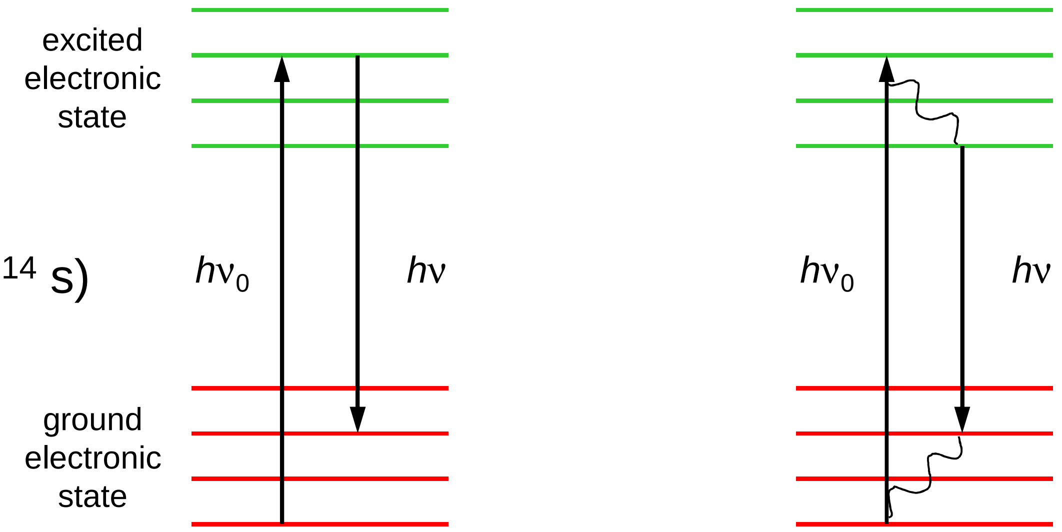
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



excited electronic state

fast (10^{-14} s)

$h\nu_0$

$h\nu$

ground electronic state

$h\nu_0$

$h\nu$

slow (10^{-9}–10^{-6} s)

Resonance Raman scattering

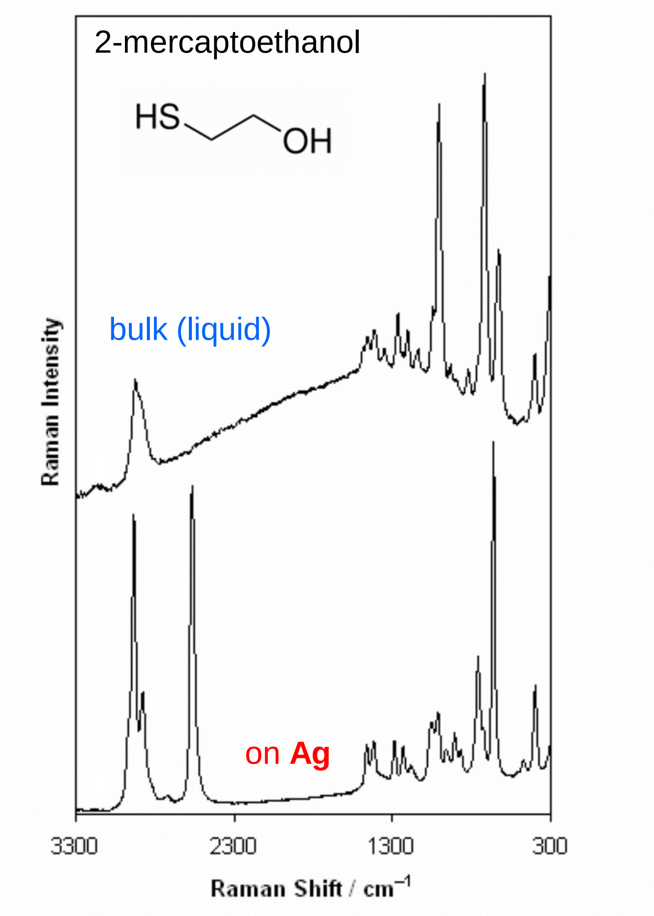
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

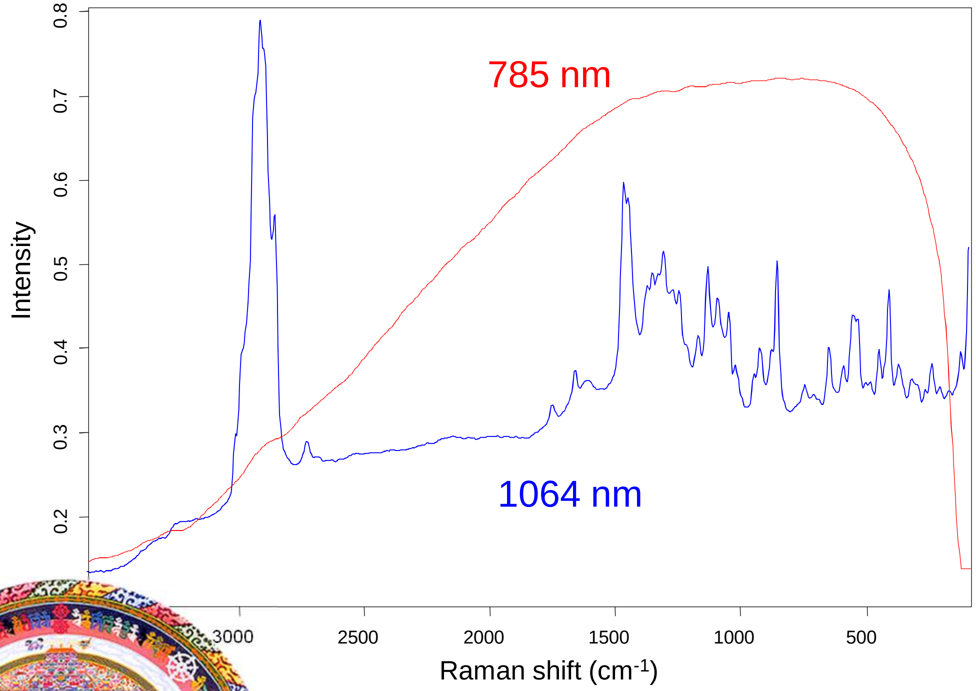
- Remarks:

  - rough surface; nanoparticles (10–100 nm) or kinks, steps etc. (E always perpendicular to surface, locally)
  - vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



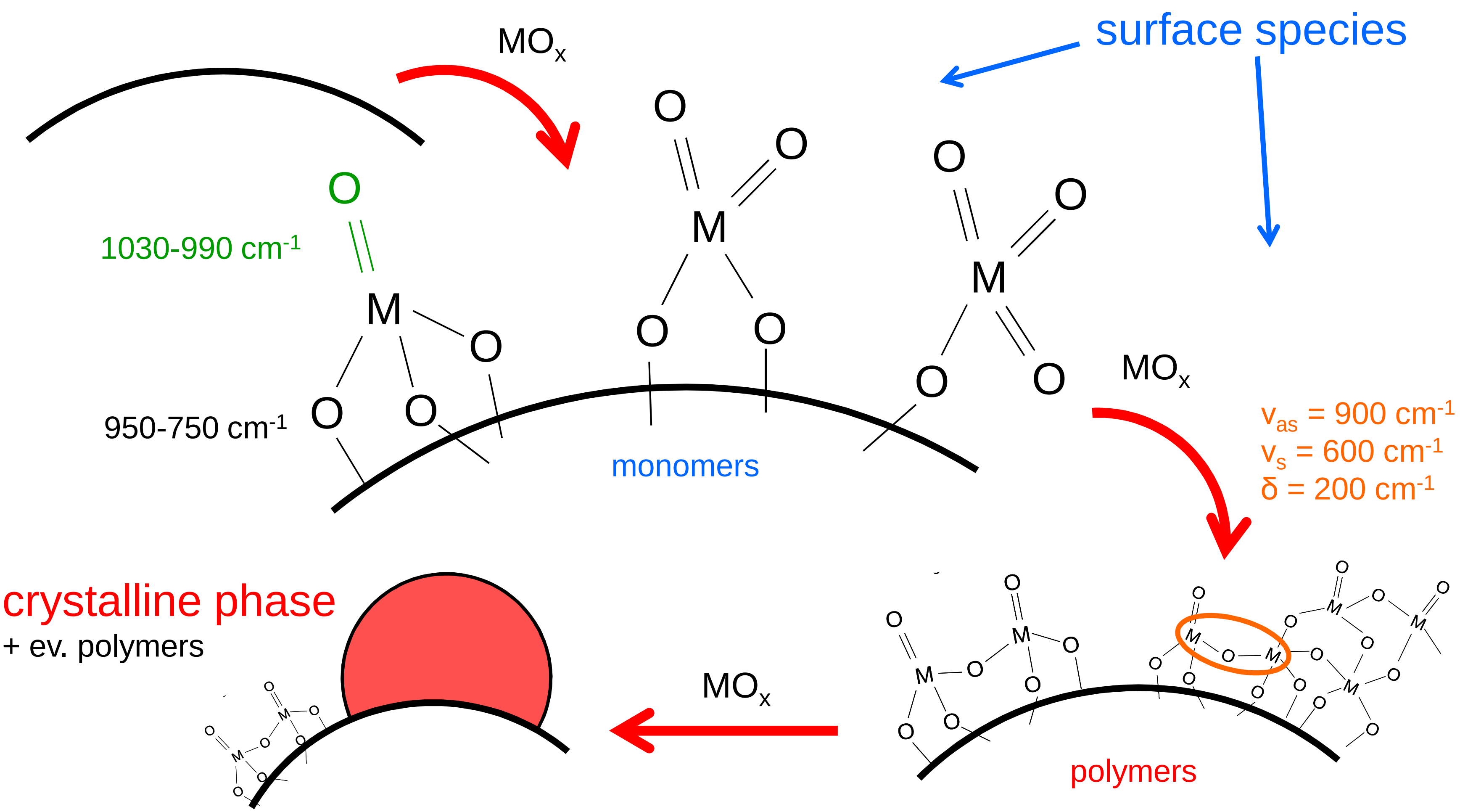
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



surface species

MO_x

1030-990 cm^{-1}

950-750 cm^{-1}

monomers

MO_x

ν_{as} = 900 cm^{-1}
ν_s = 600 cm^{-1}
δ = 200 cm^{-1}

polymers

MO_x

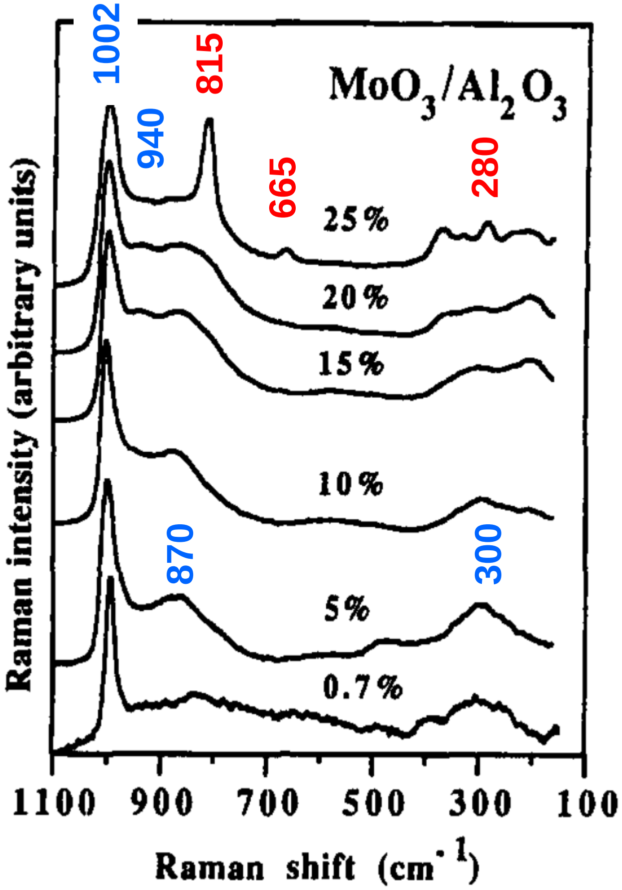
crystalline phase
+ ev. polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



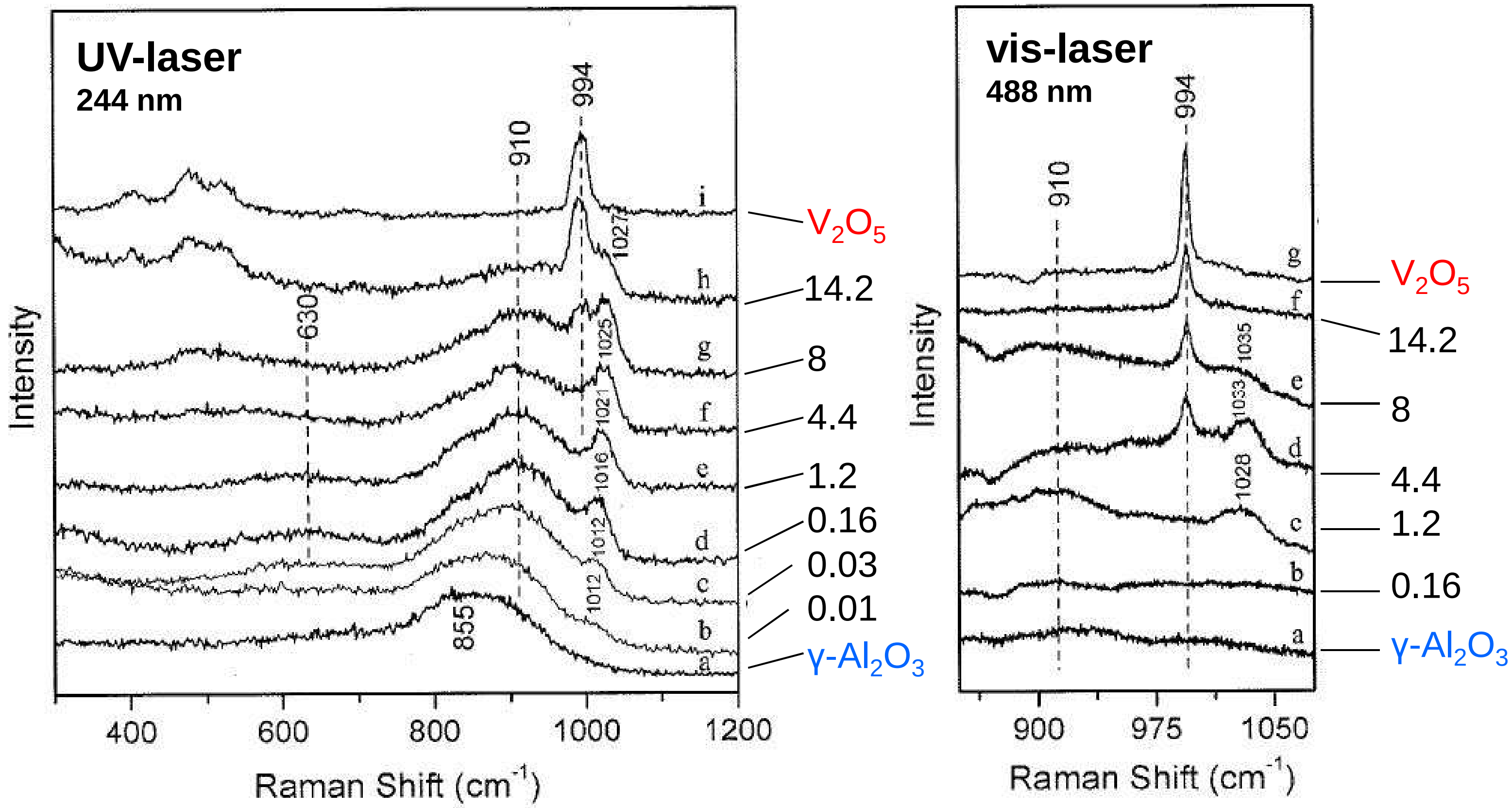
surface MoO_3
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

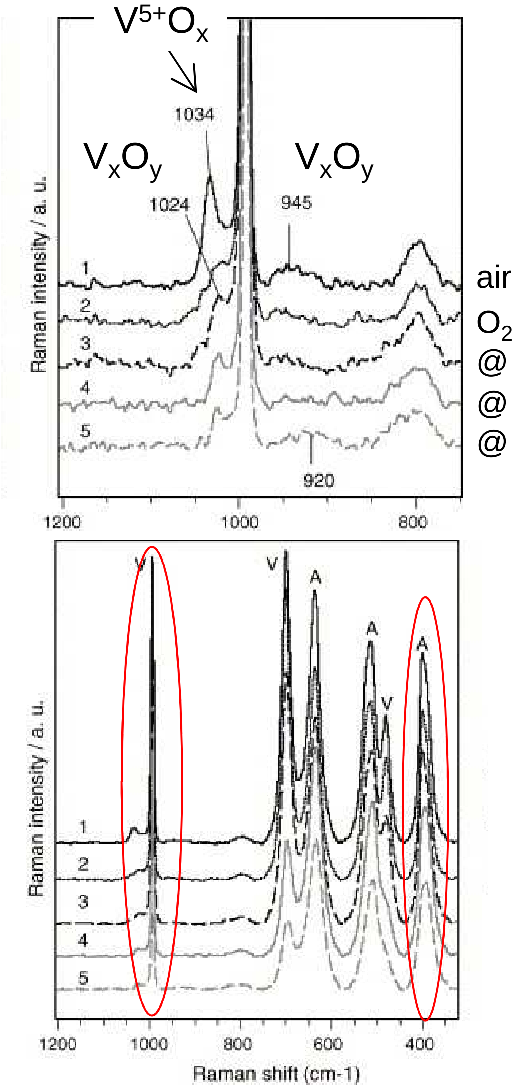
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

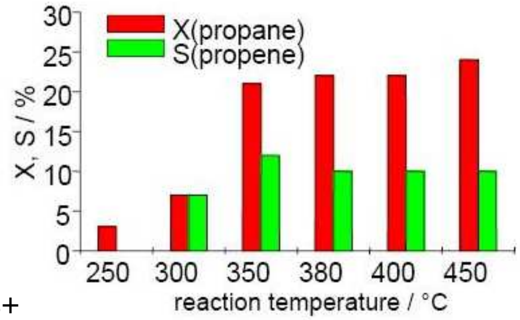
Applications

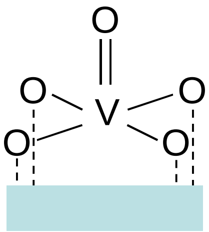
- Reactivity of V/TiO_2 after oxidative treatment

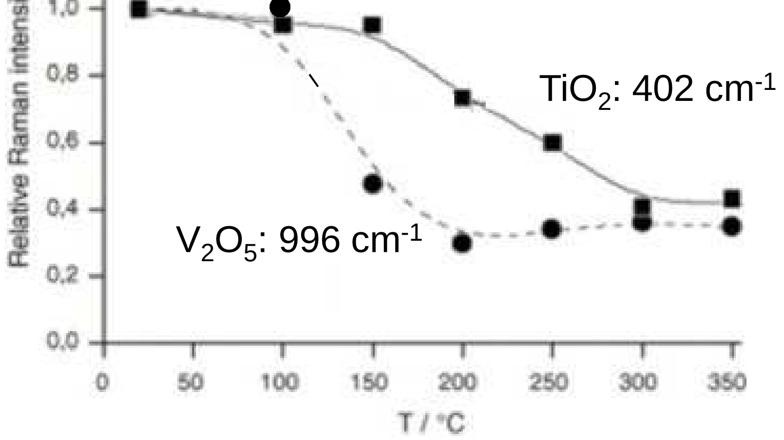


air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$







Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

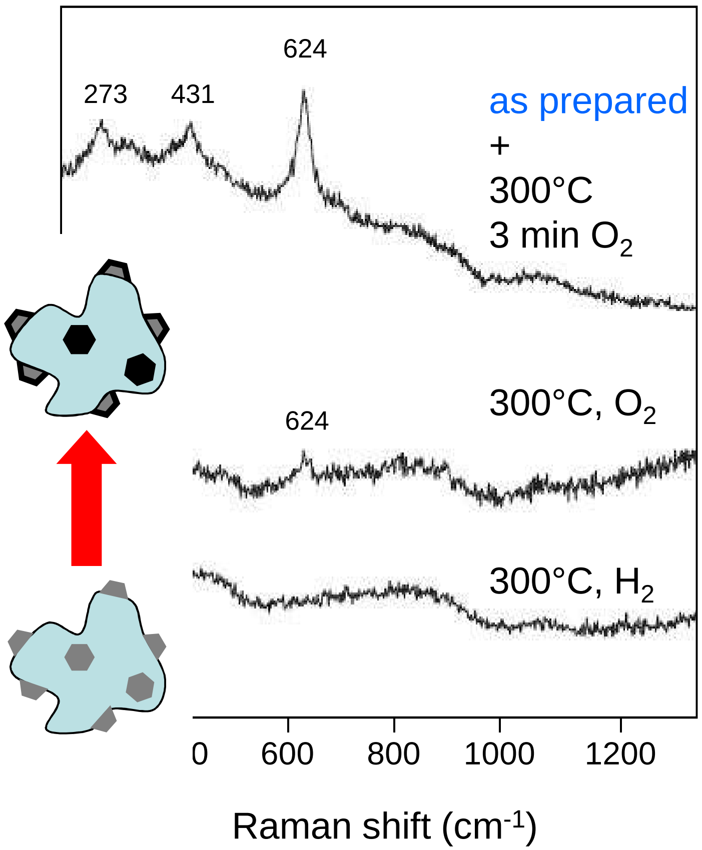
M/MO$_X$ (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

Question: what is the state of Pd during reaction?

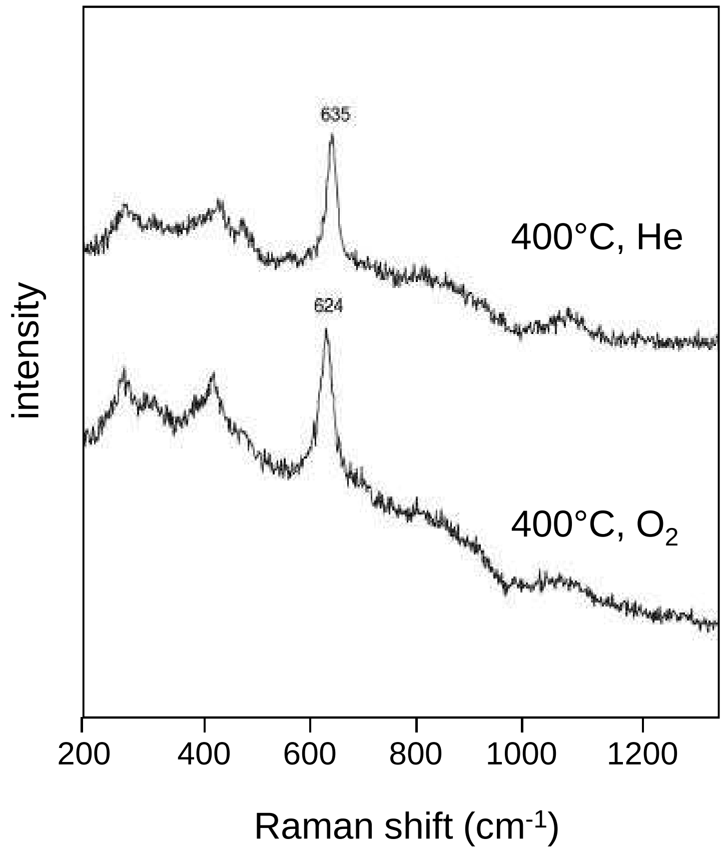
Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

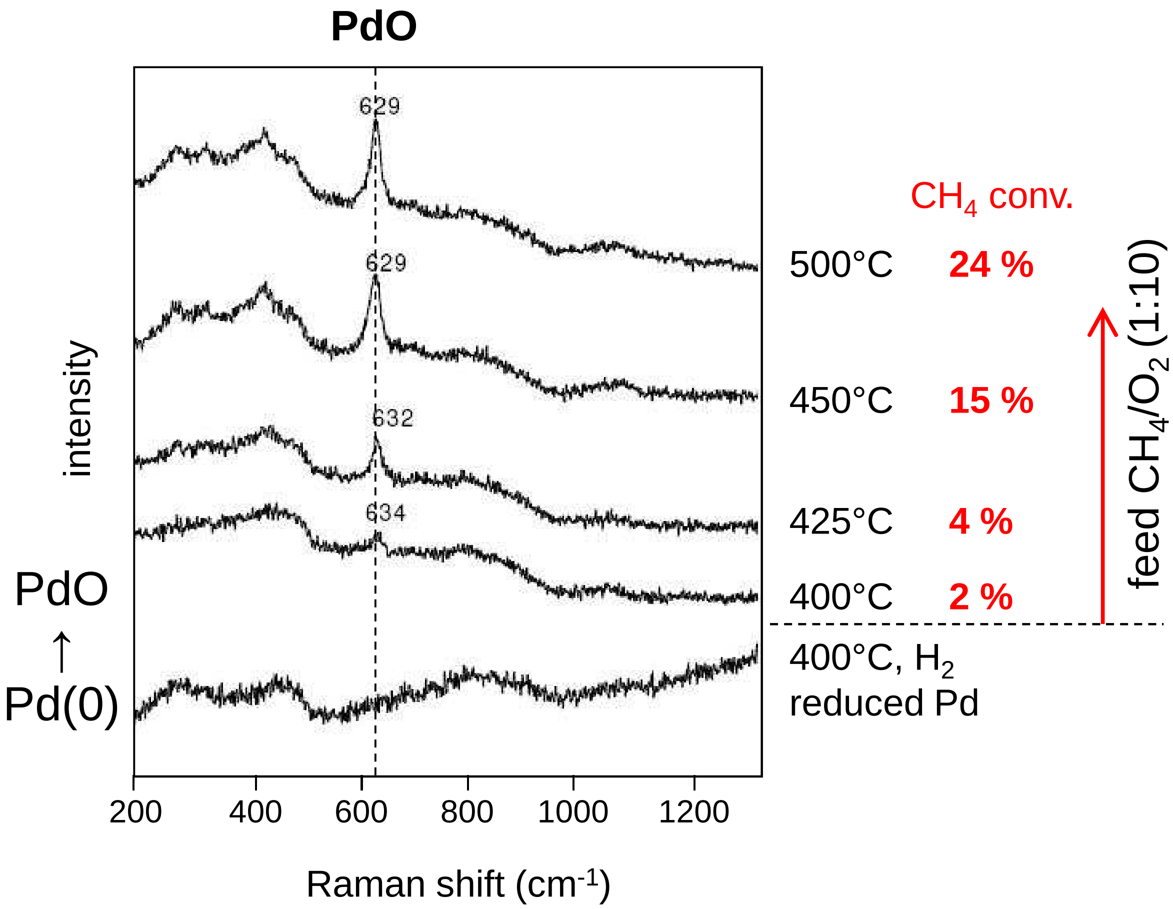


Demoulin et al., *PCCP* **5** (2003) 4394

Applications

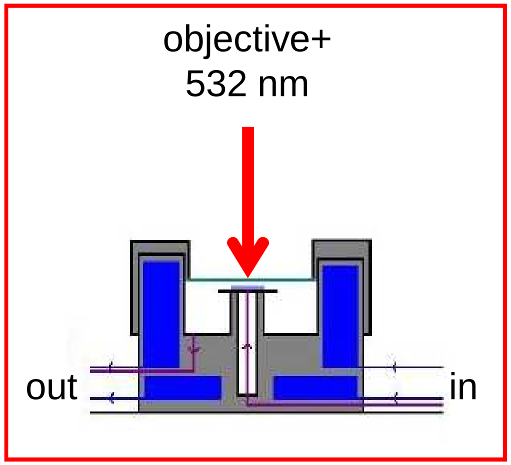
- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



	CH_4 conv.
500°C	**24 %**
450°C	**15 %**
425°C	**4 %**
400°C	**2 %**
400°C, H_2 reduced Pd	

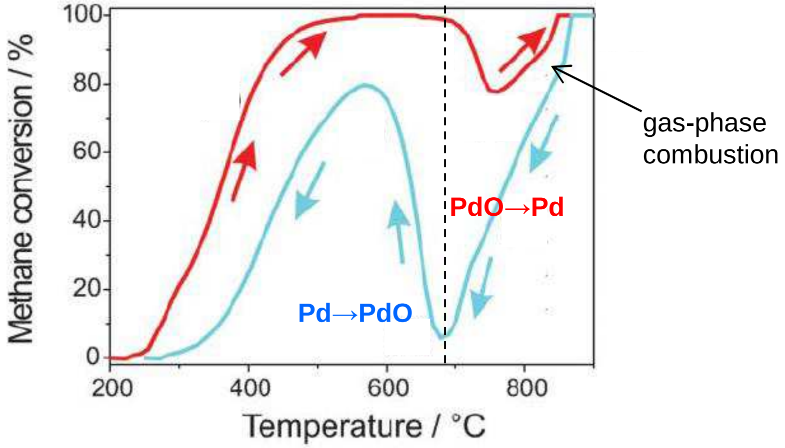
near PdO mode

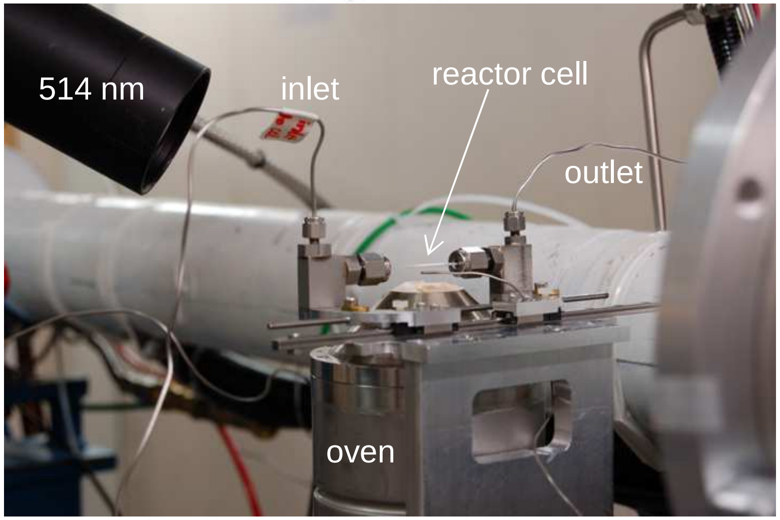


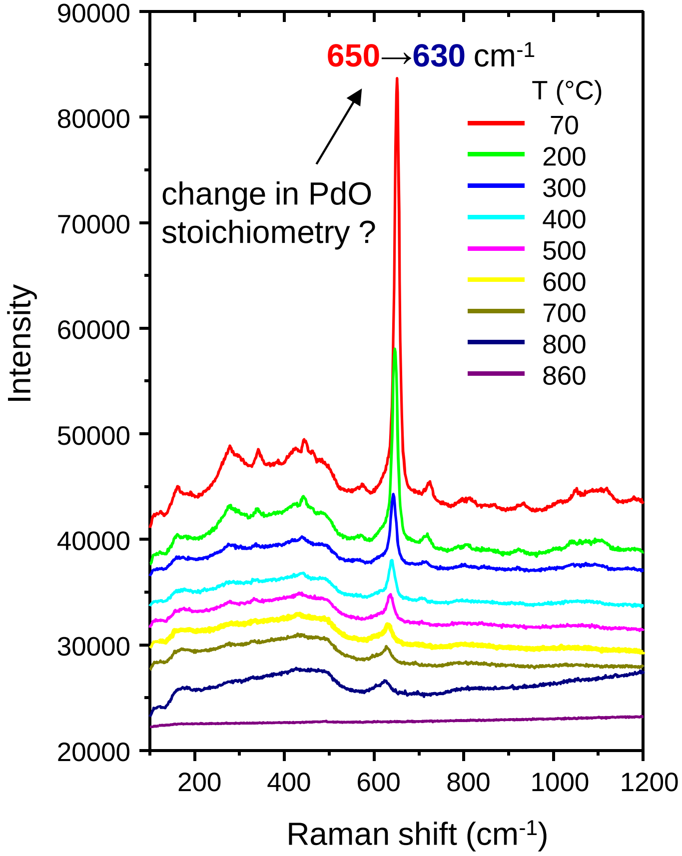
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

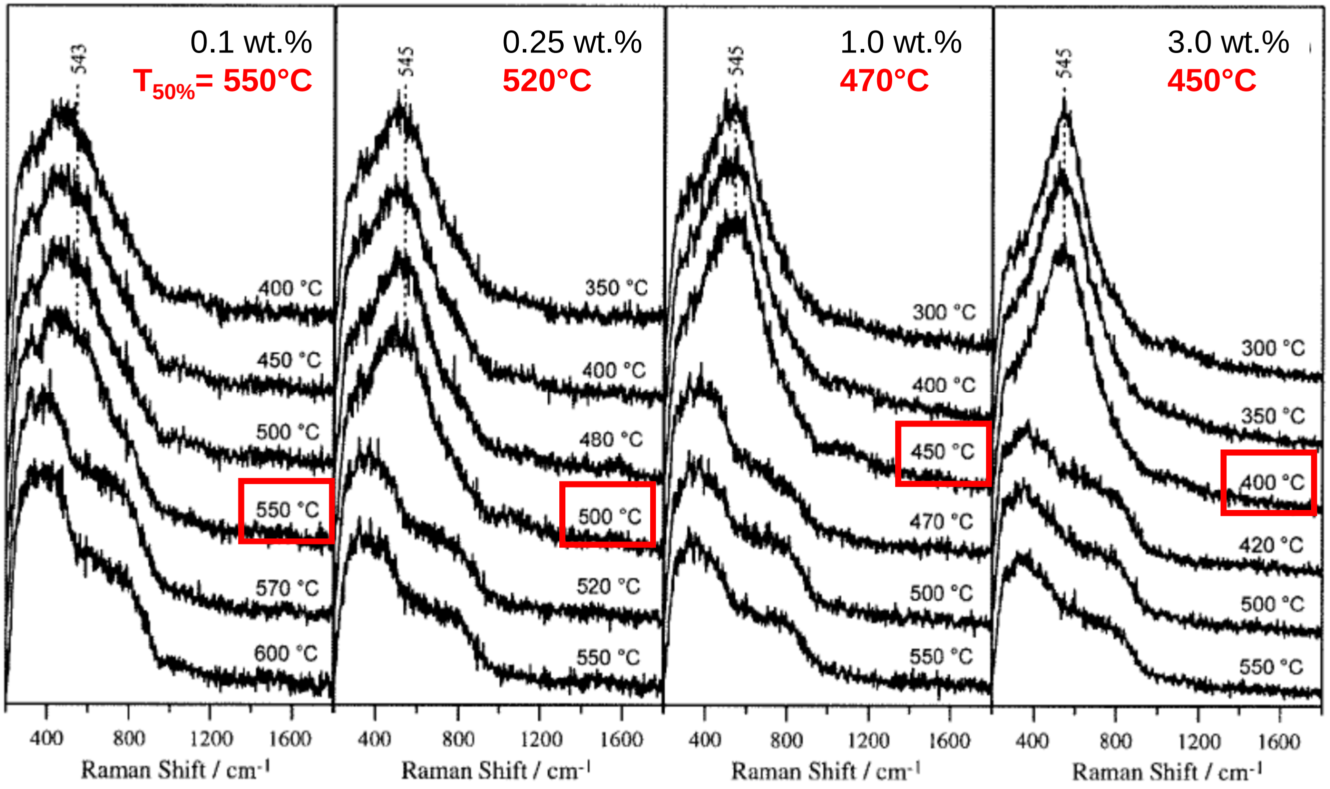
- Methane partial oxidation over Rh/Al_2O_3

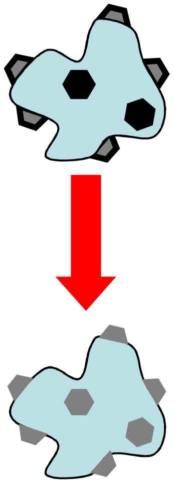
3 mW, 325 nm
$CH_4/O_2/Ar$ = 2/1/45

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content
Activity

RhOx
↓
Rh(0)





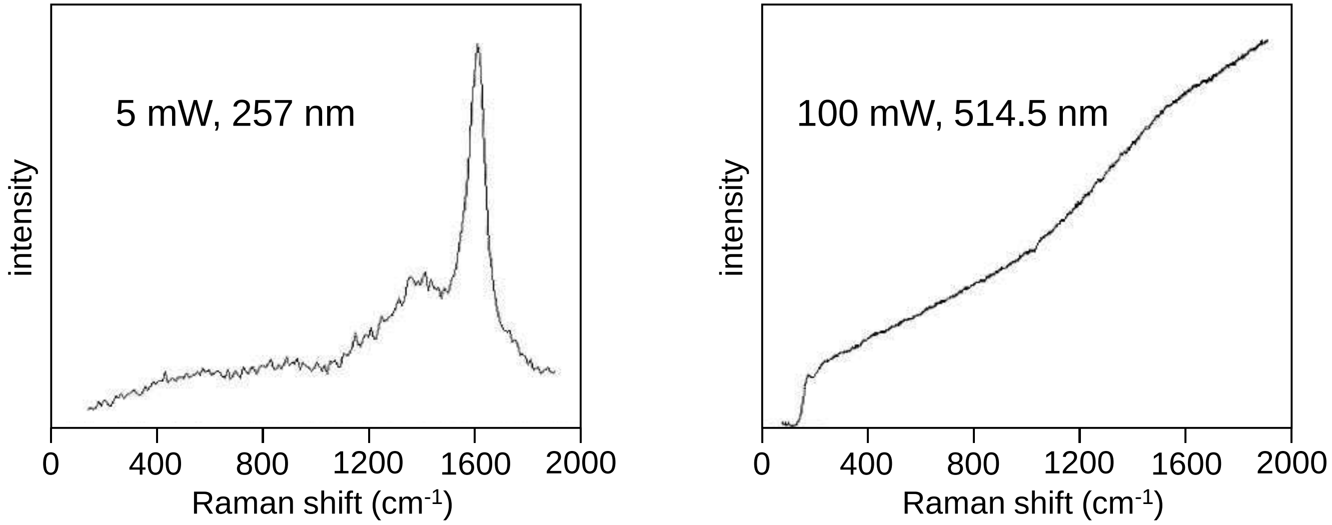
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - ☐ No fluorescence

  (only few molecules fluoresce below 260 nm)

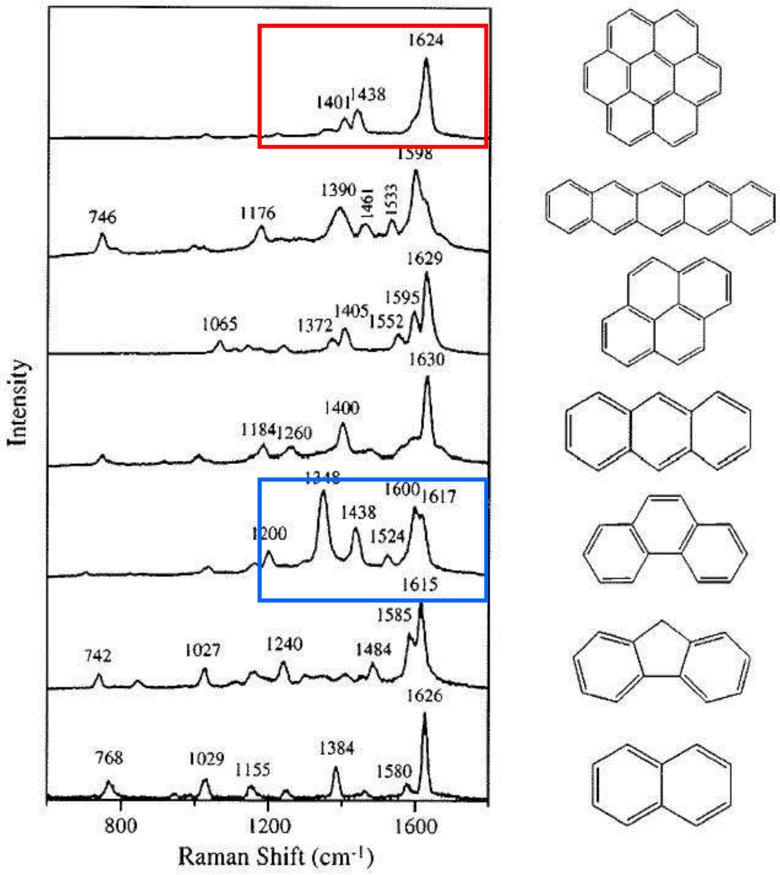
Rh/Al_2O_3, coked 500°C in naphtha

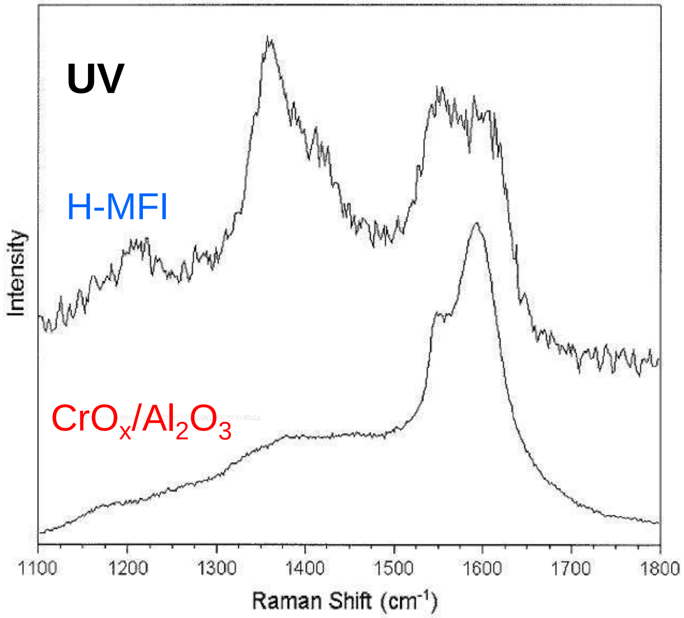


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





Coke classification

1D topology, chain-like

2D topology, sheet-like

Coke from:

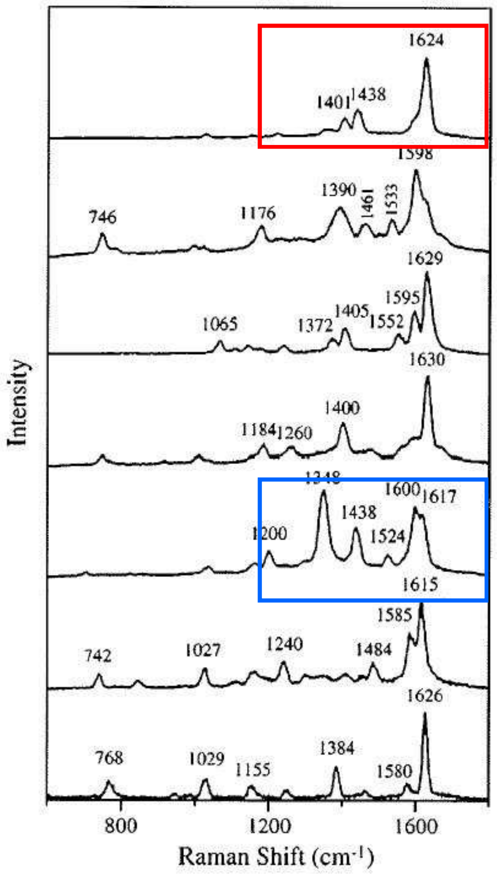
H-MFI: methanol-to-hydrocarbons (MTH)

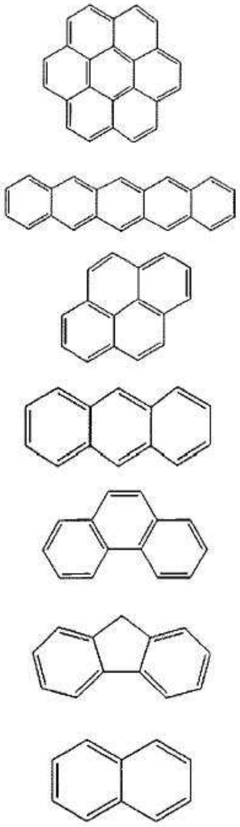
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

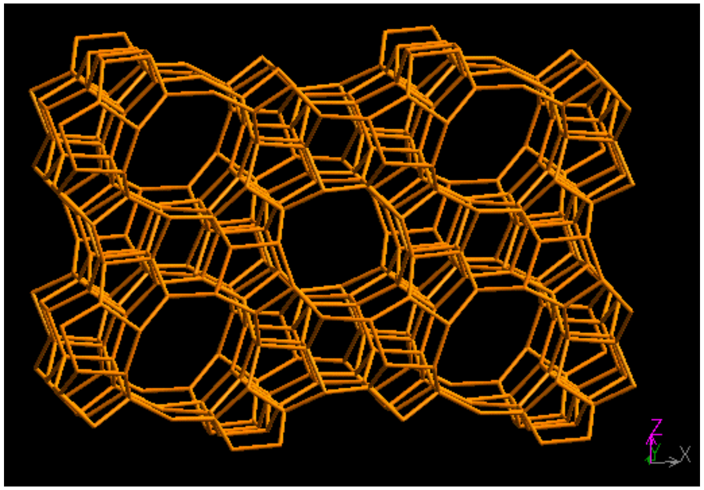
Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization







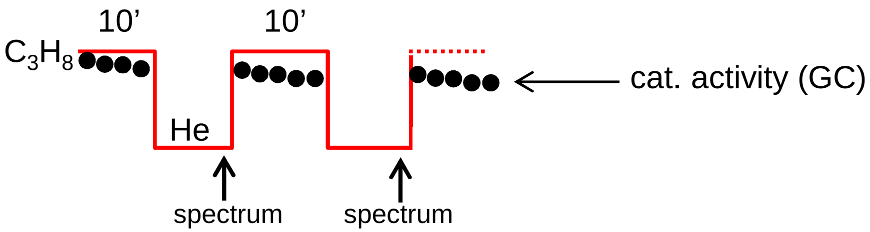
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

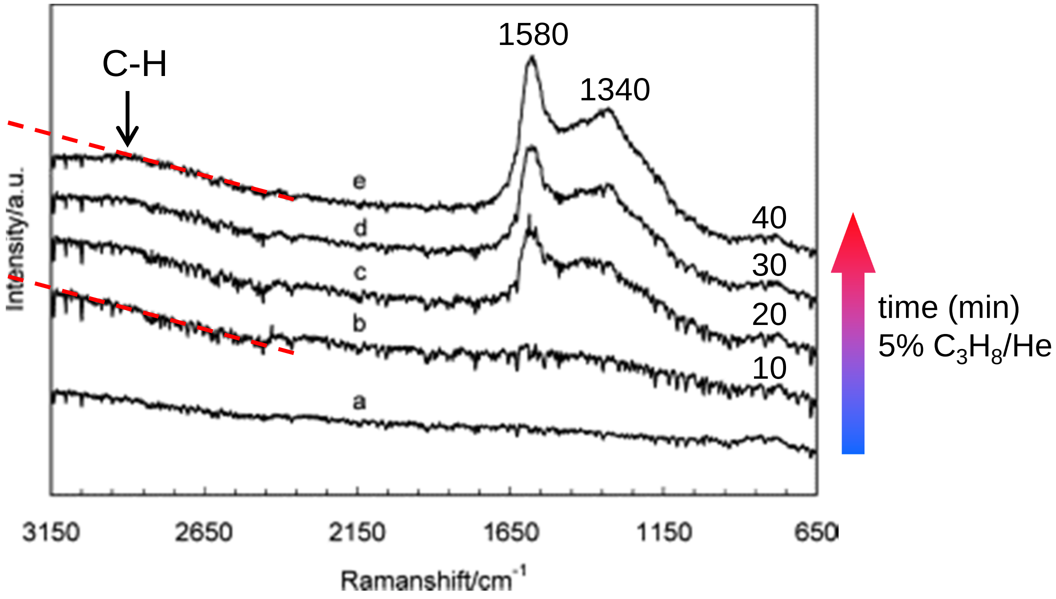
Stair, *Adv. Catal.* **51** (2007) 75

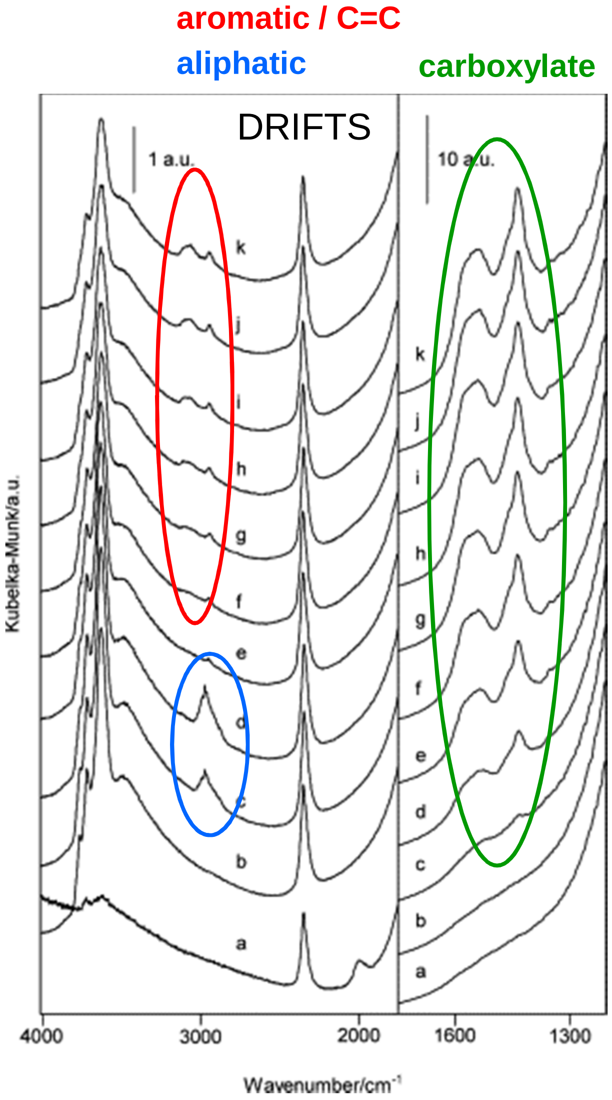
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

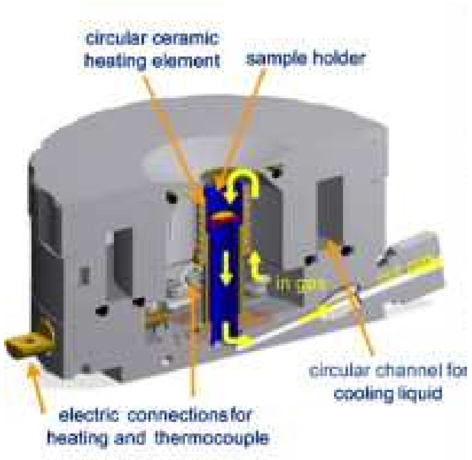


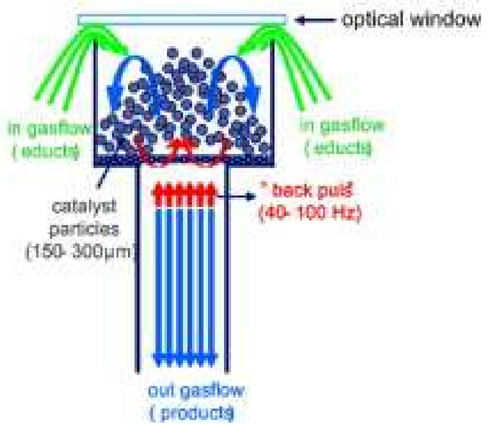


Airaksinen et al., *J. Catal.* **230** (2005) 507

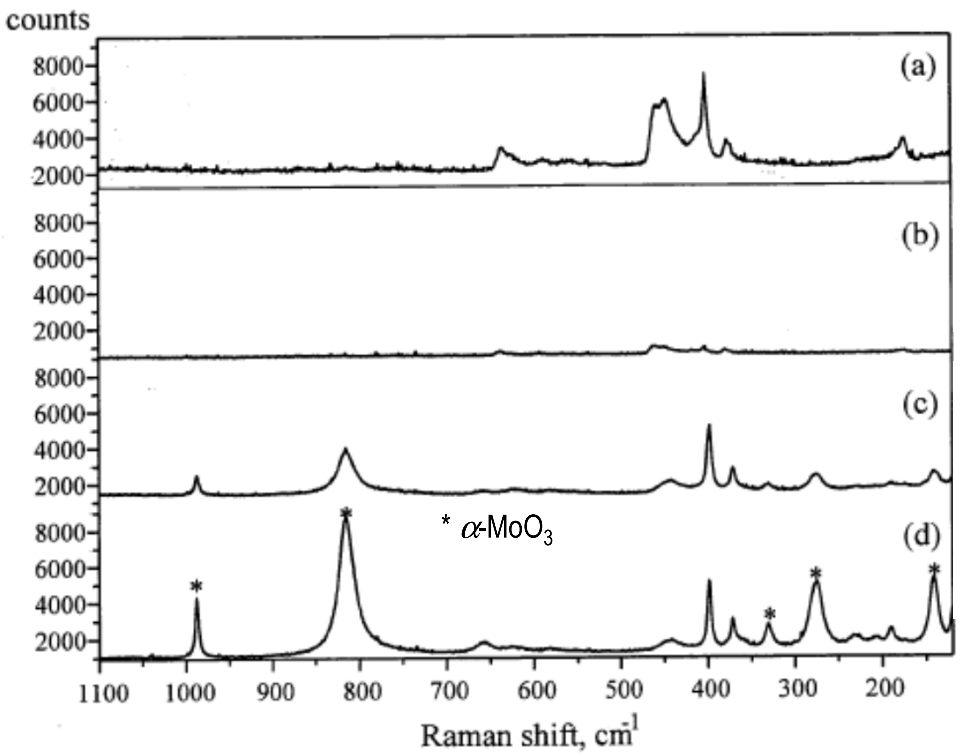
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min
full power, FB

MoS_2, 6 min
1/8 power

MoS_2, 1 min
full power

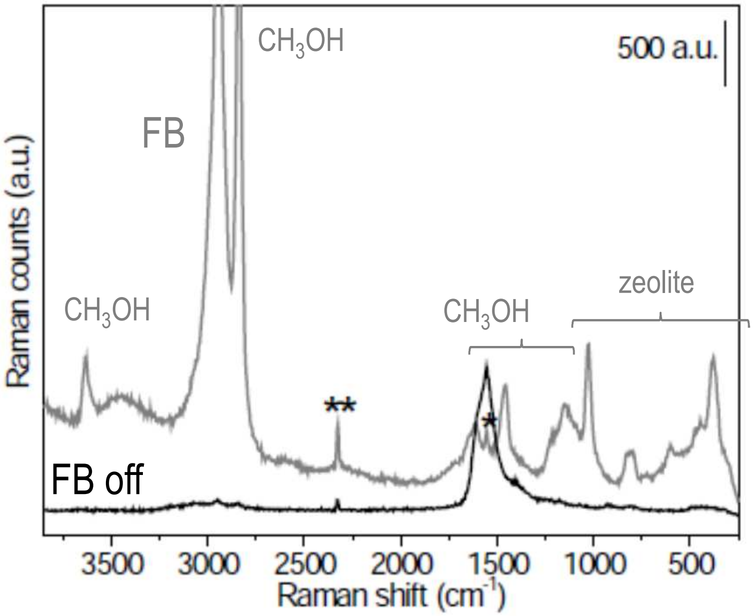
MoS_2, 6 min
full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

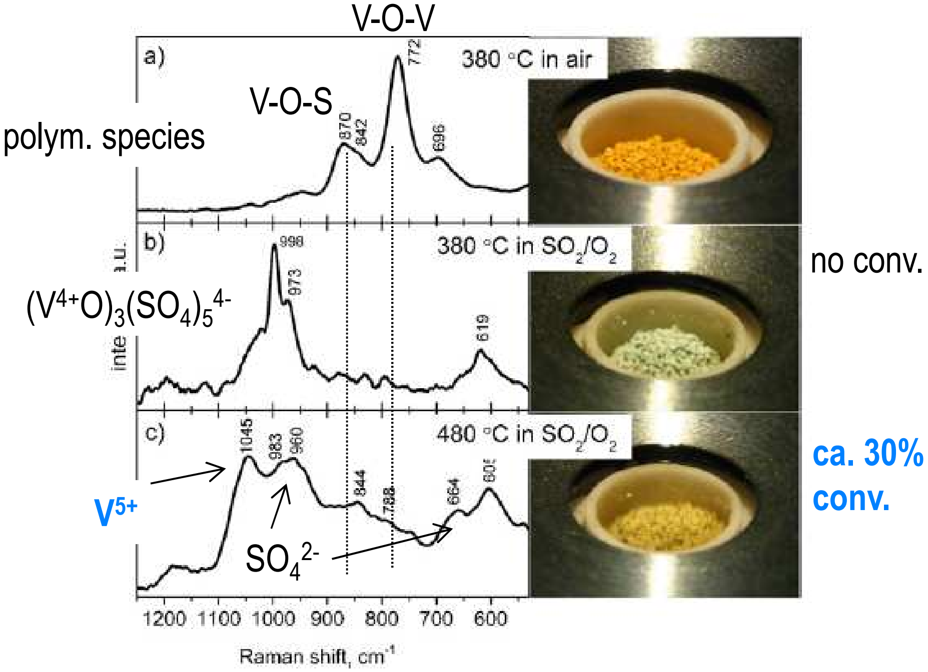
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

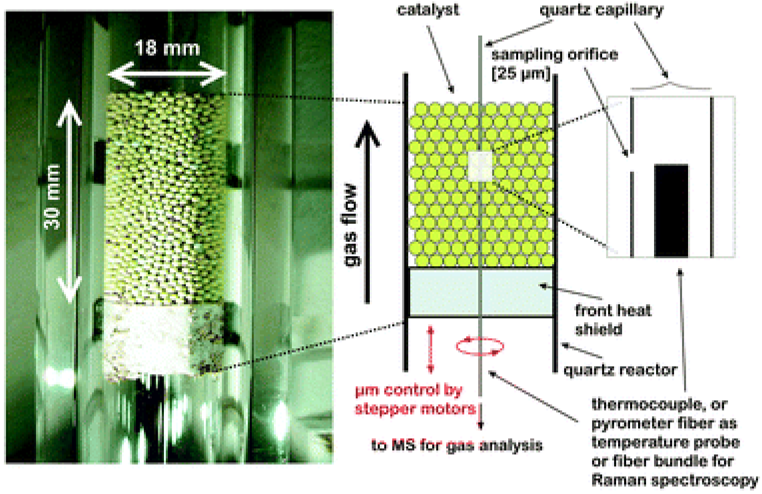


active species: mono- & dimeric V^{5+} oxosulfate species

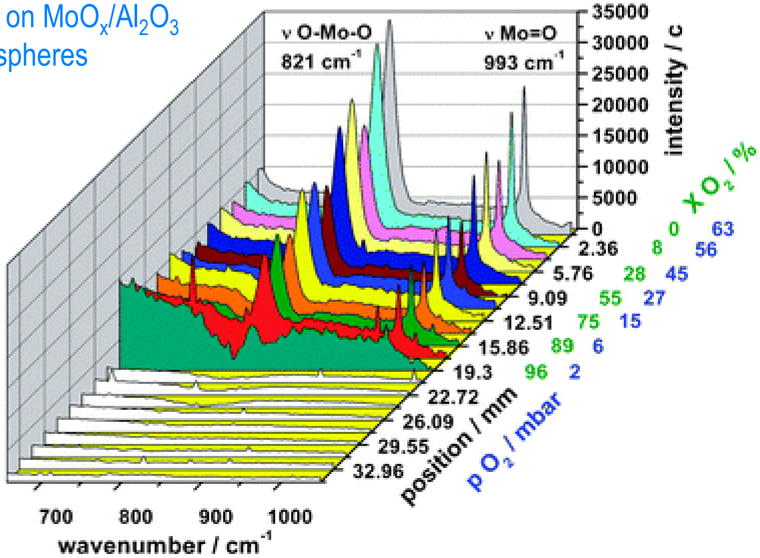
Beato et al., *Catal. Today* 205 (2013) 128

Applications

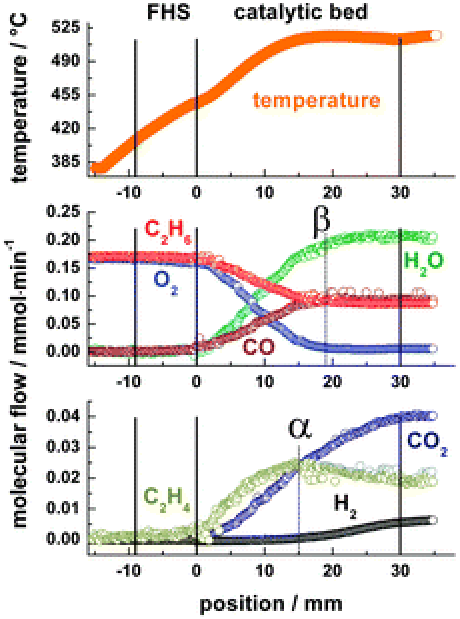
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

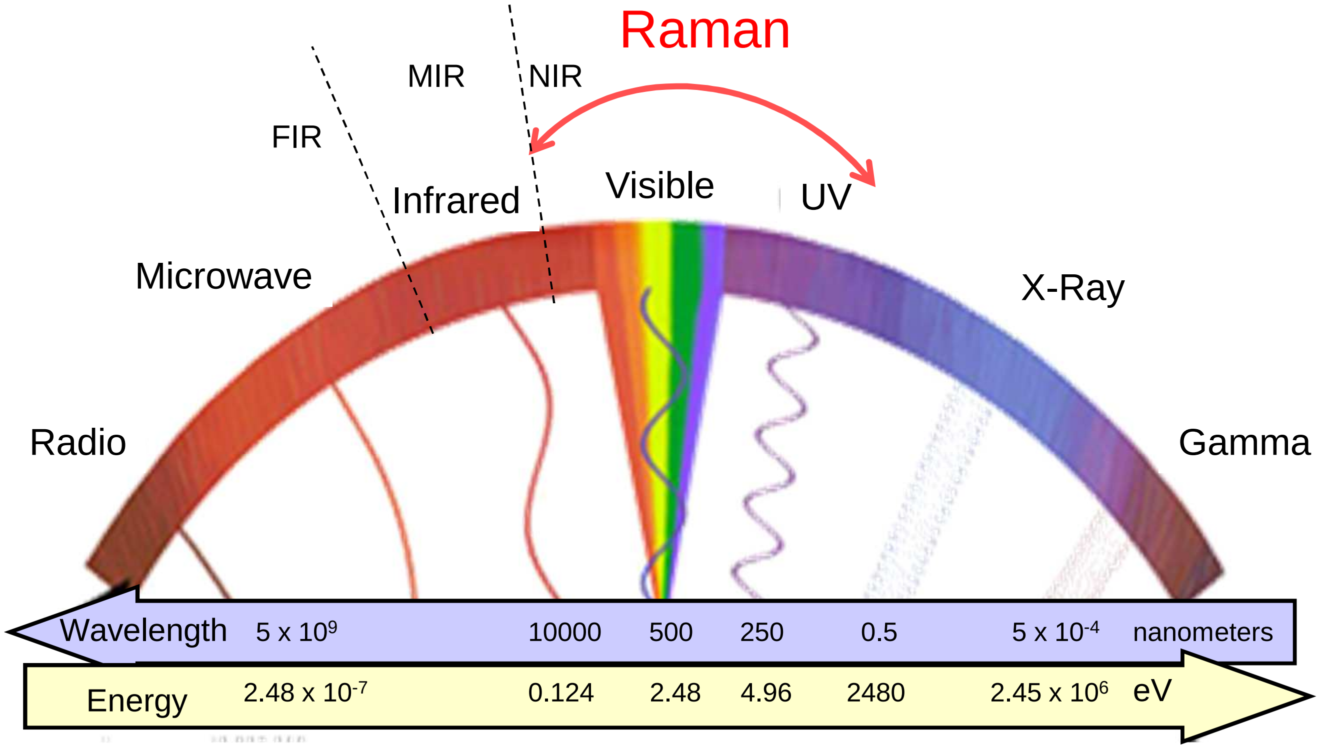
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

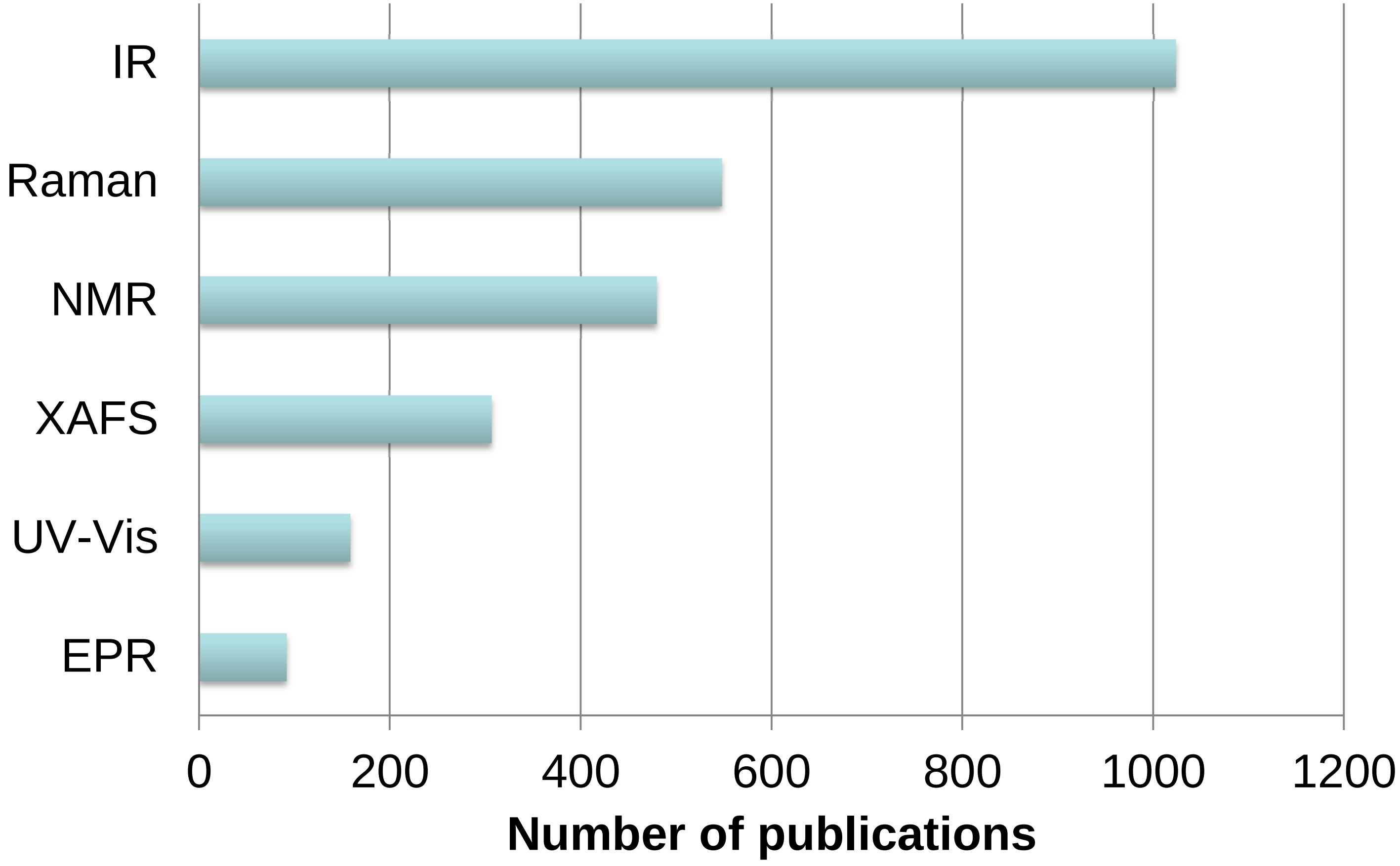
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

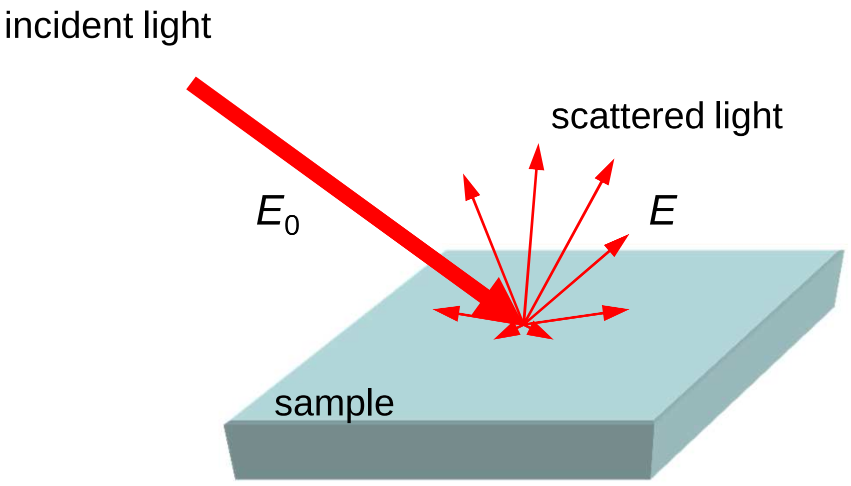


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

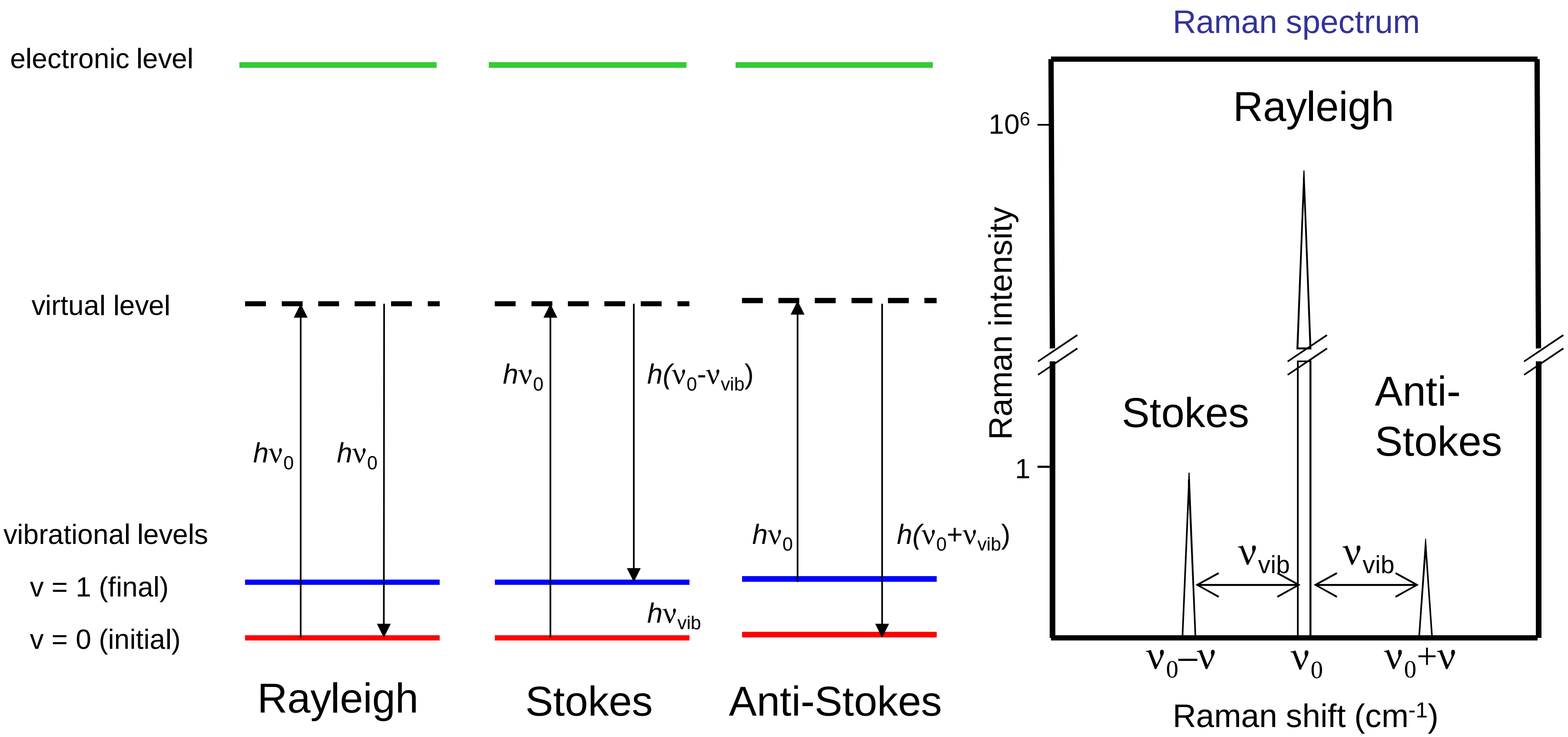
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x \cdot \cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



electronic level

virtual level

vibrational levels

v = 1 (final)

v = 0 (initial)

$h\nu_0$ $h\nu_0$

$h\nu_0$ $h(\nu_0-\nu_{vib})$ $h\nu_{vib}$

$h\nu_0$ $h(\nu_0+\nu_{vib})$

Rayleigh Stokes Anti-Stokes

Raman spectrum

10^6

1

Raman intensity

Rayleigh

Stokes

Anti-Stokes

ν_{vib} ν_{vib}

$\nu_0-\nu$ ν_0 $\nu_0+\nu$

Raman shift (cm^{-1})

Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\ (\text{Anti-Stokes})}{I\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

- ❑ 4th power of ν (4th power law)
- ❑ 2nd power of $\Delta\alpha$
  - properties of molecules
  - strength of bonds

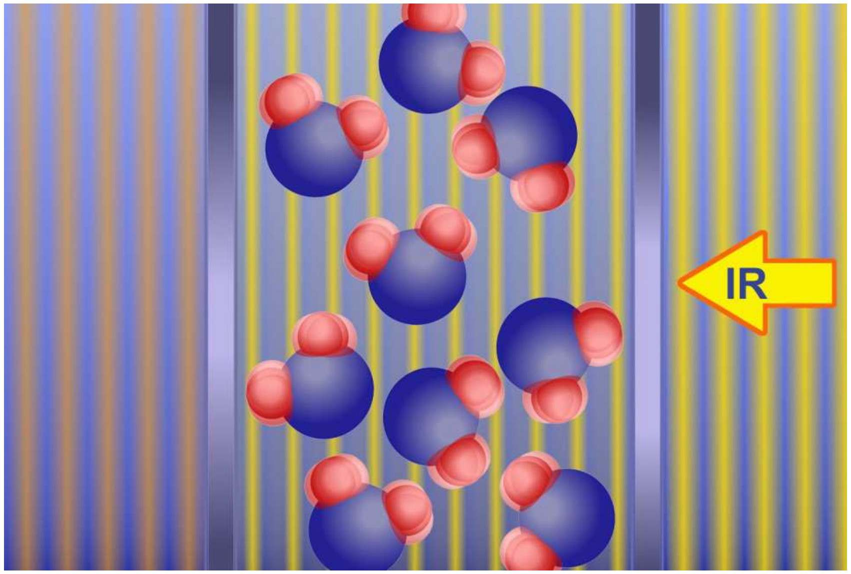
↓

covalent bond	STRONG bands	(catalysis!)
ionic bond	WEAK bands	

- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

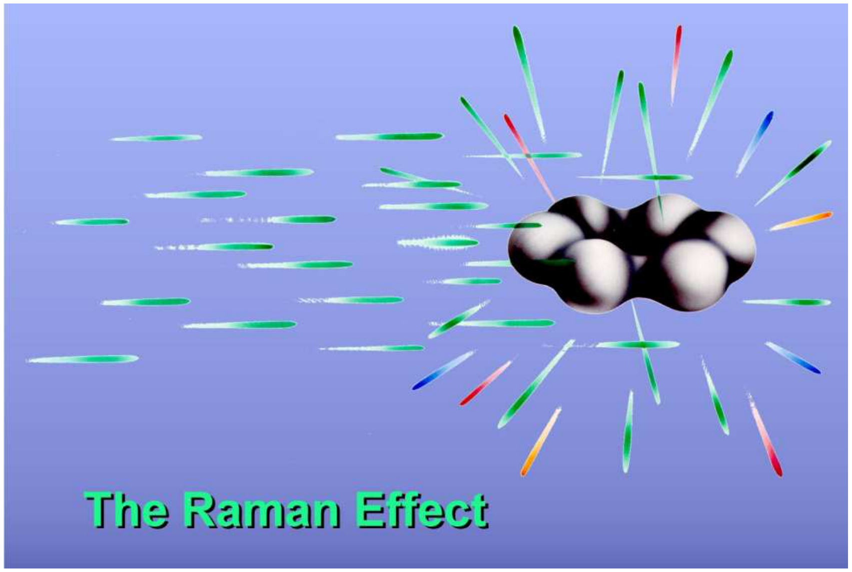
Raman *vs.* Infrared

Infrared



Absorption of IR light

Raman



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

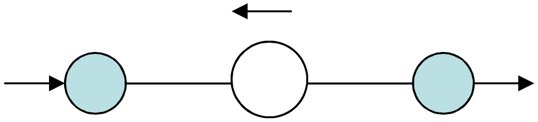
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
    - ☐ large electron clouds
    - ☐ not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

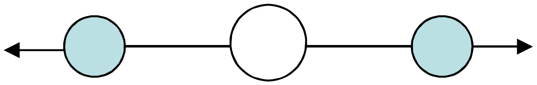
Raman *vs.* Infrared

CO_2



ν_{as}

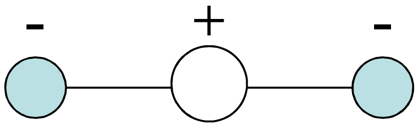
2349 cm^{-1}



ν_s

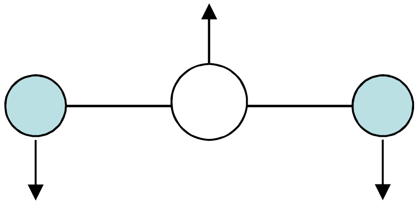
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



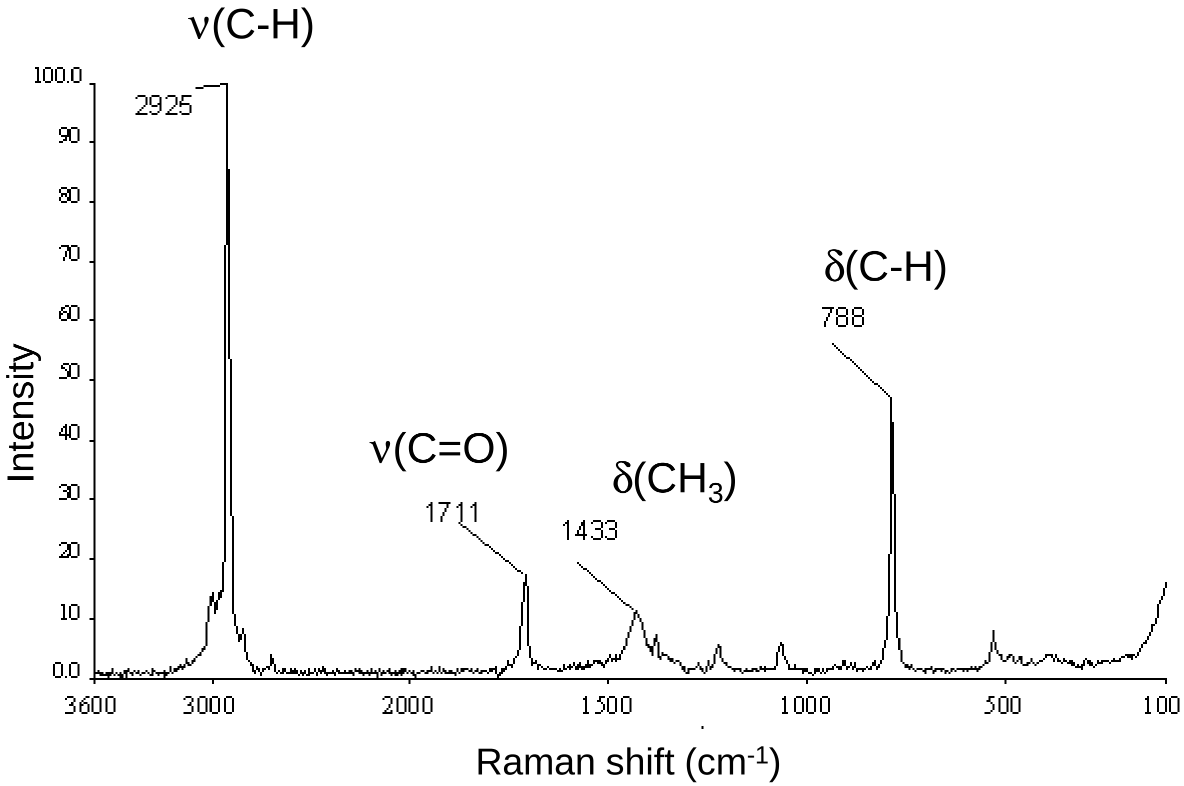
δ

667 cm^{-1}

degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared

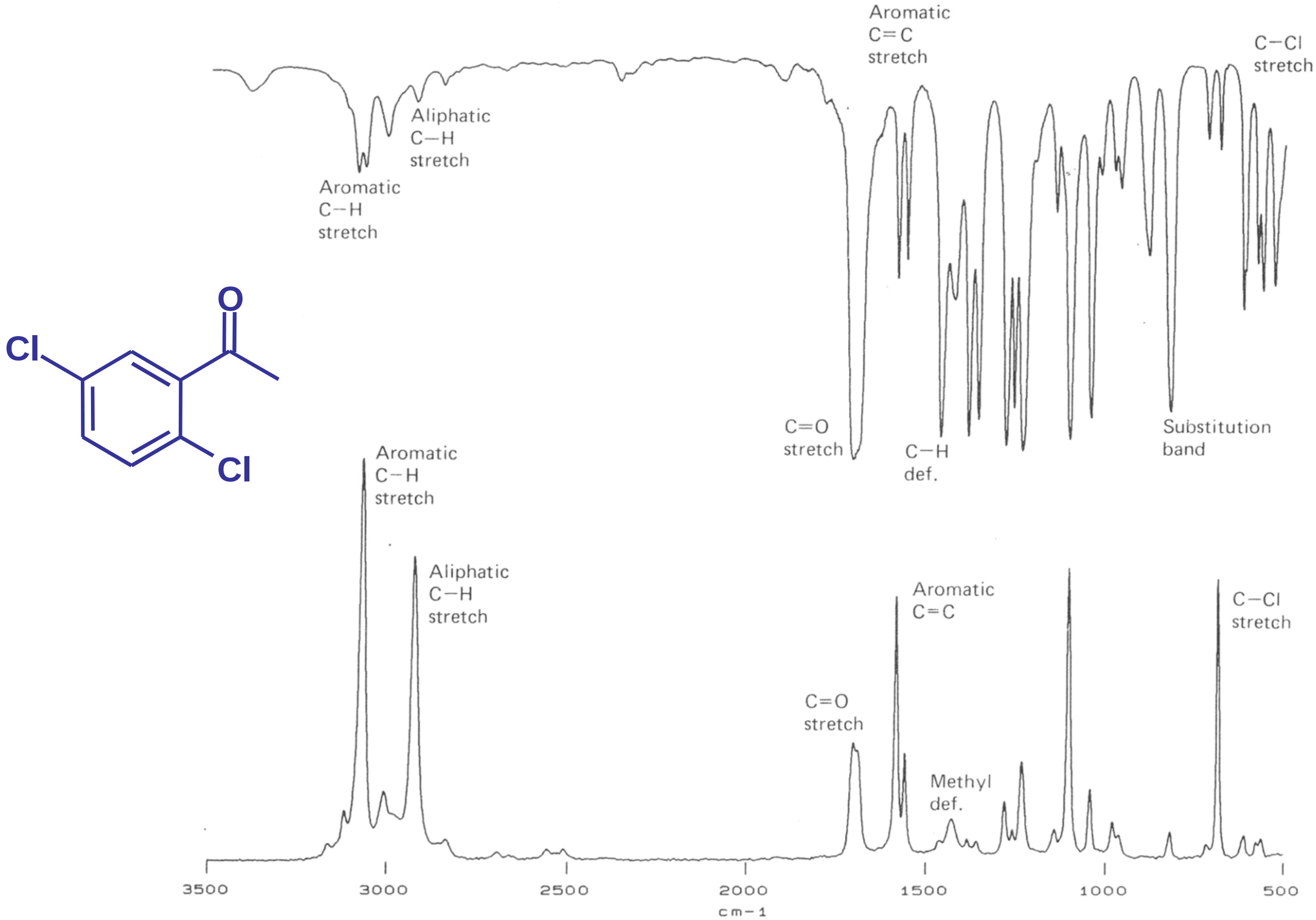


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

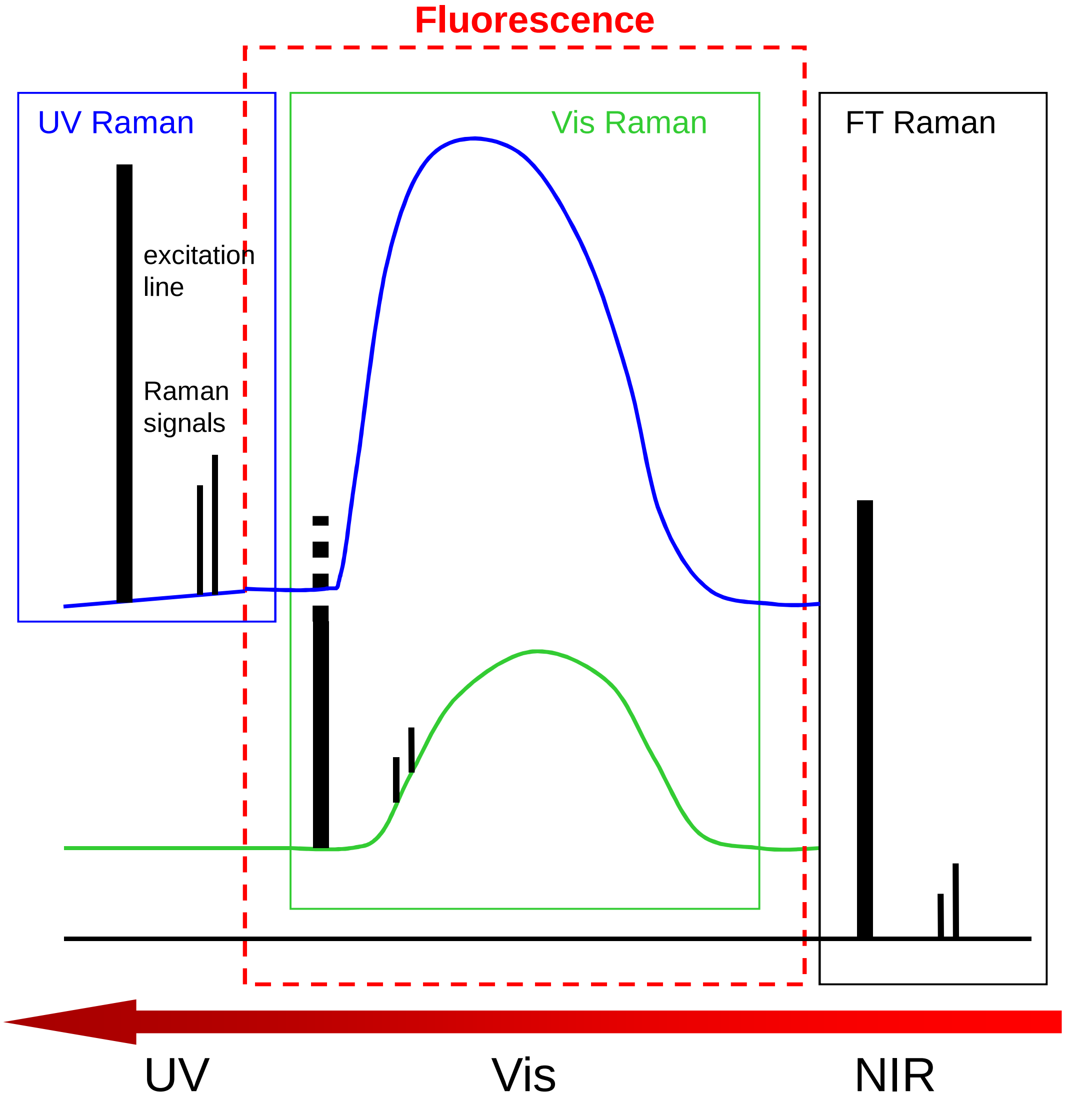
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 µm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

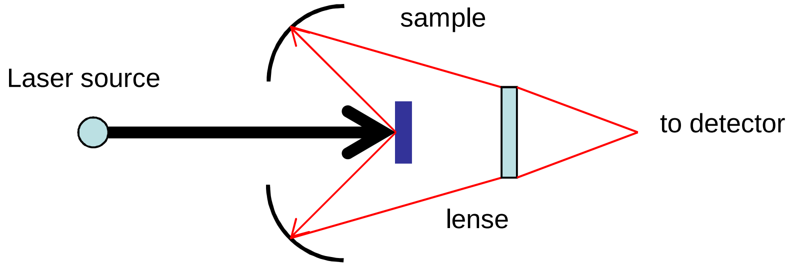
Fluorescence proportional to ν

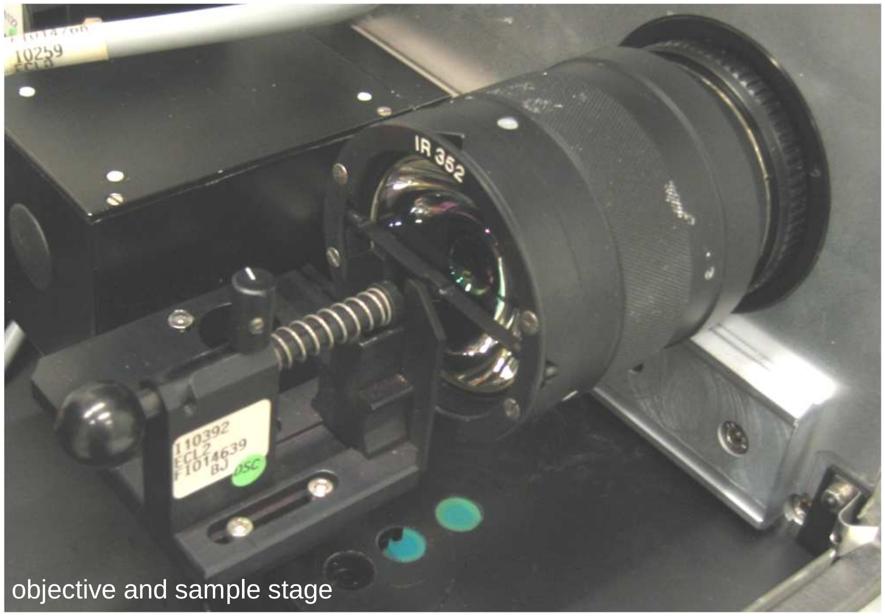
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation




objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

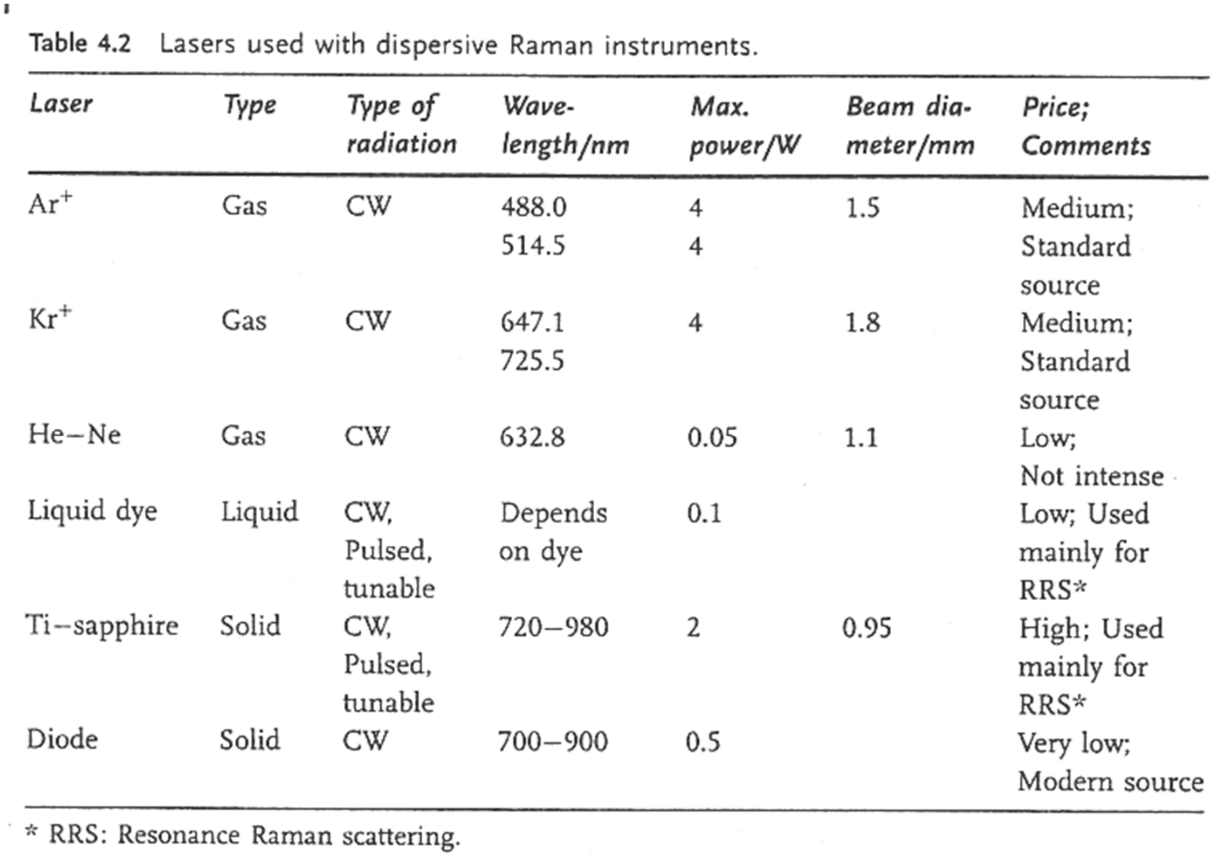


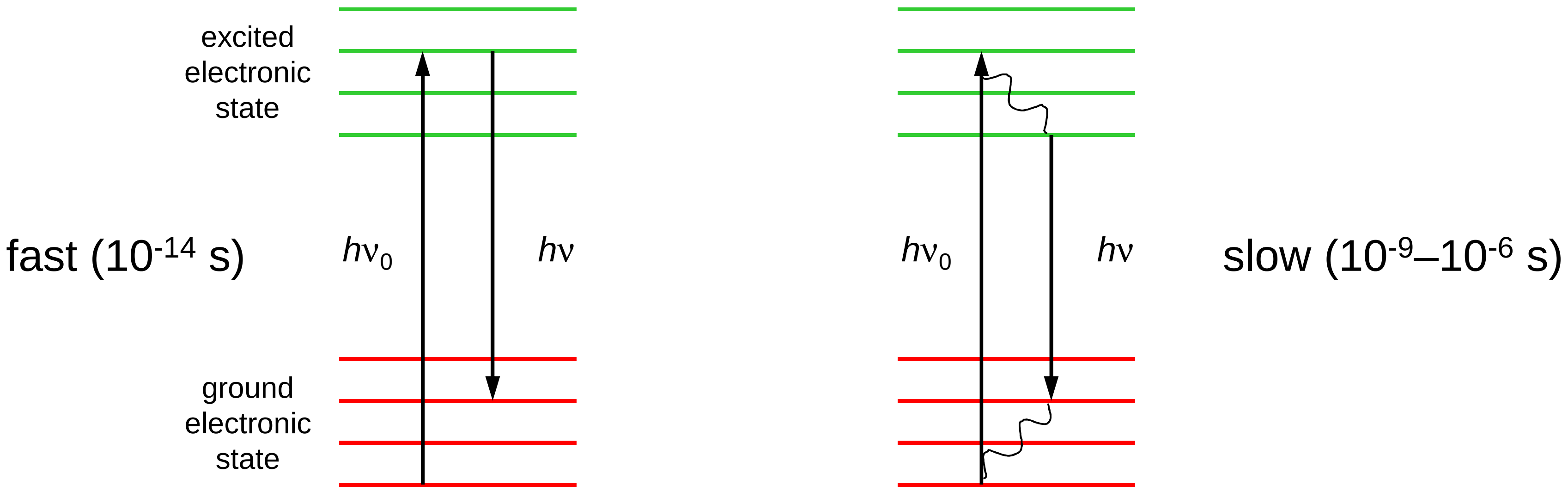
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



Resonance Raman scattering

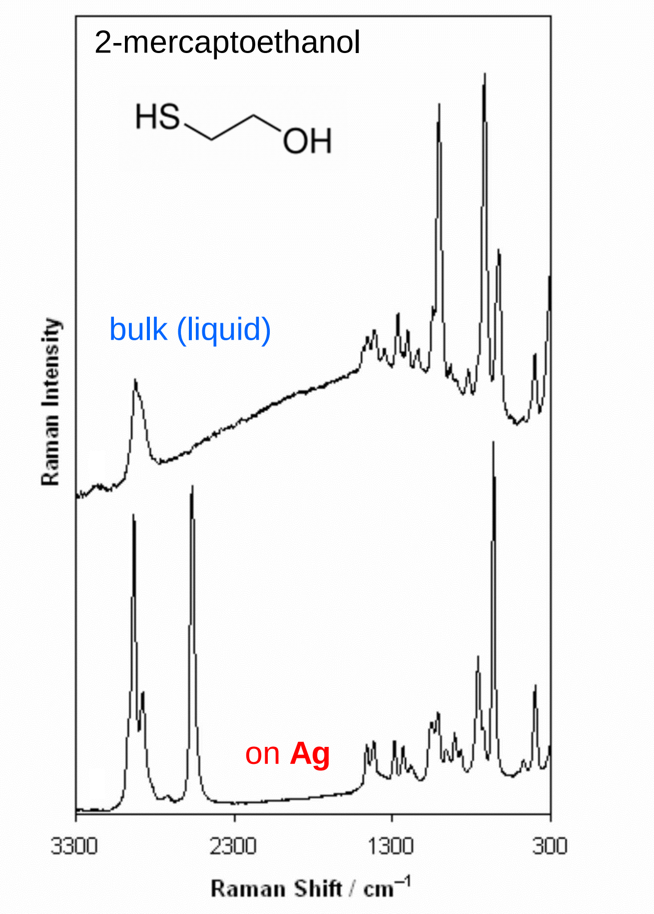
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

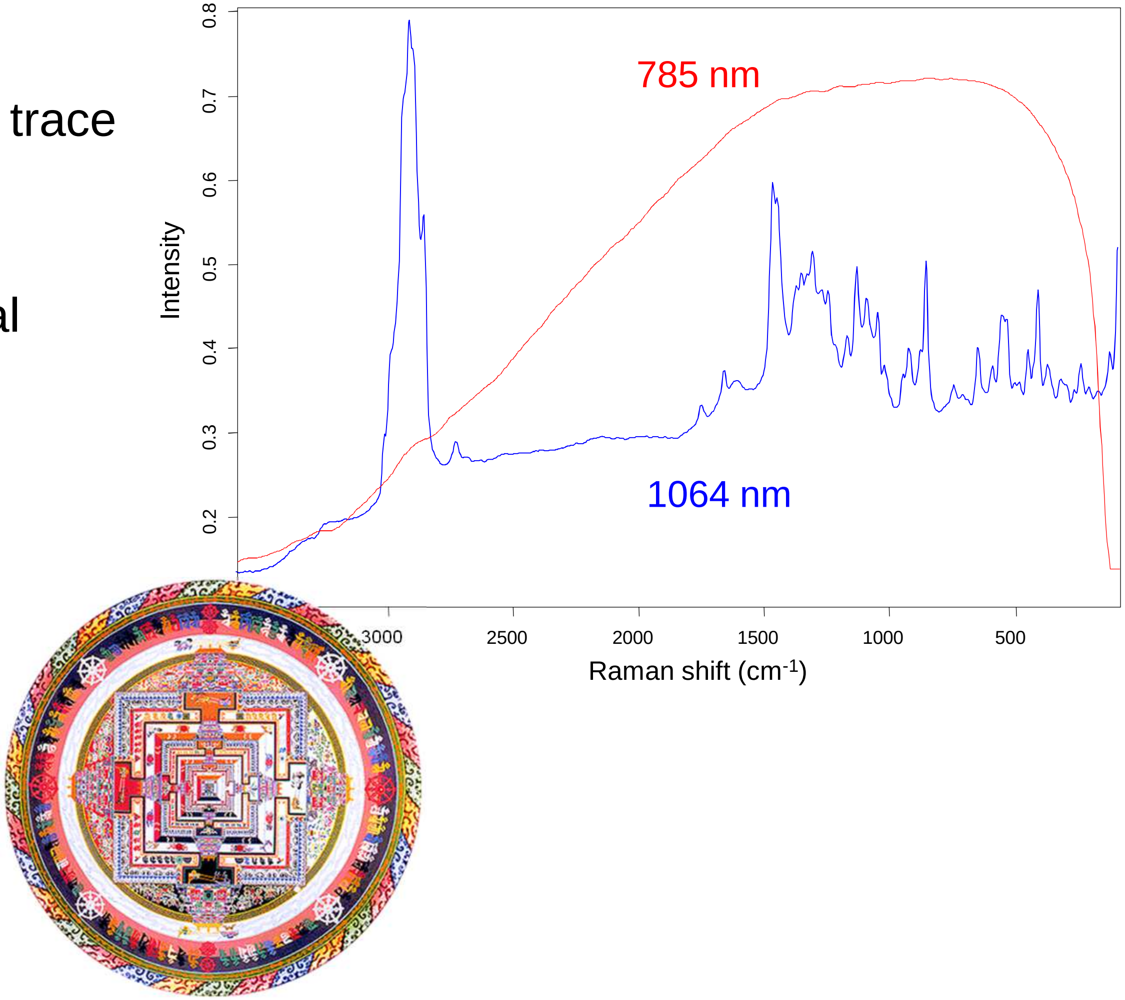
- Remarks:

❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



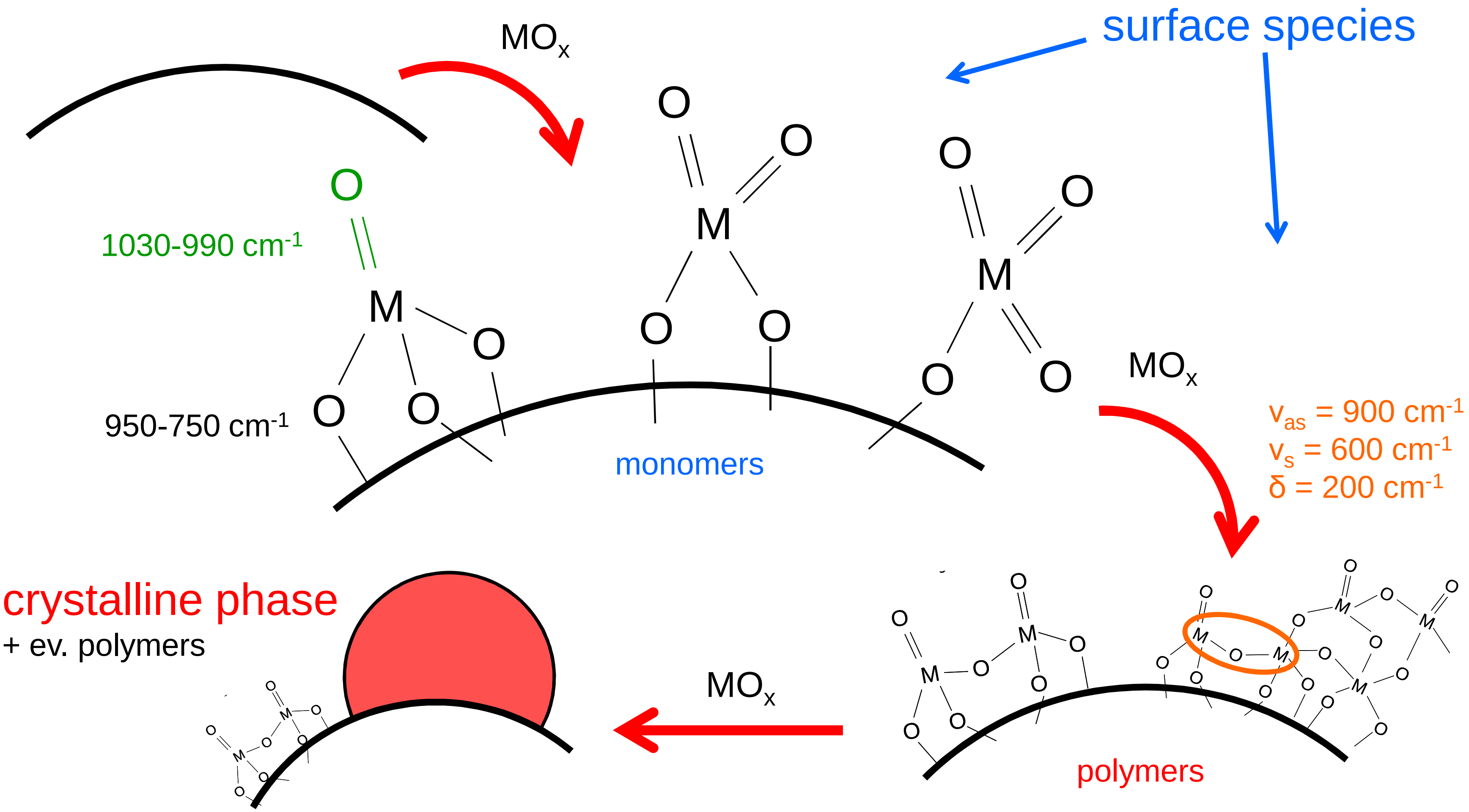
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



MO_x

surface species

1030-990 cm^{-1}

950-750 cm^{-1}

monomers

MO_x

$\nu_{as} = 900\ cm^{-1}$
$\nu_s = 600\ cm^{-1}$
$\delta = 200\ cm^{-1}$

crystalline phase
+ ev. polymers

MO_x

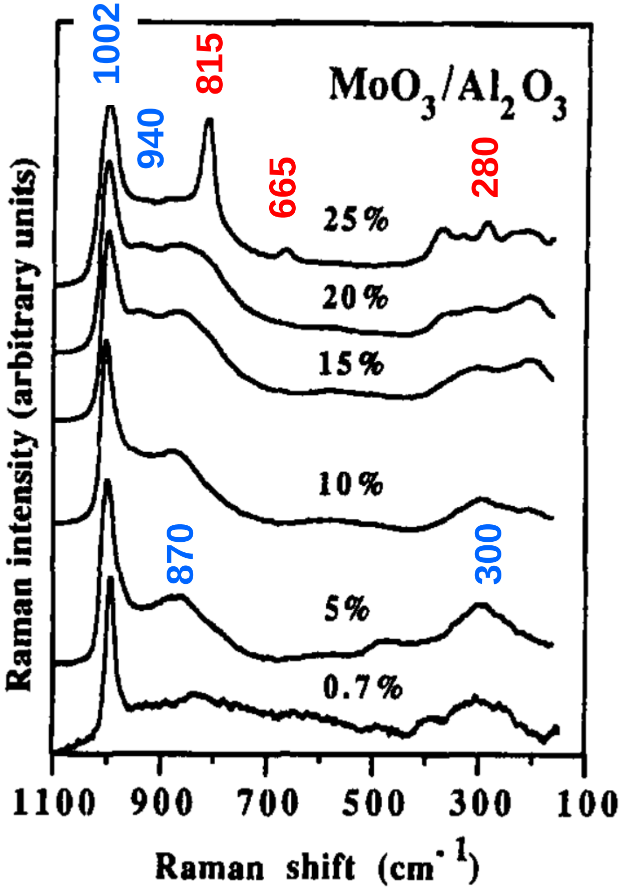
polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



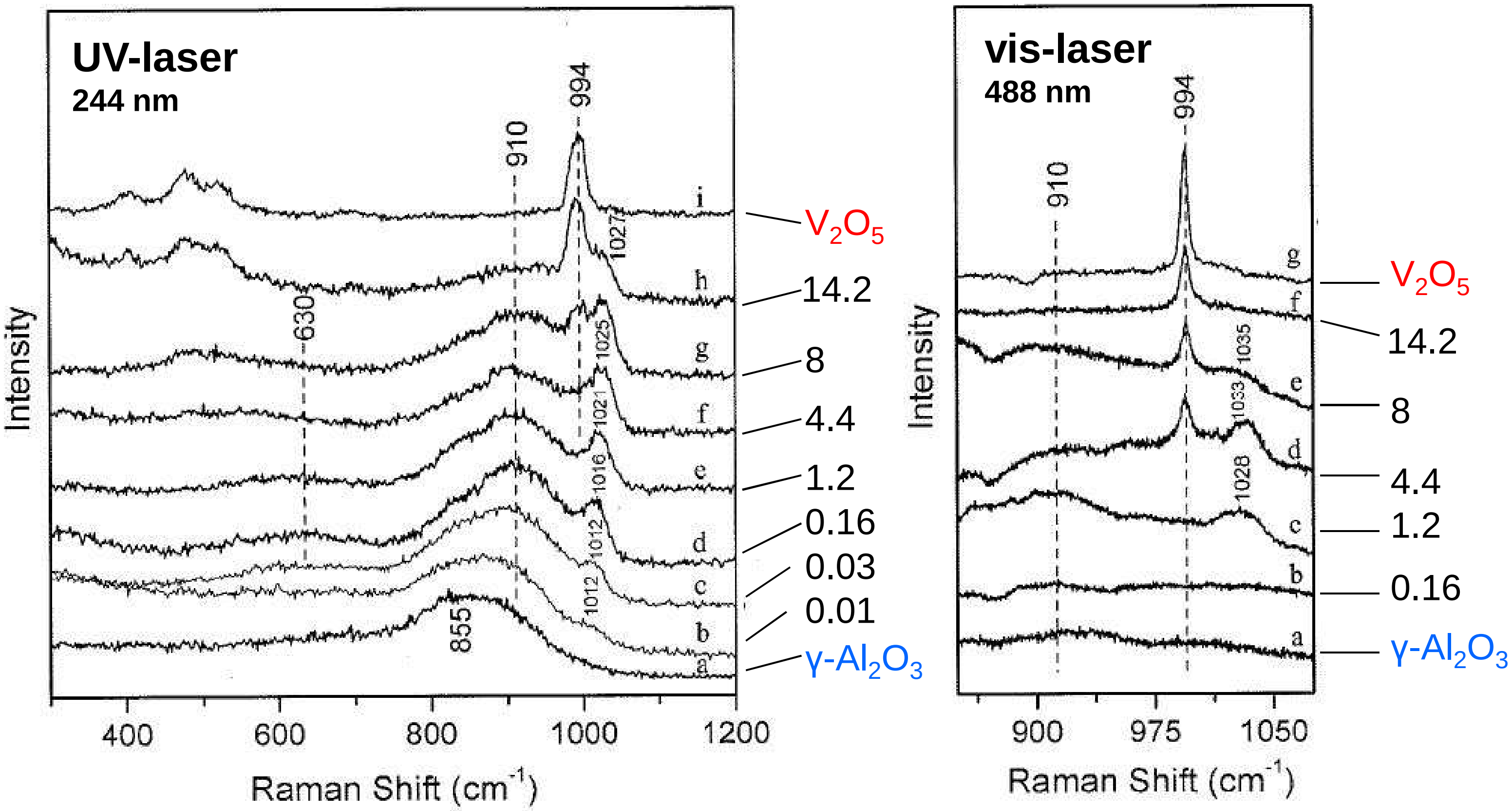
surface MoO_3
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

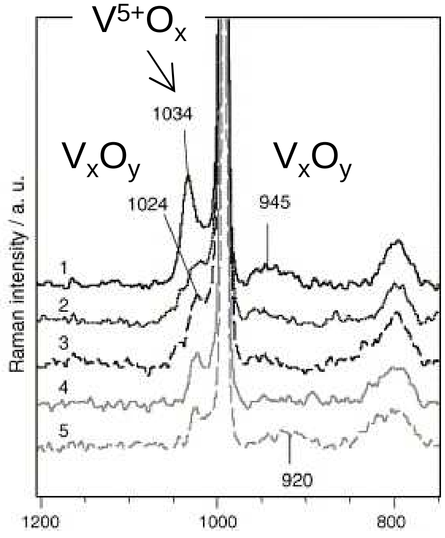
- Monomeric & polymeric species



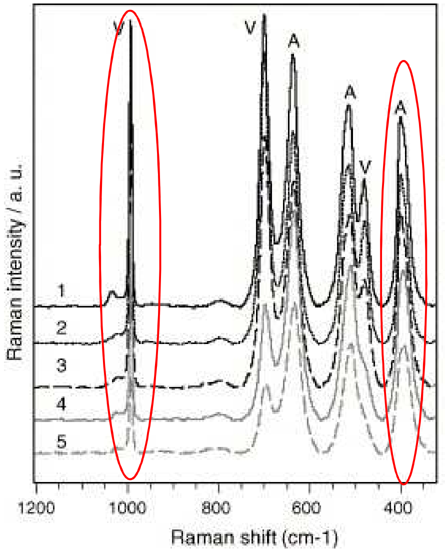
Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

Applications

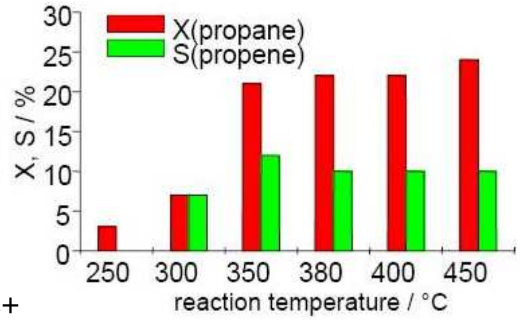
- Reactivity of V/TiO_2 after oxidative treatment

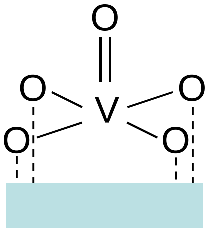


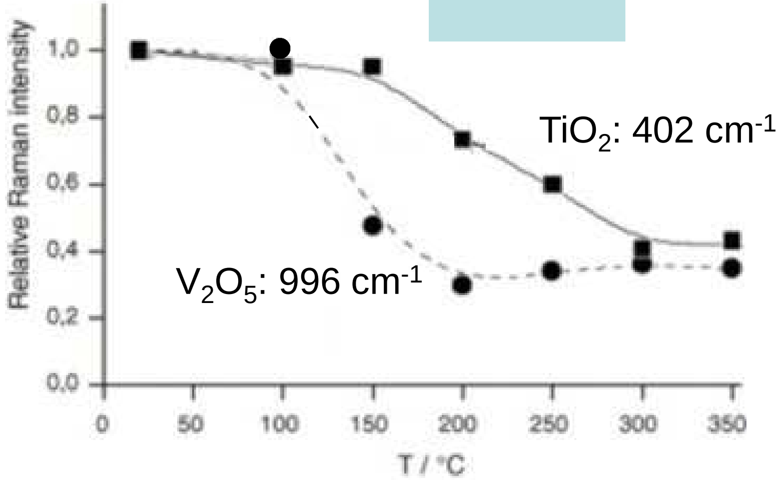
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C



$V^{5+} \longrightarrow V^{4+}$







Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

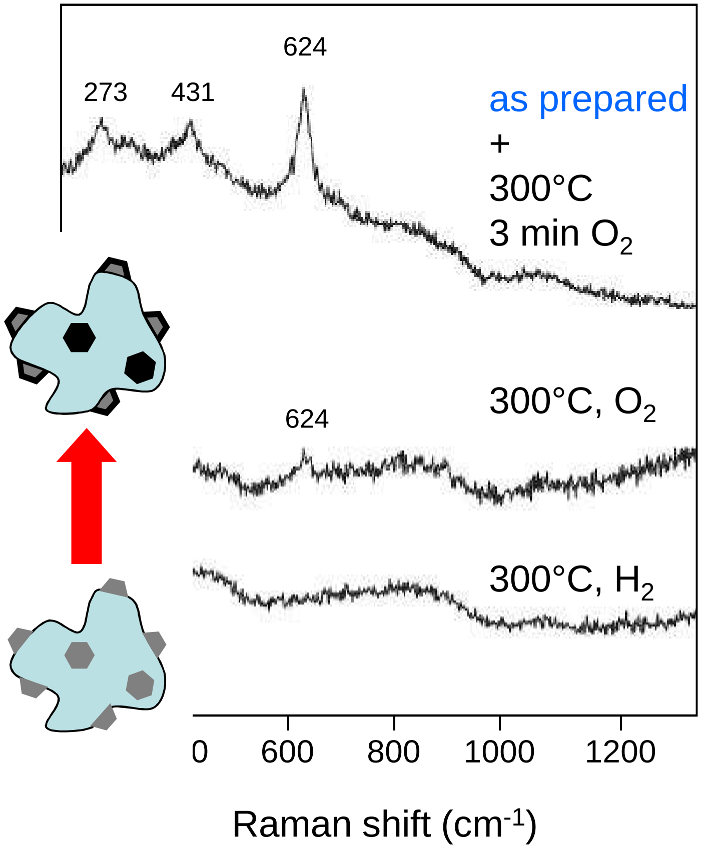
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…) used for total and partial oxidation reactions

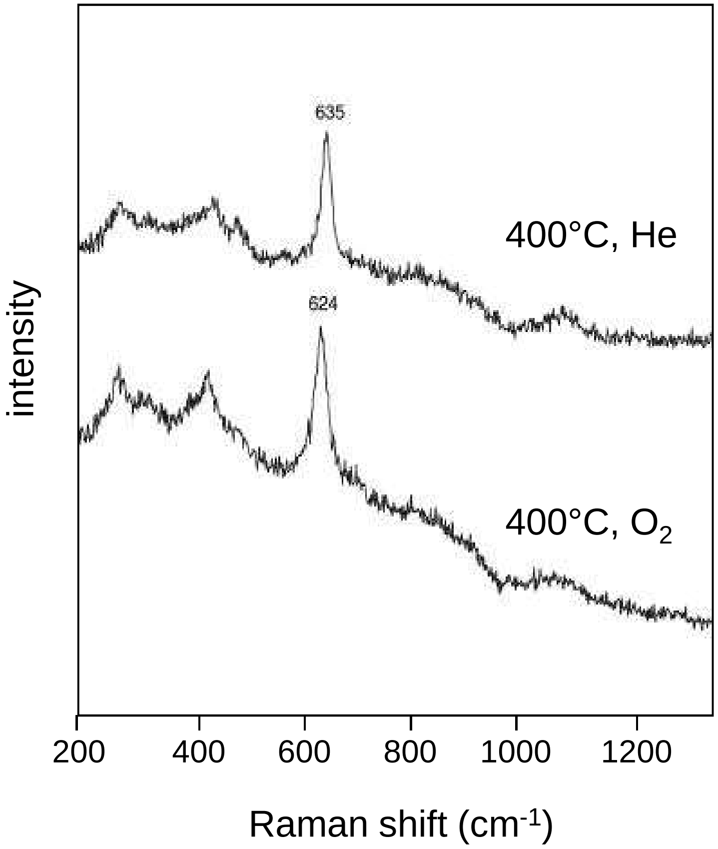
Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3





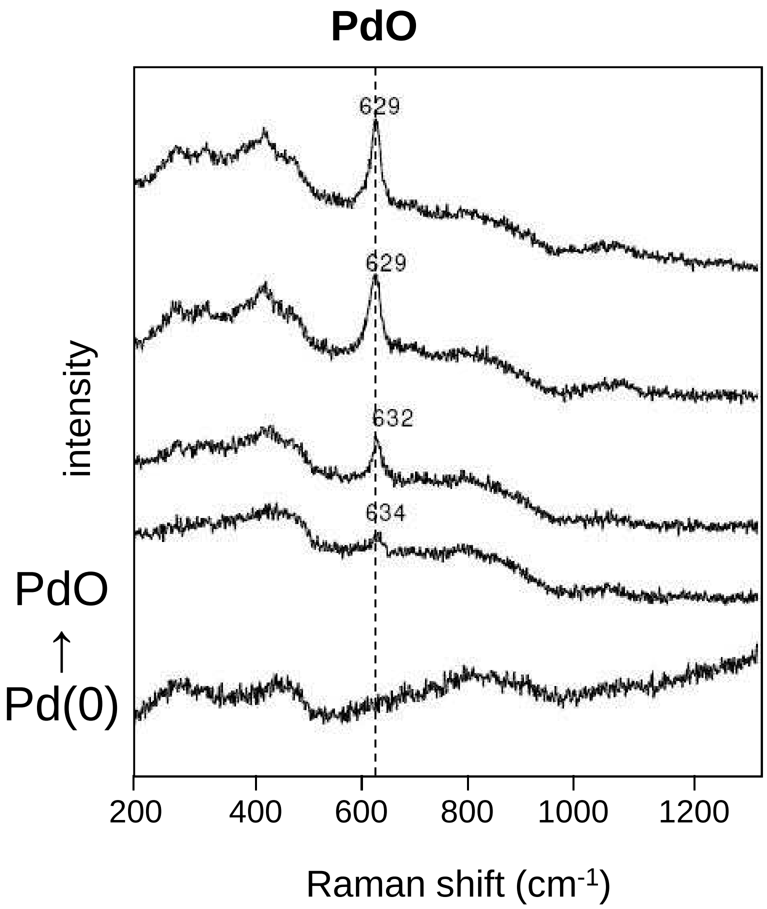
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



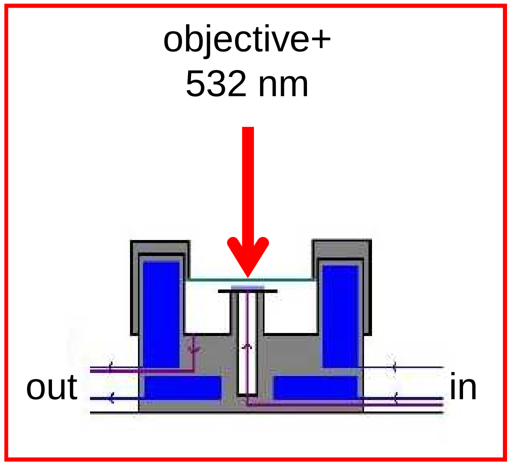
CH_4 conv.

500°C	**24 %**
450°C	**15 %**
425°C	**4 %**
400°C	**2 %**

400°C, H_2
reduced Pd

feed CH_4/O_2 (1:10)

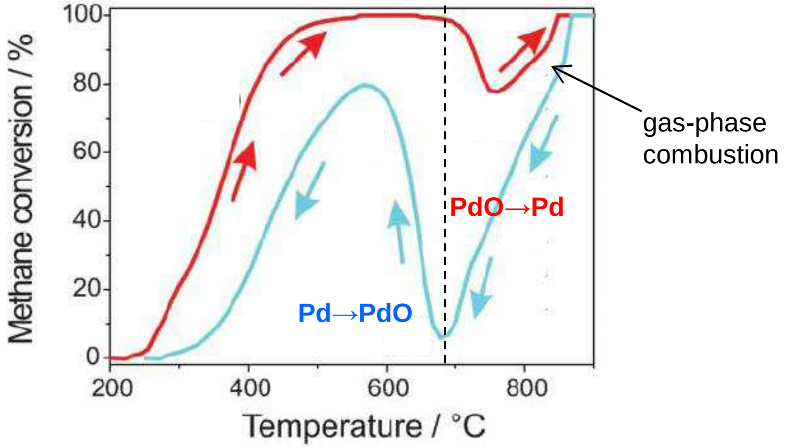
near PdO mode

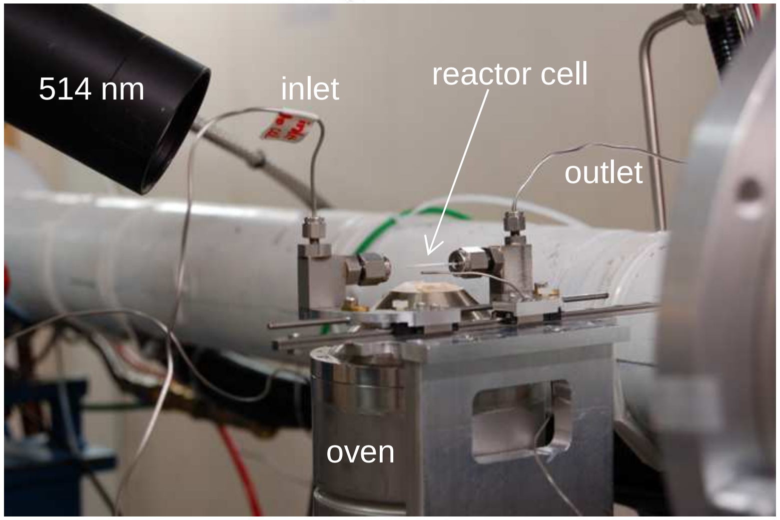


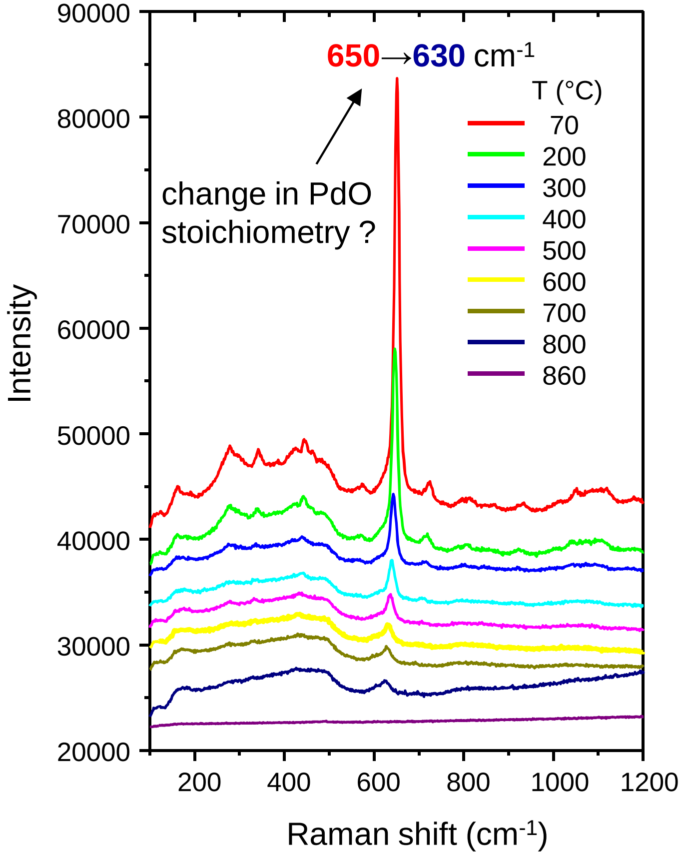
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

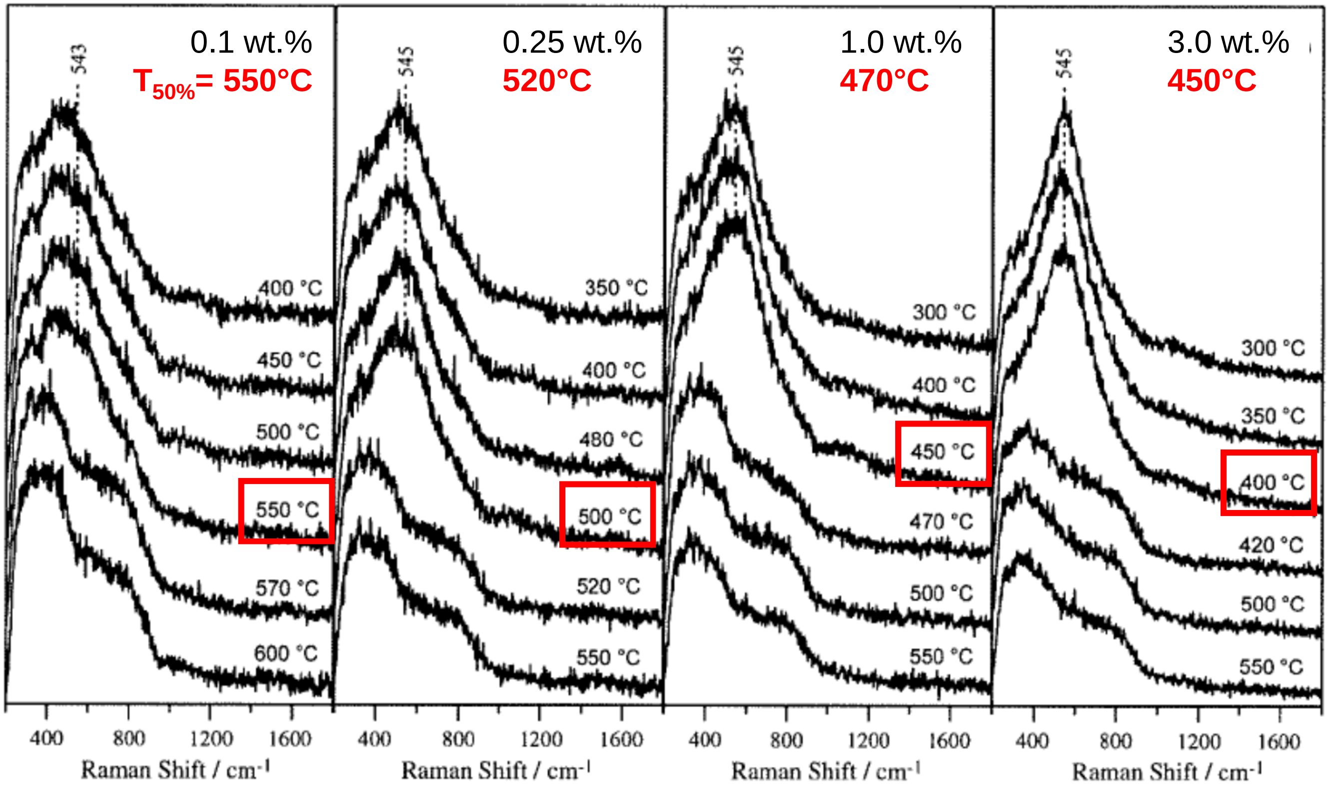
- Methane partial oxidation over Rh/Al_2O_3

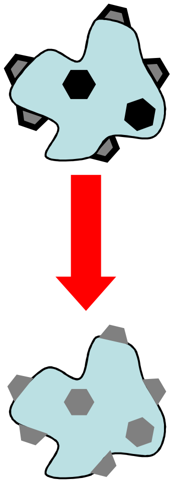
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content →
Activity →

RhO_x
↓
Rh(0)





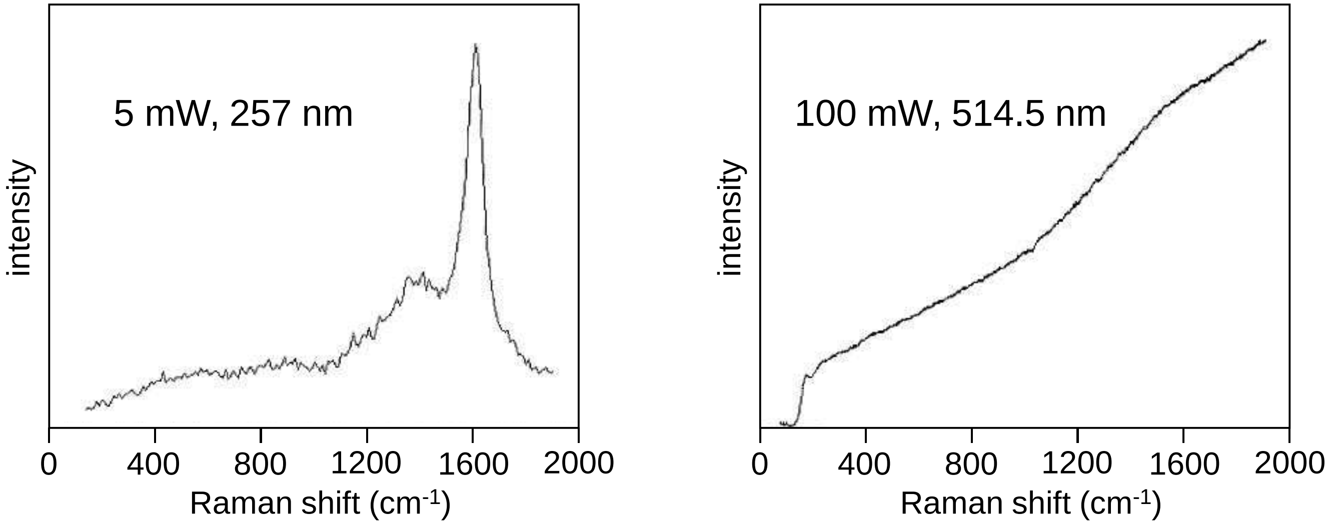
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - ☐ No fluorescence

    (only few molecules fluoresce below 260 nm)

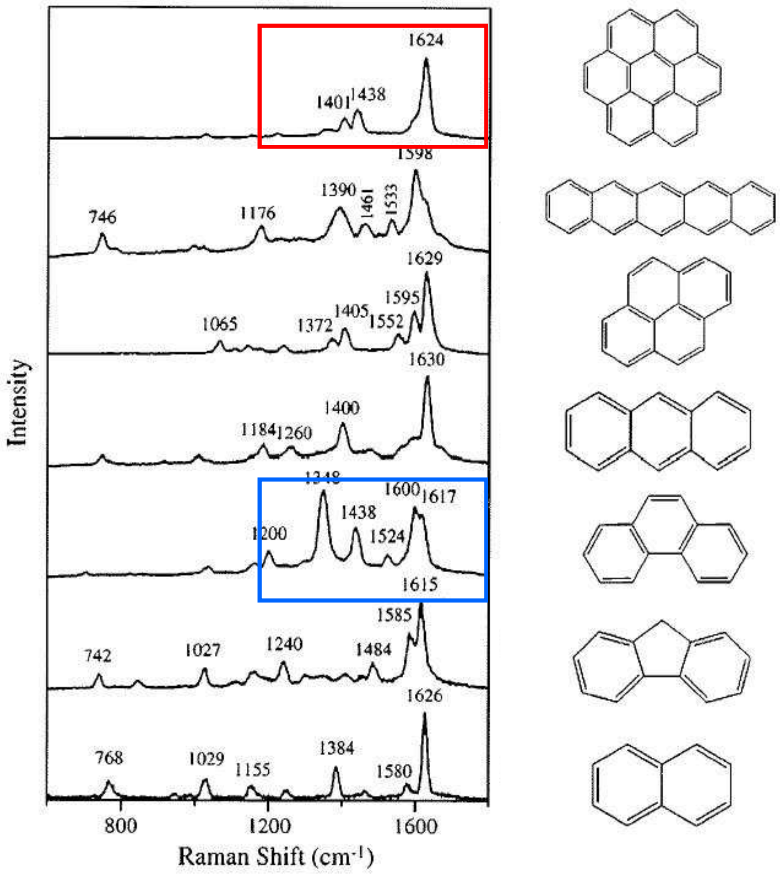
Rh/Al_2O_3, coked 500°C in naphtha

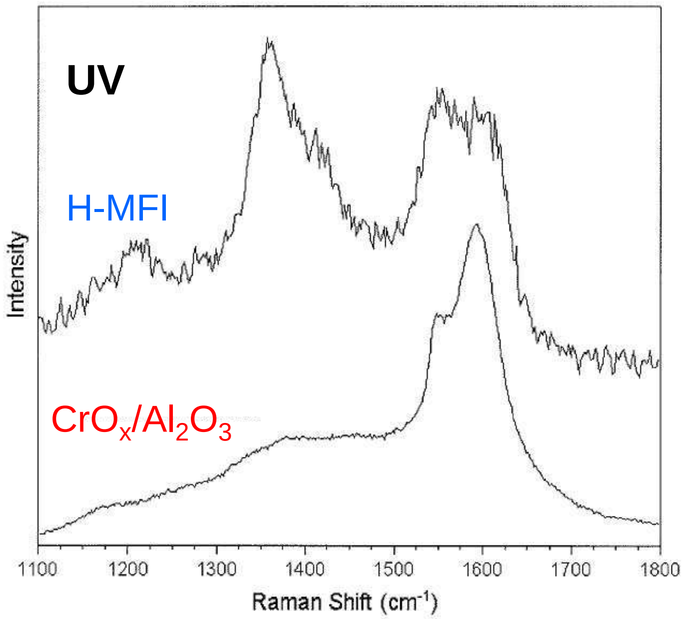


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





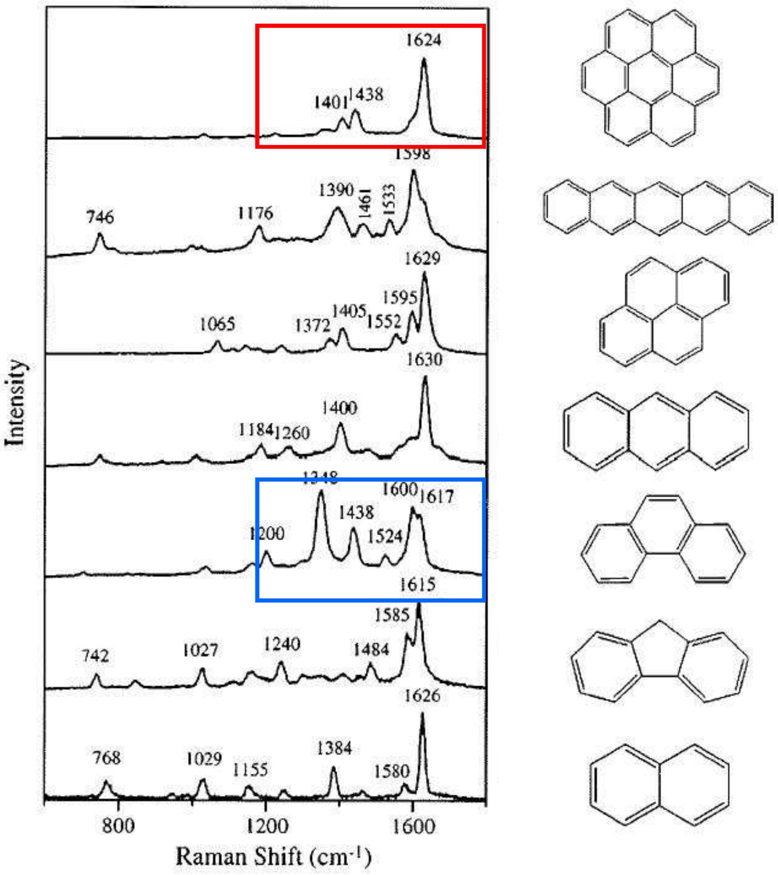
Coke classification
1D topology, chain-like
2D topology, sheet-like

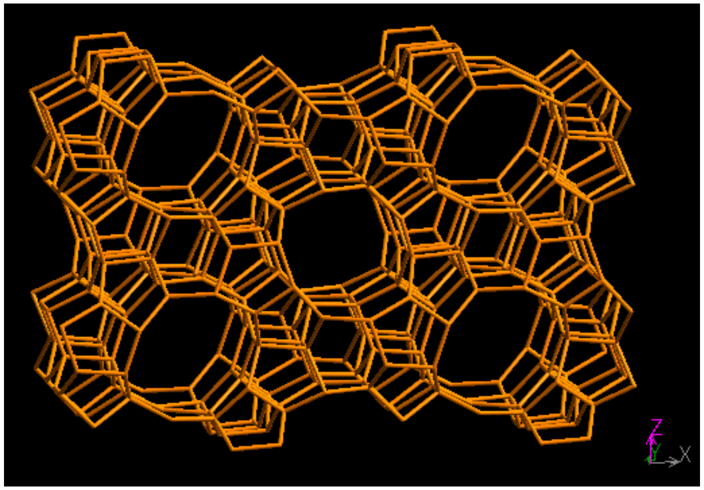
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





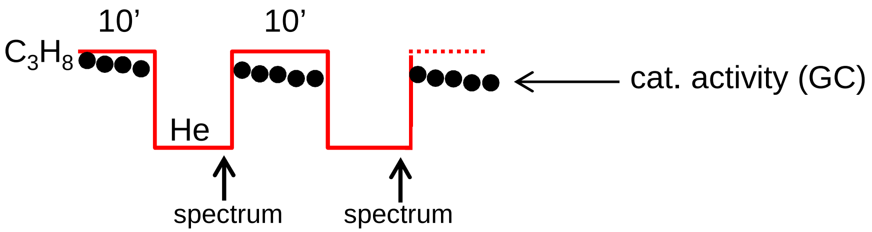
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

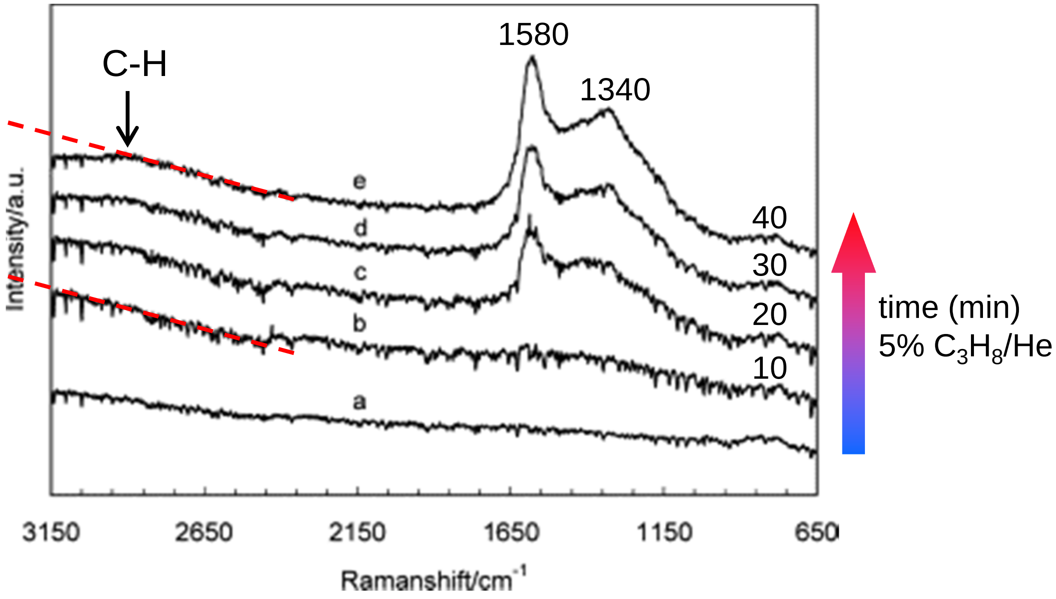
Stair, *Adv. Catal.* **51** (2007) 75

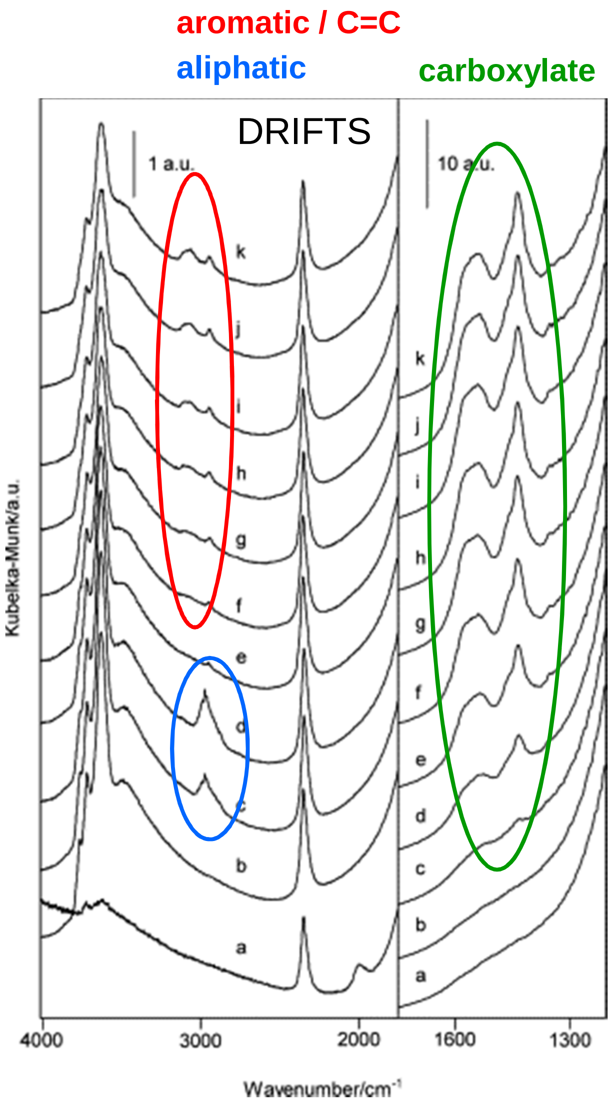
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

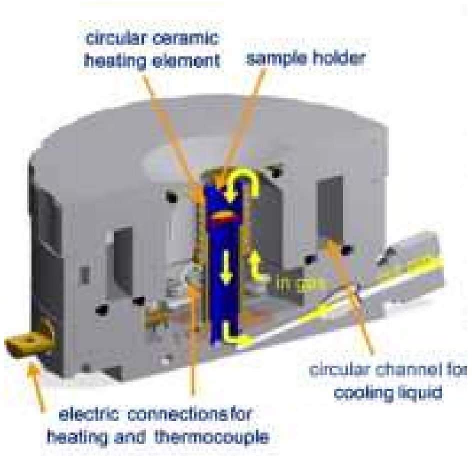


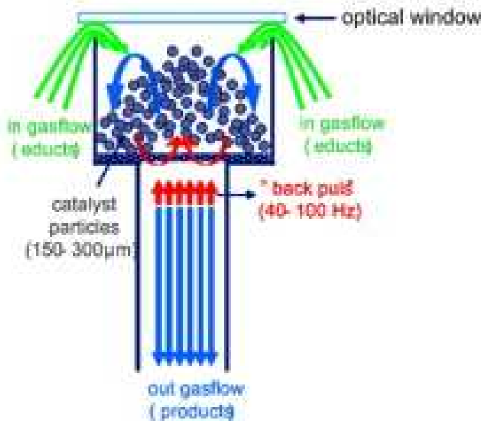


Airaksinen et al., *J. Catal.* **230** (2005) 507

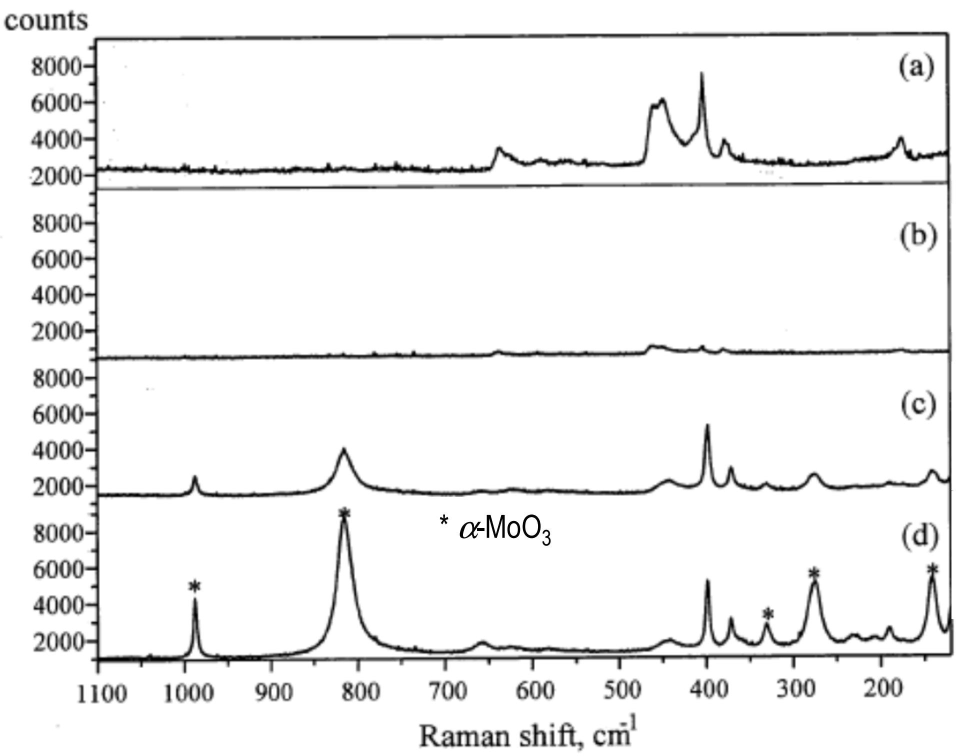
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min full power, FB

MoS_2, 6 min 1/8 power

MoS_2, 1 min full power

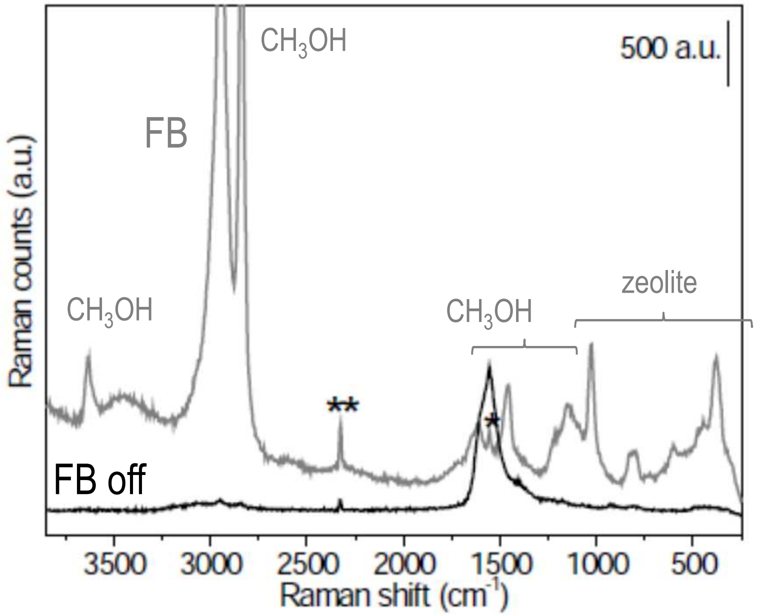
MoS_2, 6 min full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

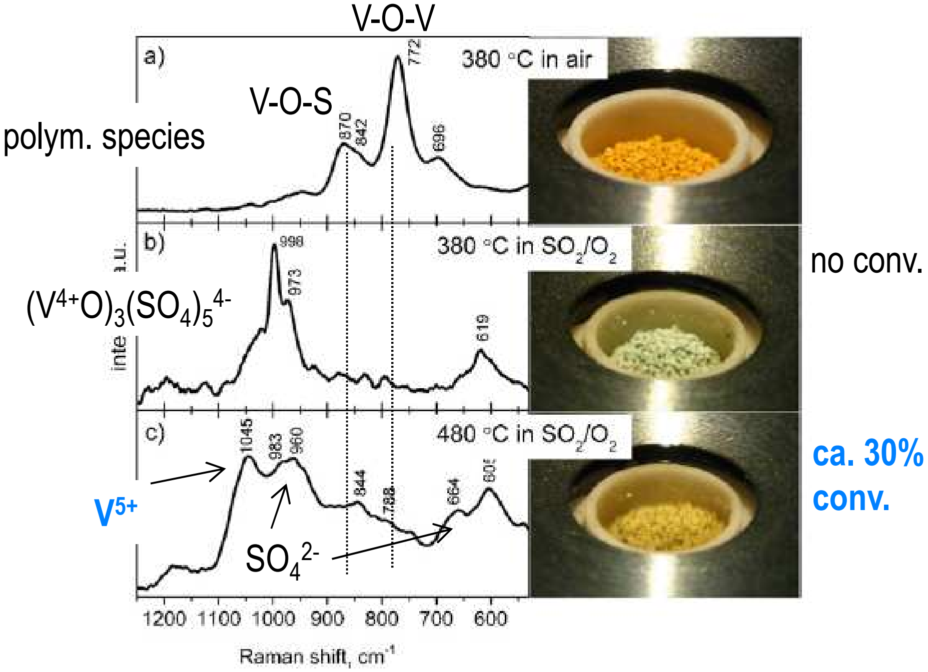
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

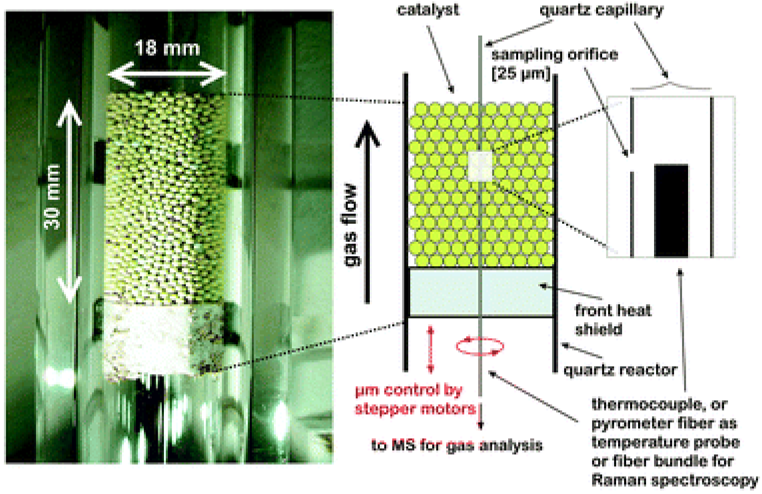


active species: mono- & dimeric V^{5+} oxosulfate species

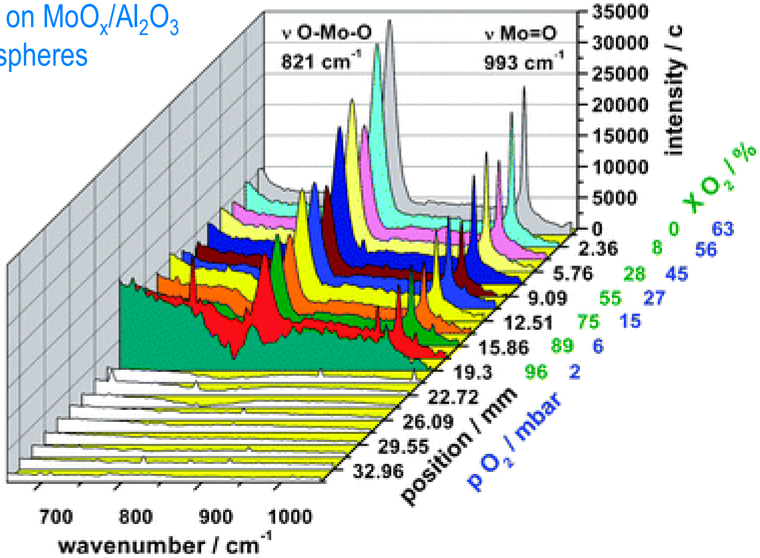
Beato et al., *Catal. Today* 205 (2013) 128

Applications

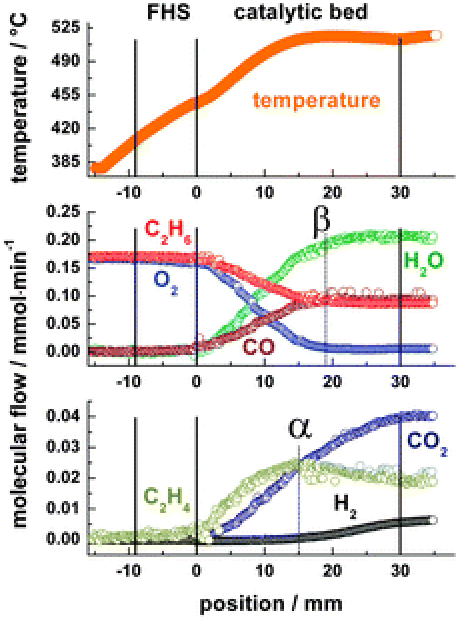
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

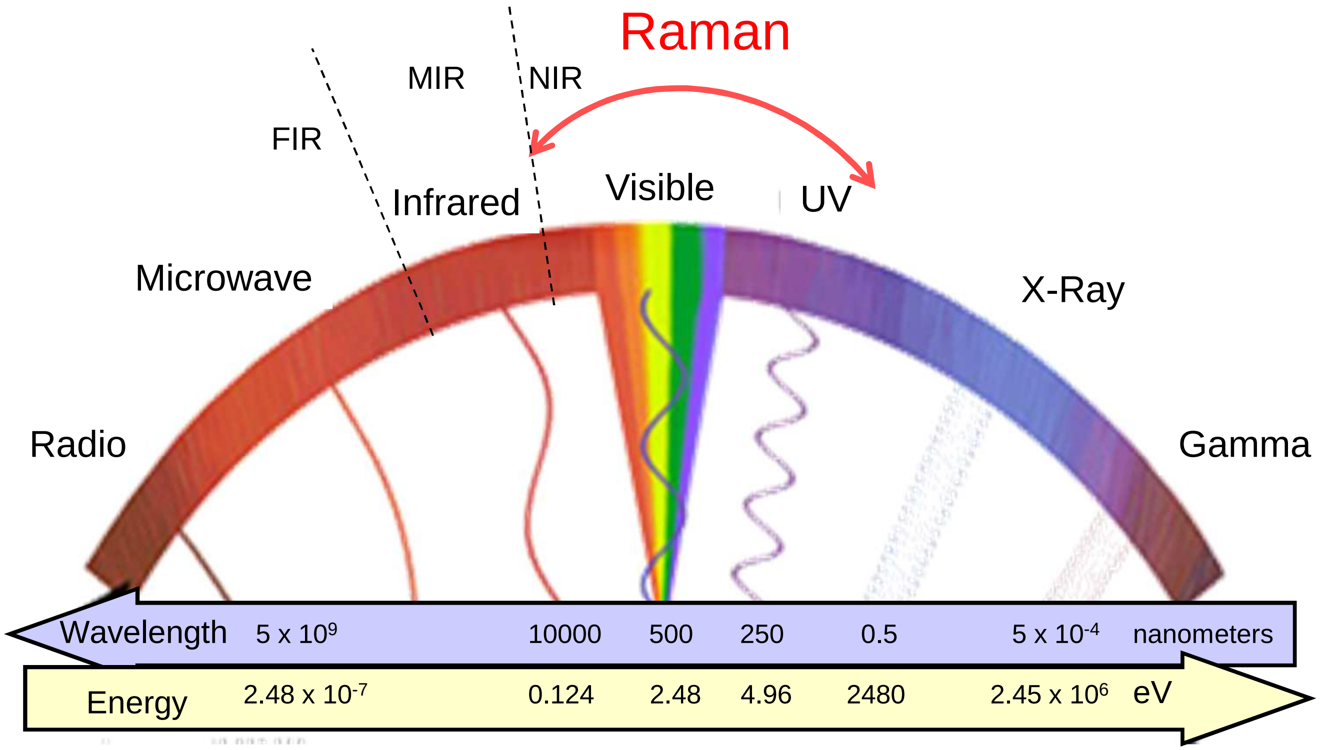
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

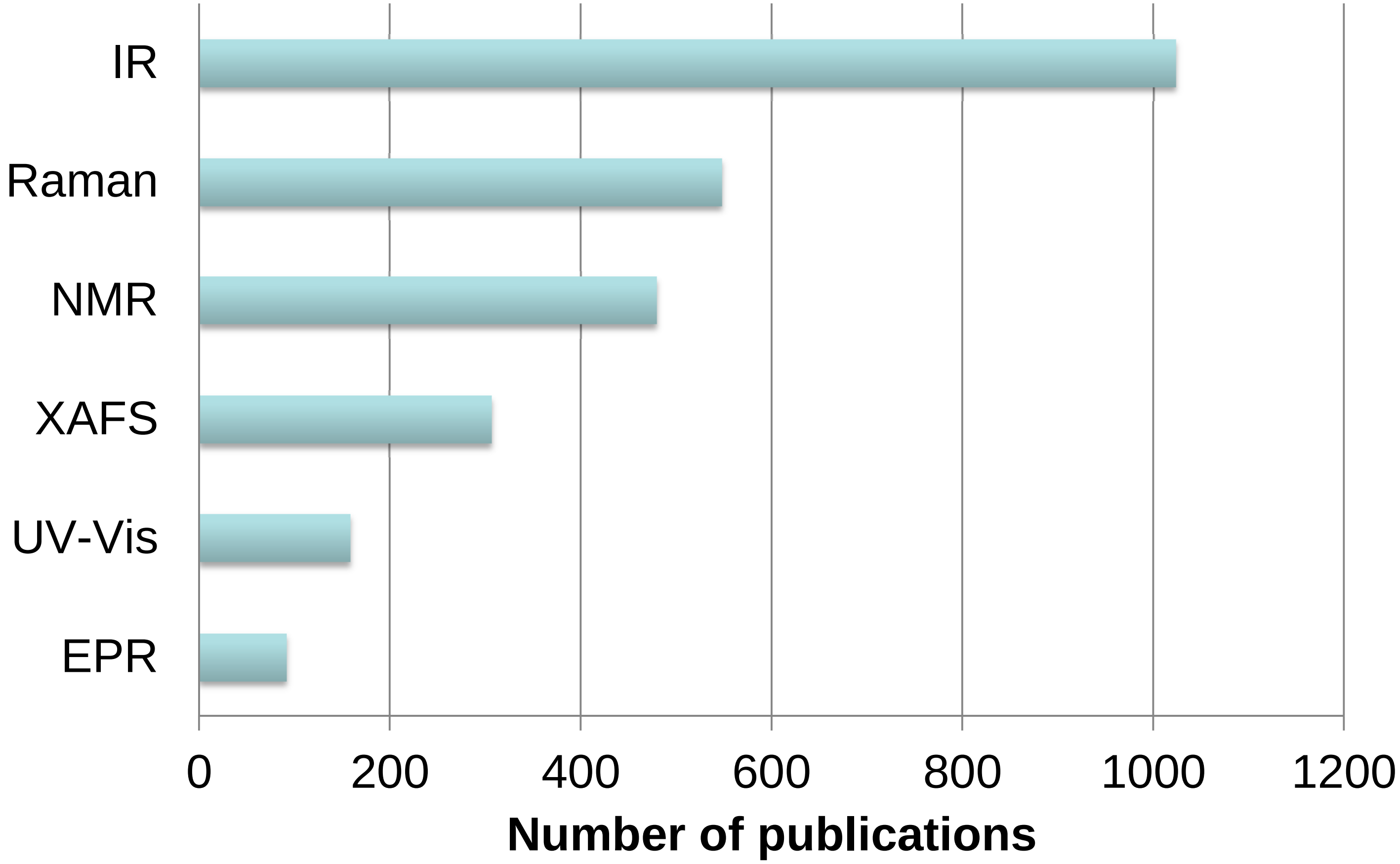
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

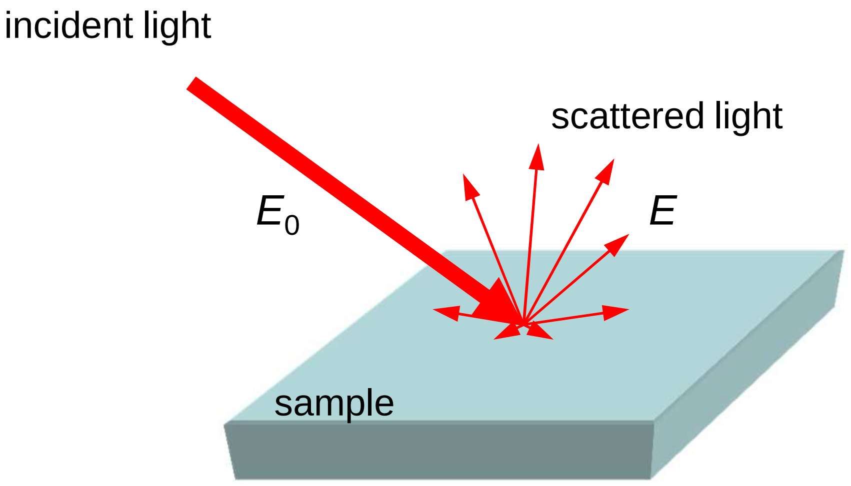


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
    - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

- E_0 = incident beam irradiance
- α = polarizability of the particle (ease of distortion of the electron cloud)
- λ = wavelength of the incident radiation
- θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

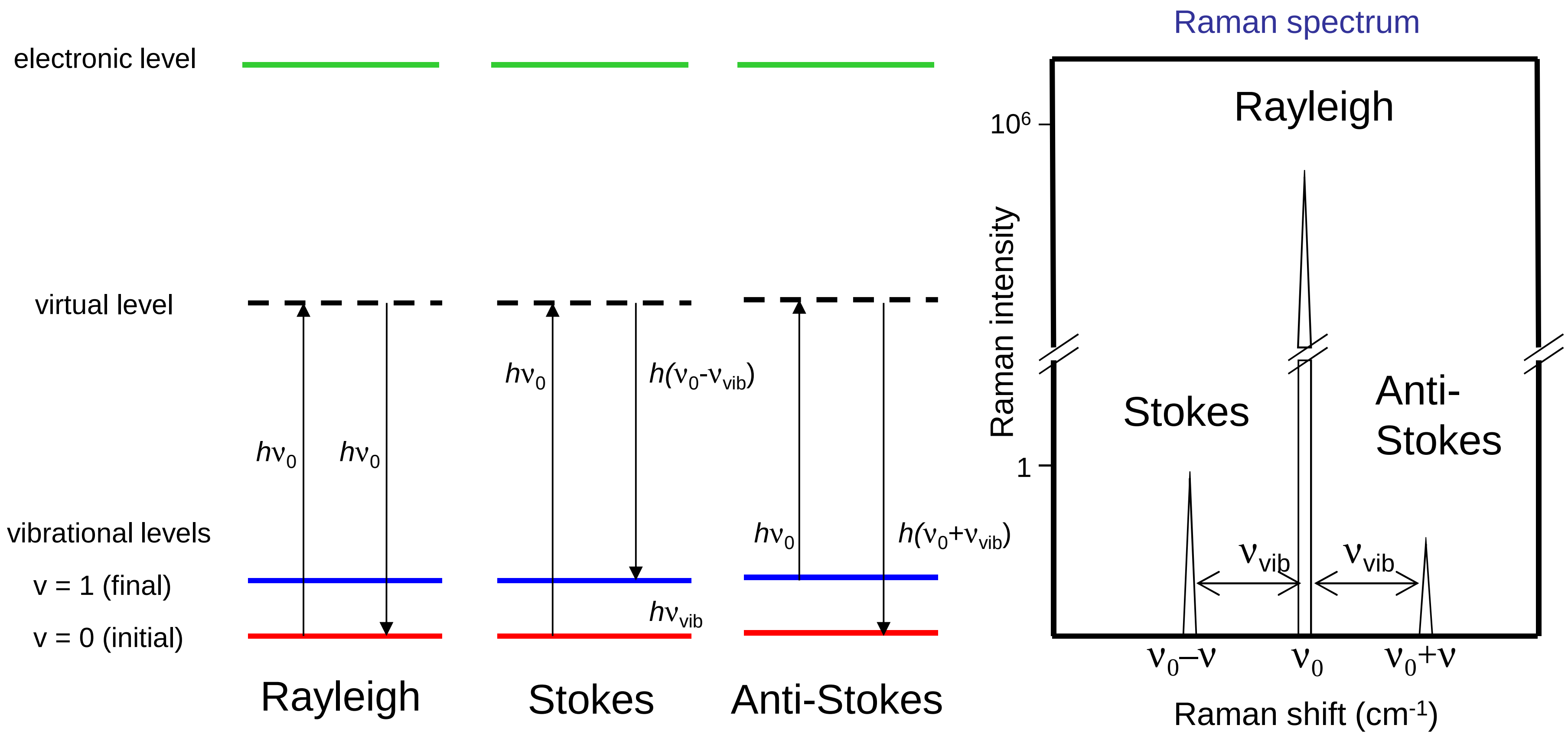
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\ [\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\ (\text{Anti-Stokes})}{I\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:
  - 4th power of ν (4th power law)
  - 2nd power of $\Delta\alpha$
    - properties of molecules
    - strength of bonds

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

↓

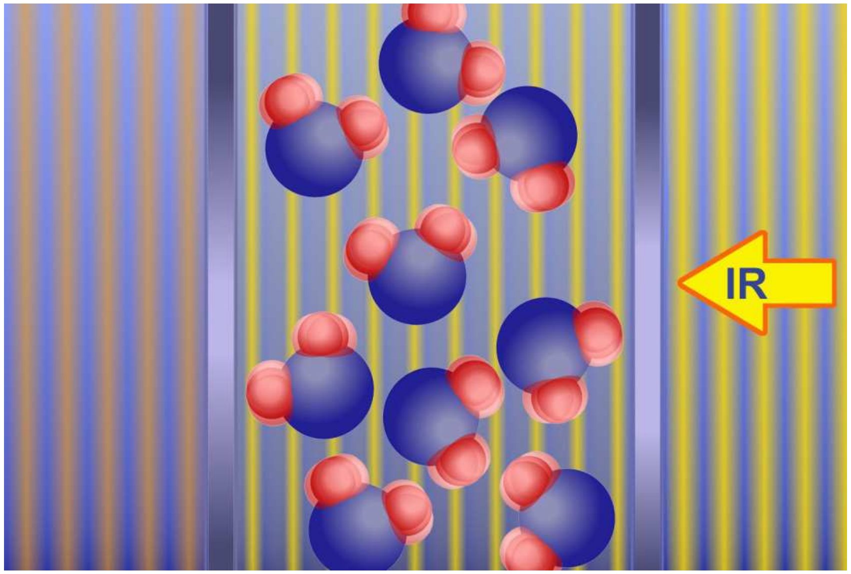
covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

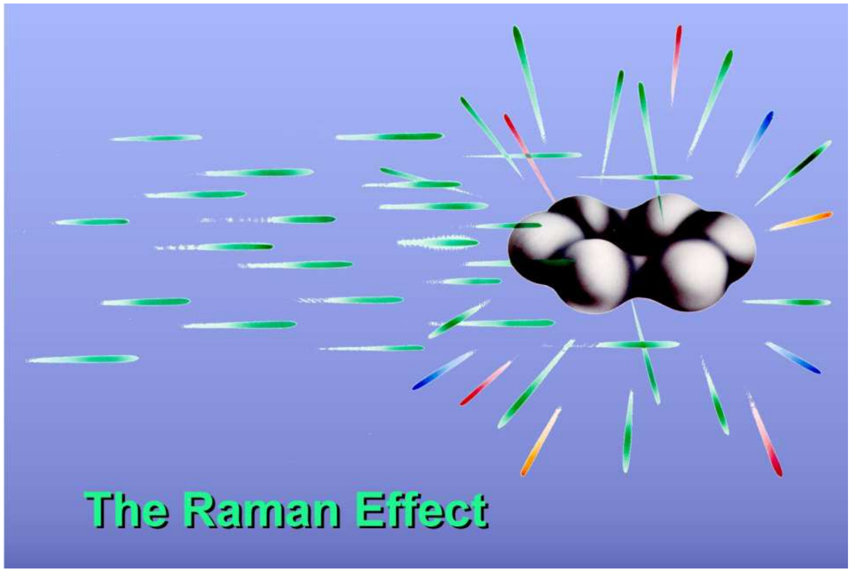
- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

Raman *vs.* Infrared

Infrared

Raman





Absorption of IR light

Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

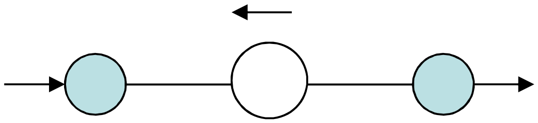
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - ❑ large electron clouds
  - ❑ not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

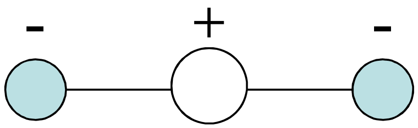
Raman *vs.* Infrared

CO_2



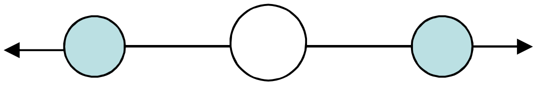
ν_{as}

2349 cm^{-1}



δ

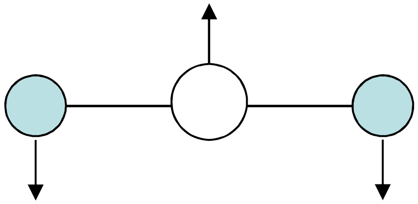
667 cm^{-1}



ν_s

1340 cm^{-1}

Raman active



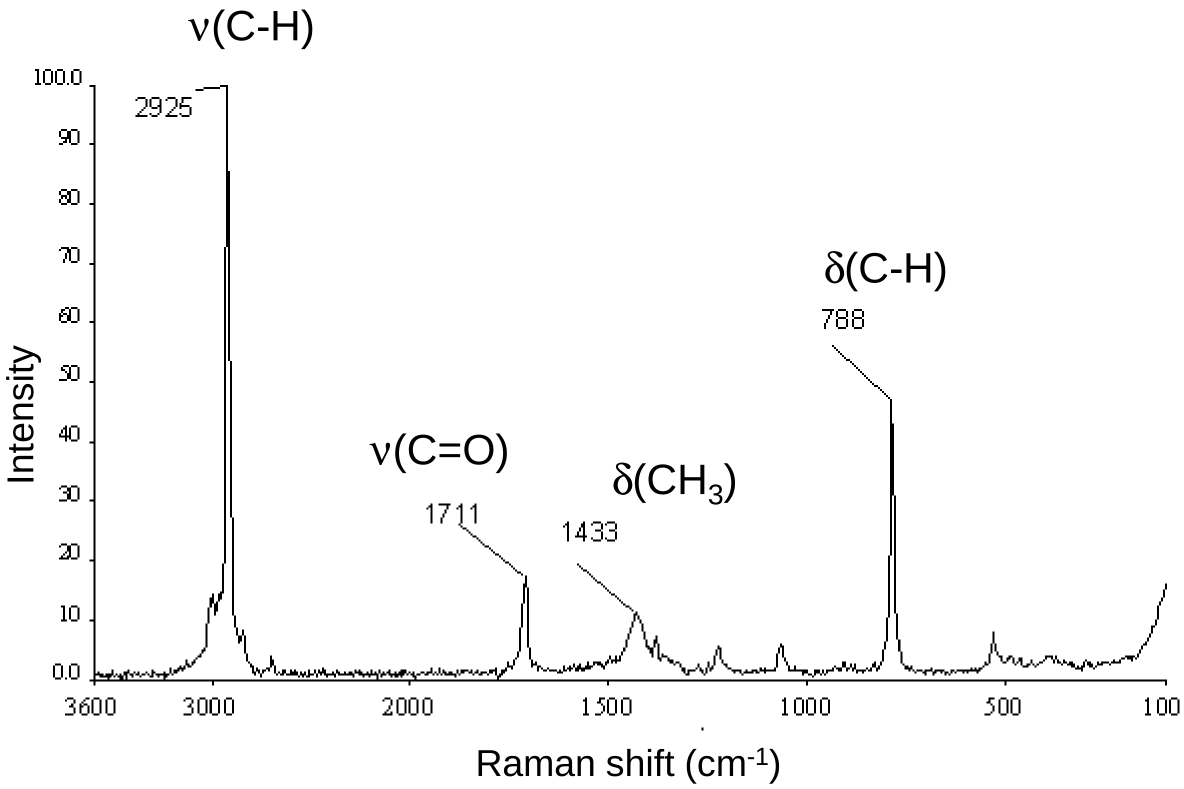
δ

667 cm^{-1}

degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared

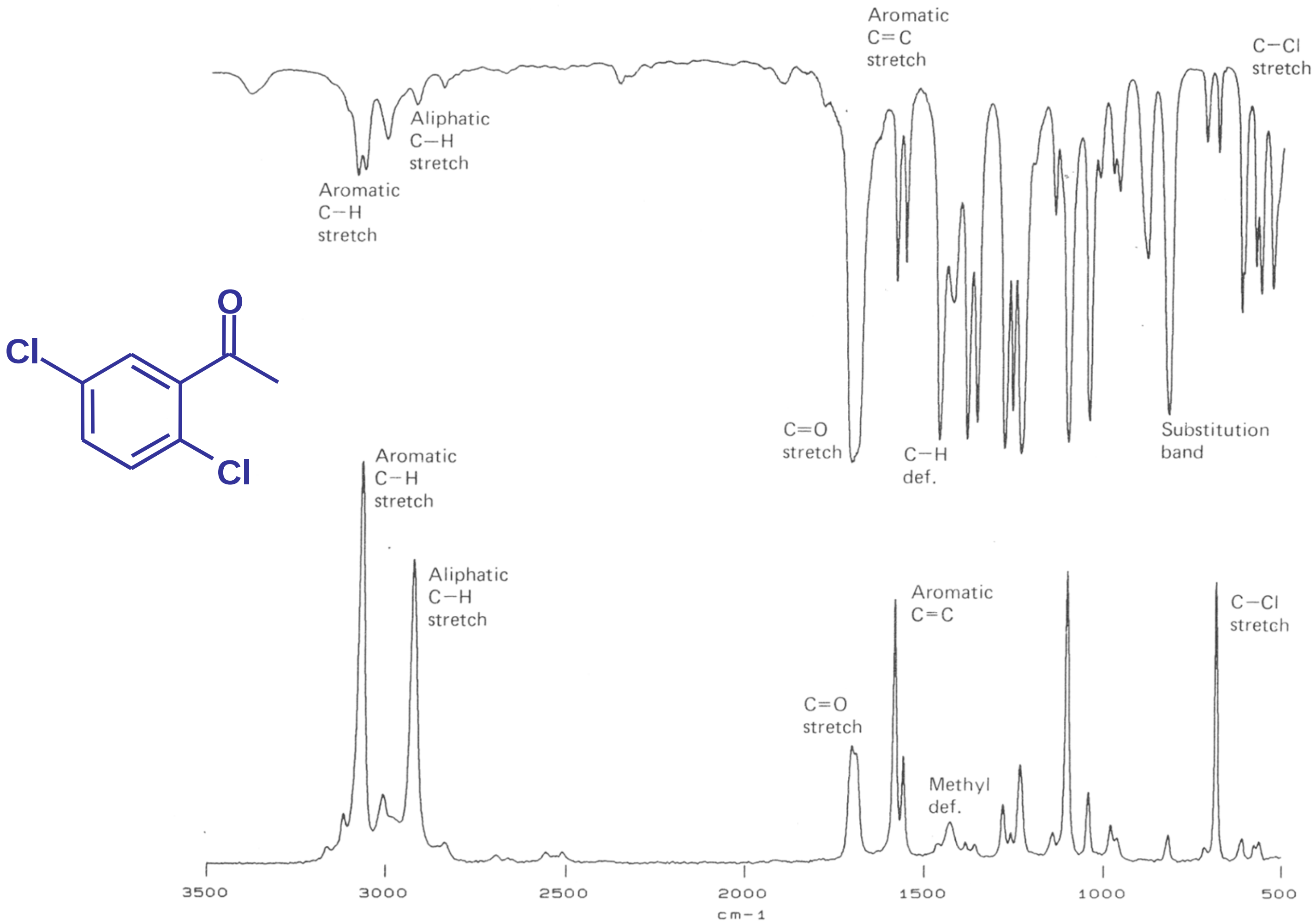


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

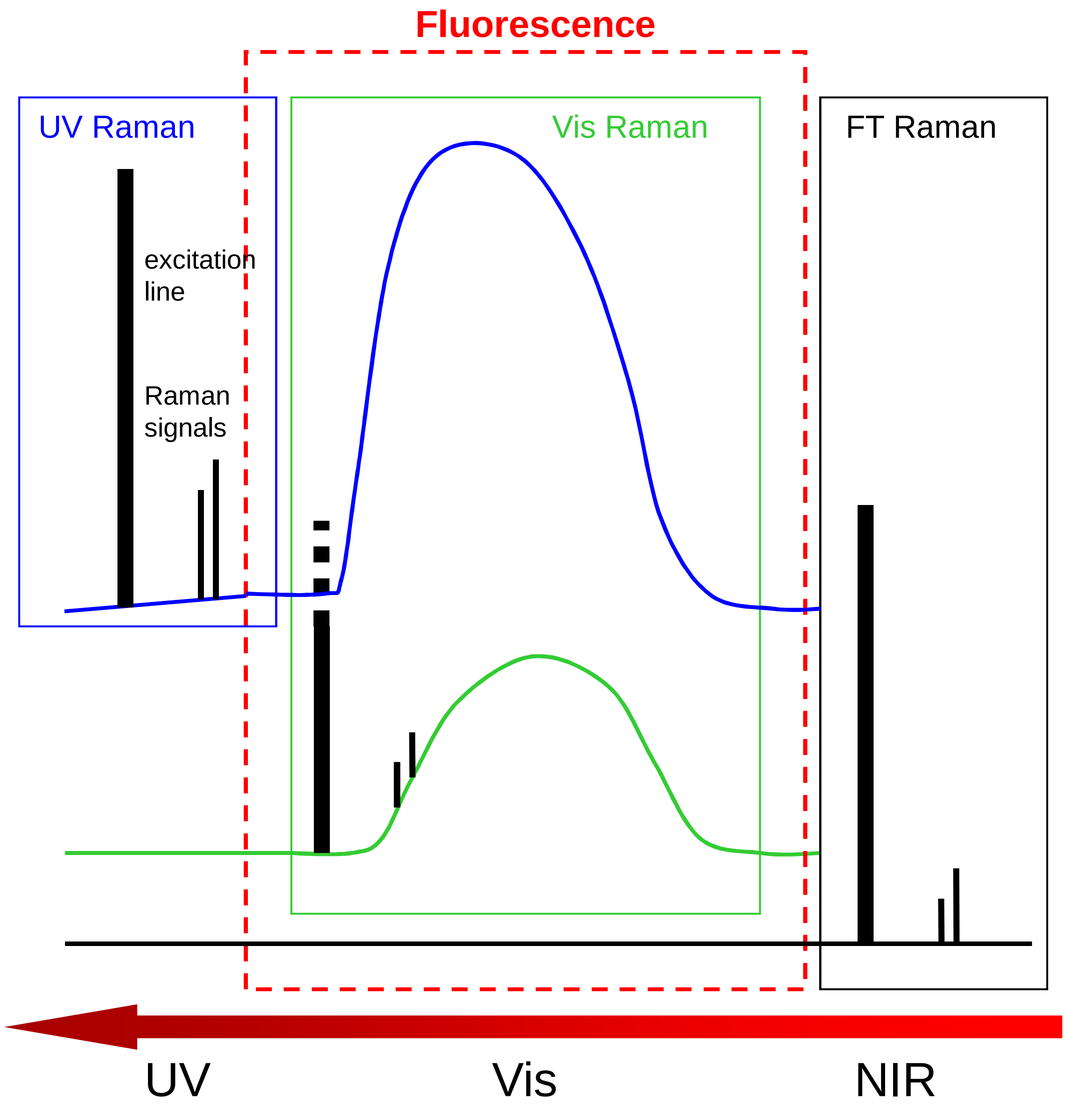
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 µm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

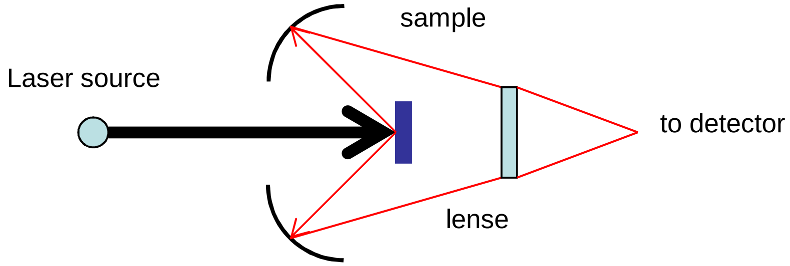
Fluorescence proportional to ν

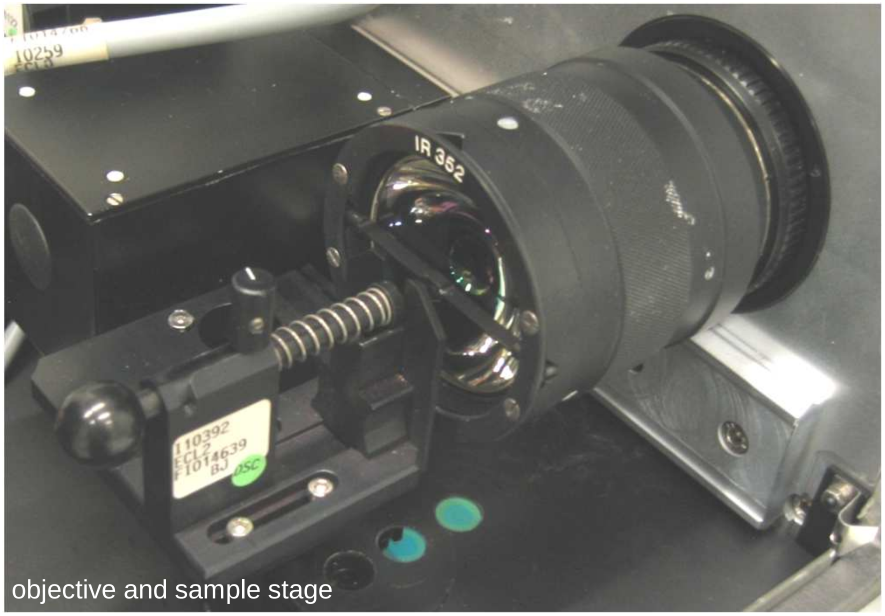
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers

Excitation wavelengths

UV	250 nm
Vis (green)	514 nm
Vis (red)	633 nm
NIR	780 nm
IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

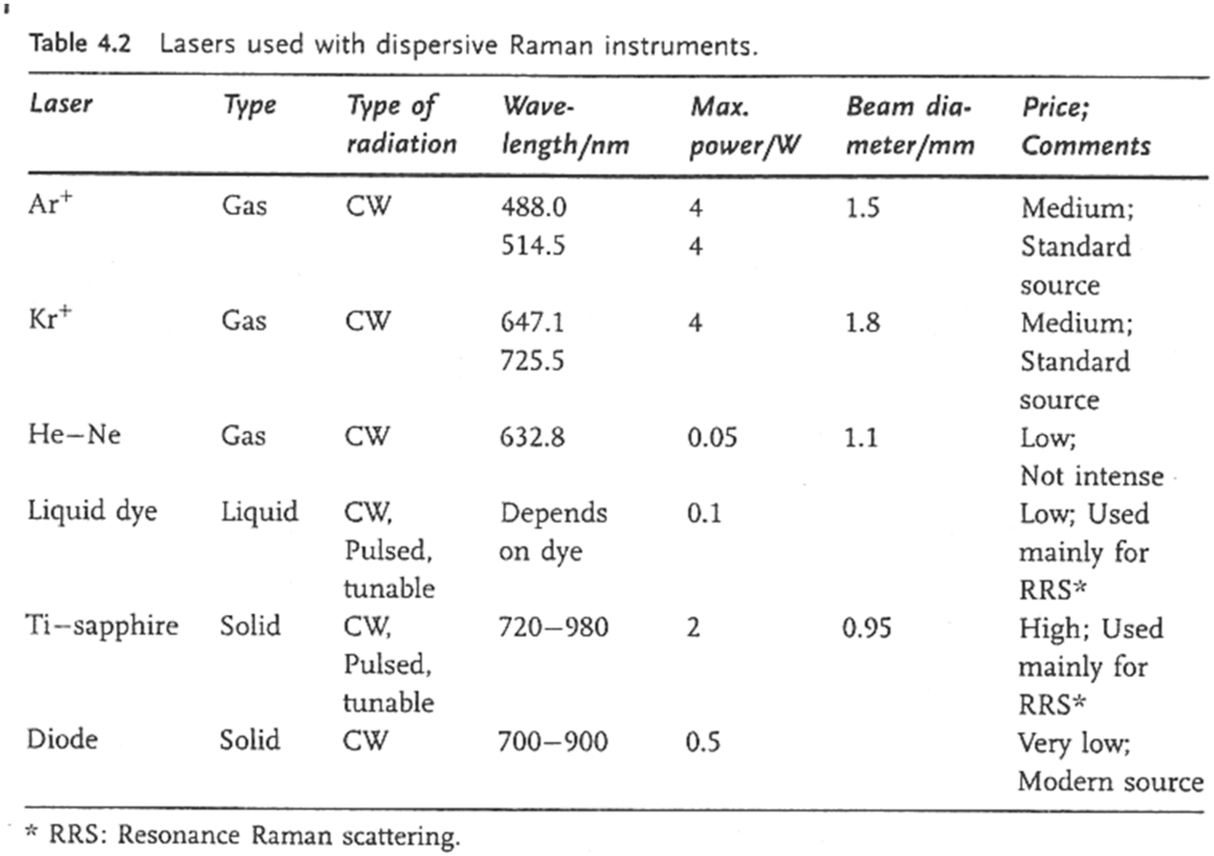


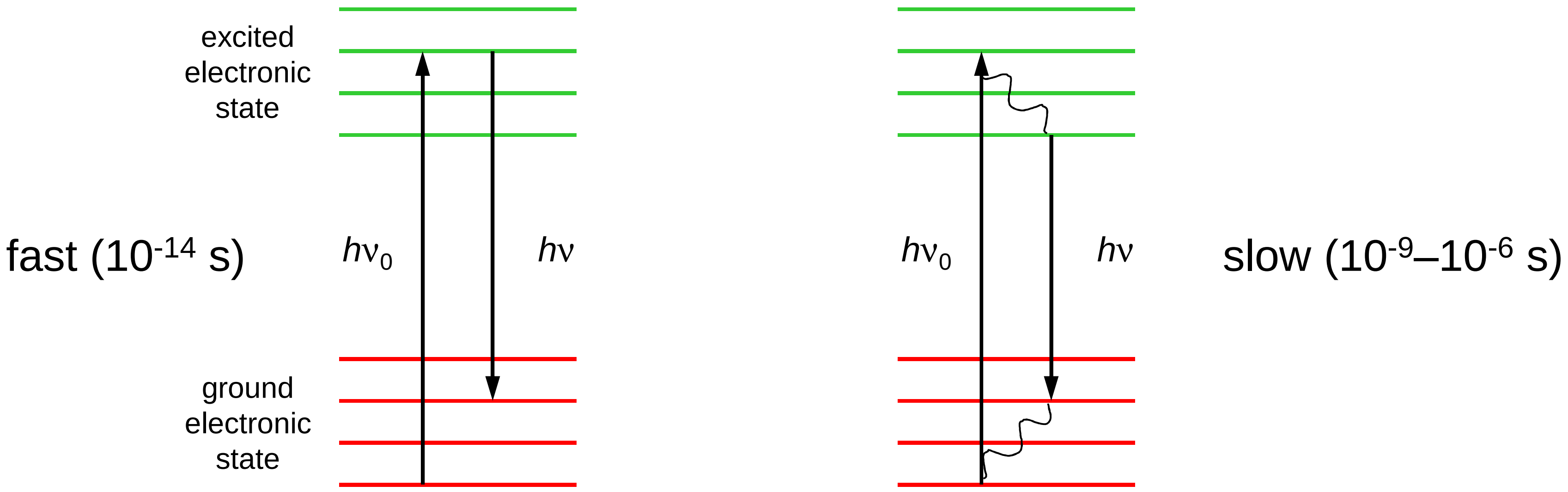
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



Resonance Raman scattering

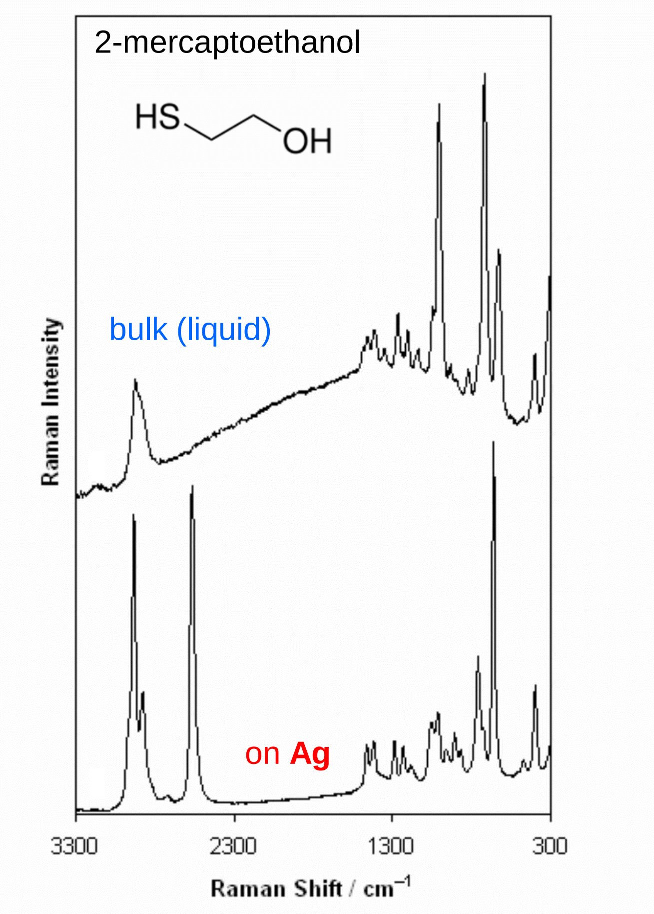
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

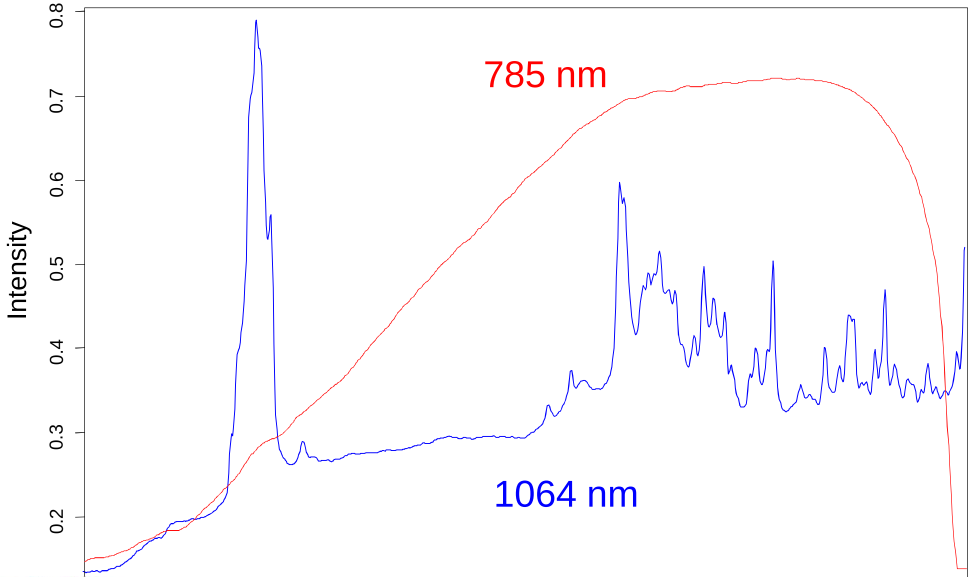
- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

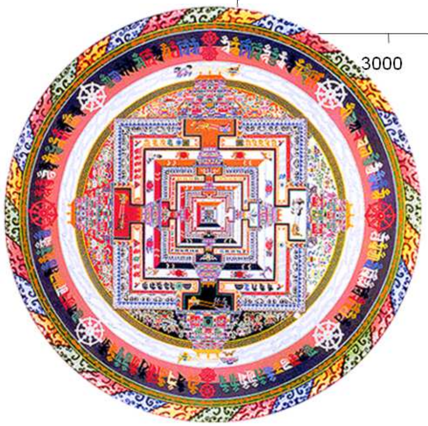
- Remarks:
  - rough surface; nanoparticles (10–100 nm) or kinks, steps etc. (E always perpendicular to surface, locally)
  - vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring





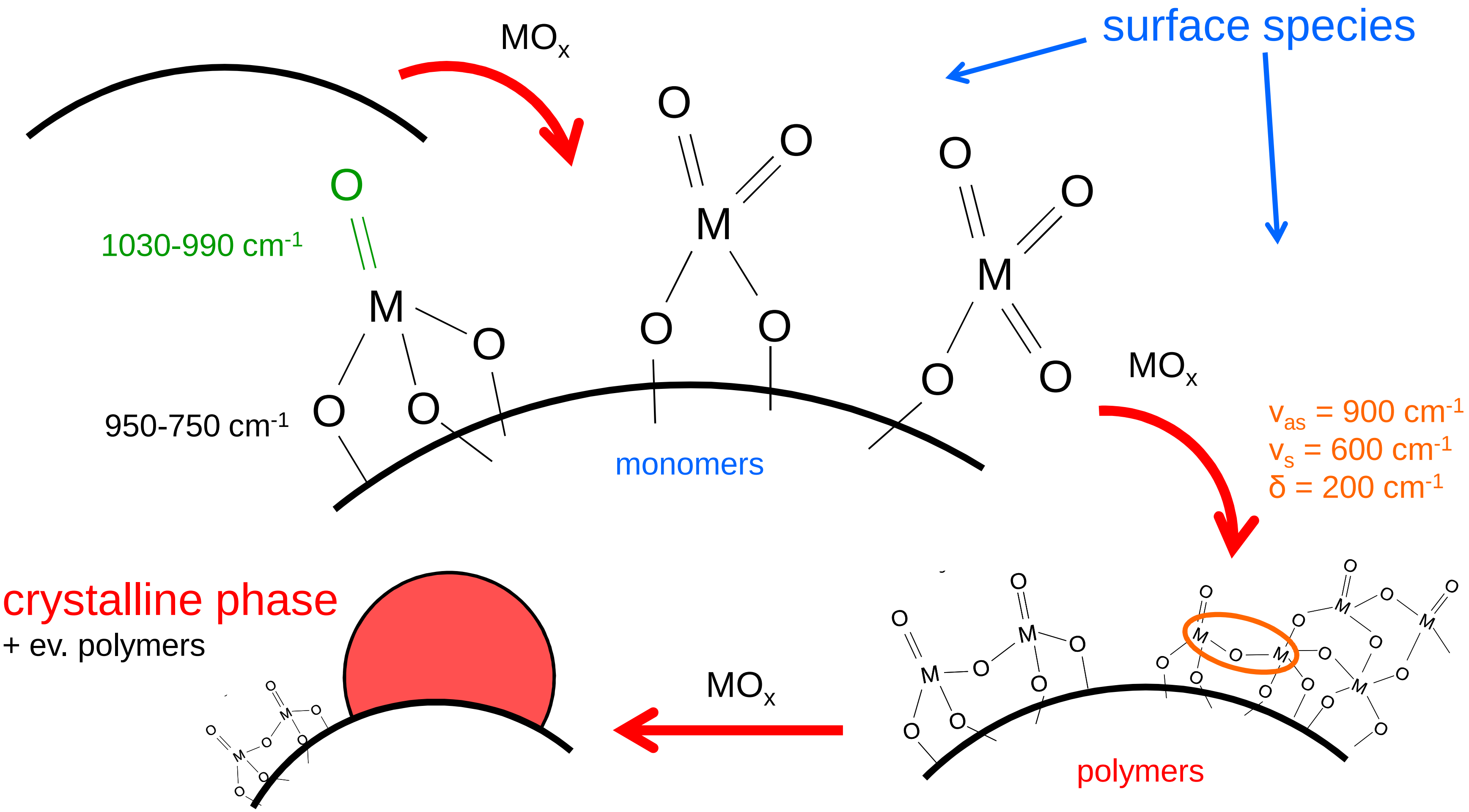
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species

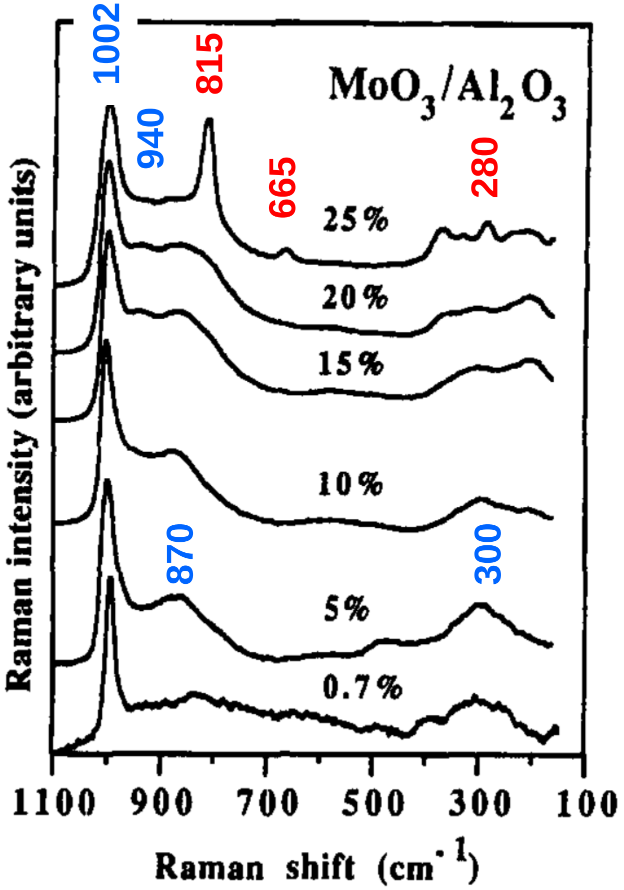


Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



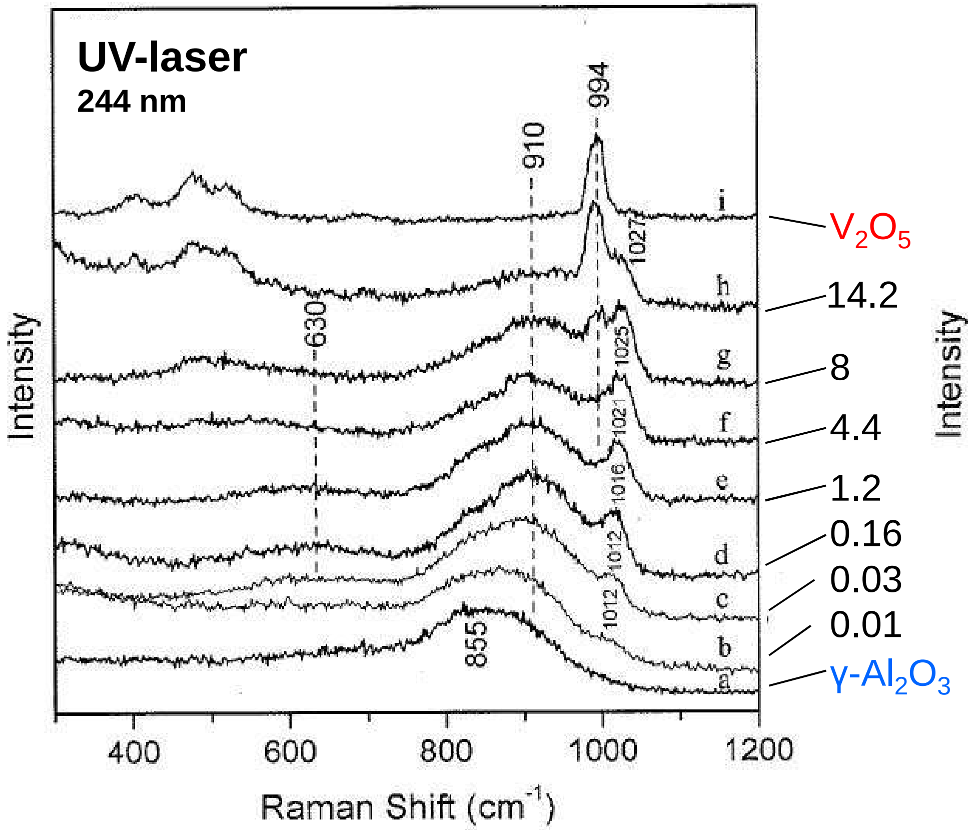
surface MoO_3
crystalline MoO_3

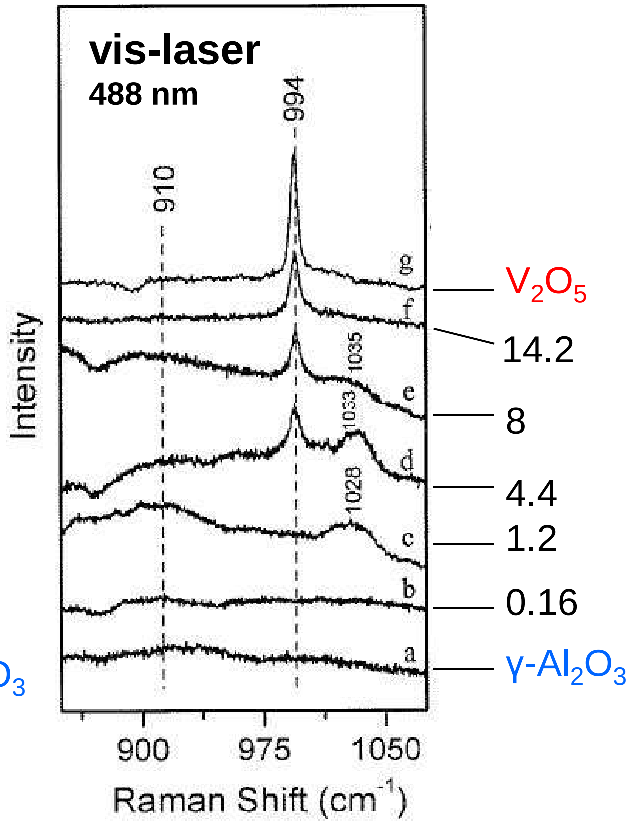
MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

- Monomeric & polymeric species

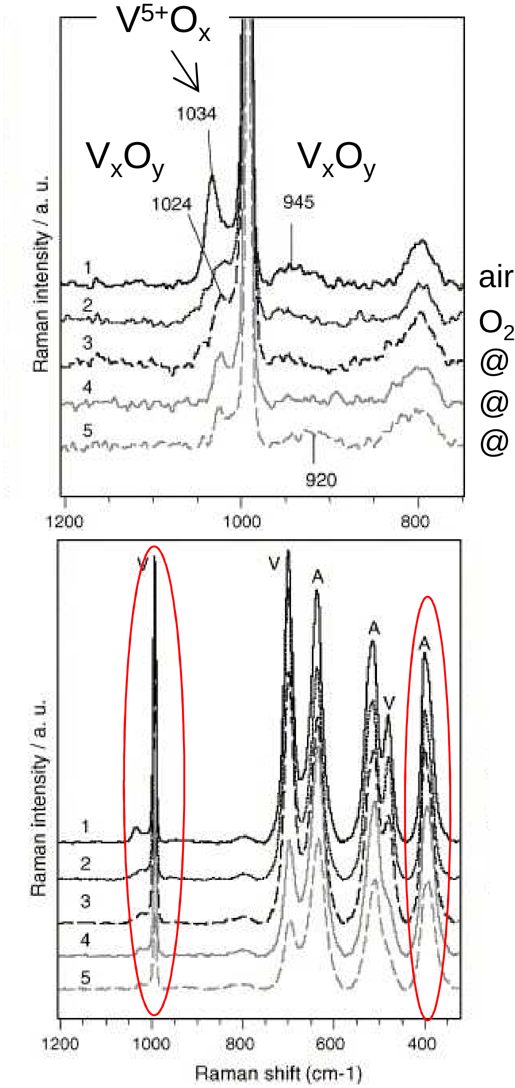




Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

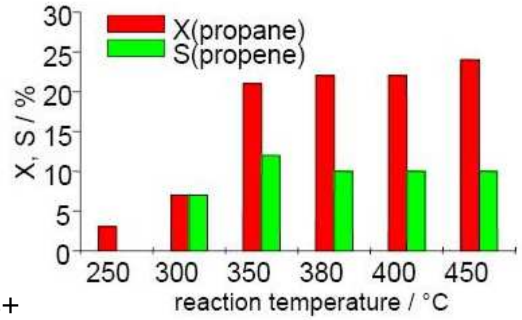
Applications

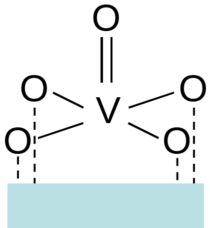
- Reactivity of V/TiO_2 after oxidative treatment

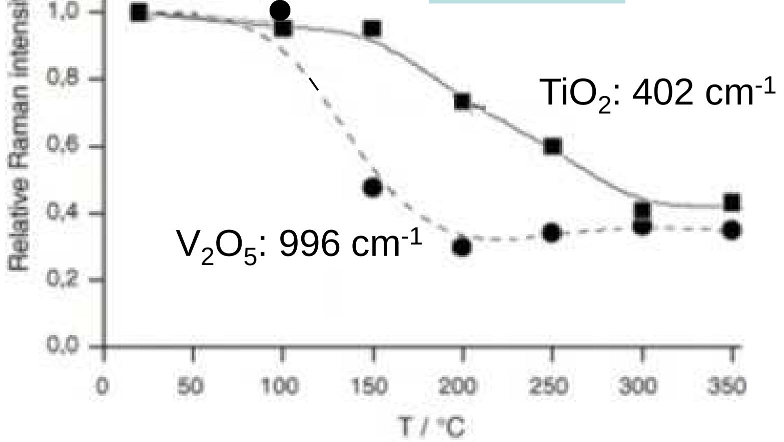


air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$







TiO_2: 402 cm^{-1}

V_2O_5: 996 cm^{-1}

Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

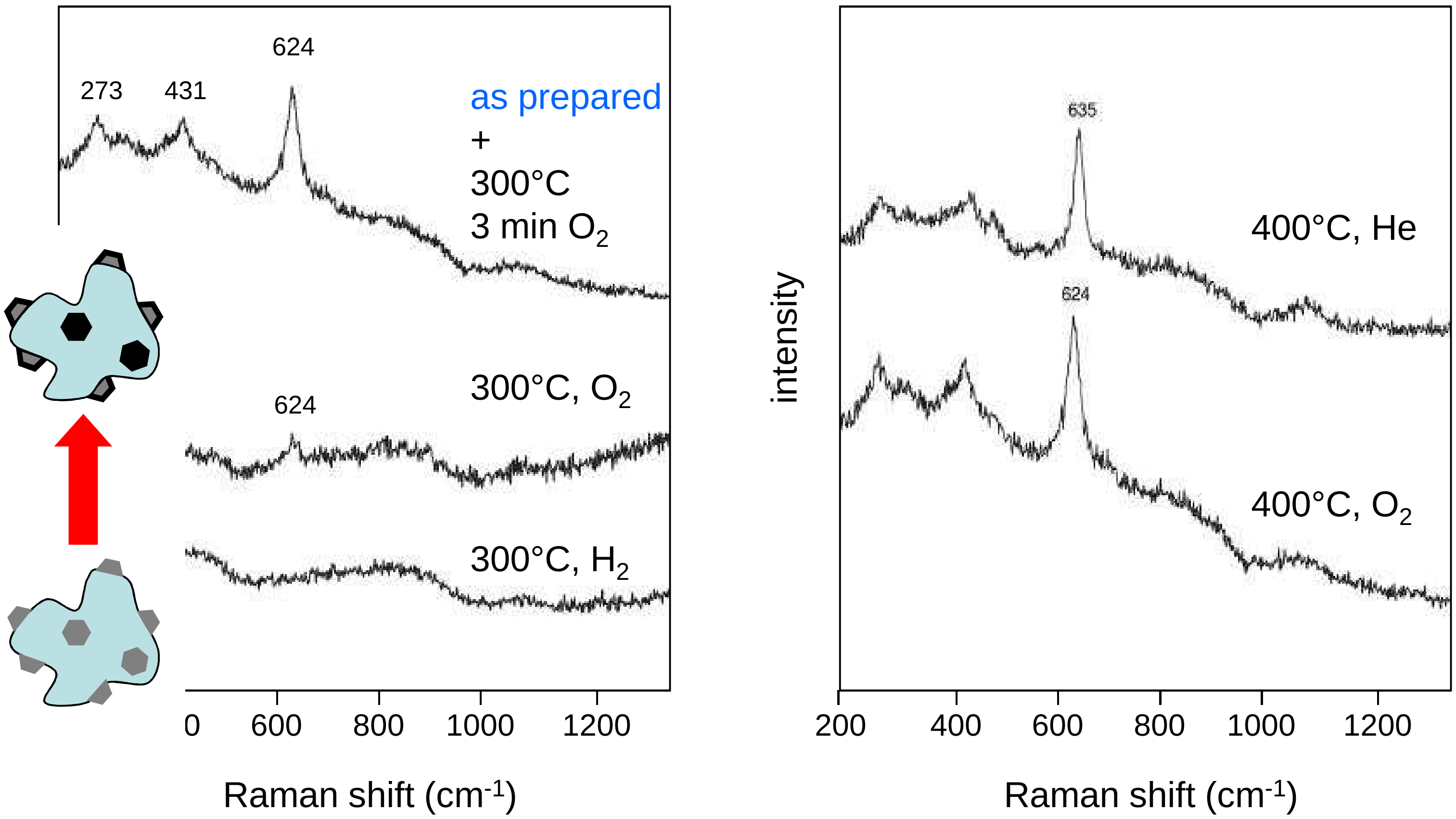
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



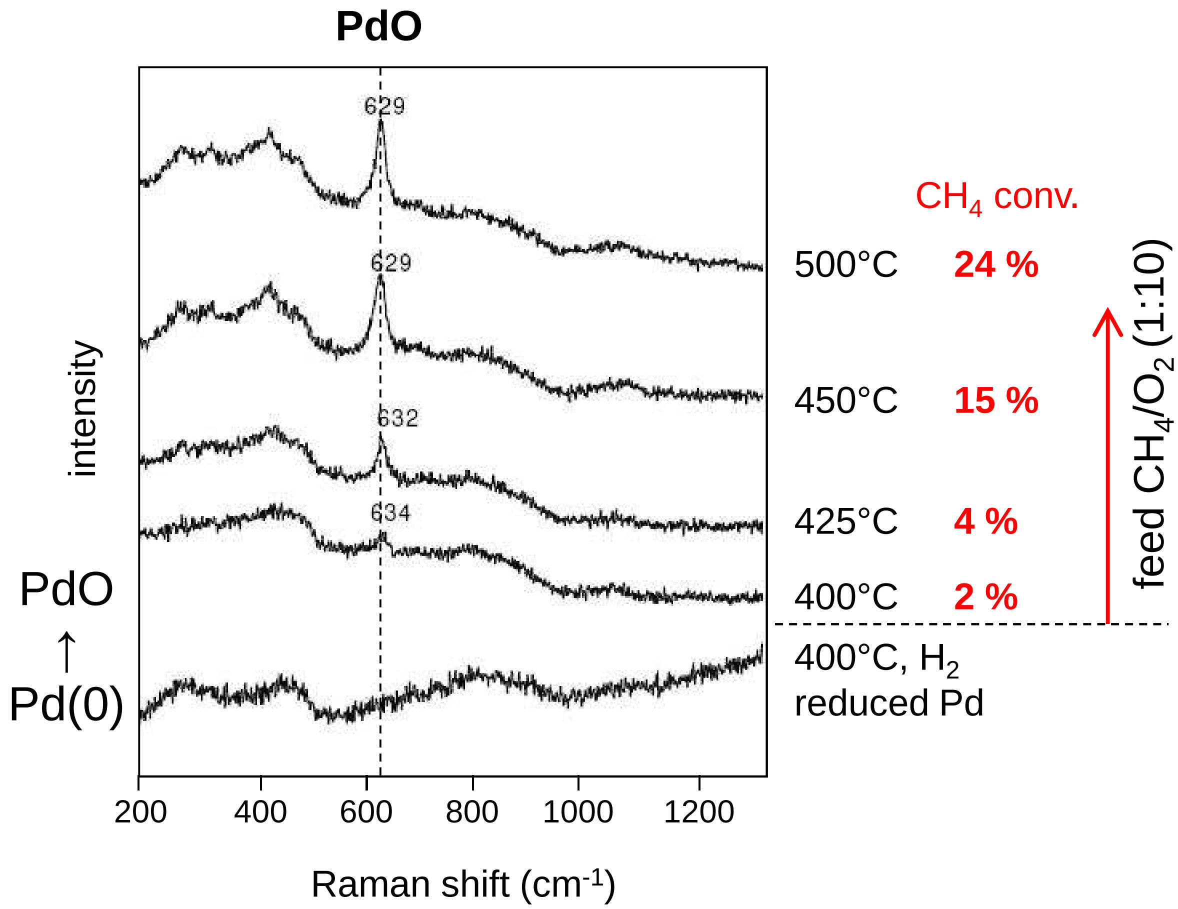
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

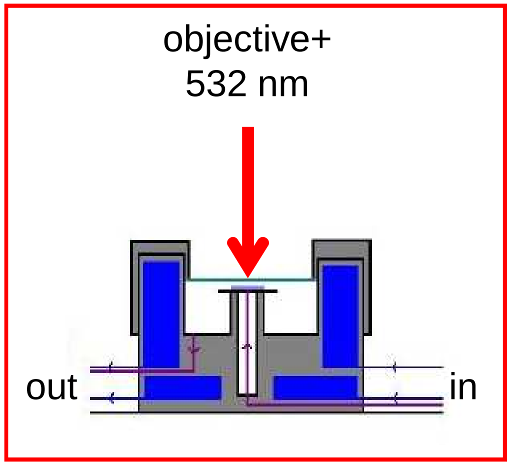
Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



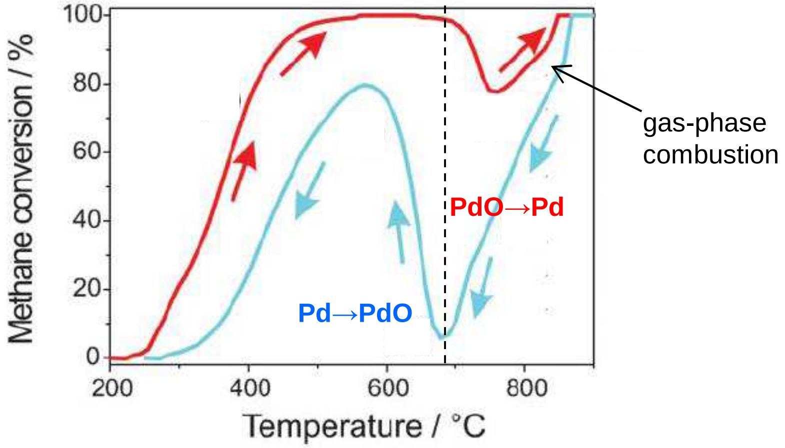
near PdO mode

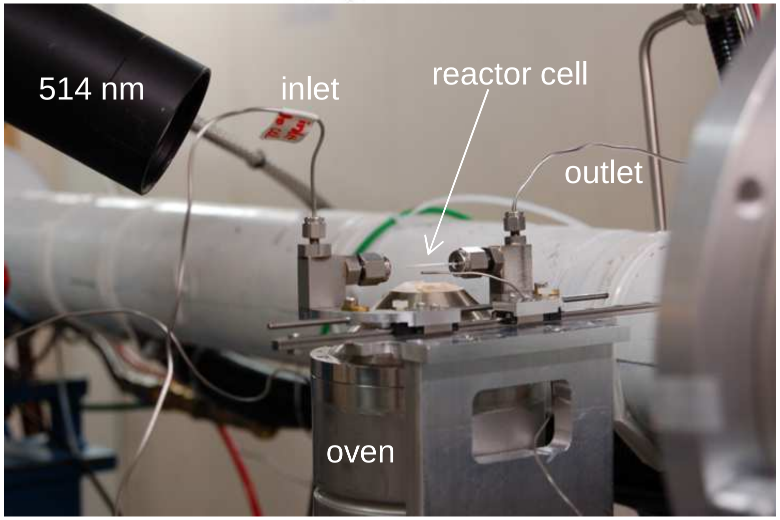


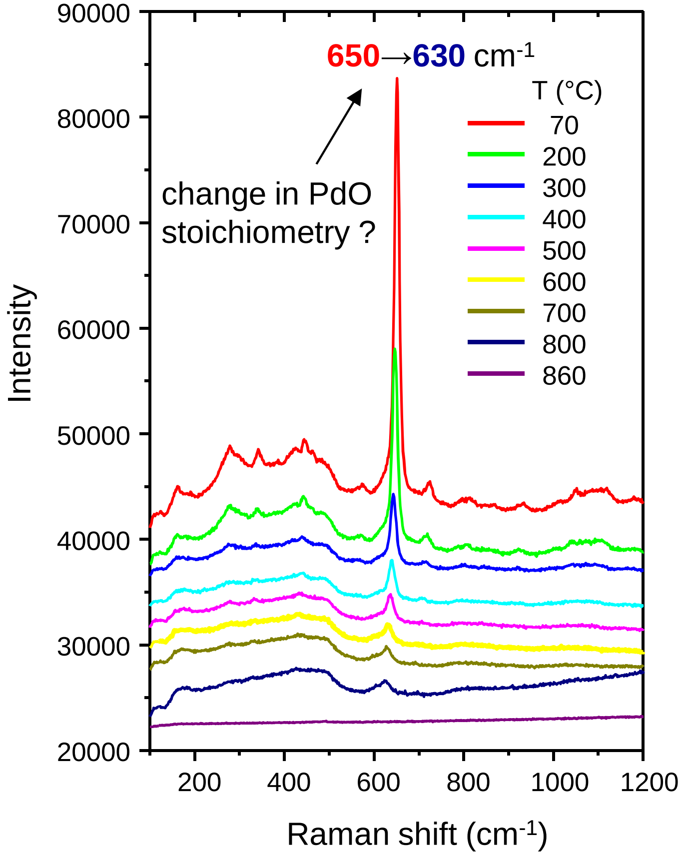
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

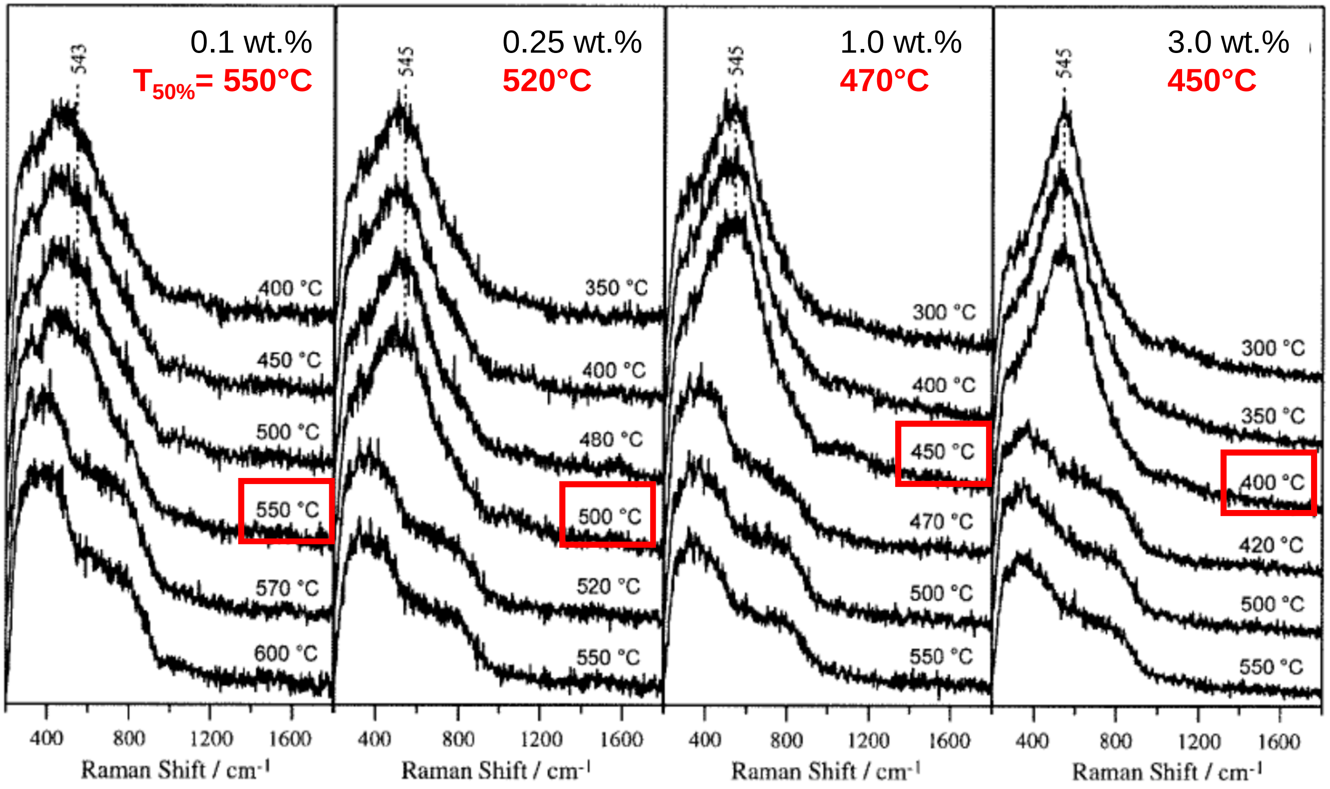
- Methane partial oxidation over Rh/Al_2O_3

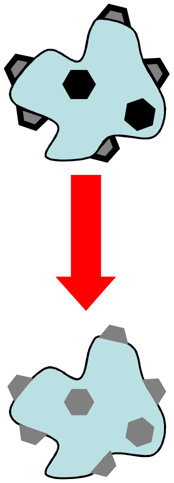
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$


Rh content
Activity

RhO_x
↓
Rh(0)





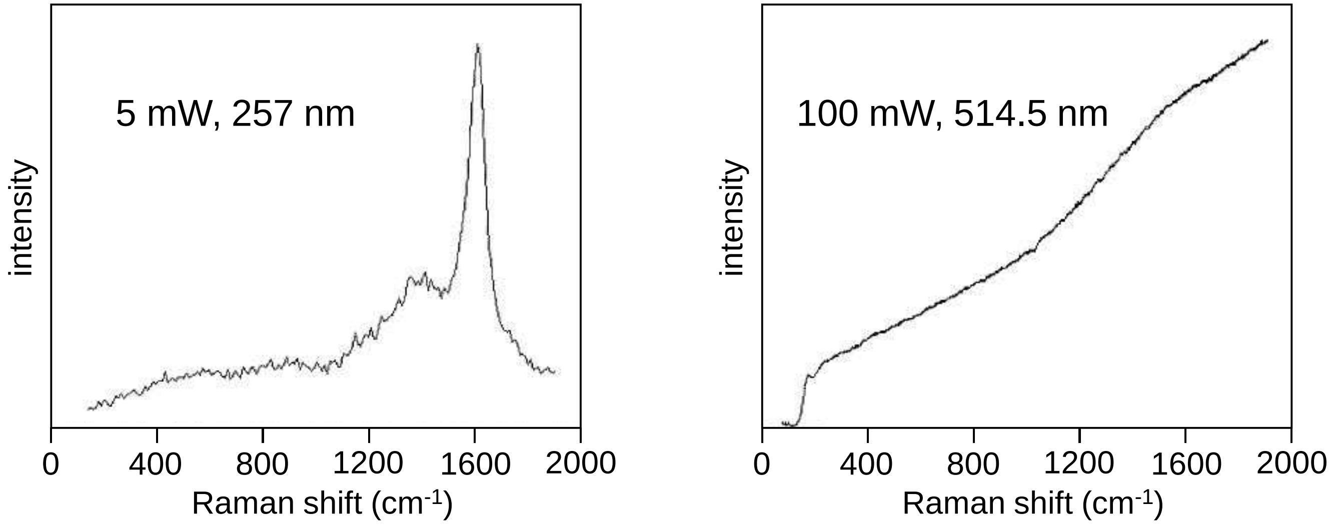
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

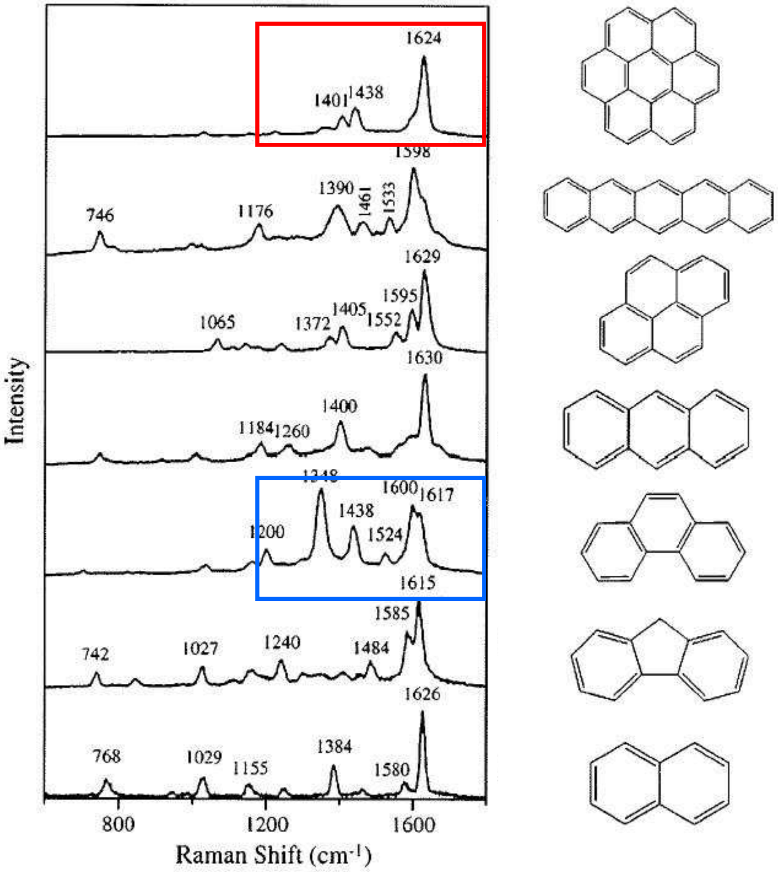
Rh/Al_2O_3, coked 500°C in naphtha

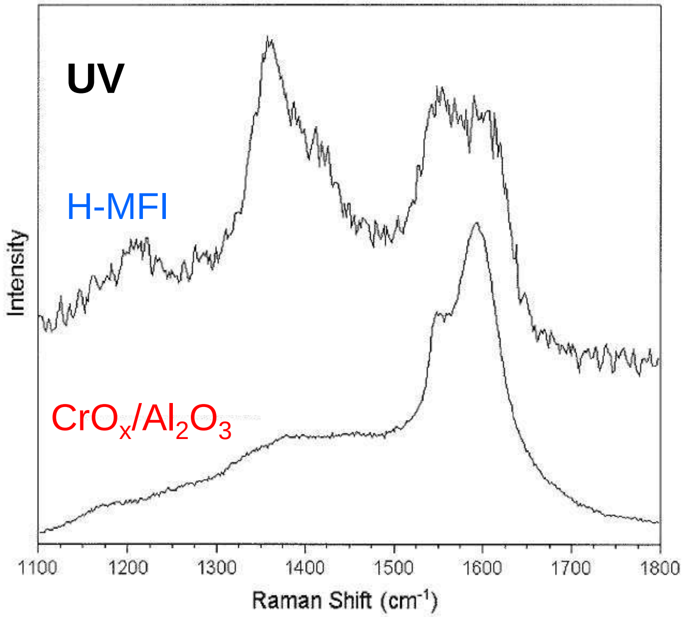


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





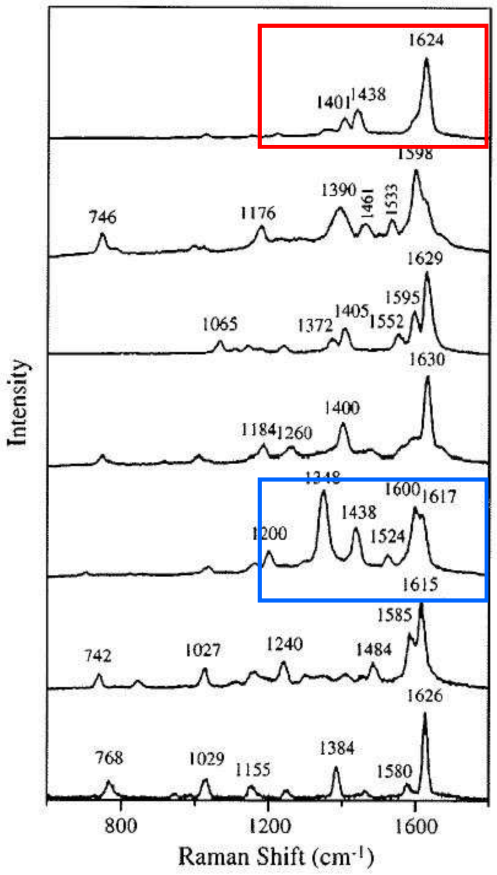
Coke classification
1D topology, chain-like
2D topology, sheet-like

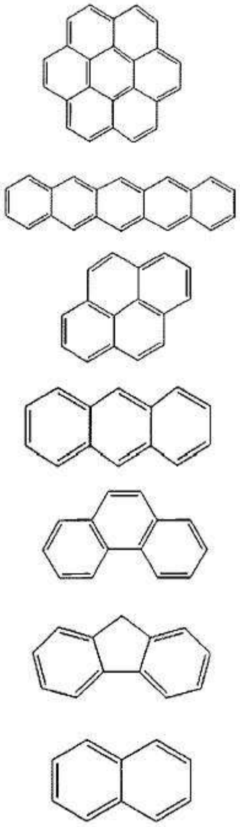
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

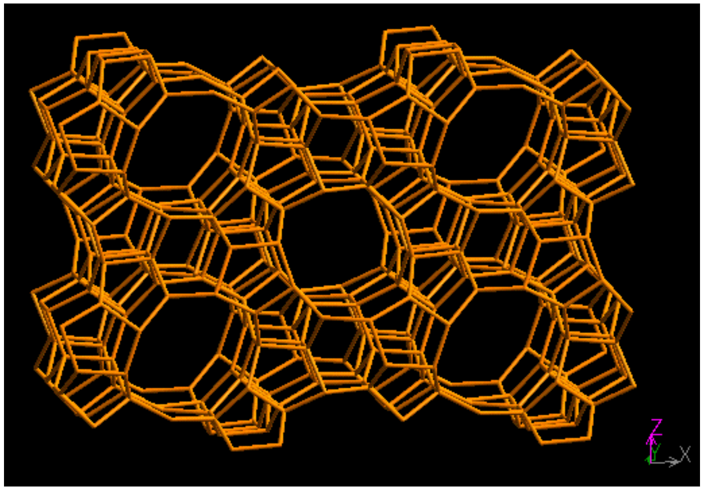
Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization







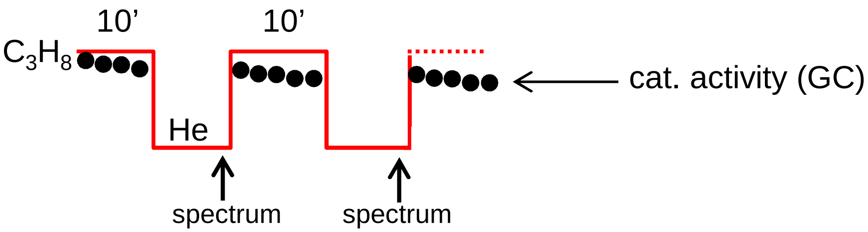
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

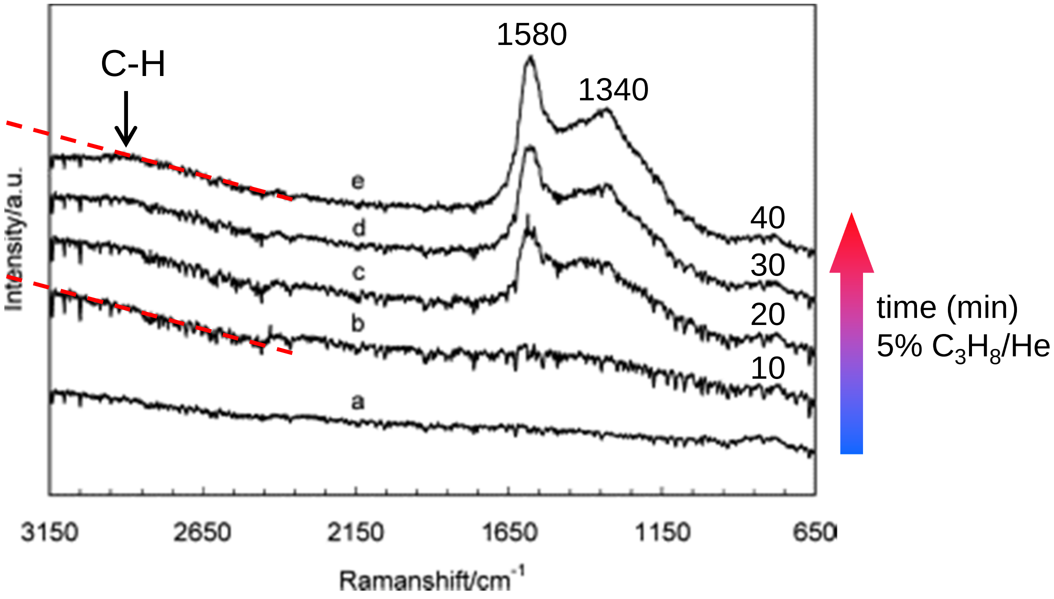
Stair, *Adv. Catal.* **51** (2007) 75

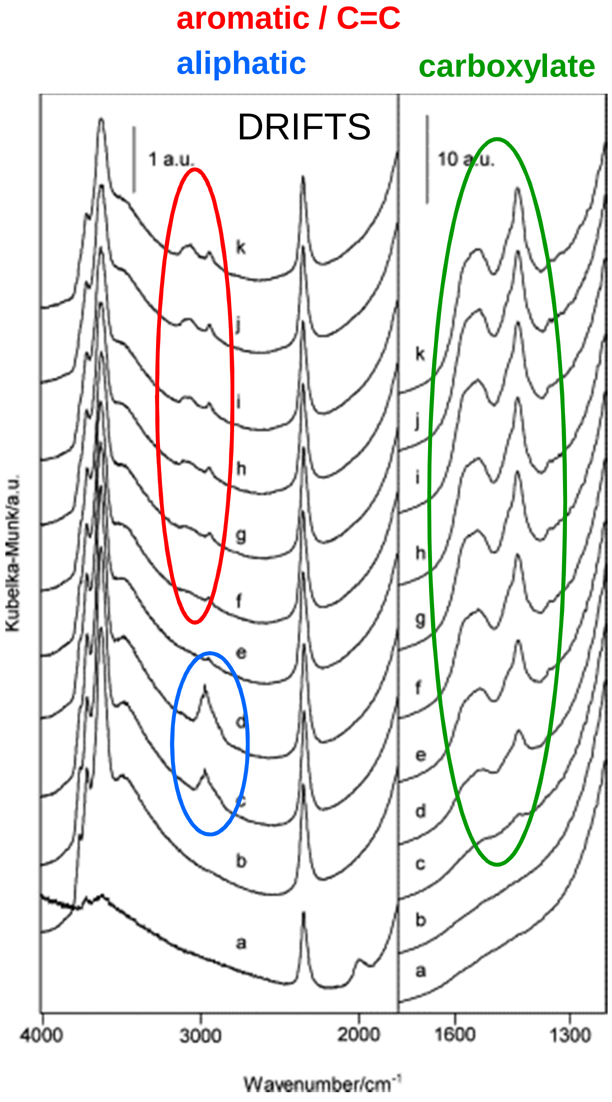
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

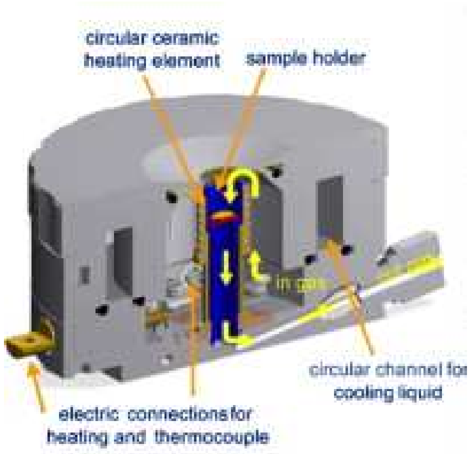


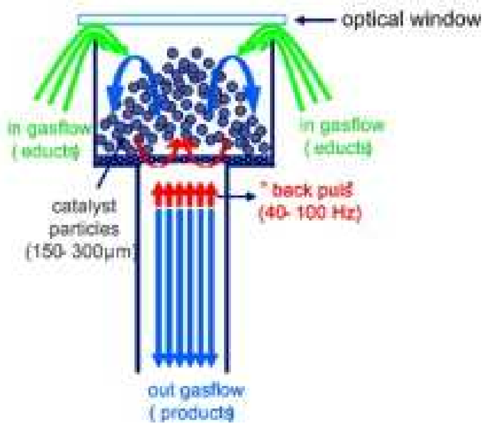


Airaksinen et al., *J. Catal.* **230** (2005) 507

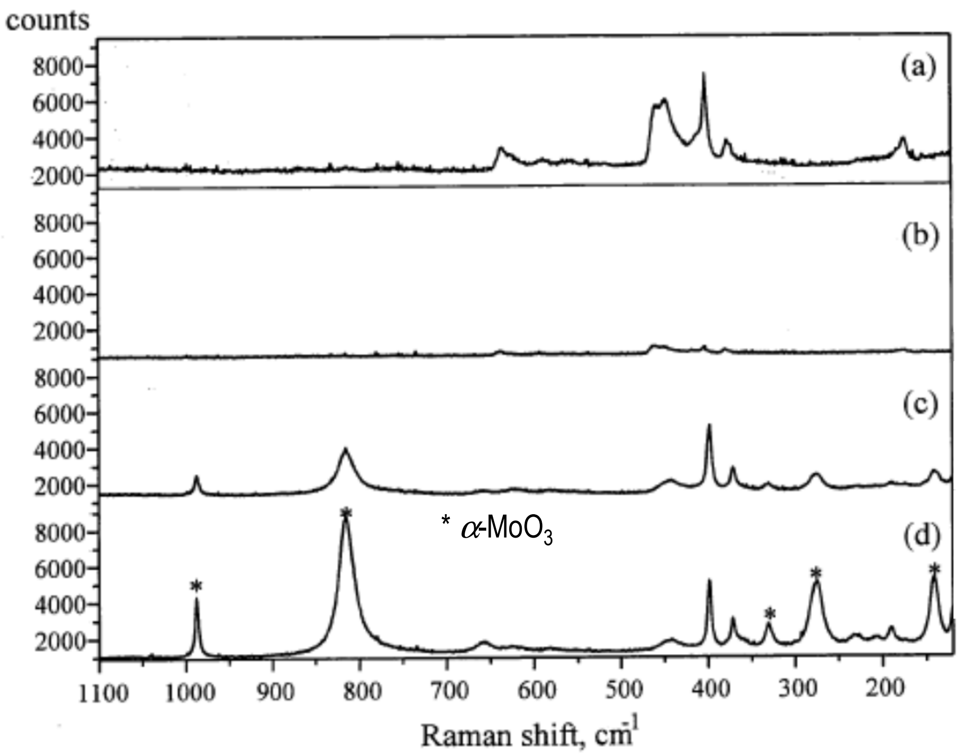
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min full power, FB

MoS_2, 6 min 1/8 power

MoS_2, 1 min full power

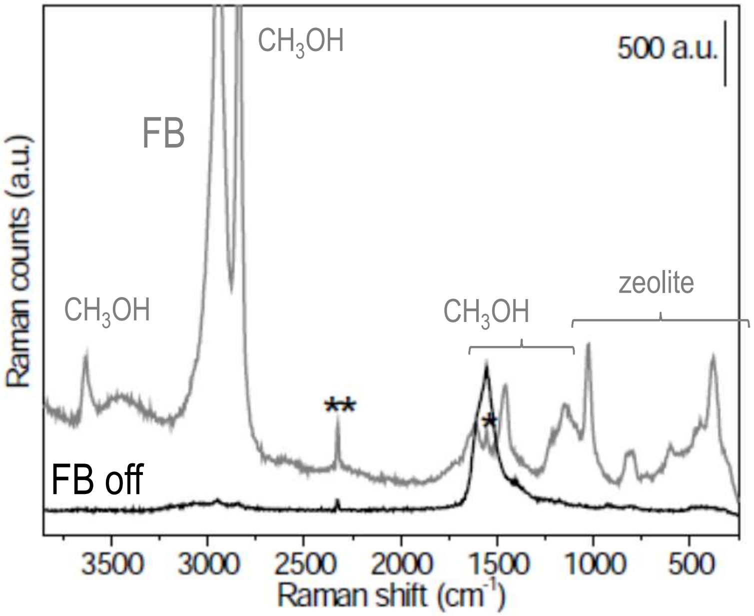
MoS_2, 6 min full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

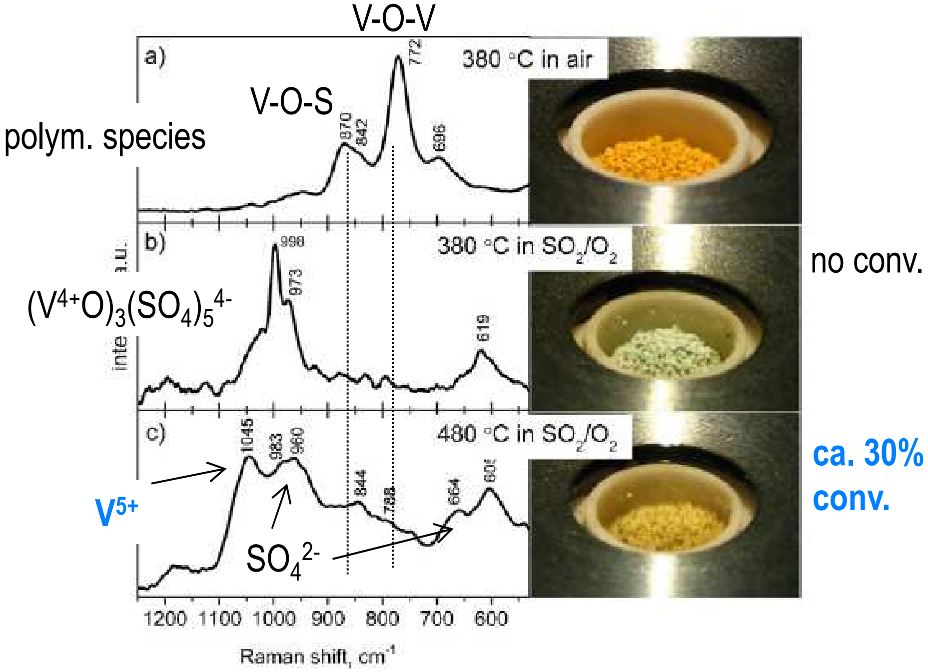
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

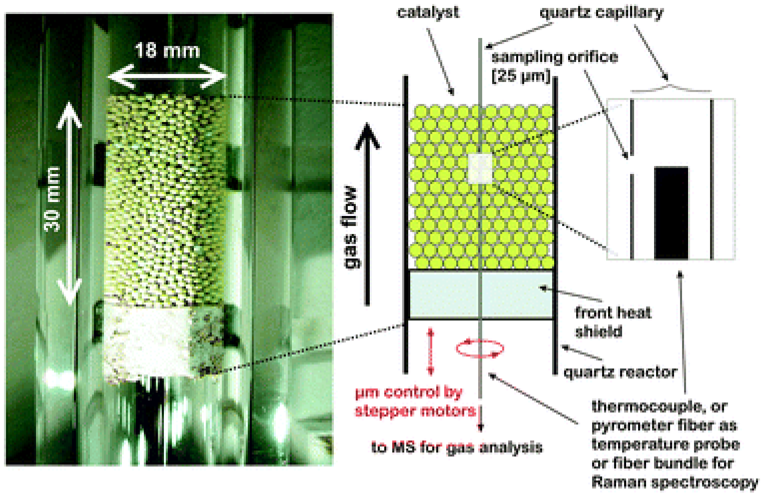


active species: mono- & dimeric V^{5+} oxosulfate species

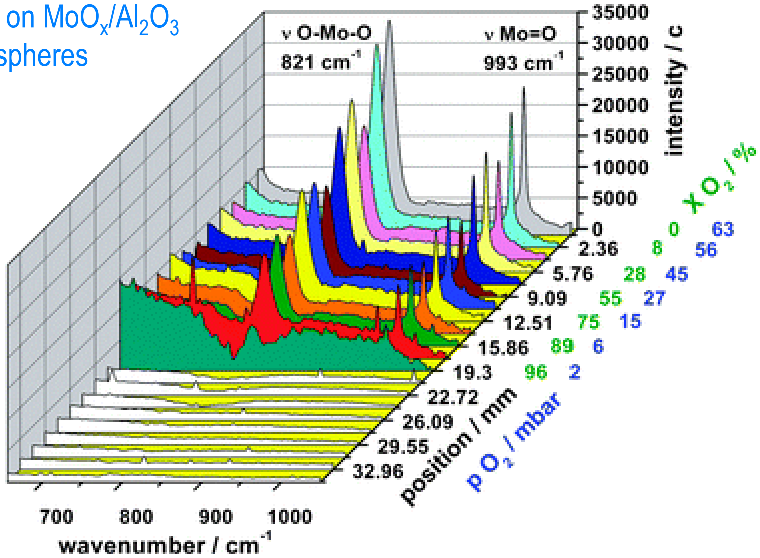
Beato et al., *Catal. Today* 205 (2013) 128

Applications

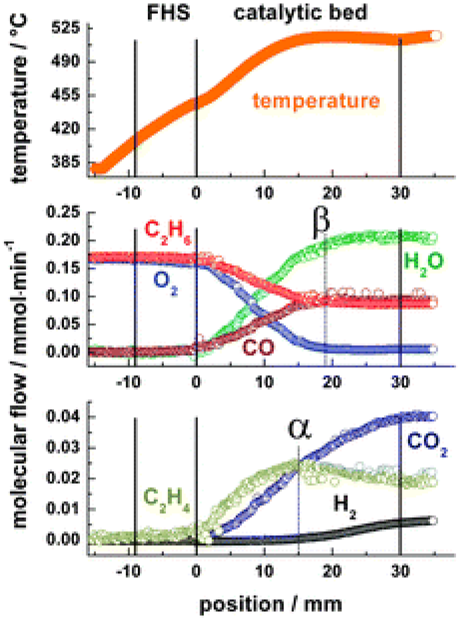
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

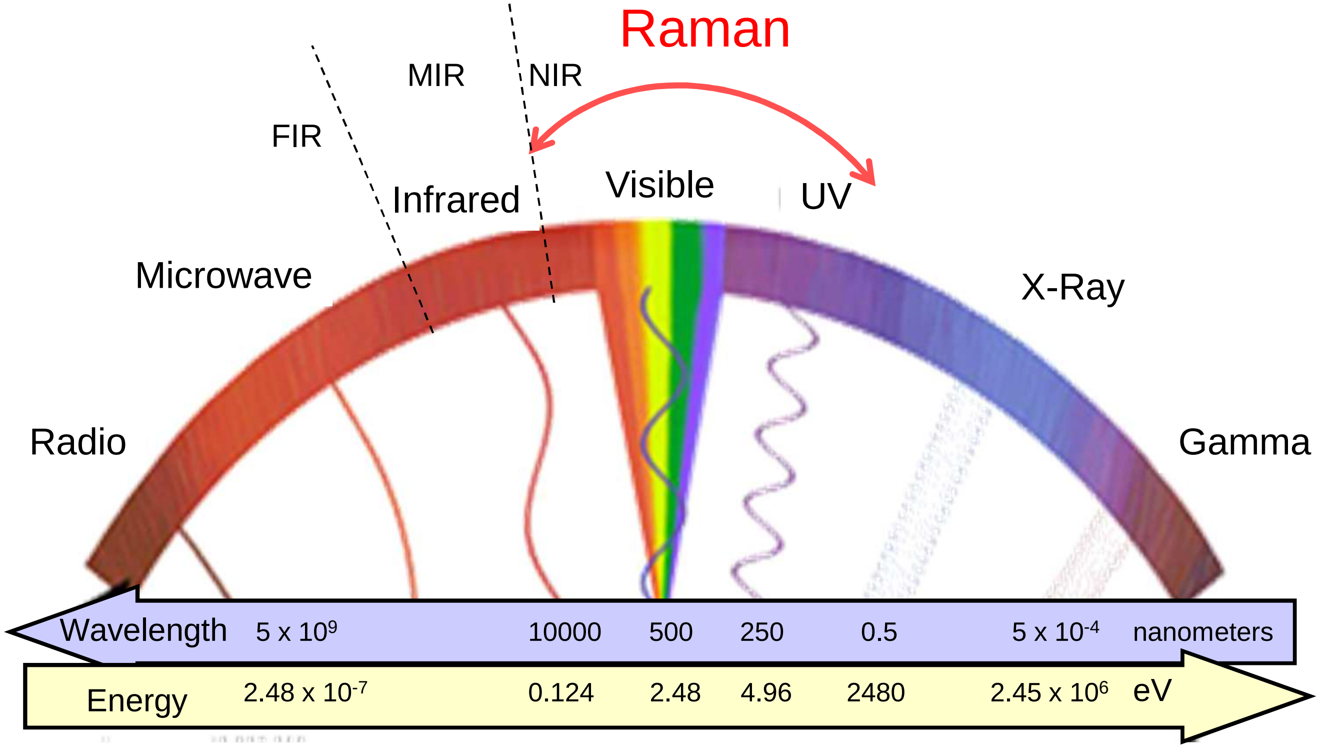
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

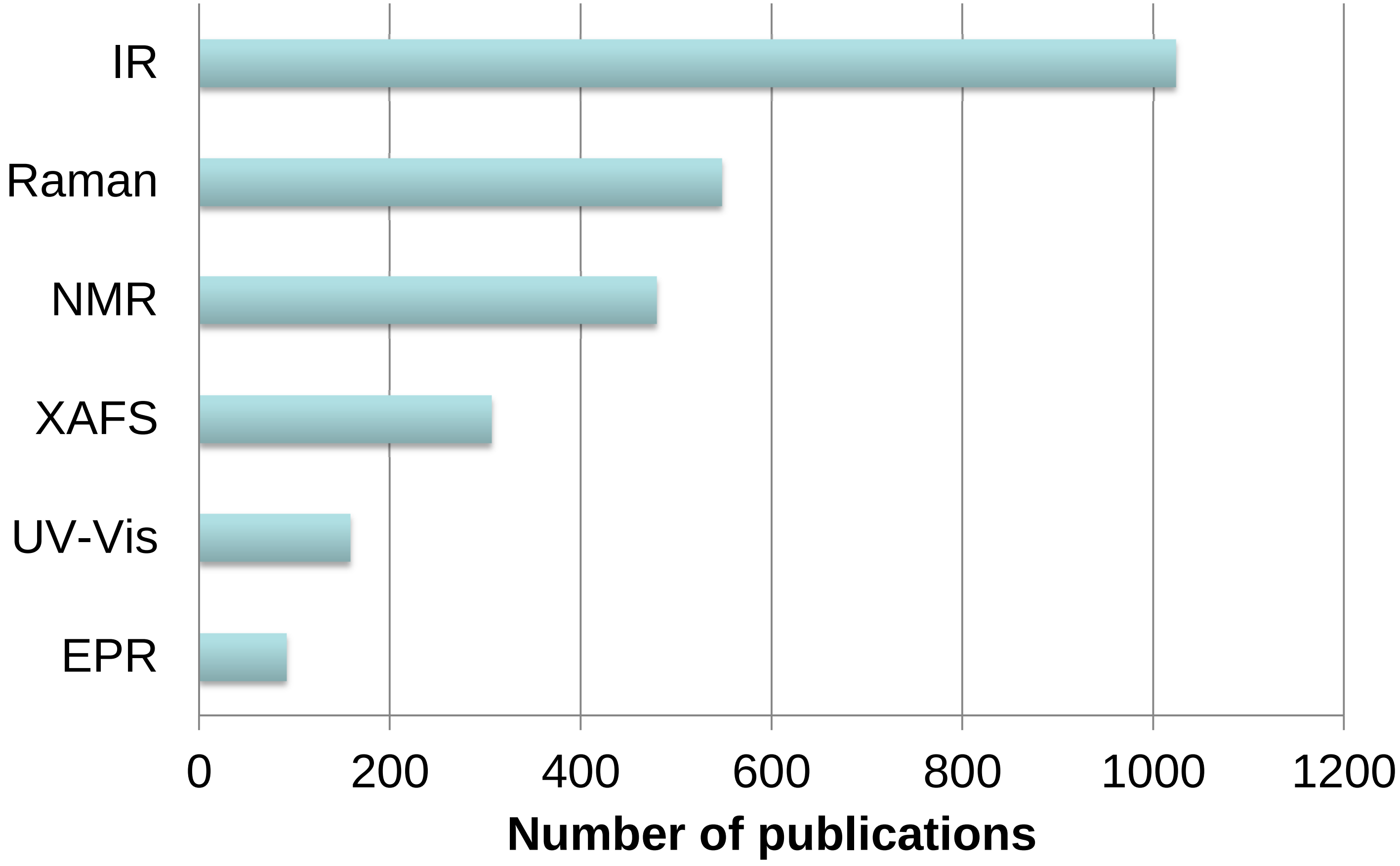
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

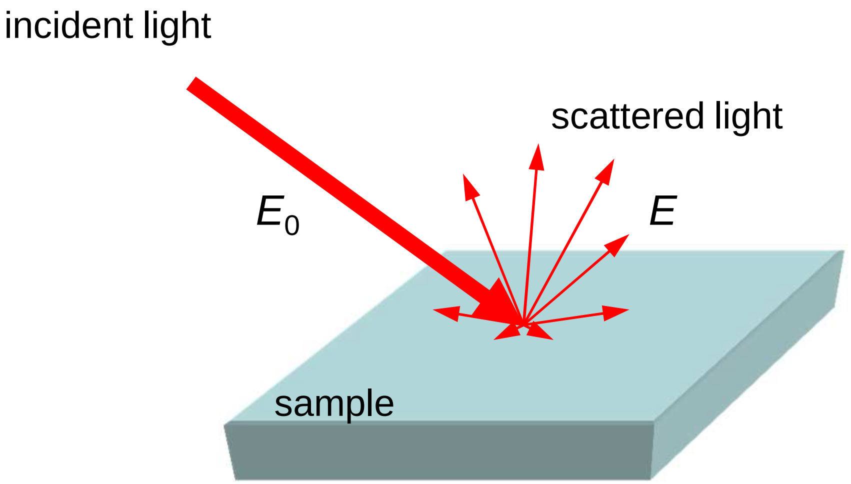


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

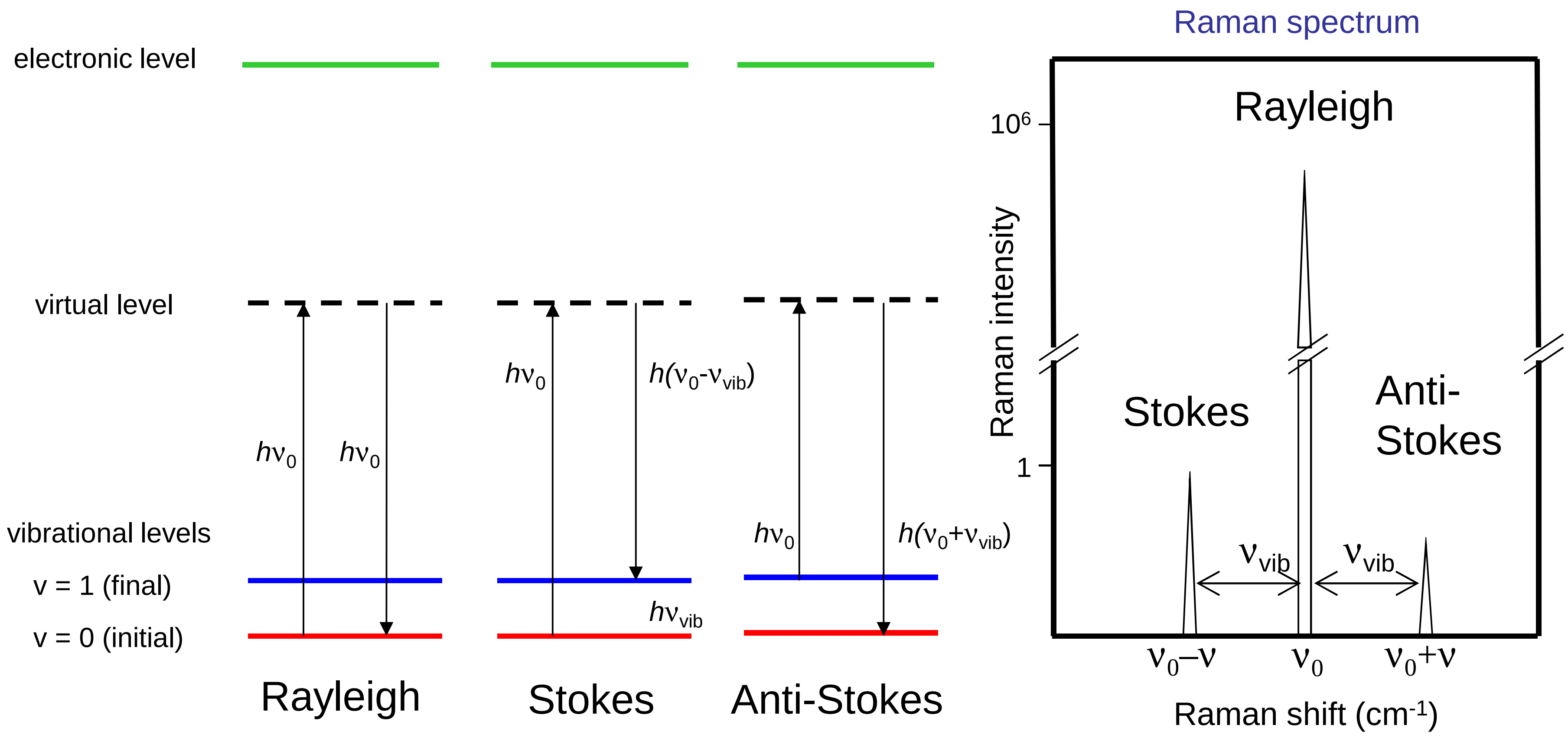
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2 E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2 E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{\mathrm{I}\ (\text{Anti-Stokes})}{\mathrm{I}\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

- ❑ 4th power of ν (4th power law)
- ❑ 2nd power of $\Delta\alpha$
  - properties of molecules
  - strength of bonds

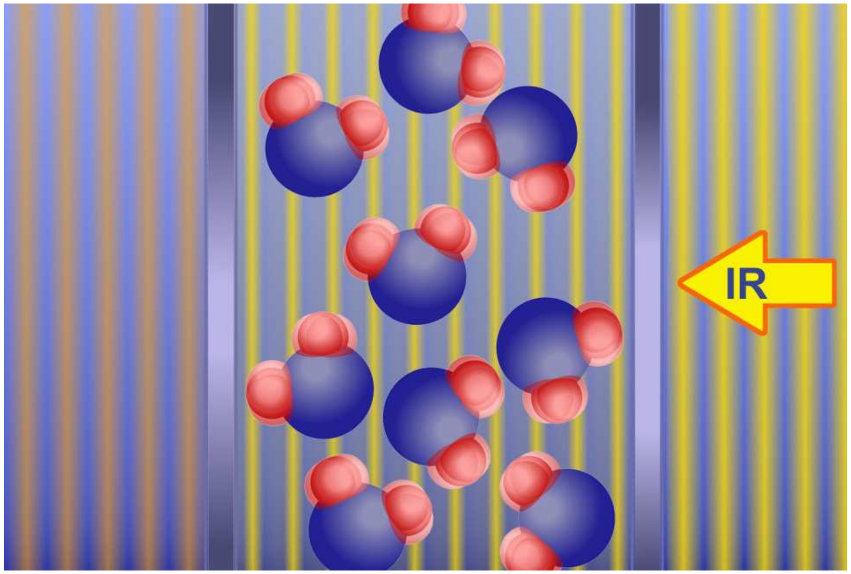
↓

covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

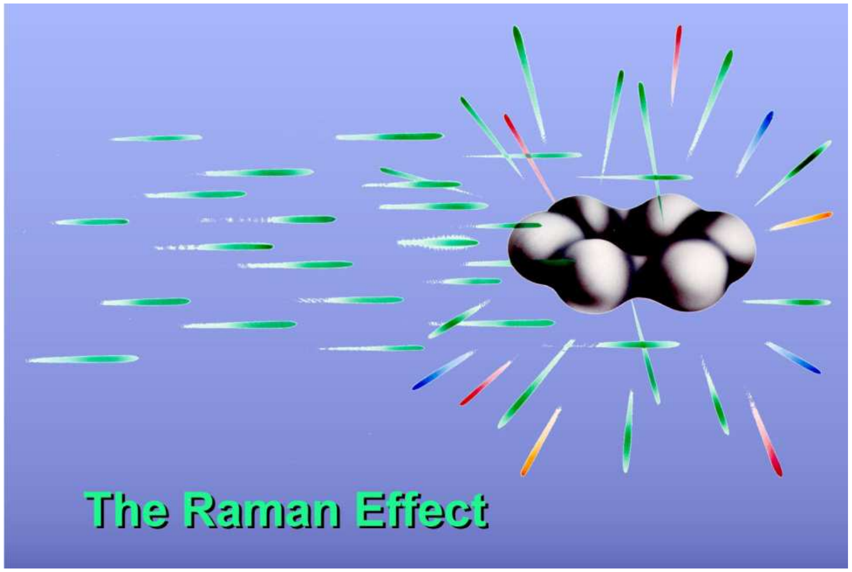
Raman *vs.* Infrared

Infrared



Absorption of IR light

Raman



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial\mu}{\partial Q}\right)^2 \neq 0$$

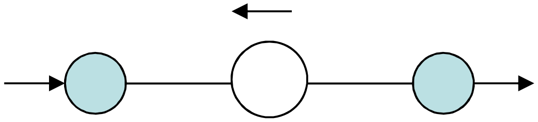
- high absorption for polar bonds ($C=O$, H_2O, NH, etc.)

$$\left(\frac{\partial\alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - ❑ large electron clouds
  - ❑ not polar
- H_2O is a very weak Raman scatterer
- $C=C$ double bonds strong Raman scatterers

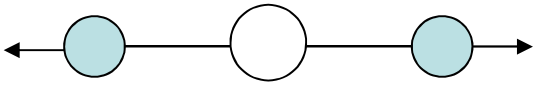
Raman *vs.* Infrared

CO_2



ν_{as}

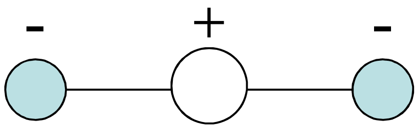
2349 cm^{-1}



ν_s

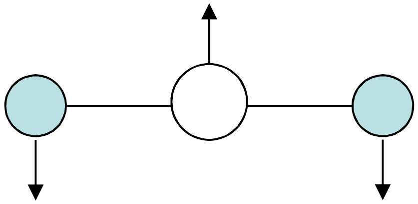
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



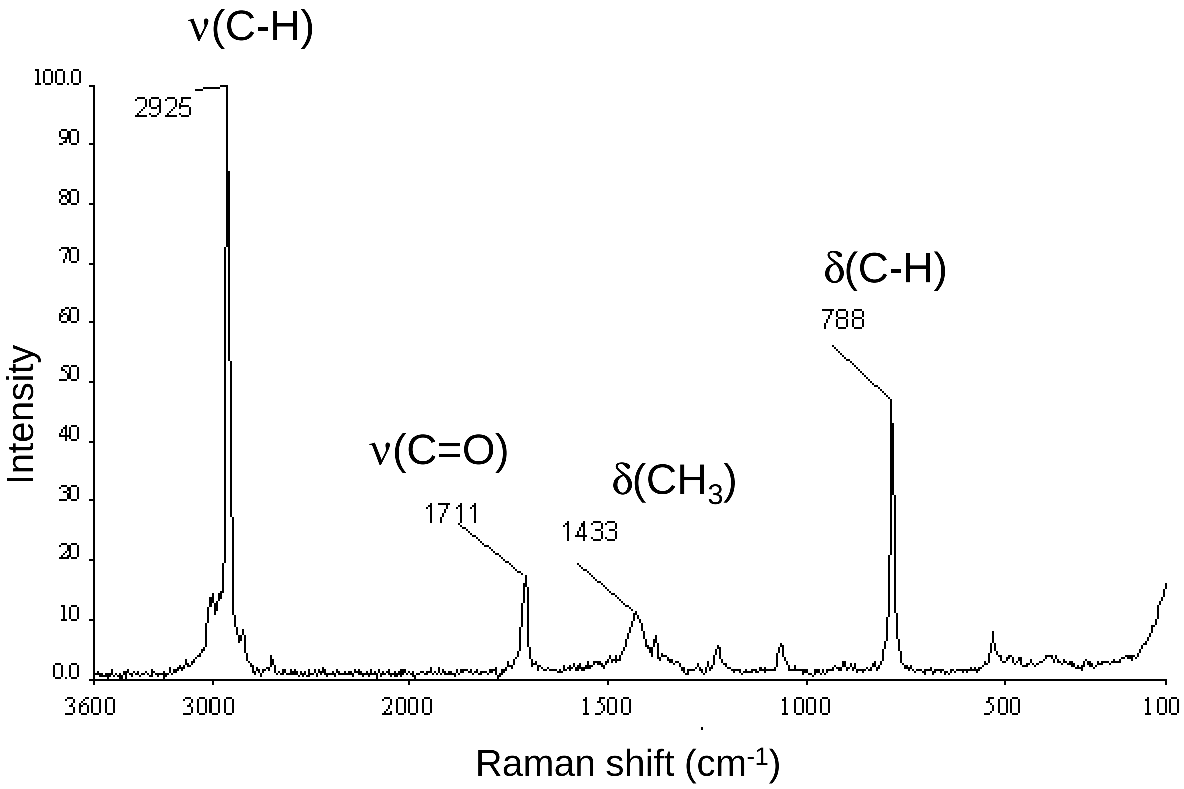
δ

667 cm^{-1}

degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared

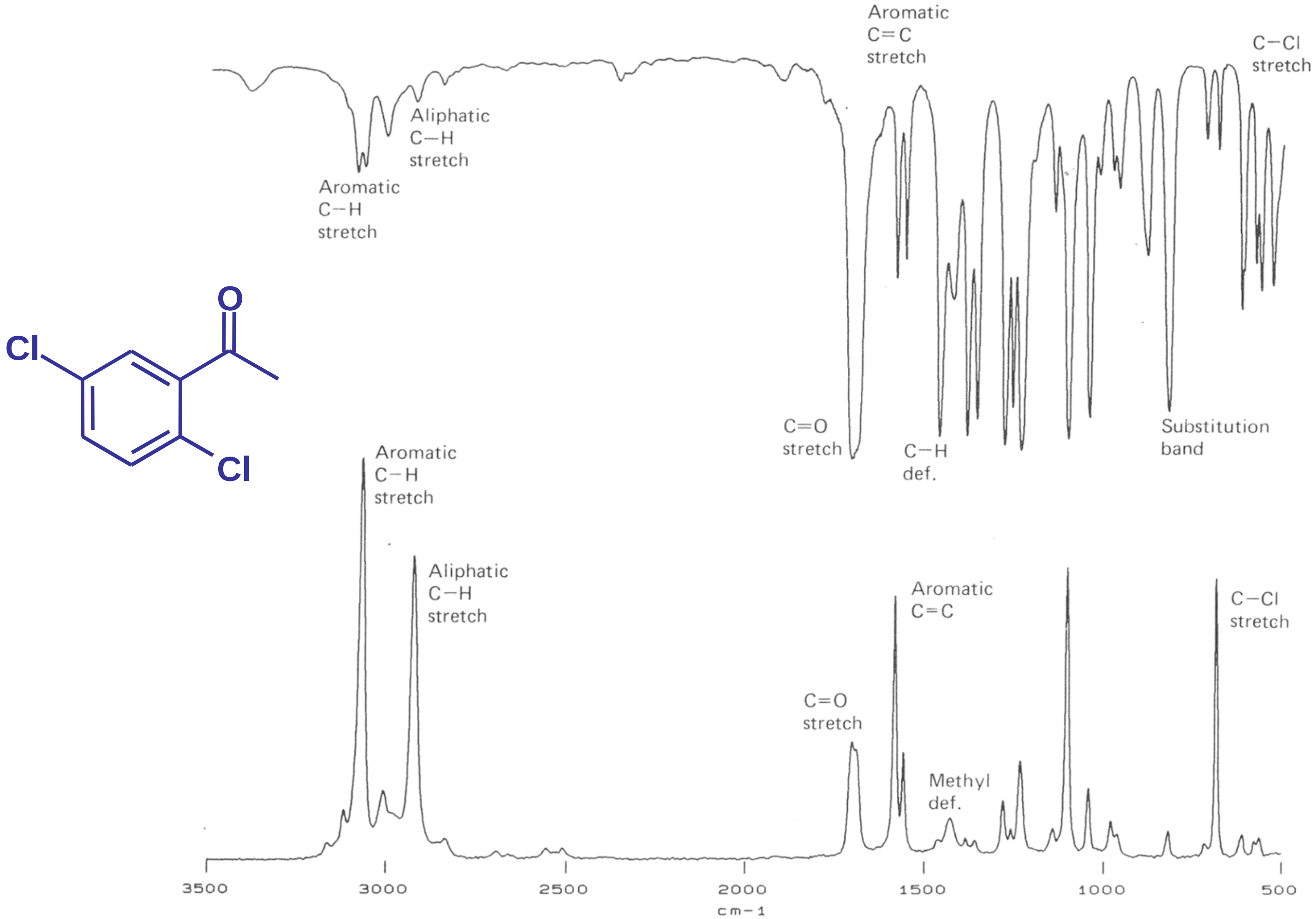


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

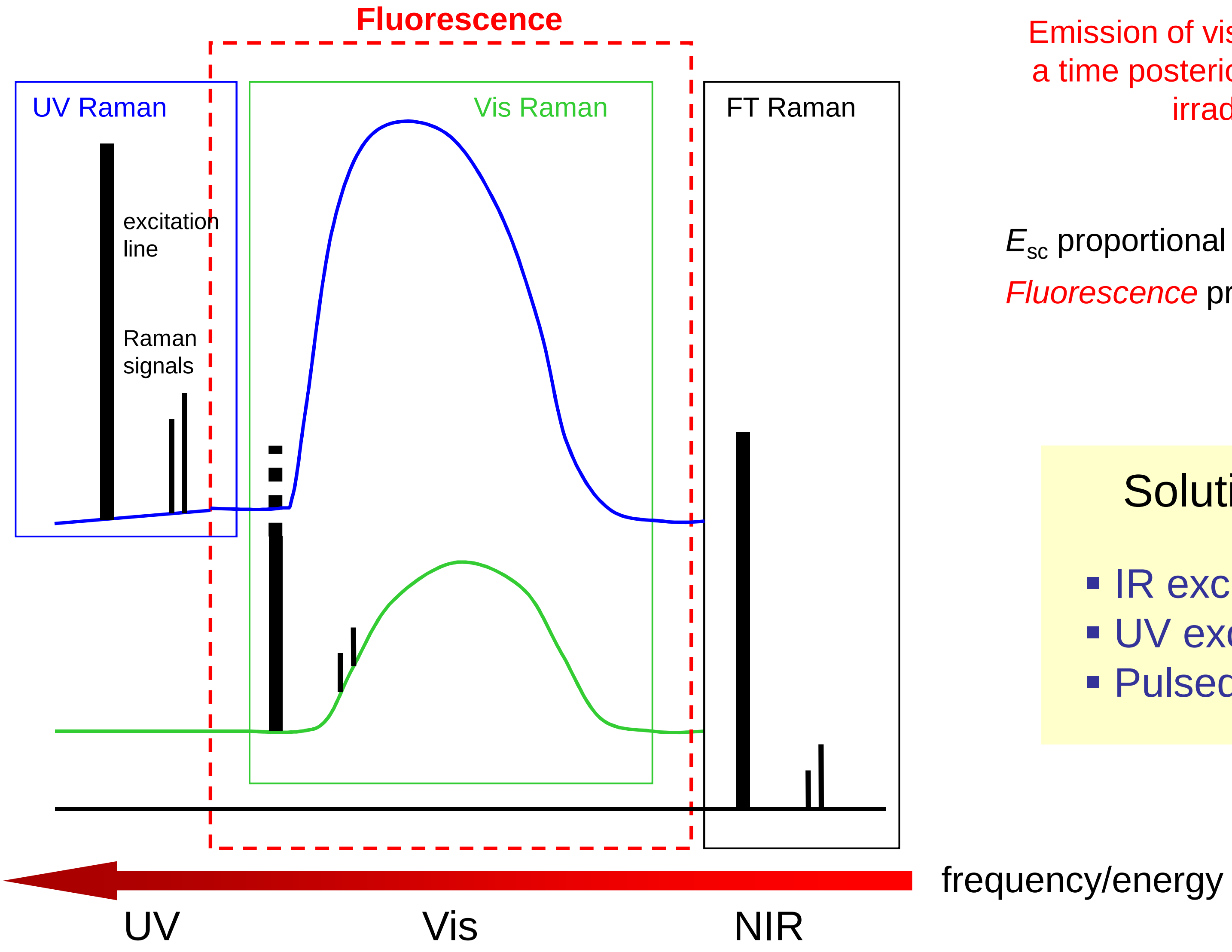
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 µm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

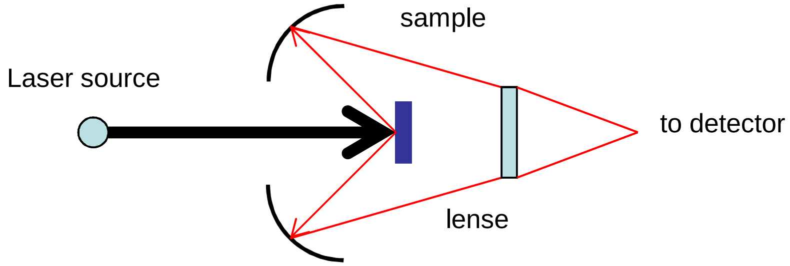
Fluorescence proportional to ν

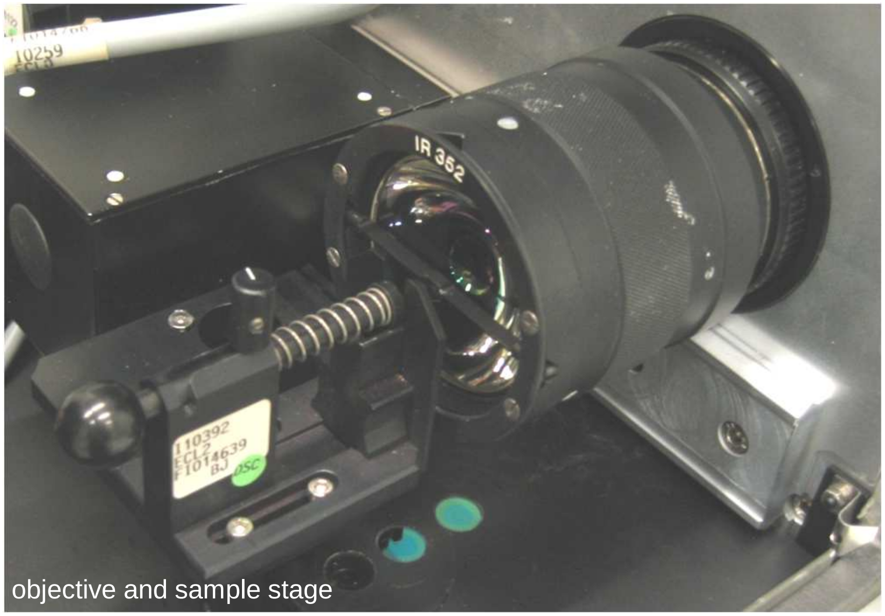
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation




objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

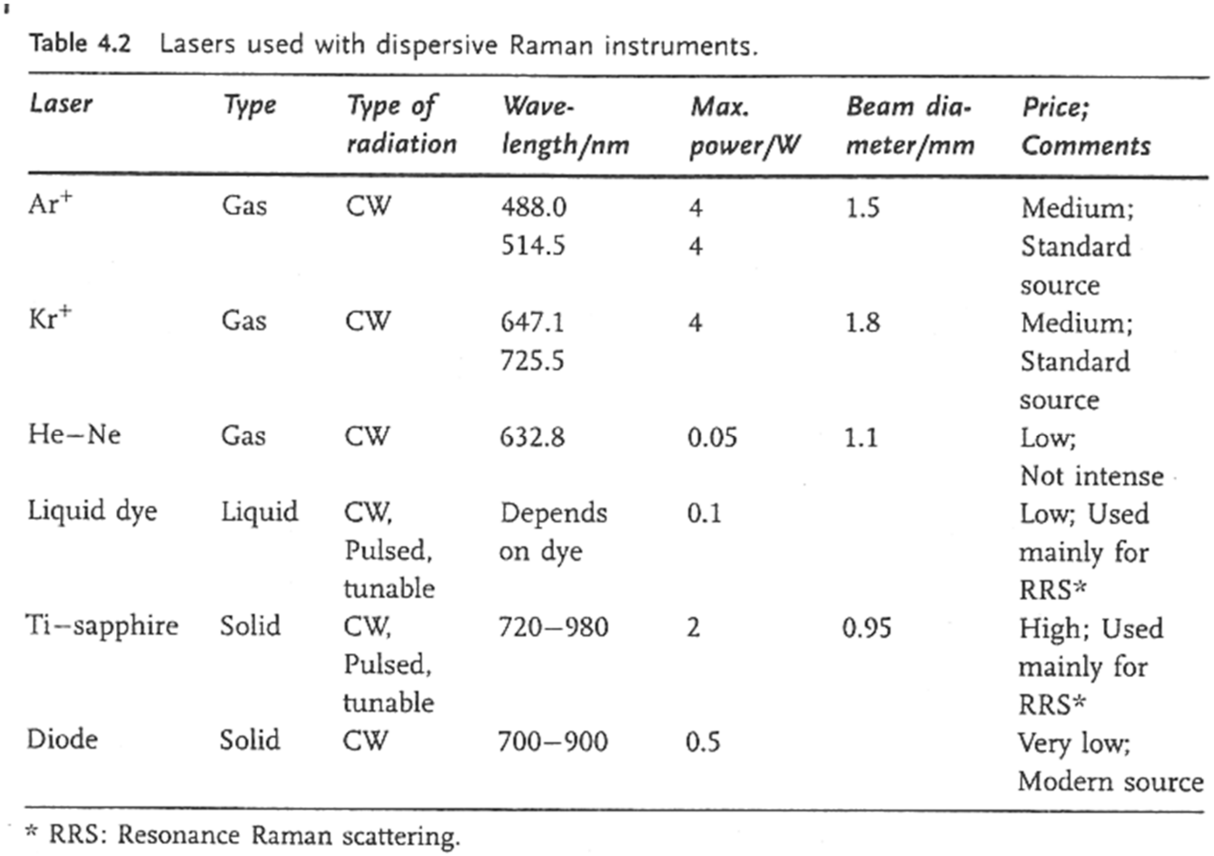


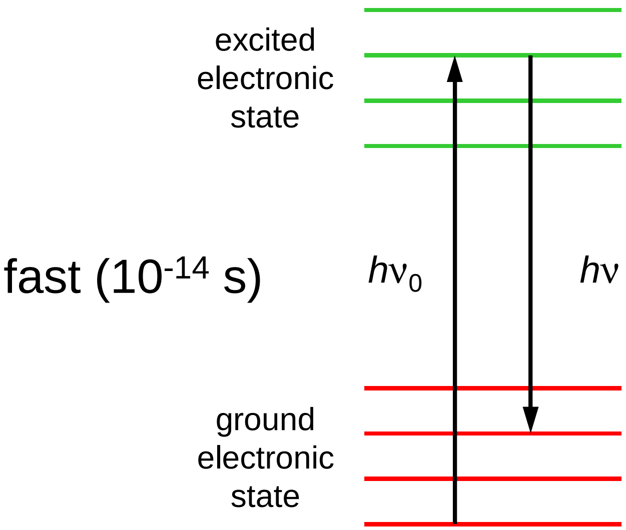
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

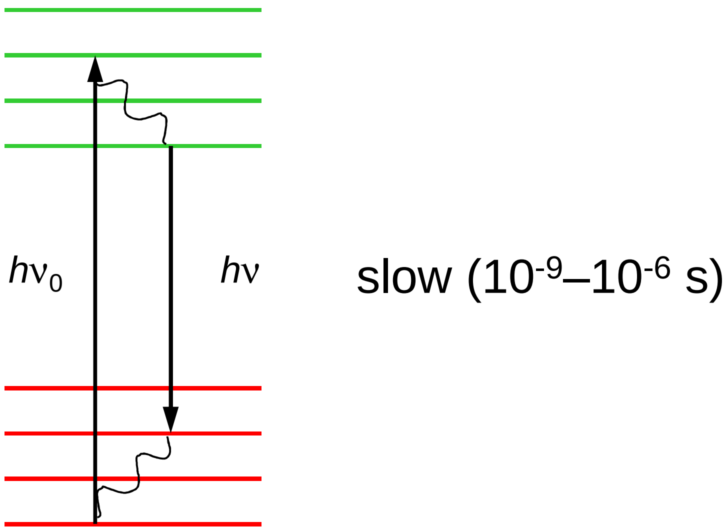
* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



Resonance Raman scattering



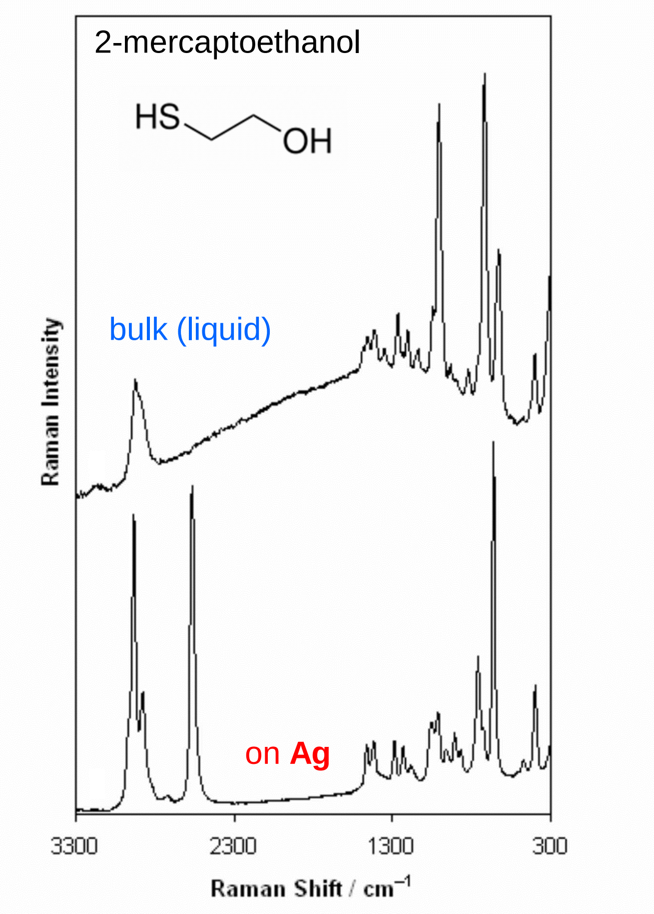
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

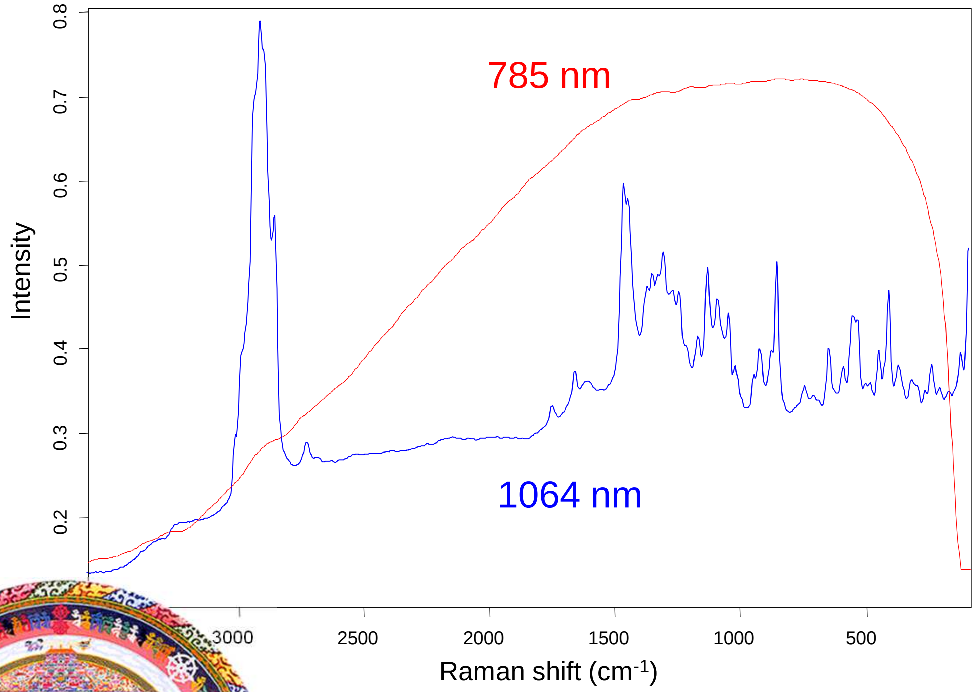
- Remarks:

❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



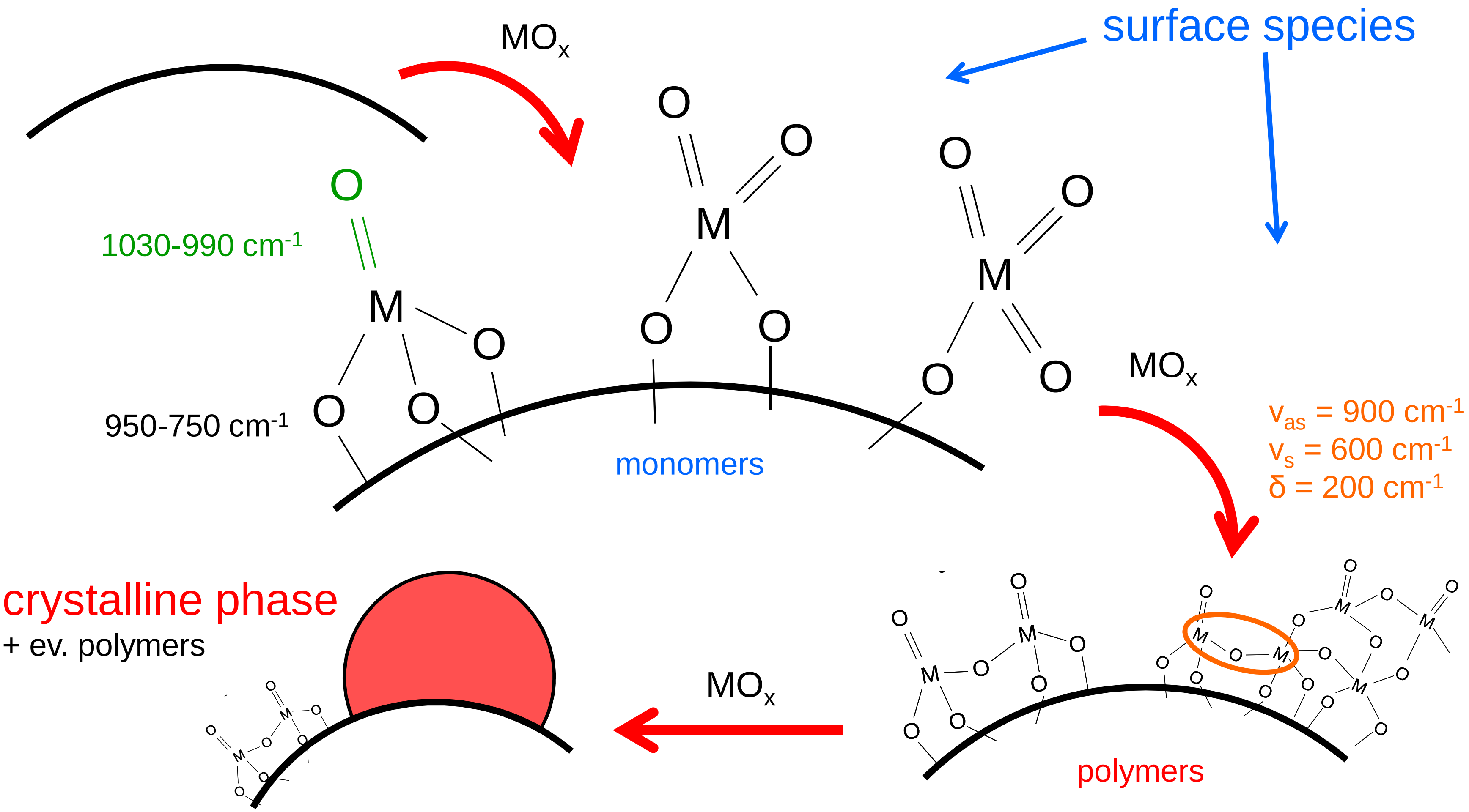
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



MO_x

surface species

1030-990 cm^{-1}

950-750 cm^{-1}

monomers

MO_x

ν_{as} = 900 cm^{-1}
ν_s = 600 cm^{-1}
δ = 200 cm^{-1}

polymers

MO_x

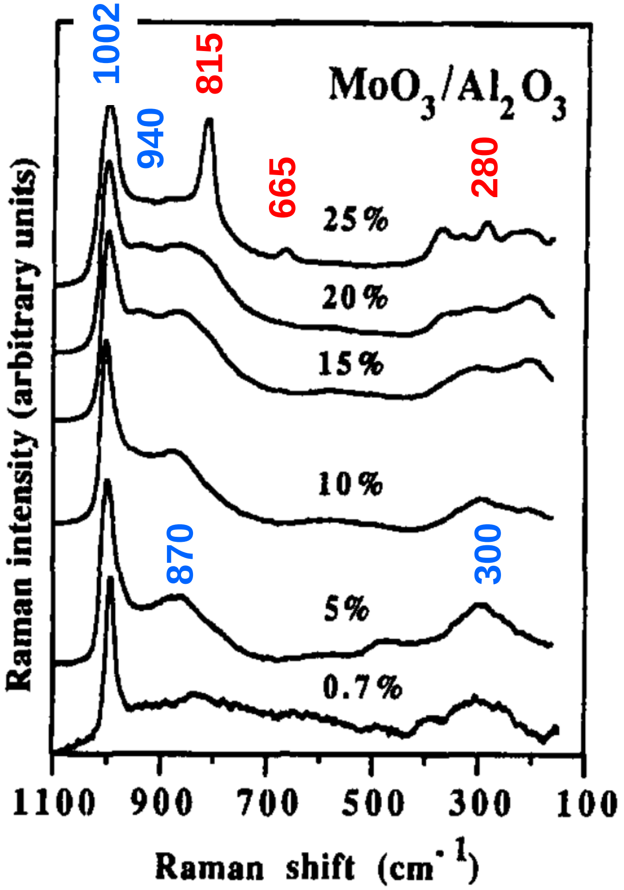
crystalline phase
+ ev. polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



surface MoO_3

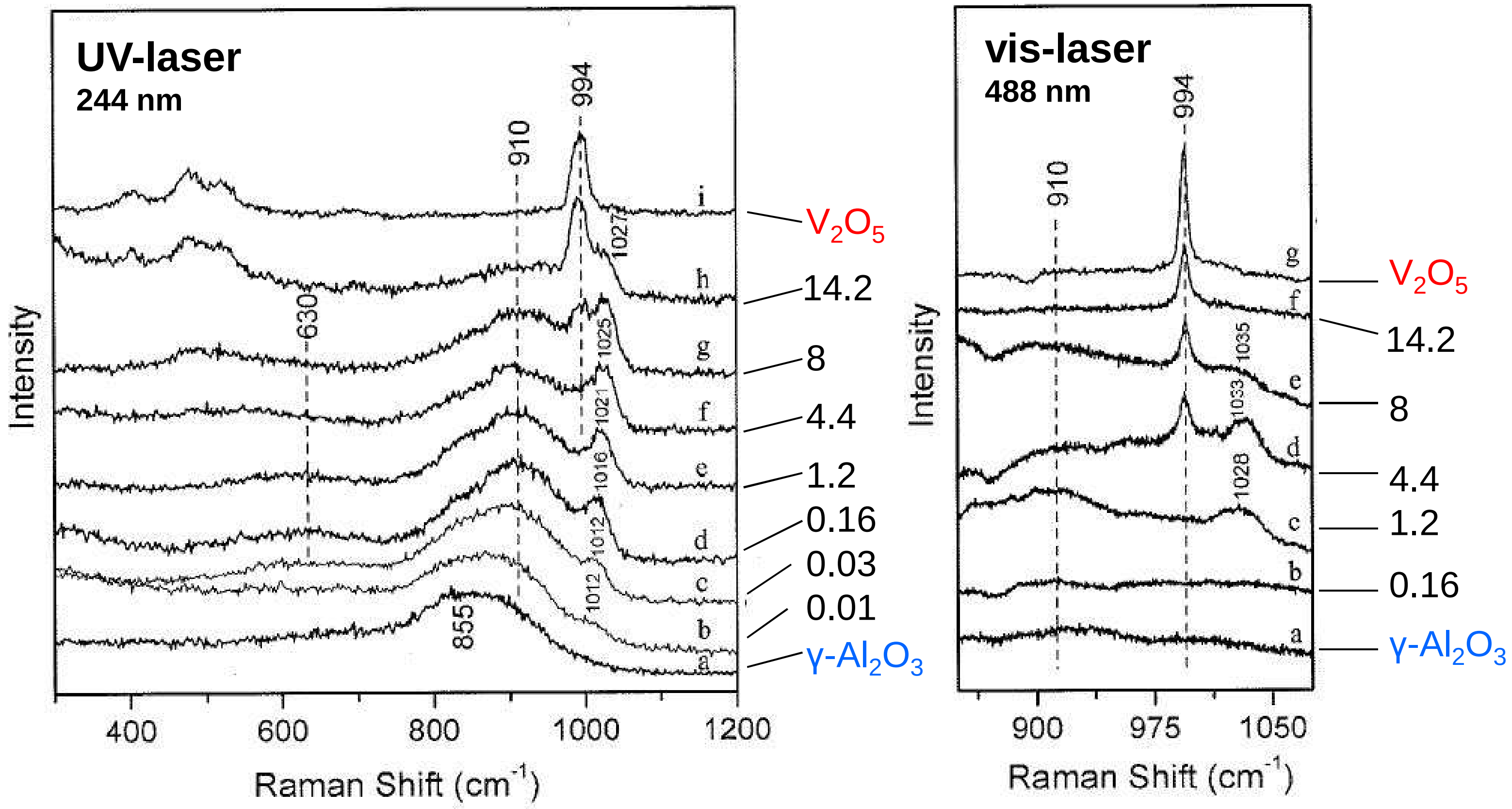
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

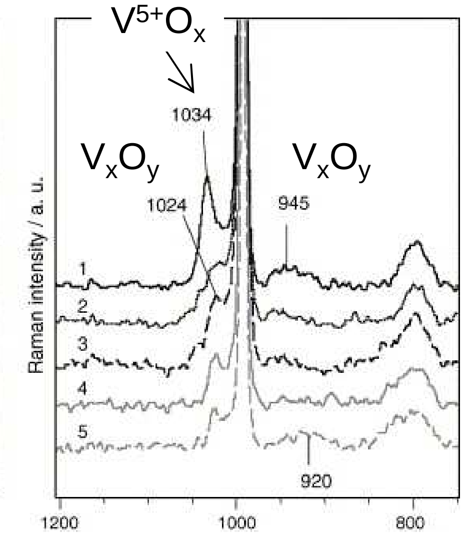
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

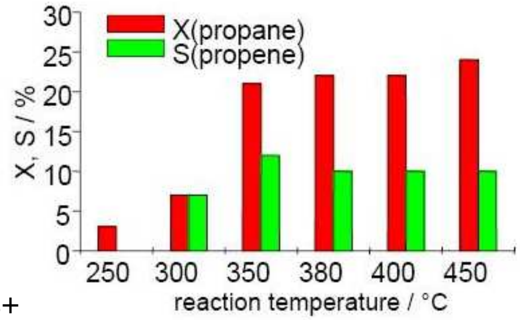
Applications

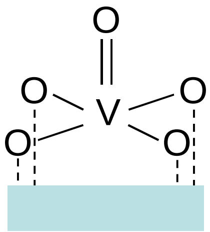
- Reactivity of V/TiO_2 after oxidative treatment

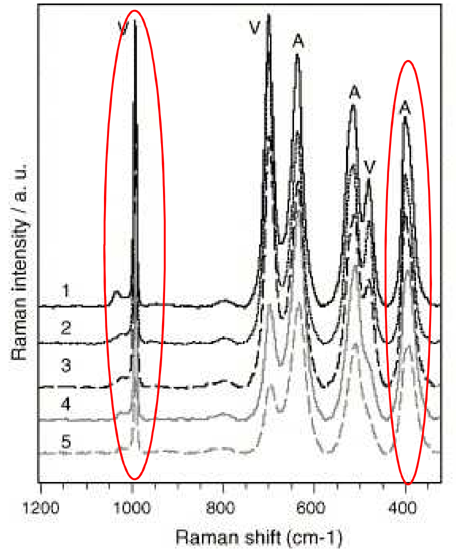


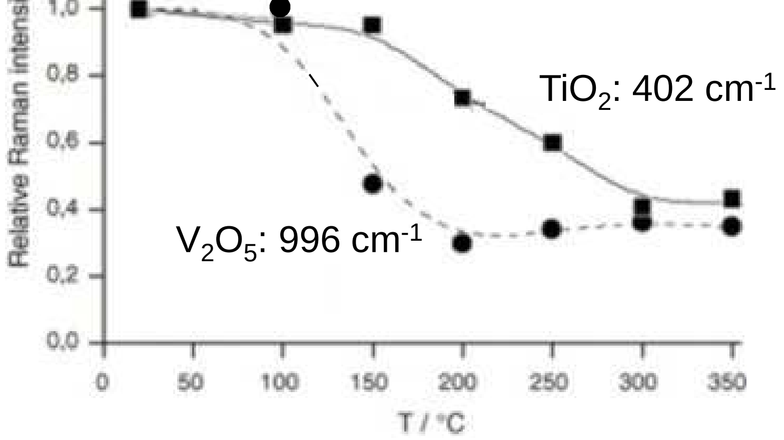
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

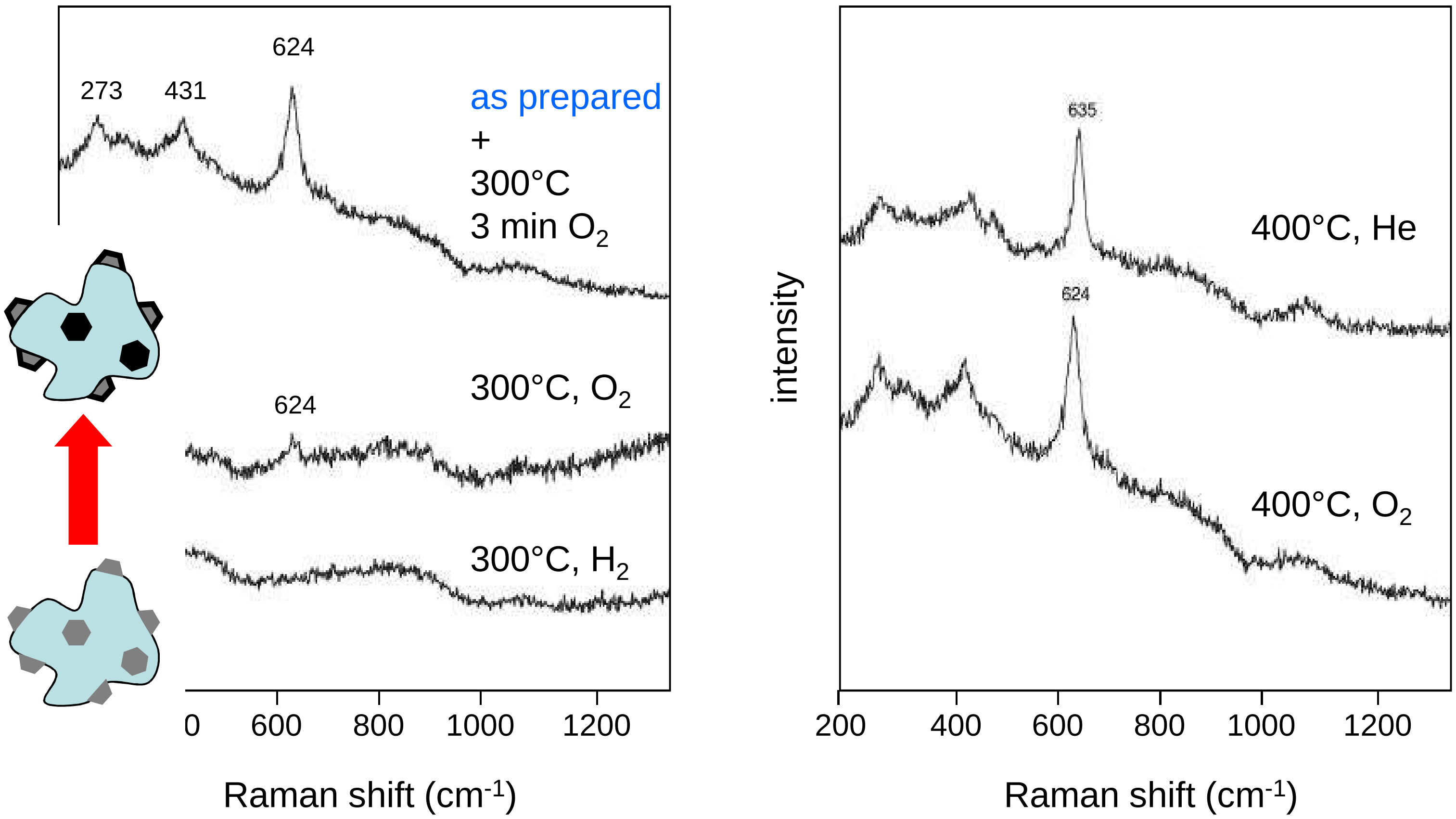
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



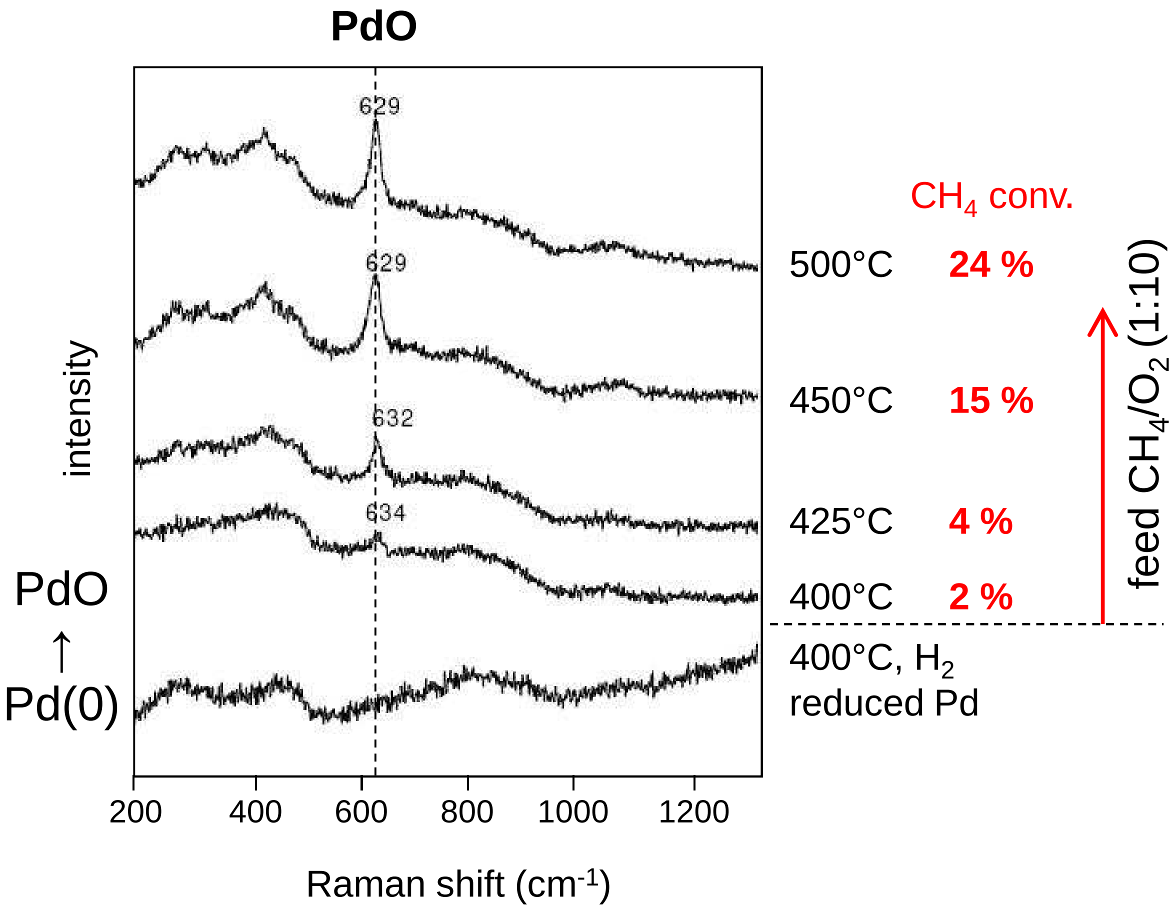
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

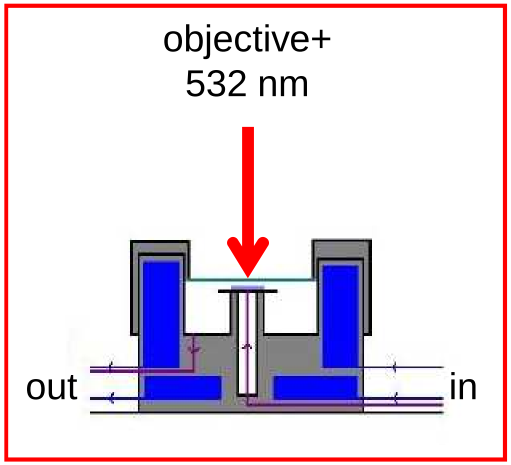
Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



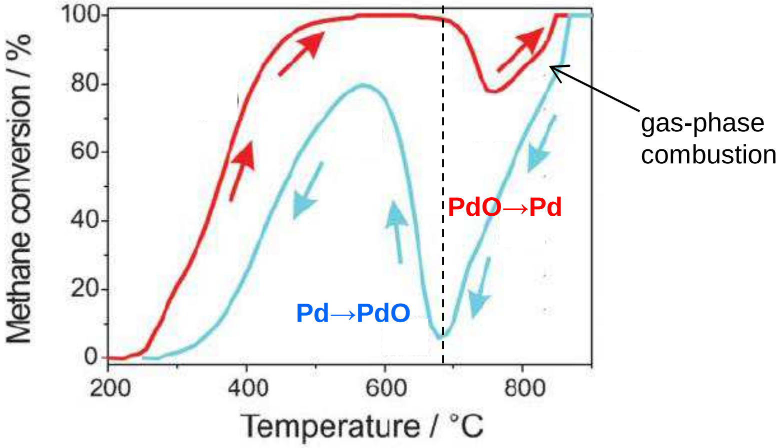
near PdO mode

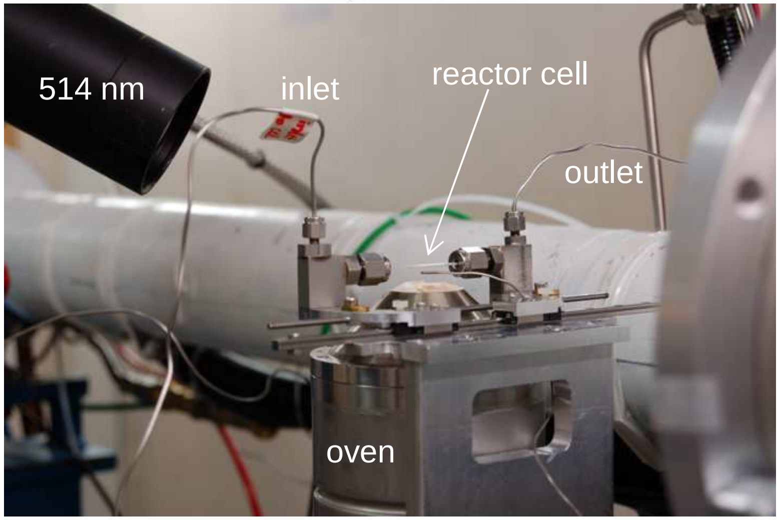


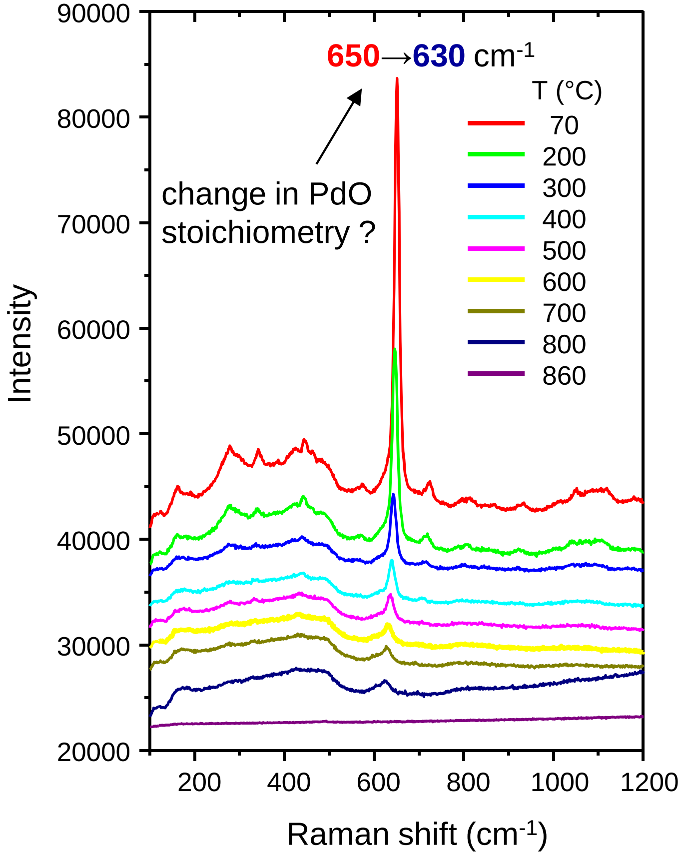
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







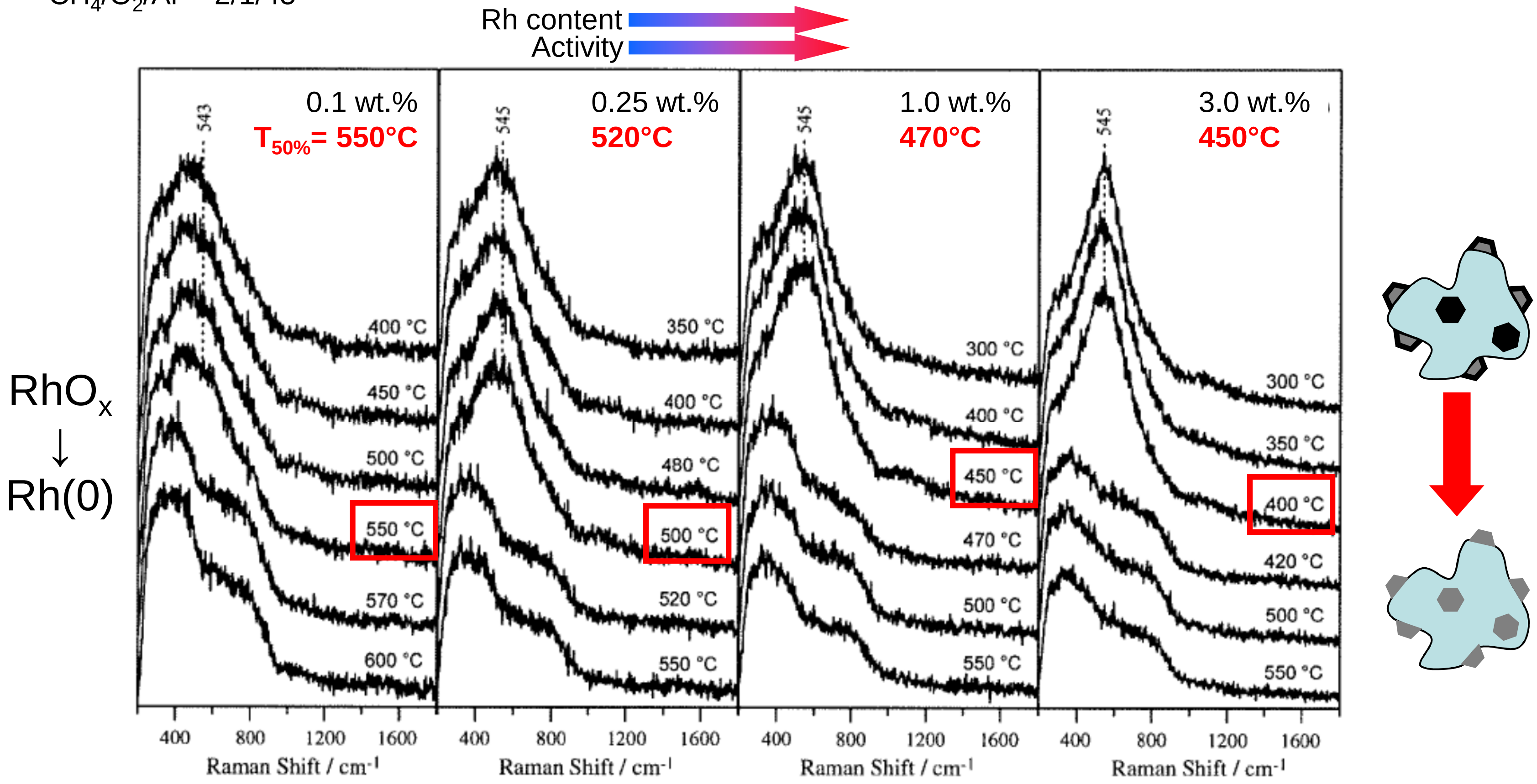
1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

- Methane partial oxidation over Rh/Al_2O_3

3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$$



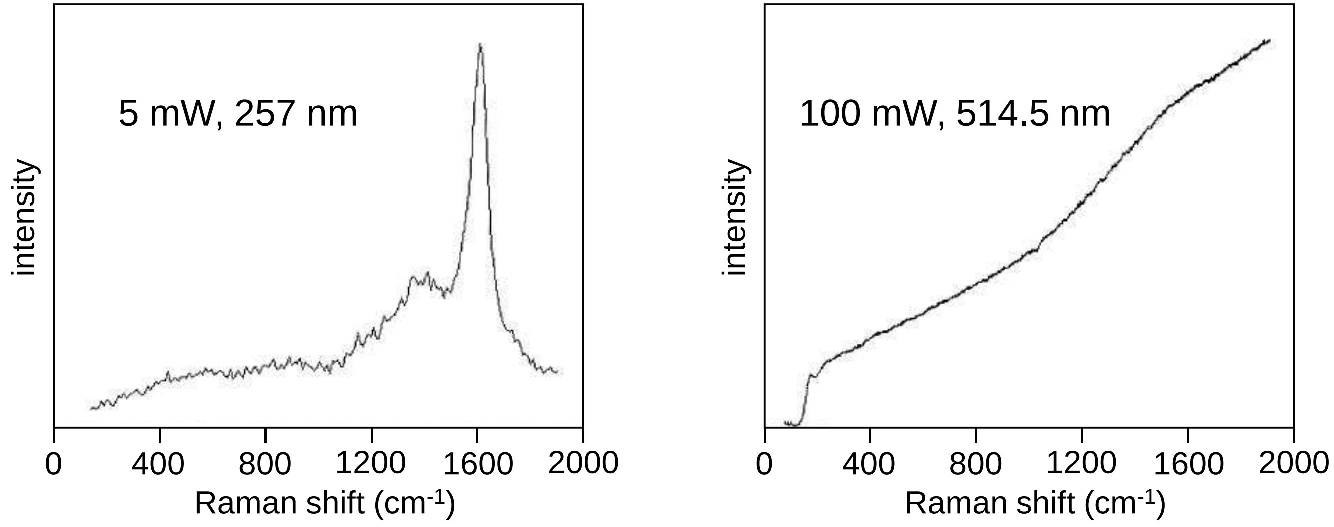
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

    (only few molecules fluoresce below 260 nm)

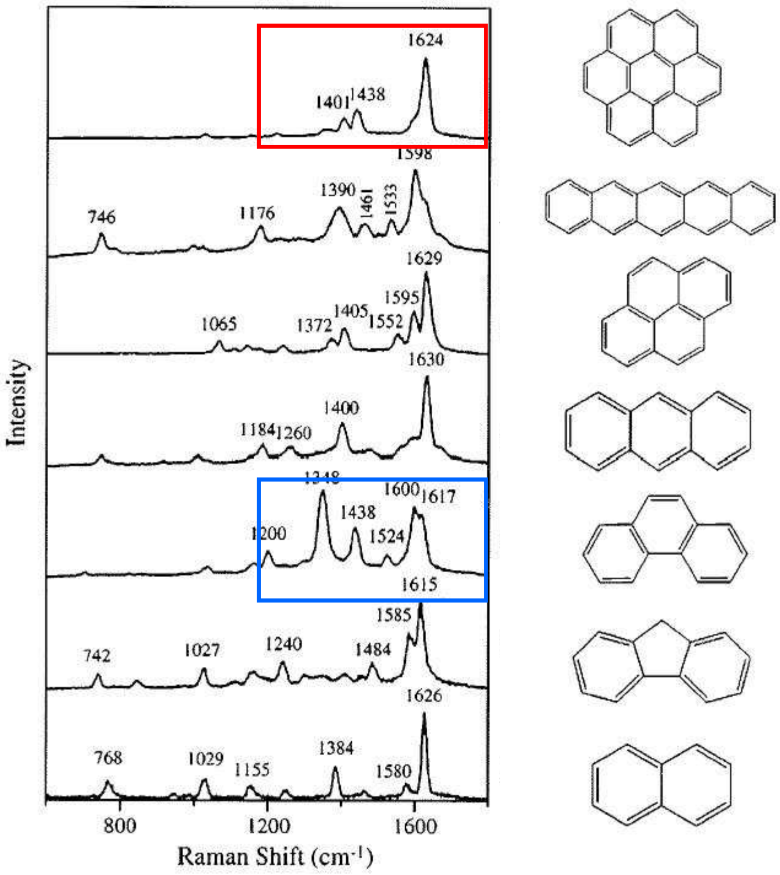
Rh/Al_2O_3, coked 500°C in naphtha

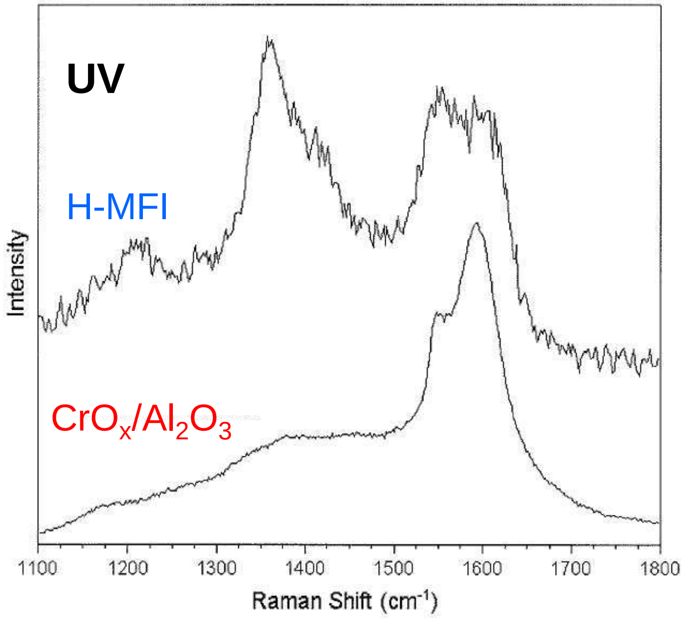


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





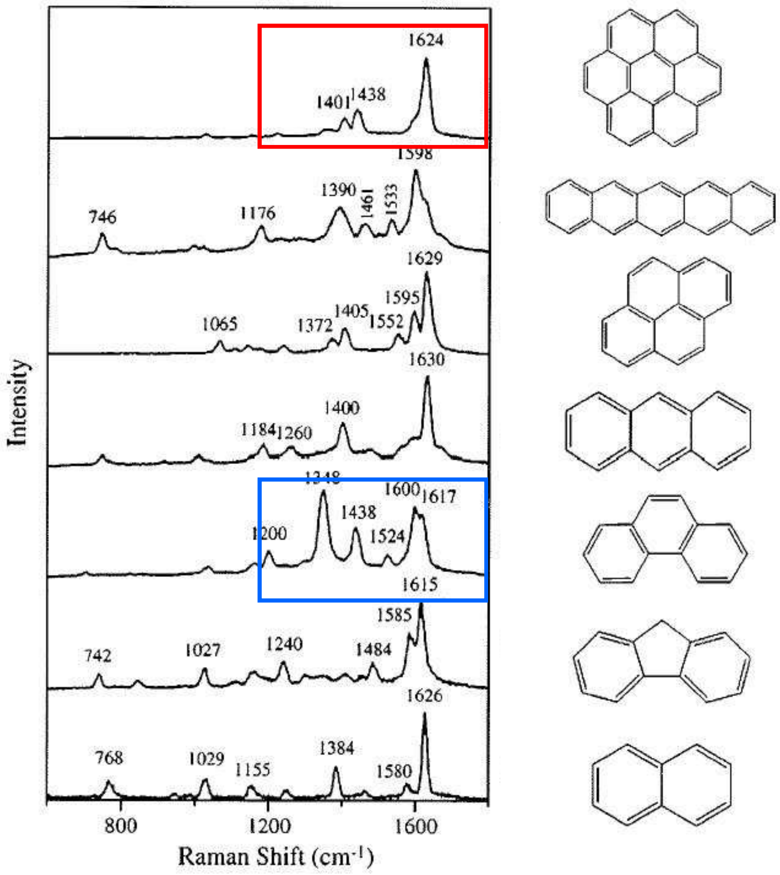
Coke classification
1D topology, chain-like
2D topology, sheet-like

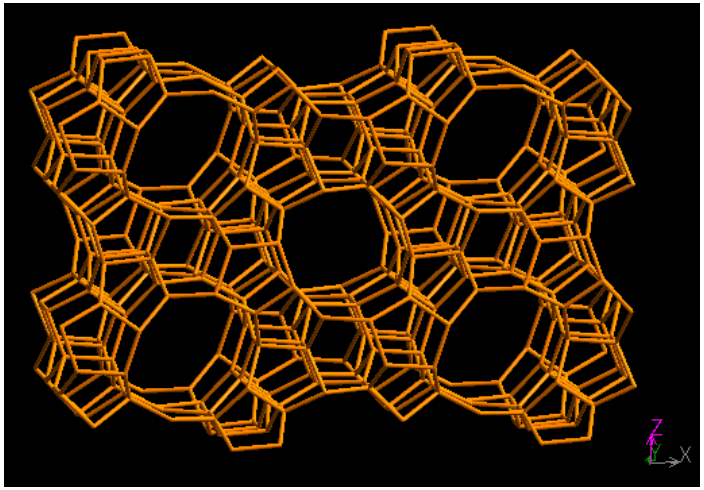
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





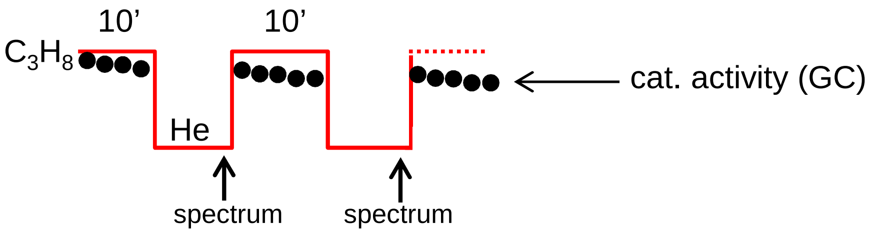
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

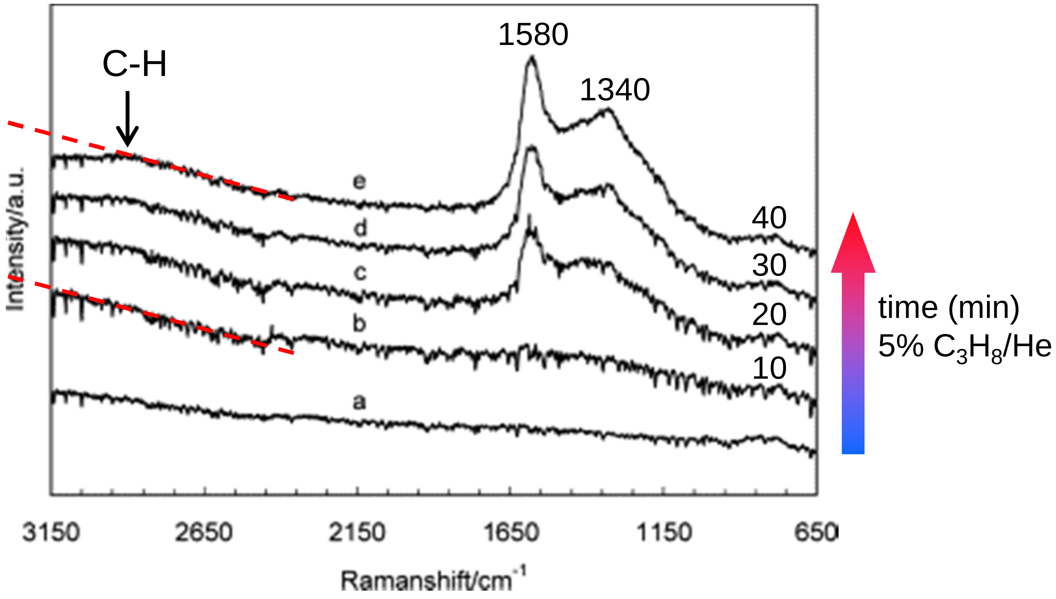
Stair, *Adv. Catal.* **51** (2007) 75

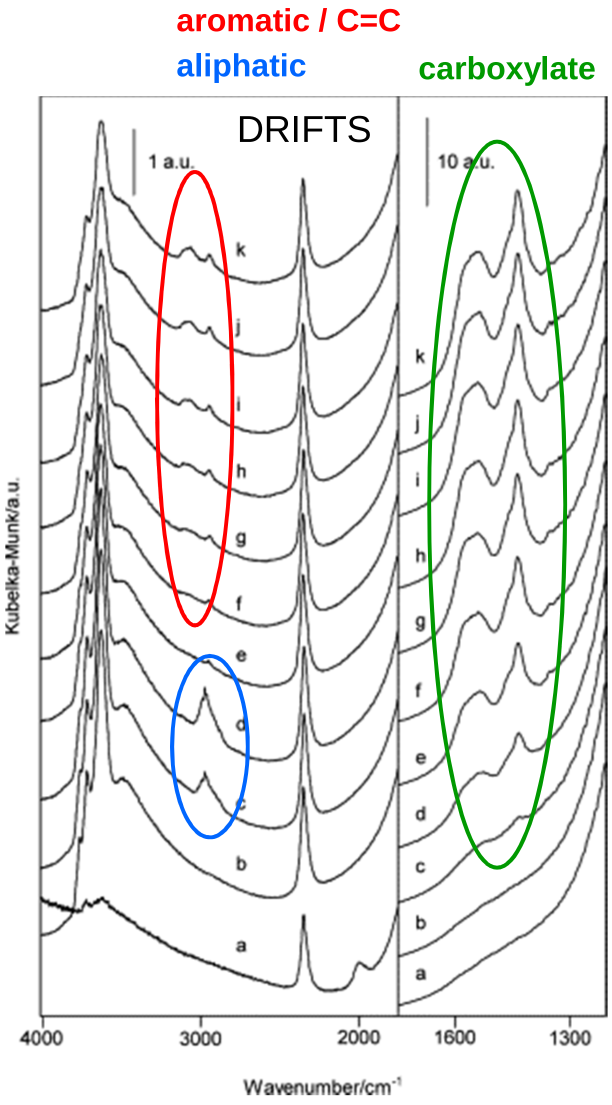
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

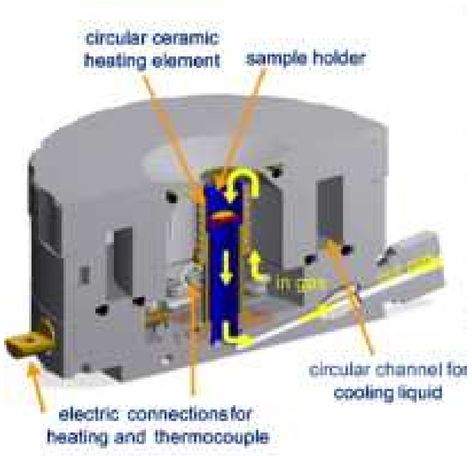


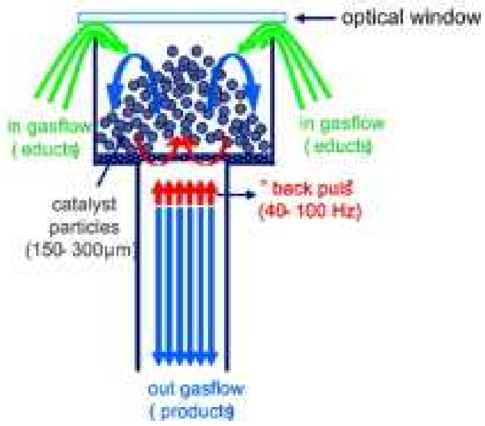


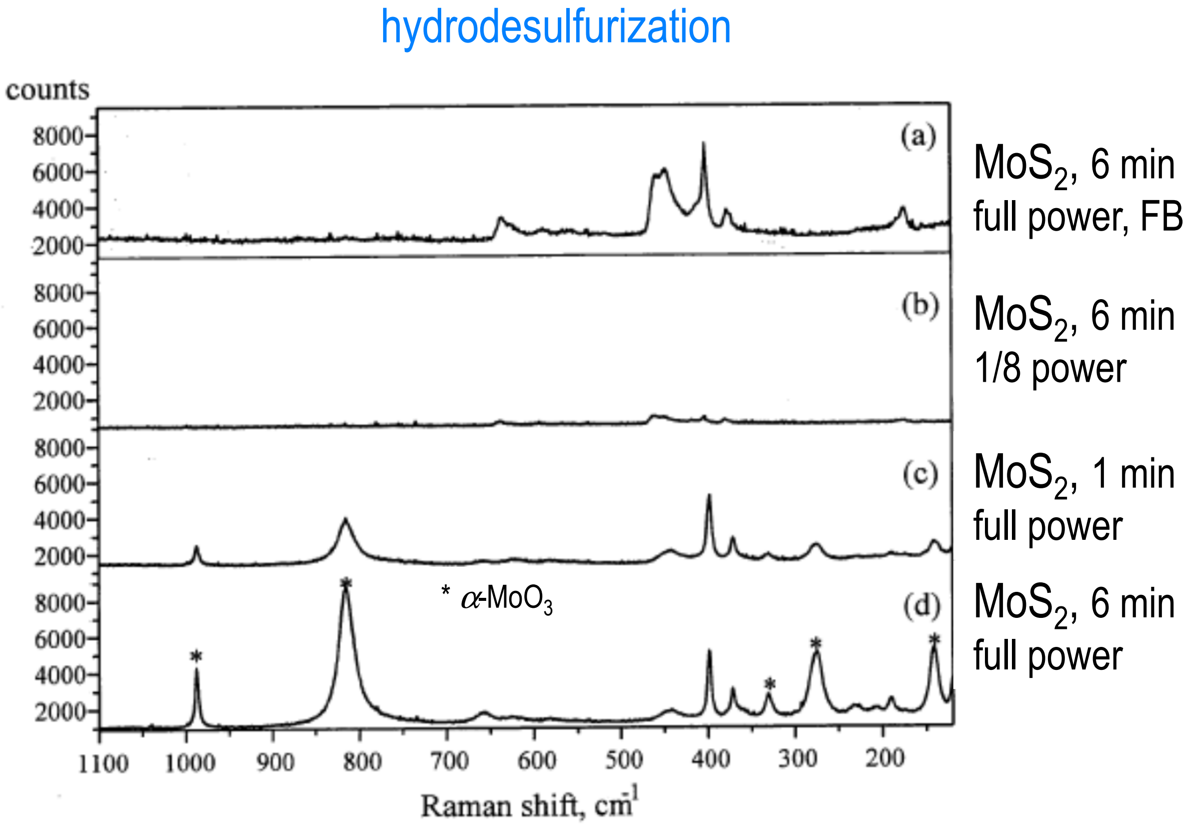
Airaksinen et al., *J. Catal.* **230** (2005) 507

Applications

- Fluidized bed reactor cell





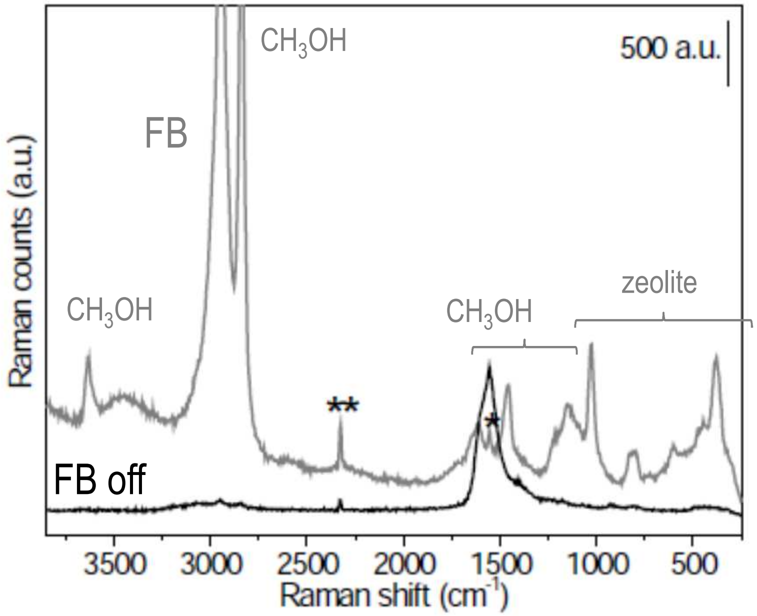


Beato et al., *Catal. Today* 205 (2013) 128

Applications

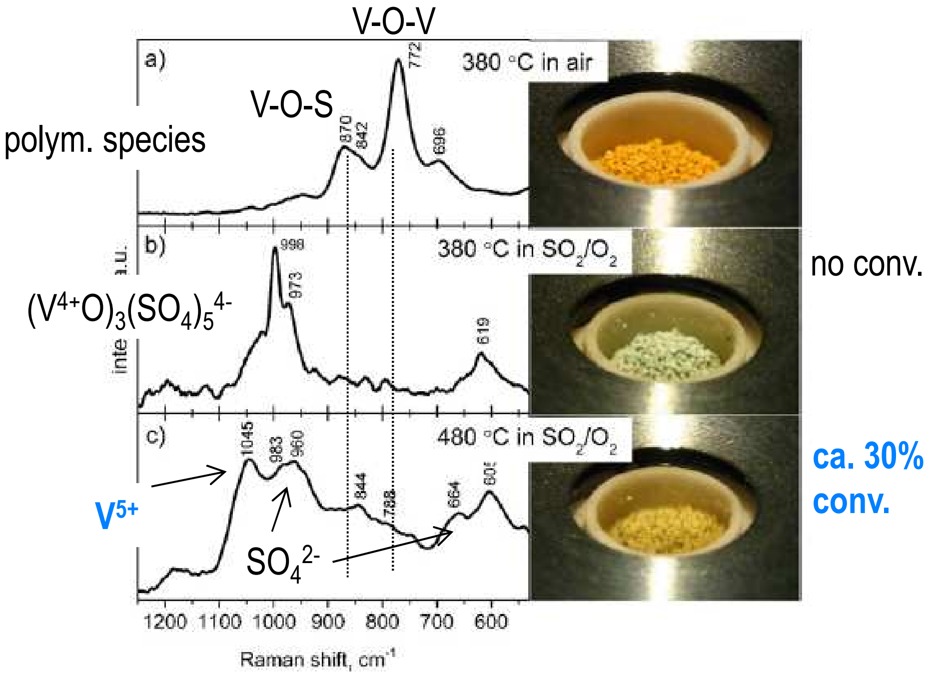
- Fluidized bed reactor cell

CH$_3$OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH$_3$OH decomposition

Sulfuric acid V$_2$O$_5$/pyrosulfate catalyst
λ= 514 nm

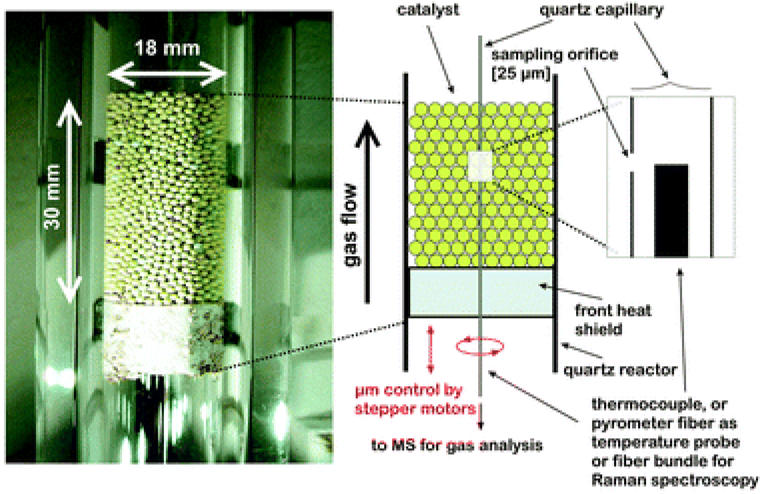


active species: mono- & dimeric V^{5+} oxosulfate species

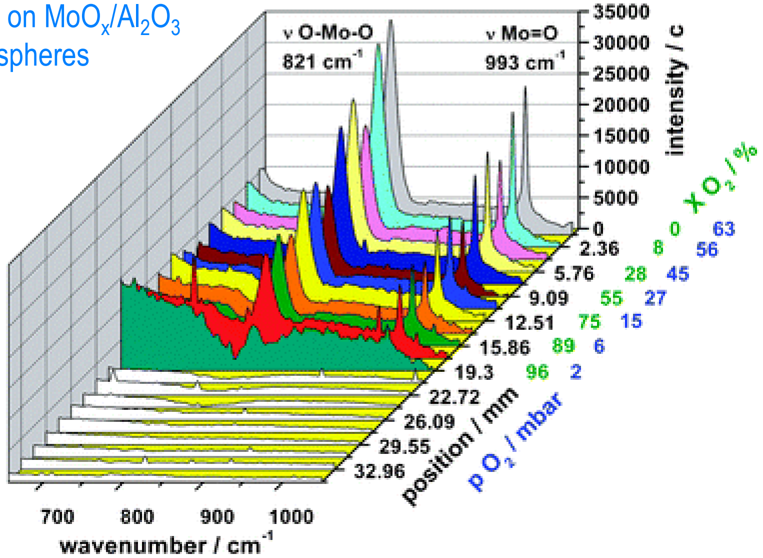
Beato et al., *Catal. Today* 205 (2013) 128

Applications

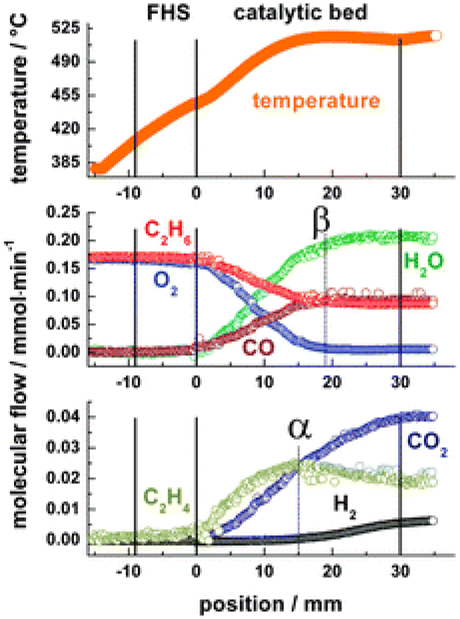
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

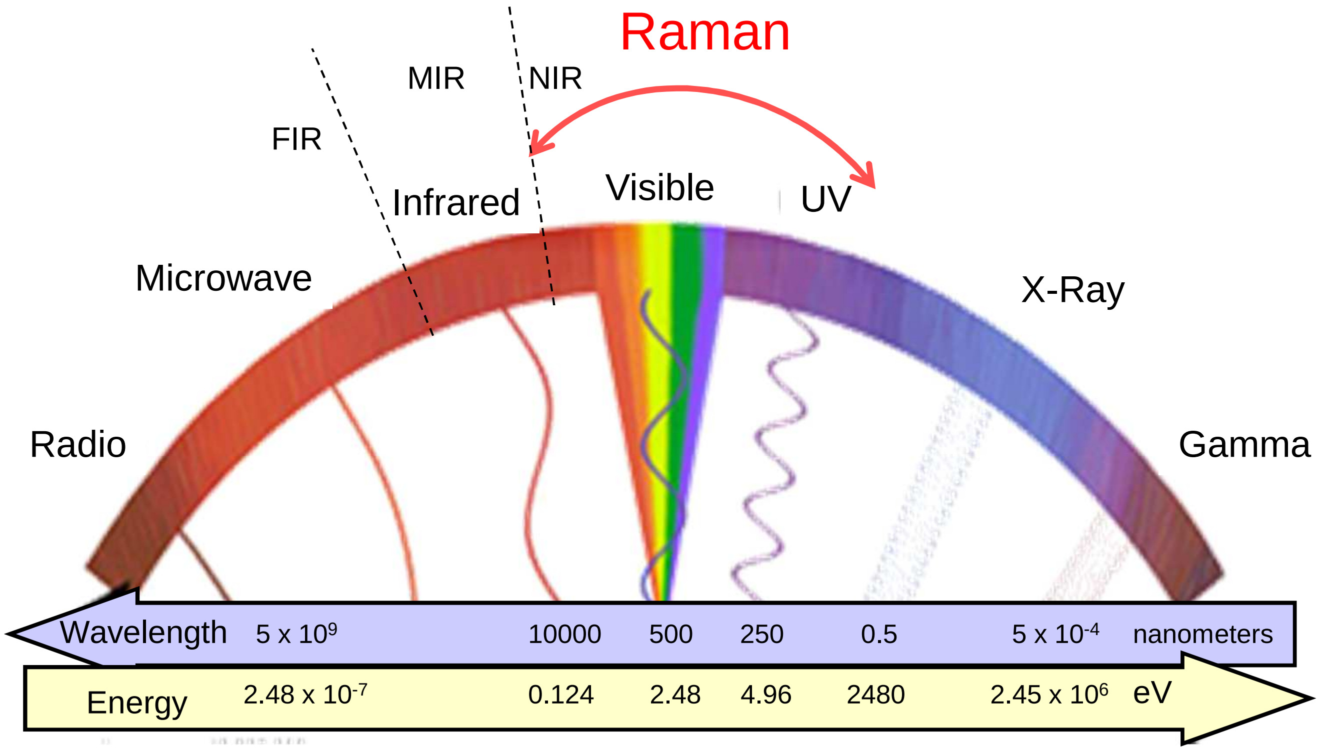
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

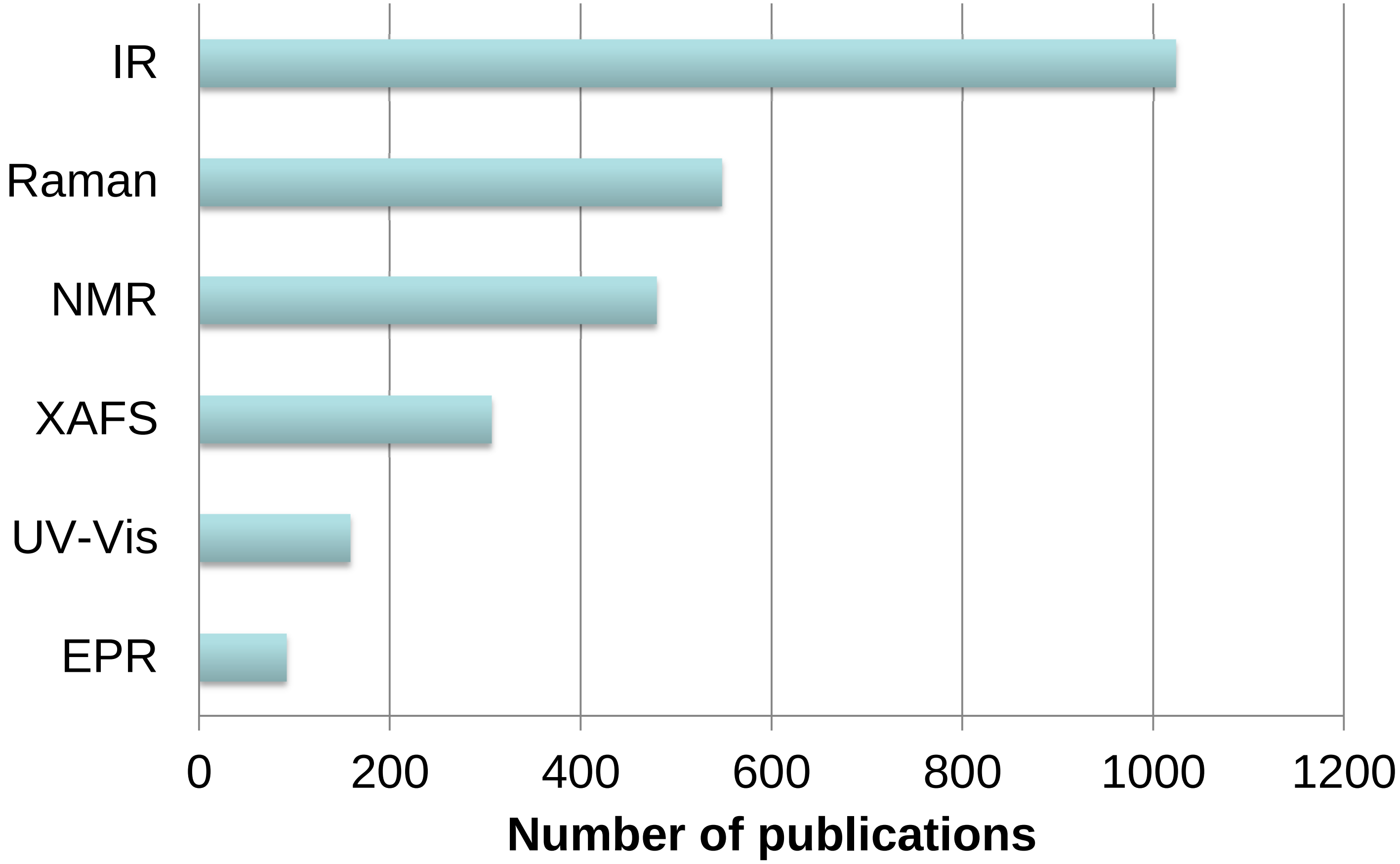
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

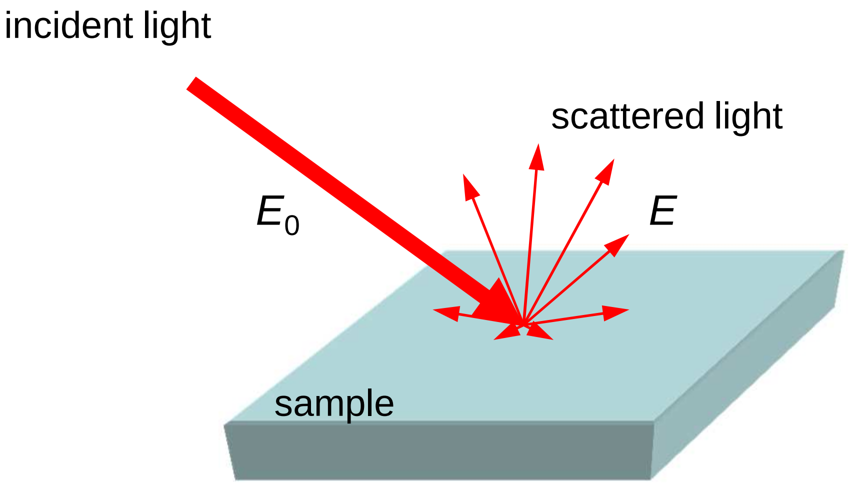


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$E_{vib} = E_0 - E$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

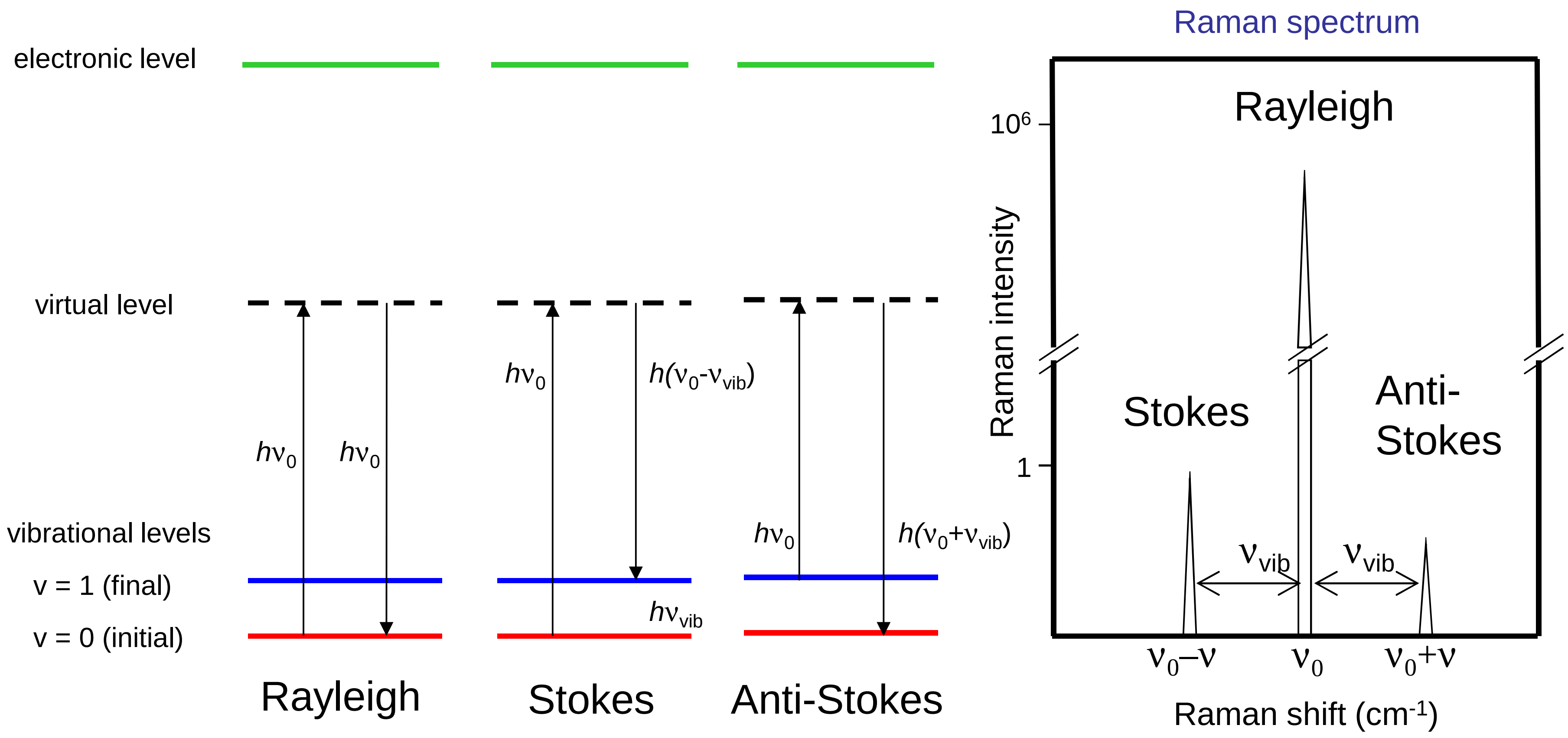
$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

$$\text{and}\quad \boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\ (\text{Anti-Stokes})}{I\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:
  - 4th power of ν (4th power law)
  - 2nd power of $\Delta\alpha$
    - properties of molecules
    - strength of bonds

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

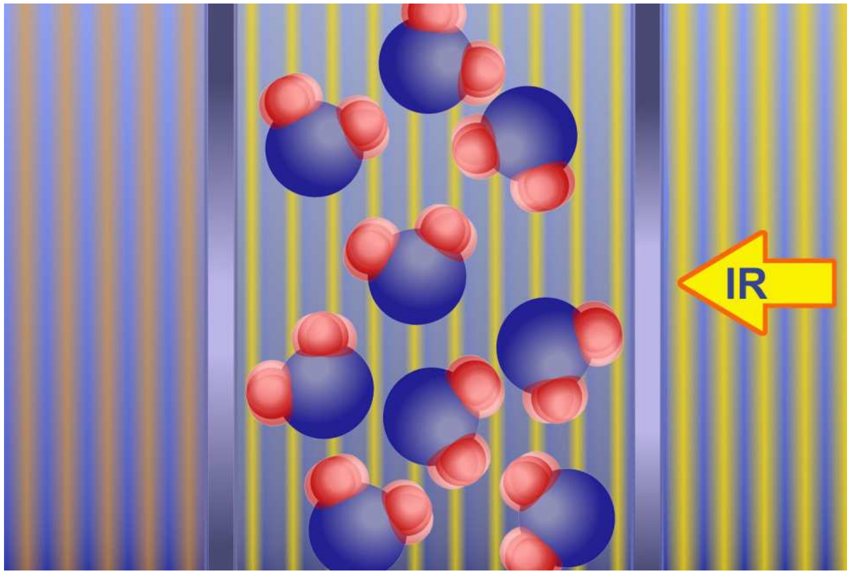
covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

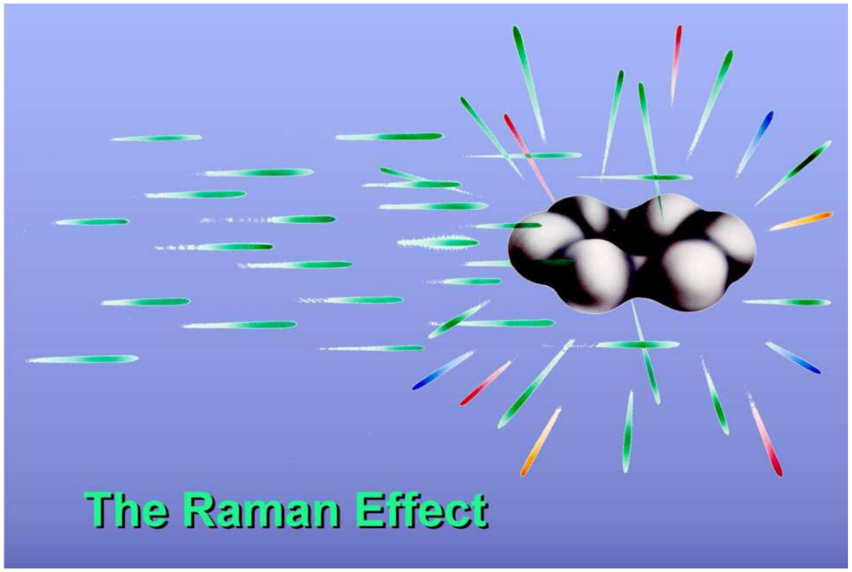
- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

Raman *vs.* Infrared

Infrared

Raman





Absorption of IR light

Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

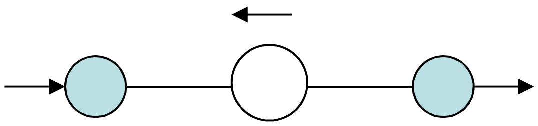
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - ❑ large electron clouds
  - ❑ not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

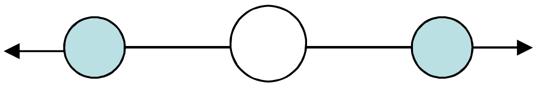
Raman *vs.* Infrared

CO_2



ν_{as}

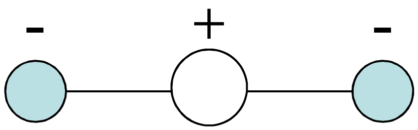
2349 cm^{-1}



ν_s

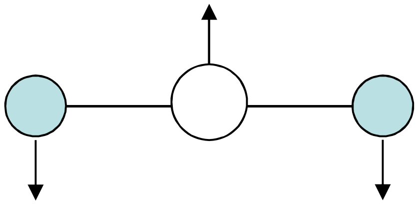
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



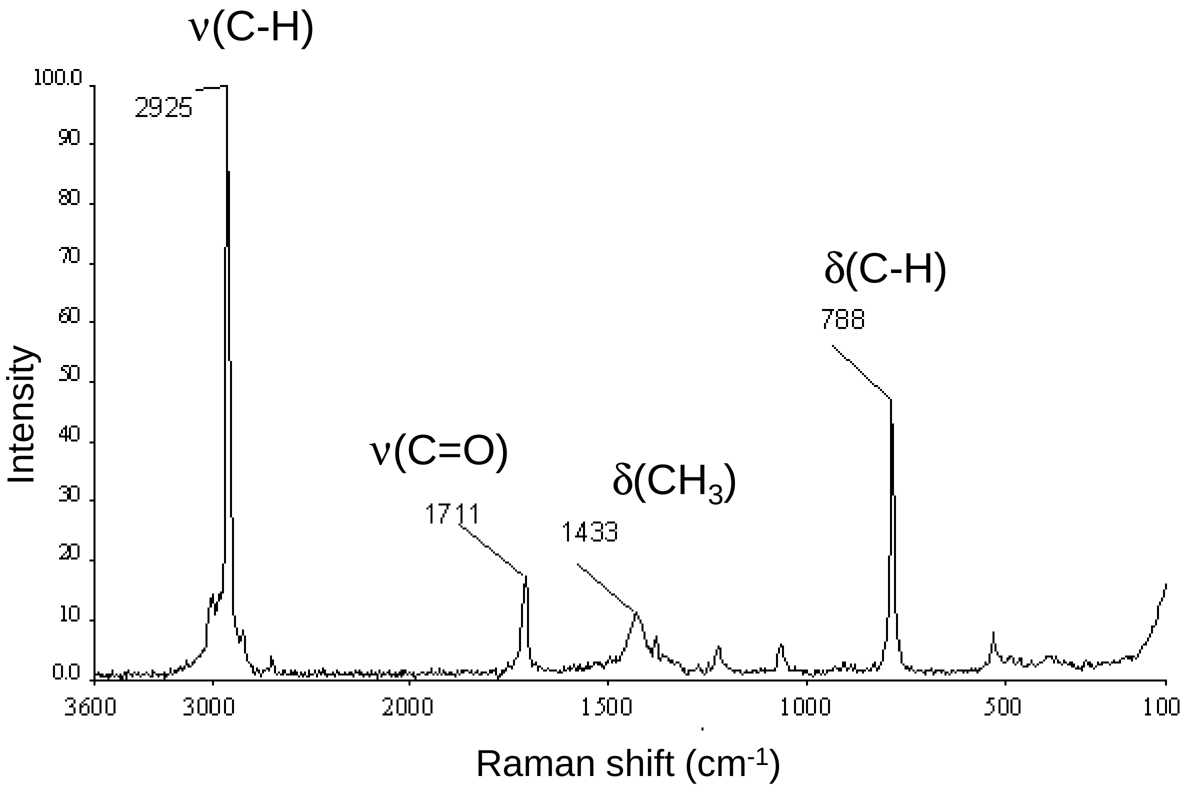
δ

667 cm^{-1}

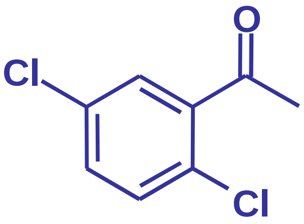
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



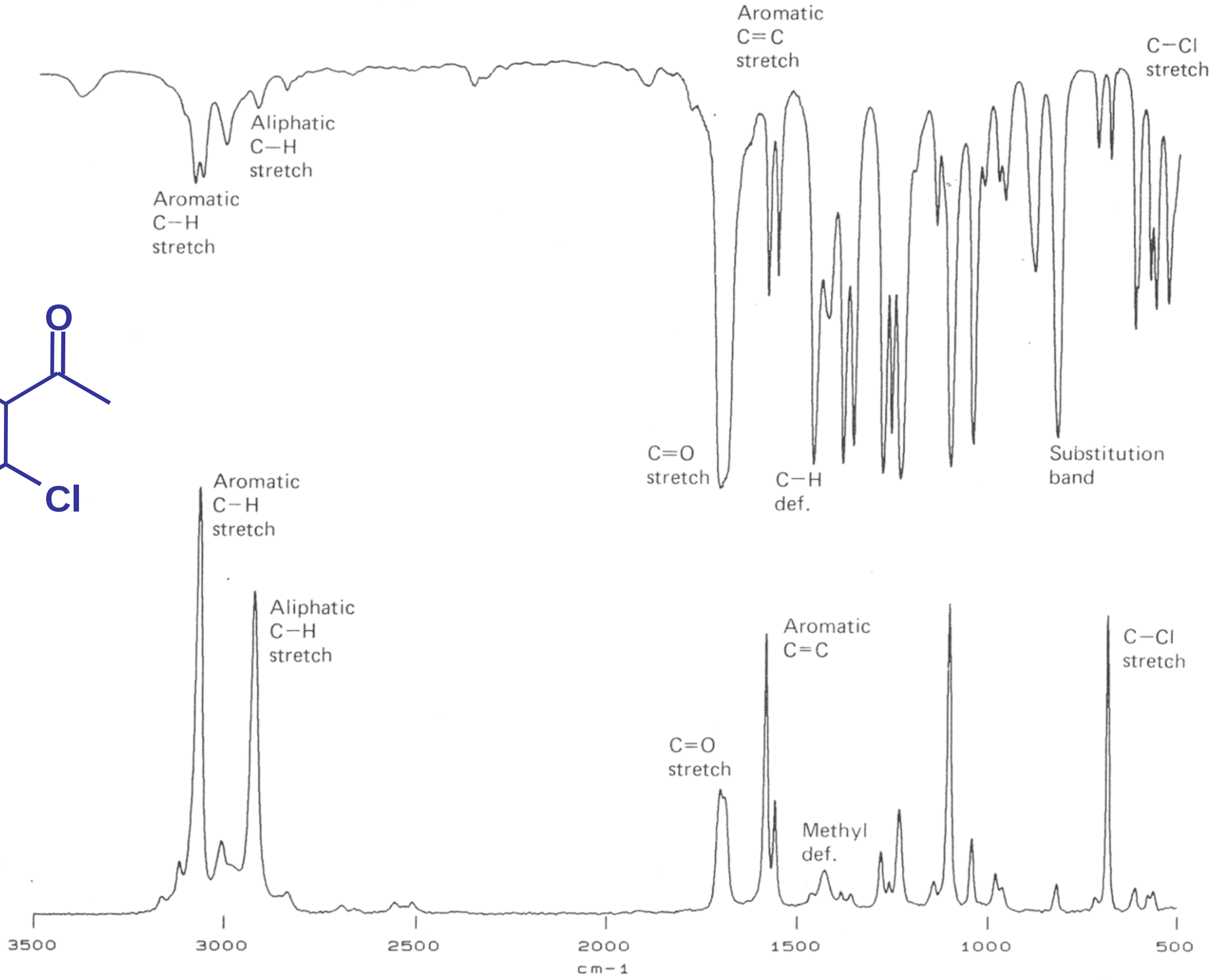


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

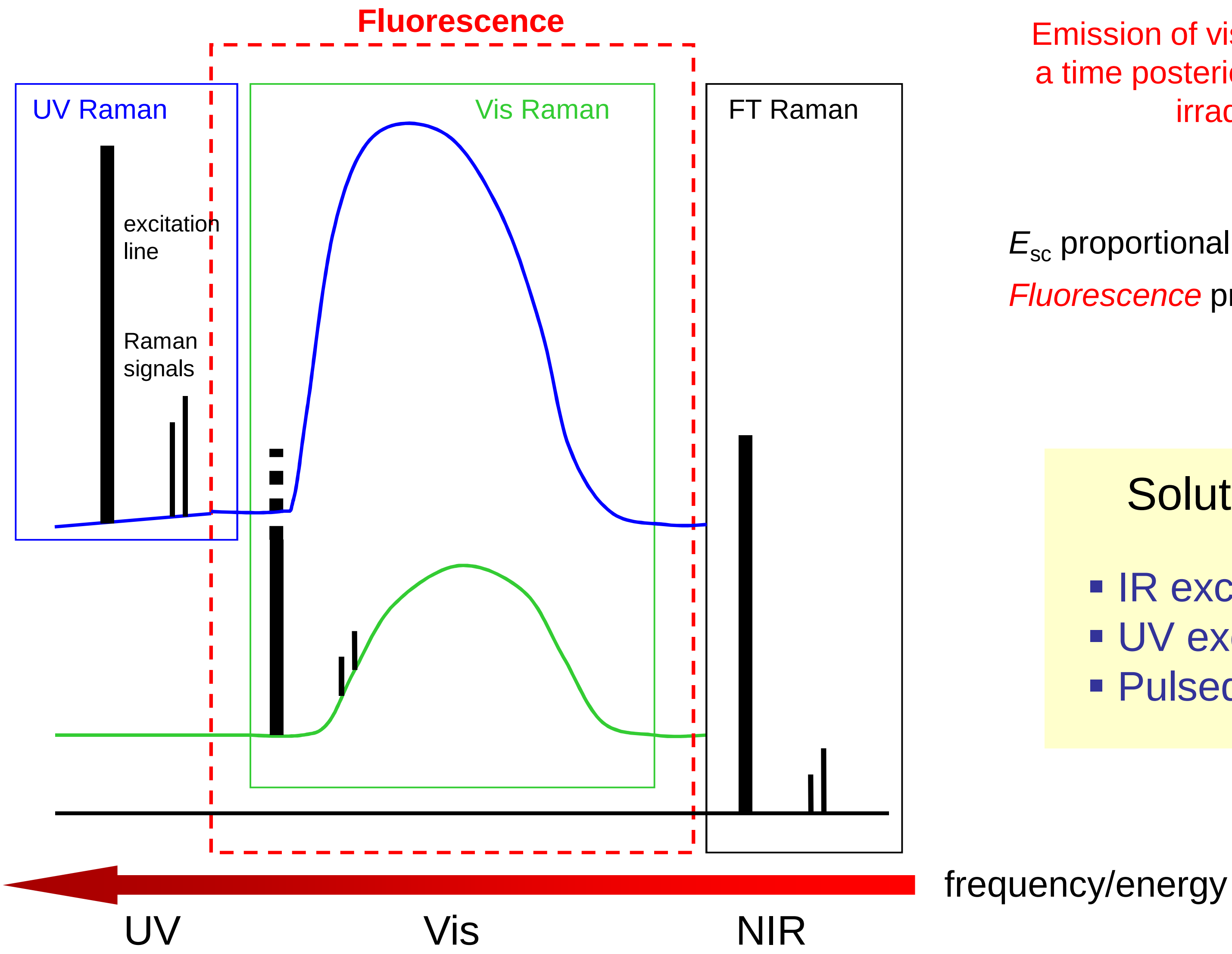
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 µm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during
a time posterior to the sample
irradiation

E_{sc} proportional to ν^4

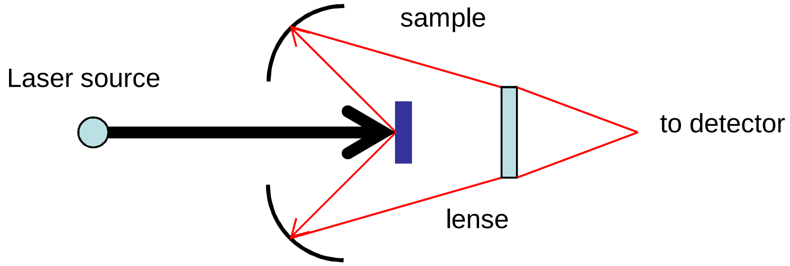
Fluorescence proportional to ν

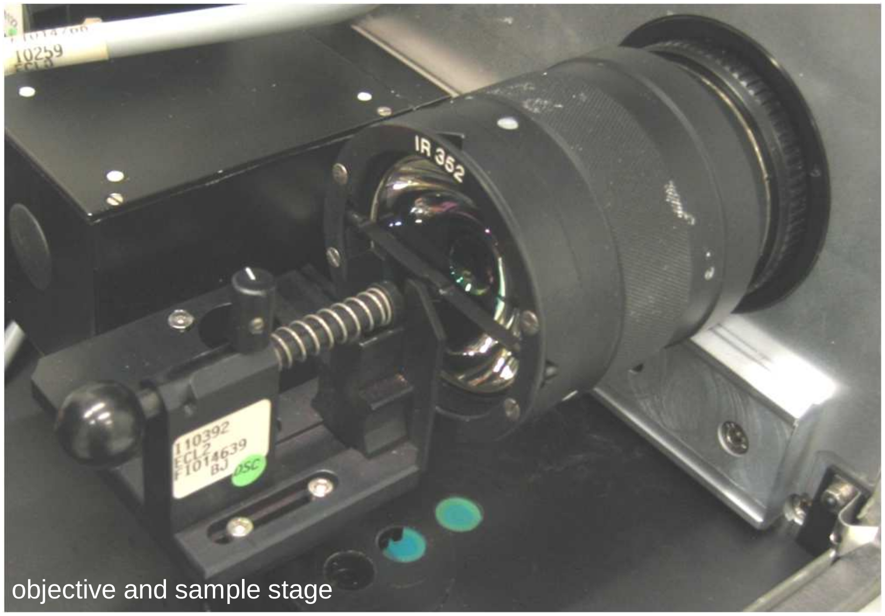
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

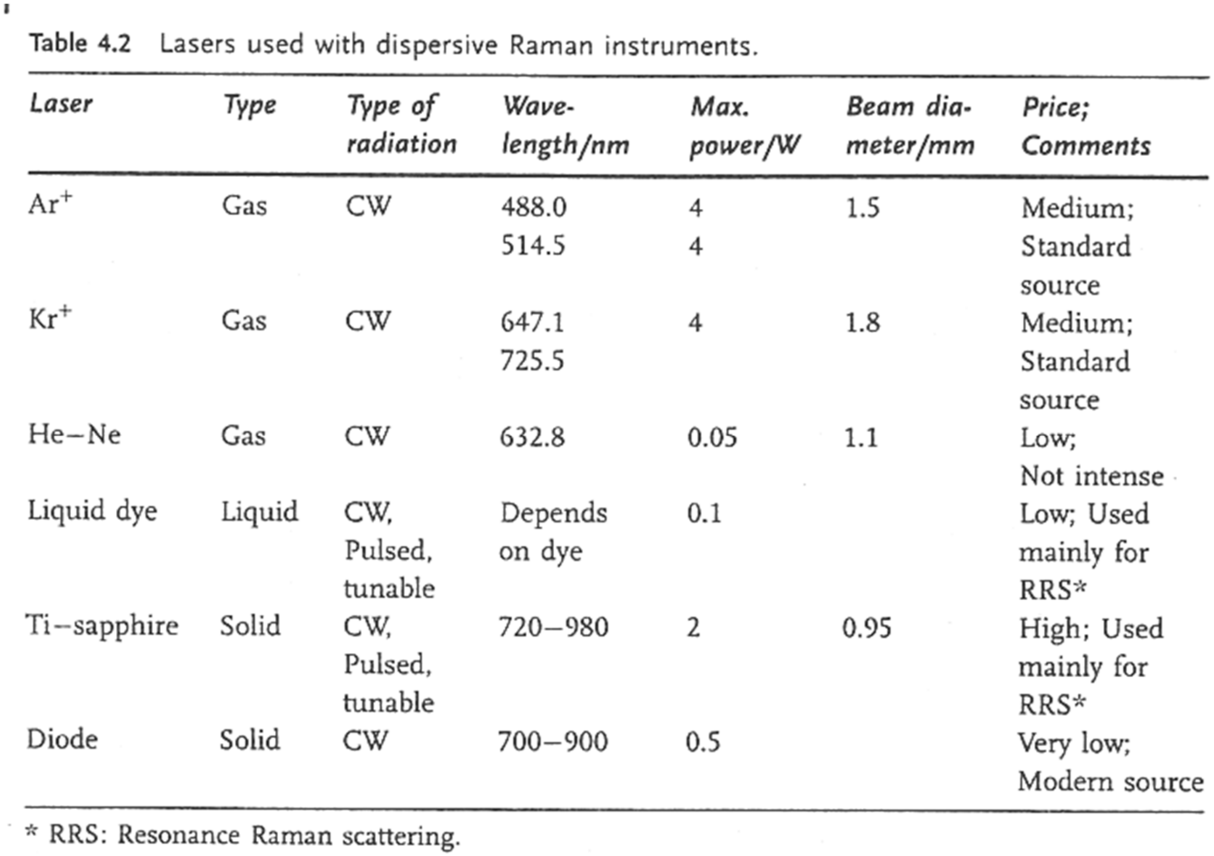


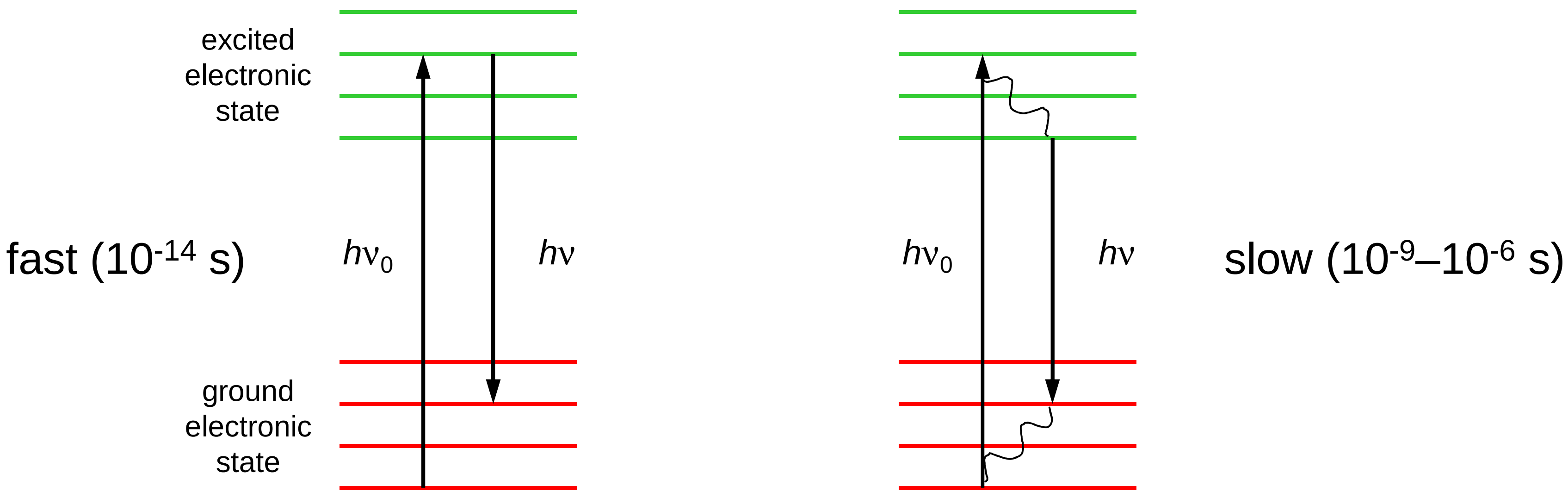
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



Resonance Raman scattering

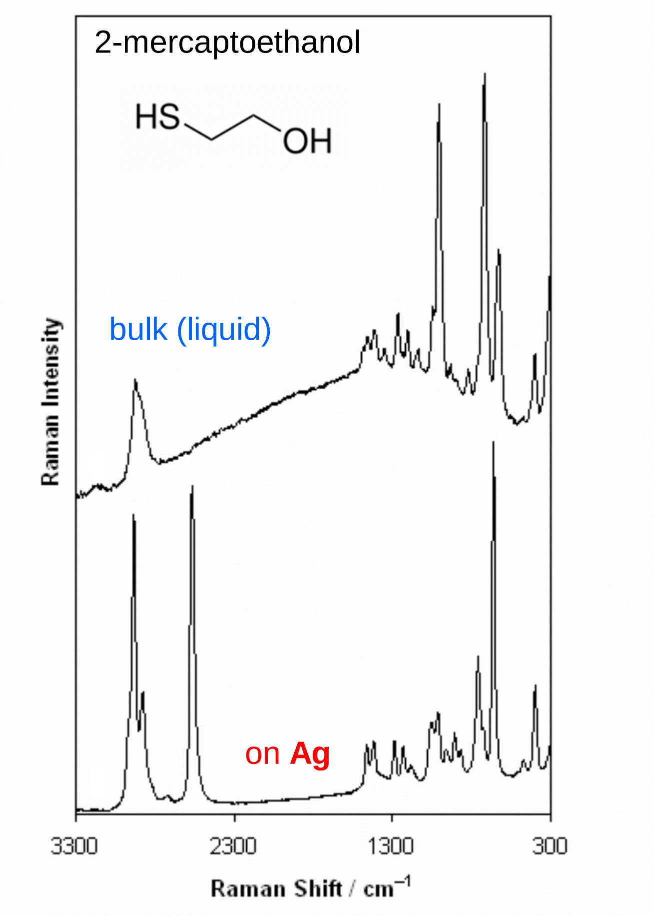
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

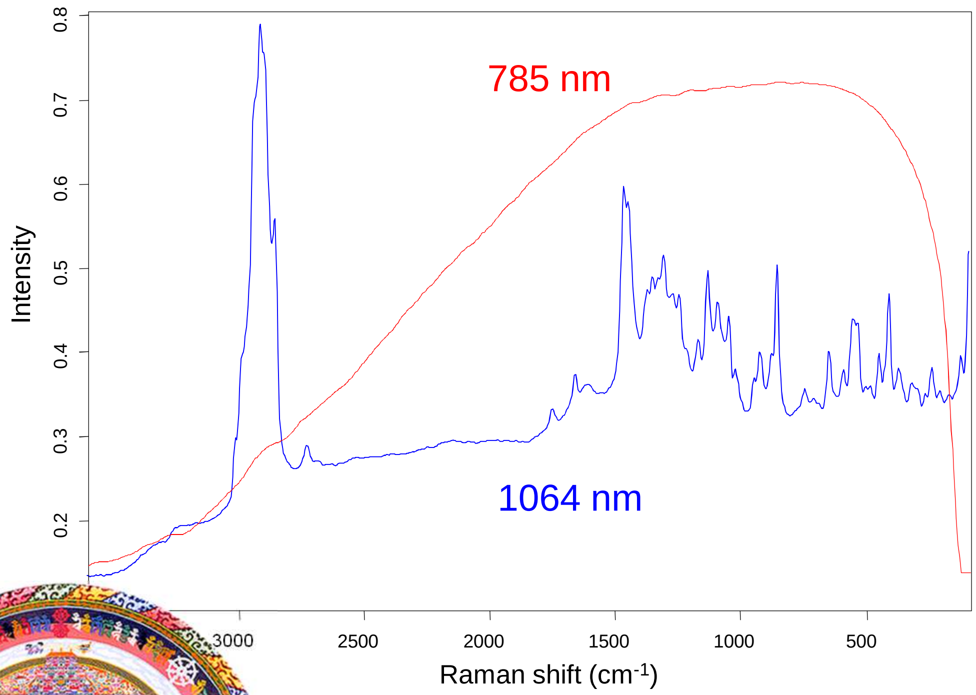
- Remarks:

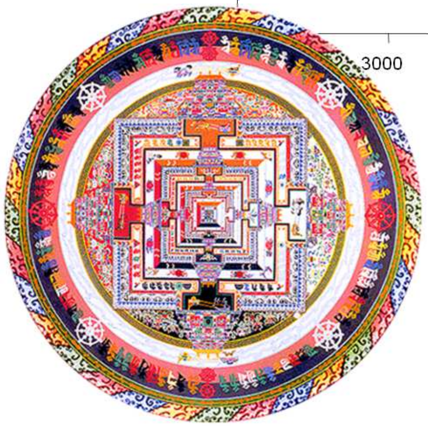
❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring





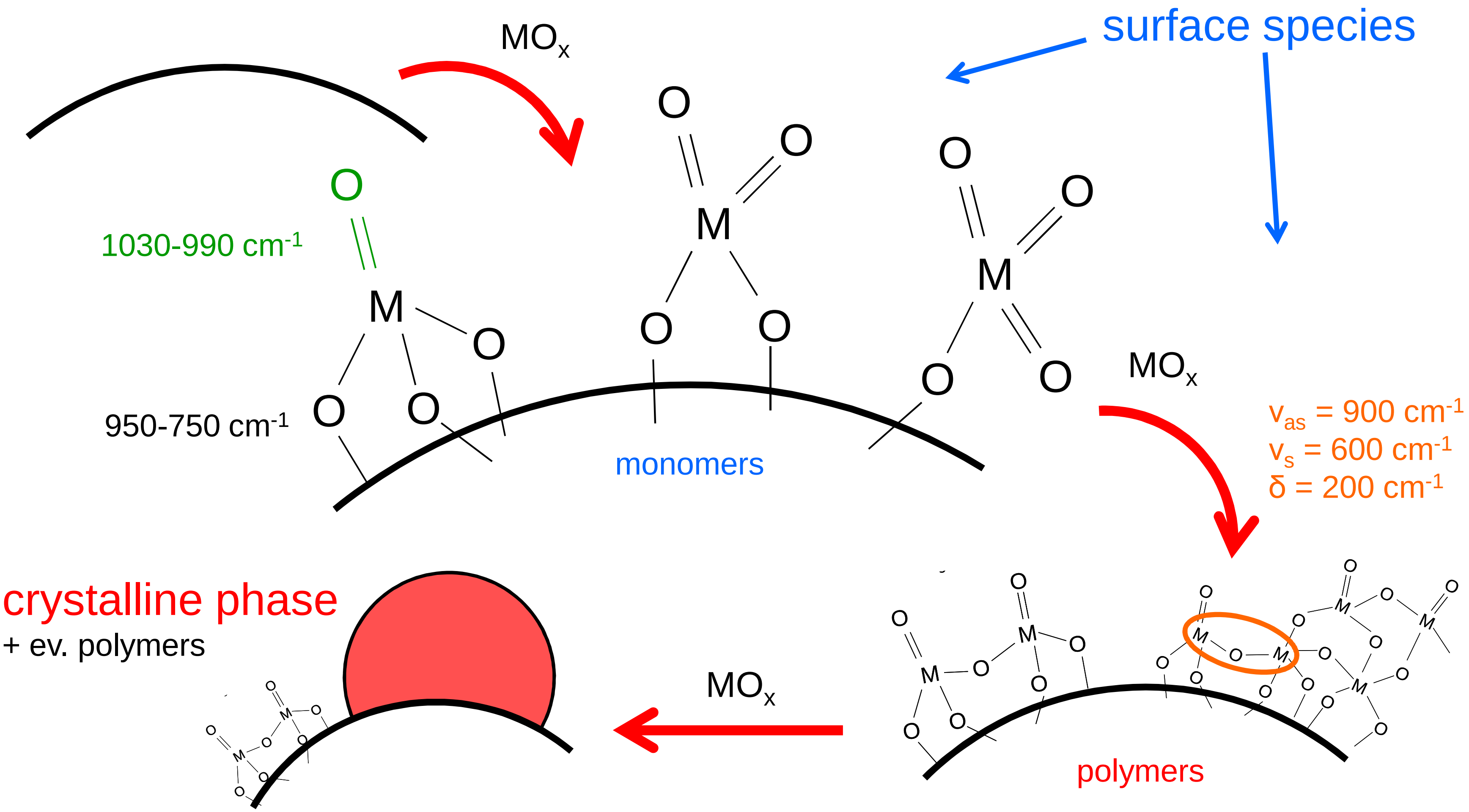
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species

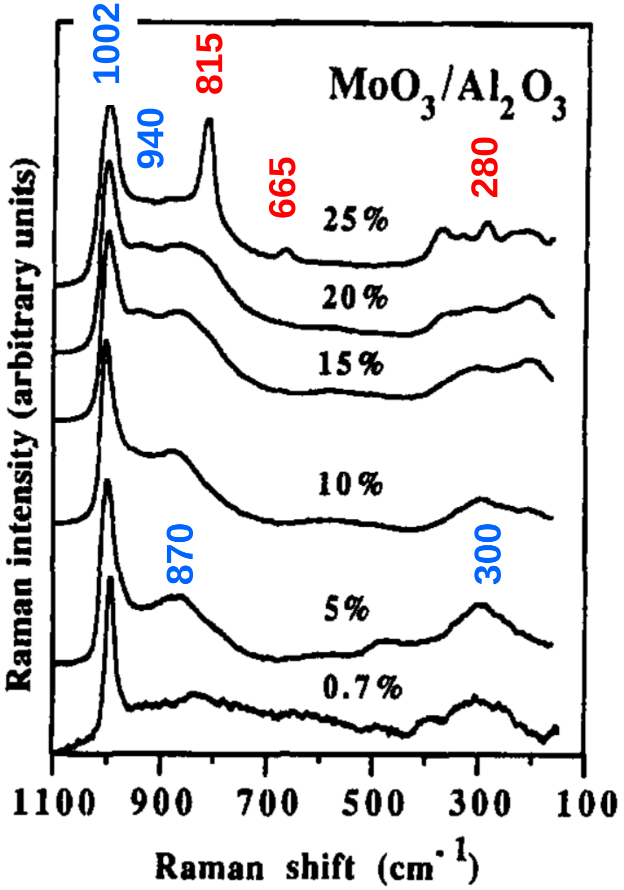


Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



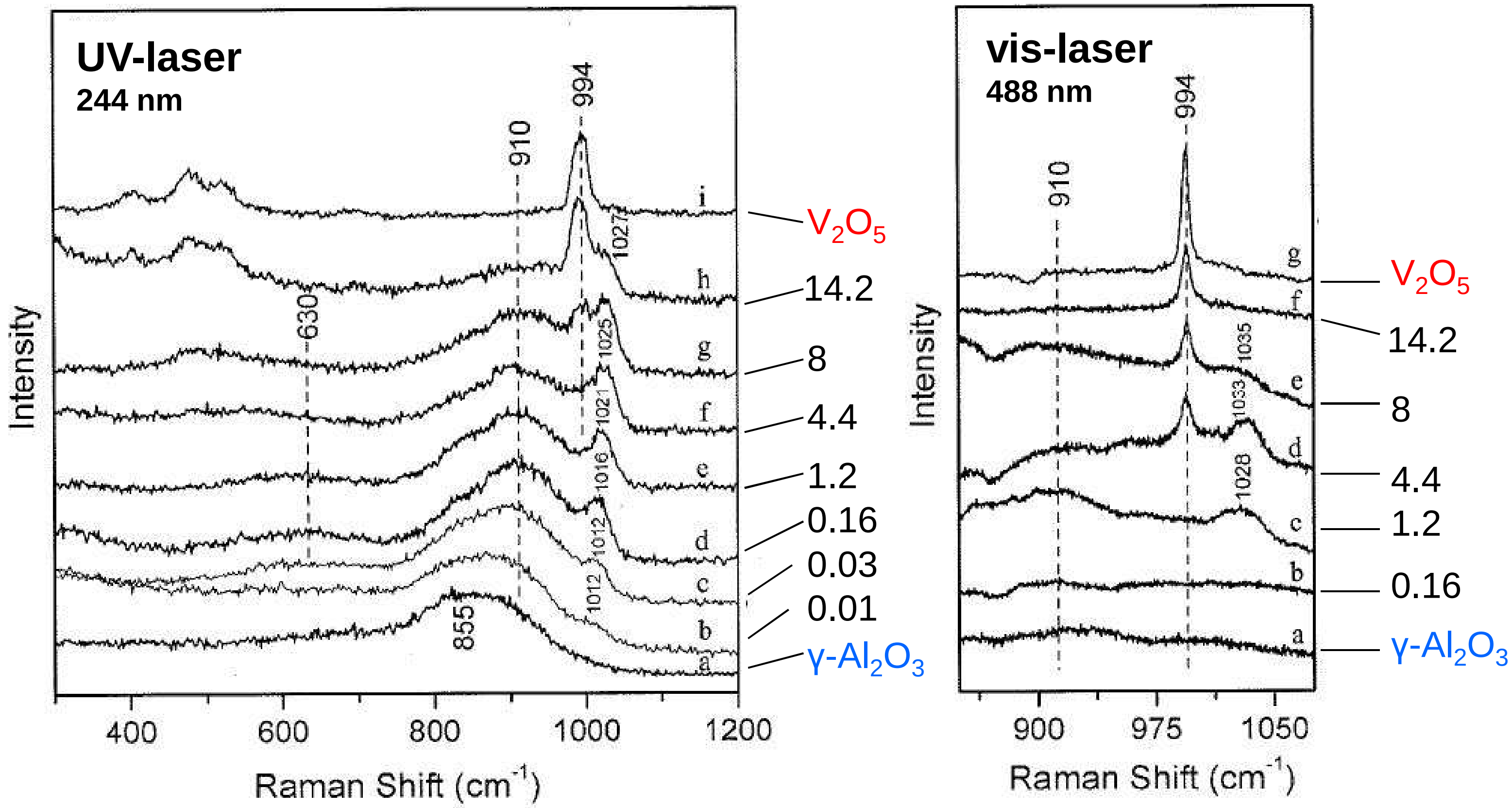
surface MoO_3
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

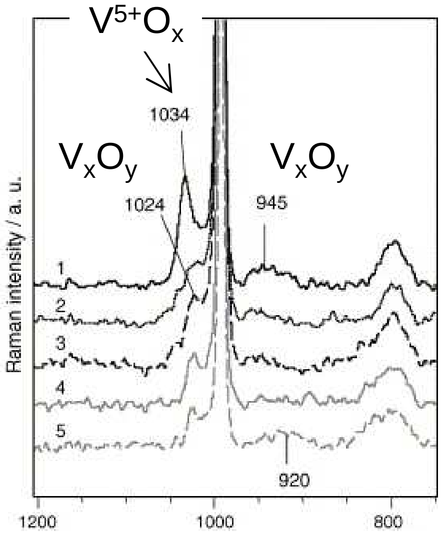
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

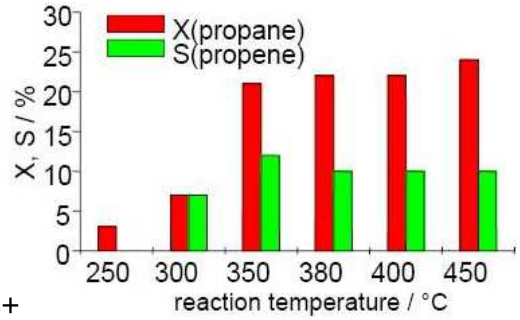
Applications

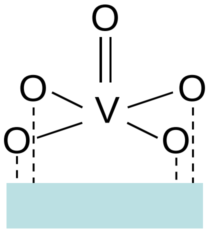
- Reactivity of V/TiO_2 after oxidative treatment

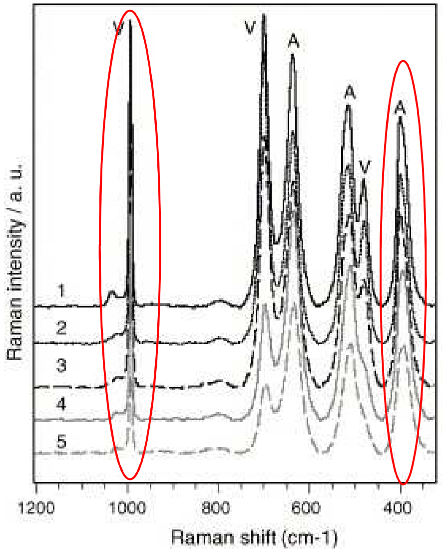


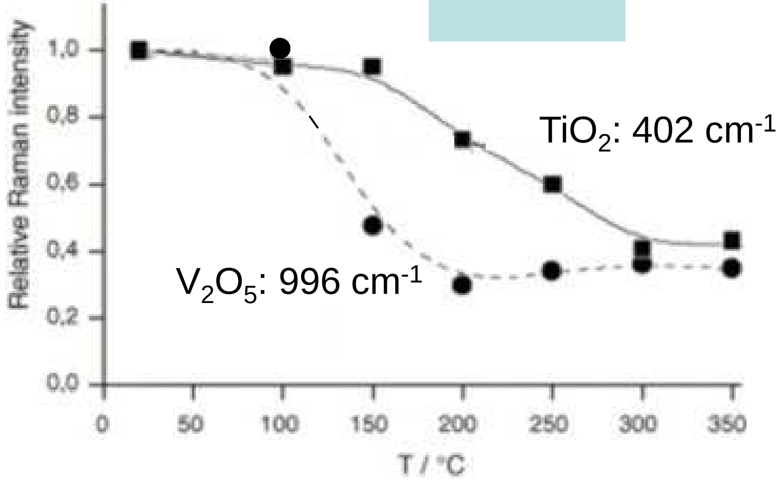
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









TiO_2: 402 cm^{-1}

V_2O_5: 996 cm^{-1}

Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

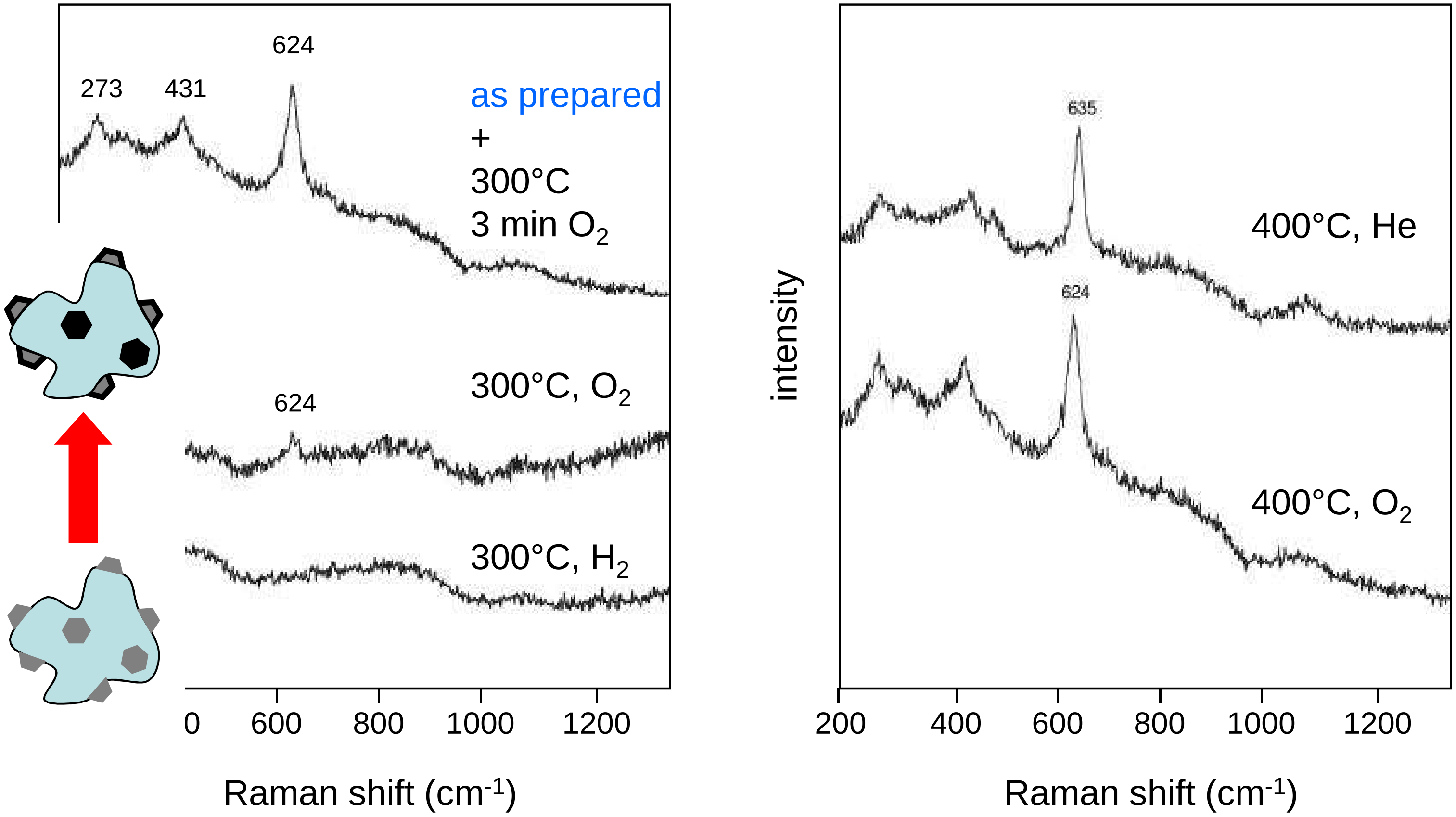
M/MO$_X$ (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



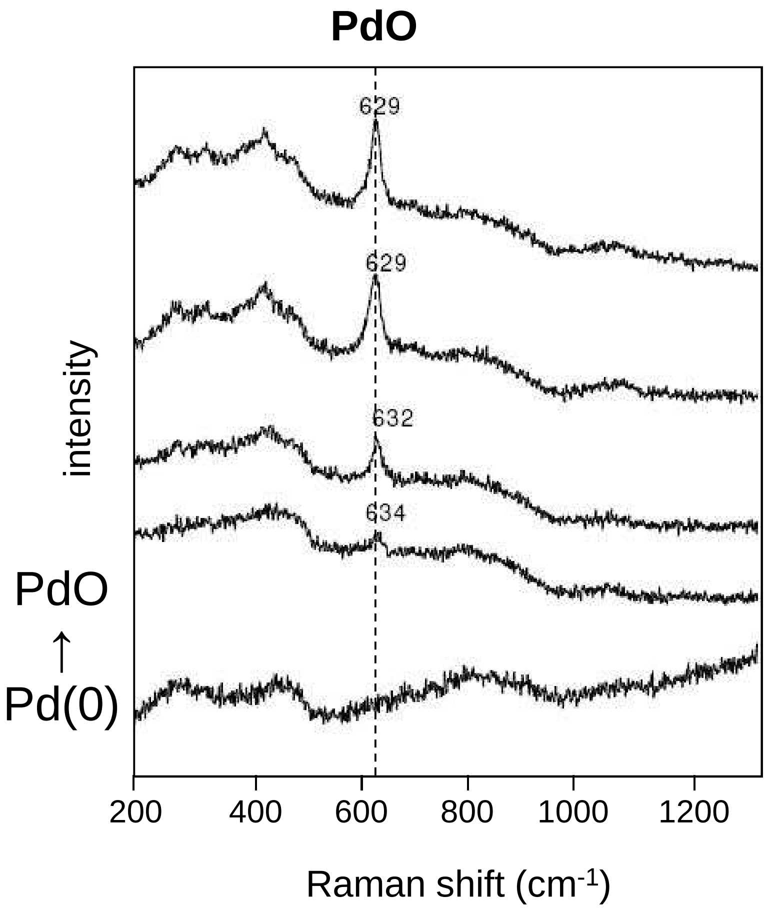
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

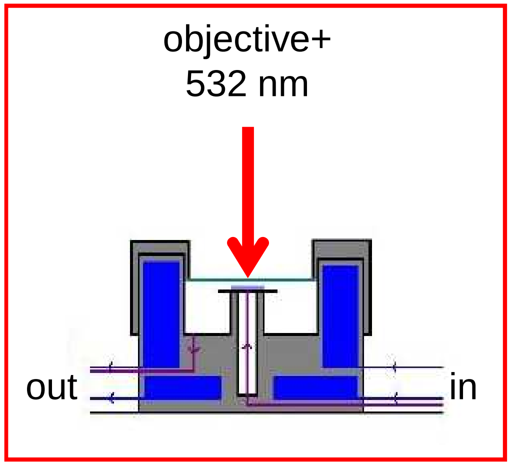
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



	CH_4 conv.
500°C	**24 %**
450°C	**15 %**
425°C	**4 %**
400°C	**2 %**
400°C, H_2 reduced Pd	

↑ feed CH_4/O_2 (1:10)

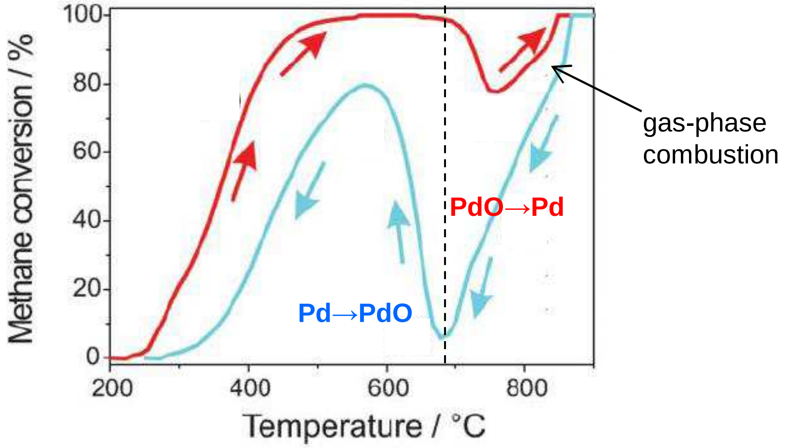
near PdO mode

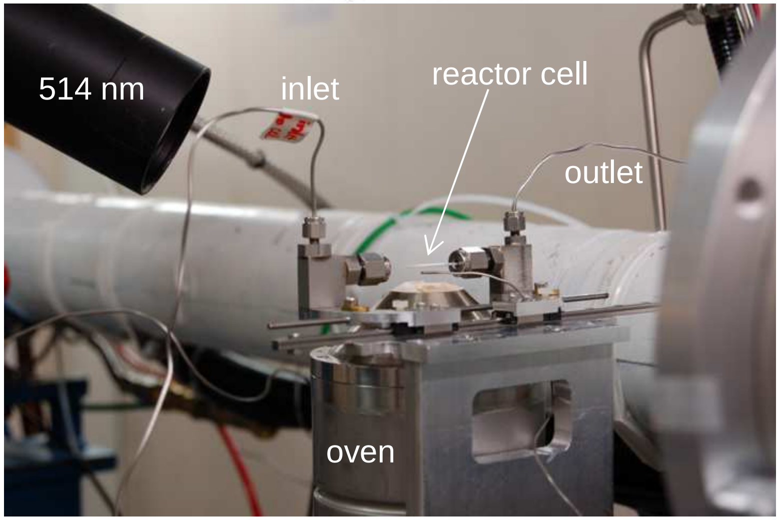


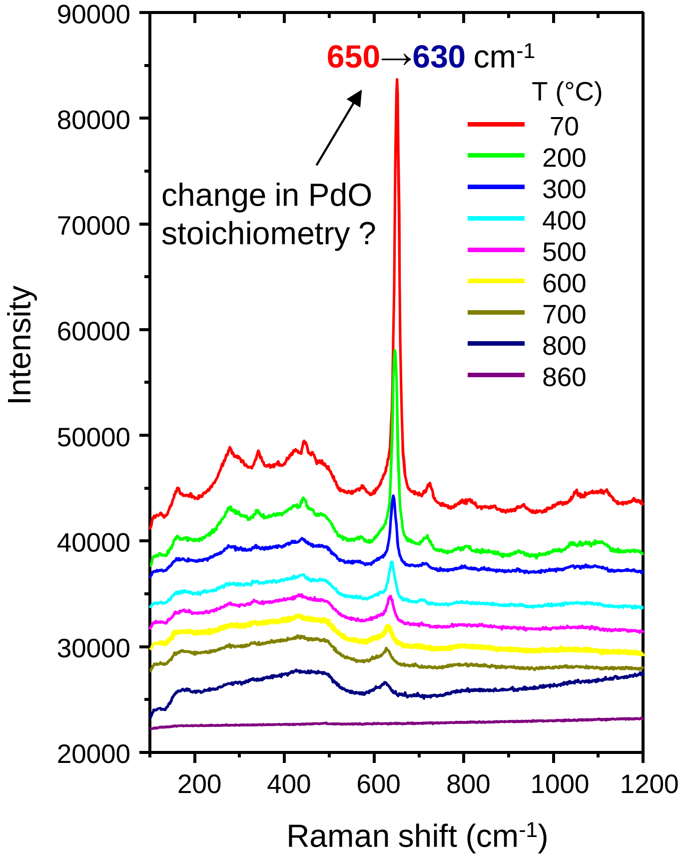
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

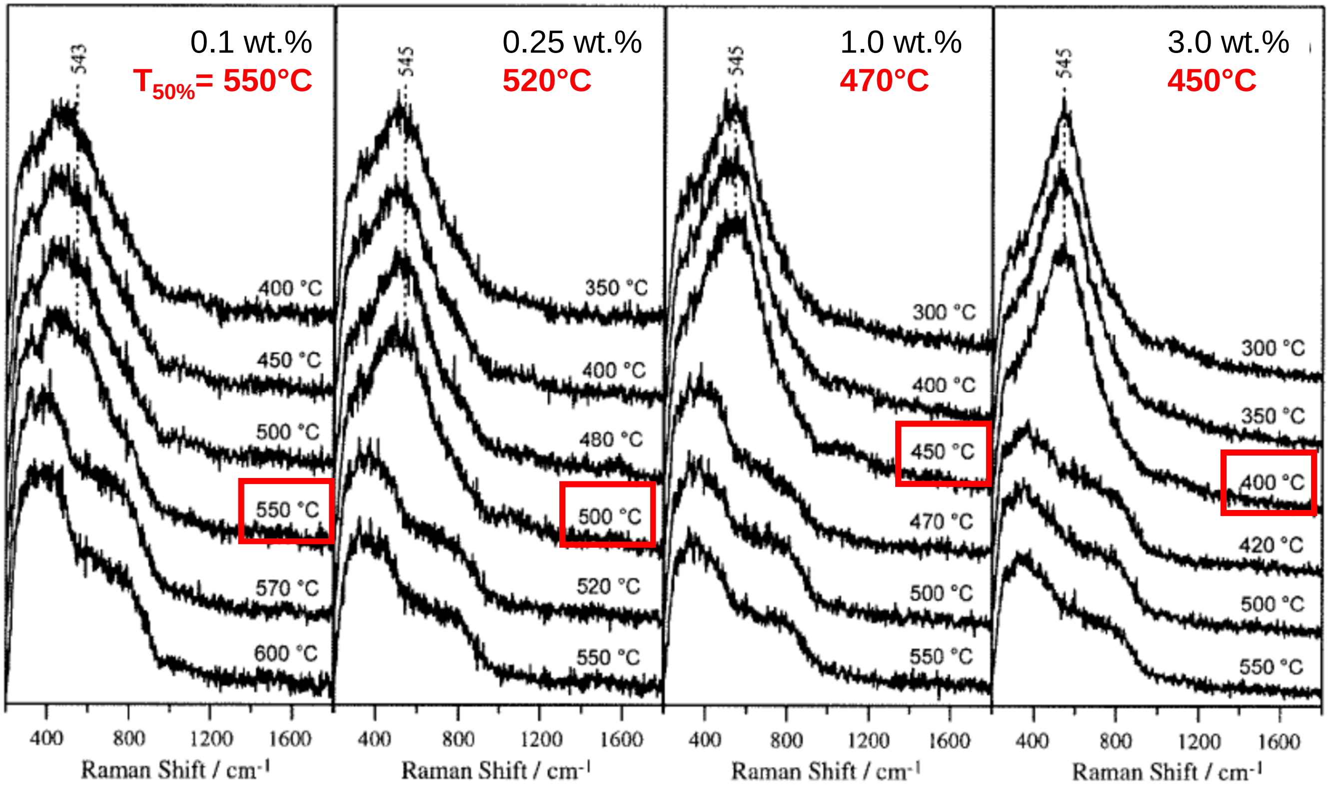
- Methane partial oxidation over Rh/Al_2O_3

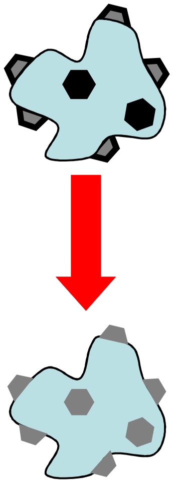
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content →
Activity →

RhO_x
↓
Rh(0)





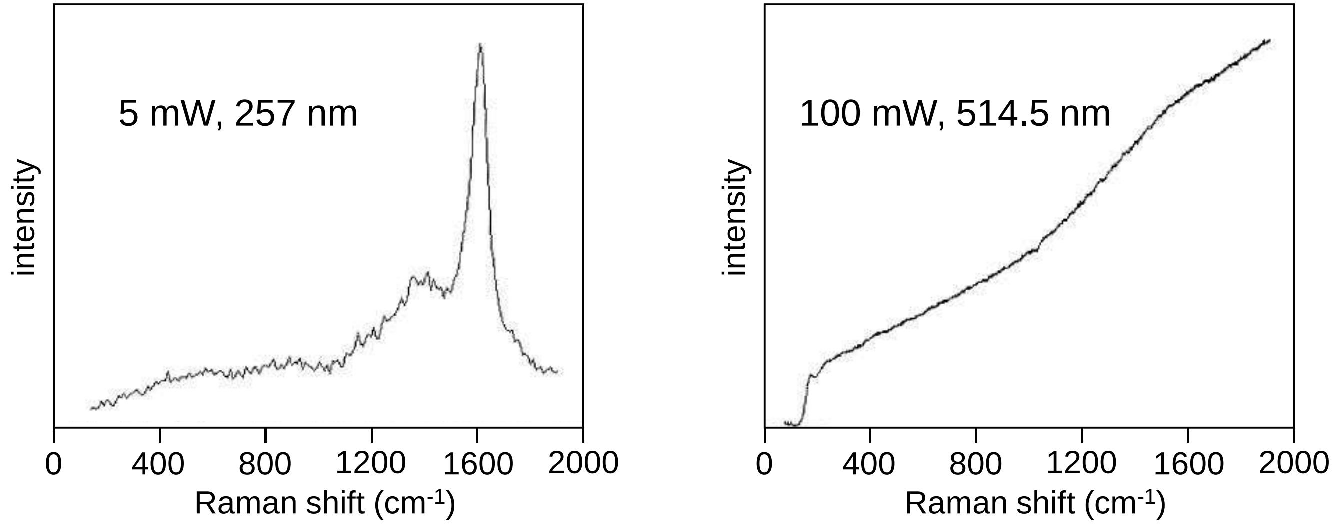
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - ❑ No fluorescence

  (only few molecules fluoresce below 260 nm)

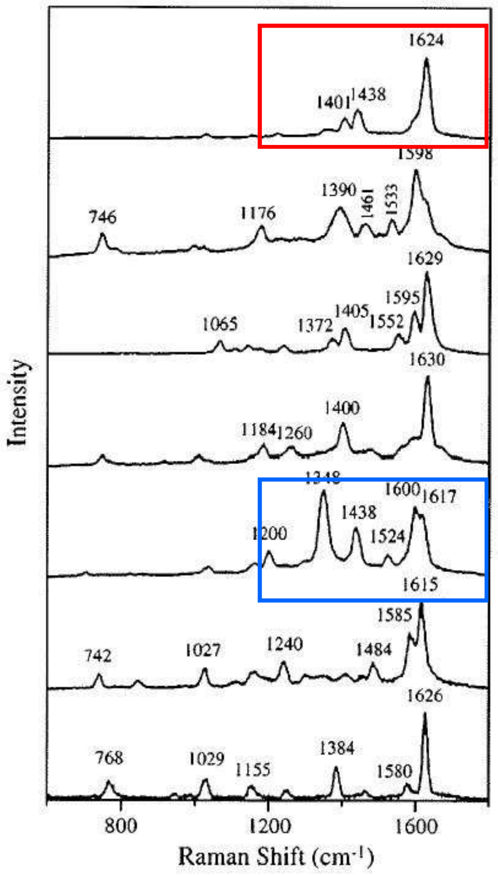
Rh/Al$_2$O$_3$, coked 500°C in naphtha

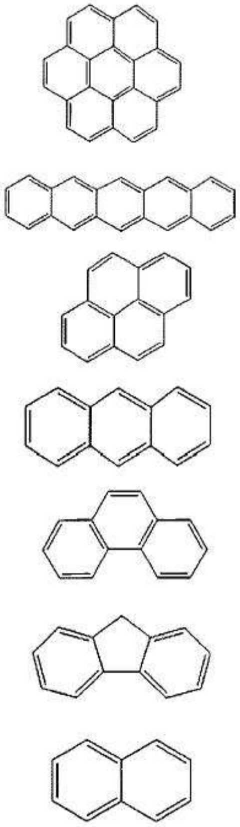


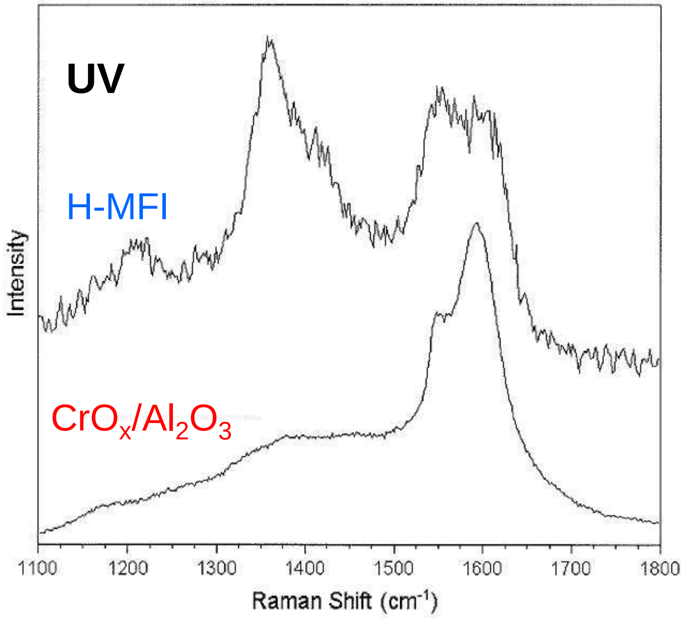
Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization







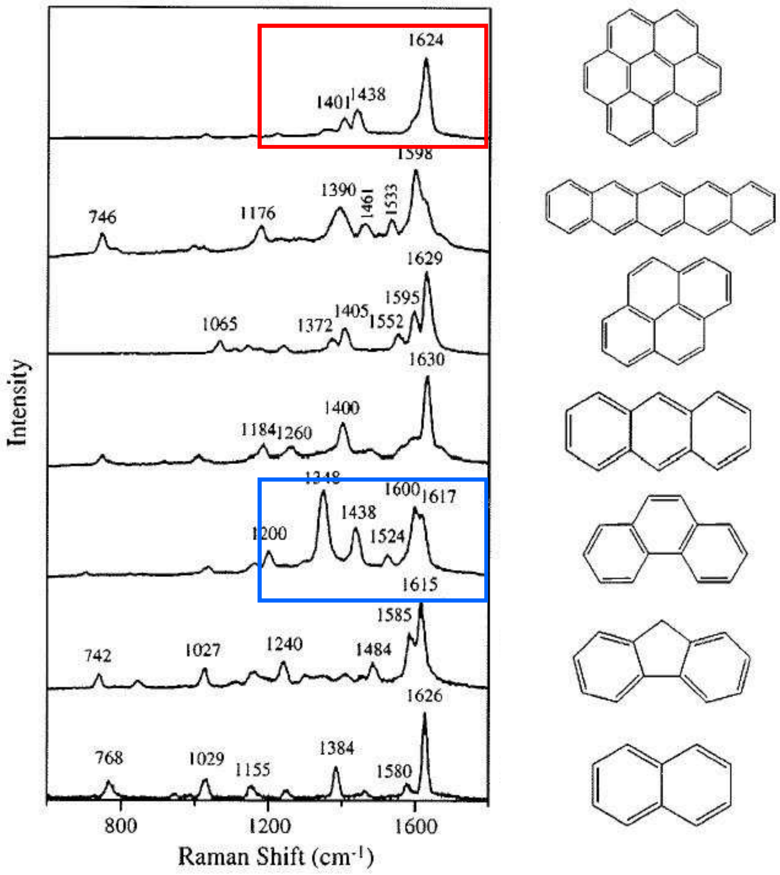
Coke classification
1D topology, chain-like
2D topology, sheet-like

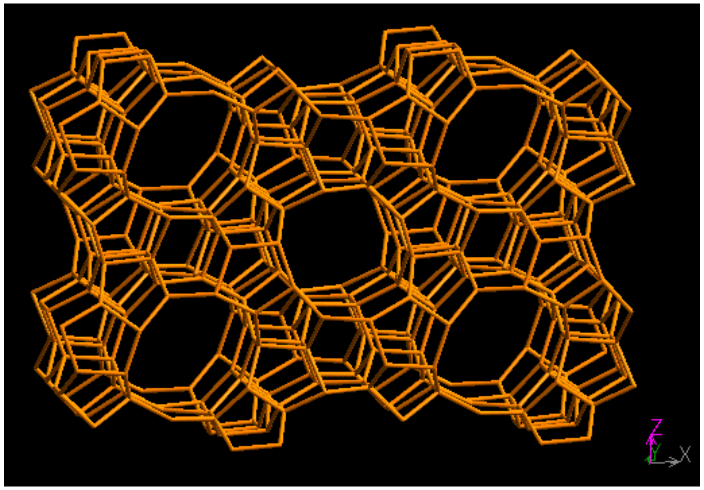
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





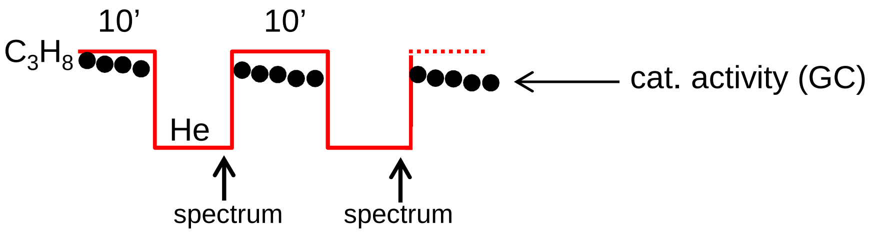
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

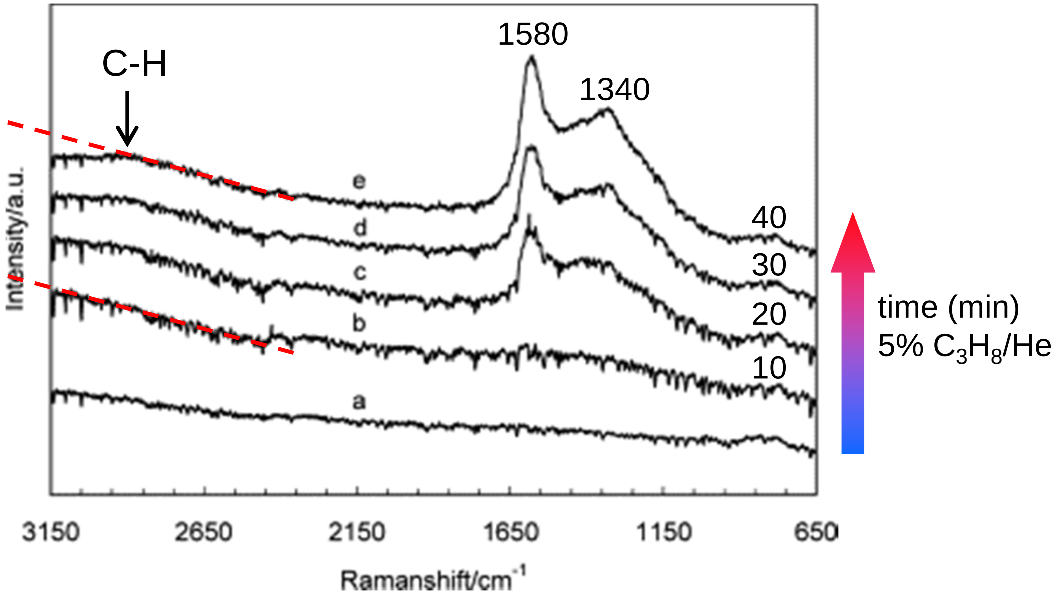
Stair, *Adv. Catal.* **51** (2007) 75

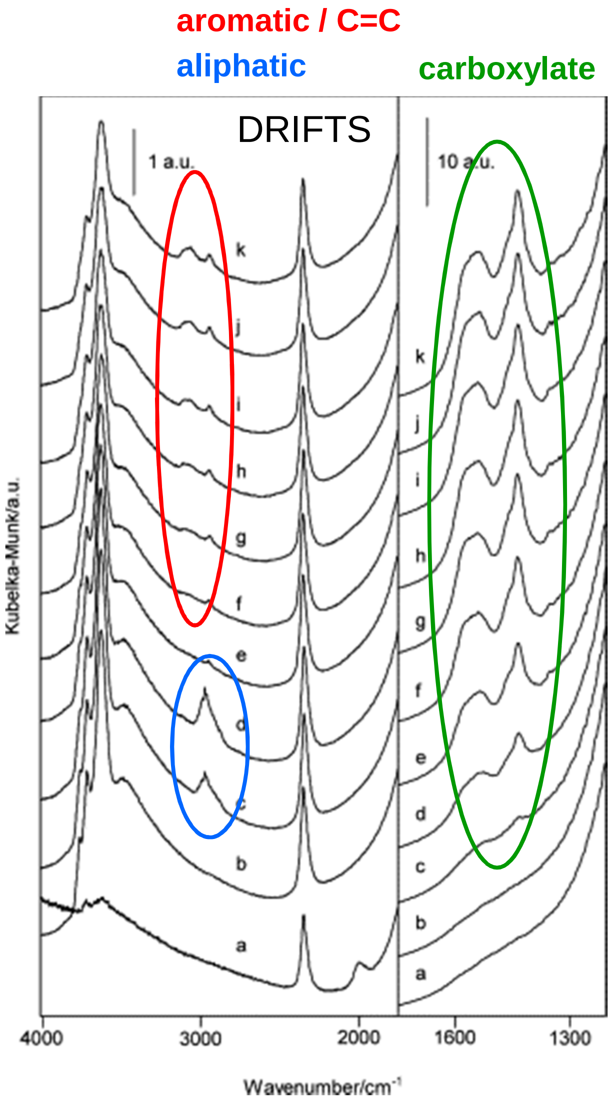
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

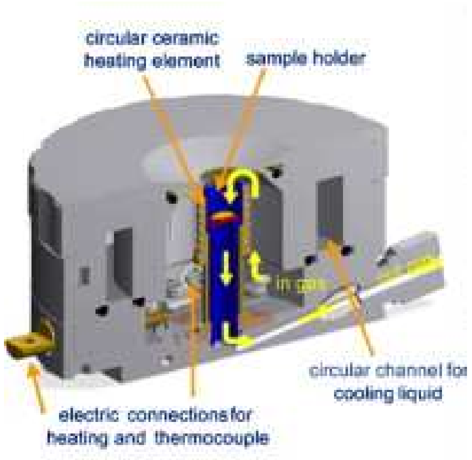


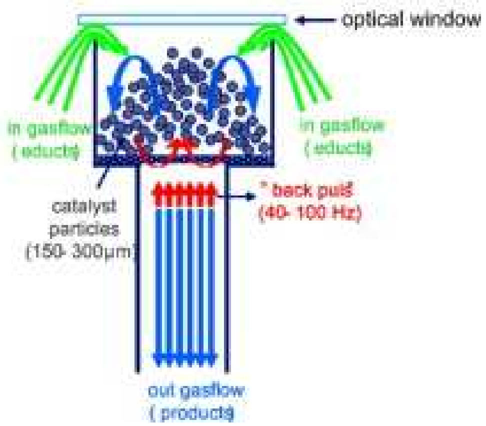


Airaksinen et al., *J. Catal.* **230** (2005) 507

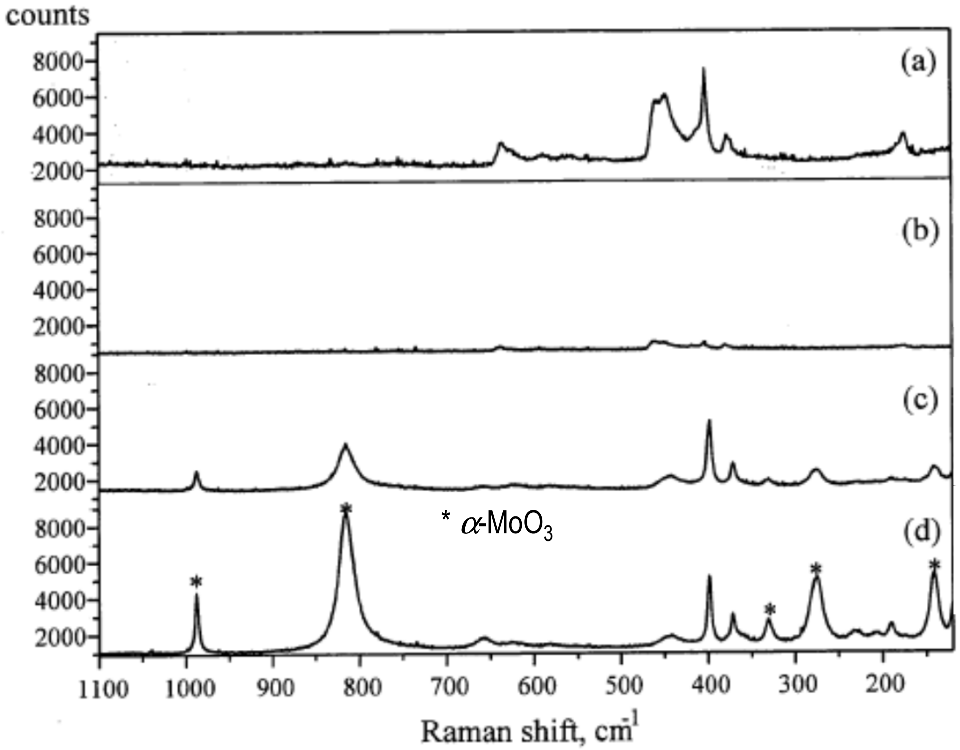
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min
full power, FB

MoS_2, 6 min
1/8 power

MoS_2, 1 min
full power

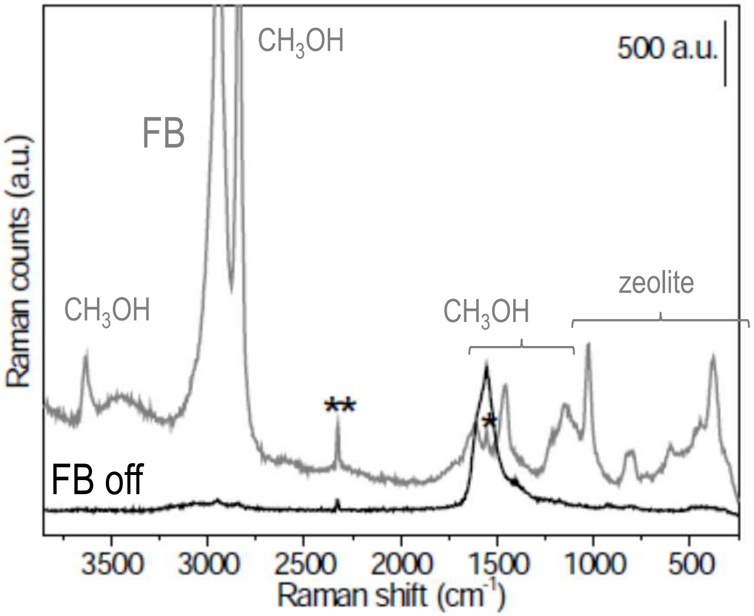
MoS_2, 6 min
full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

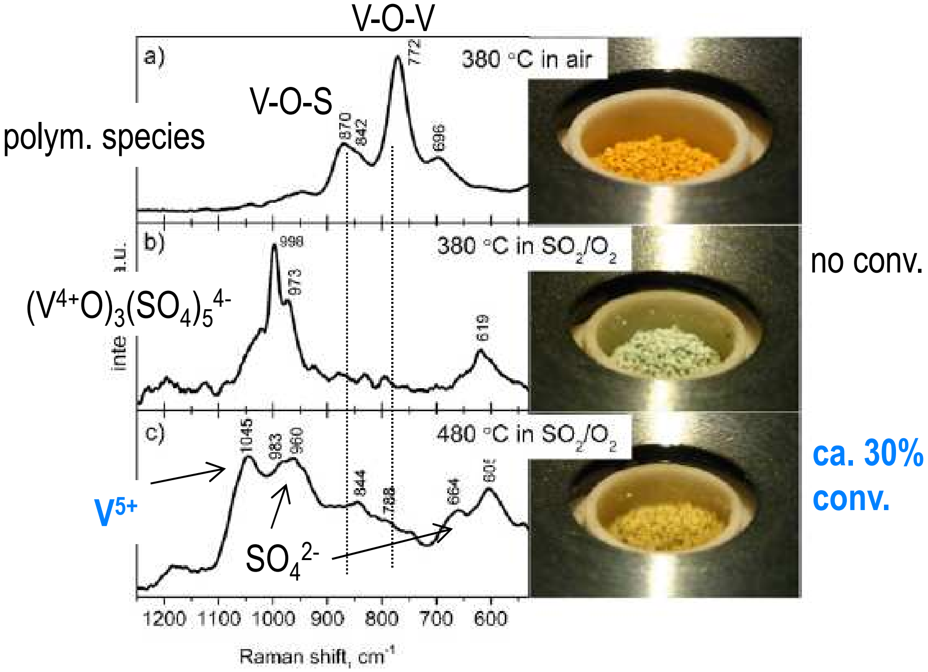
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

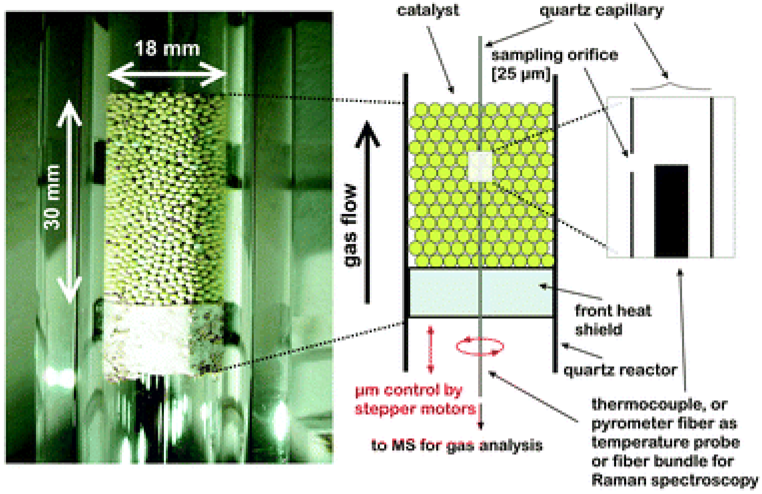


active species: mono- & dimeric V^{5+} oxosulfate species

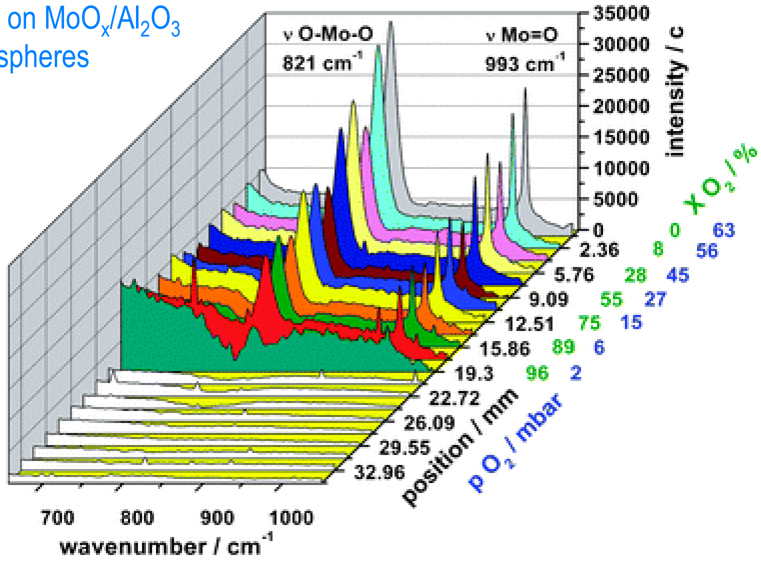
Beato et al., *Catal. Today* 205 (2013) 128

Applications

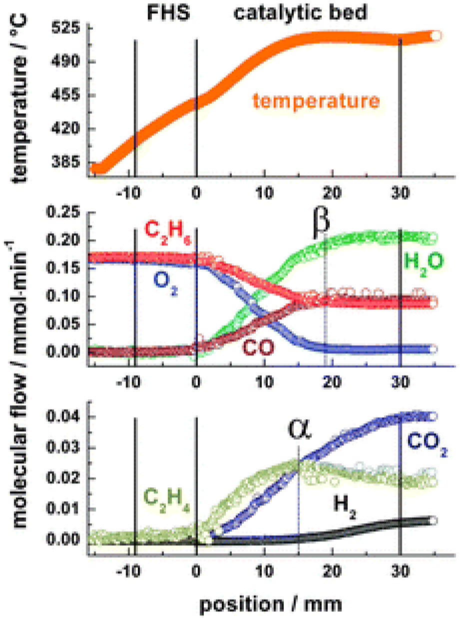
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

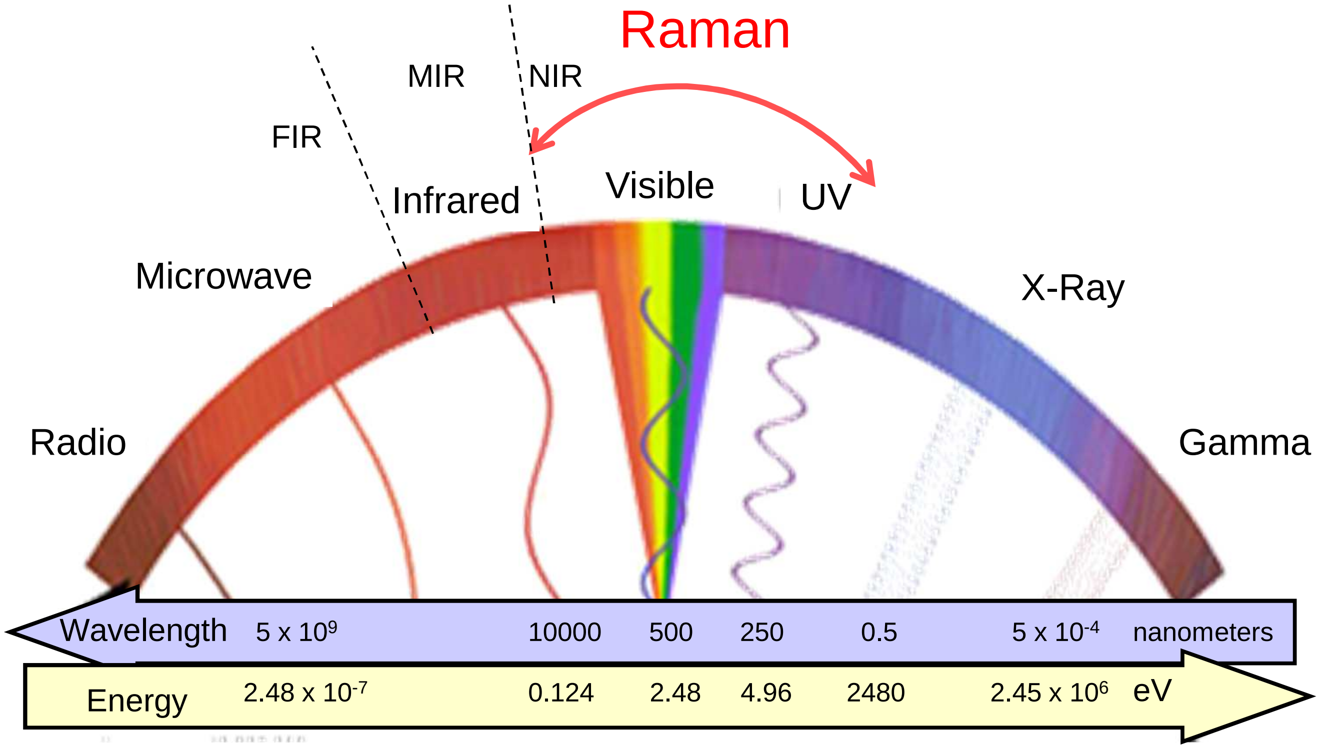
February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

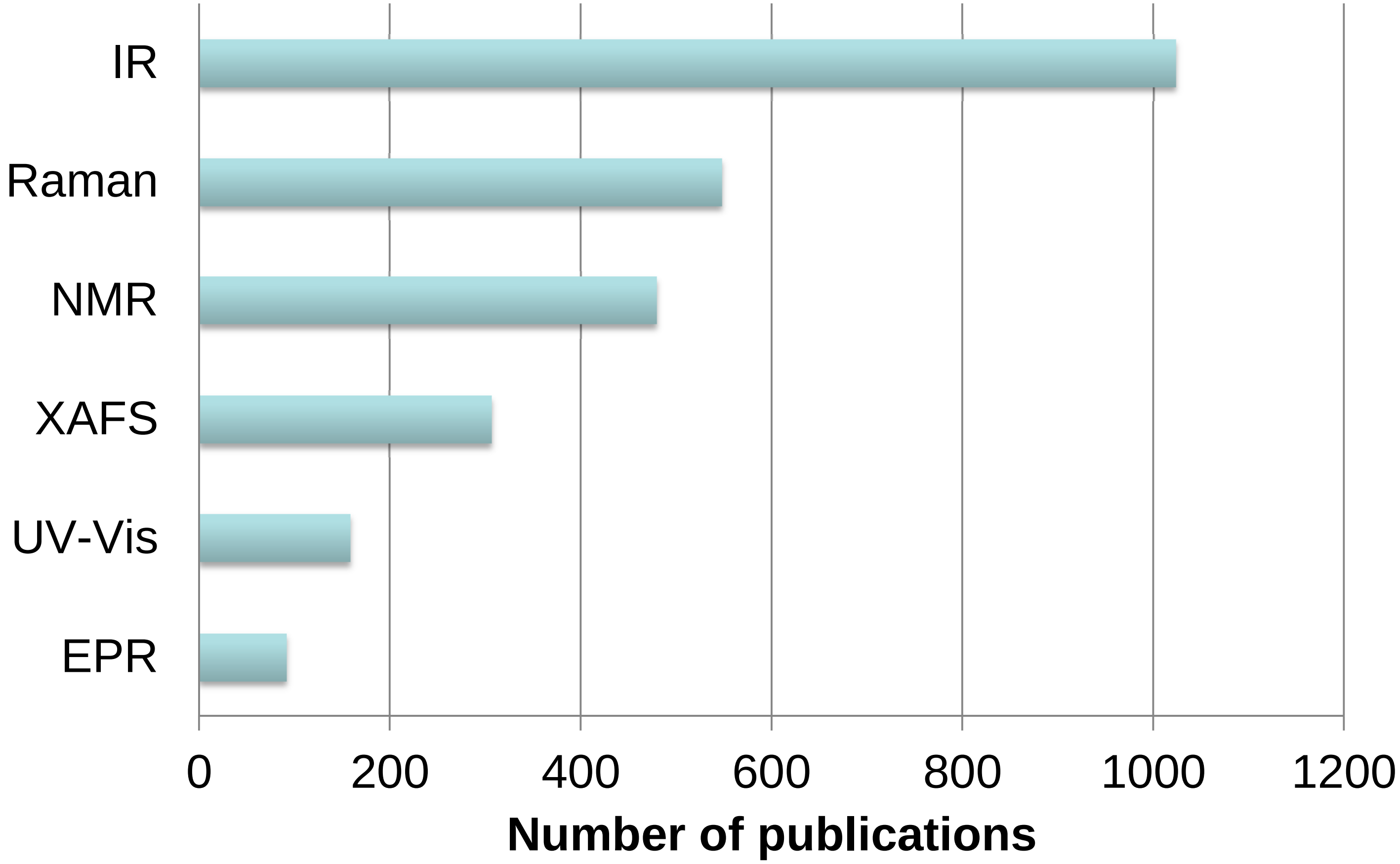
Literature:

M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104
Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1
http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

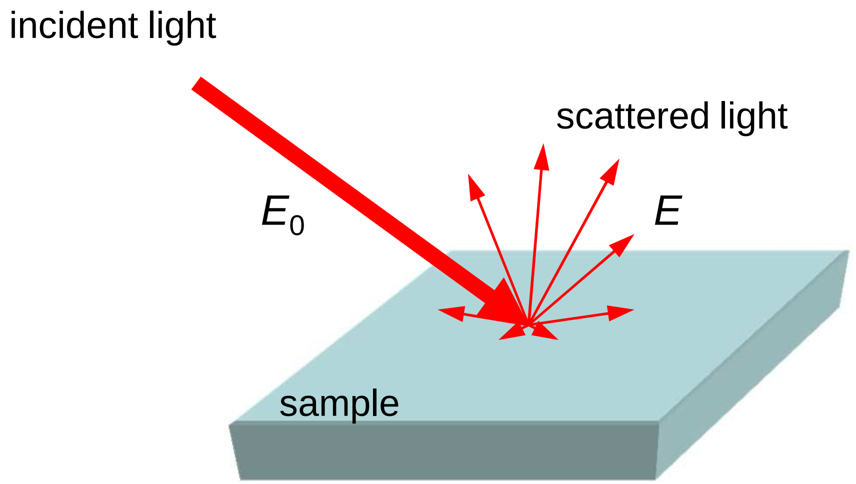


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and $$\boxed{\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha/2 E_0\cos[2\pi(\nu_0+\nu_{vib})t] + \alpha/2 E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}$$

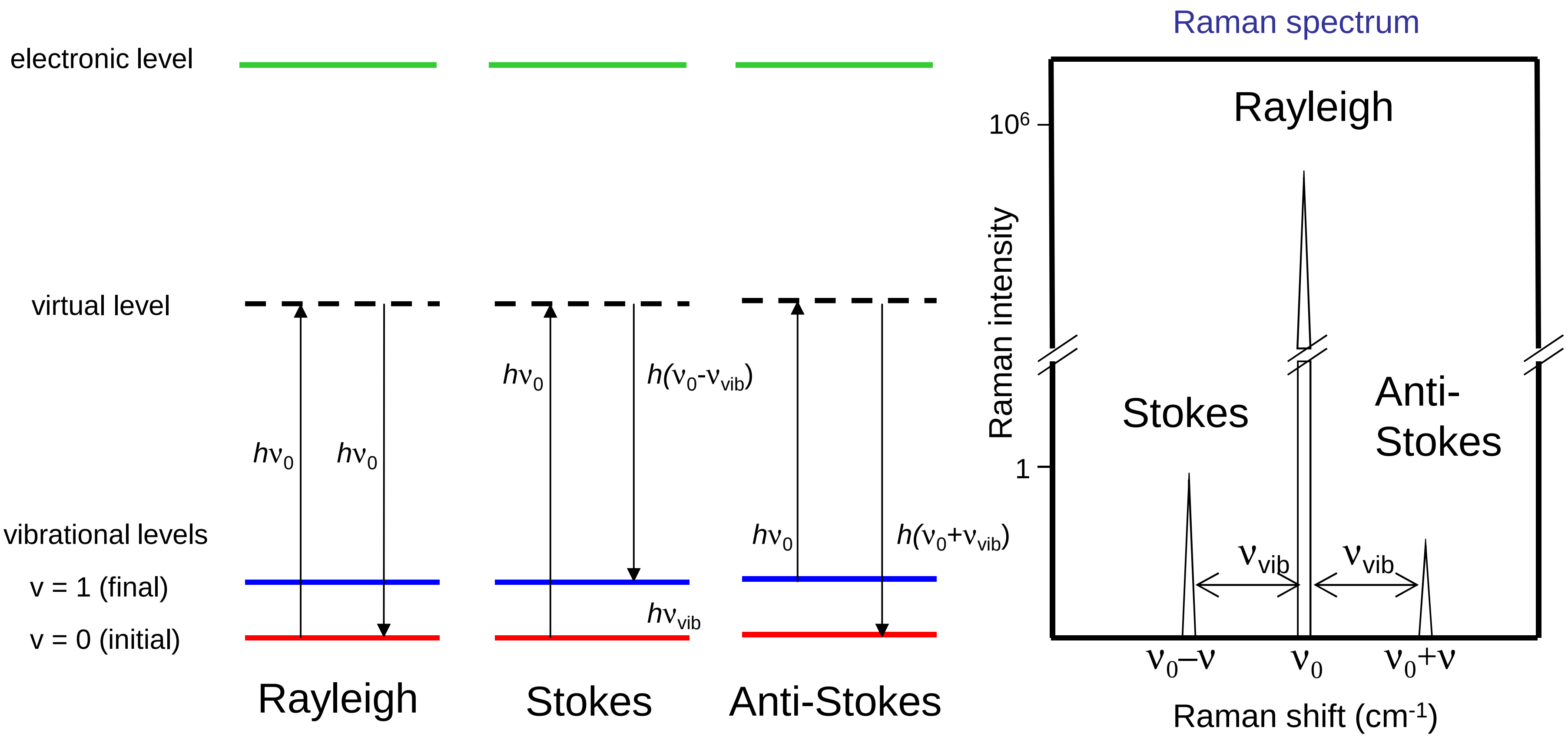
Rayleigh

Anti-Stokes

Stokes

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\ (\text{Anti-Stokes})}{I\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

  - 4th power of ν (4th power law)

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

  - 2nd power of $\Delta\alpha$
    - properties of molecules
    - strength of bonds

↓

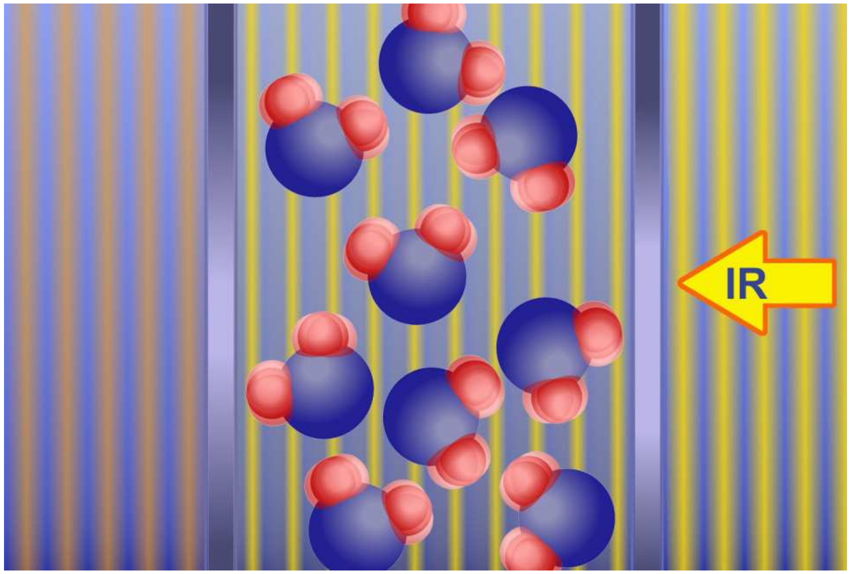
covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

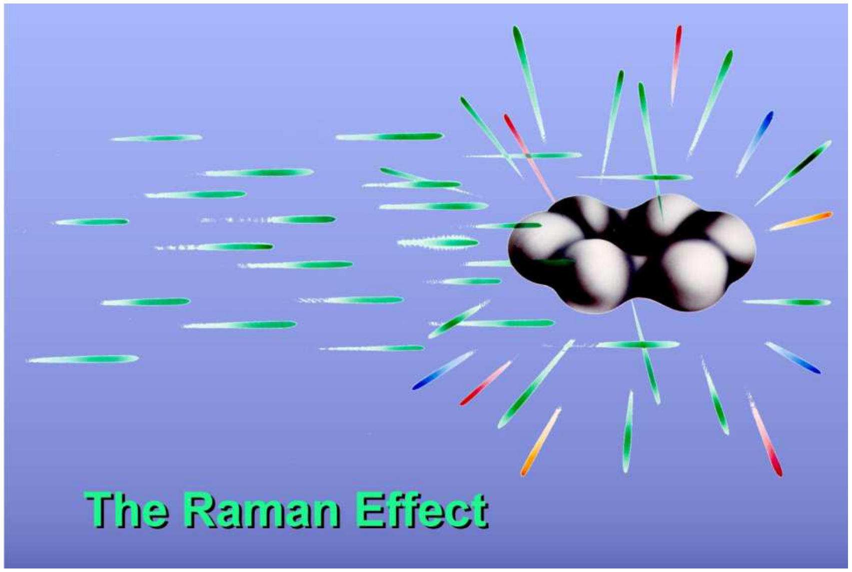
- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

Raman *vs.* Infrared

Infrared

Raman





Absorption of IR light

Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial\mu}{\partial Q}\right)^2 \neq 0$$

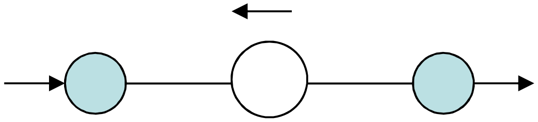
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial\alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - large electron clouds
  - not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

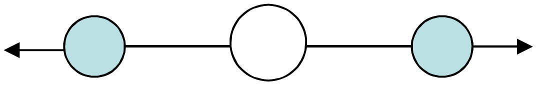
Raman *vs.* Infrared

CO_2



ν_{as}

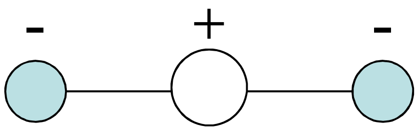
2349 cm^{-1}



ν_s

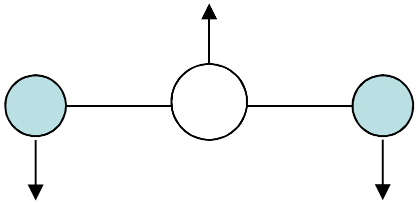
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



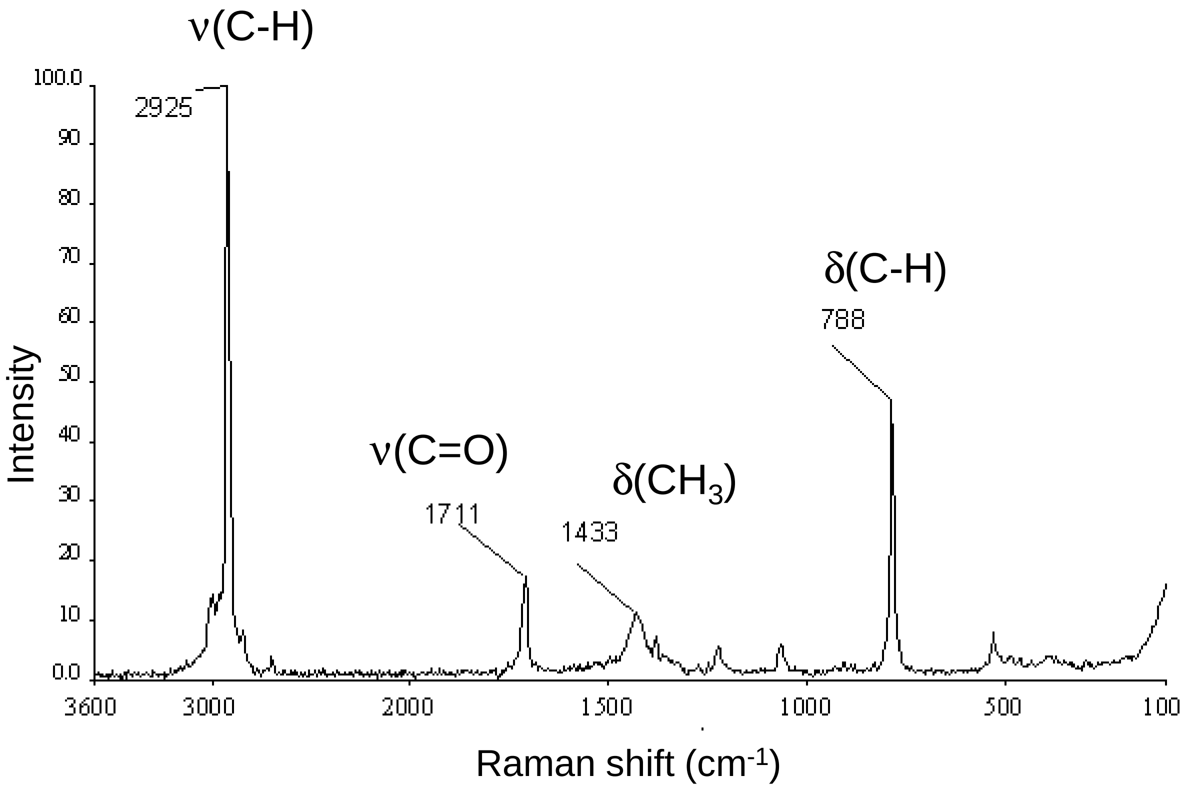
δ

667 cm^{-1}

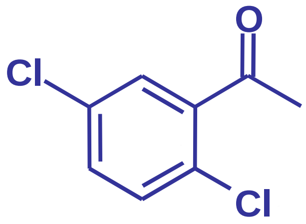
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



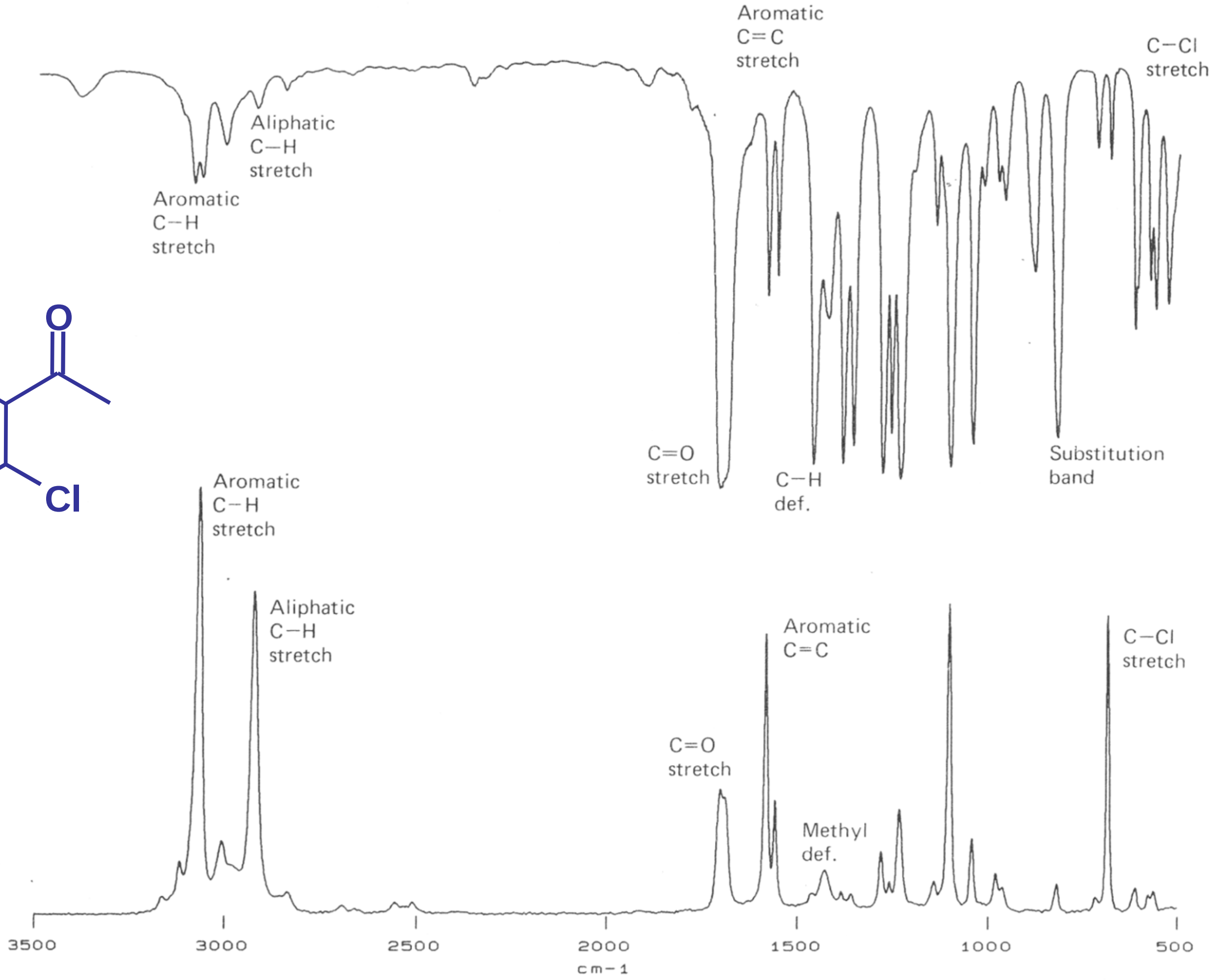


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

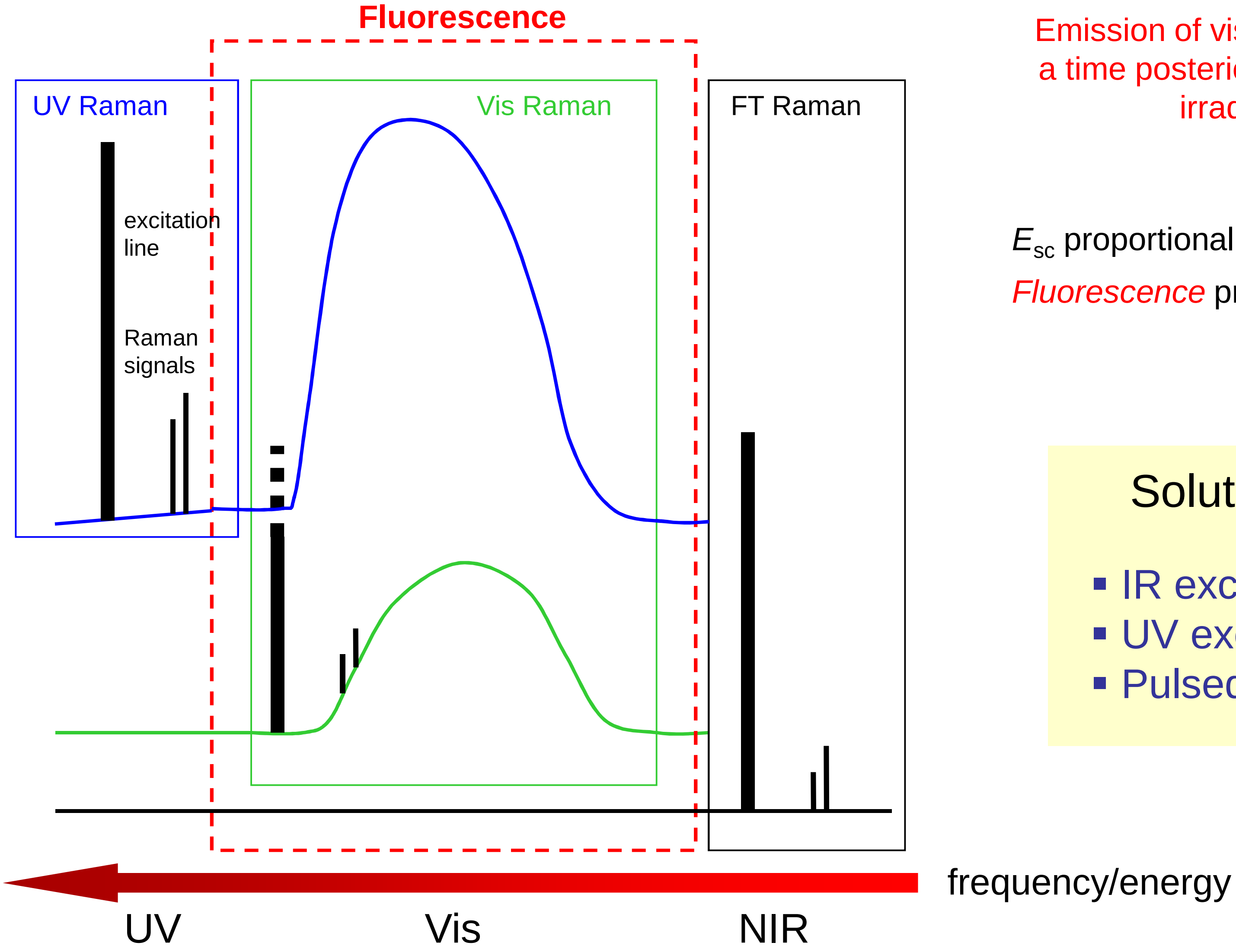
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 μm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

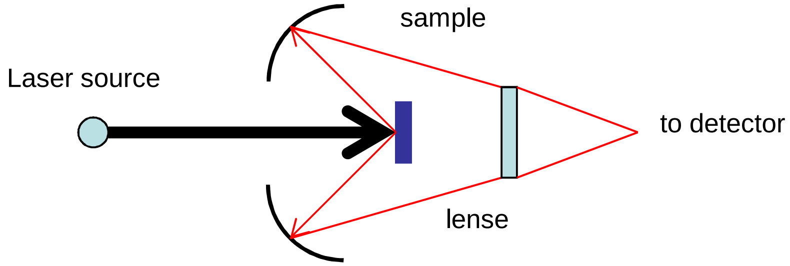
Fluorescence proportional to ν

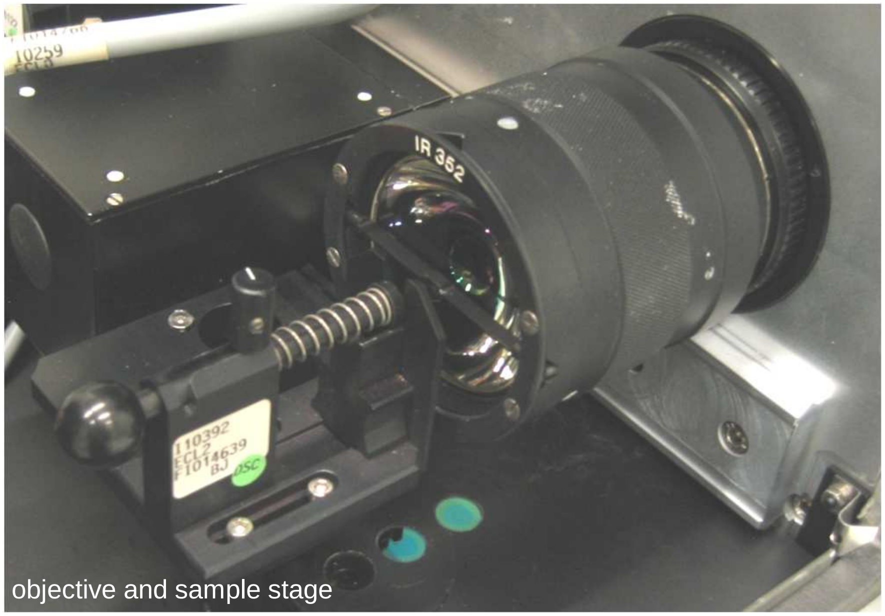
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers
Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

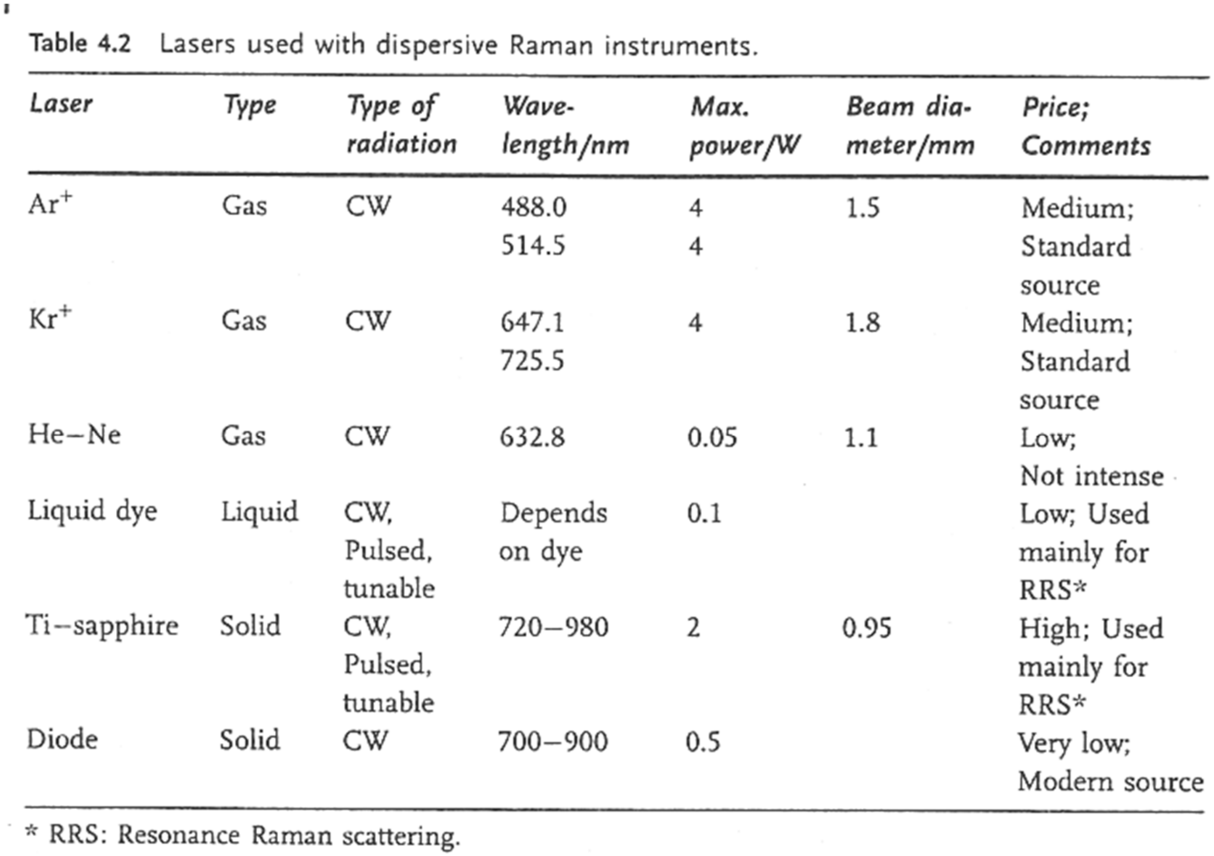


Table 4.2 Lasers used with dispersive Raman instruments.

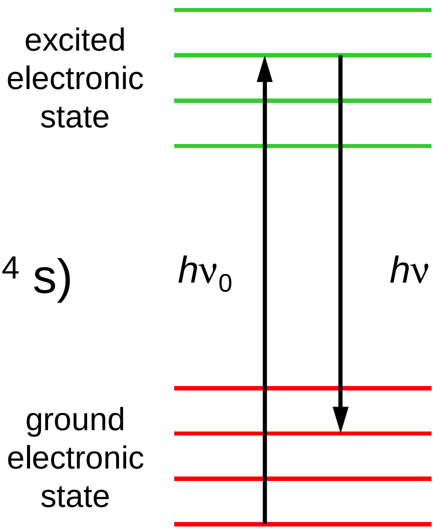
Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

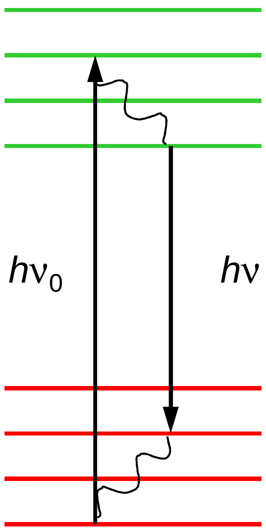
Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited

fast (10^{-14} s)



Resonance Raman scattering



Fluorescence

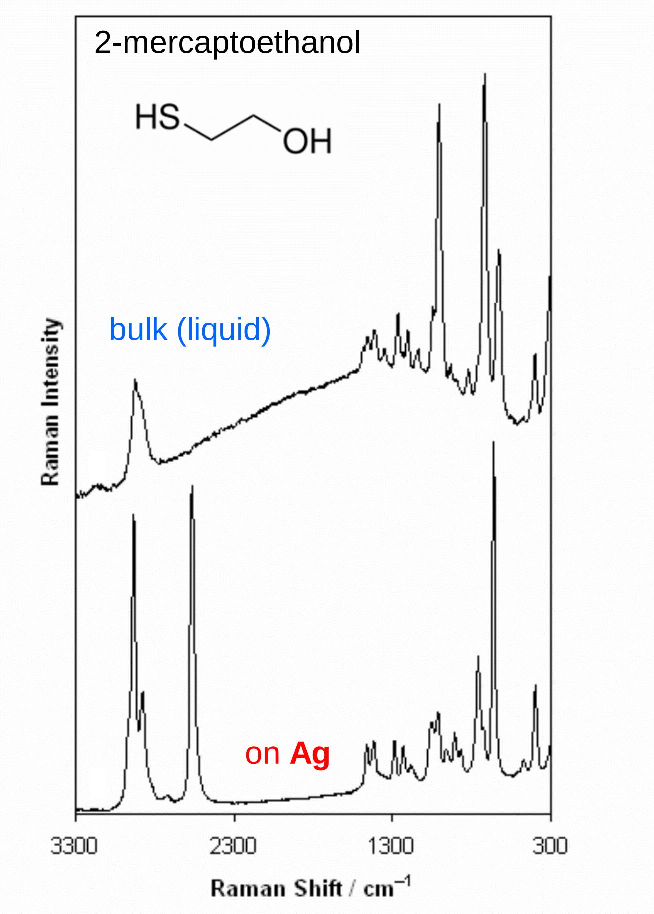
slow (10^{-9}–10^{-6} s)

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

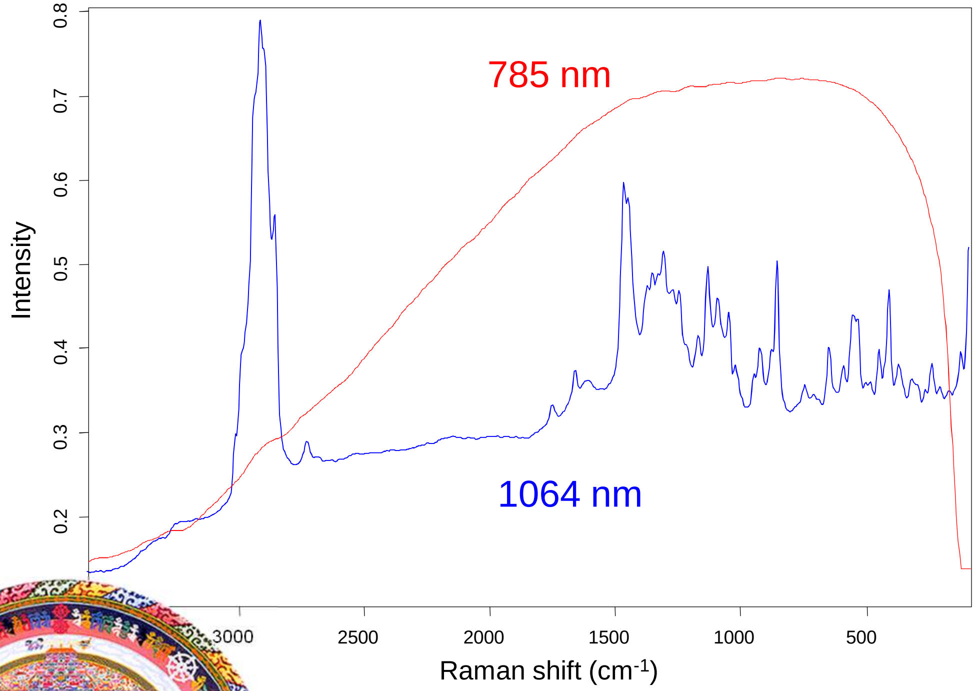
- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

- Remarks:
  - rough surface; nanoparticles (10–100 nm) or kinks, steps etc. (E always perpendicular to surface, locally)
  - vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



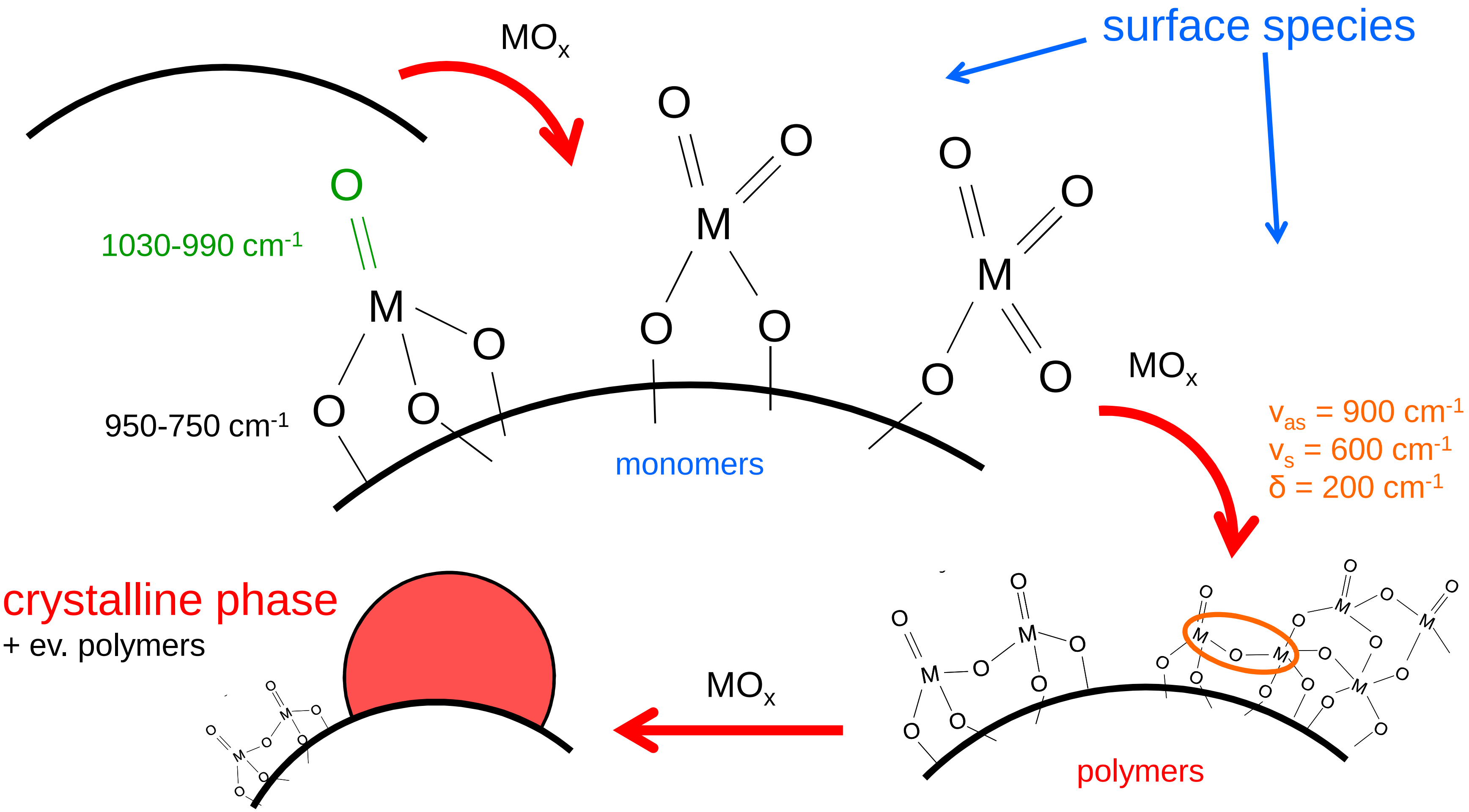
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



MO_x

surface species

1030-990 cm^{-1}

950-750 cm^{-1}

monomers

MO_x

ν_{as} = 900 cm^{-1}
ν_s = 600 cm^{-1}
δ = 200 cm^{-1}

polymers

MO_x

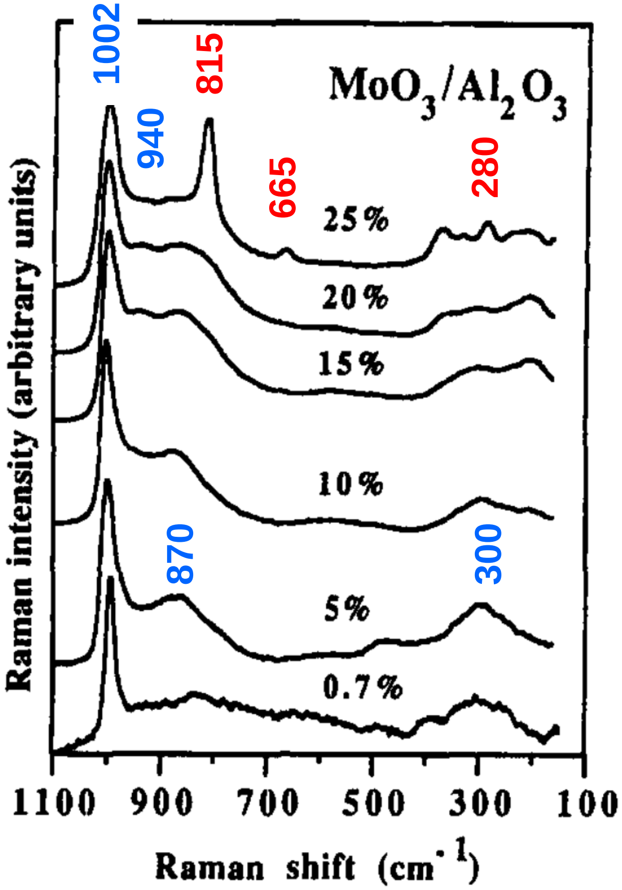
crystalline phase
+ ev. polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



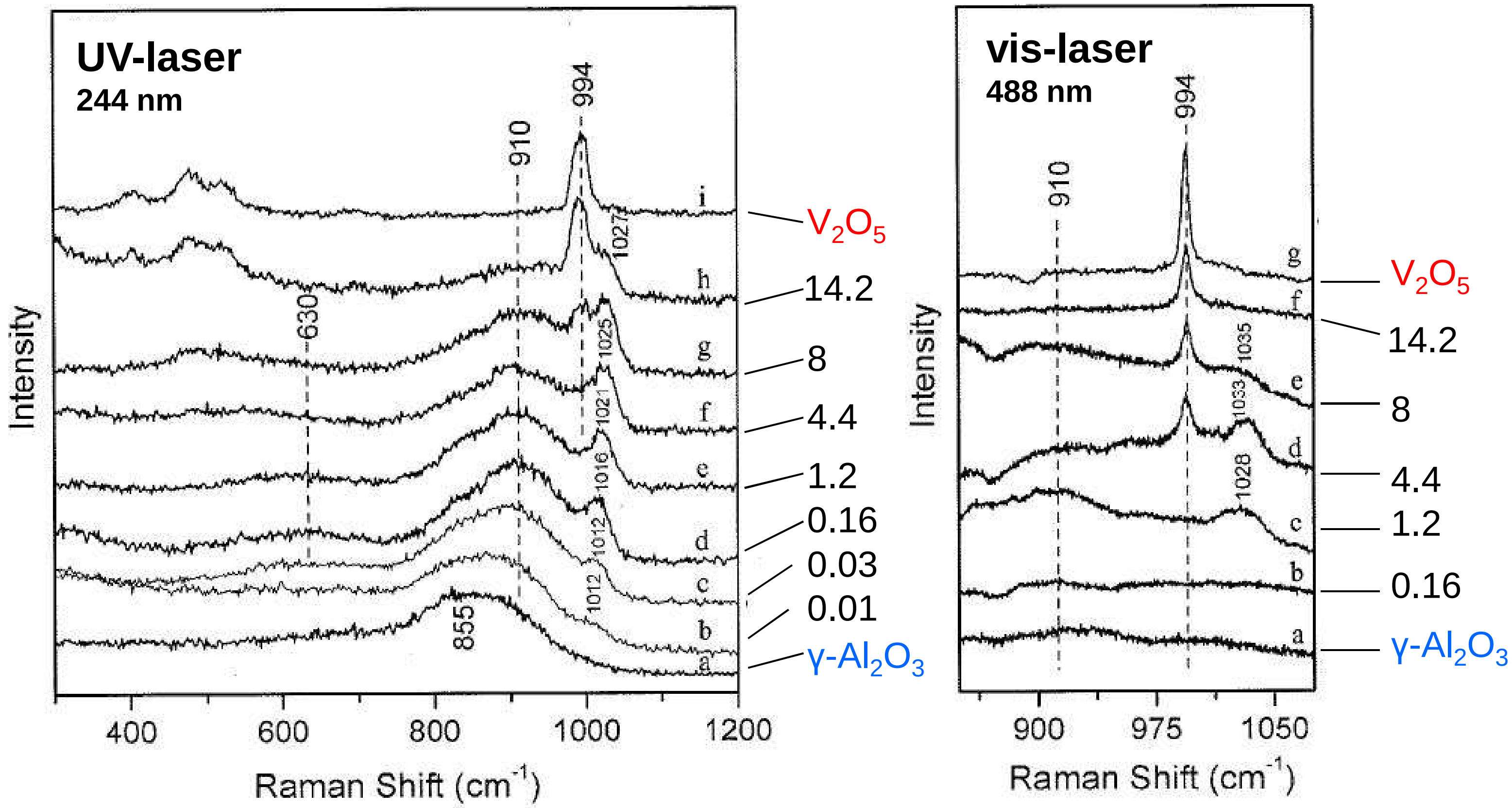
surface MoO_3
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

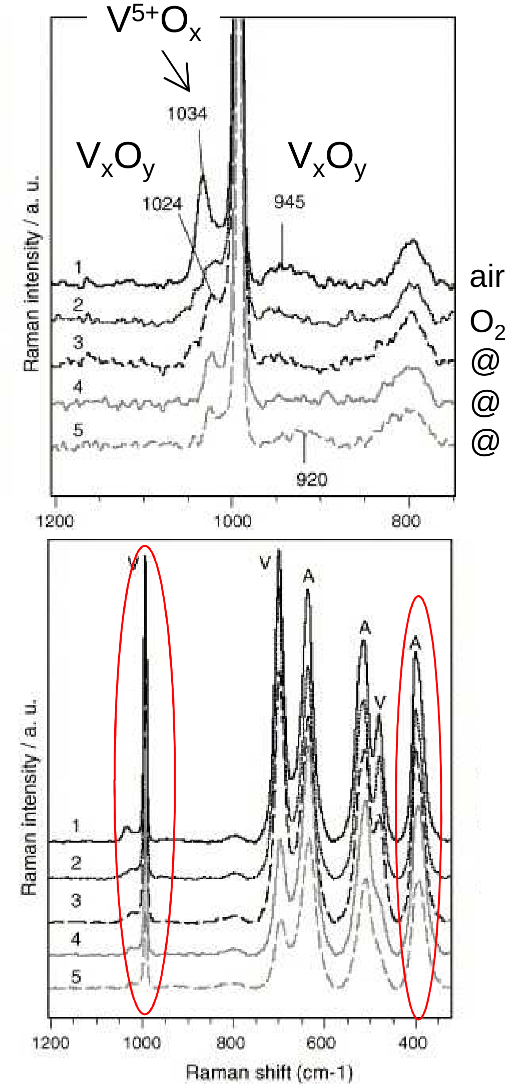
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

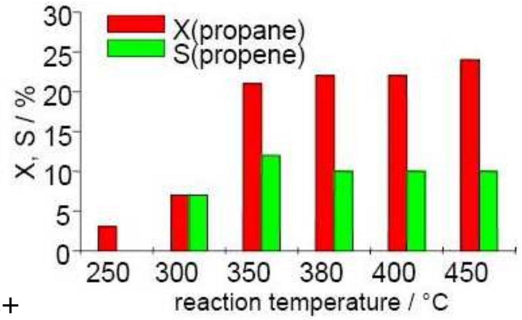
Applications

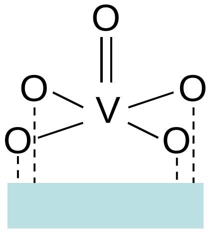
- Reactivity of V/TiO$_2$ after oxidative treatment

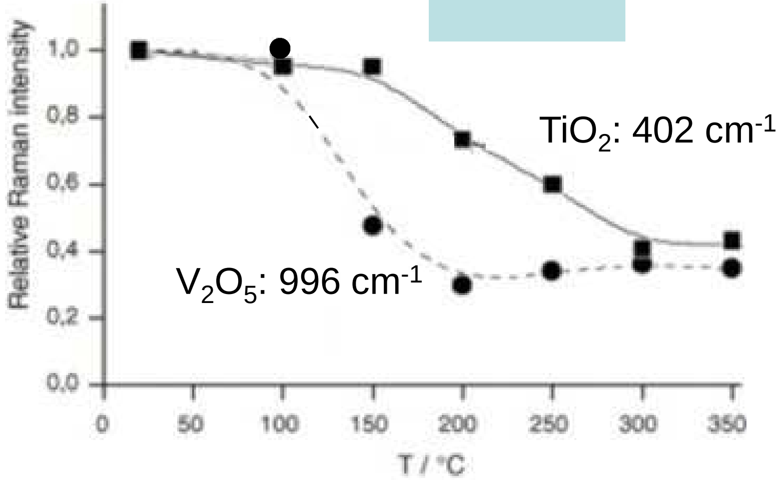


air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$







TiO$_2$: 402 cm^{-1}

V$_2$O$_5$: 996 cm^{-1}

Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

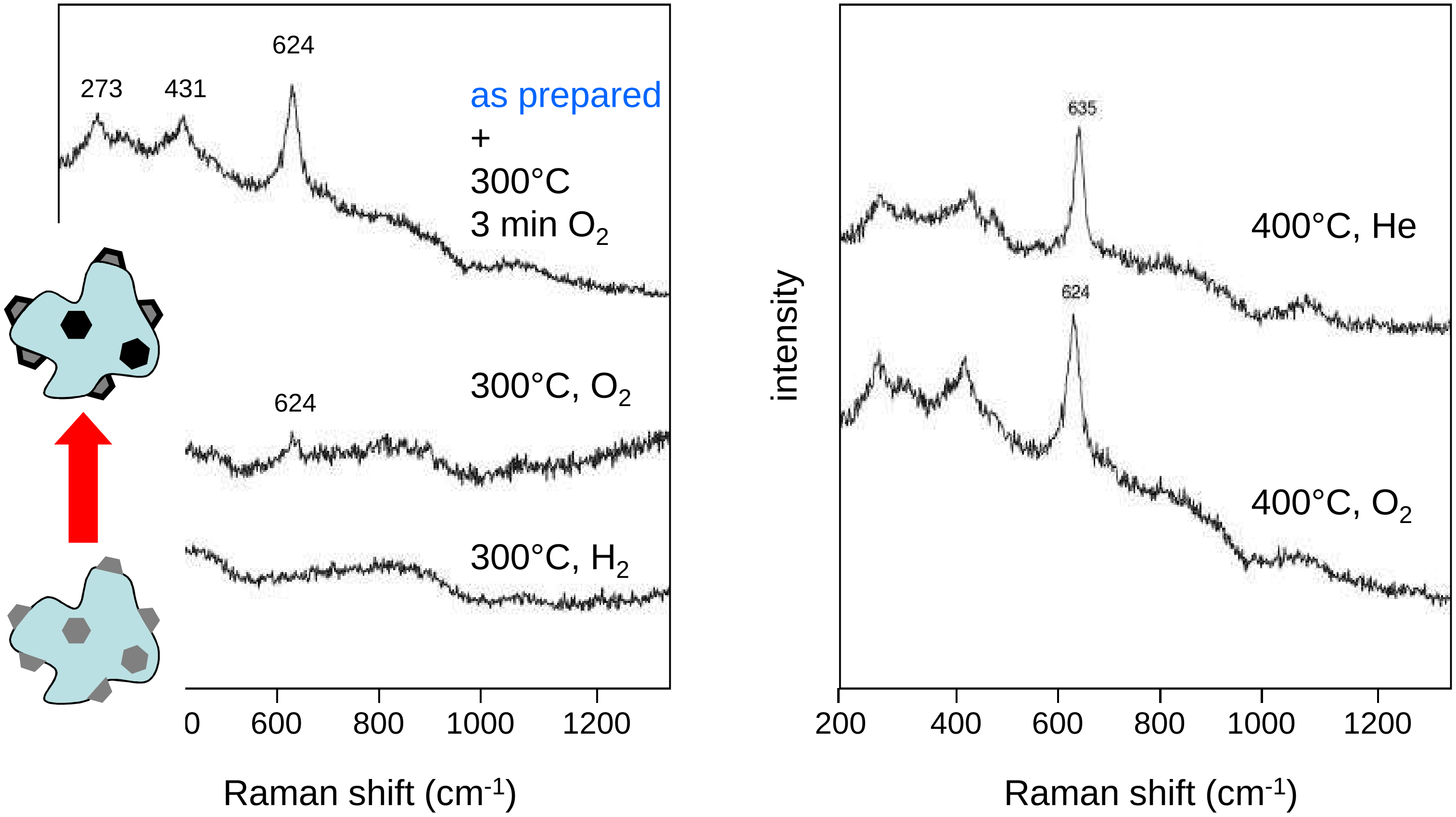
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



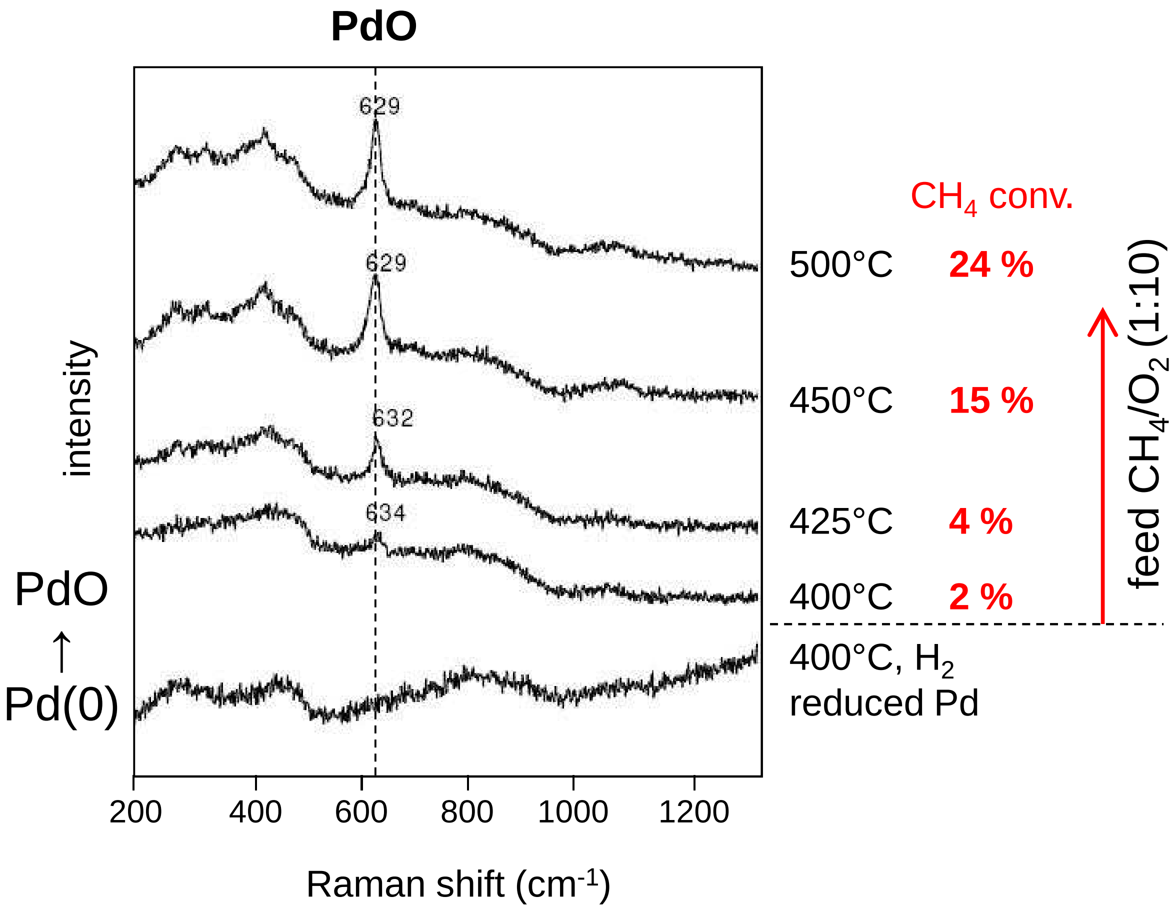
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

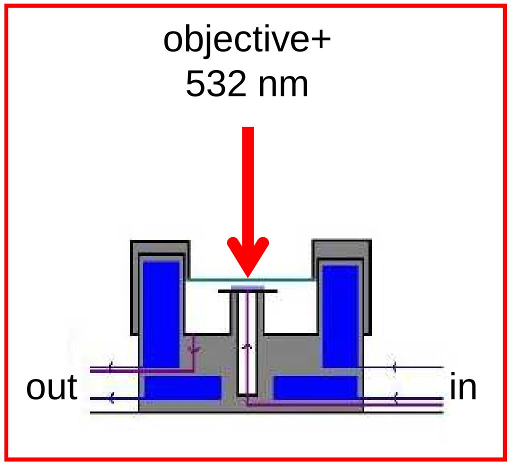
Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



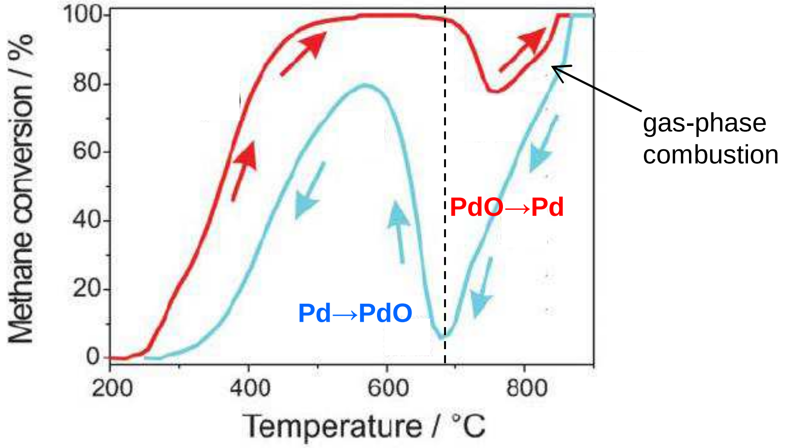
near PdO mode

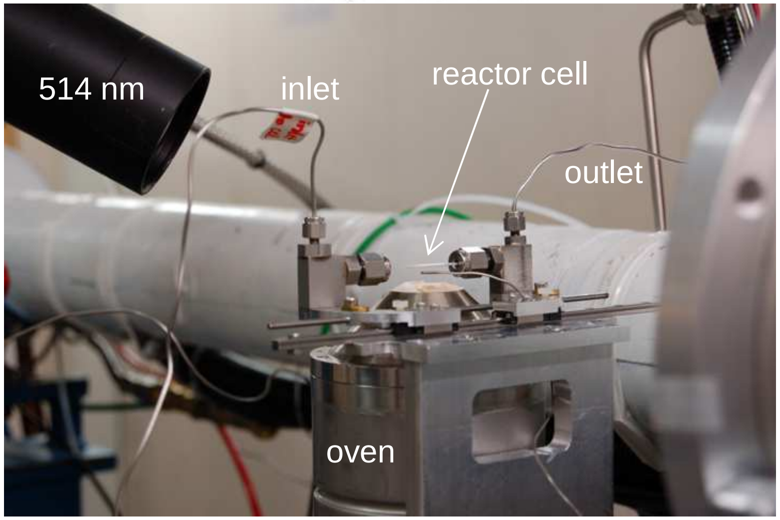


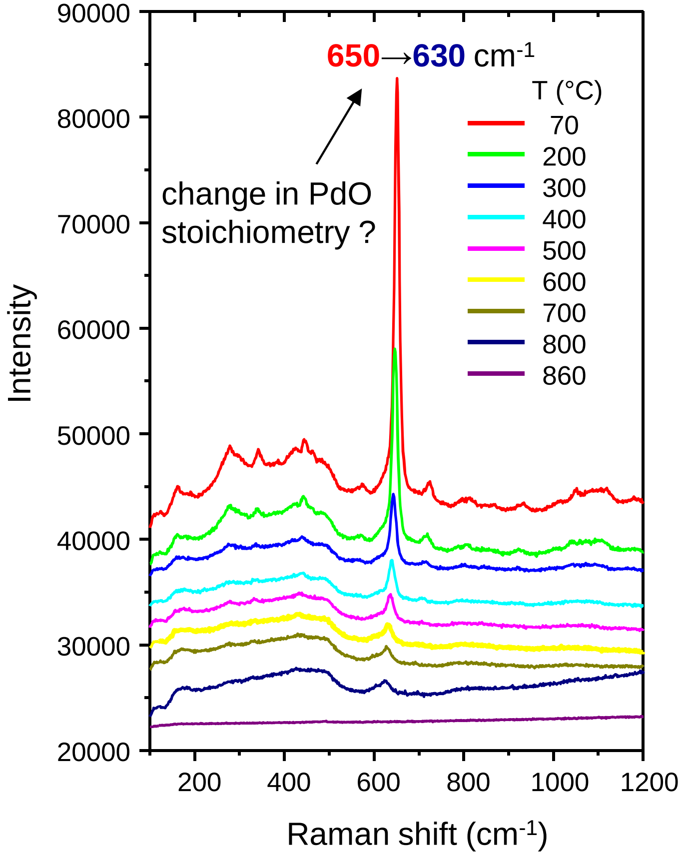
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

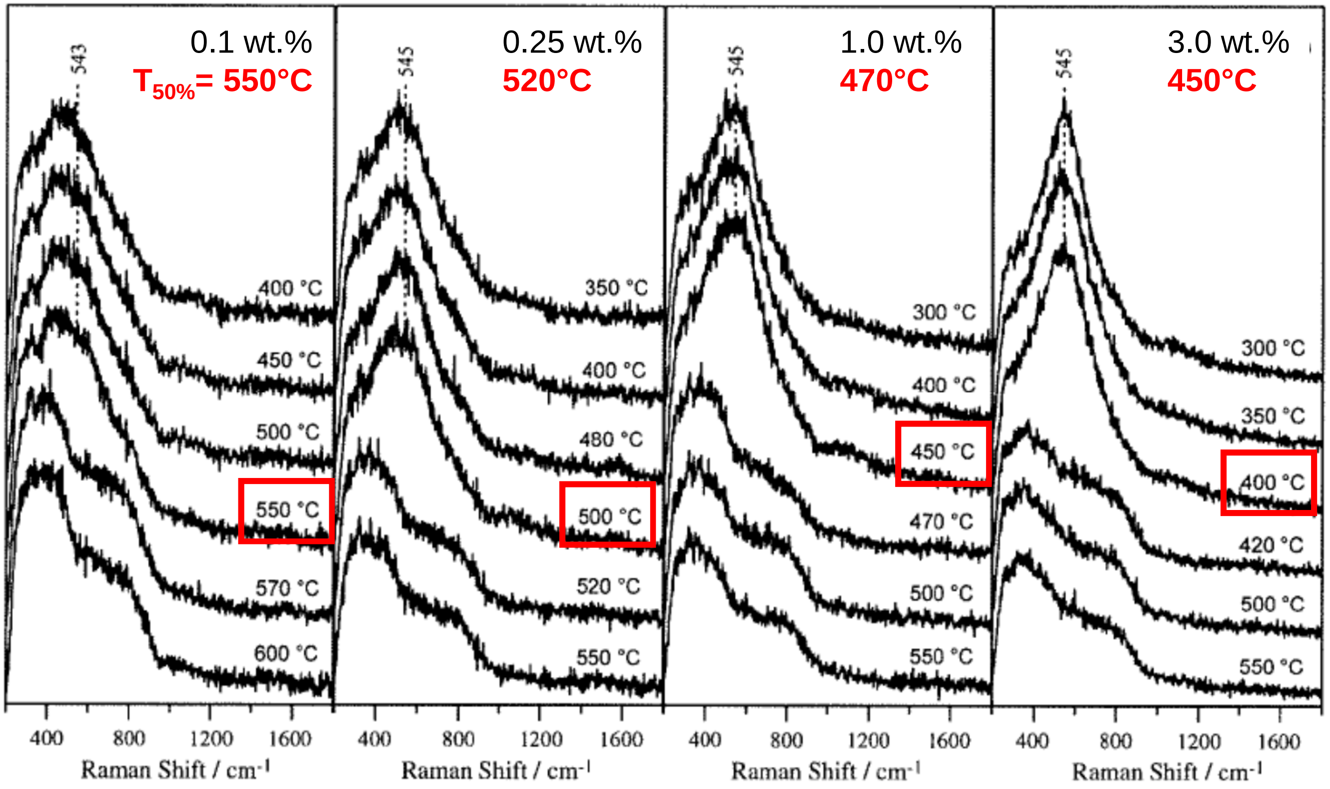
- Methane partial oxidation over Rh/Al_2O_3

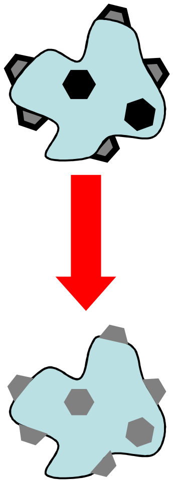
3 mW, 325 nm
$CH_4/O_2/Ar$ = 2/1/45

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content →
Activity →

RhO_x
↓
Rh(0)





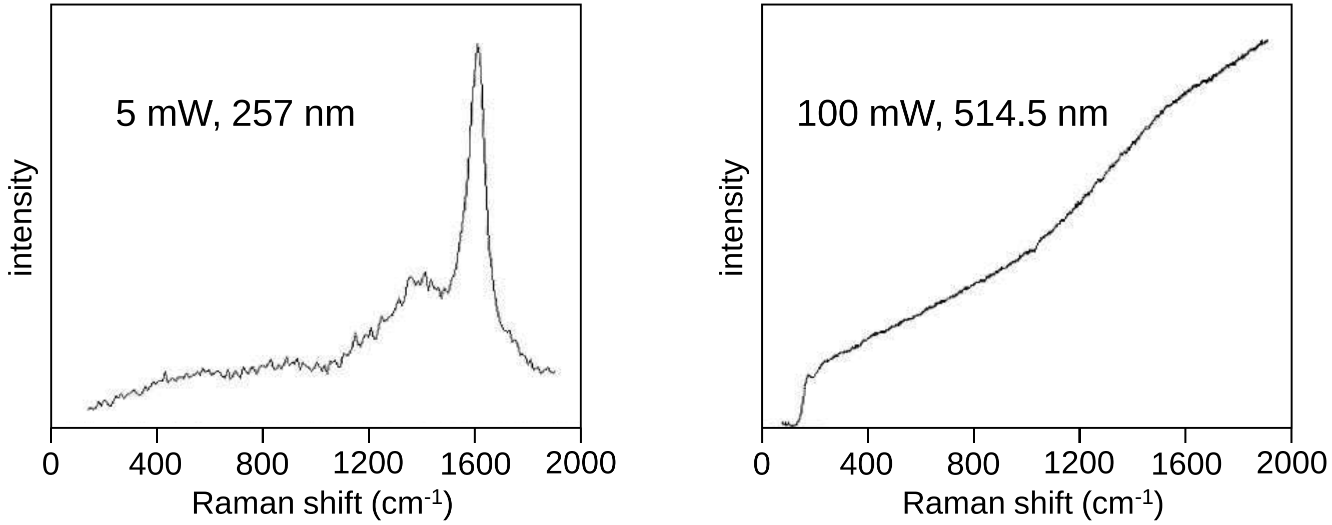
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

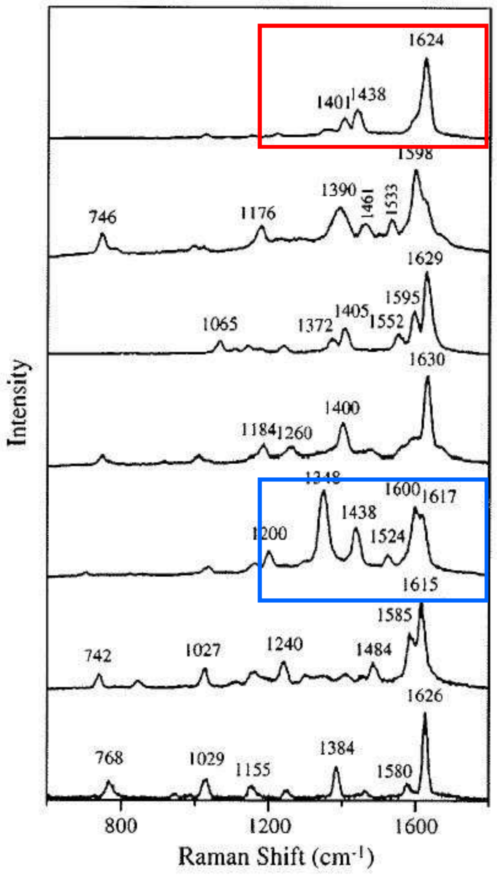
Rh/Al_2O_3, coked 500°C in naphtha

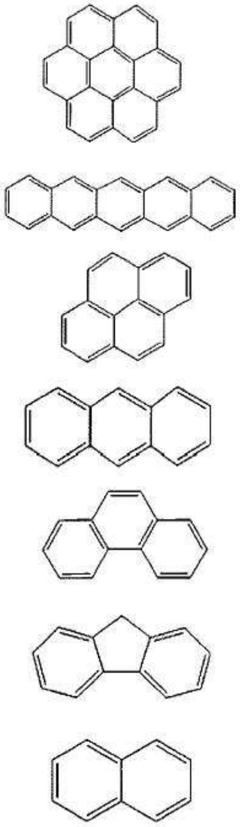


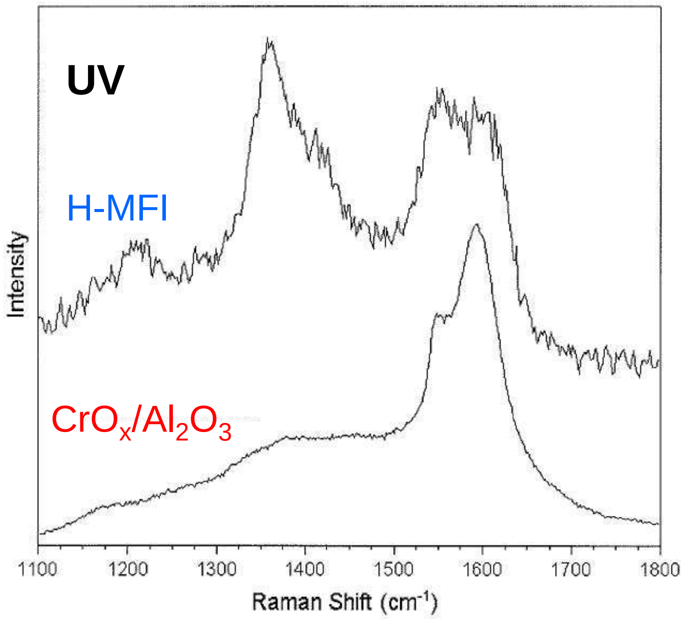
Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization







Coke classification

1D topology, chain-like

2D topology, sheet-like

Coke from:

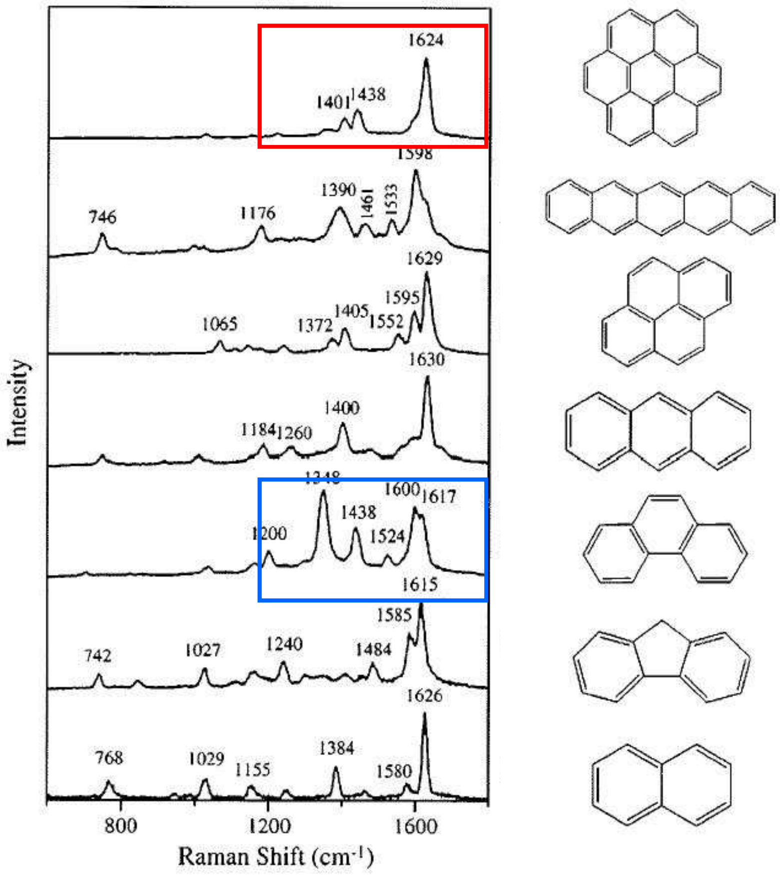
H-MFI: methanol-to-hydrocarbons (MTH)

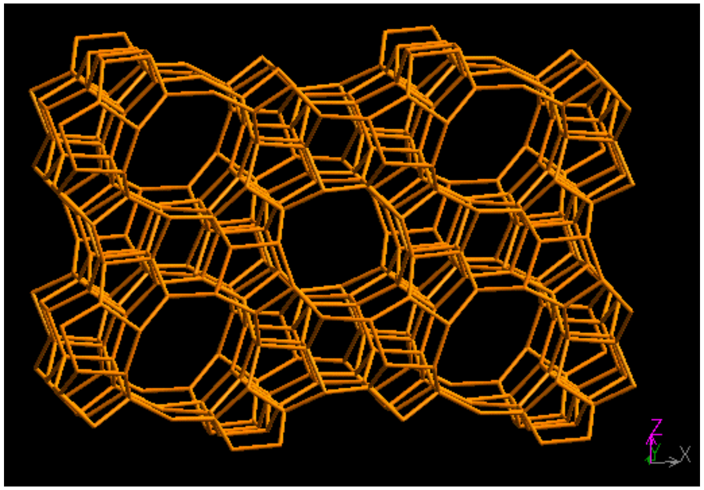
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





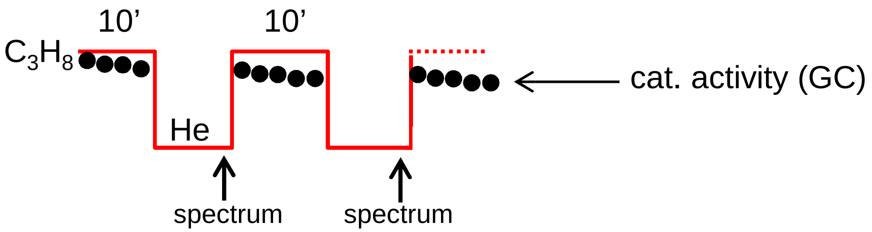
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- Propane dehydrogenation



10’ 10’

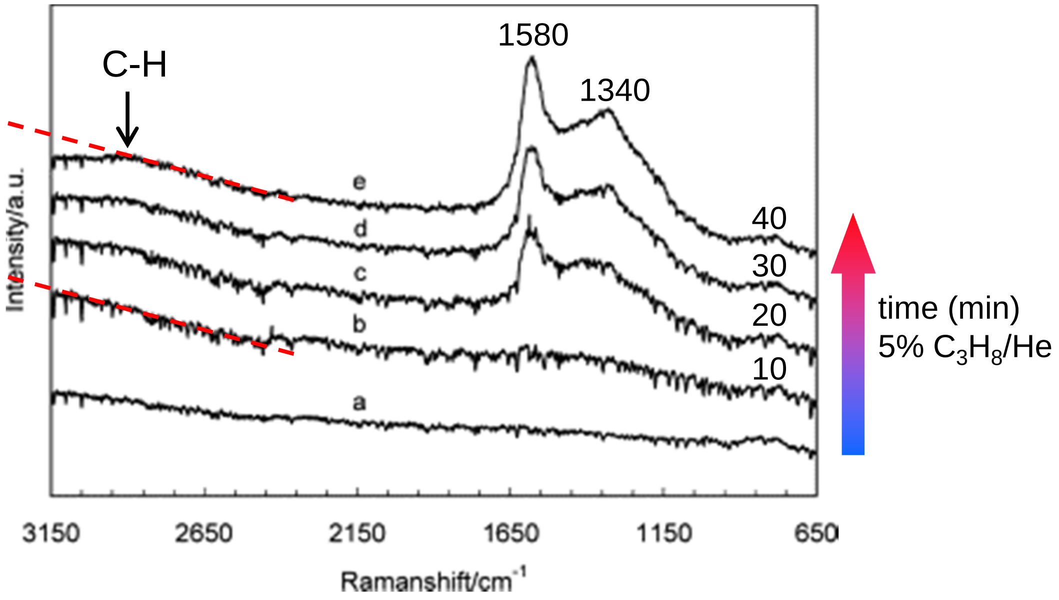
C_3H_8

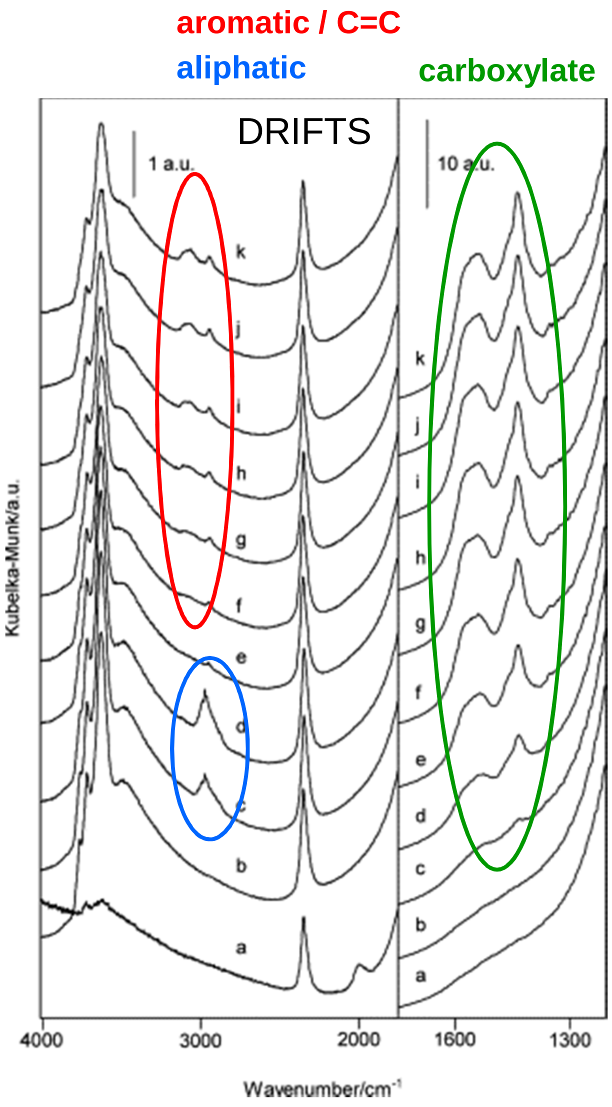
He

spectrum spectrum

cat. activity (GC)

Cr_2O_3/Al_2O_3, 580°C, 514 nm

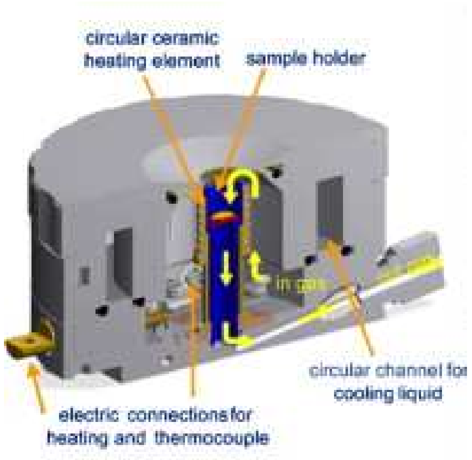


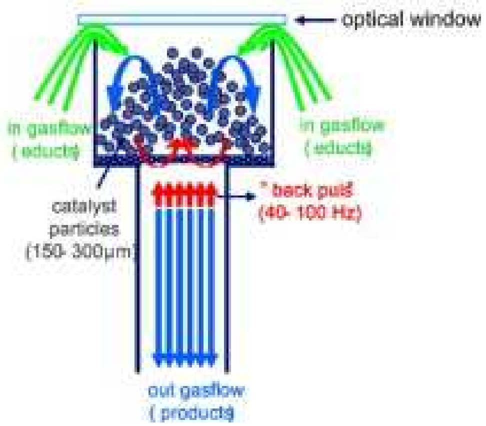


Airaksinen et al., *J. Catal.* **230** (2005) 507

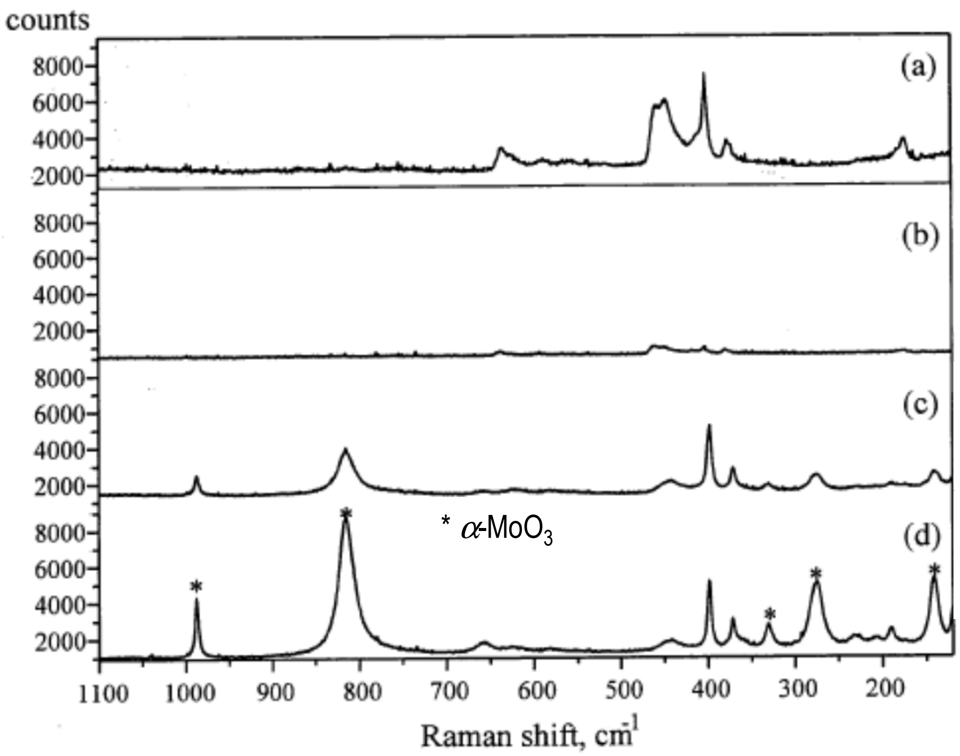
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min full power, FB

MoS_2, 6 min 1/8 power

MoS_2, 1 min full power

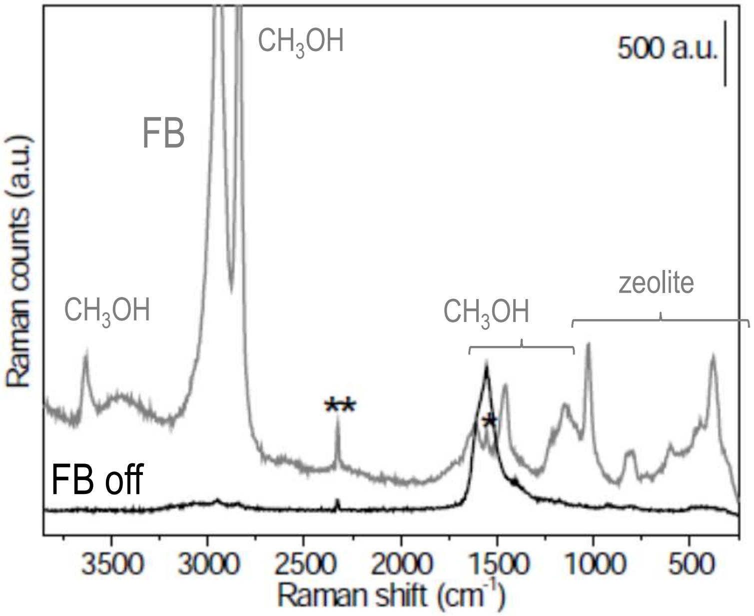
MoS_2, 6 min full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

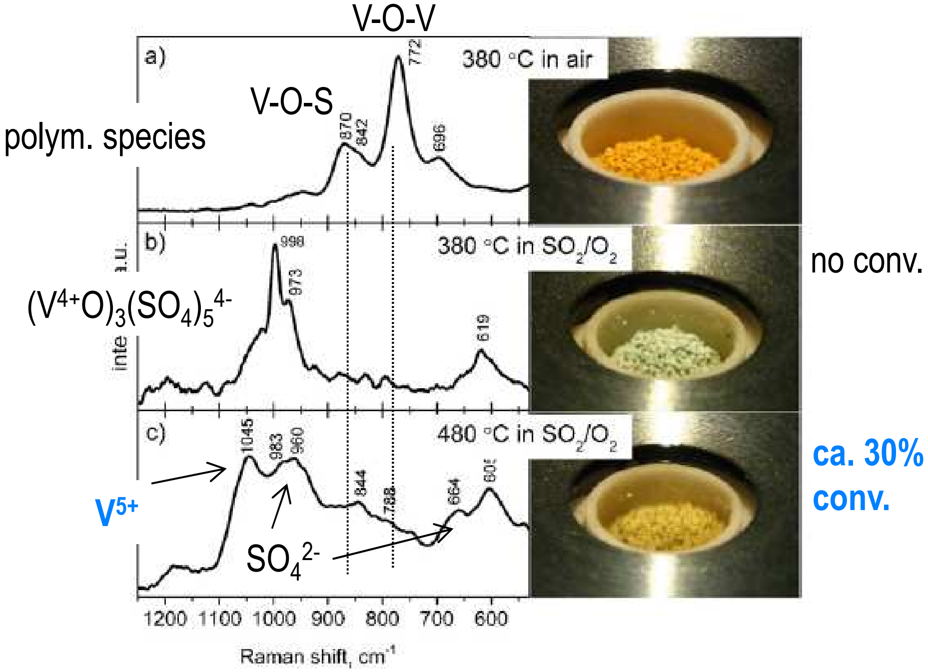
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm



no conv.

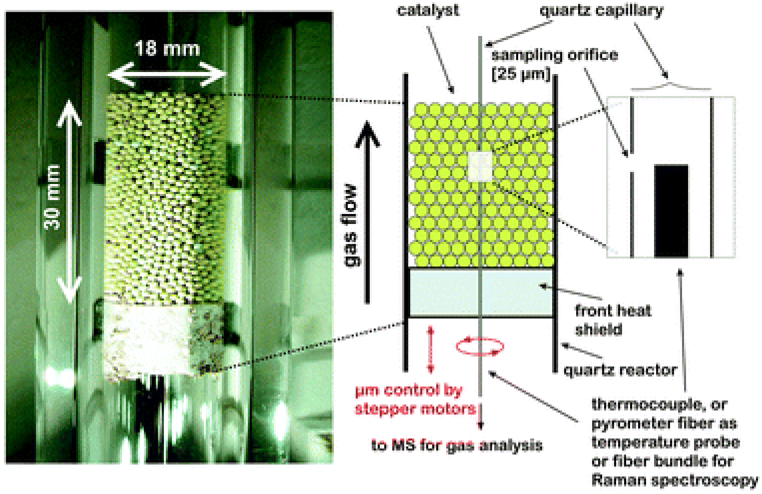
ca. 30% conv.

active species: mono- & dimeric V^{5+} oxosulfate species

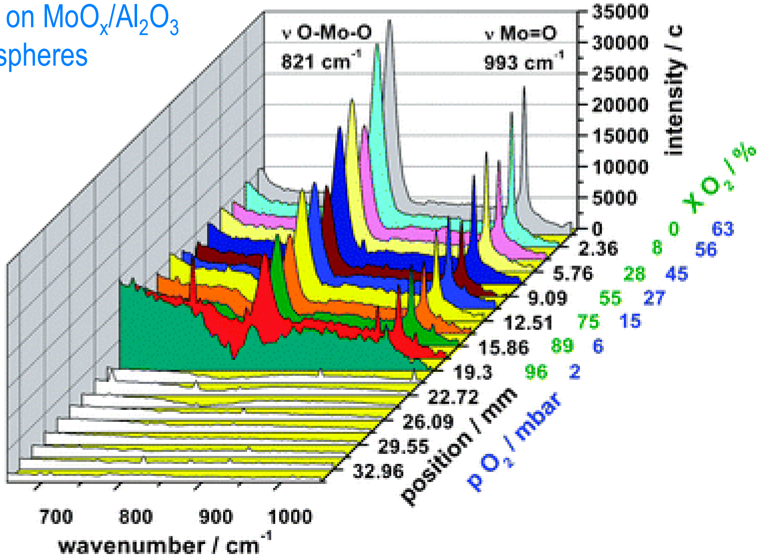
Beato et al., *Catal. Today* 205 (2013) 128

Applications

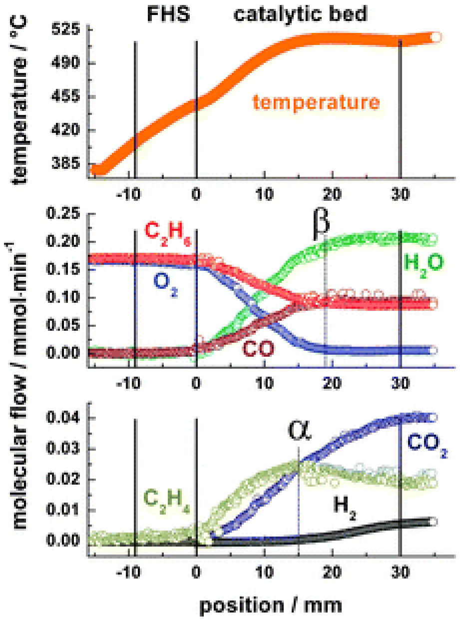
- Fixed bed reactor

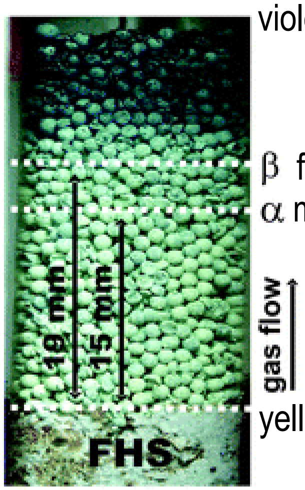


ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm





violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

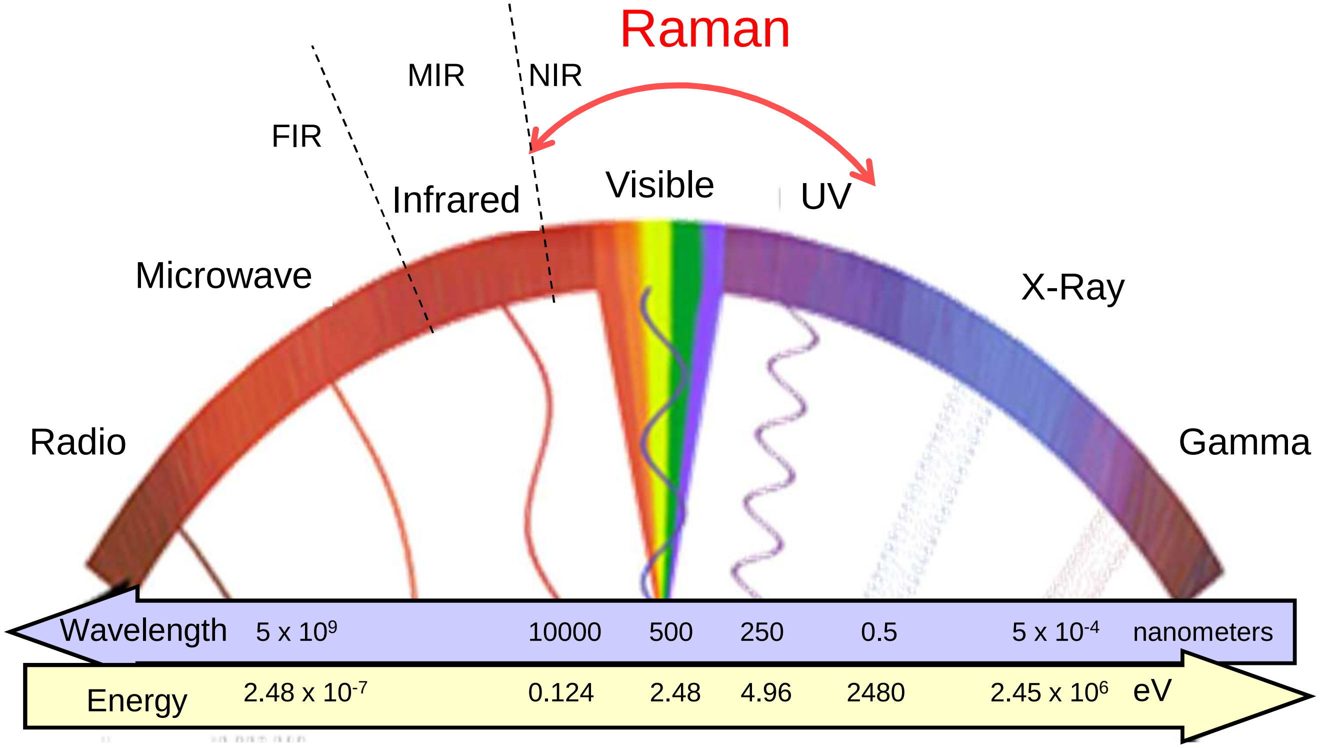
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

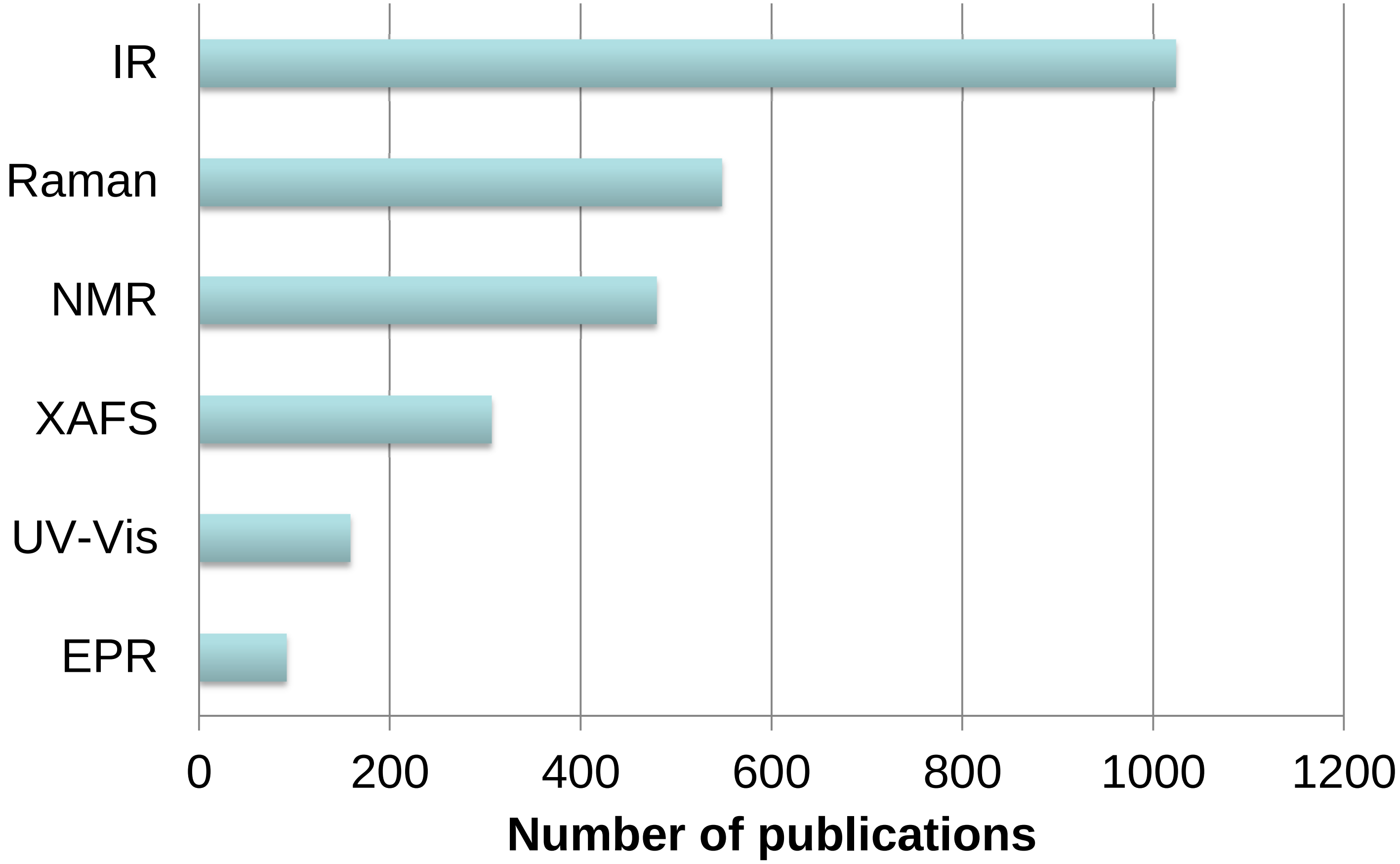
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

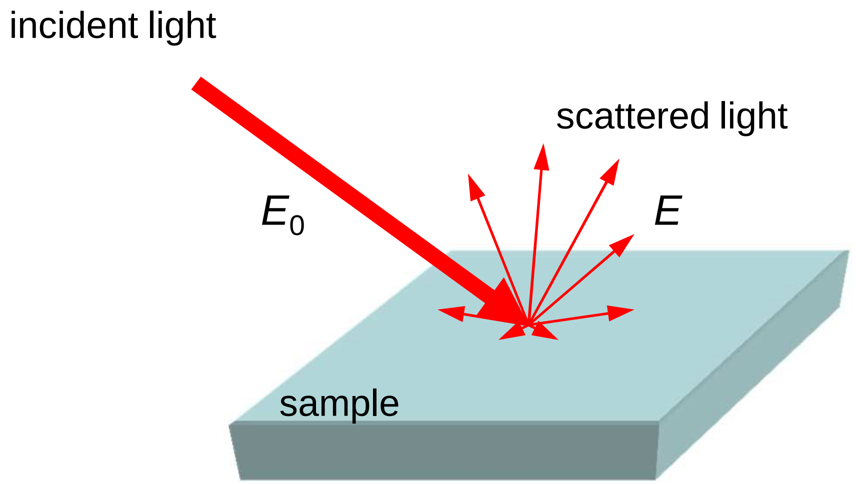


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

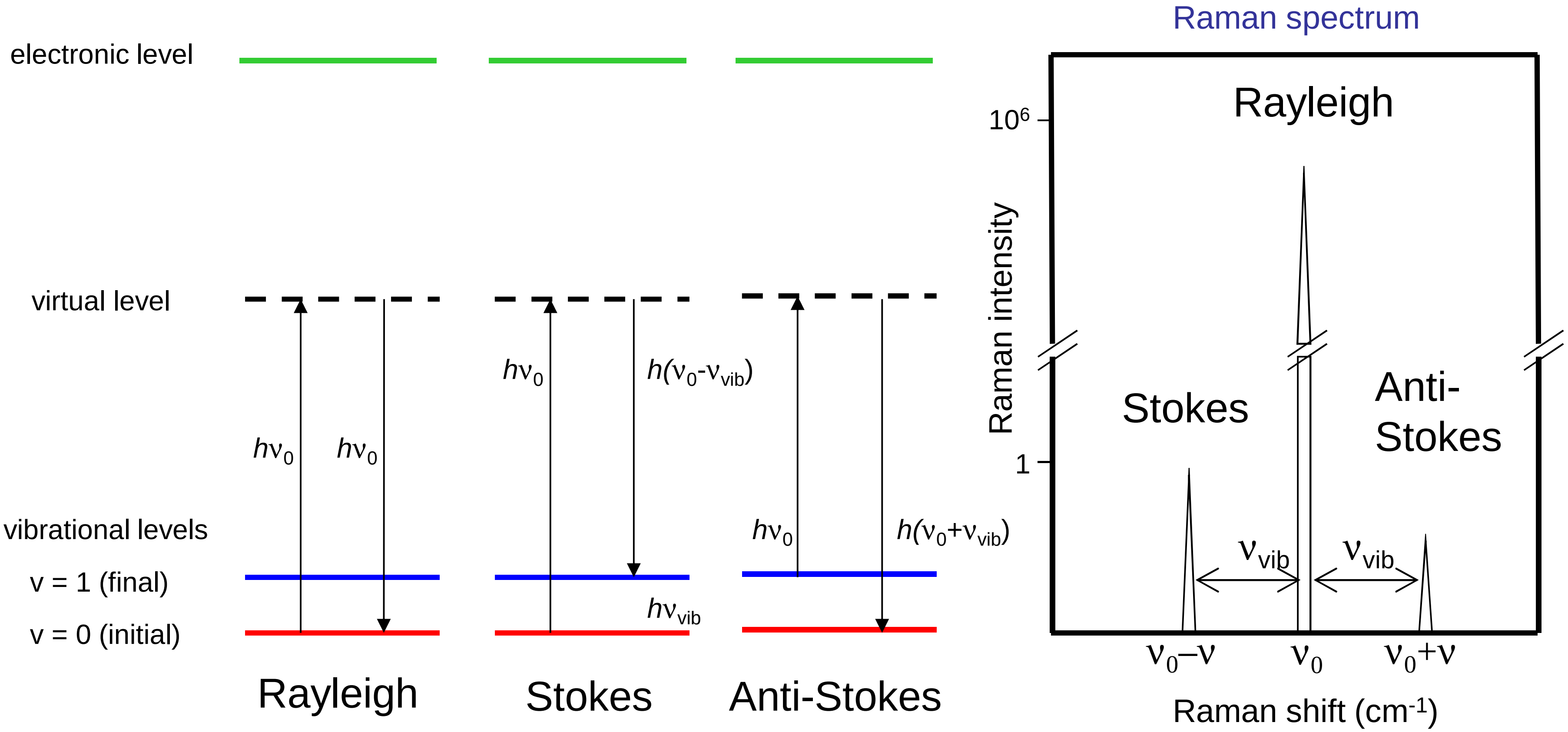
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\ (\text{Anti-Stokes})}{I\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

- 4th power of ν (4th power law)
- 2nd power of $\Delta\alpha$
  - properties of molecules
  - strength of bonds

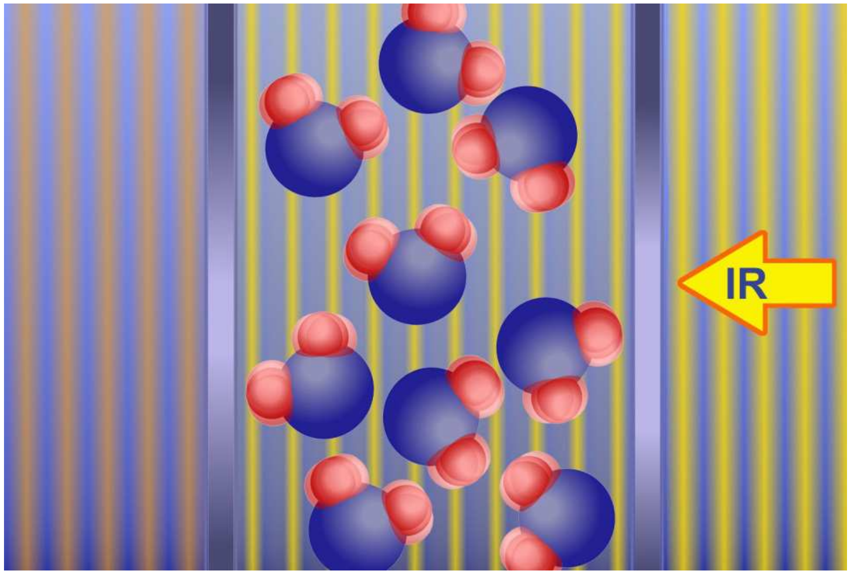
covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

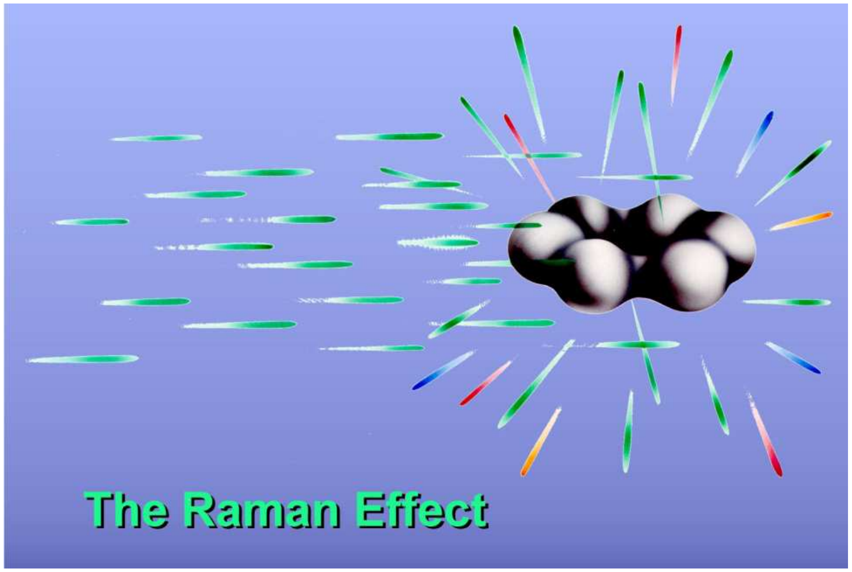
- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

Raman *vs.* Infrared

Infrared

Raman





Absorption of IR light

Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

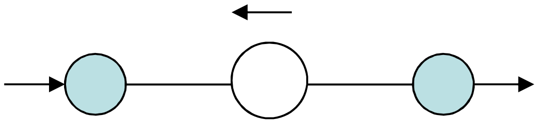
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - ❑ large electron clouds
  - ❑ not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

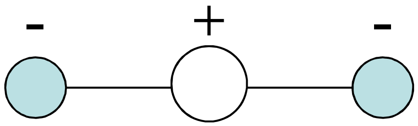
Raman *vs.* Infrared

CO_2



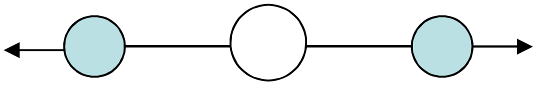
ν_{as}

2349 cm^{-1}



δ

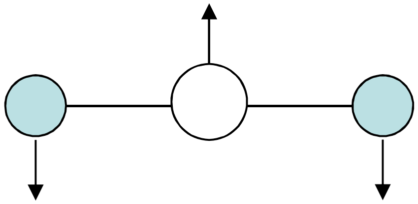
667 cm^{-1}



ν_s

1340 cm^{-1}

Raman active



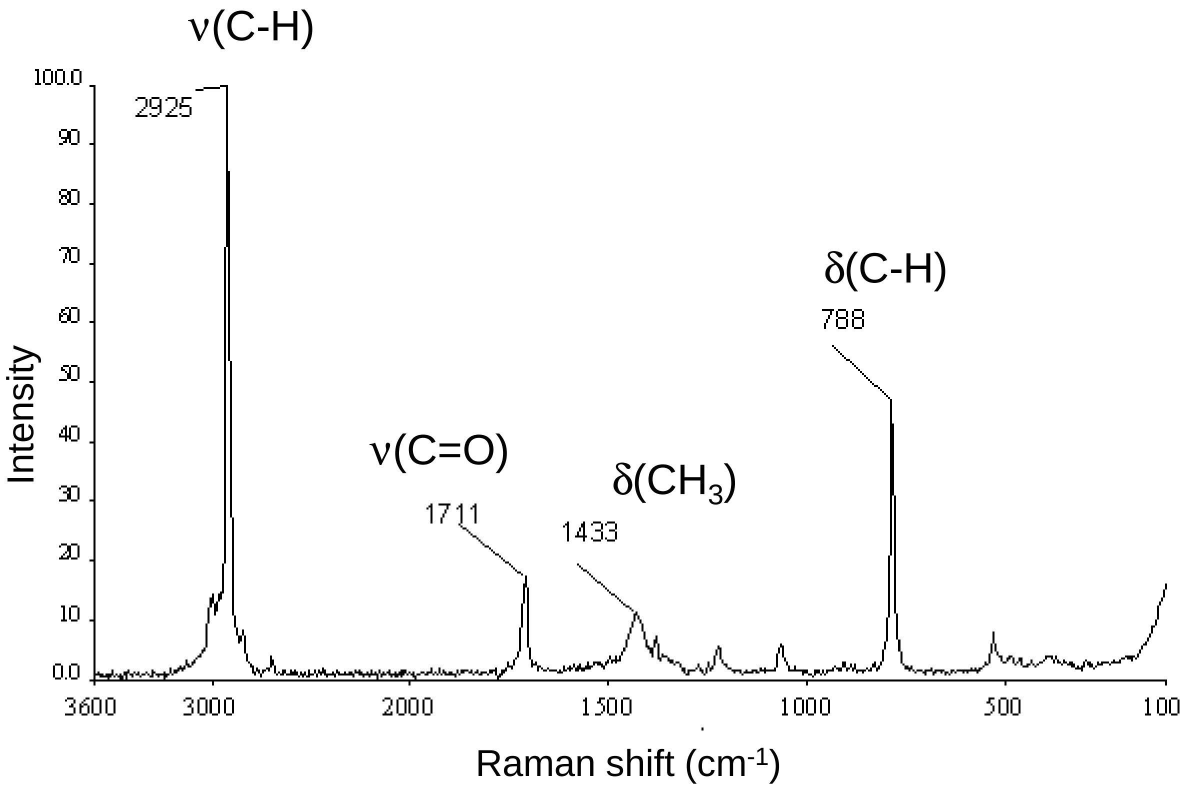
δ

667 cm^{-1}

degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared

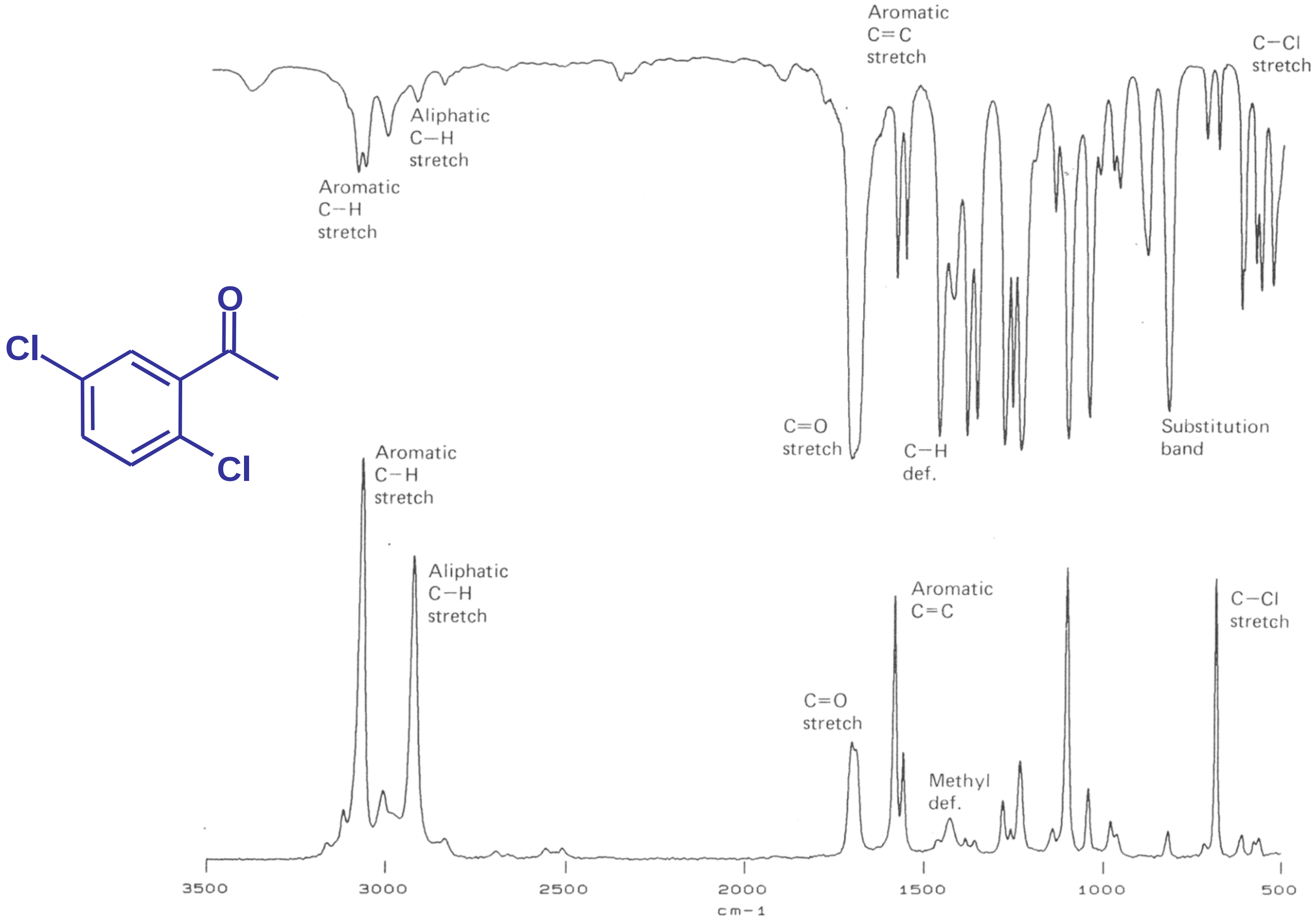


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

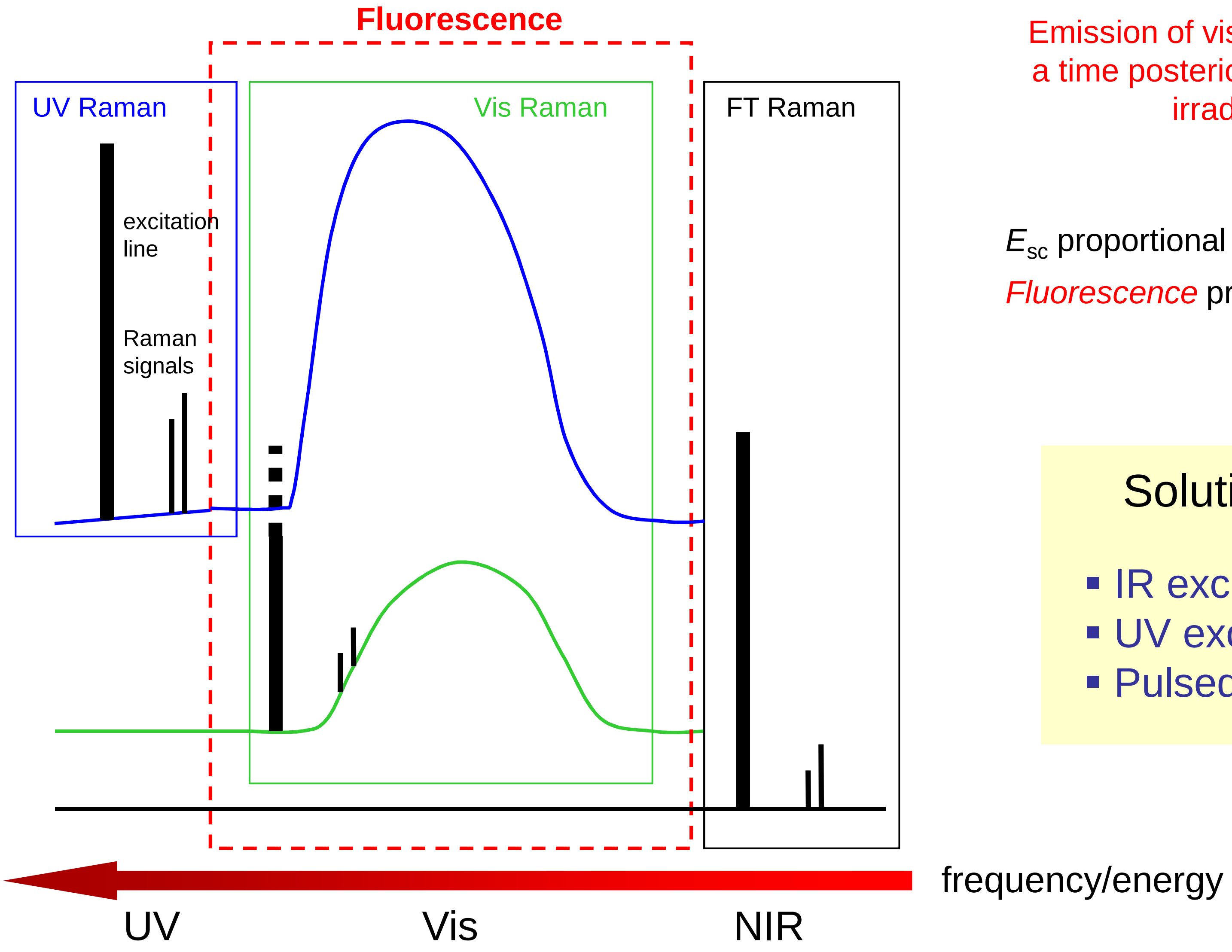
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 μm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during
a time posterior to the sample
irradiation

E_{sc} proportional to ν^4

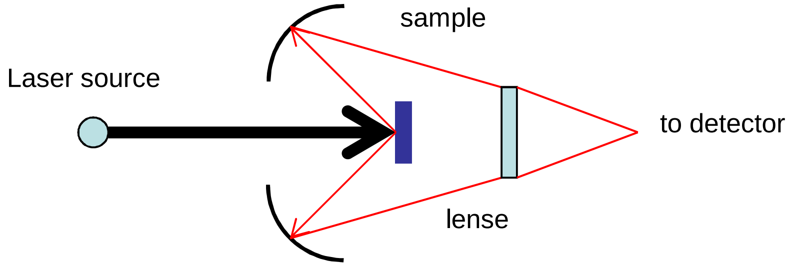
Fluorescence proportional to ν

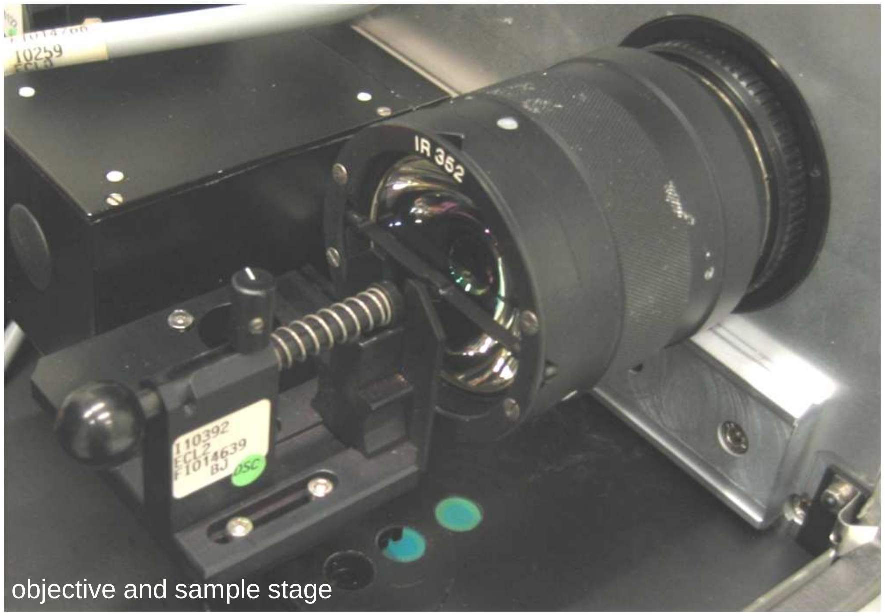
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers

Excitation wavelengths

UV	250 nm
Vis (green)	514 nm
Vis (red)	633 nm
NIR	780 nm
IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

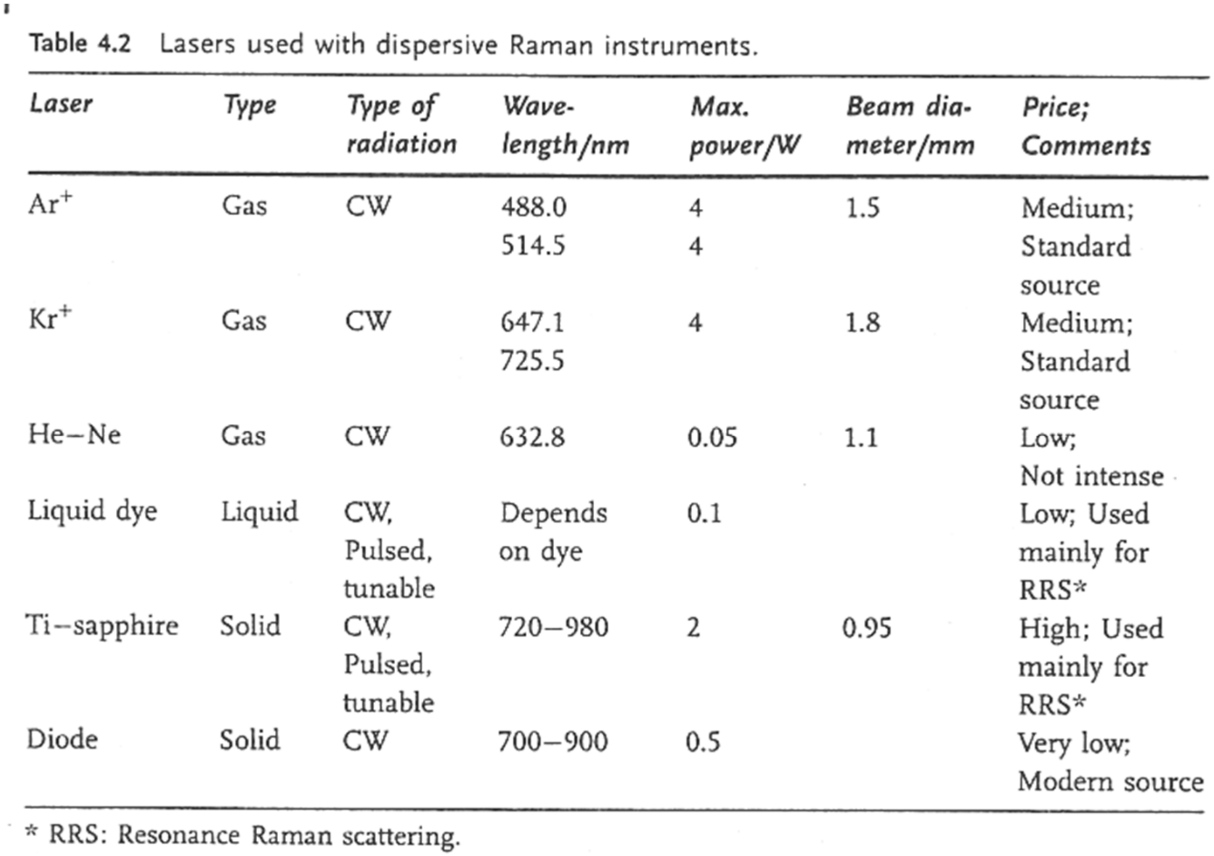


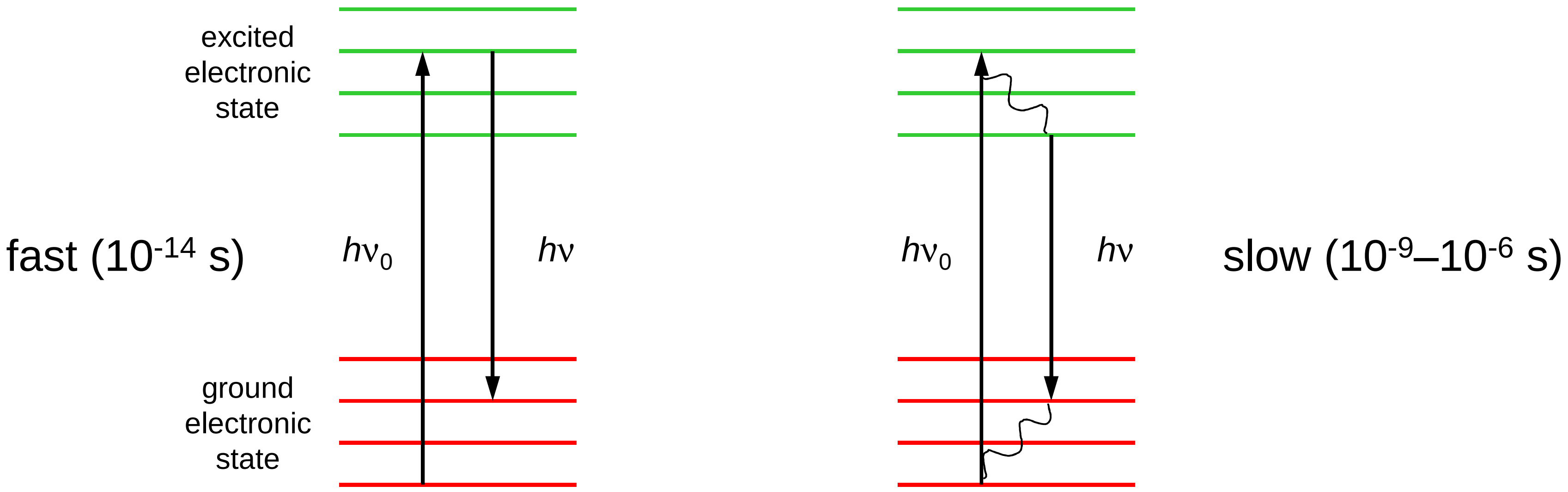
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



fast (10^{-14} s)

slow (10^{-9}–10^{-6} s)

Resonance Raman scattering

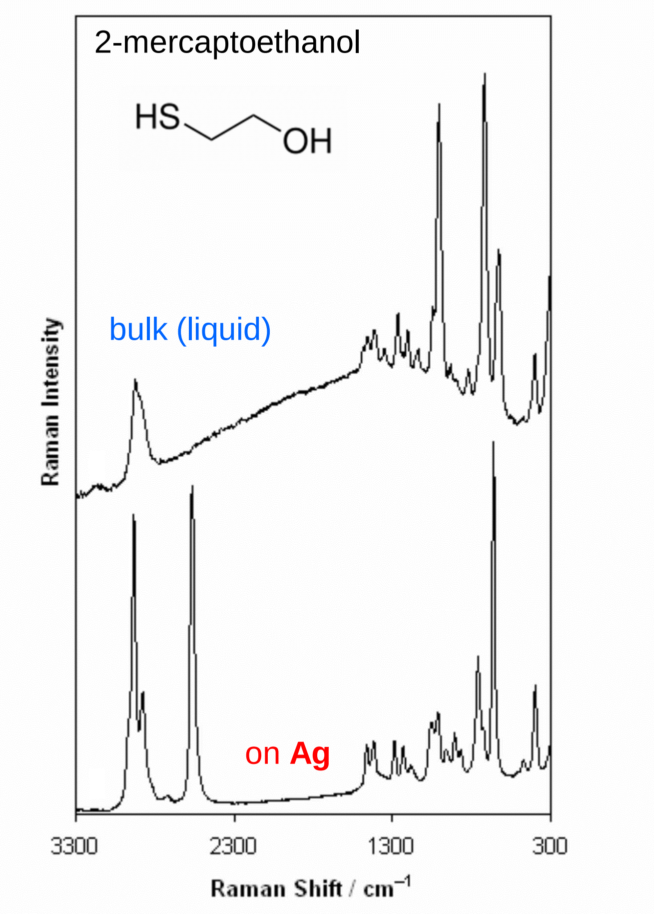
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

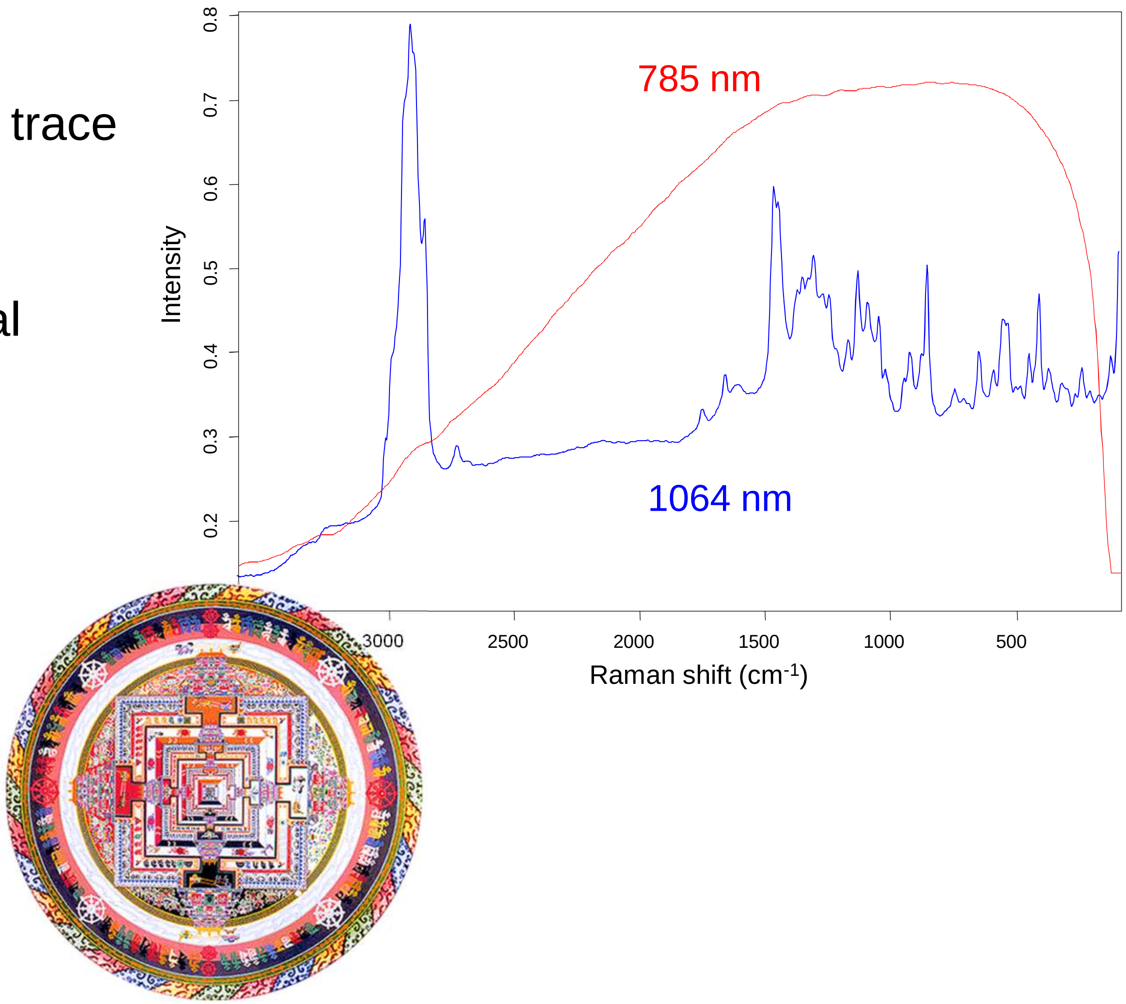
- Remarks:

  - rough surface; nanoparticles (10–100 nm) or kinks, steps etc. (E always perpendicular to surface, locally)
  - vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



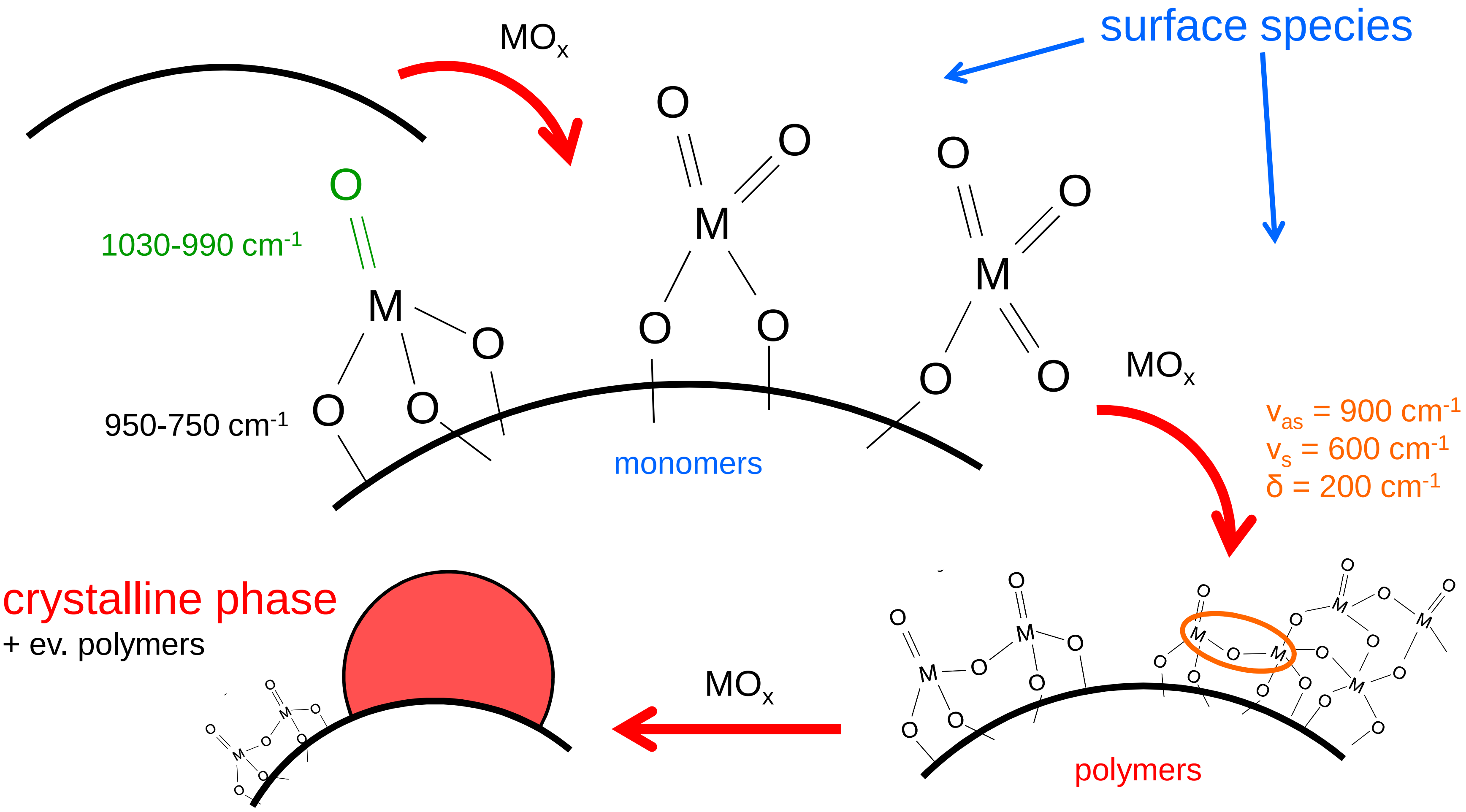
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



surface species

MO_x

1030-990 cm^{-1}

950-750 cm^{-1}

monomers

MO_x

ν_{as} = 900 cm^{-1}
ν_s = 600 cm^{-1}
δ = 200 cm^{-1}

polymers

MO_x

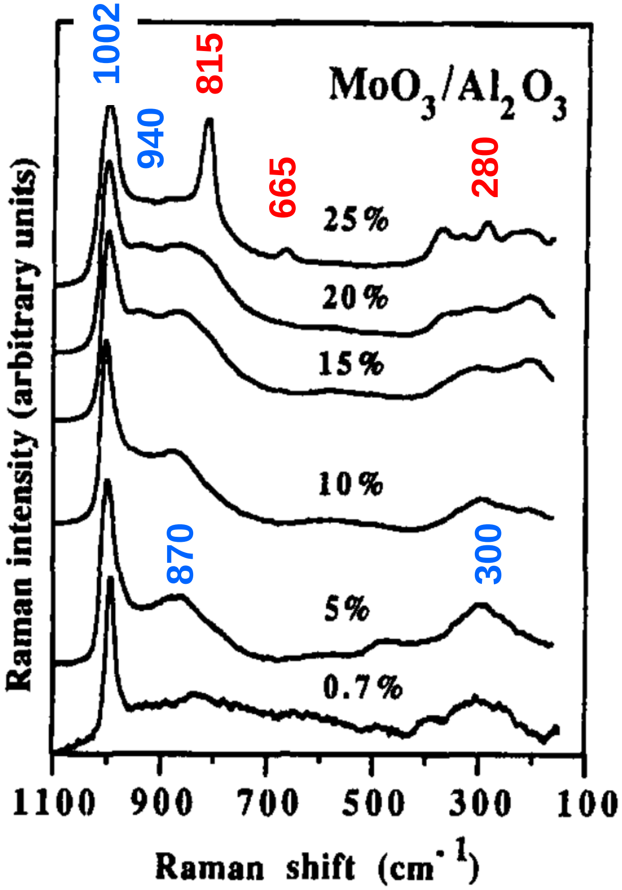
crystalline phase
+ ev. polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



surface MoO_3

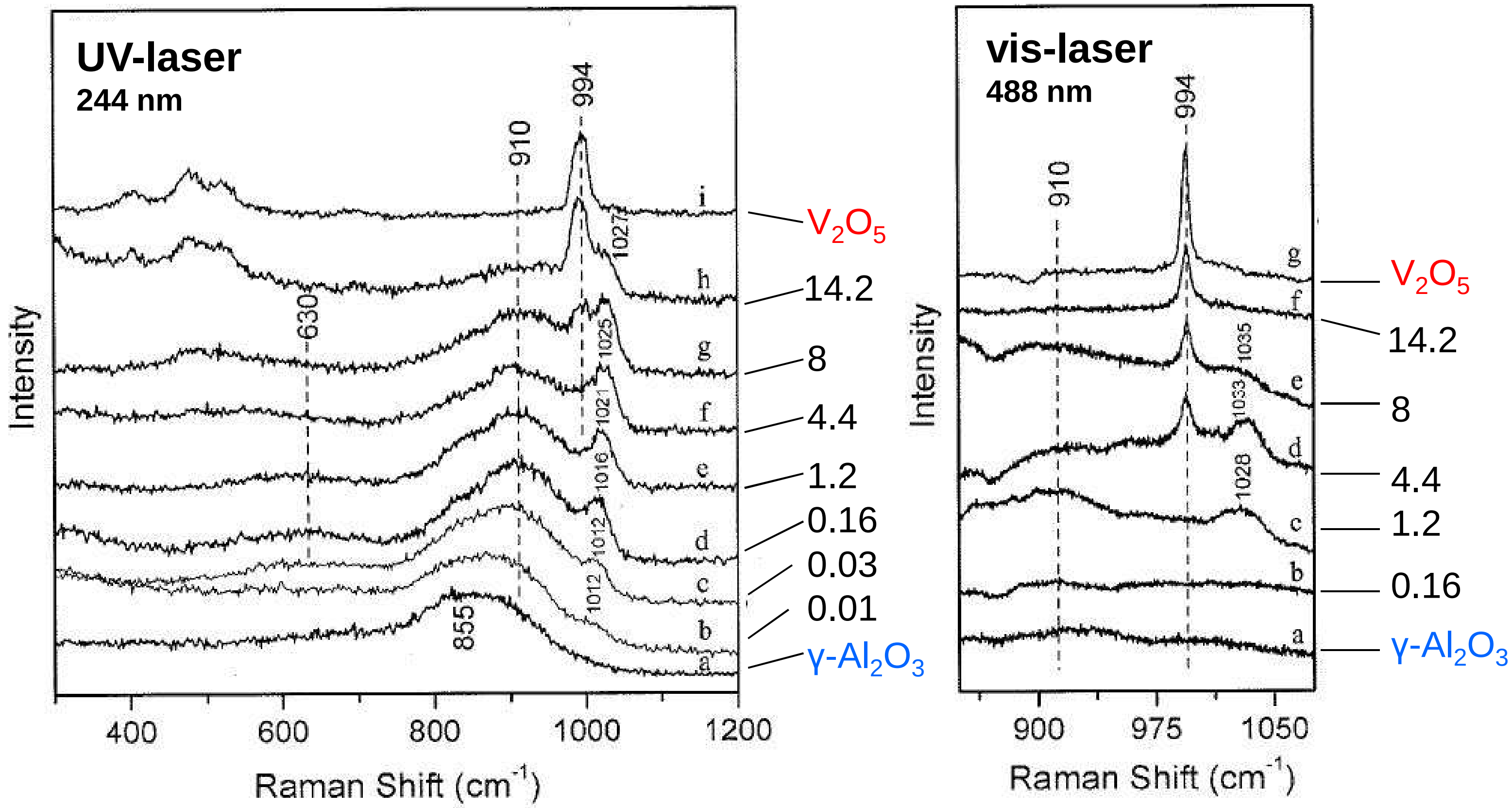
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

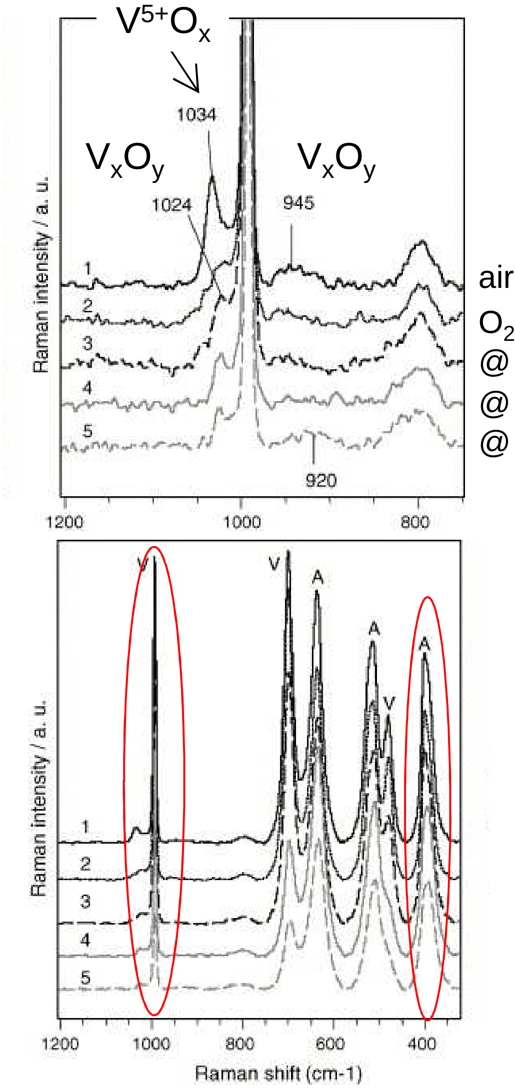
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

Applications

- Reactivity of V/TiO_2 after oxidative treatment



air flow @ 450°C

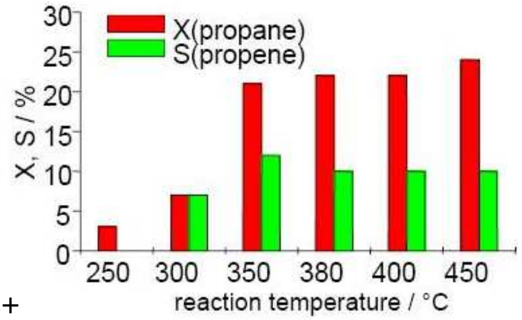
O_2/C_3H_8 @ 20°C

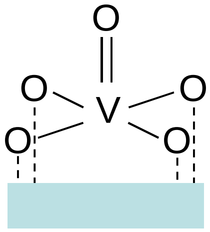
@ 100°C

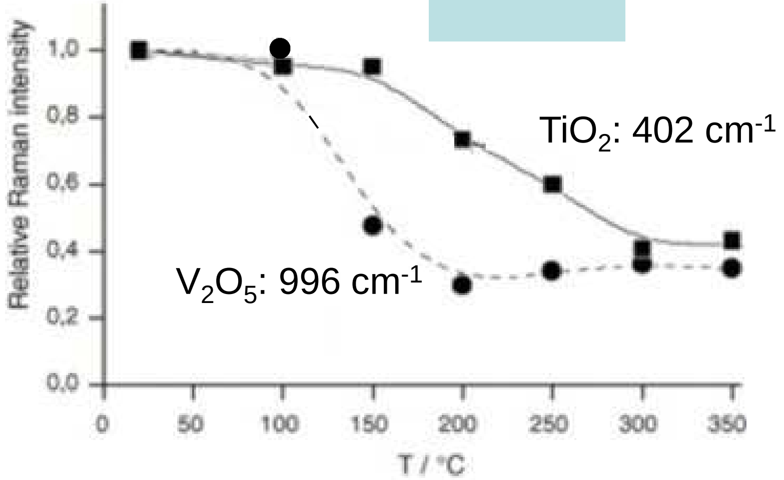
@ 150°C

@ 200°C

$V^{5+} \longrightarrow V^{4+}$







TiO_2: 402 cm^{-1}

V_2O_5: 996 cm^{-1}

Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

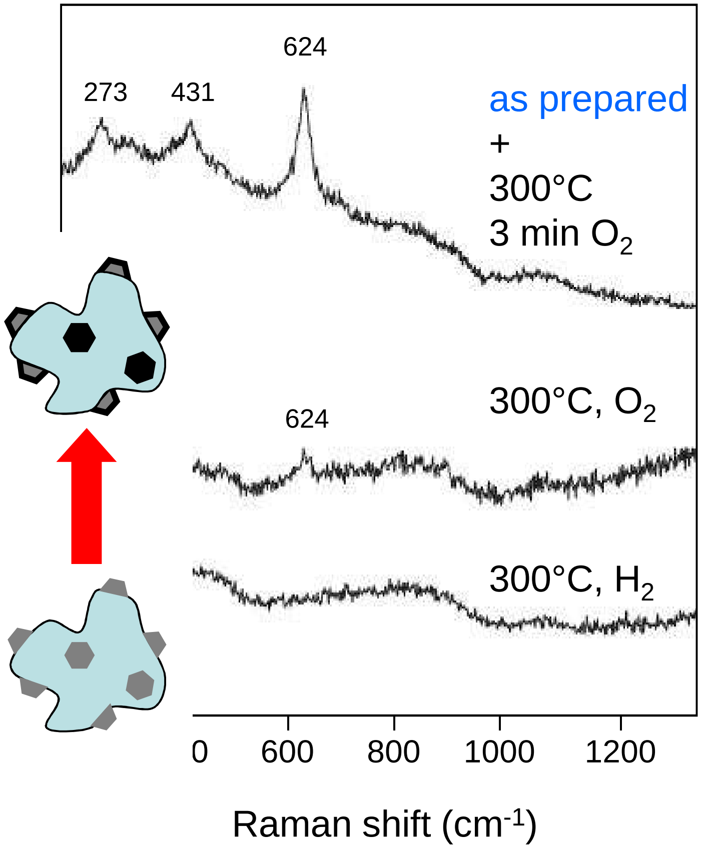
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

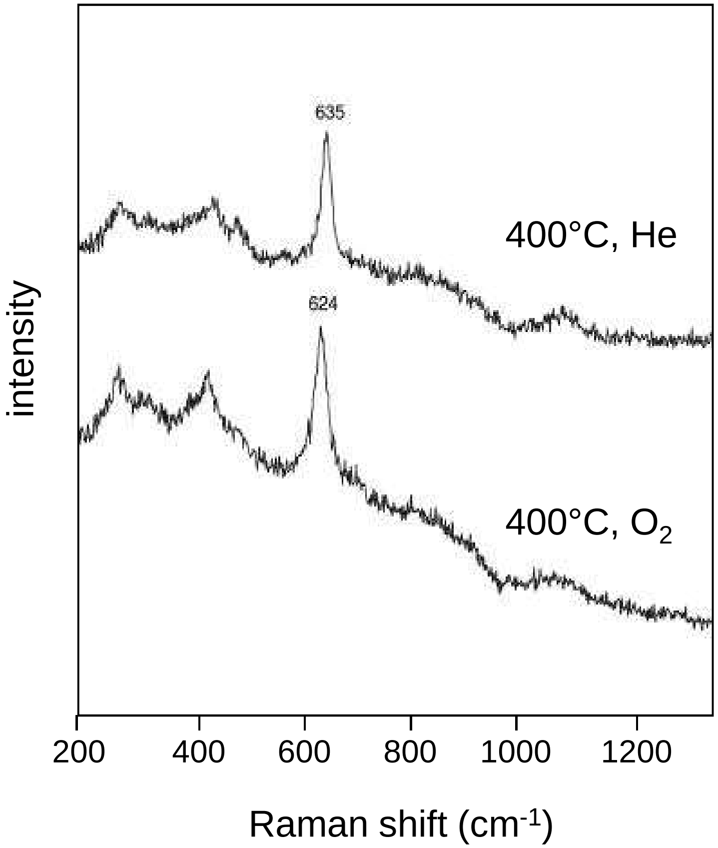
Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3





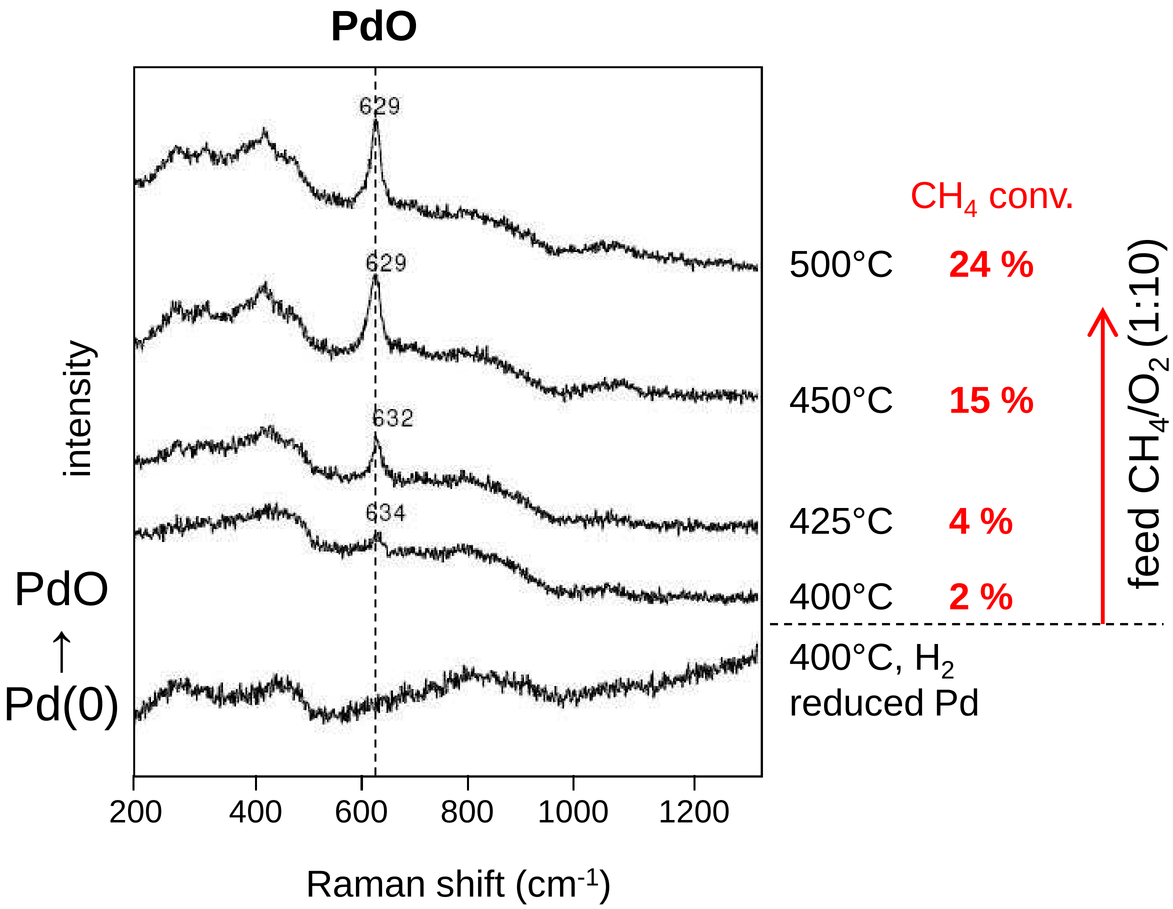
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

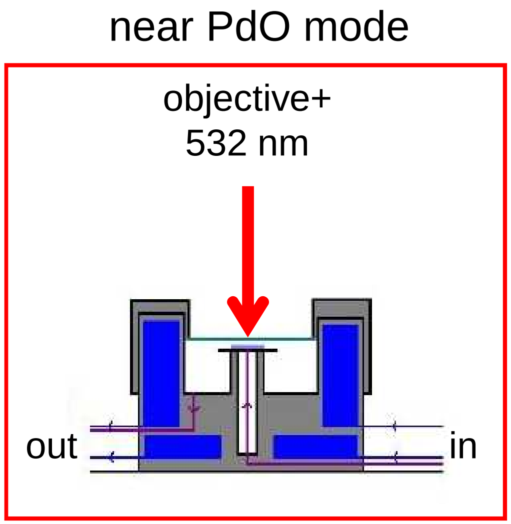
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

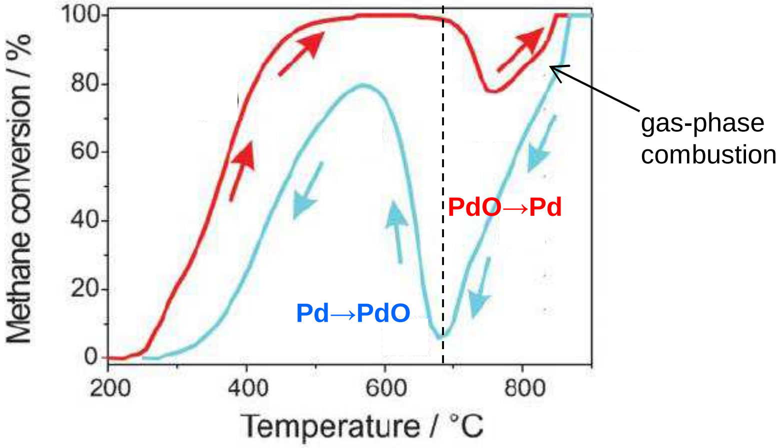


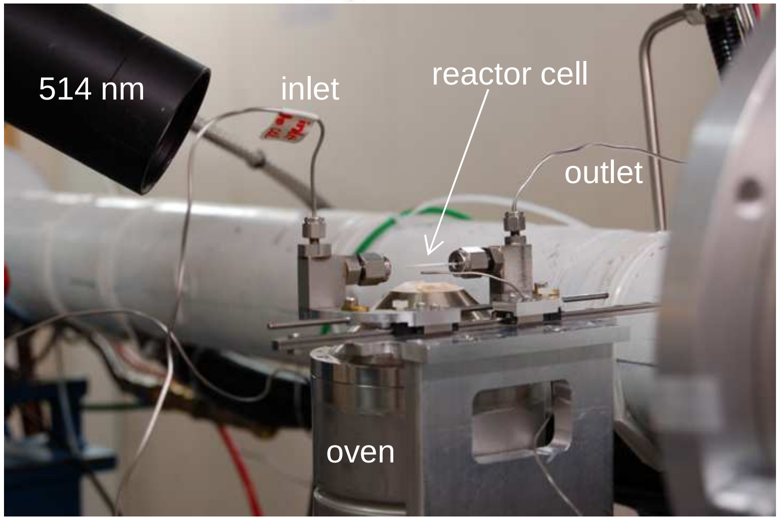


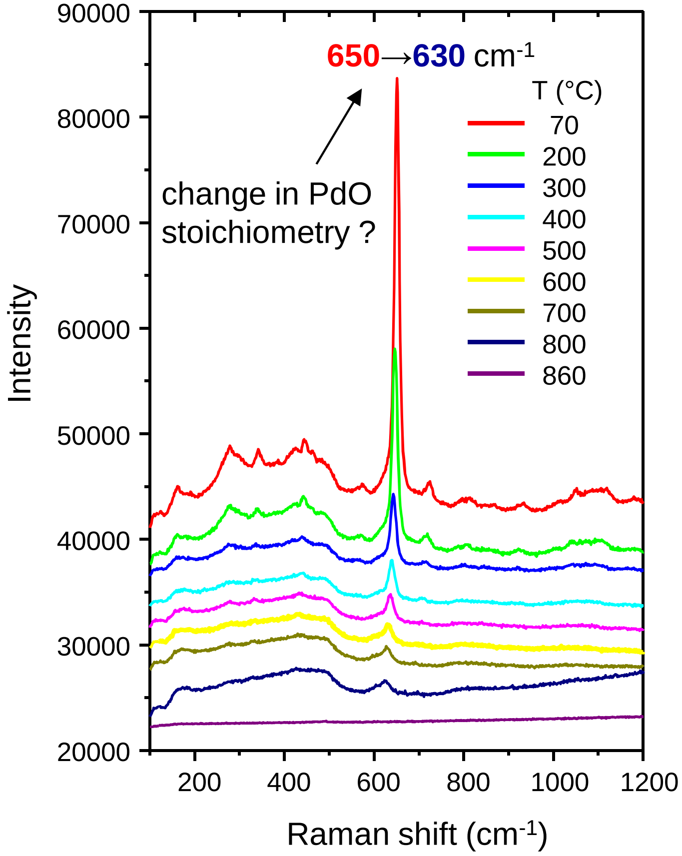
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

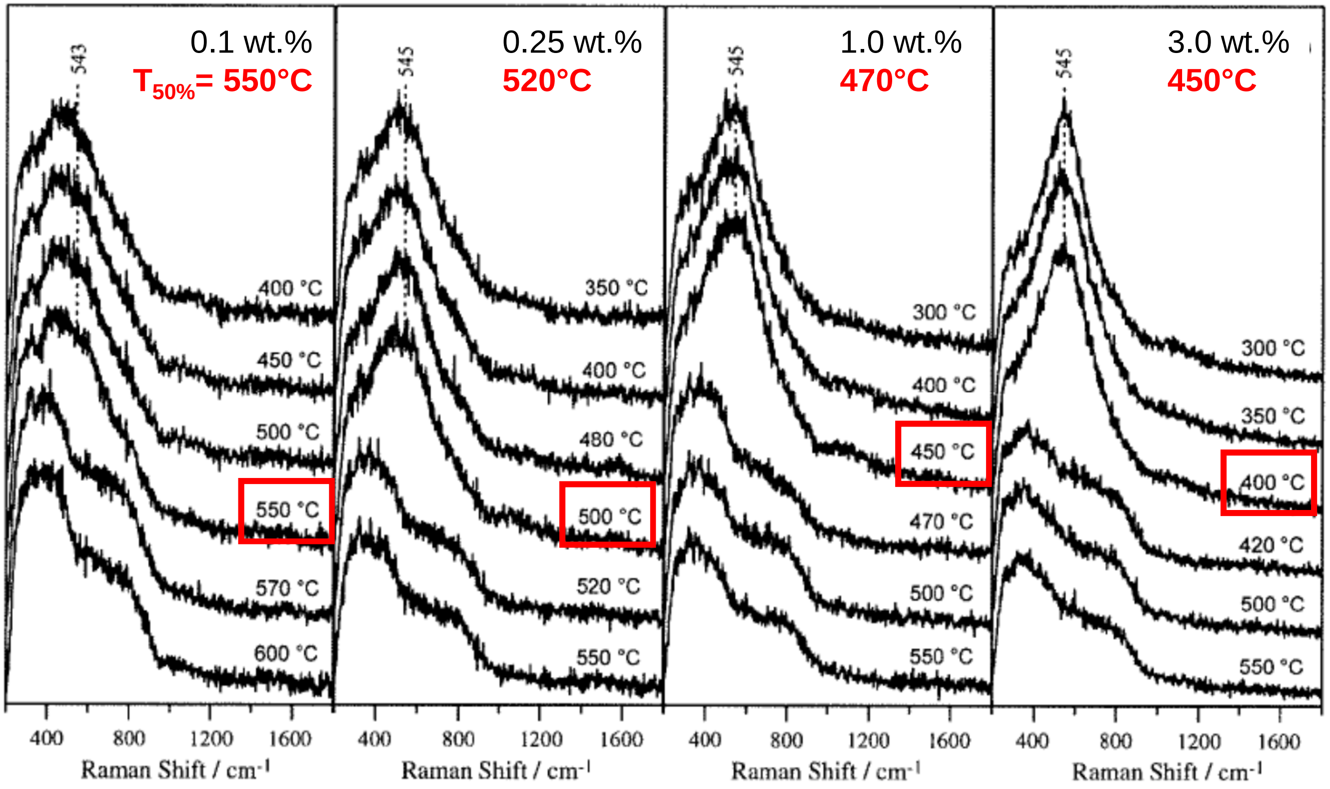
- Methane partial oxidation over Rh/Al_2O_3

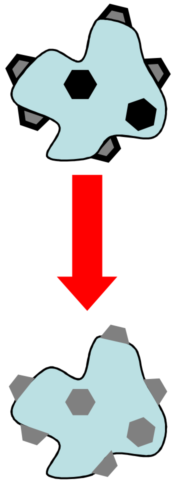
3 mW, 325 nm
$CH_4/O_2/Ar$ = 2/1/45

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content
Activity

RhO$_x$
↓
Rh(0)





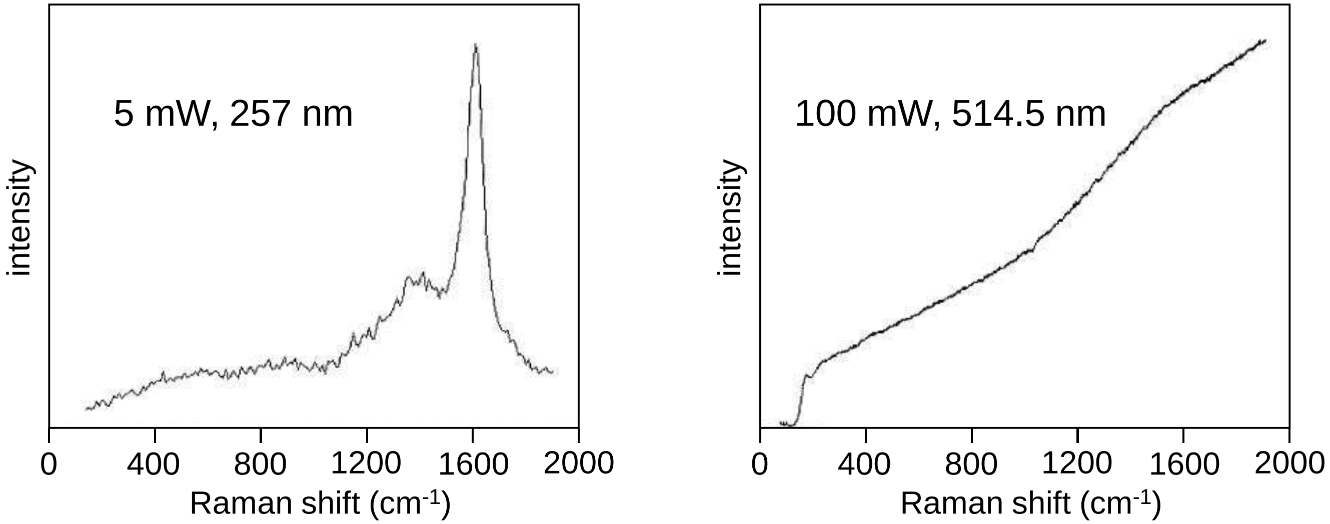
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

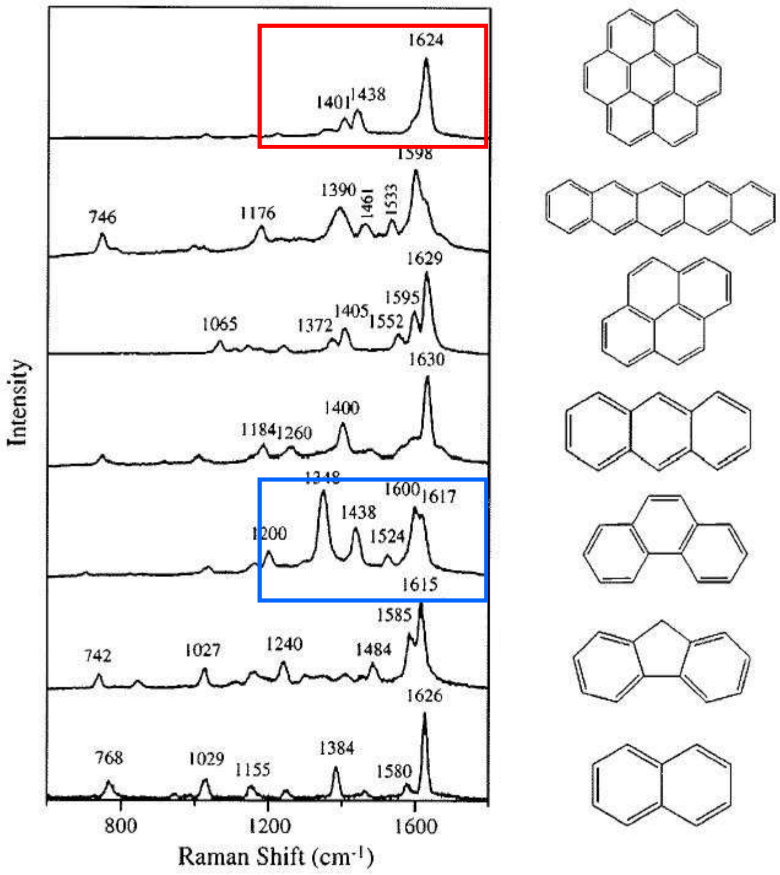
Rh/Al_2O_3, coked 500°C in naphtha

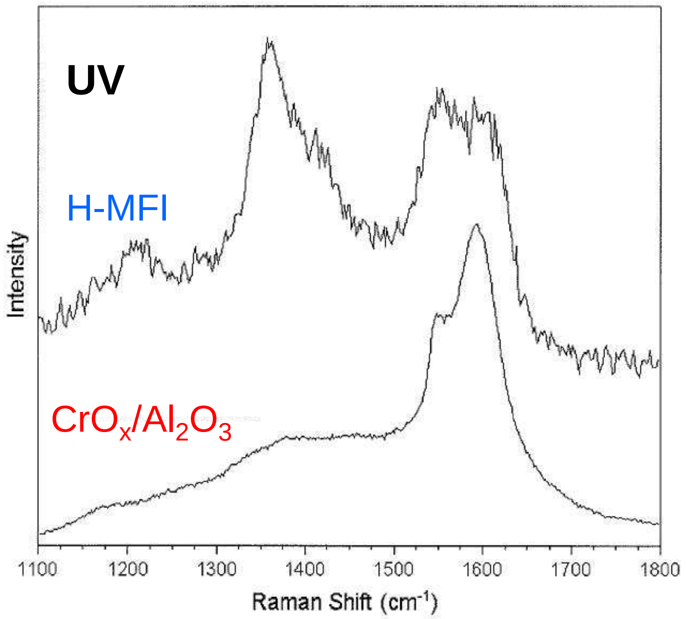


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





Coke classification

1D topology, chain-like

2D topology, sheet-like

Coke from:

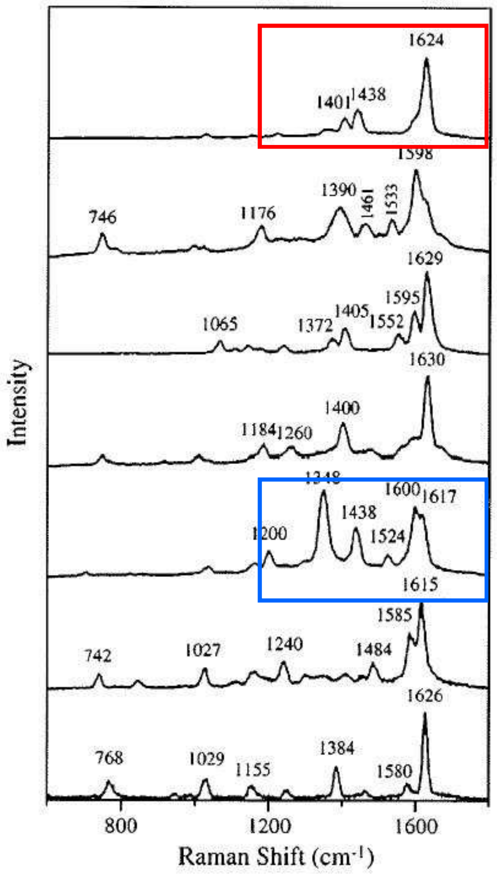
H-MFI: methanol-to-hydrocarbons (MTH)

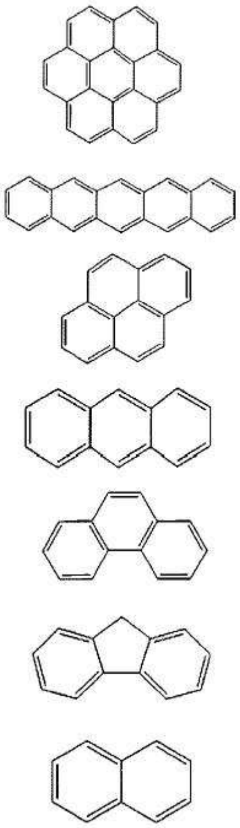
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

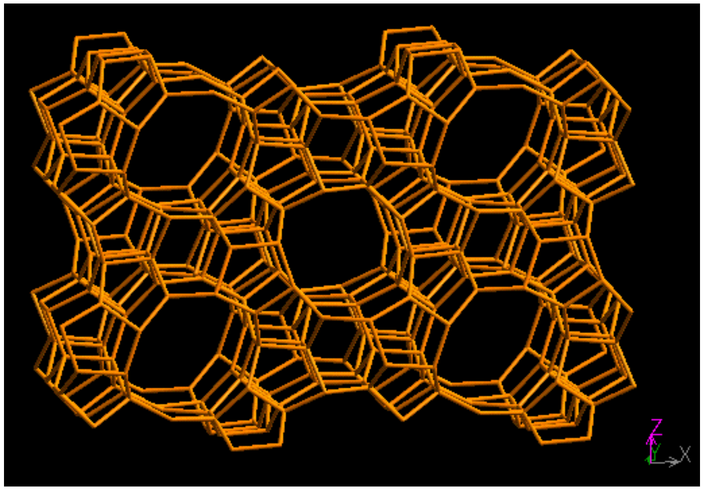
Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization







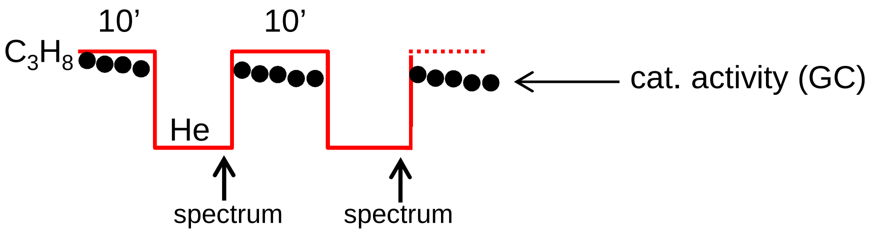
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

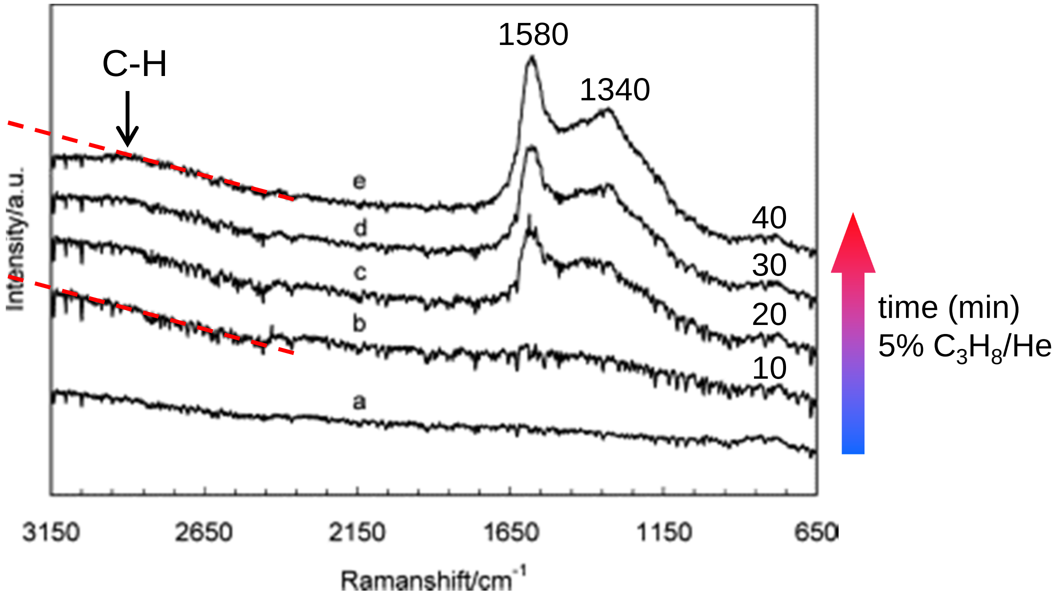
Stair, *Adv. Catal.* **51** (2007) 75

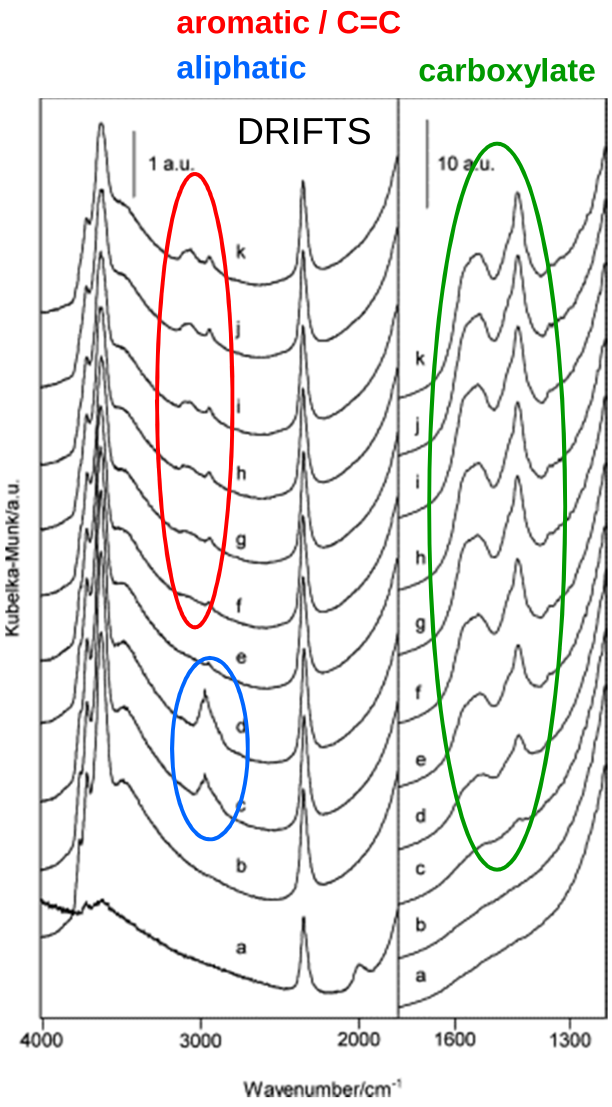
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

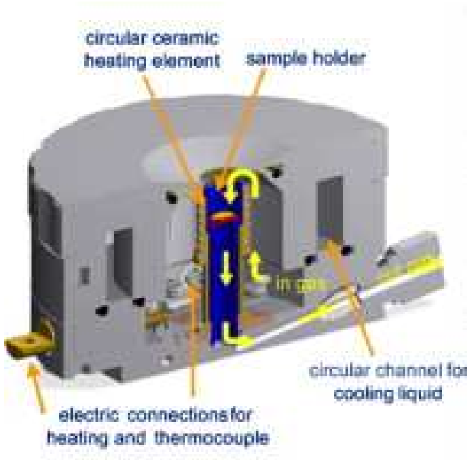


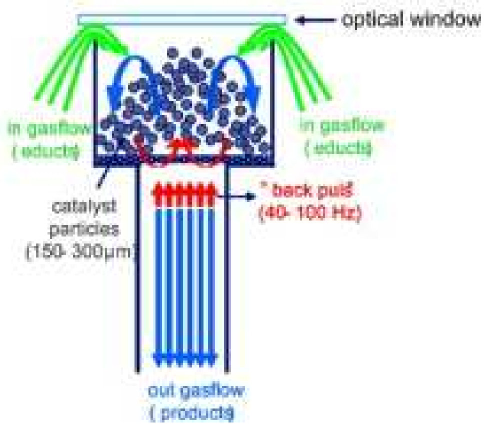


Airaksinen et al., *J. Catal.* **230** (2005) 507

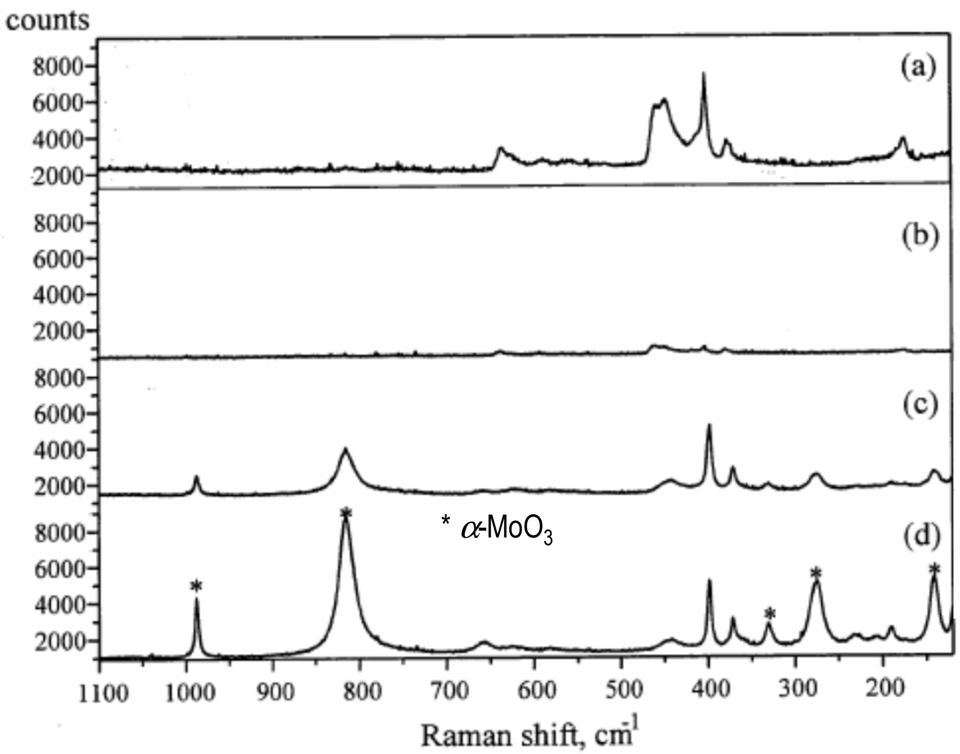
Applications

- Fluidized bed reactor cell





hydrodesulfurization



(a) MoS_2, 6 min full power, FB

(b) MoS_2, 6 min 1/8 power

(c) MoS_2, 1 min full power

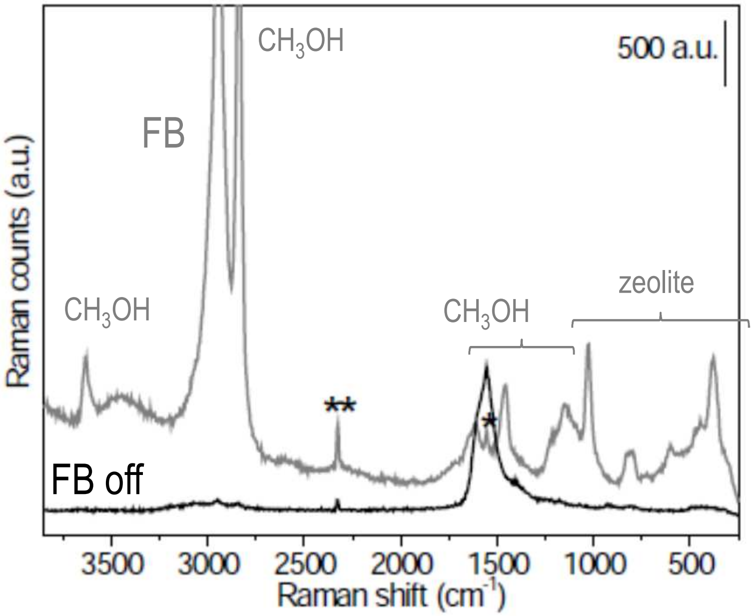
(d) MoS_2, 6 min full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

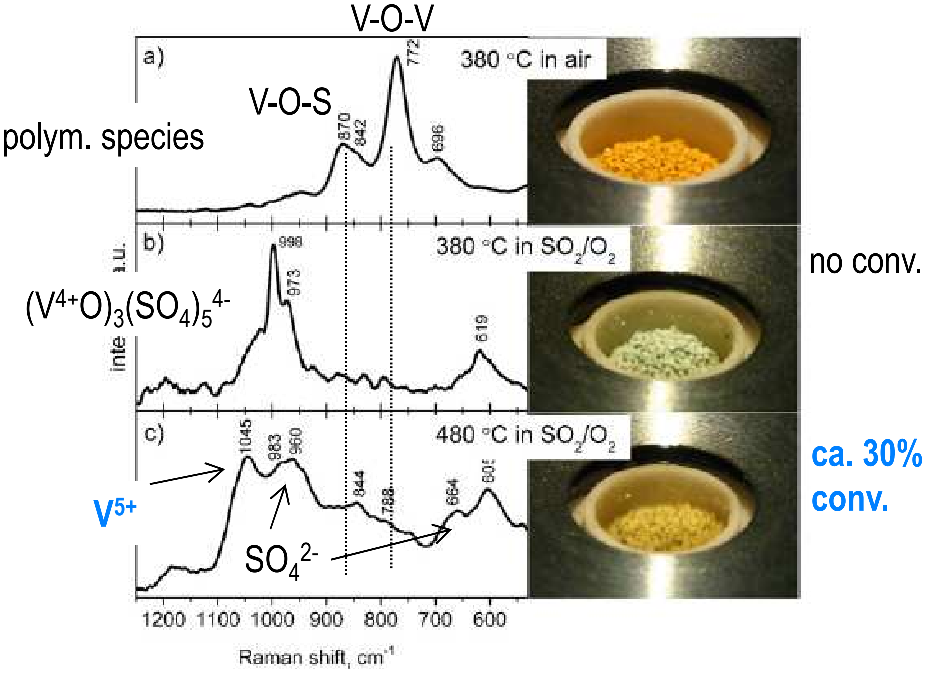
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm



V-O-V

V-O-S

polym. species

$(V^{4+}O)_3(SO_4)_5^{4-}$

no conv.

V^{5+}

SO_4^{2-}

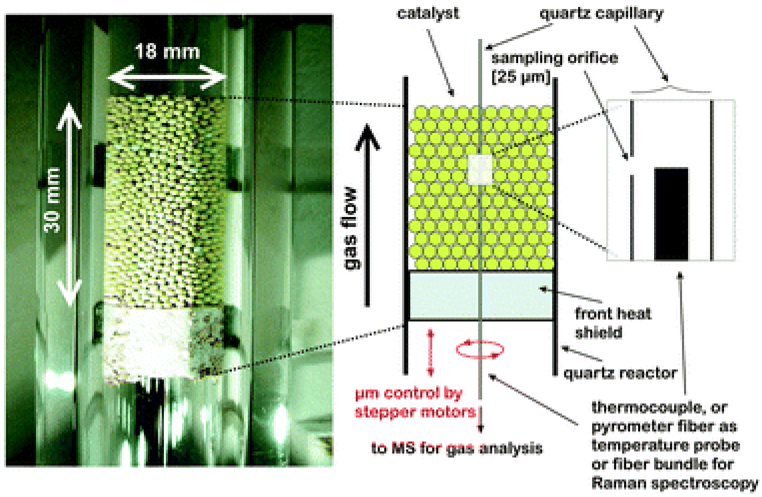
ca. 30% conv.

active species: mono- & dimeric V^{5+} oxosulfate species

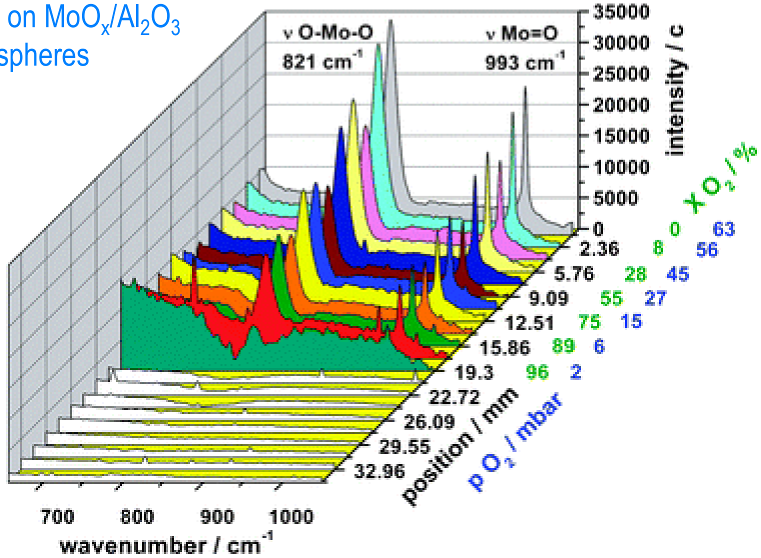
Beato et al., *Catal. Today* 205 (2013) 128

Applications

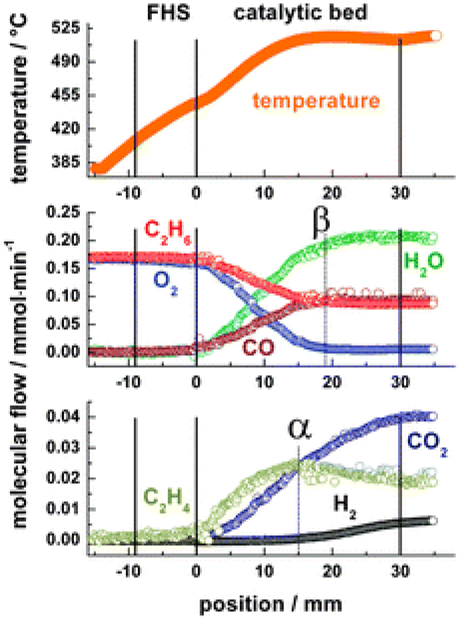
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

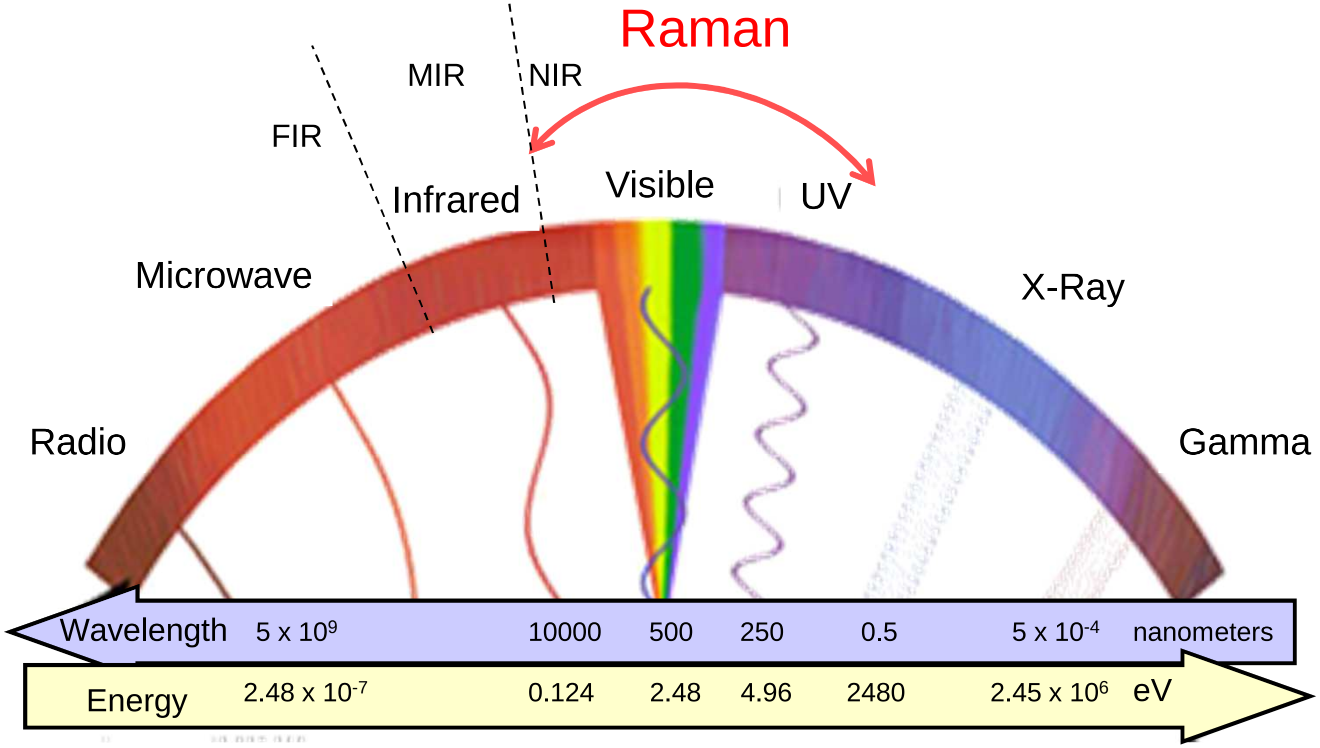
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy



Raman

FIR

MIR

NIR

Infrared

Visible

UV

Microwave

X-Ray

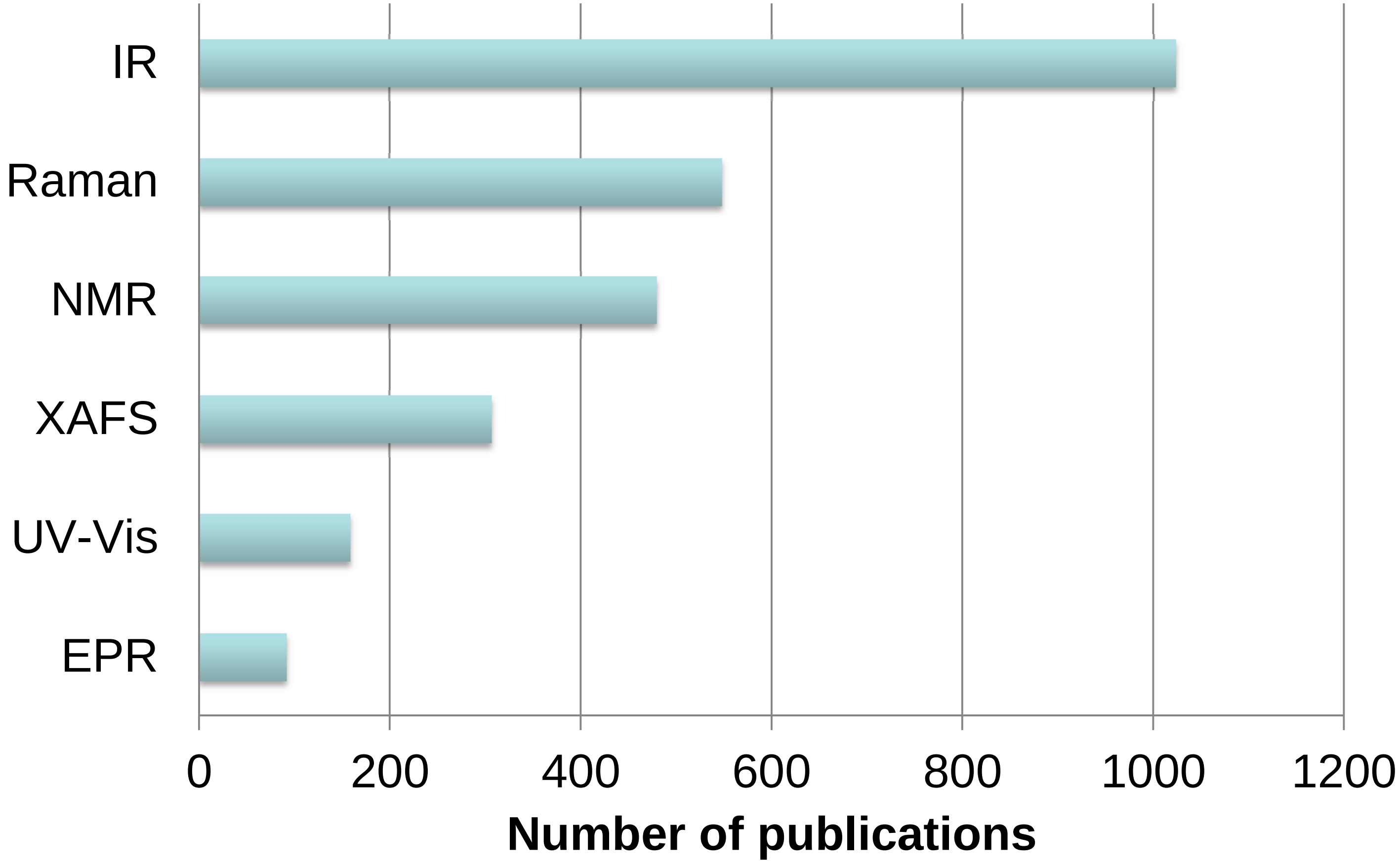
Radio

Gamma

Wavelength 5 x 10^9 10000 500 250 0.5 5 x 10^{-4} nanometers

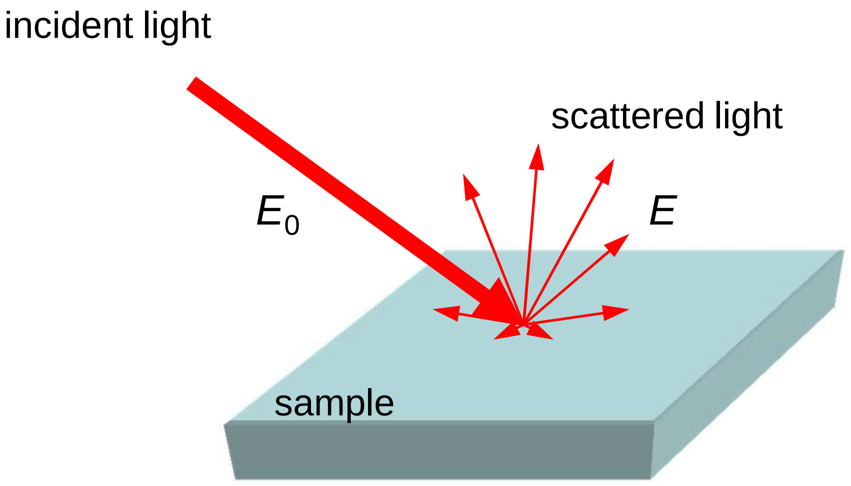
Energy 2.48 x 10^{-7} 0.124 2.48 4.96 2480 2.45 x 10^6 eV

Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib}t)]E_0\cos(2\pi\nu_0 t)$$

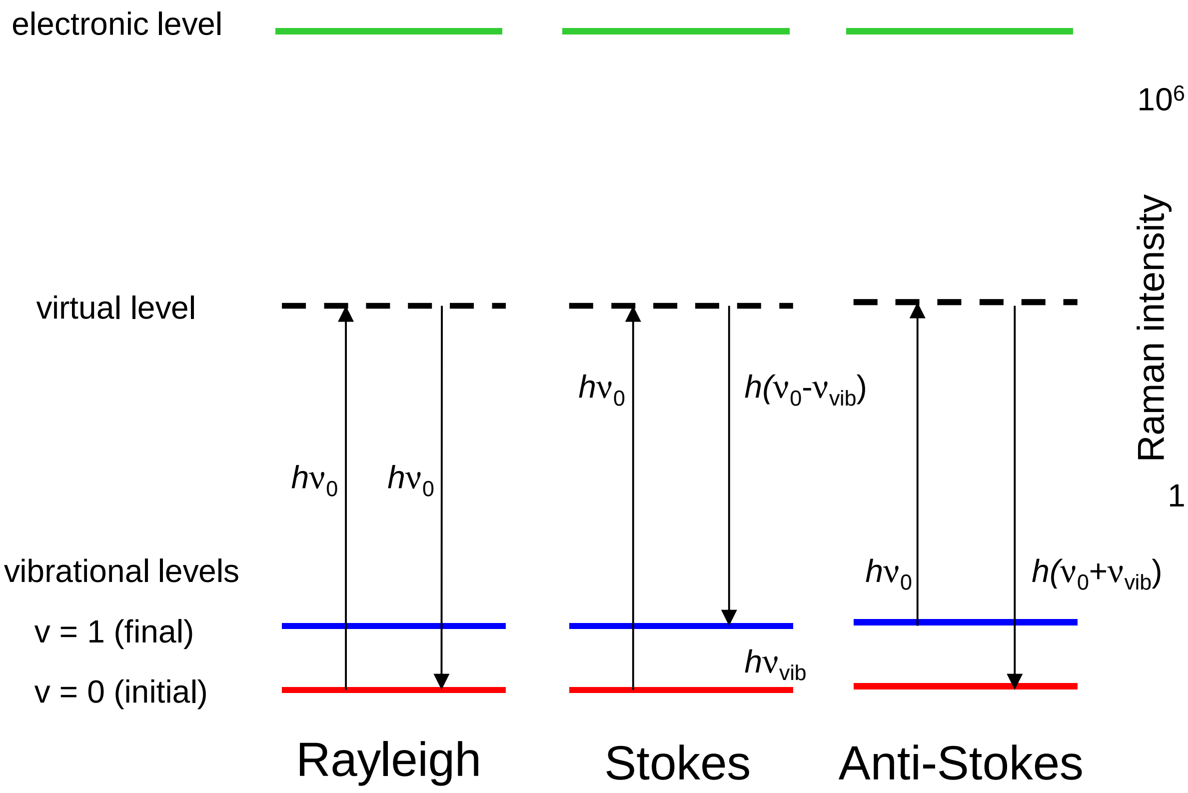
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib}t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



electronic level

virtual level

vibrational levels

v = 1 (final)

v = 0 (initial)

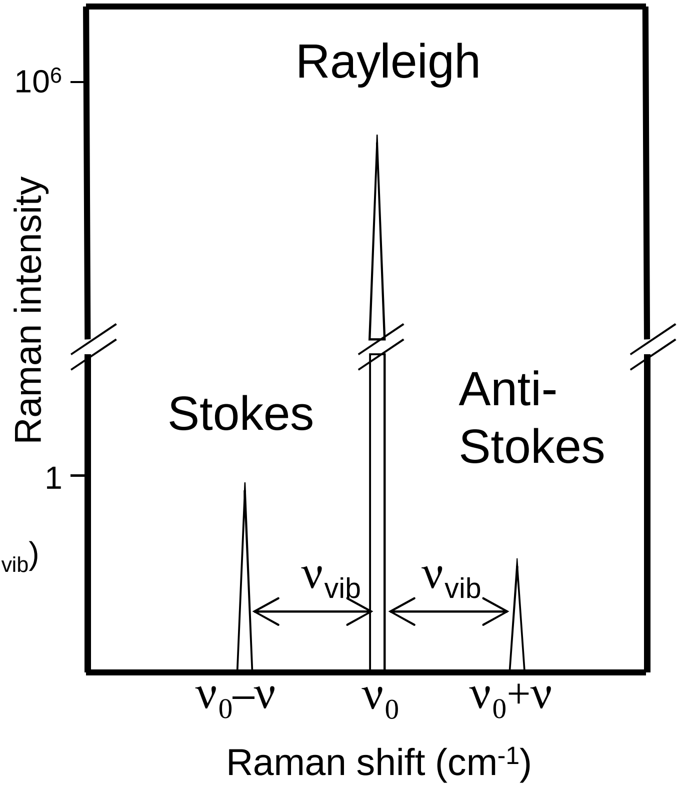
$h\nu_0$ $h\nu_0$

$h\nu_0$ $h(\nu_0 - \nu_{vib})$ $h\nu_{vib}$

$h\nu_0$ $h(\nu_0 + \nu_{vib})$

Rayleigh Stokes Anti-Stokes

Raman spectrum



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\text{ (Anti-Stokes)}}{I\text{ (Stokes)}} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

- 4th power of ν (4th power law)
- 2nd power of $\Delta\alpha$
  - properties of molecules
  - strength of bonds

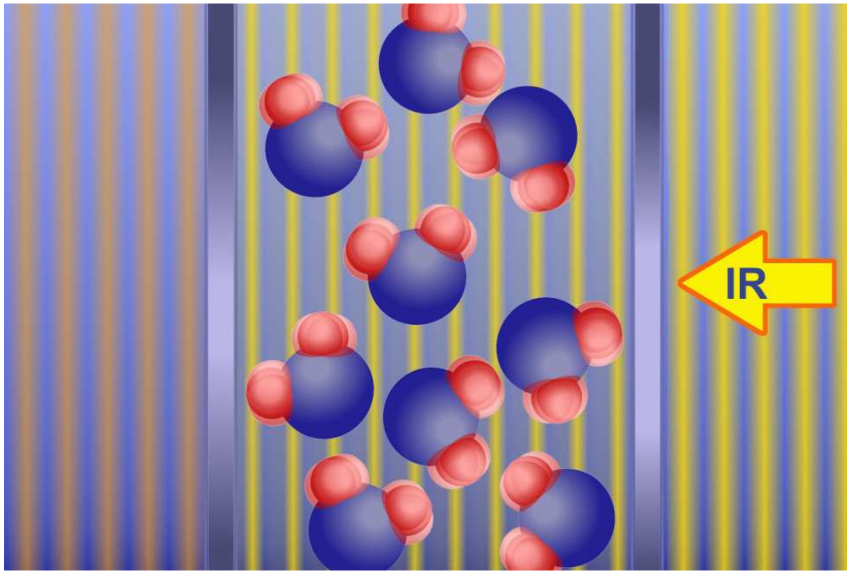
↓

covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

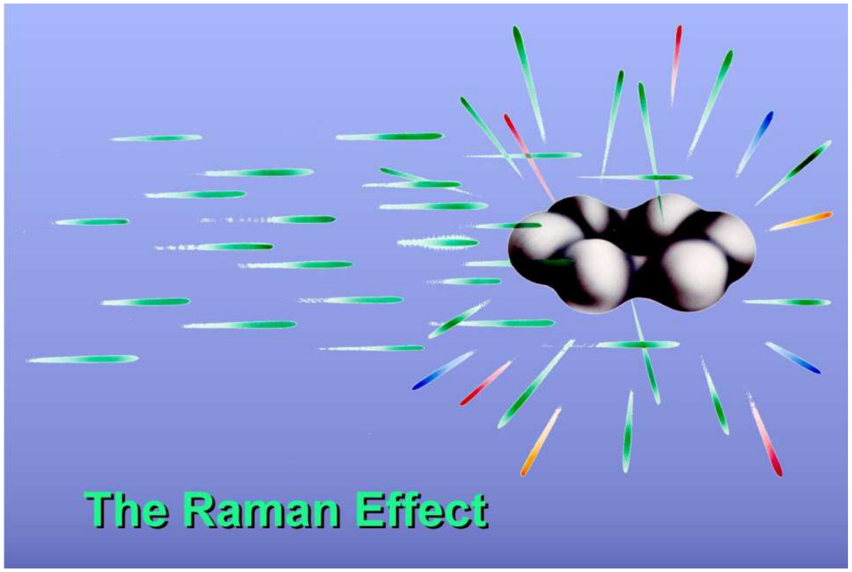
Raman *vs.* Infrared

Infrared



Absorption of IR light

Raman



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

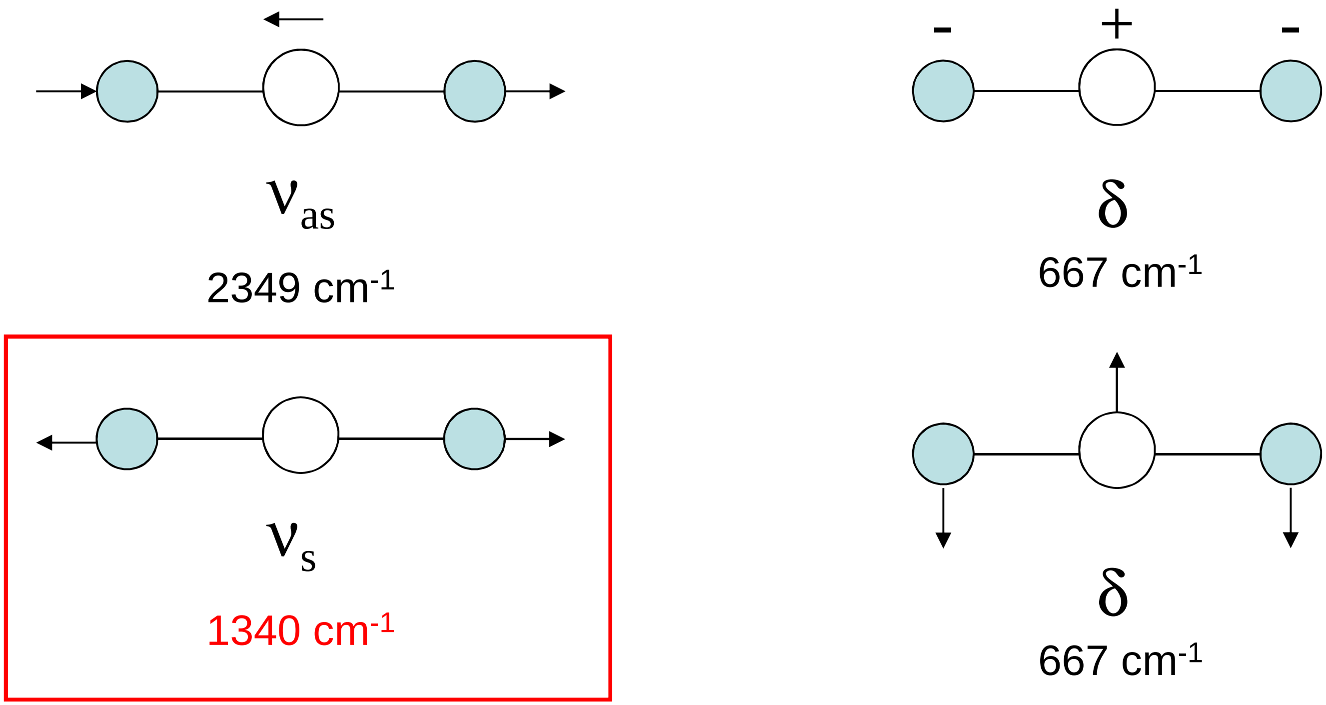
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - large electron clouds
  - not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

Raman *vs.* Infrared

CO_2



ν_{as}

2349 cm^{-1}

δ

667 cm^{-1}

ν_s

1340 cm^{-1}

Raman active

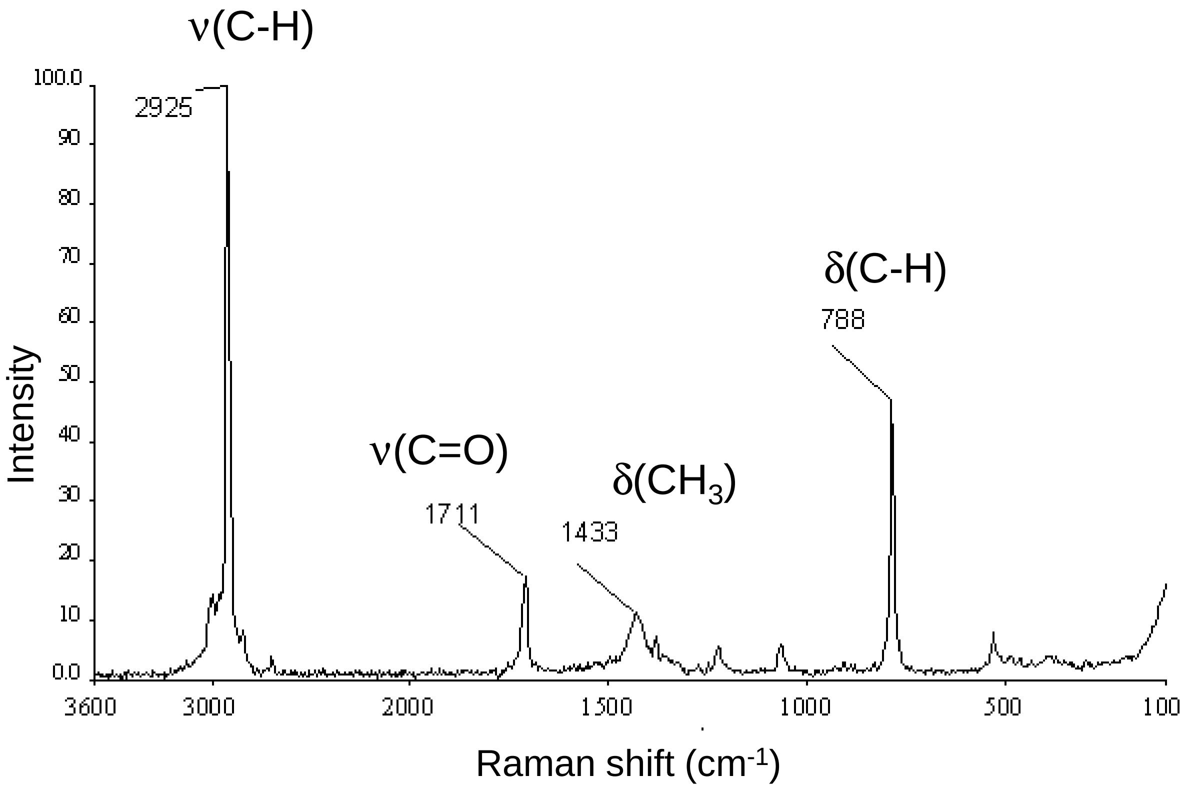
δ

667 cm^{-1}

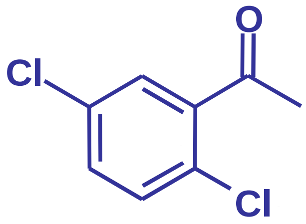
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



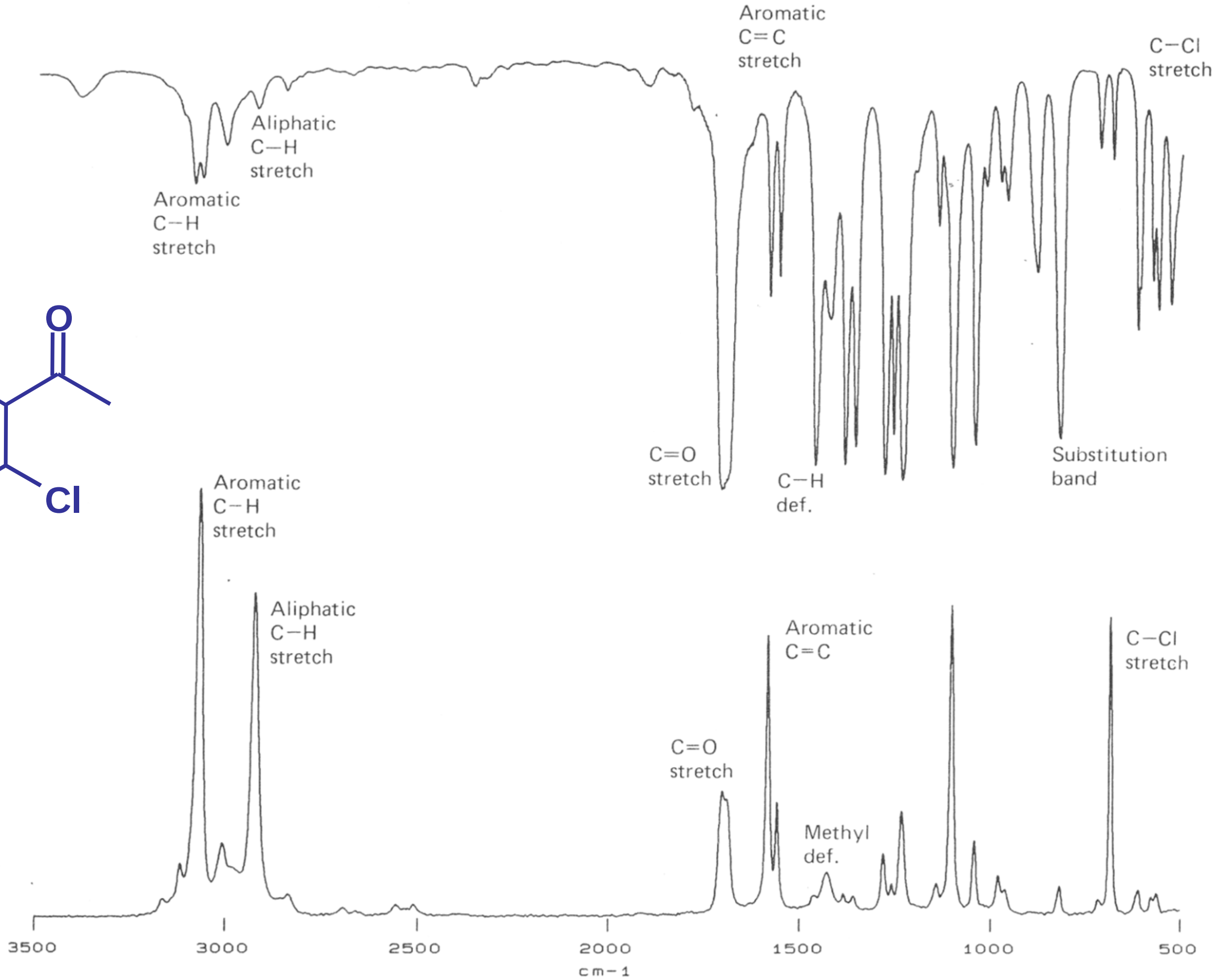


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

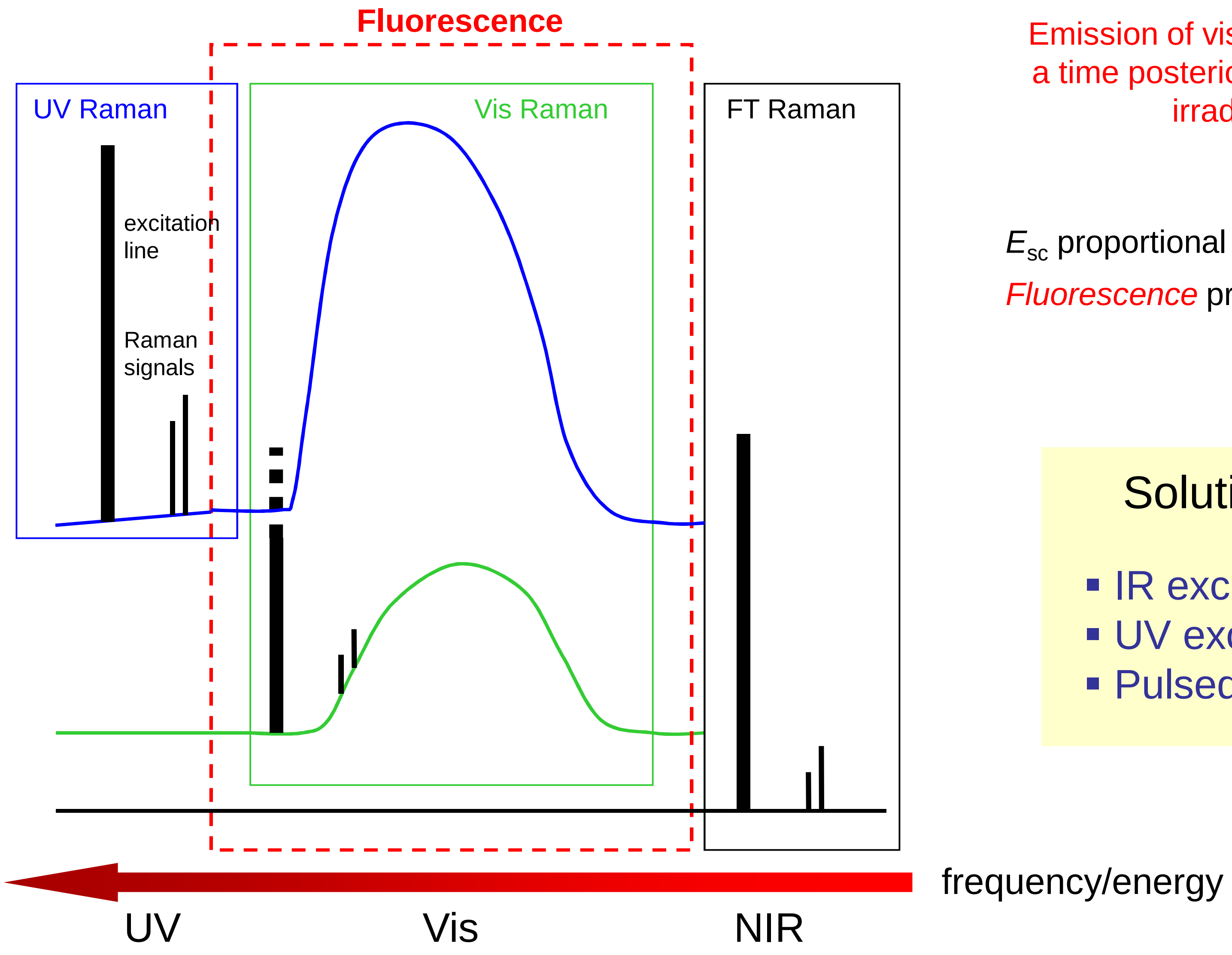
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 μm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

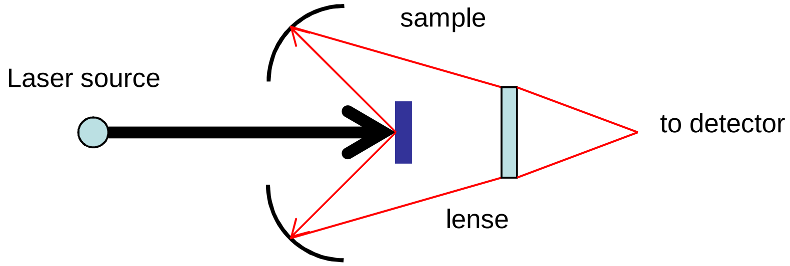
Fluorescence proportional to ν

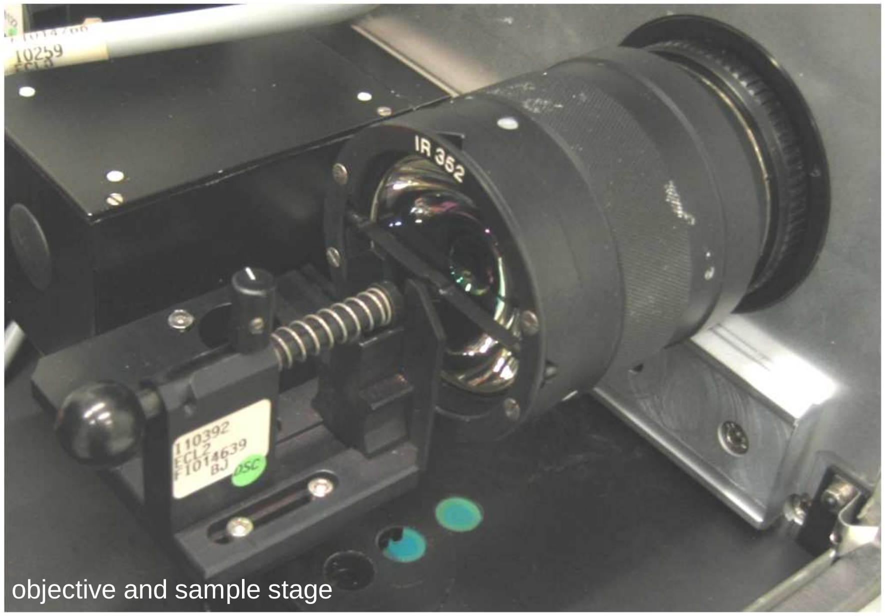
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

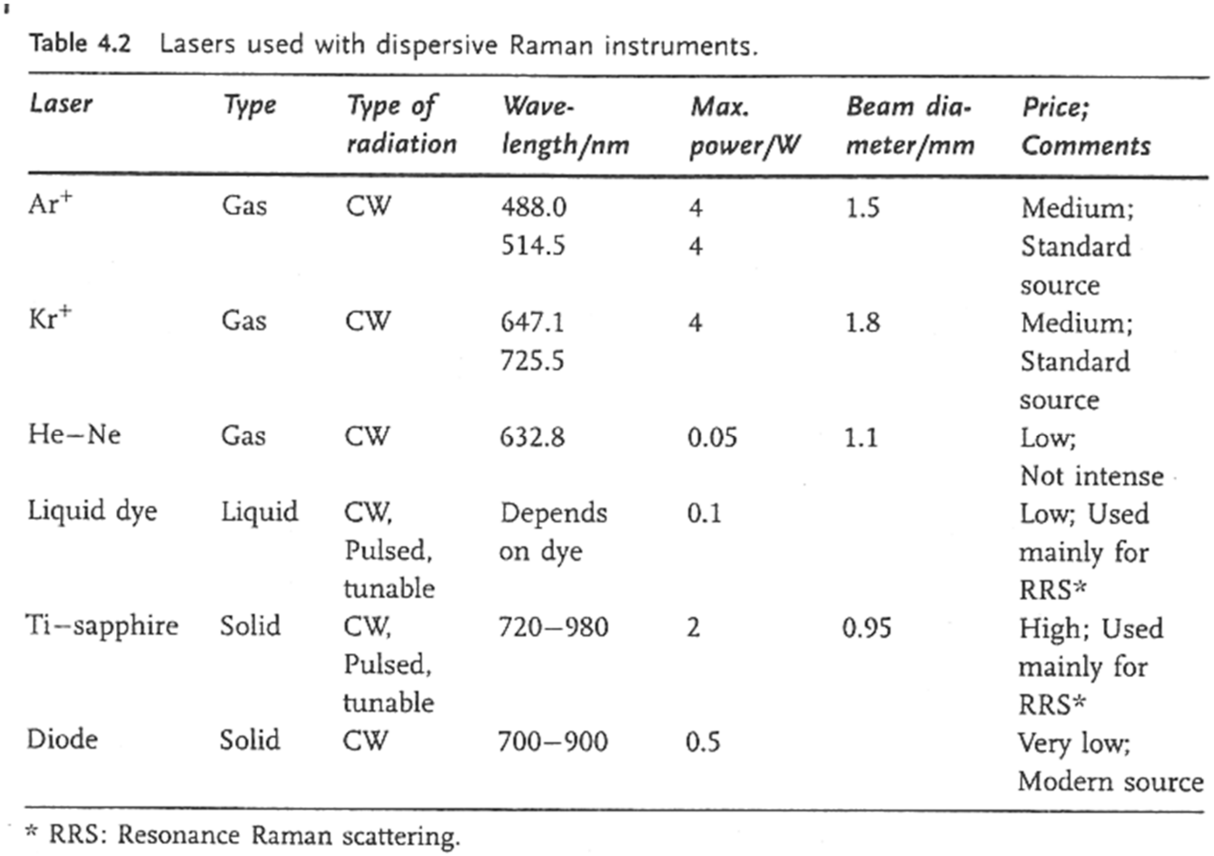


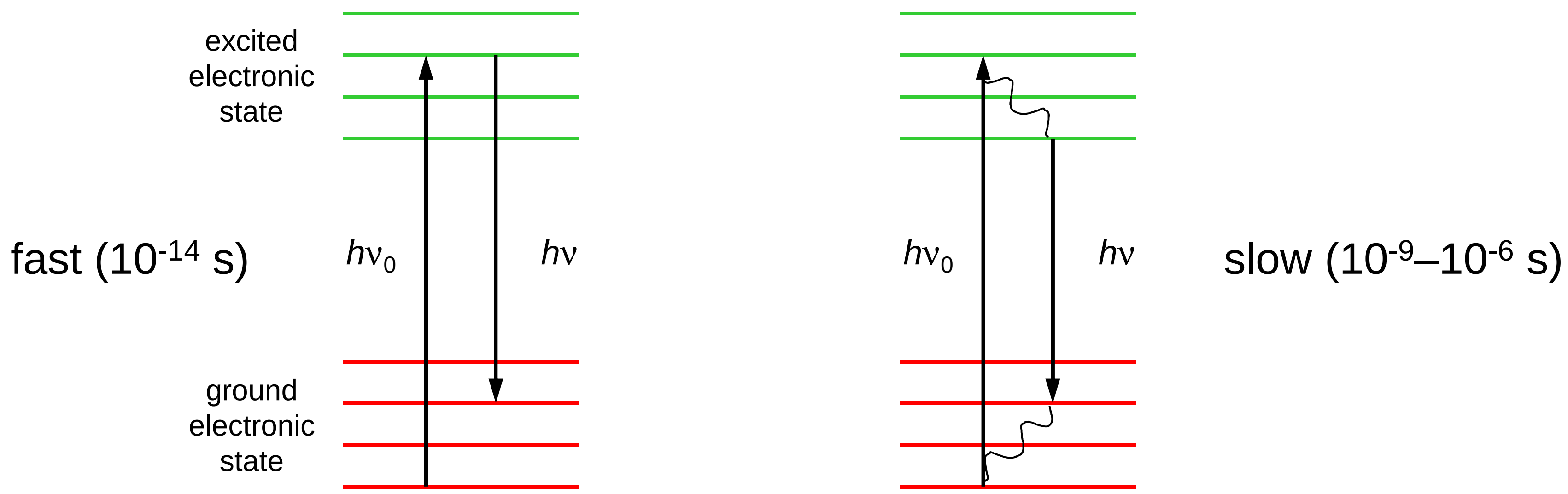
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



Resonance Raman scattering

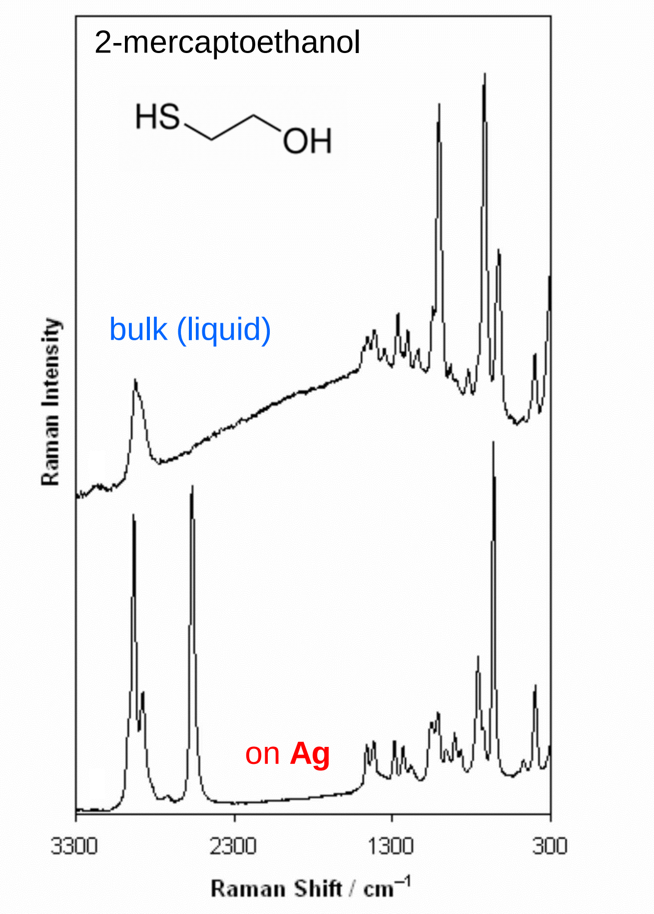
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

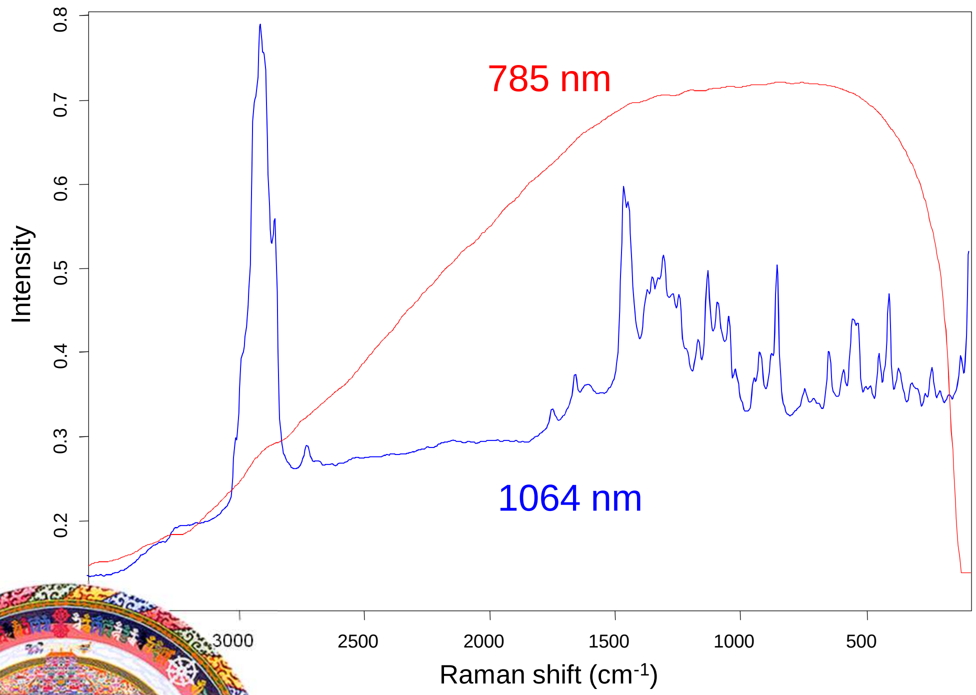
- Remarks:

- rough surface; nanoparticles (10–100 nm) or kinks, steps etc. (E always perpendicular to surface, locally)
- vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



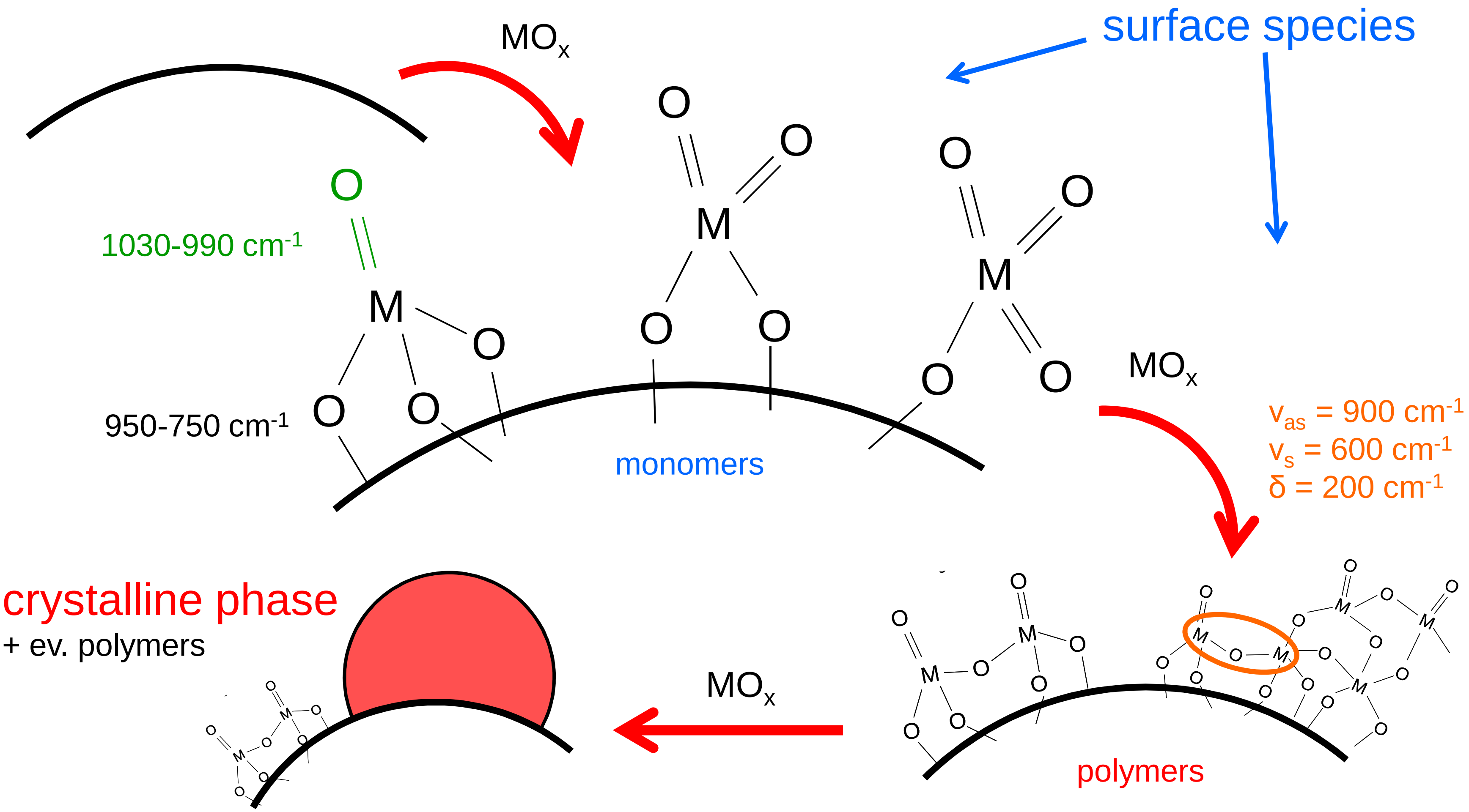
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



MO$_x$

surface species

1030-990 cm^{-1}

950-750 cm^{-1}

monomers

MO$_x$

v_{as} = 900 cm^{-1}
v_s = 600 cm^{-1}
δ = 200 cm^{-1}

crystalline phase
+ ev. polymers

MO$_x$

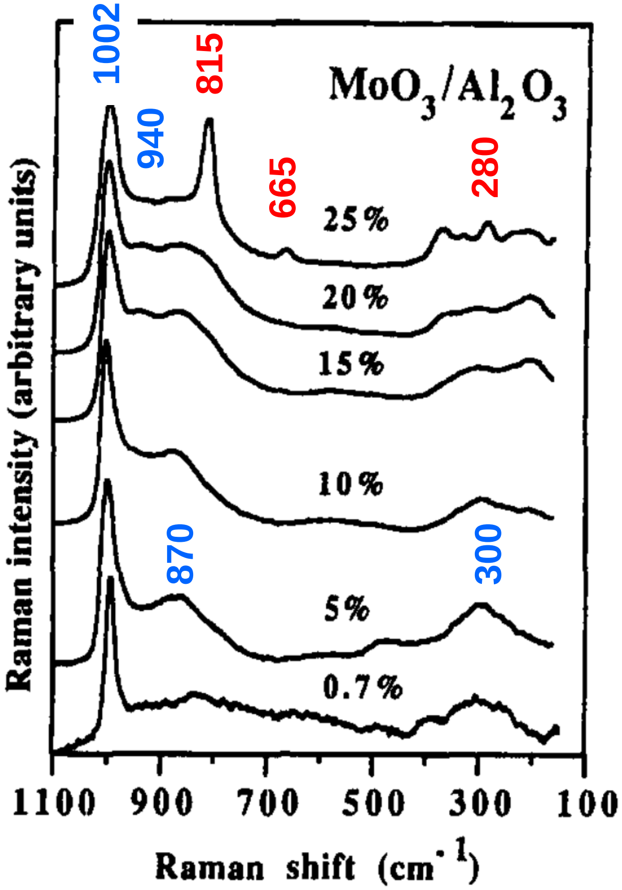
polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



surface MoO_3

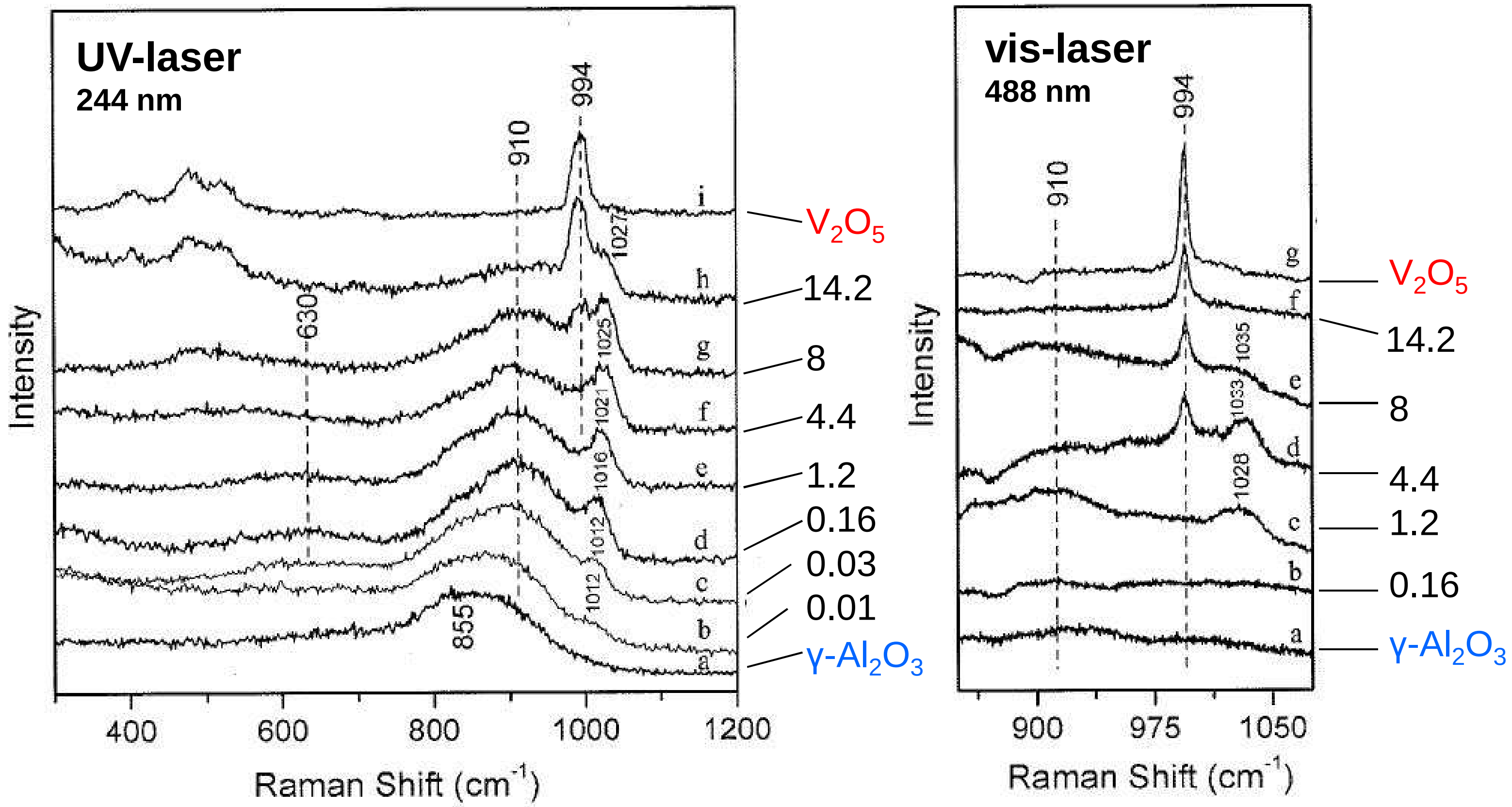
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

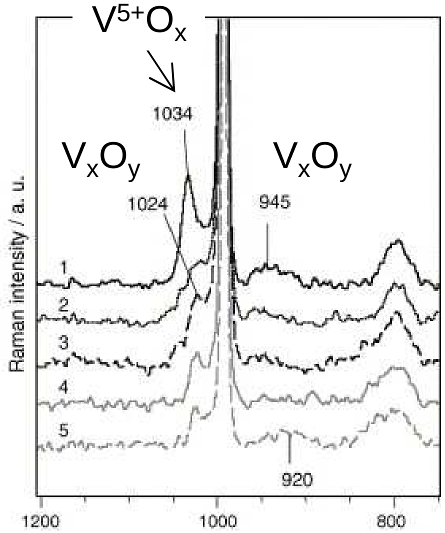
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

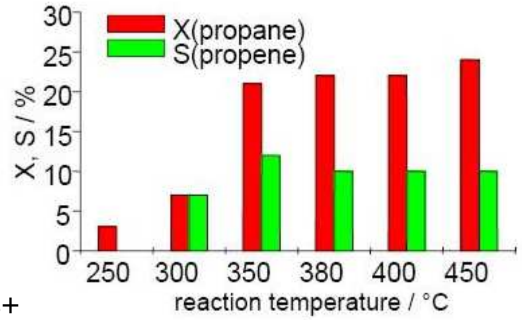
Applications

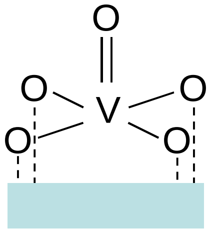
- Reactivity of V/TiO_2 after oxidative treatment

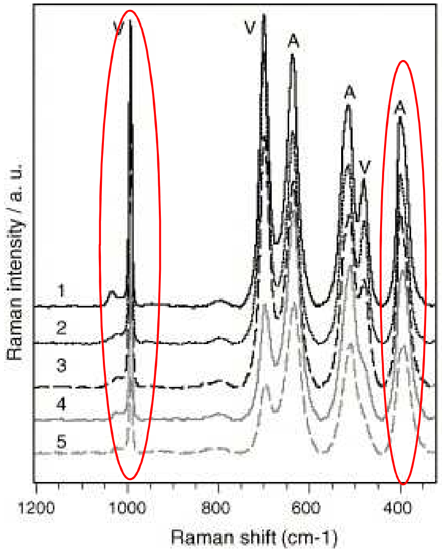


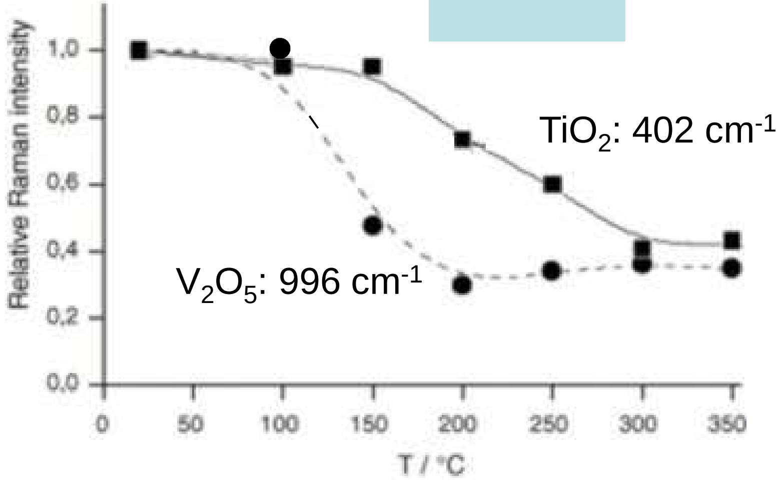
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

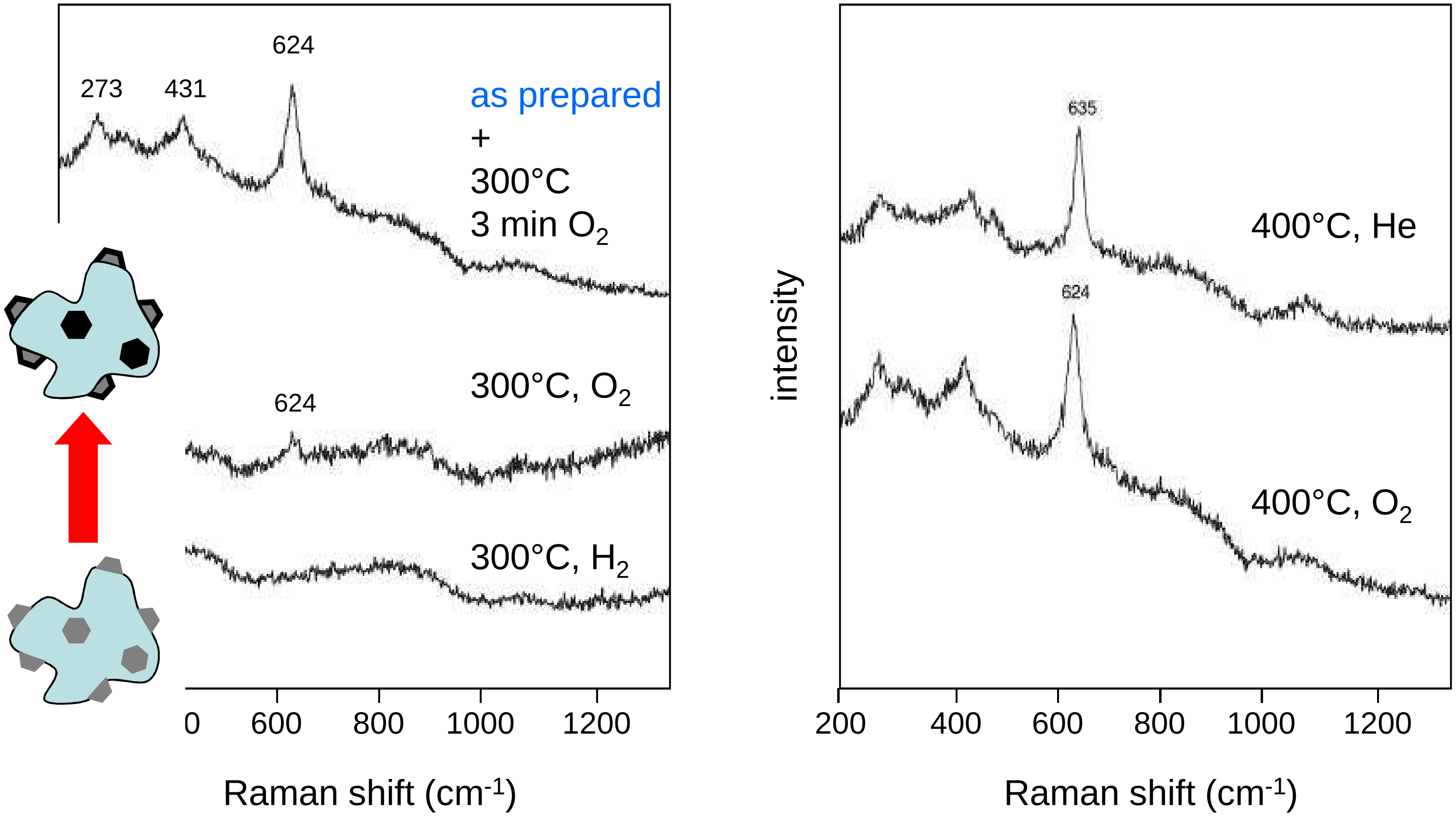
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



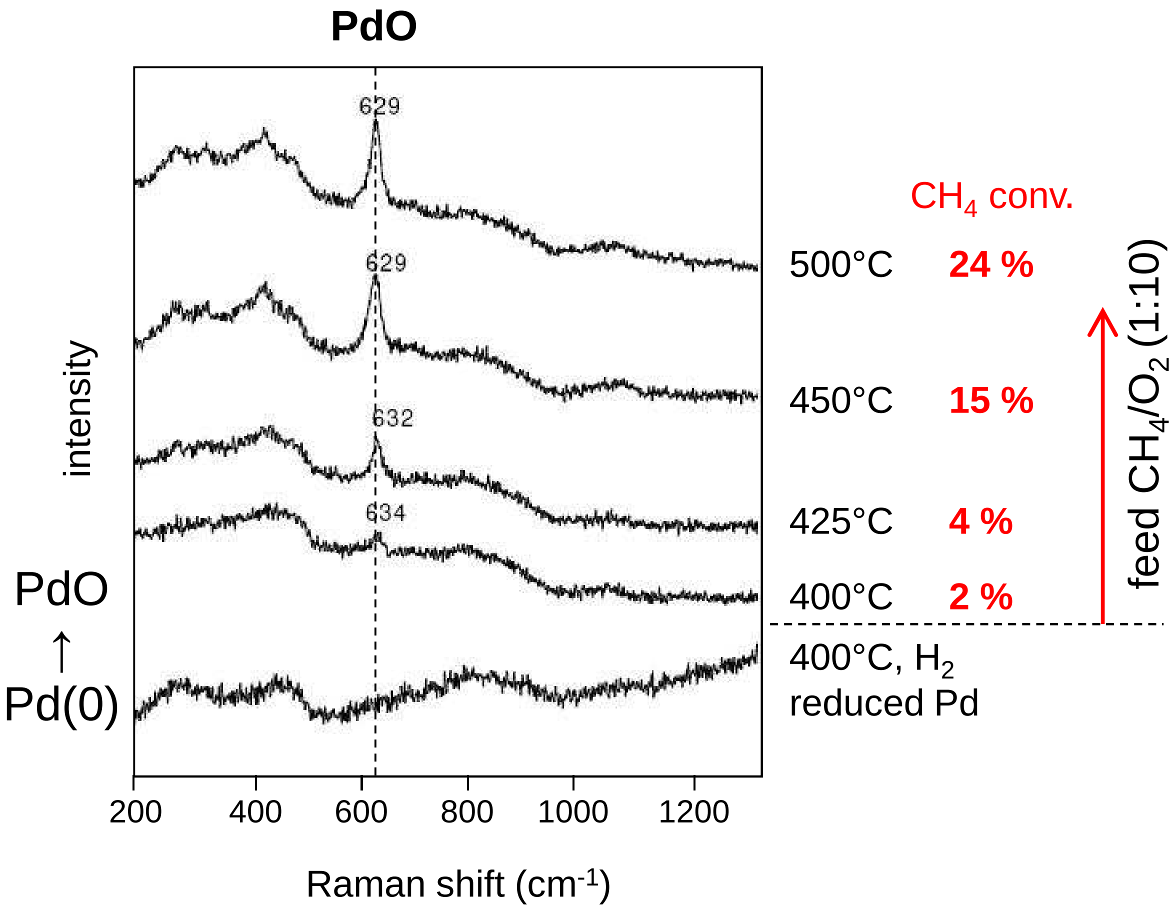
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

Applications

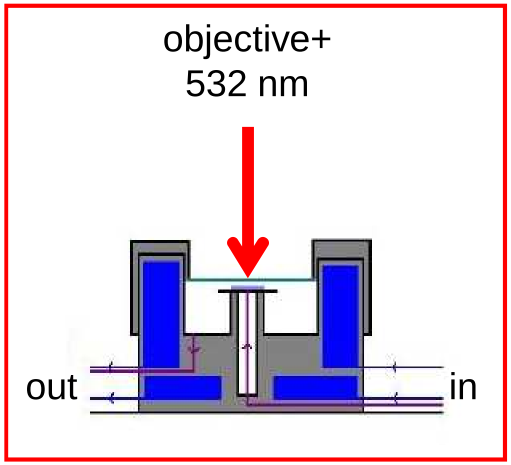
- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



	CH_4 conv.
500°C	**24 %**
450°C	**15 %**
425°C	**4 %**
400°C	**2 %**
400°C, H_2 reduced Pd	

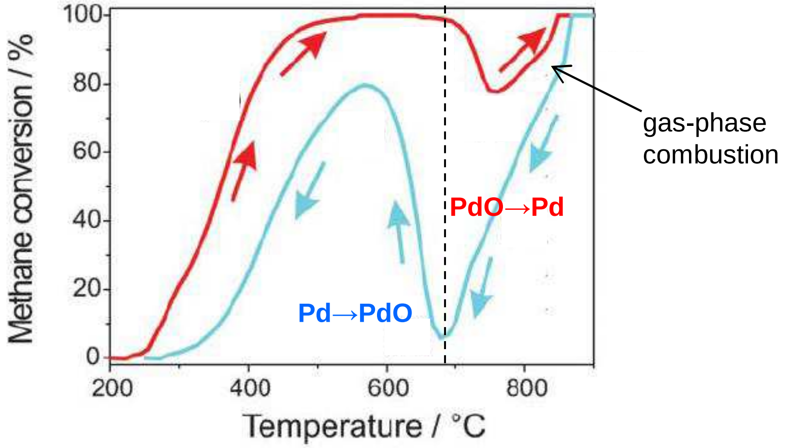
near PdO mode

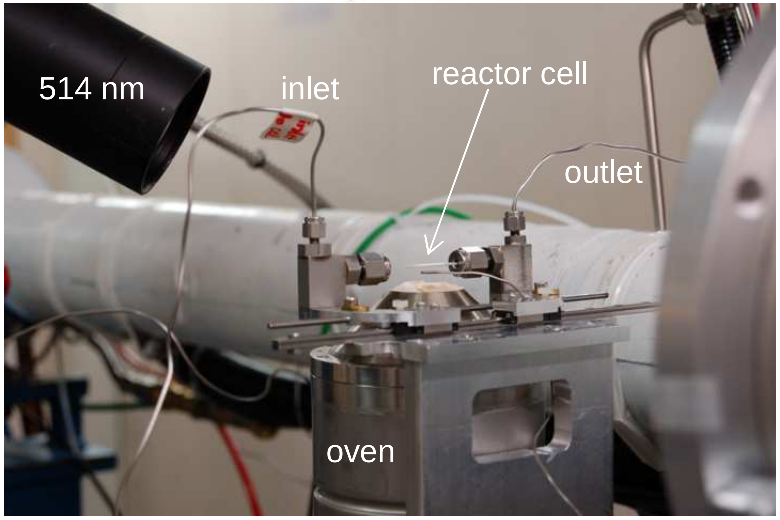


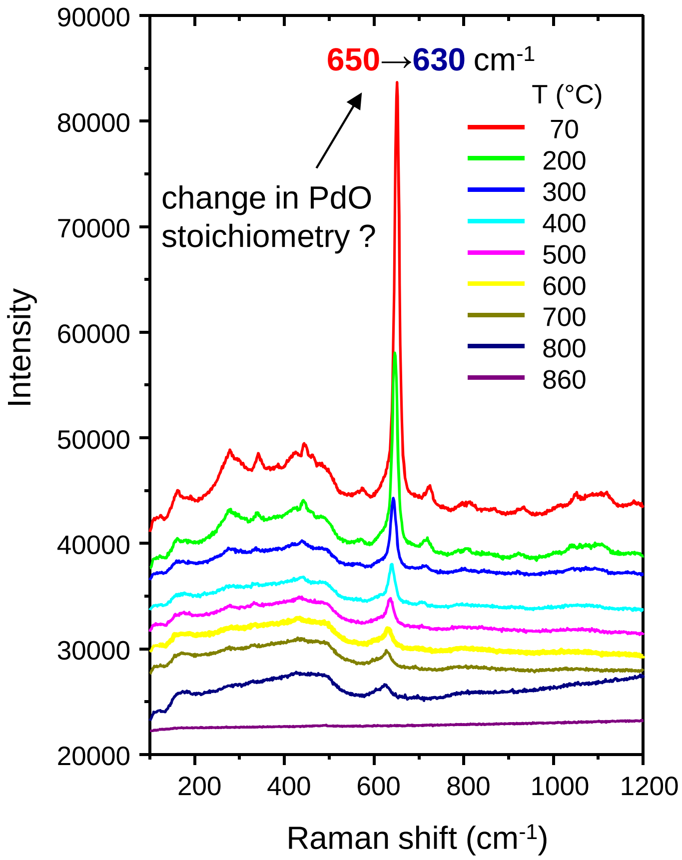
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







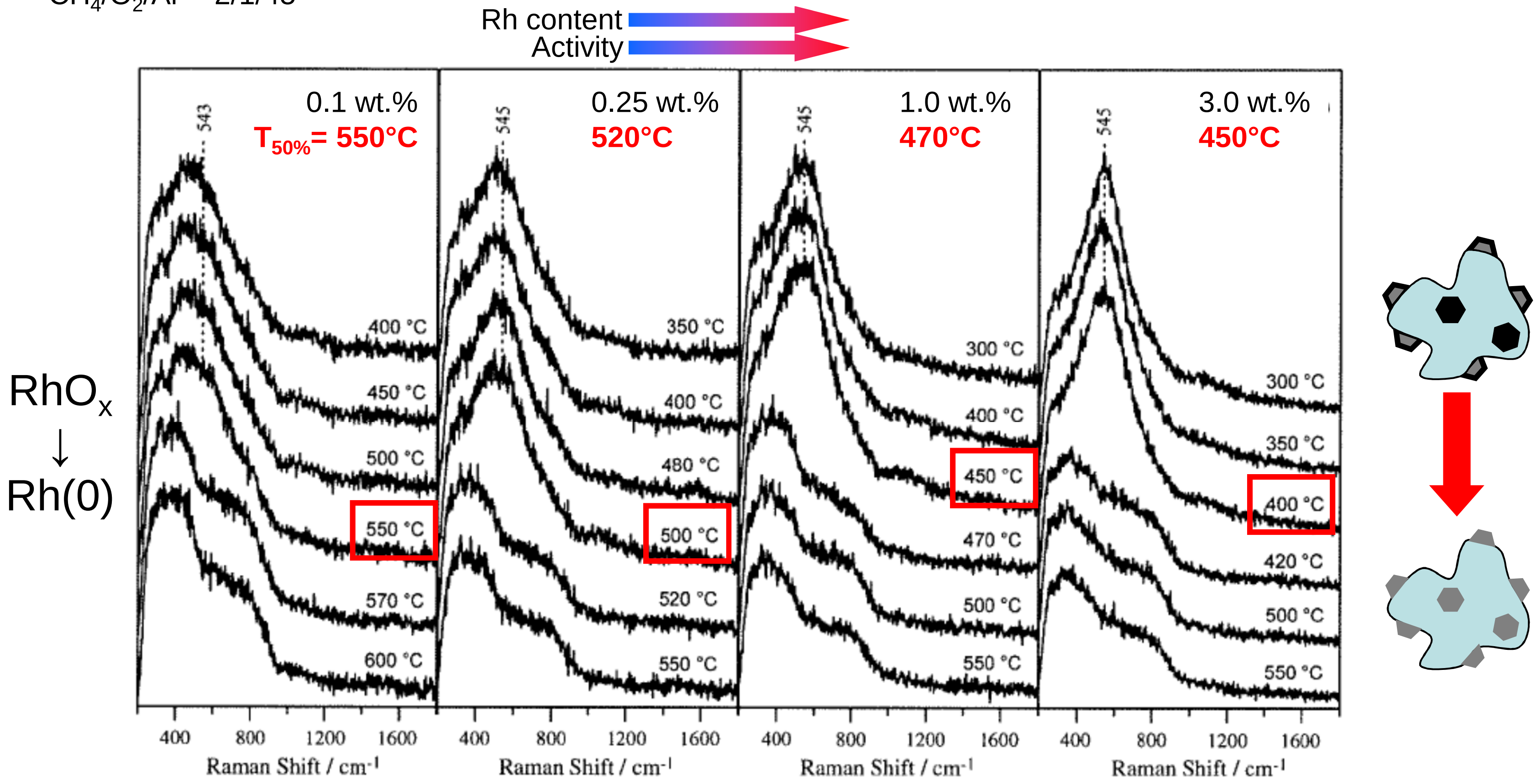
1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

- Methane partial oxidation over Rh/Al_2O_3

3 mW, 325 nm
$CH_4/O_2/Ar$ = 2/1/45

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$



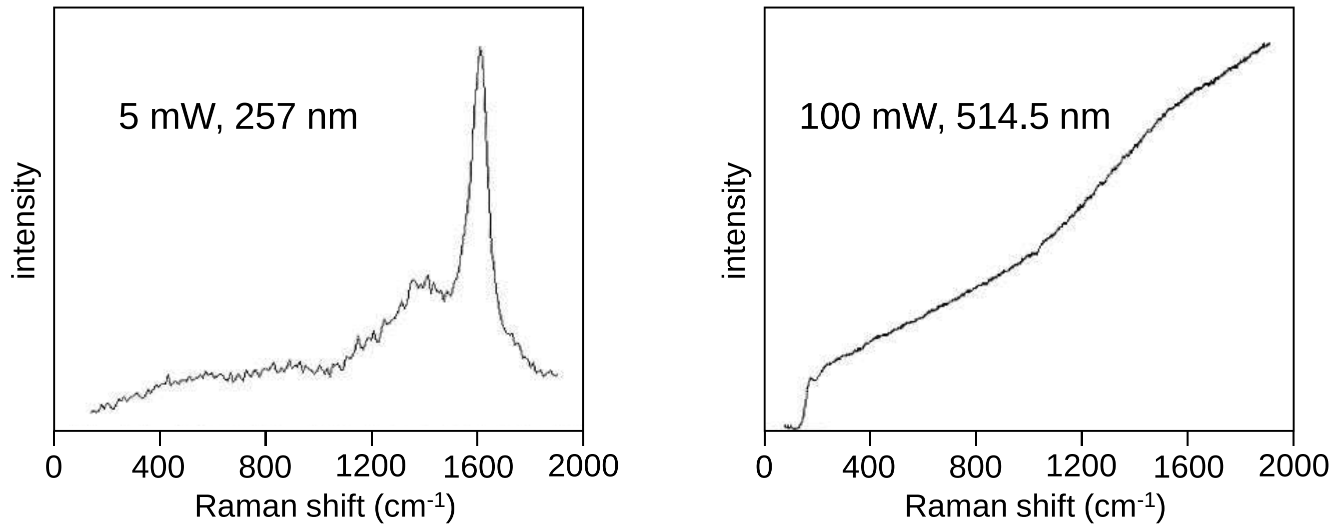
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

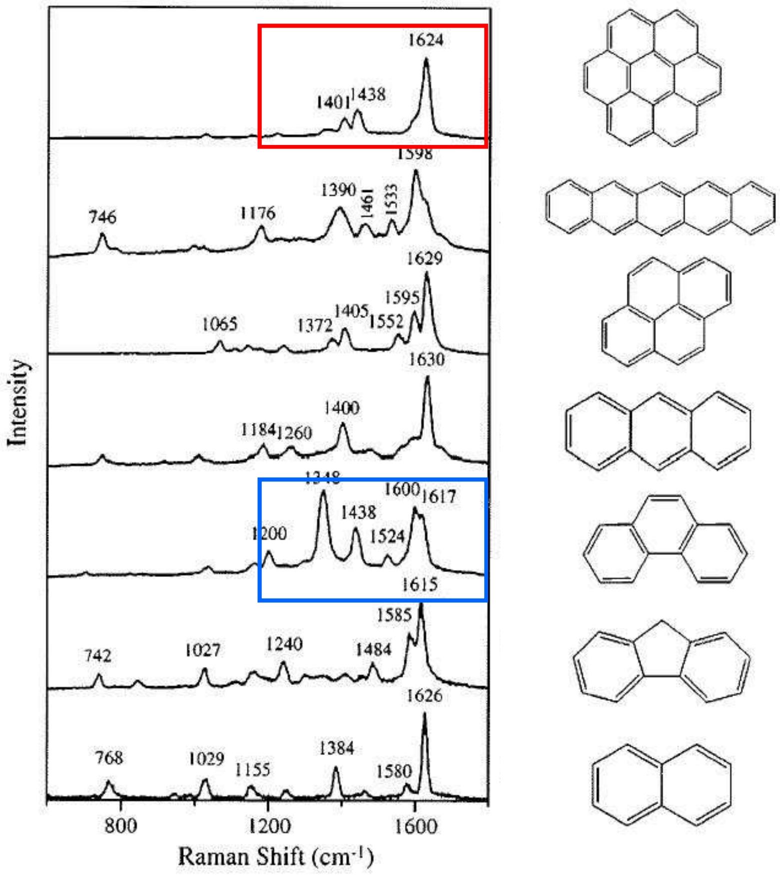
Rh/Al_2O_3, coked 500°C in naphtha

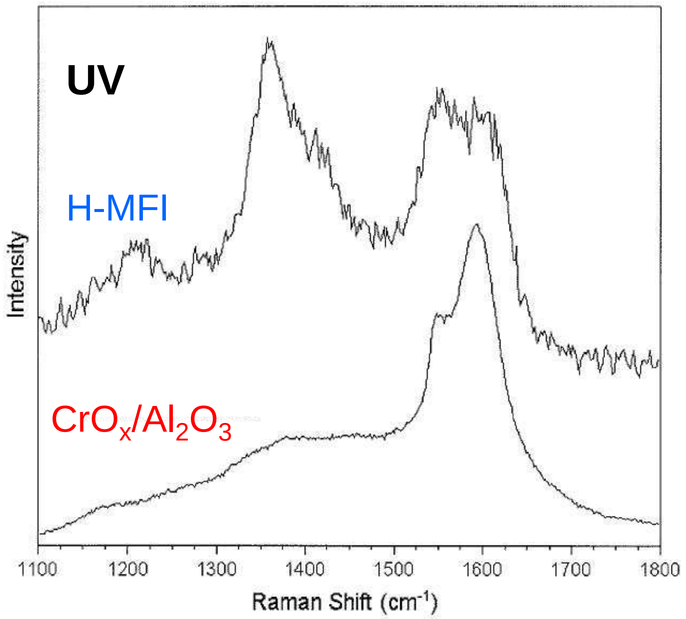


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





Coke classification

1D topology, chain-like

2D topology, sheet-like

Coke from:

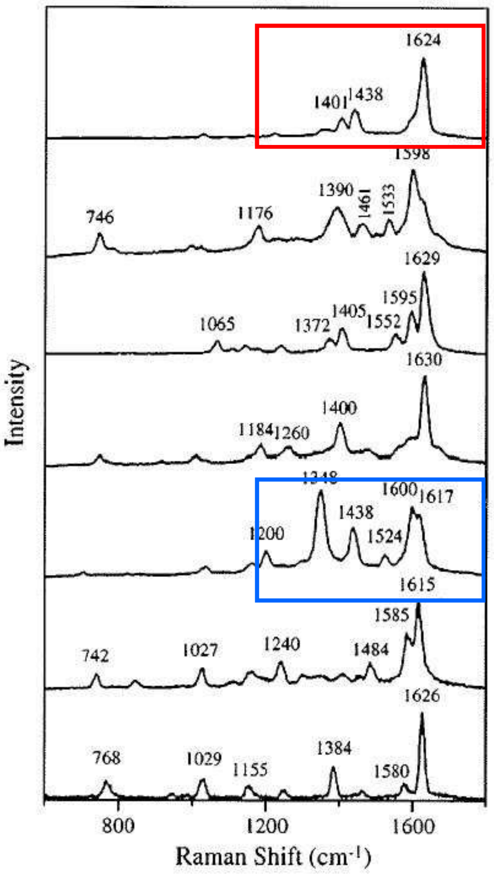
H-MFI: methanol-to-hydrocarbons (MTH)

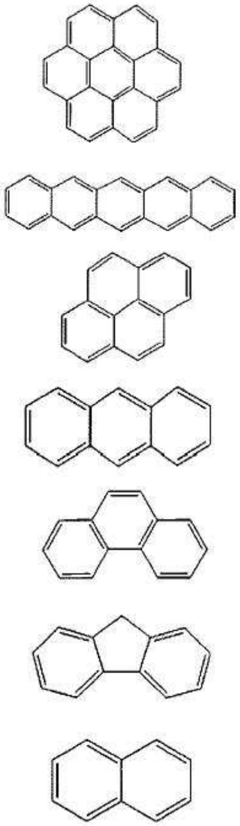
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

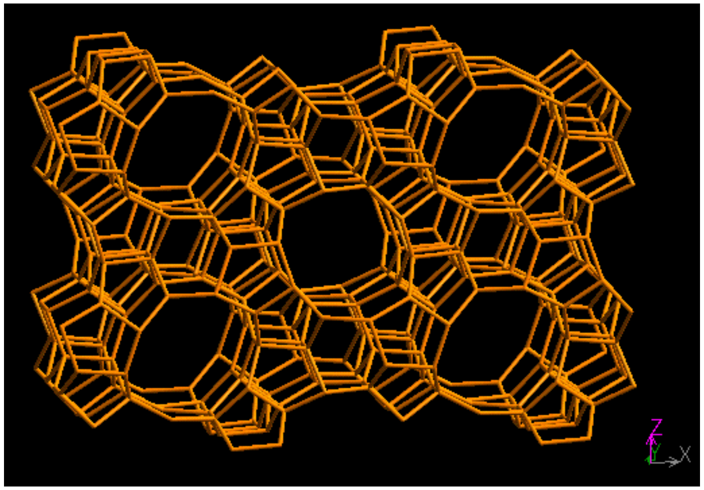
Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization







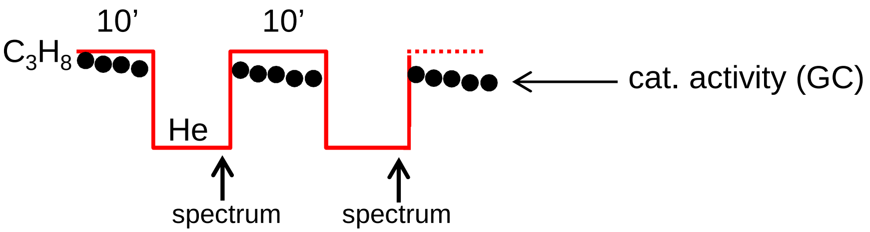
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

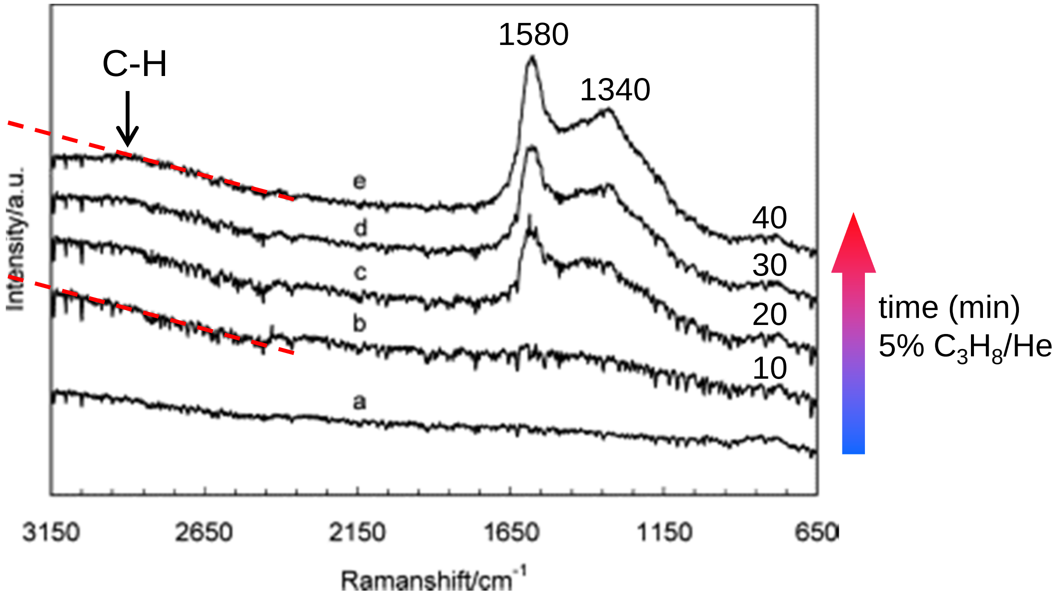
Stair, *Adv. Catal.* **51** (2007) 75

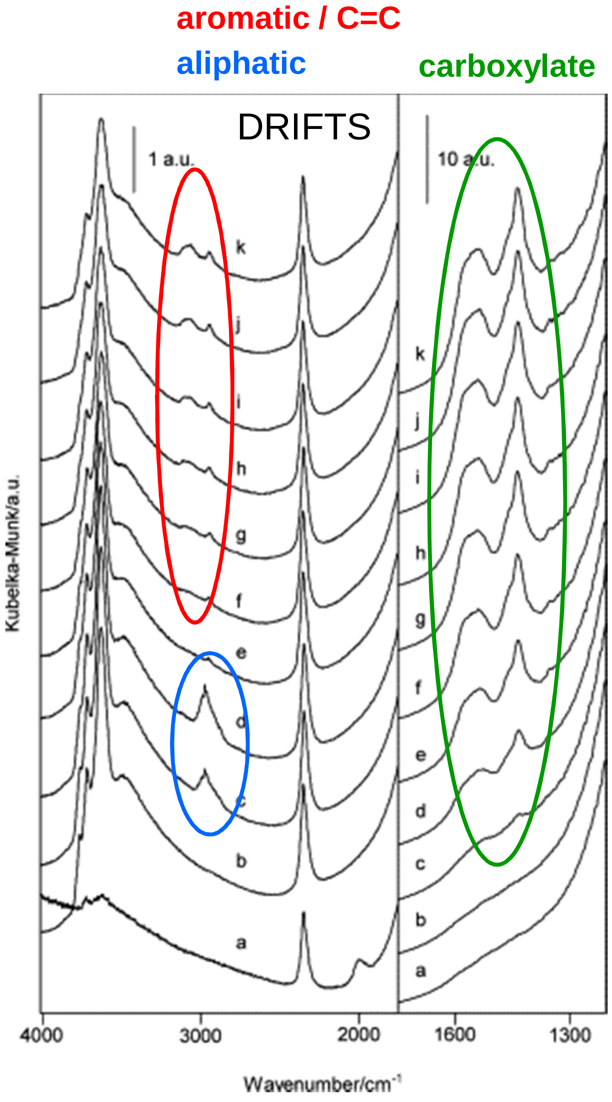
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

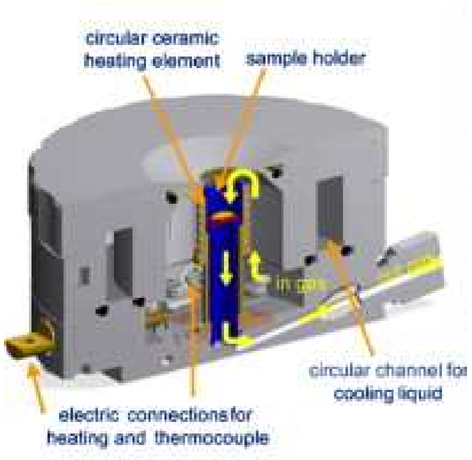


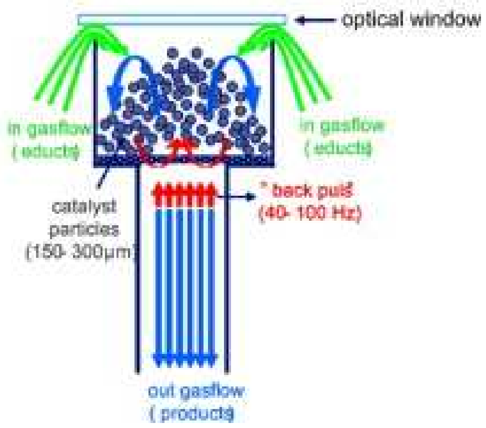


Airaksinen et al., *J. Catal.* **230** (2005) 507

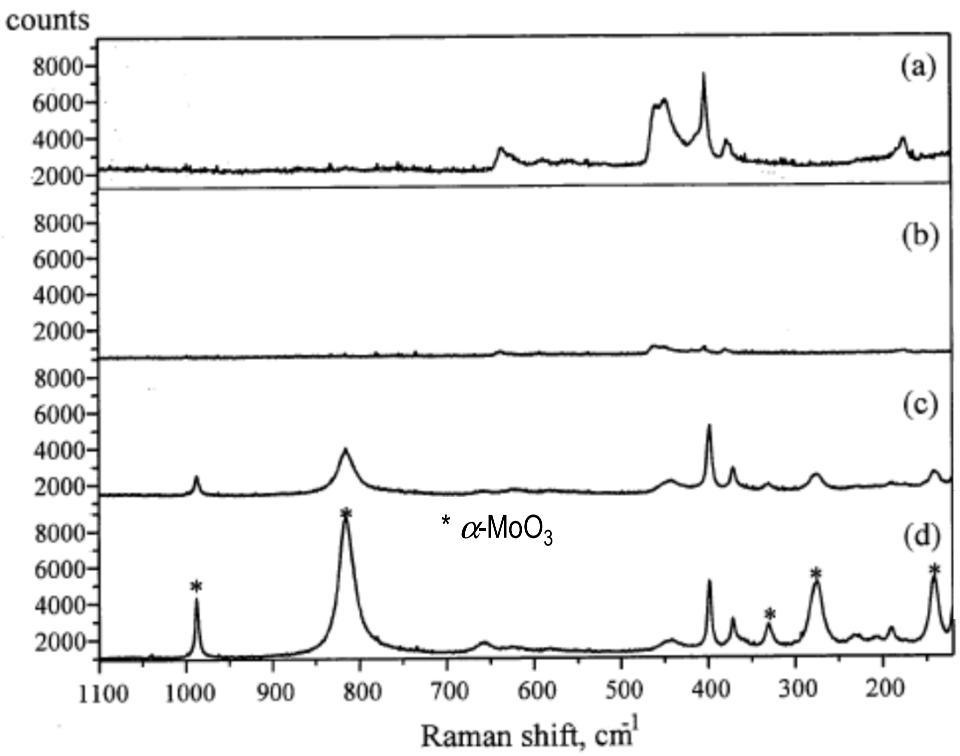
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min full power, FB

MoS_2, 6 min 1/8 power

MoS_2, 1 min full power

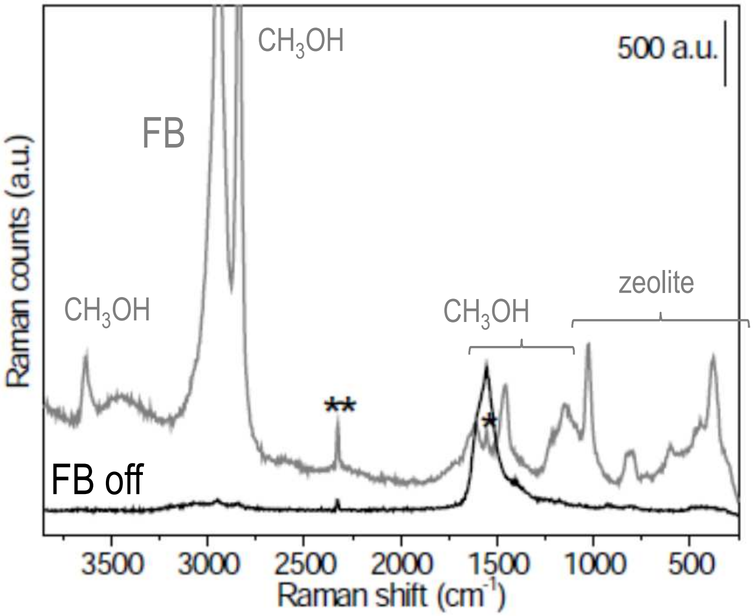
MoS_2, 6 min full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

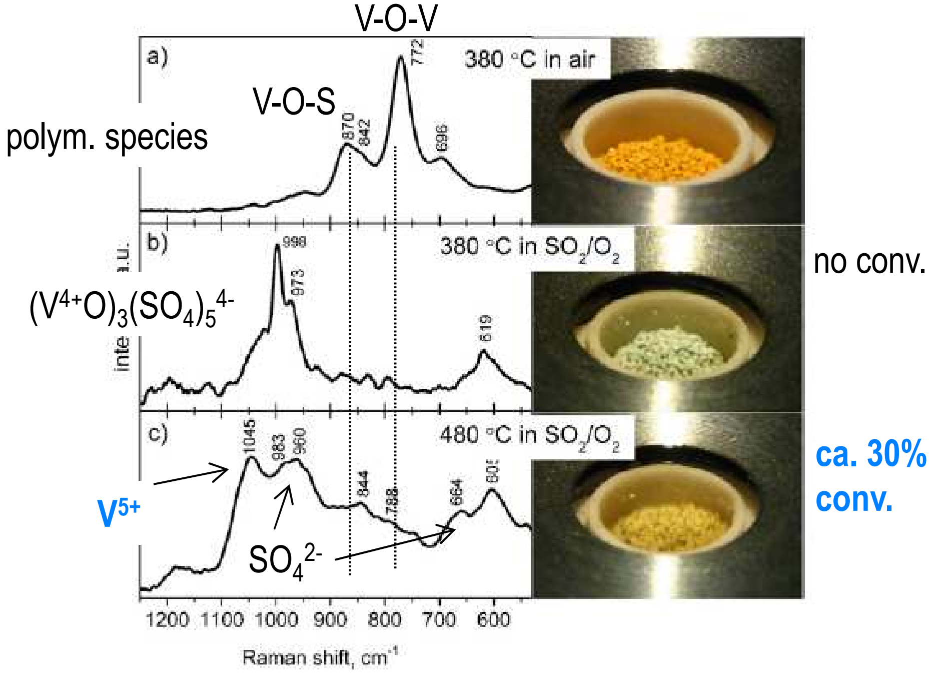
- Fluidized bed reactor cell

CH$_3$OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH$_3$OH decomposition

Sulfuric acid V$_2$O$_5$/pyrosulfate catalyst
λ= 514 nm

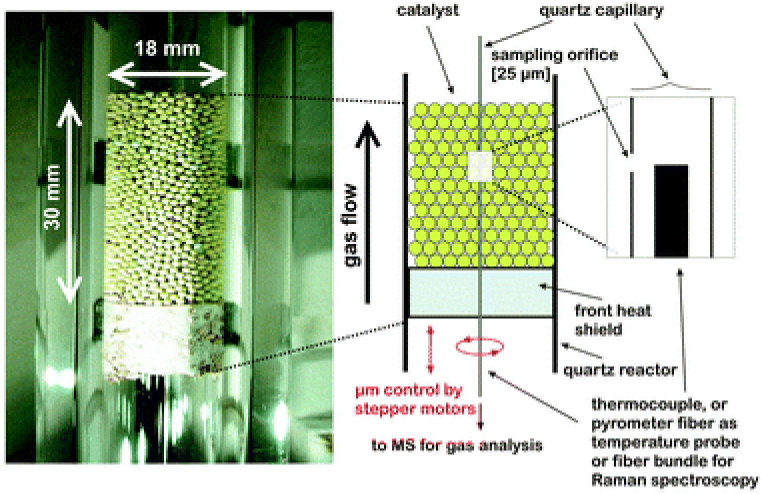


active species: mono- & dimeric V^{5+} oxosulfate species

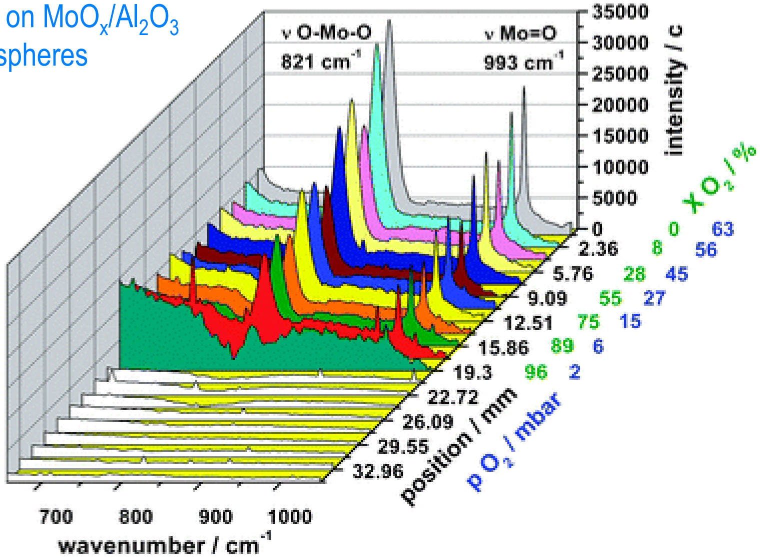
Beato et al., *Catal. Today* 205 (2013) 128

Applications

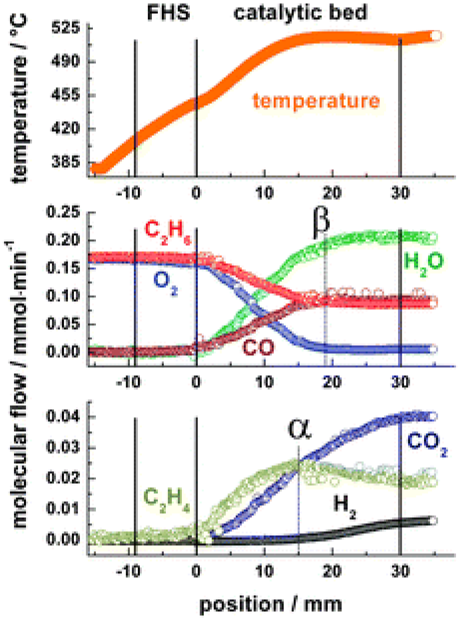
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

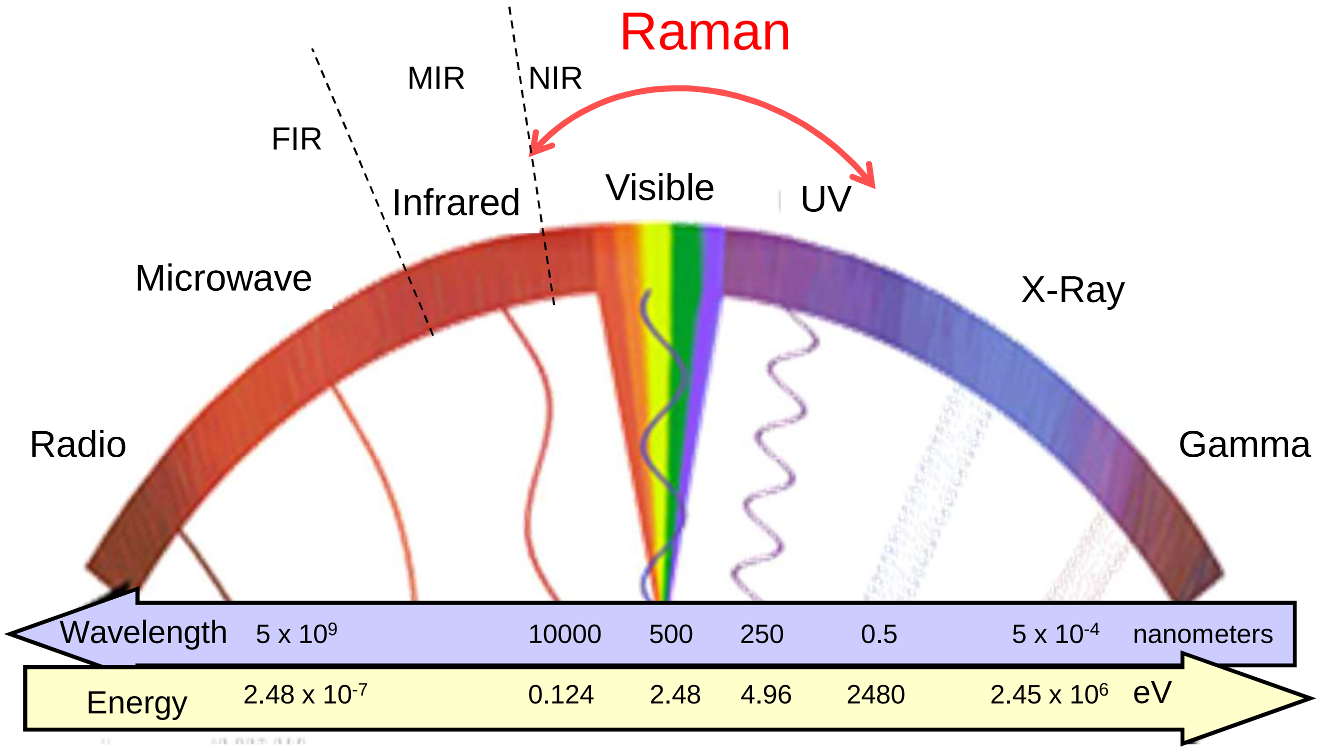
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

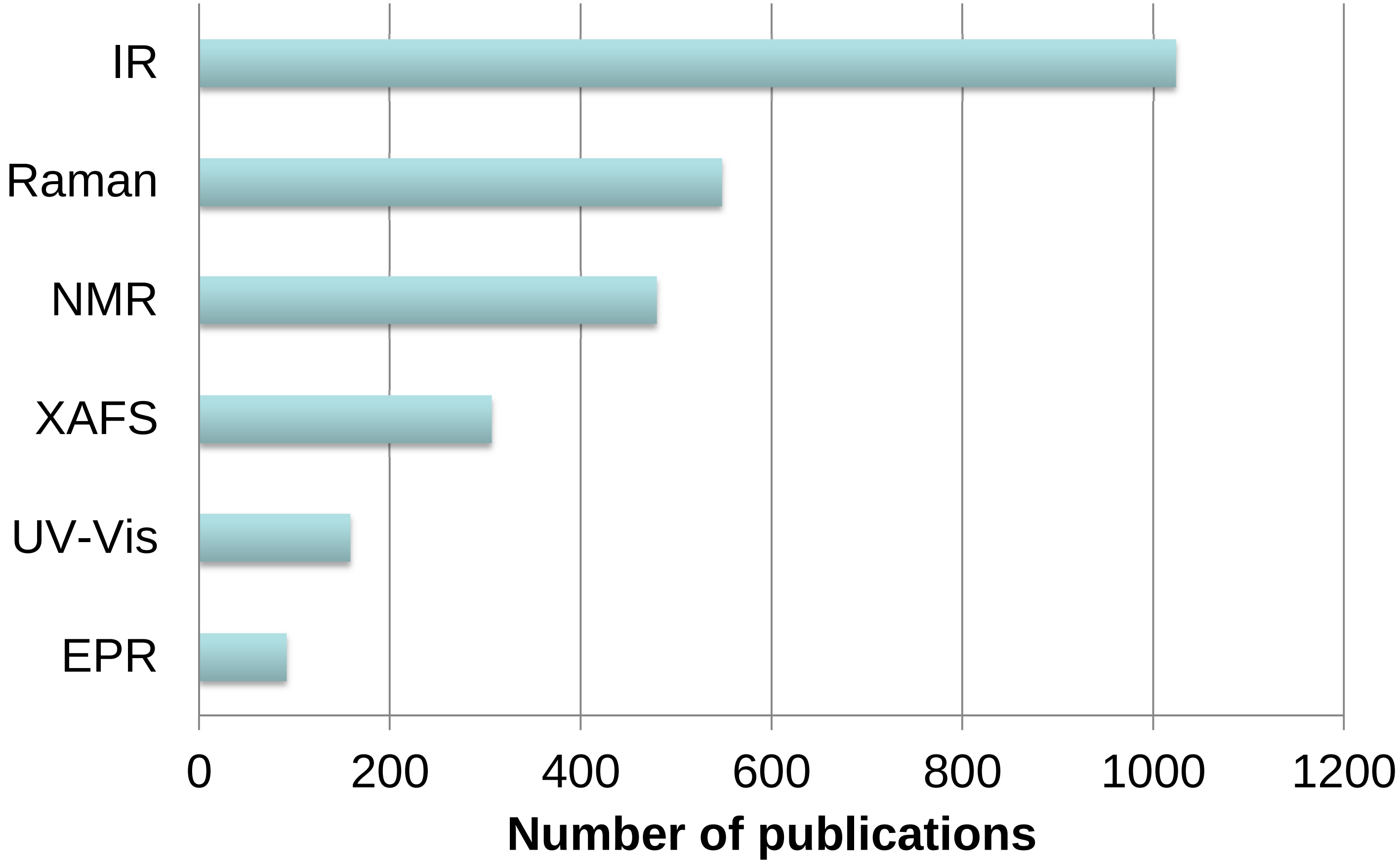
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

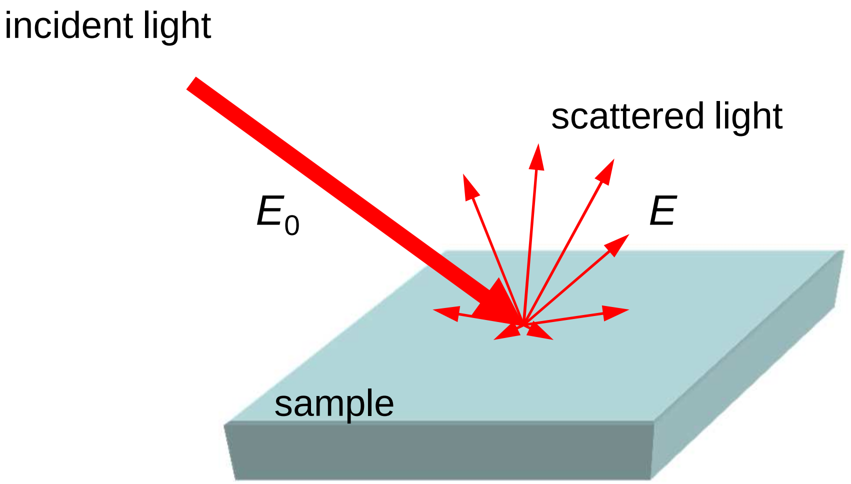


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib}t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib}t)]E_0\cos(2\pi\nu_0 t)$$

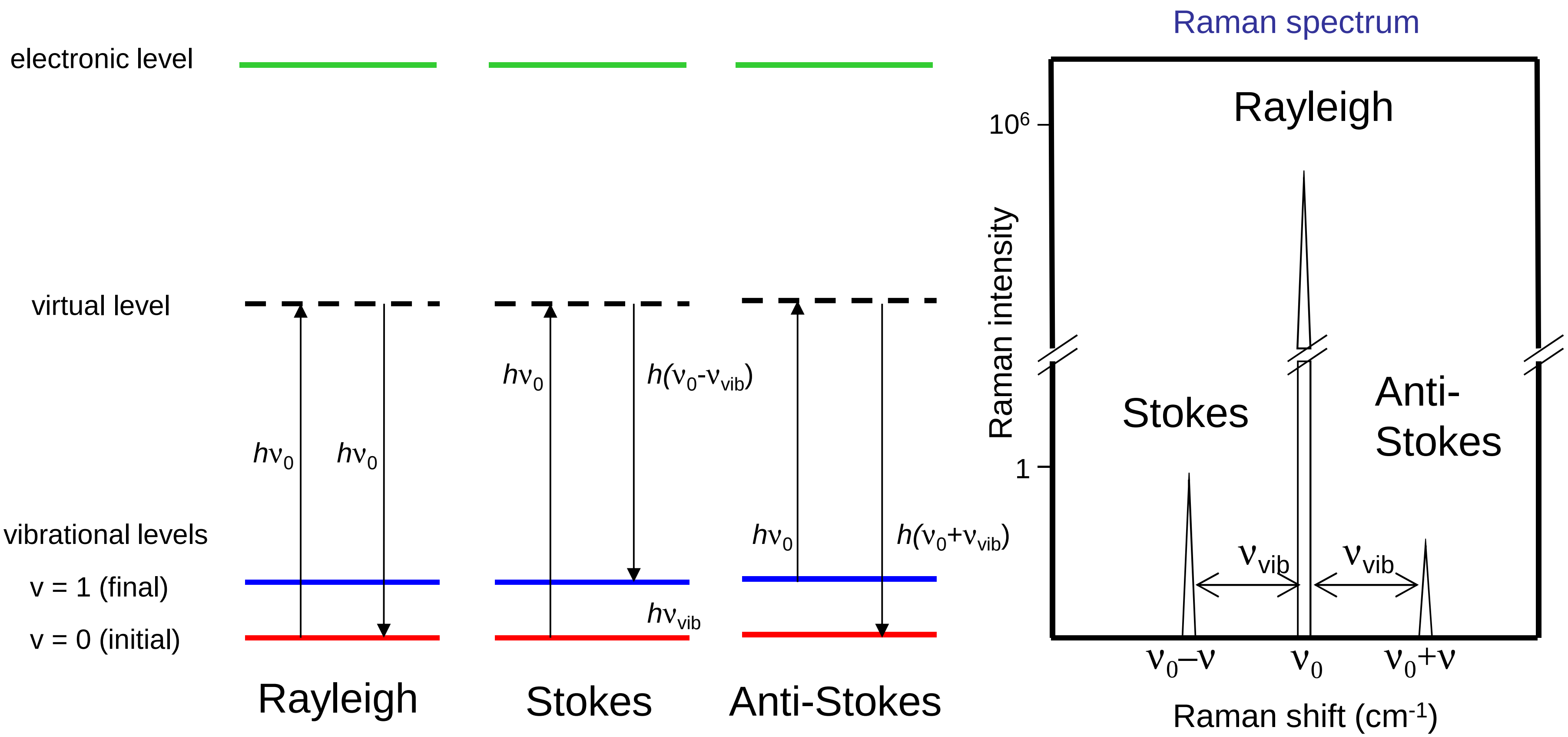
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib}t)\cos(2\pi\nu_0 t)$$

and $\boxed{\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t] + \alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}$

Rayleigh Anti-Stokes Stokes

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\text{ (Anti-Stokes)}}{I\text{ (Stokes)}} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:
  - 4th power of ν (4th power law)
  - 2nd power of $\Delta\alpha$
    - properties of molecules
    - strength of bonds

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

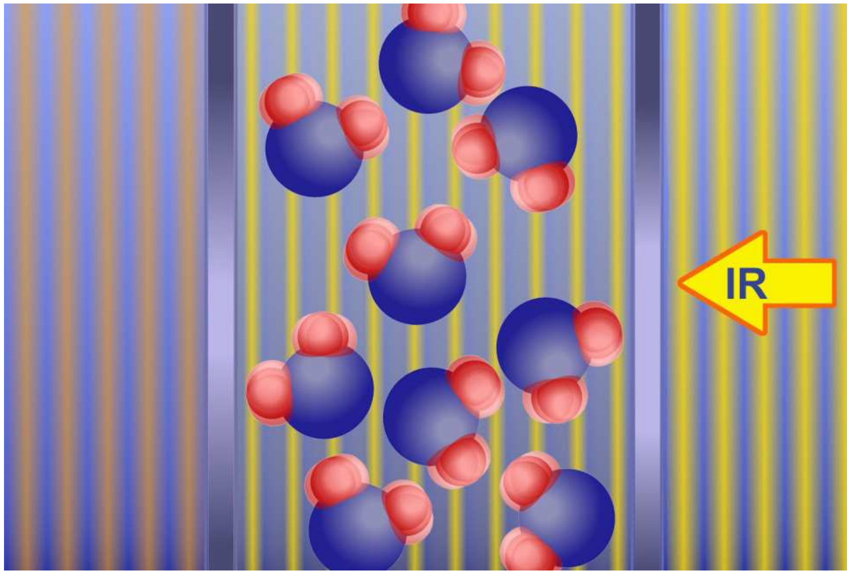
covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

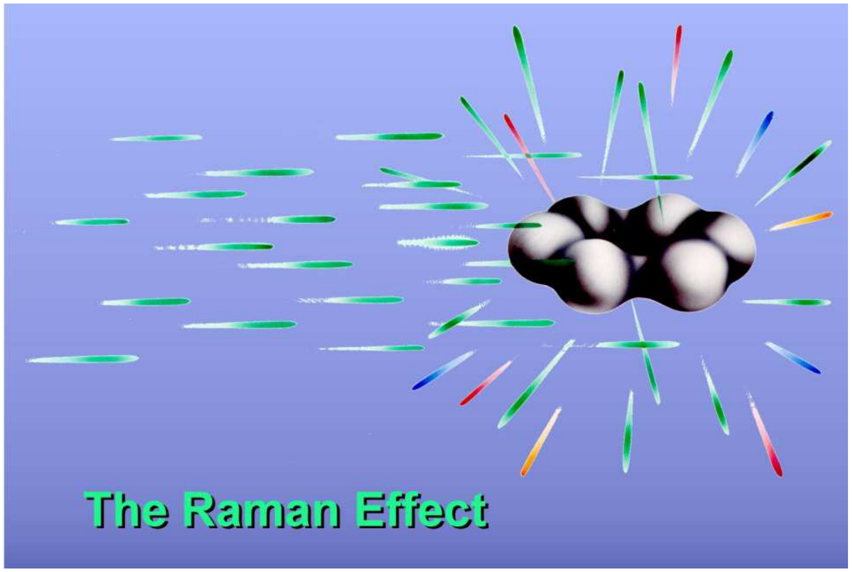
Raman *vs.* Infrared

Infrared

Raman



Absorption of IR light



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

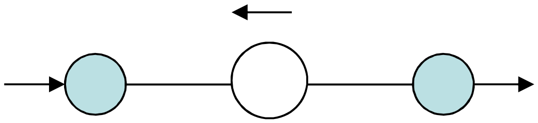
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - large electron clouds
  - not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

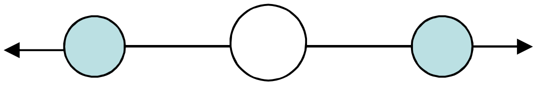
Raman *vs.* Infrared

CO_2



ν_{as}

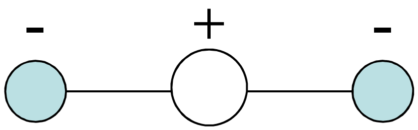
2349 cm^{-1}



ν_s

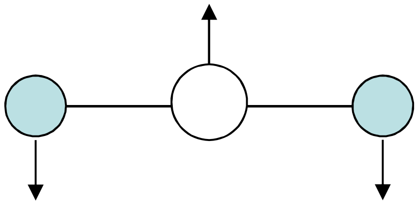
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



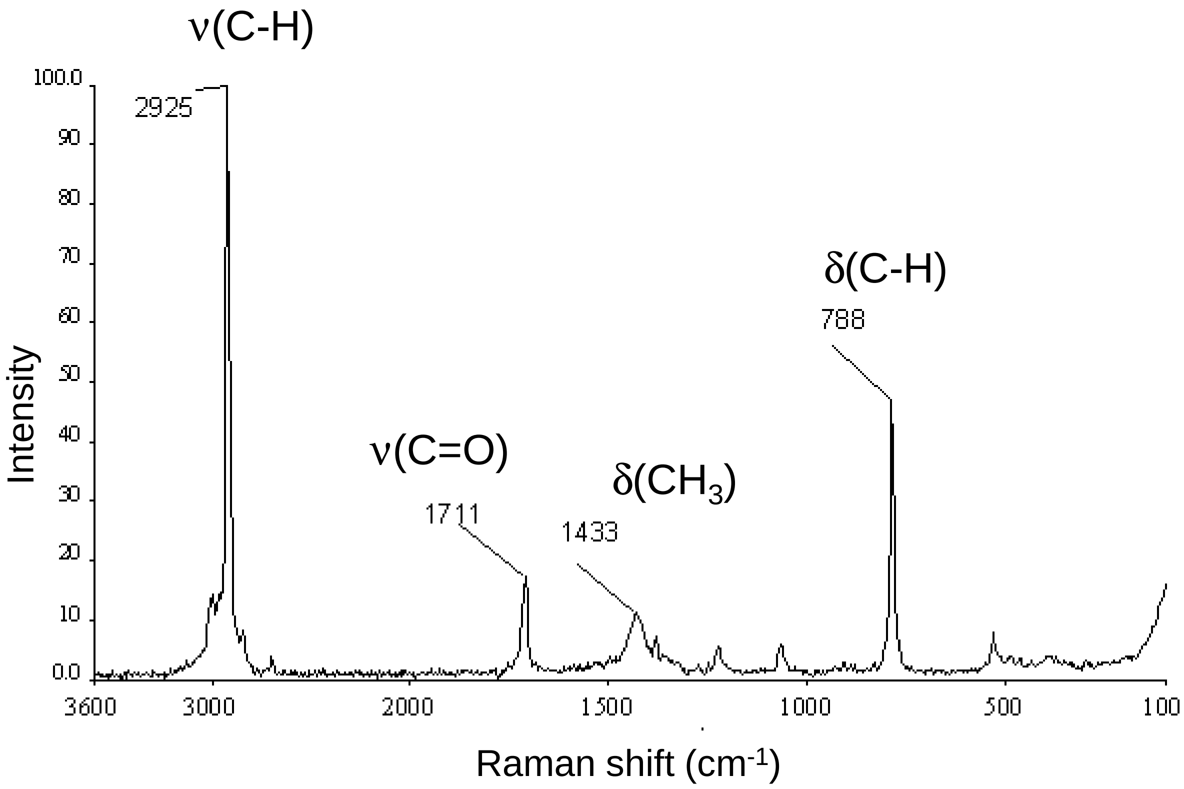
δ

667 cm^{-1}

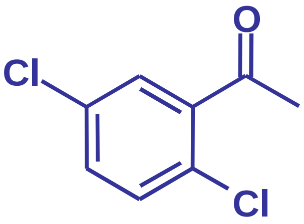
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



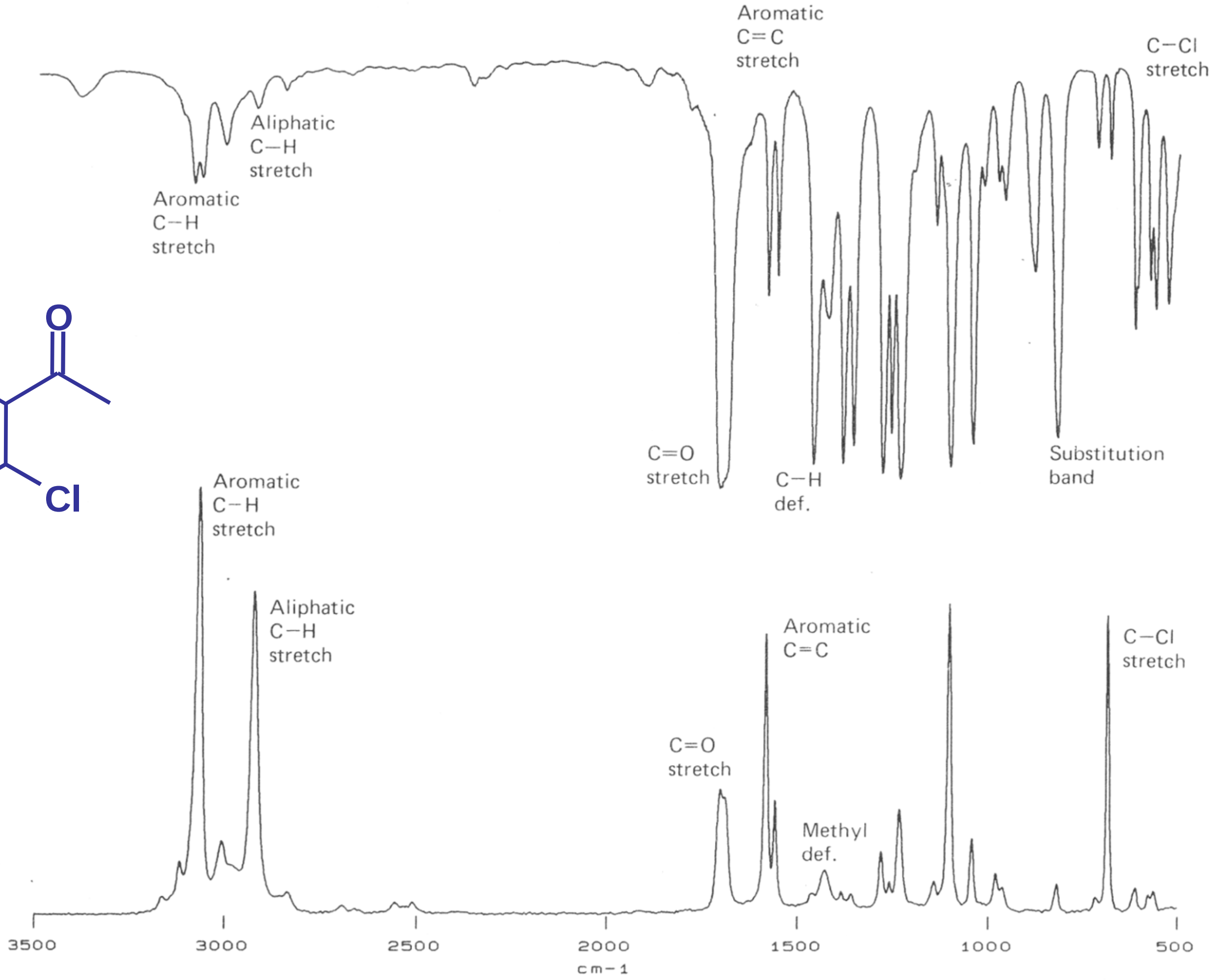


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

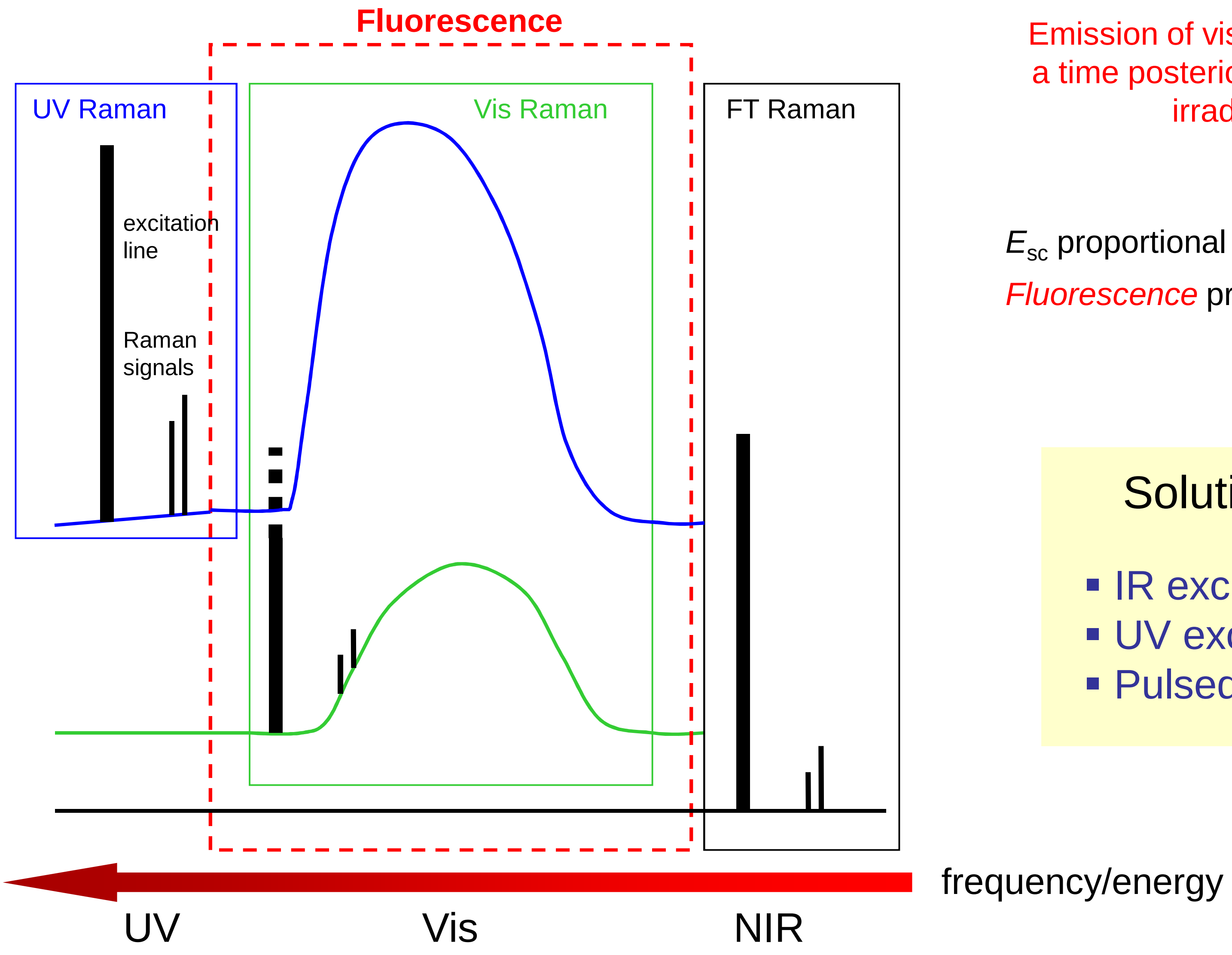
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 μm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

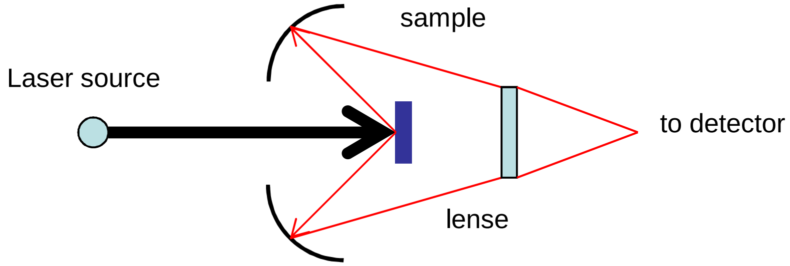
Fluorescence proportional to ν

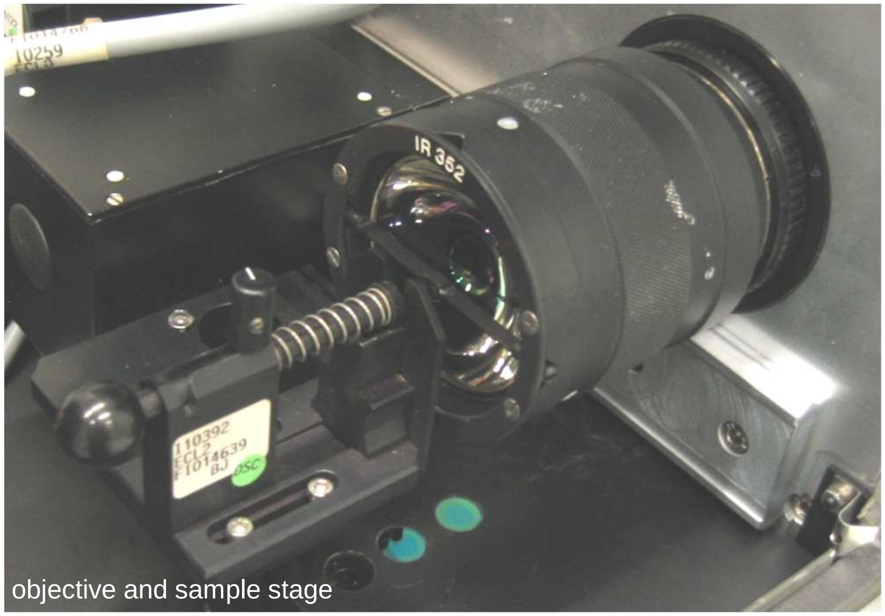
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

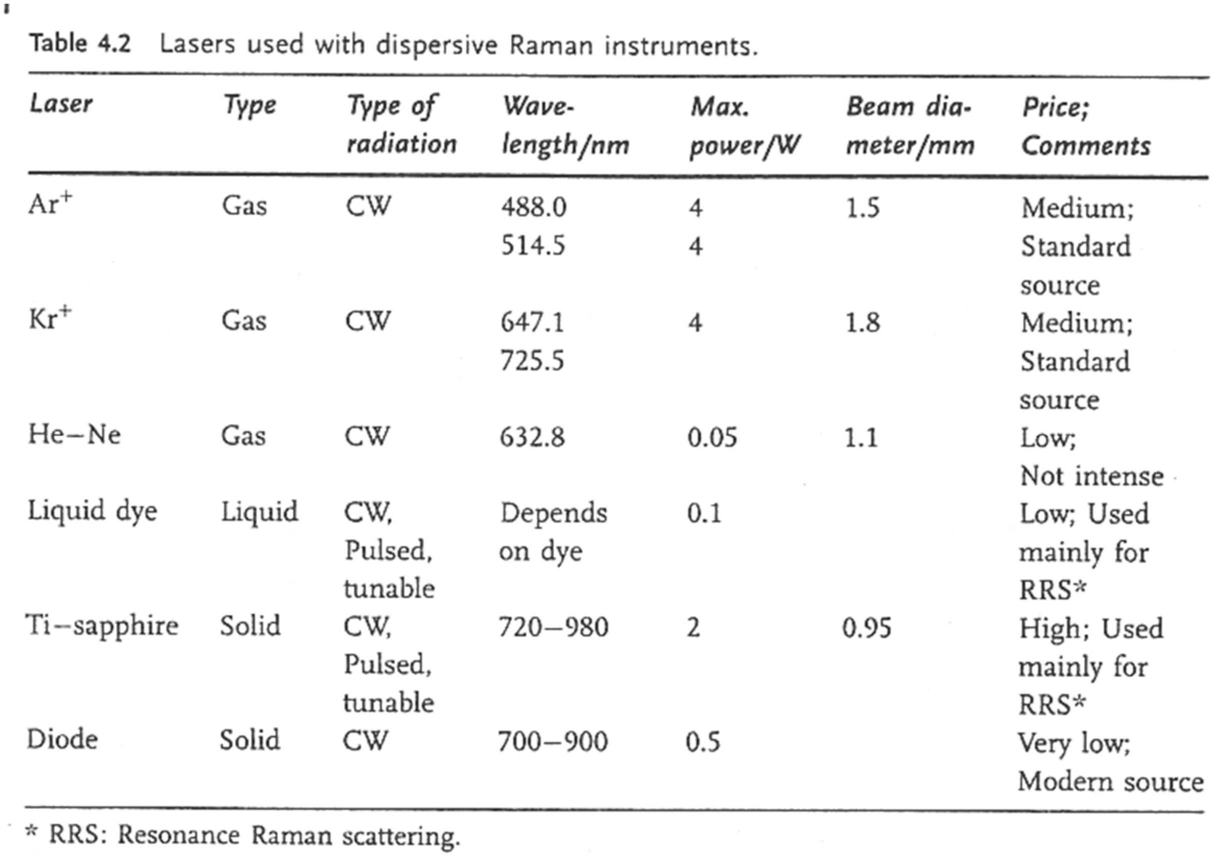


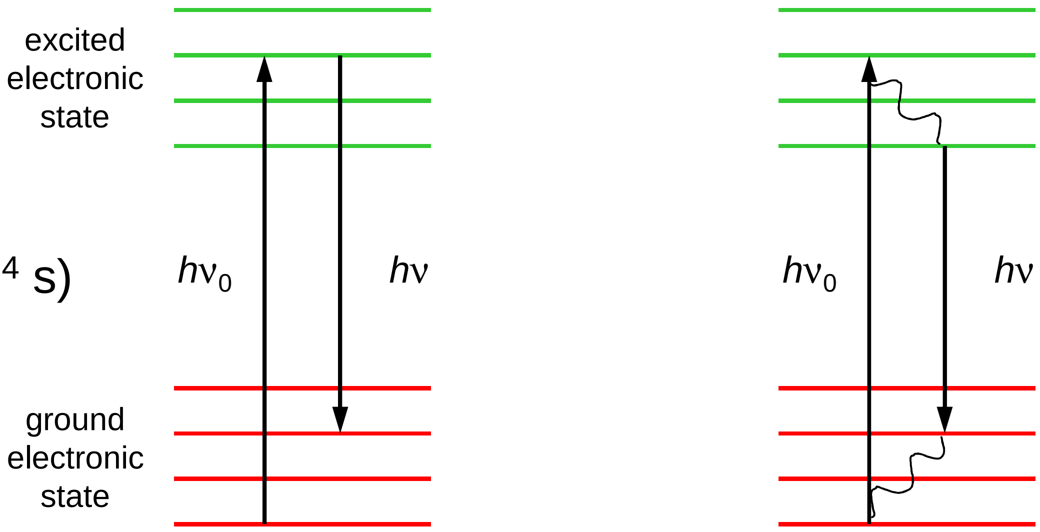
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



excited electronic state

ground electronic state

fast (10^{-14} s)

$h\nu_0$

$h\nu$

$h\nu_0$

$h\nu$

slow (10^{-9}–10^{-6} s)

Resonance Raman scattering

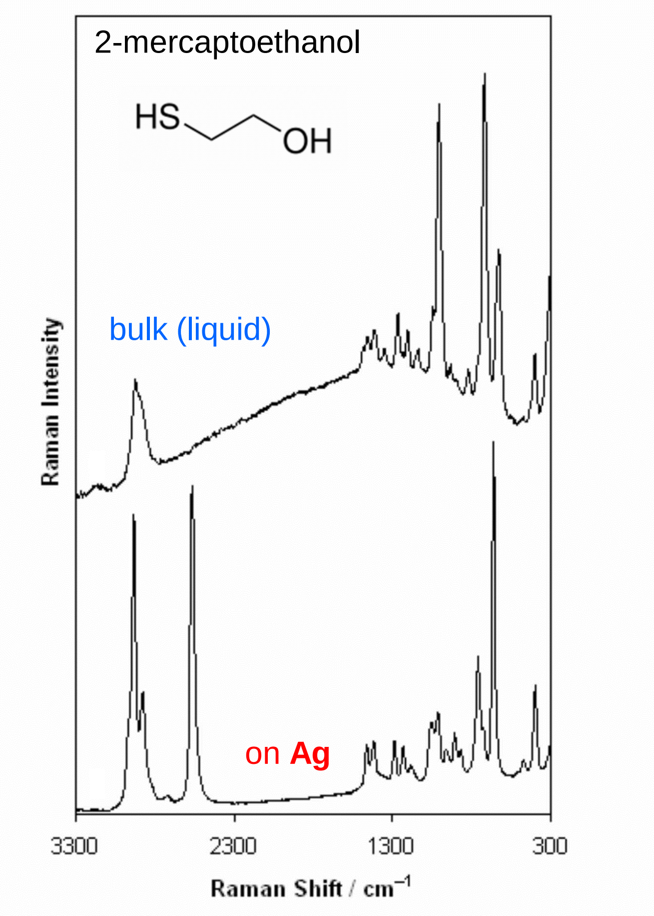
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

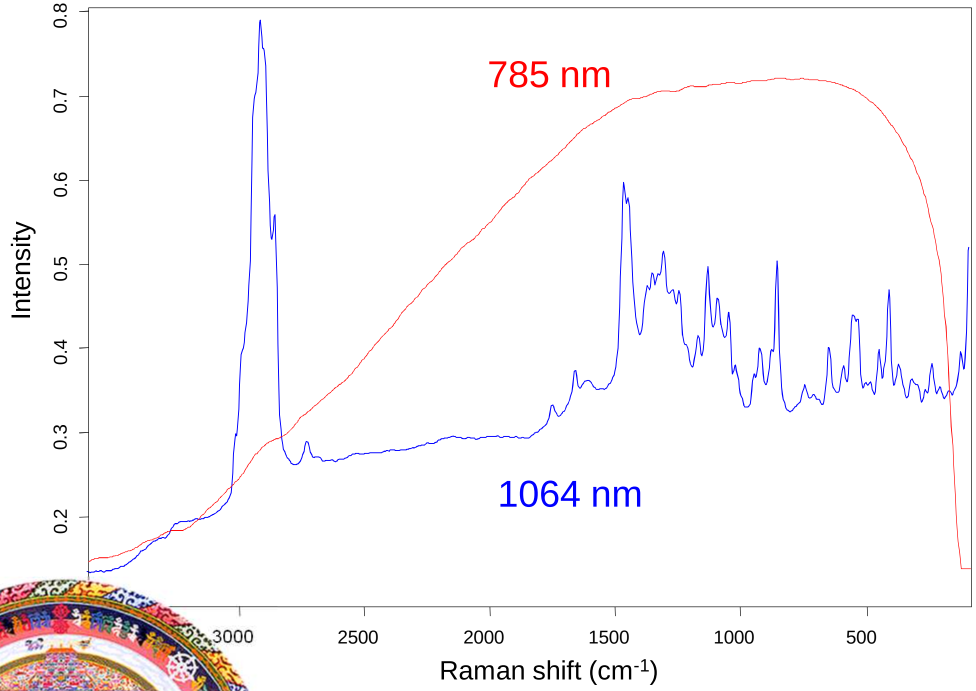
- Remarks:

❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



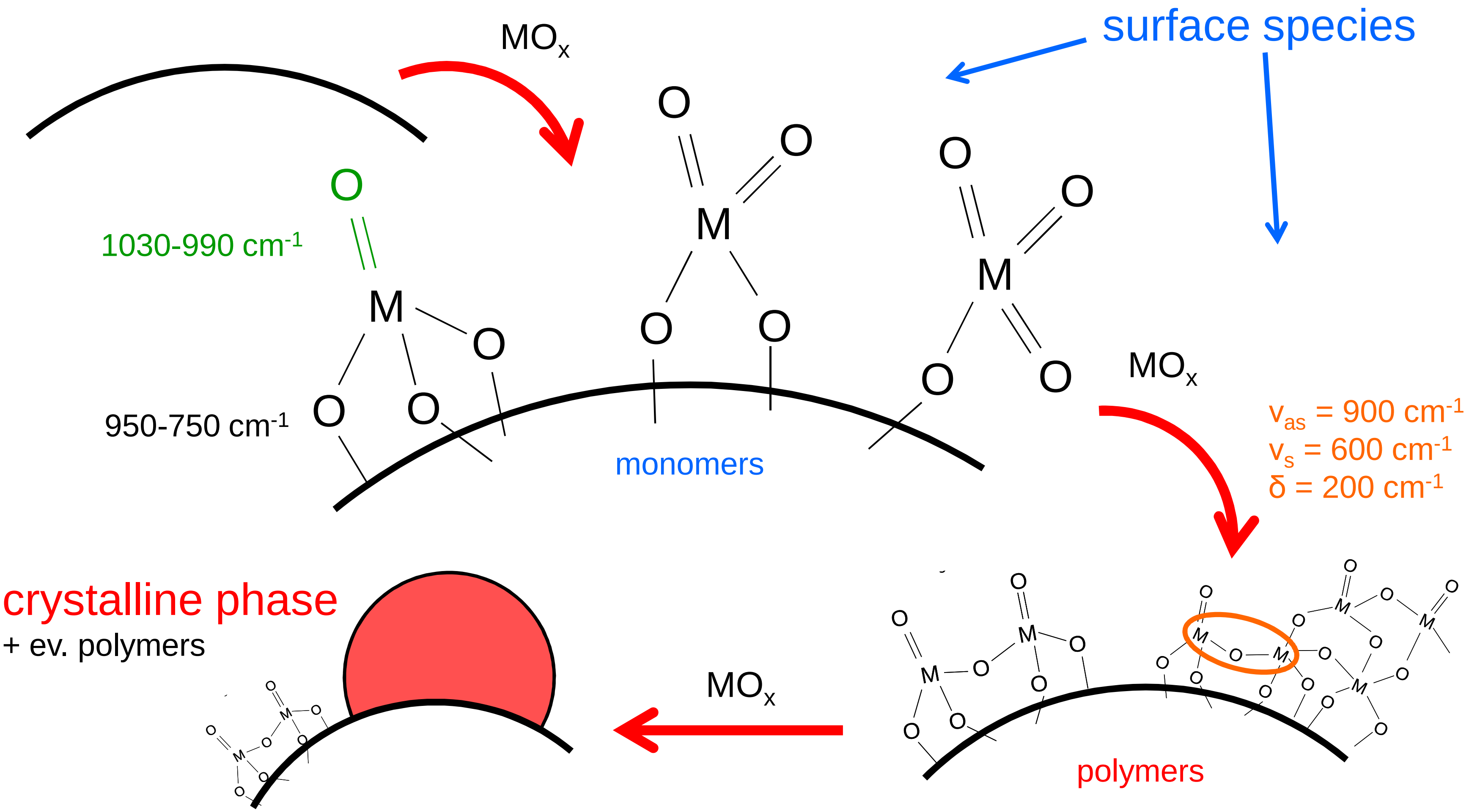
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species

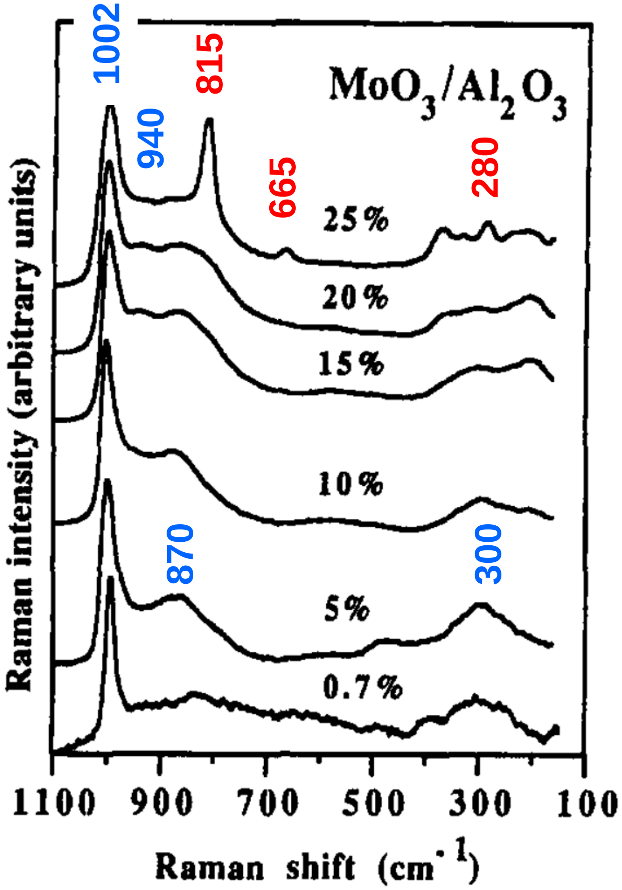


Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



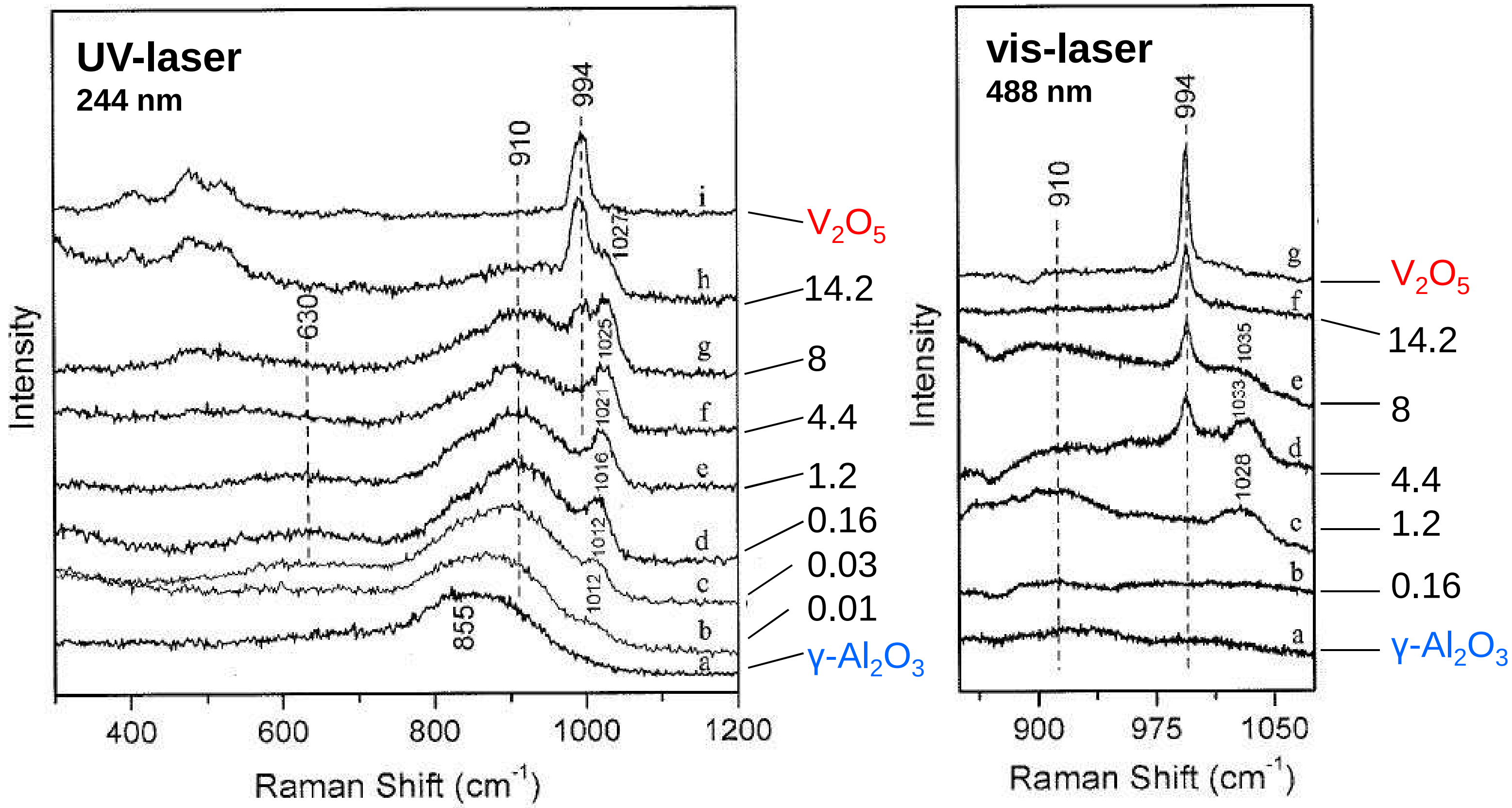
surface MoO_3
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

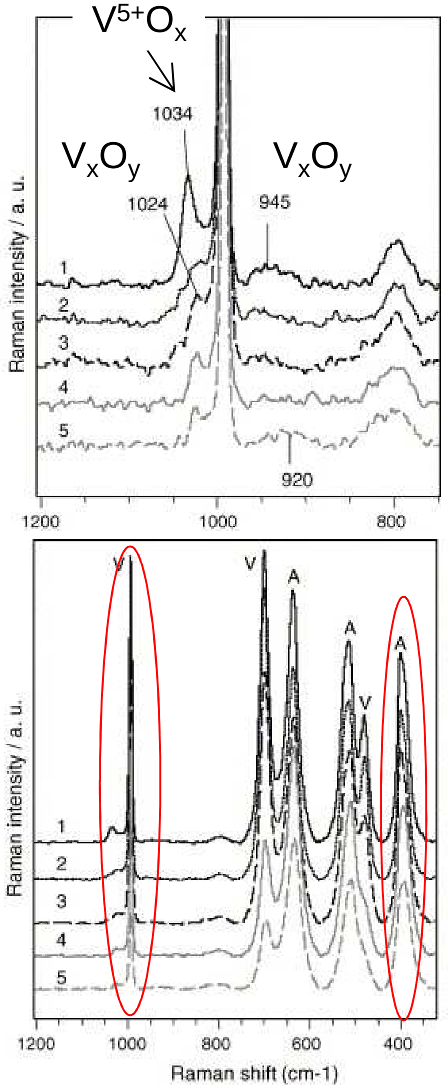
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

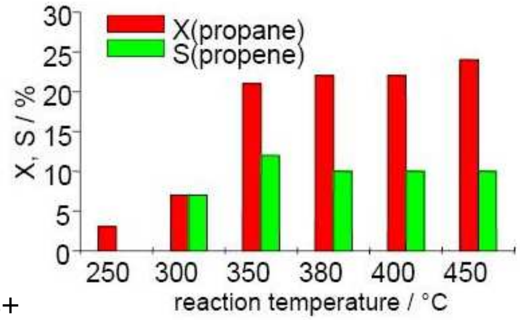
Applications

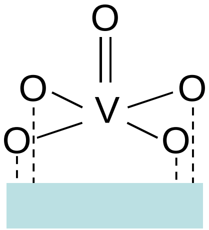
- Reactivity of V/TiO$_2$ after oxidative treatment

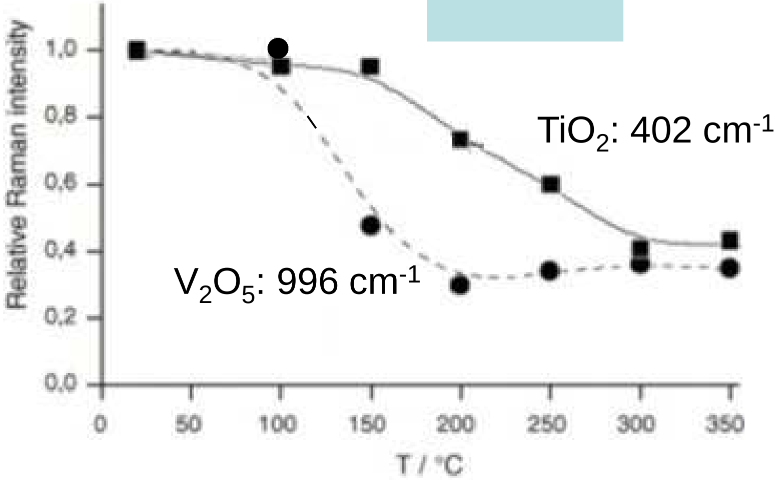


air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$







TiO$_2$: 402 cm^{-1}

V$_2$O$_5$: 996 cm^{-1}

Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

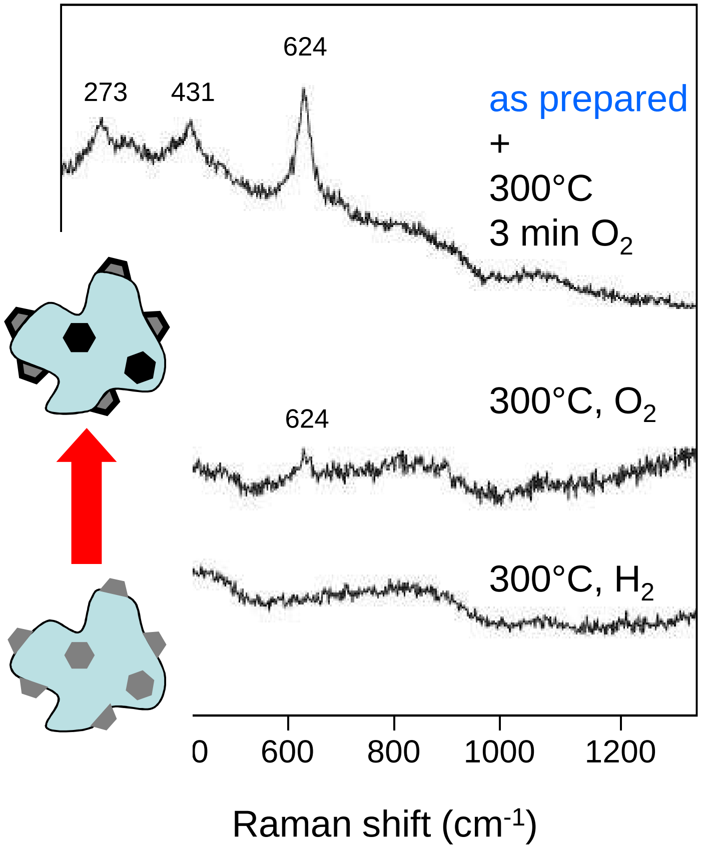
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…) used for total and partial oxidation reactions

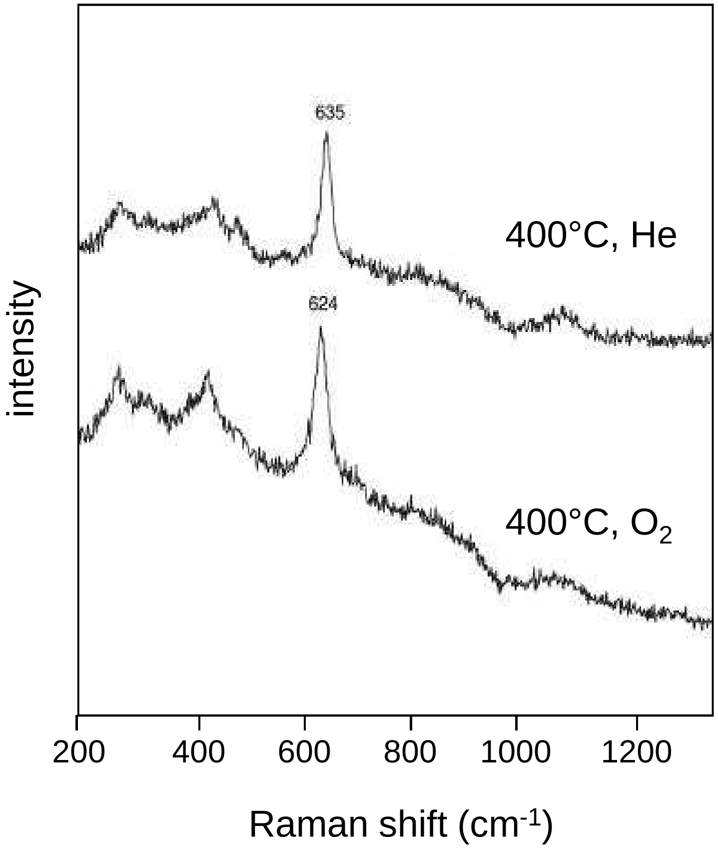
Question: what is the state of Pd during reaction?

Examples:	Pd for CH_4 combustion
	Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3





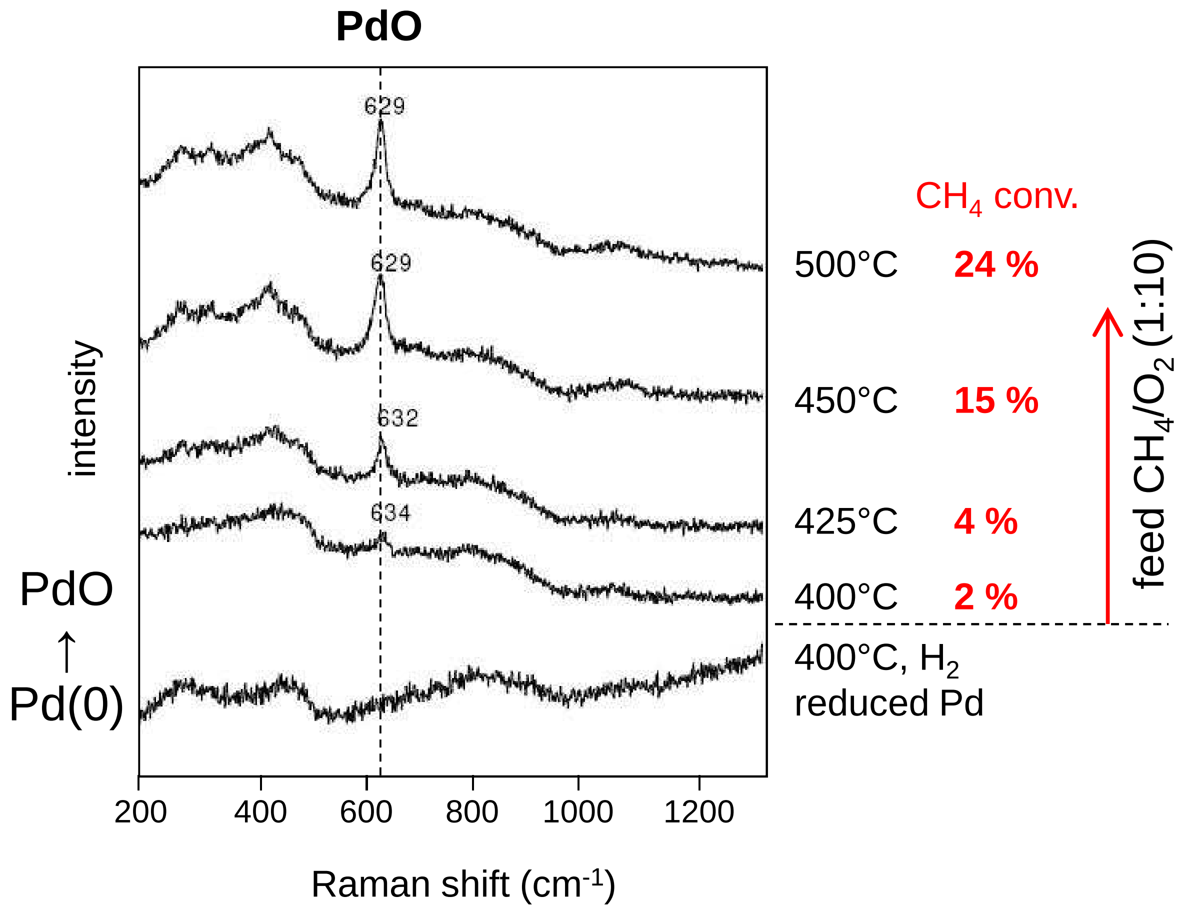
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

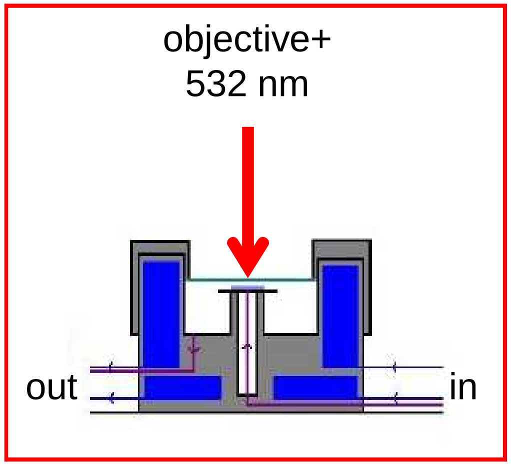
Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$



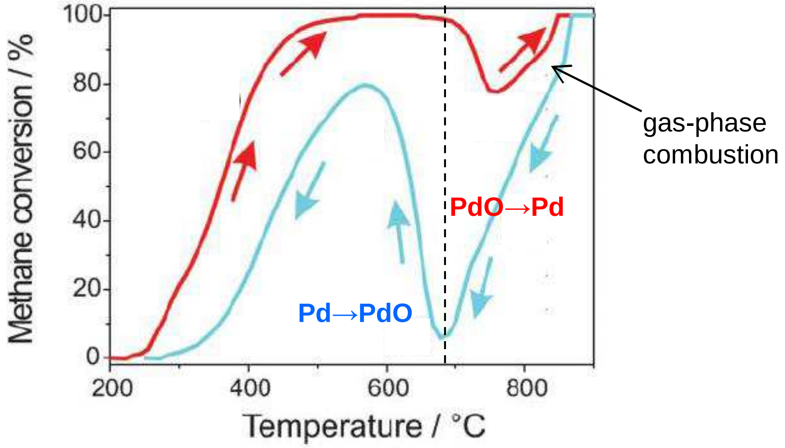
near PdO mode

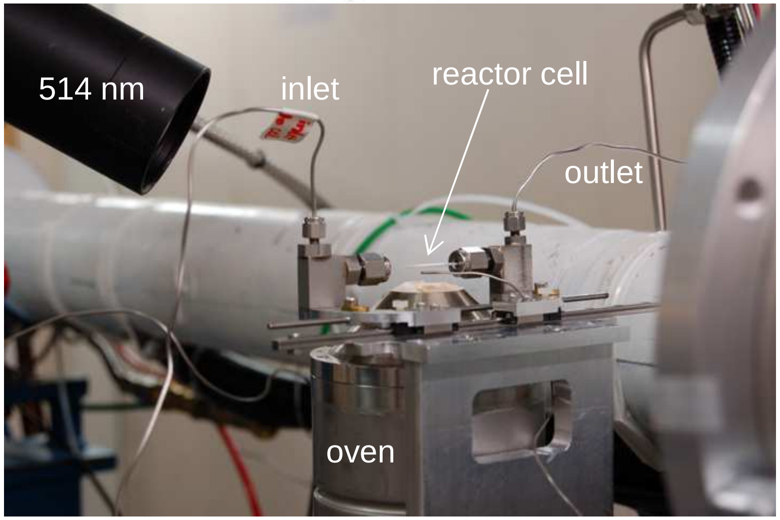


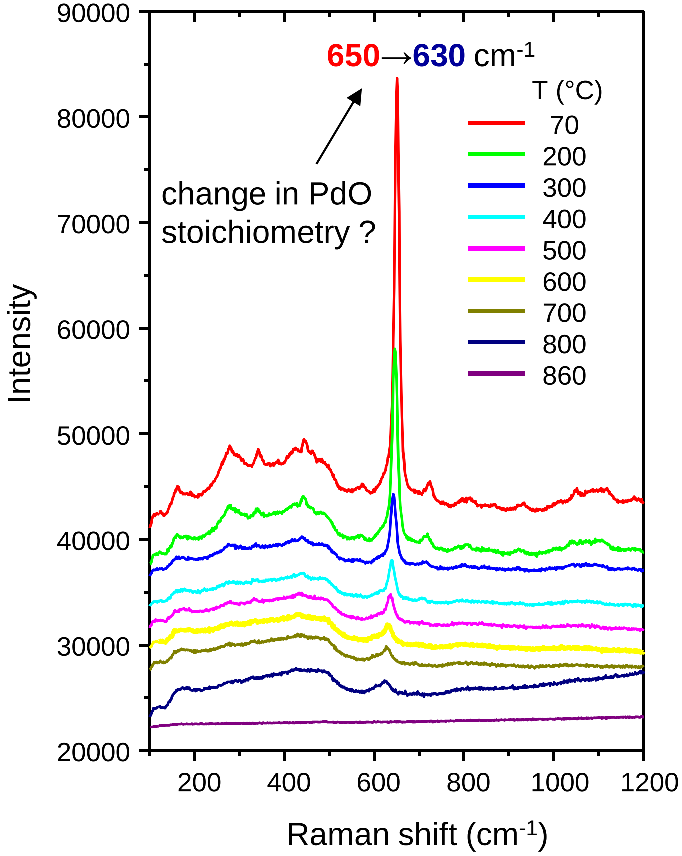
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

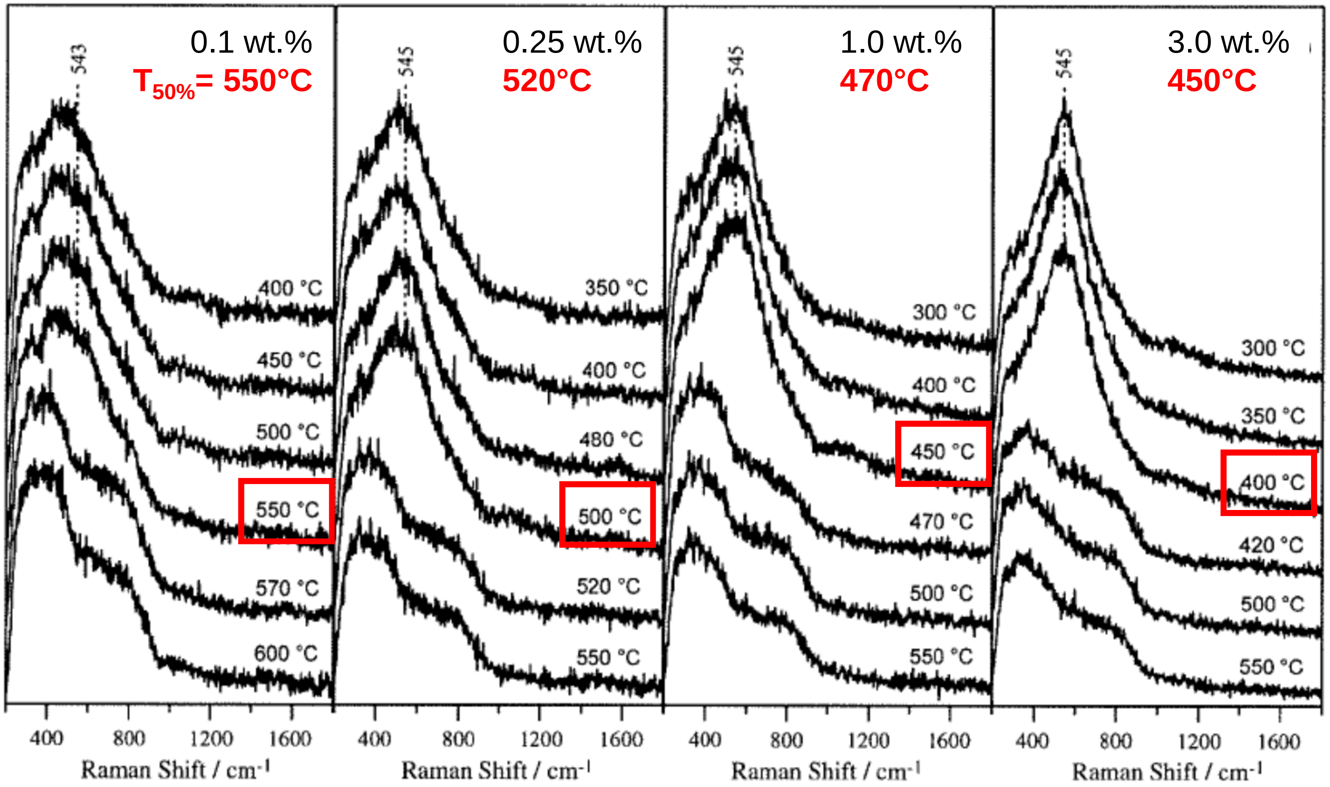
- Methane partial oxidation over Rh/Al_2O_3

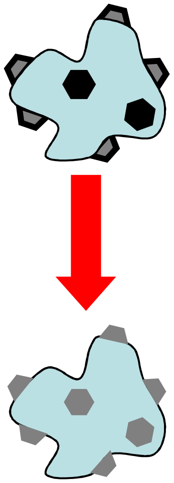
3 mW, 325 nm
$CH_4/O_2/Ar$ = 2/1/45

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content
Activity

RhO_x
↓
Rh(0)


0.1 wt.% **$T_{50\%}$= 550°C**
0.25 wt.% **520°C**
1.0 wt.% **470°C**
3.0 wt.% **450°C**



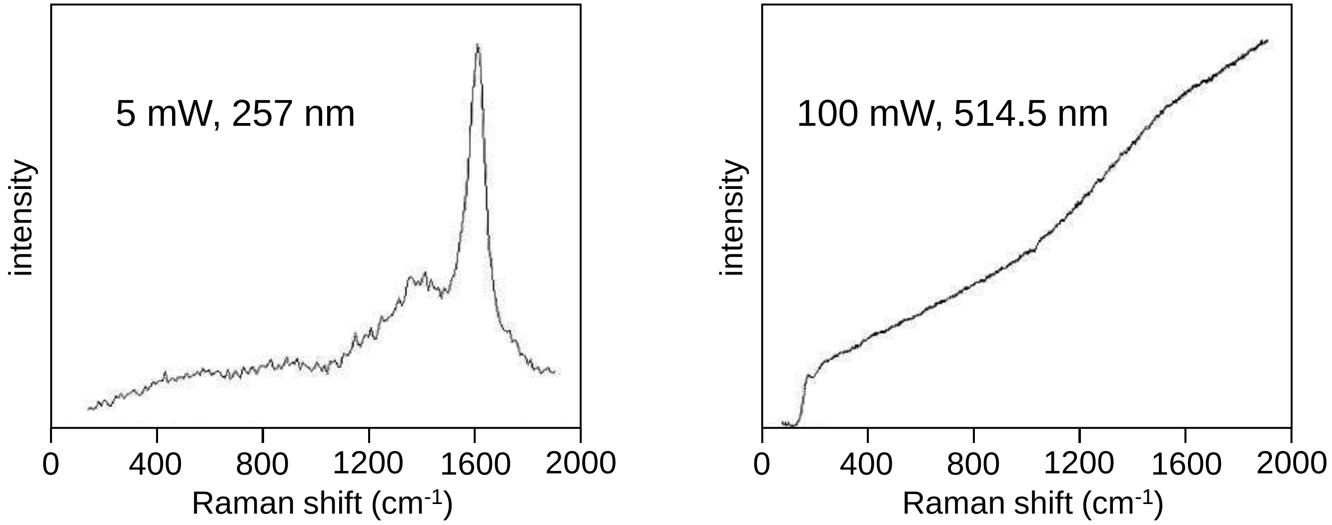
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

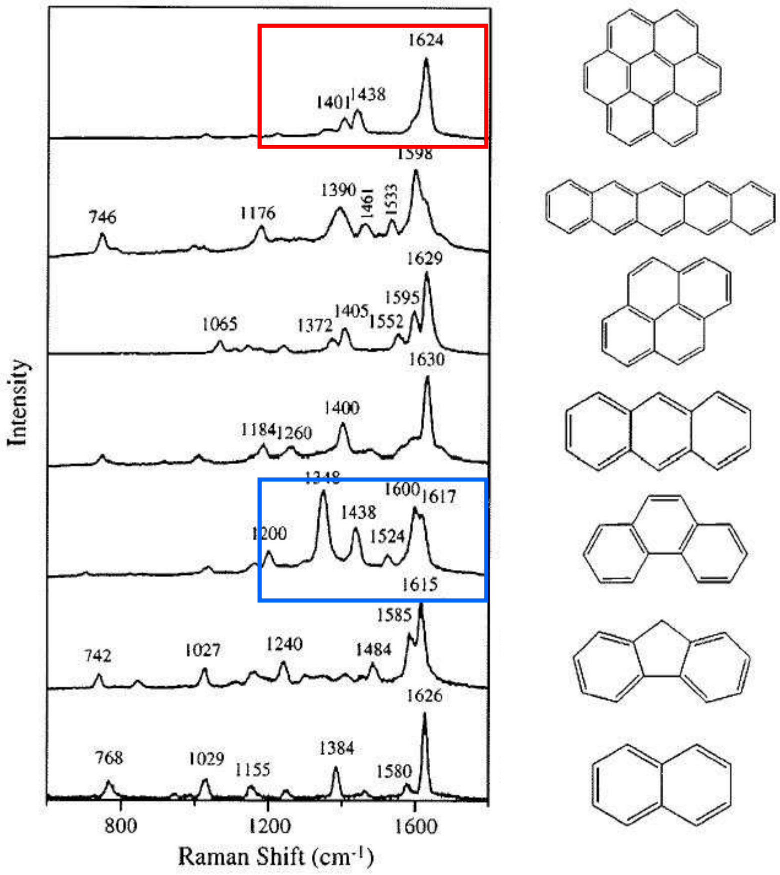
Rh/Al_2O_3, coked 500°C in naphtha

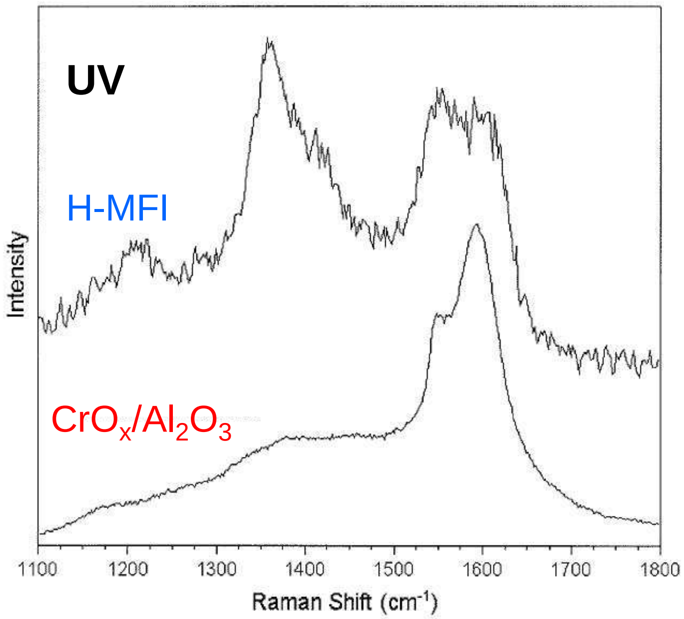


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





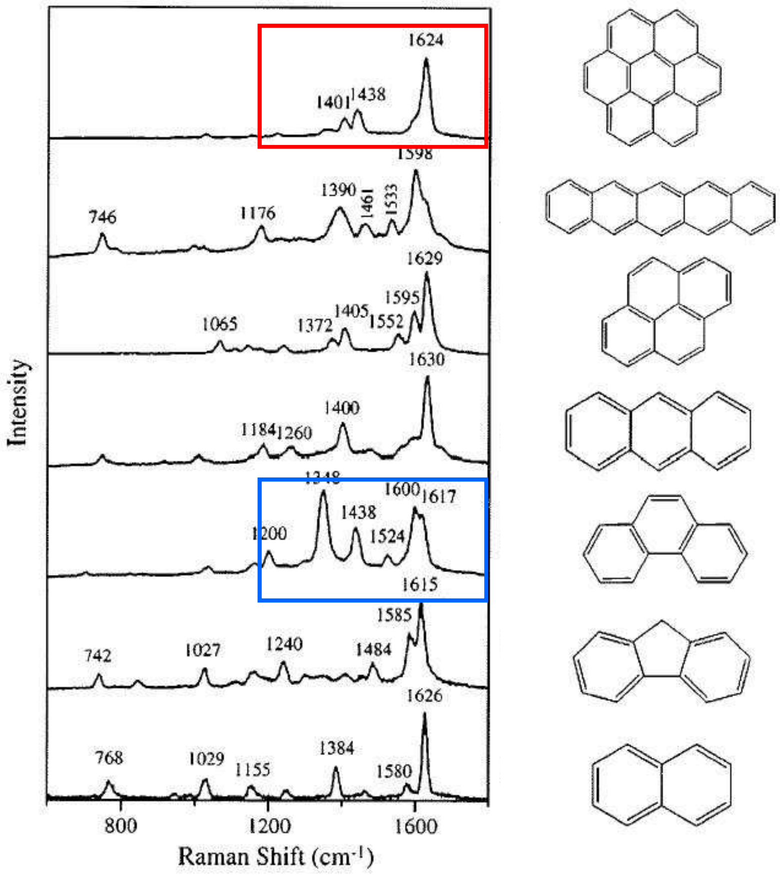
Coke classification
1D topology, chain-like
2D topology, sheet-like

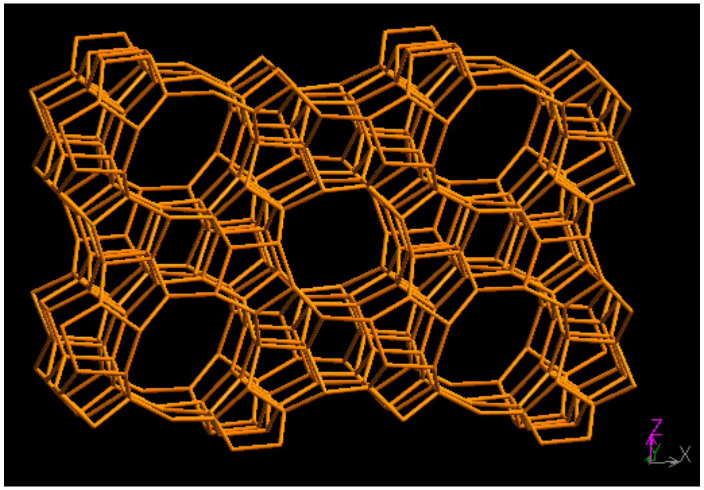
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





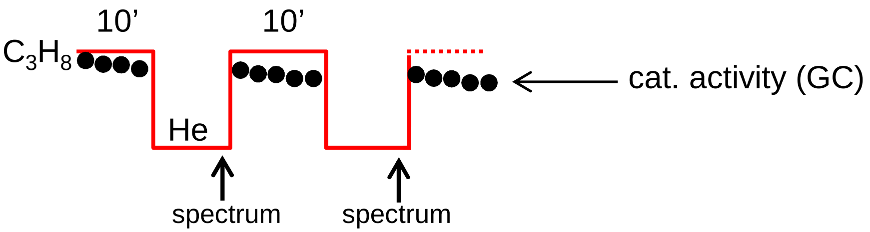
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

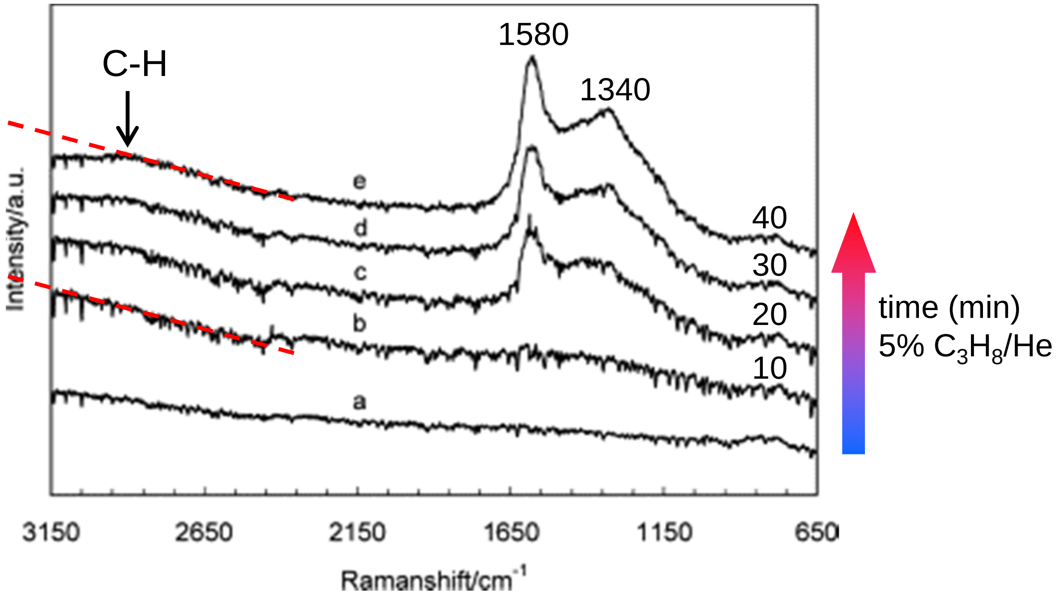
Stair, *Adv. Catal.* **51** (2007) 75

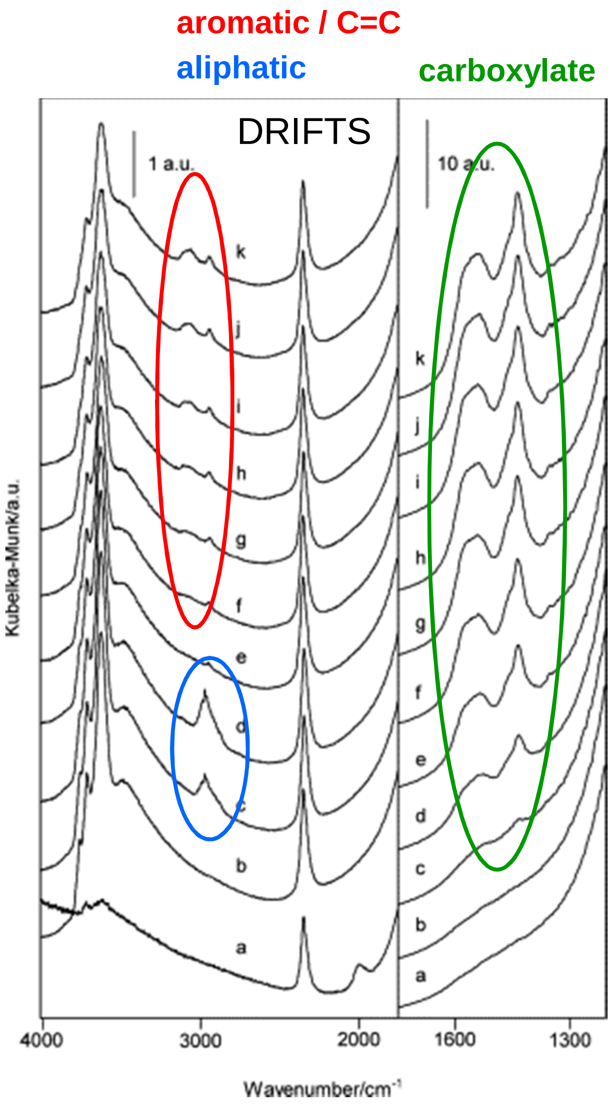
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

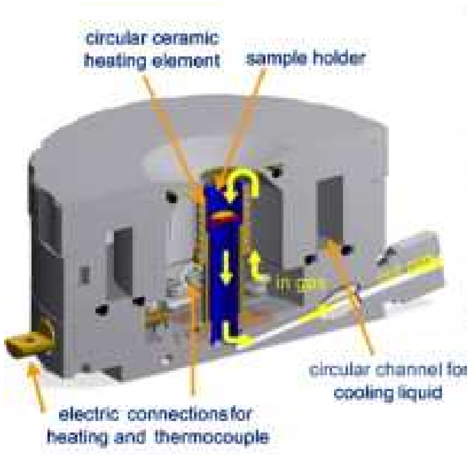


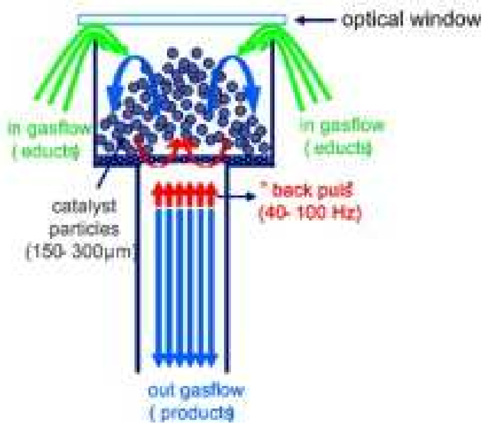


Airaksinen et al., *J. Catal.* **230** (2005) 507

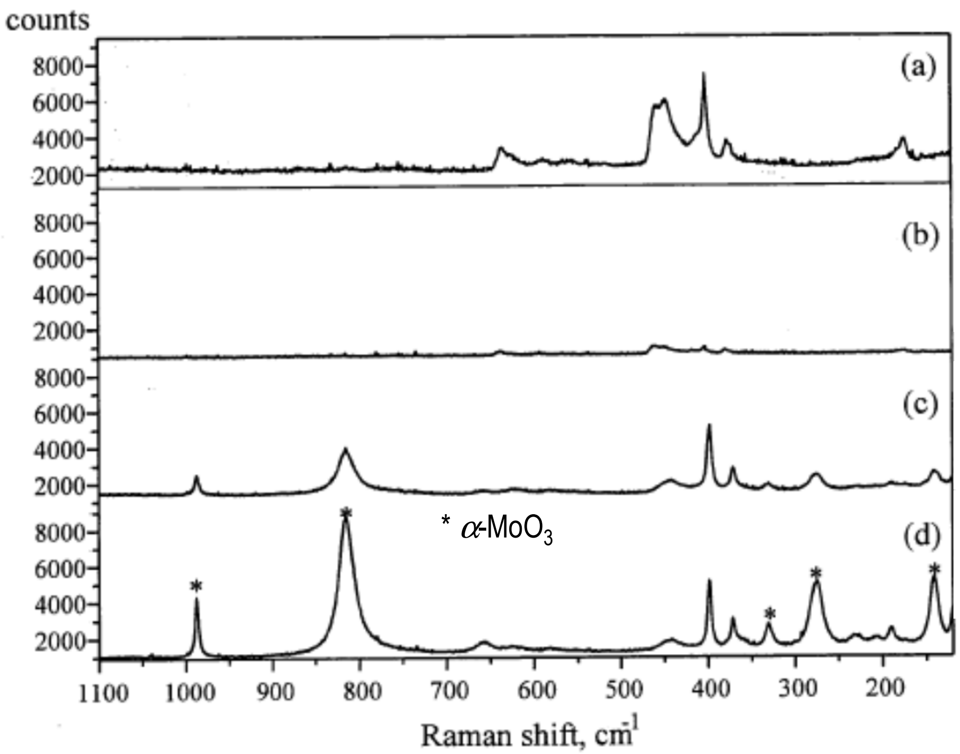
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min
full power, FB

MoS_2, 6 min
1/8 power

MoS_2, 1 min
full power

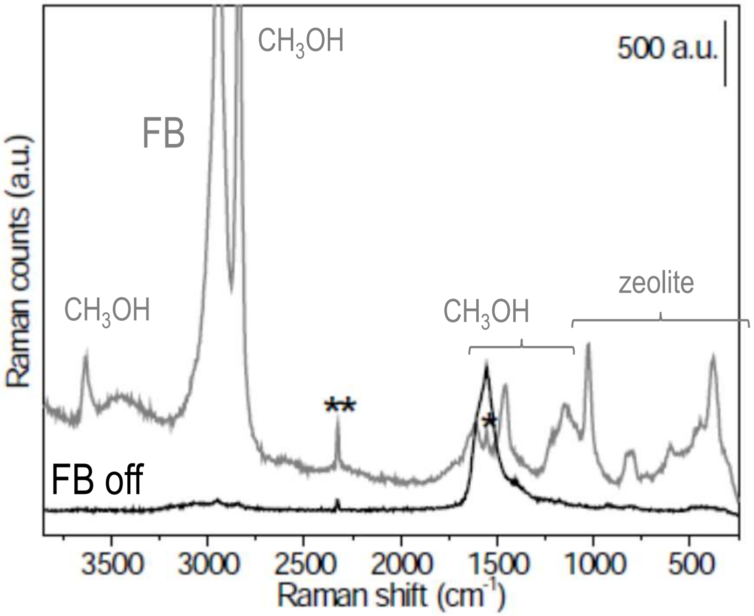
MoS_2, 6 min
full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

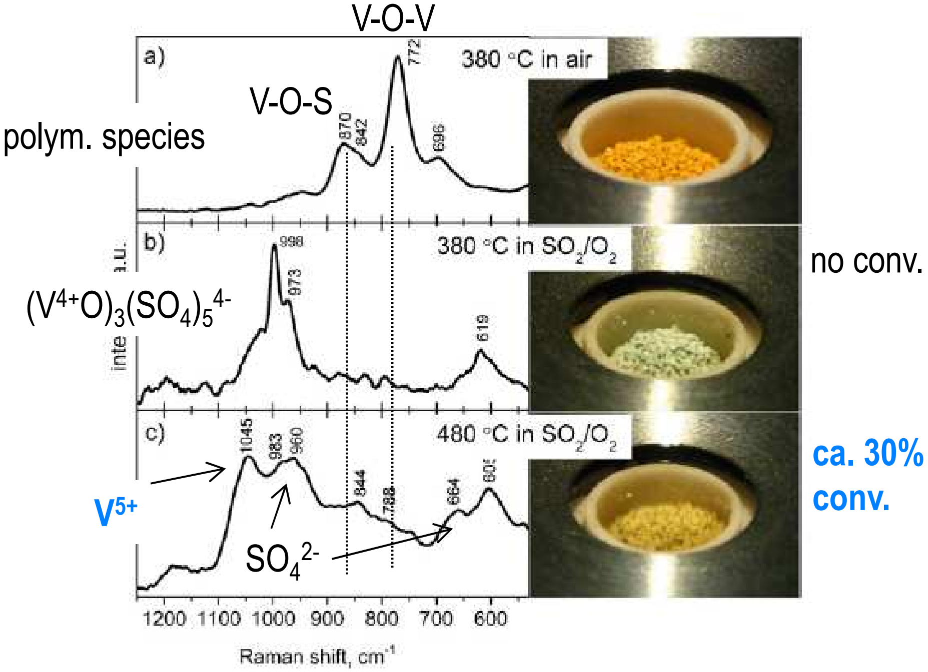
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

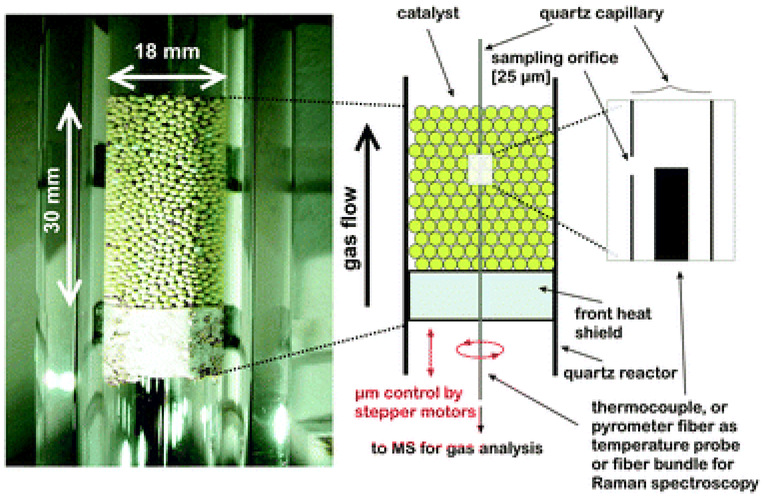


active species: mono- & dimeric V^{5+} oxosulfate species

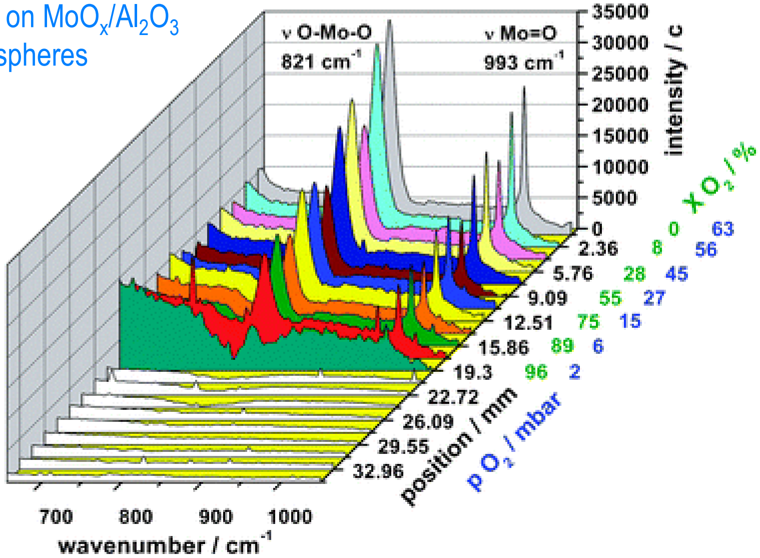
Beato et al., *Catal. Today* 205 (2013) 128

Applications

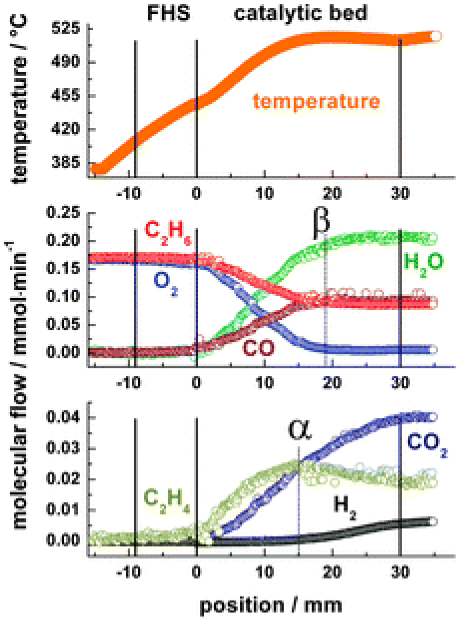
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 "*for his work on the scattering of light and for the discovery of the effect named after him*"

Literature:

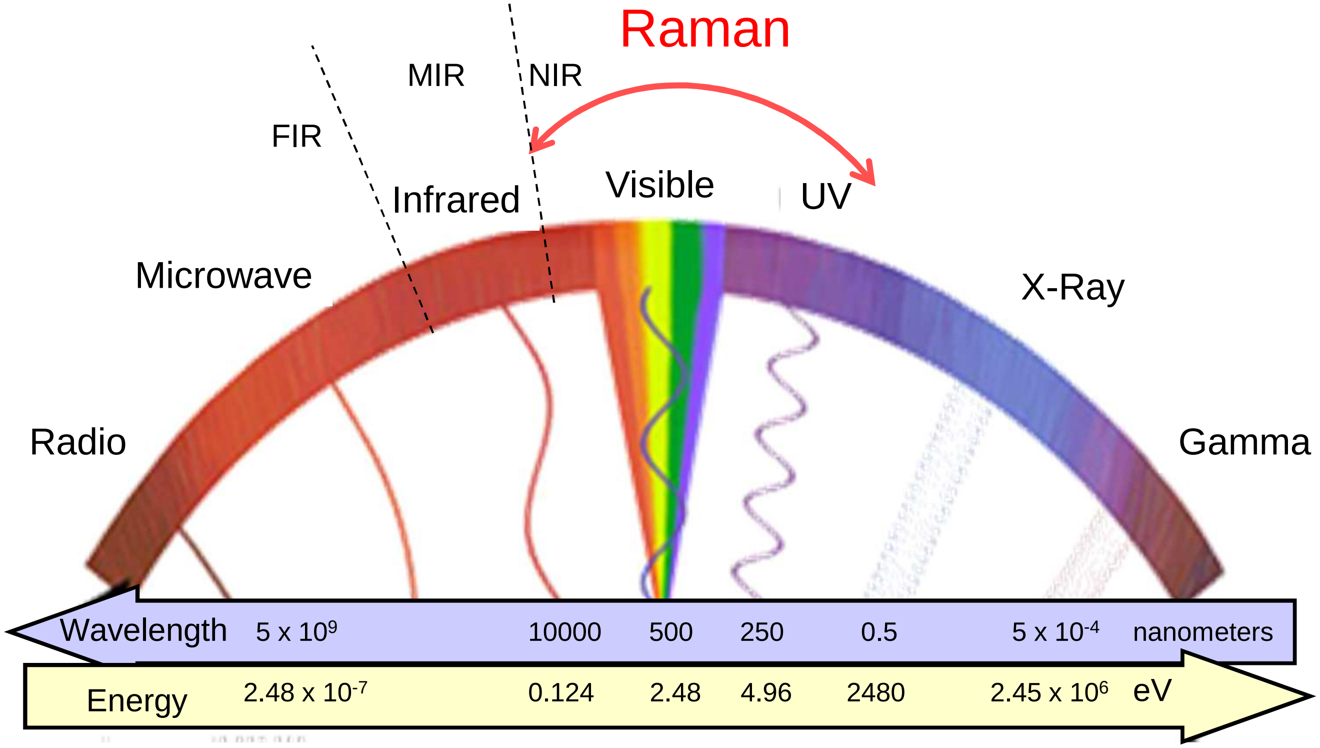
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

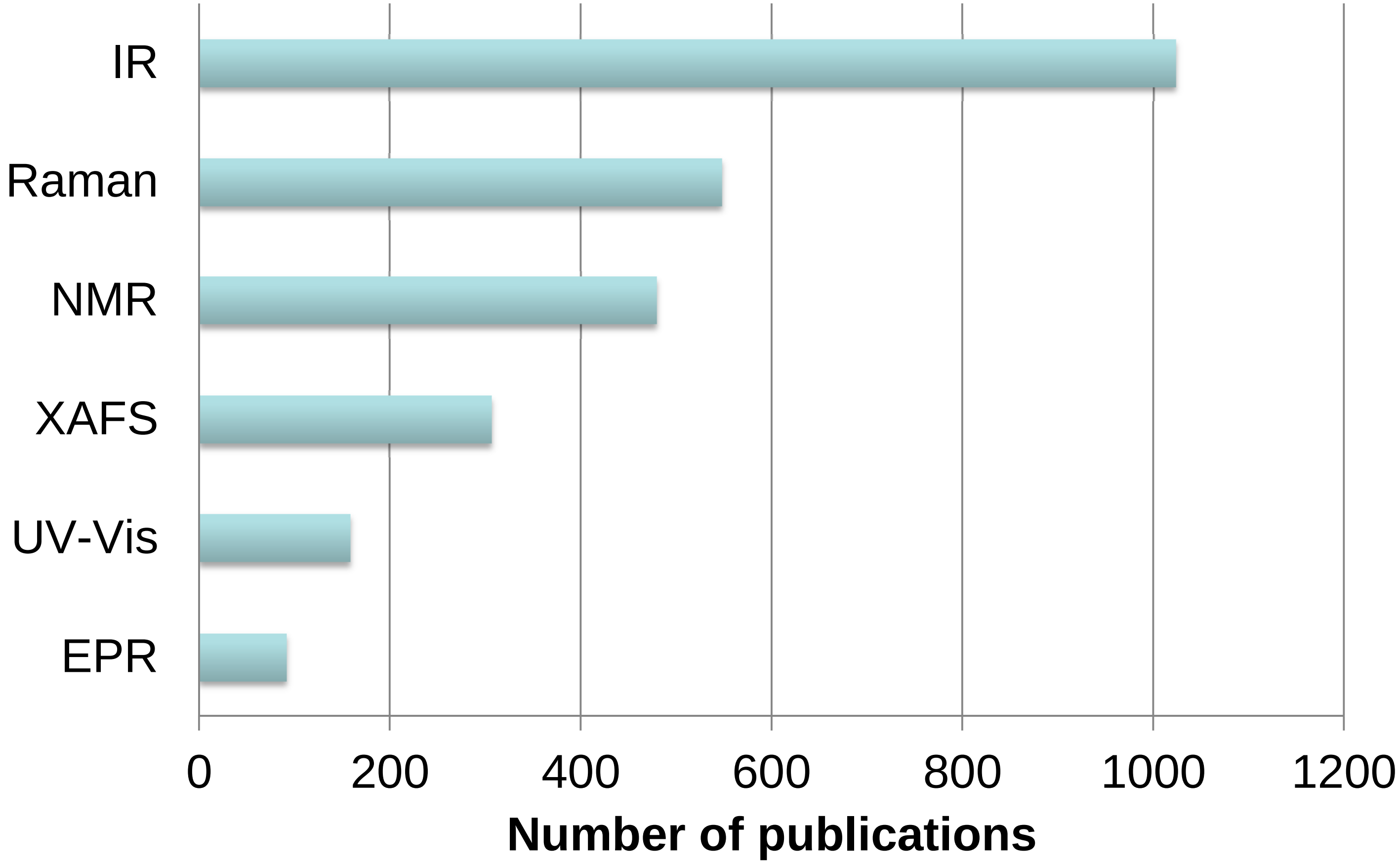
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

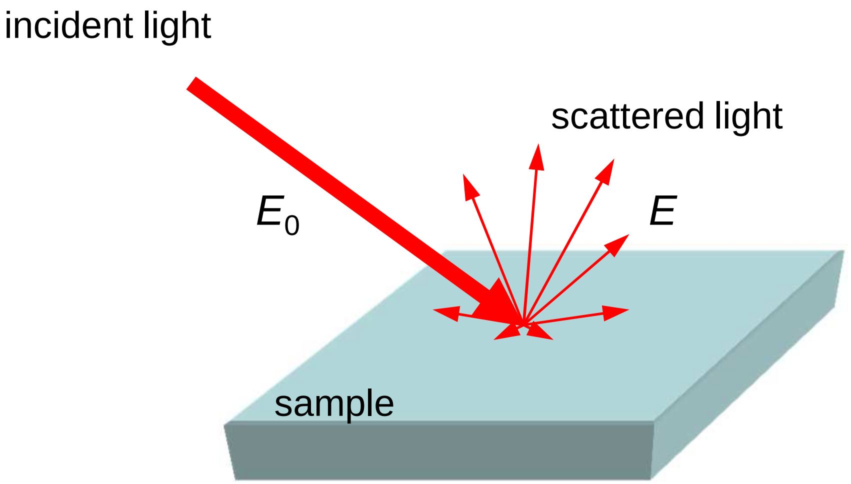


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib}t)]E_0\cos(2\pi\nu_0 t)$$

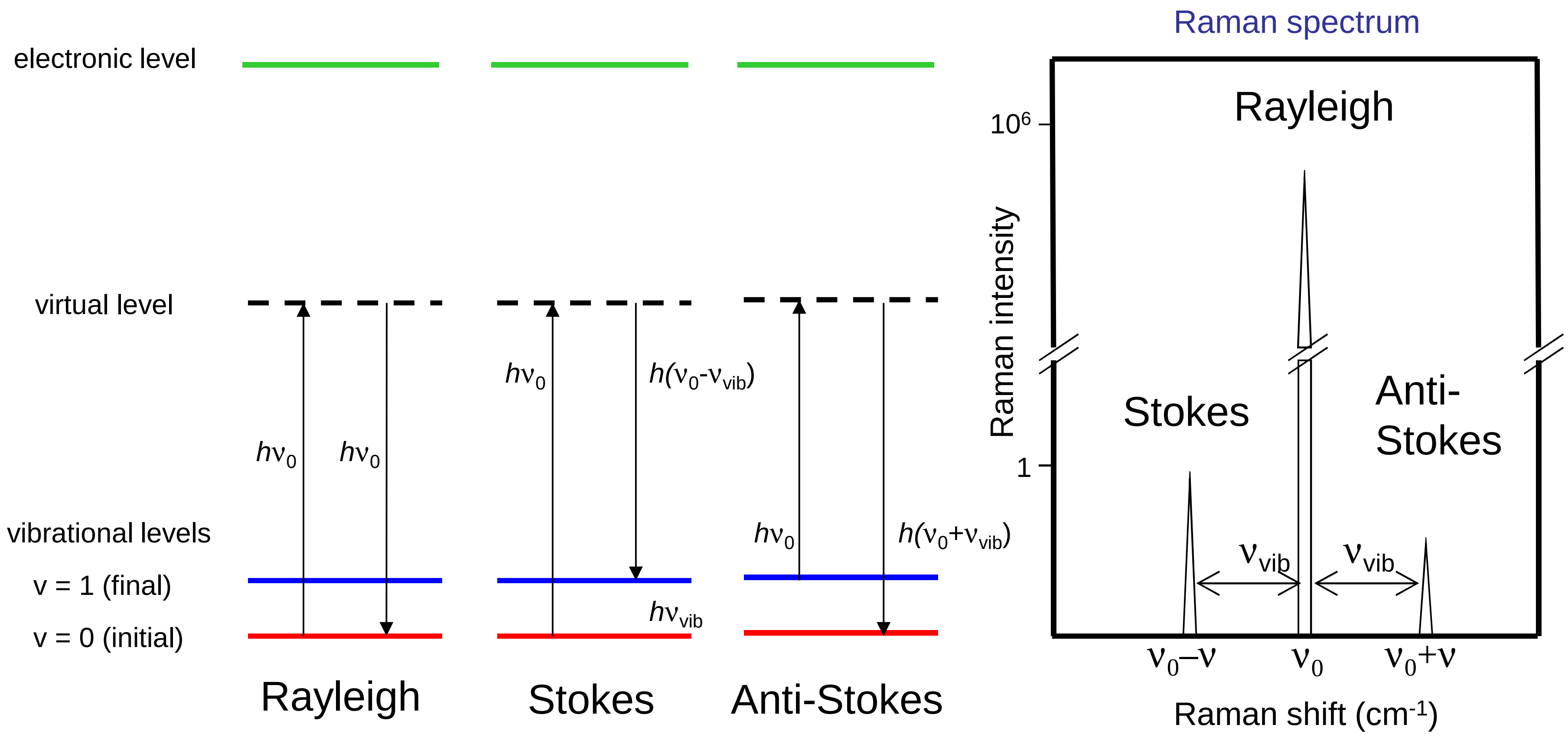
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib}t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\text{ (Anti-Stokes)}}{I\text{ (Stokes)}} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

- ❑ 4th power of ν (4th power law)
- ❑ 2nd power of $\Delta\alpha$
  - properties of molecules
  - strength of bonds

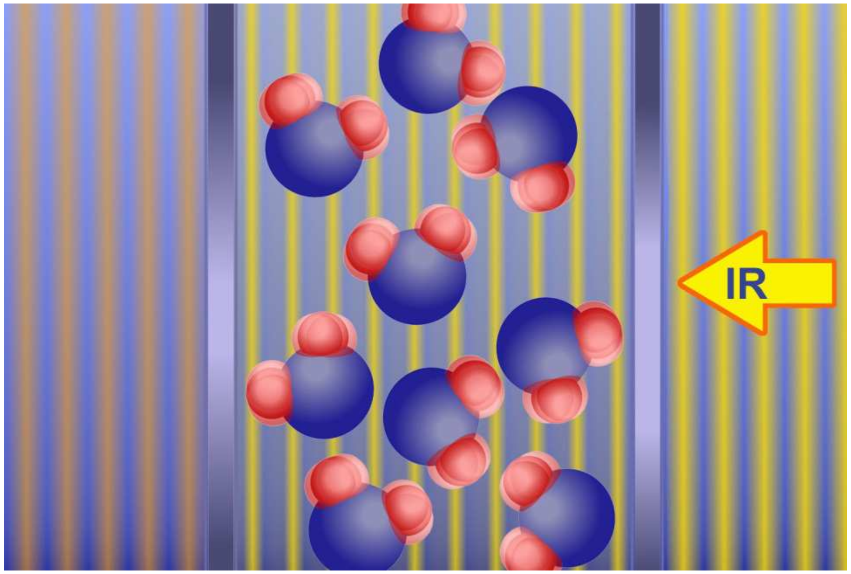
↓

covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

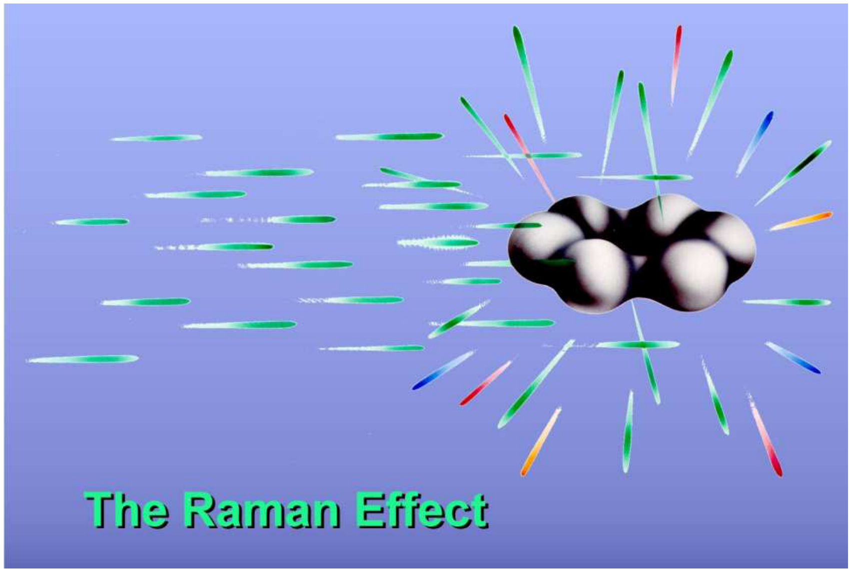
Raman *vs.* Infrared

Infrared



Absorption of IR light

Raman



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

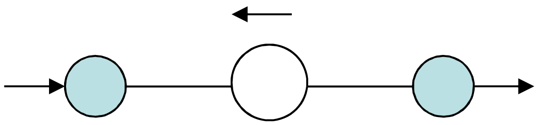
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - ❑ large electron clouds
  - ❑ not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

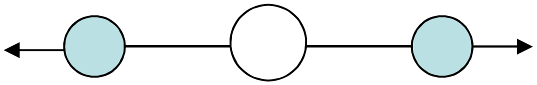
Raman *vs.* Infrared

CO_2



ν_{as}

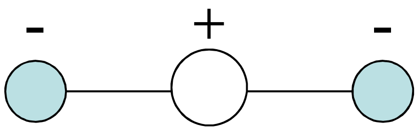
2349 cm^{-1}



ν_s

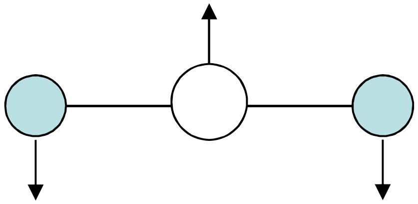
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



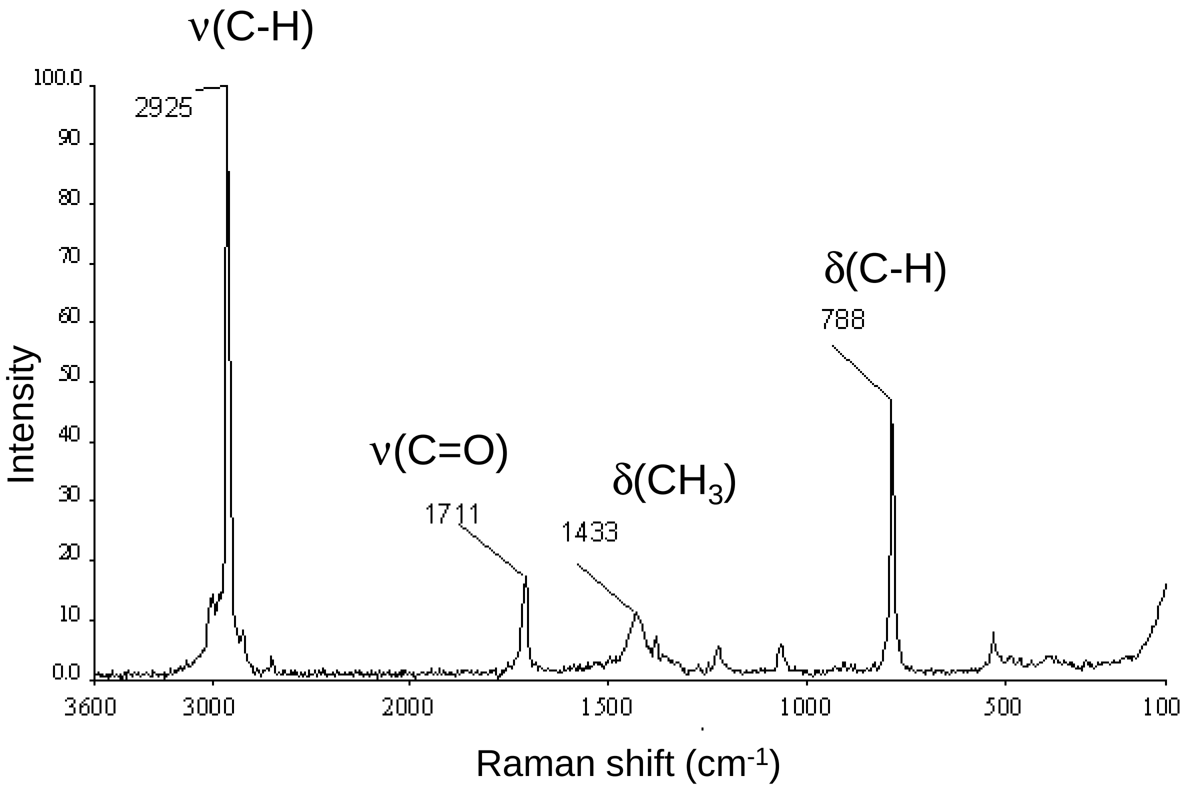
δ

667 cm^{-1}

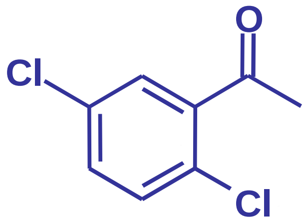
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



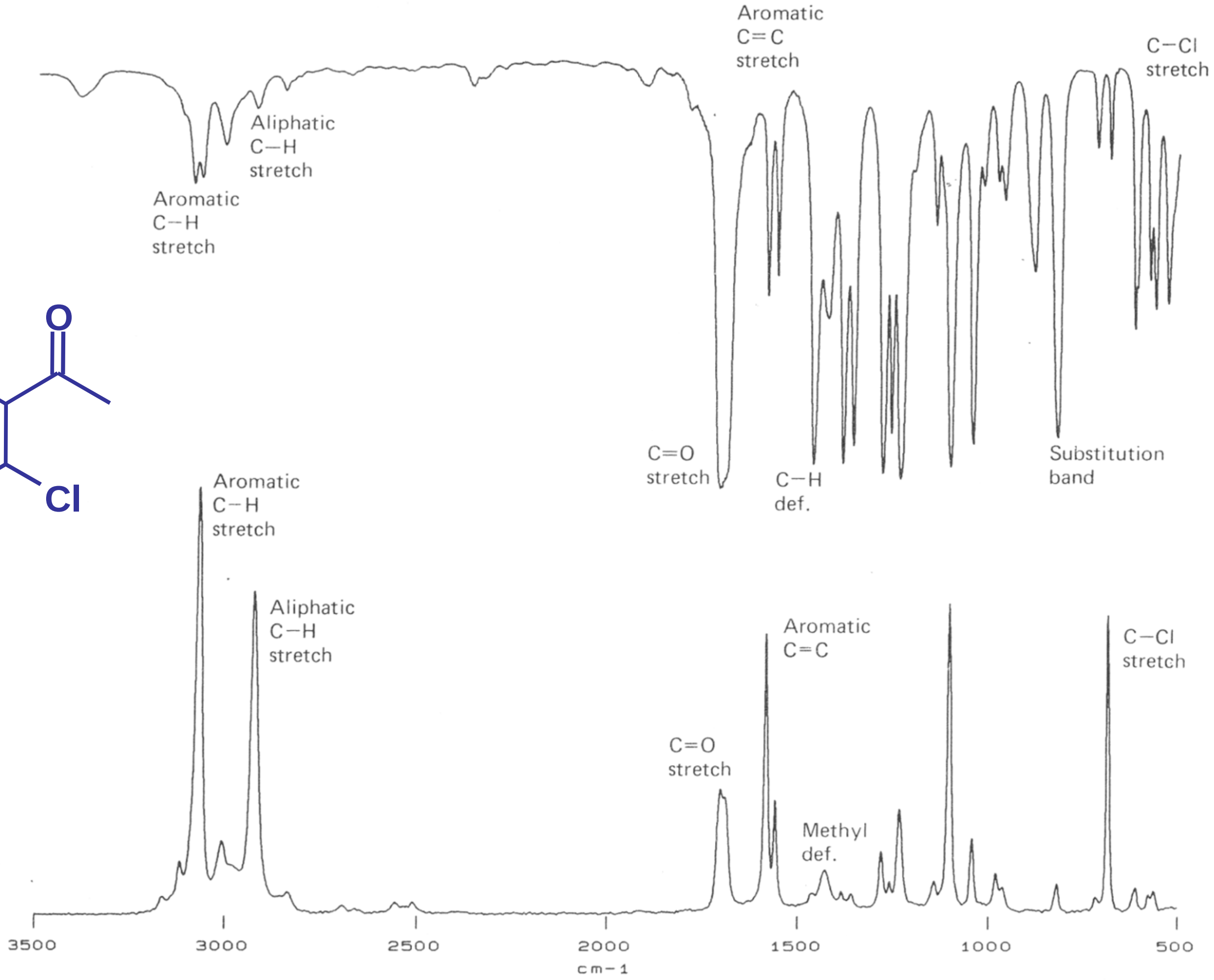


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

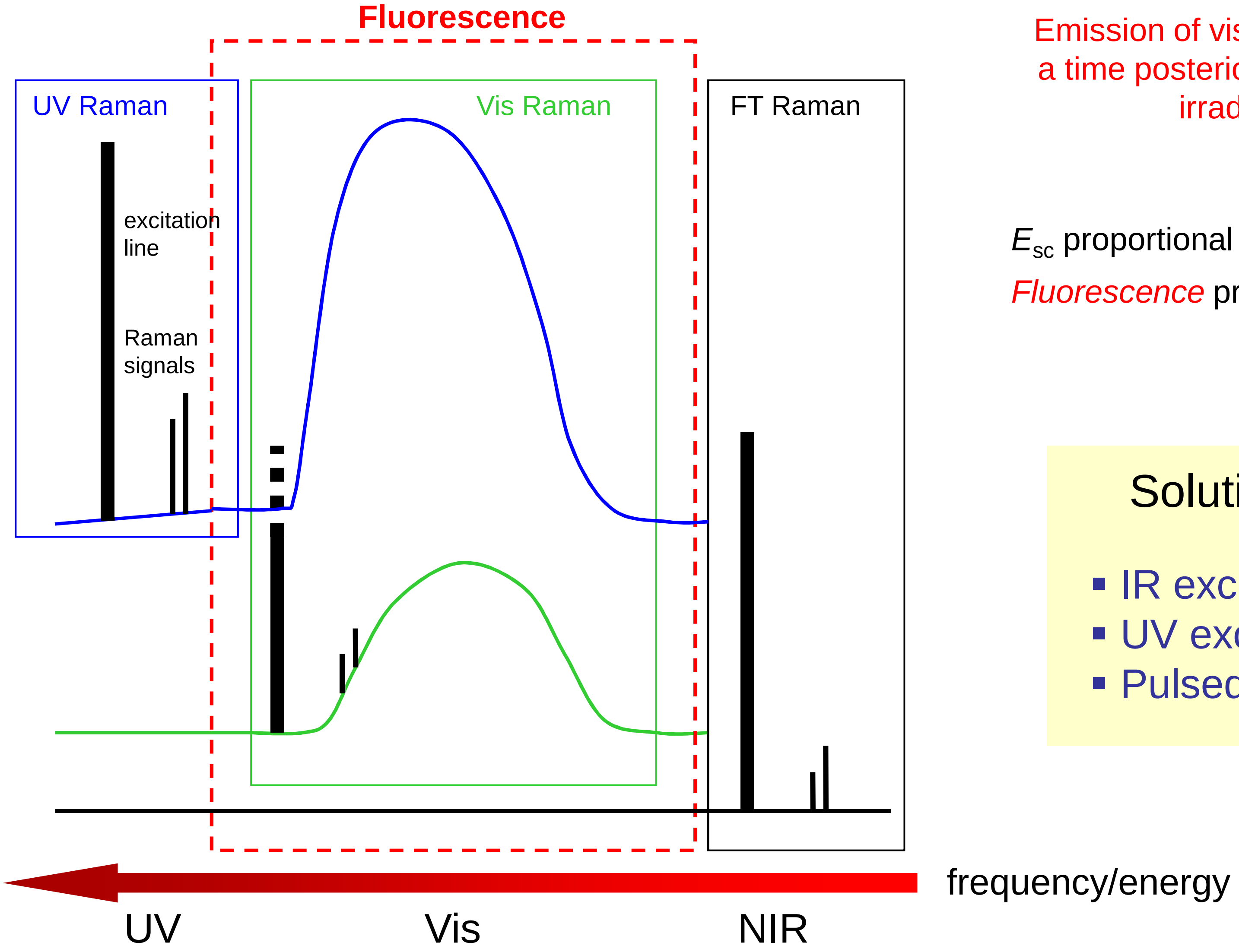
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 µm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

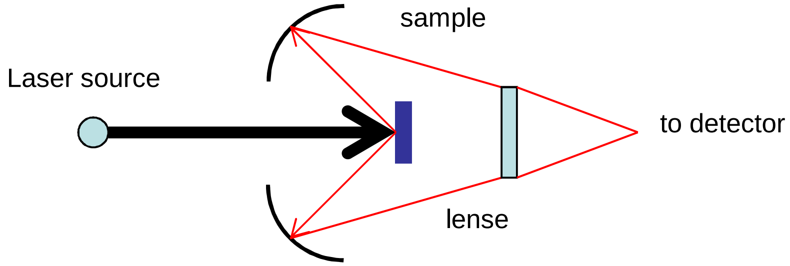
Fluorescence proportional to ν

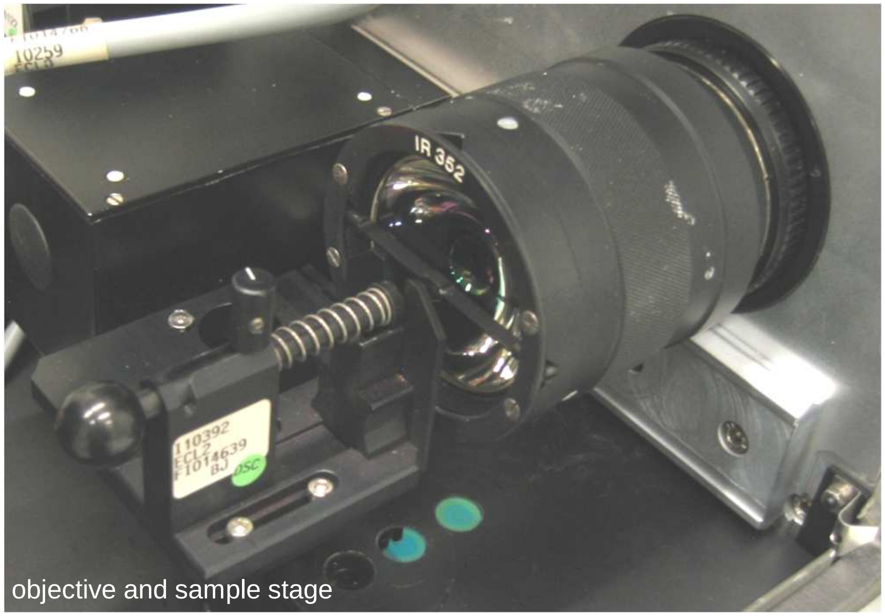
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

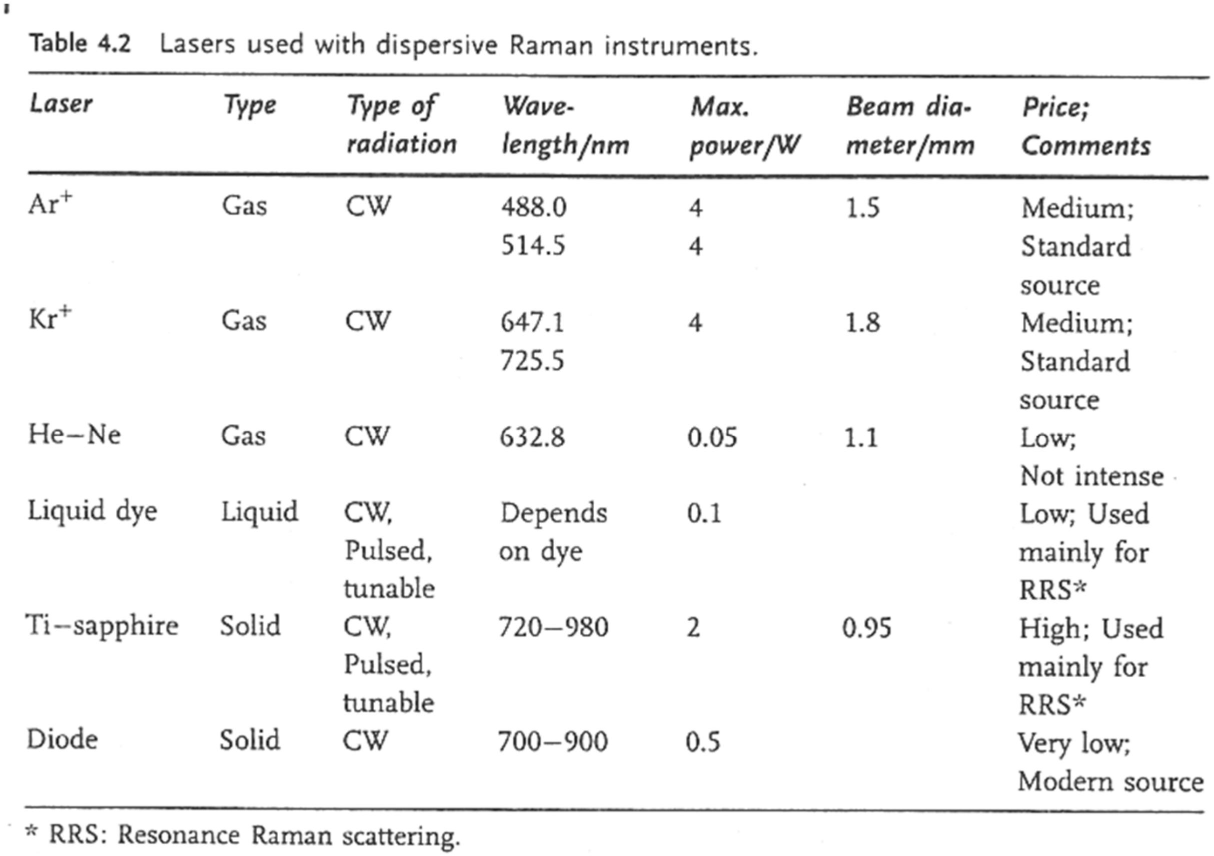


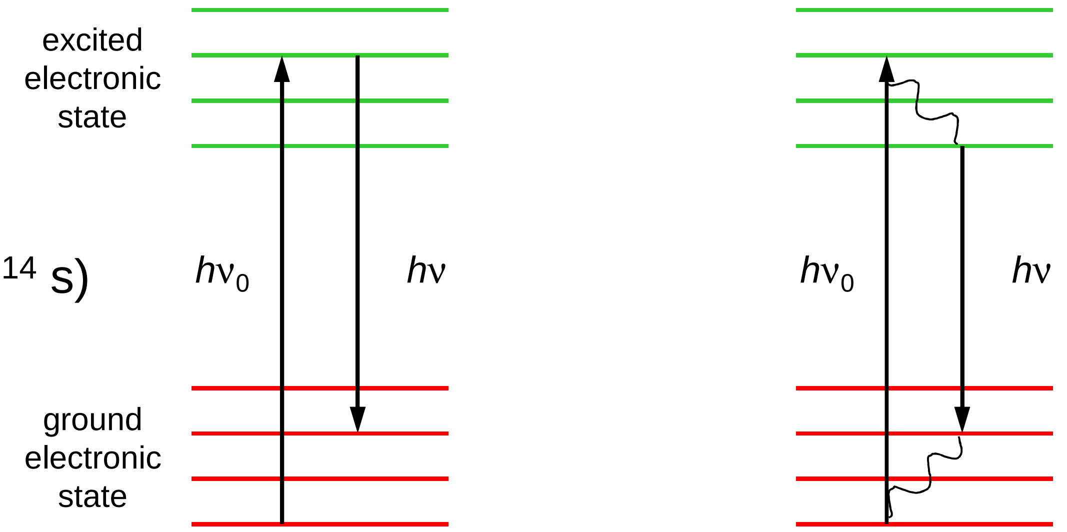
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



excited electronic state

ground electronic state

fast (10^{-14} s)

$h\nu_0$

$h\nu$

$h\nu_0$

$h\nu$

slow (10^{-9}–10^{-6} s)

Resonance Raman scattering

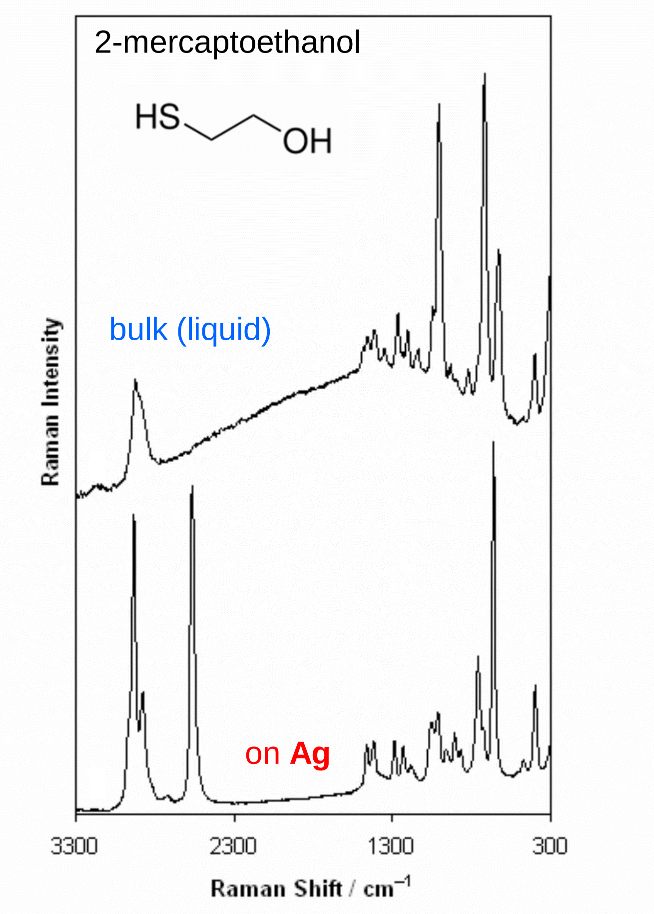
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

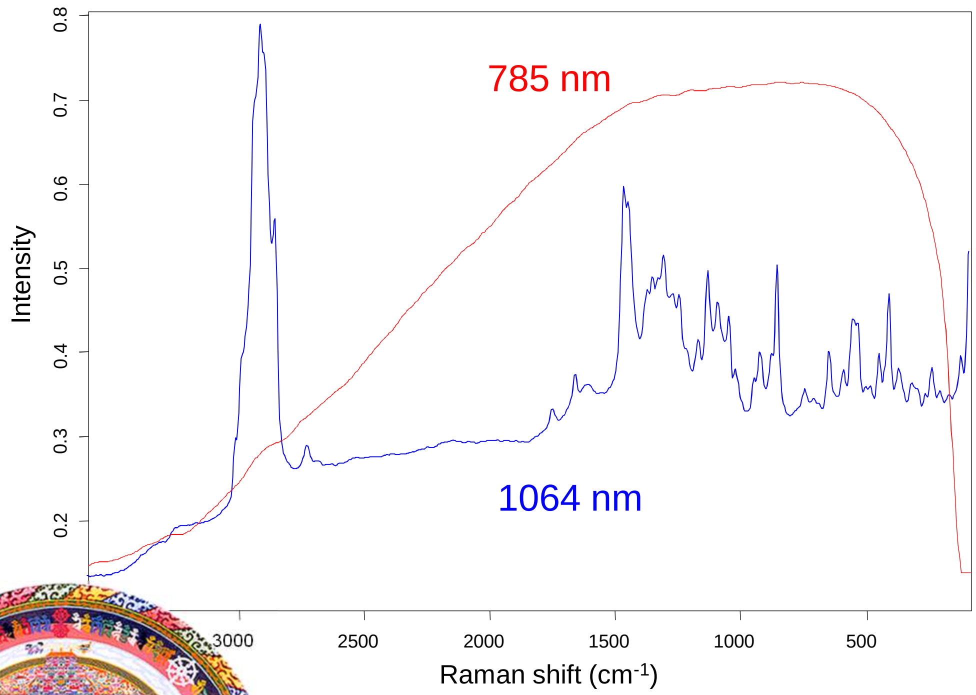
- Remarks:

❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



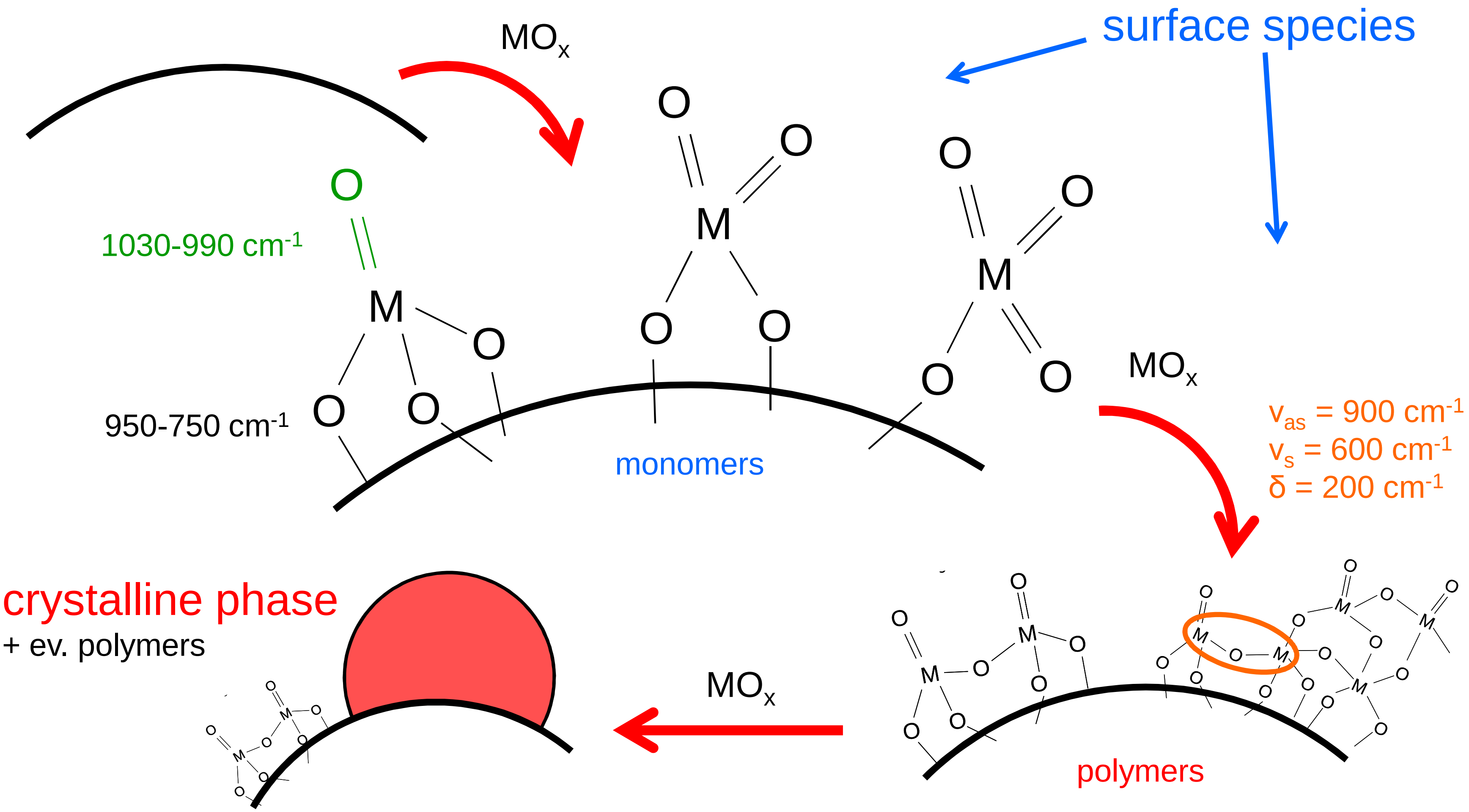
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species

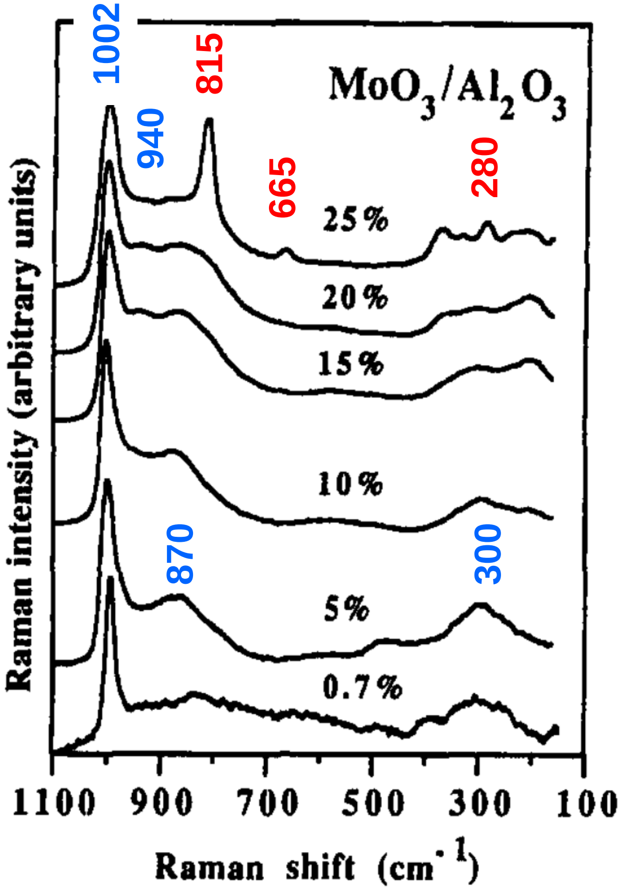


Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



surface MoO_3

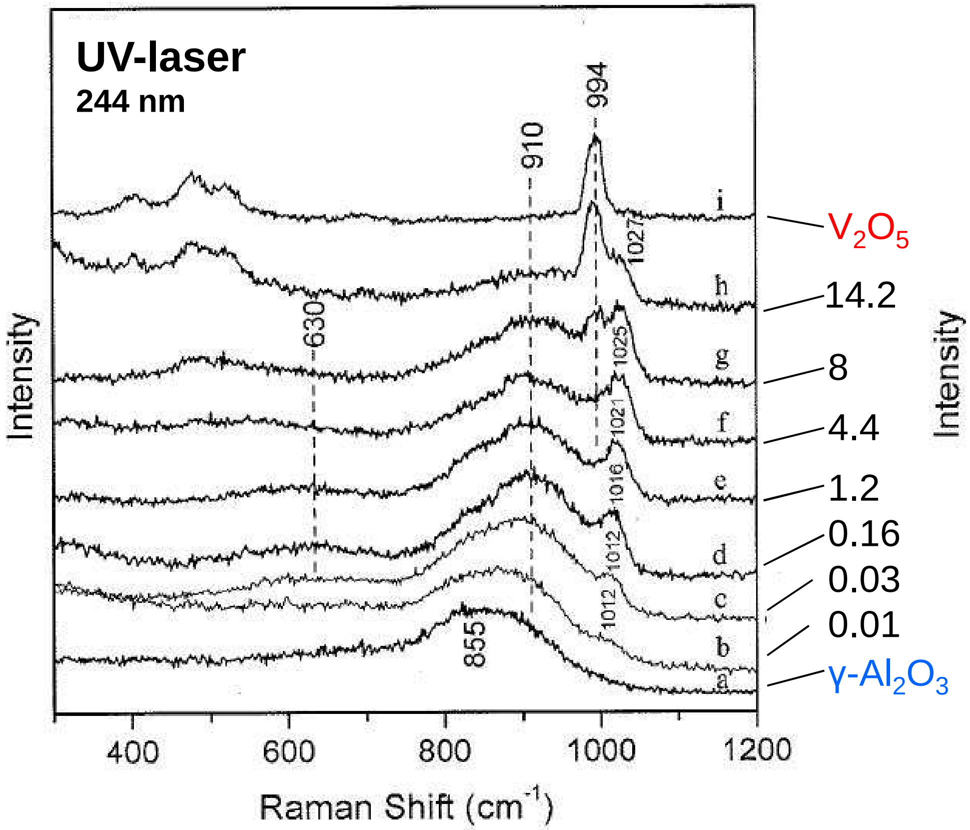
crystalline MoO_3

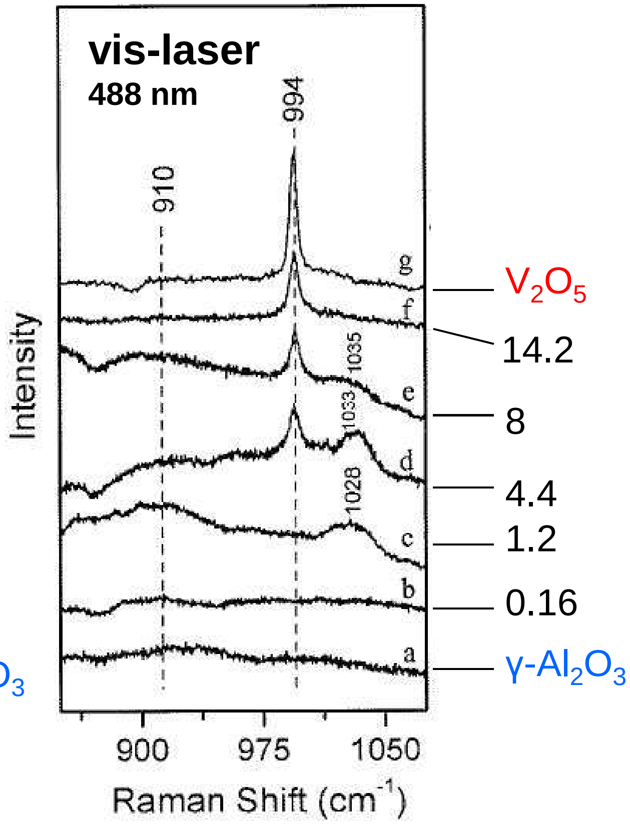
MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

- Monomeric & polymeric species

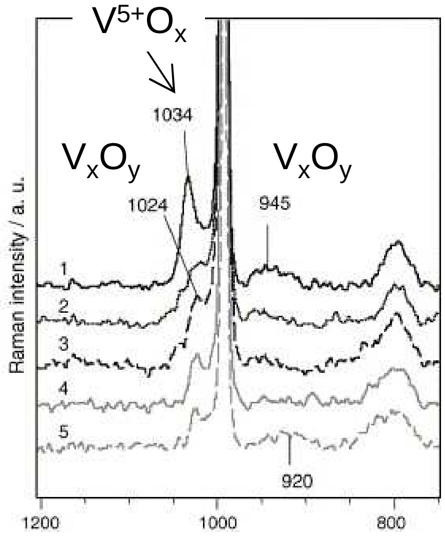




Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

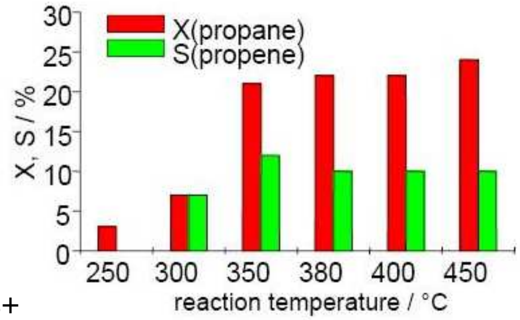
Applications

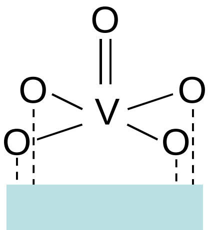
- Reactivity of V/TiO_2 after oxidative treatment

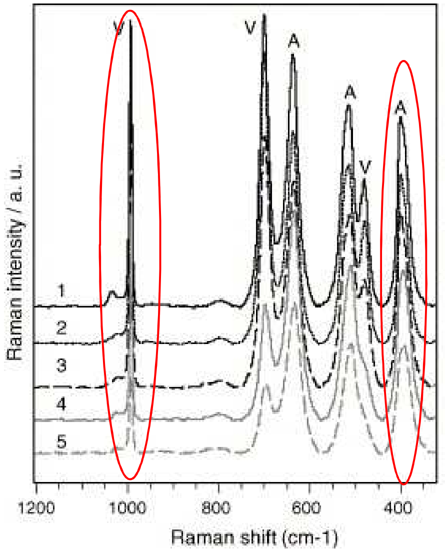


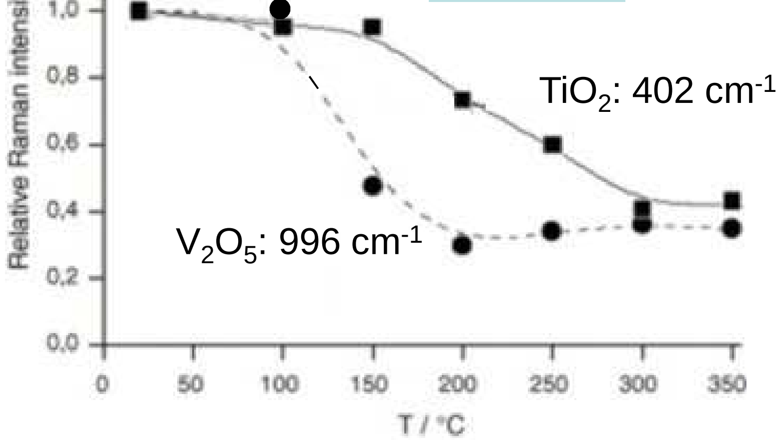
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

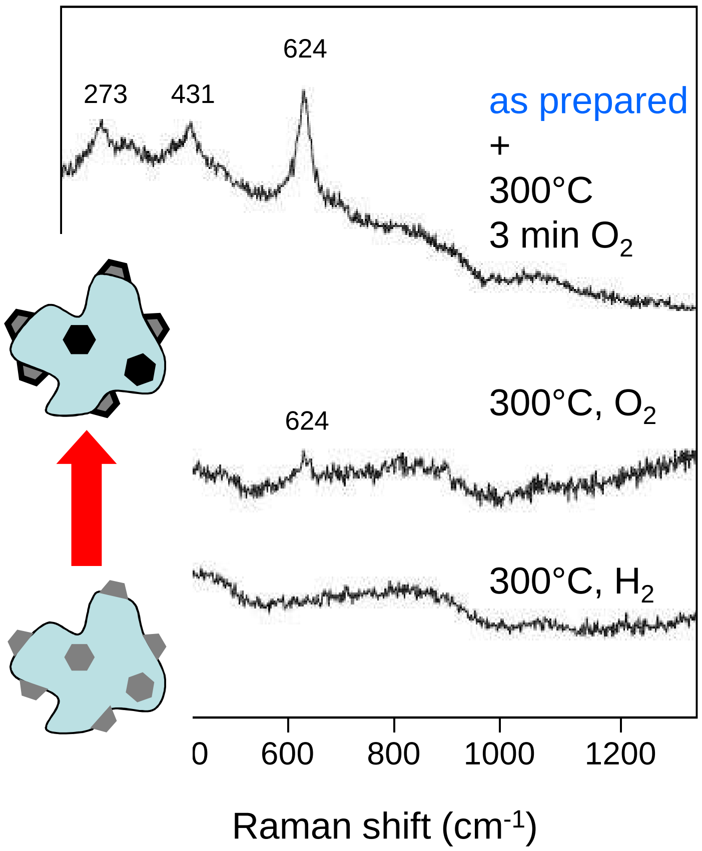
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

Question: what is the state of Pd during reaction?

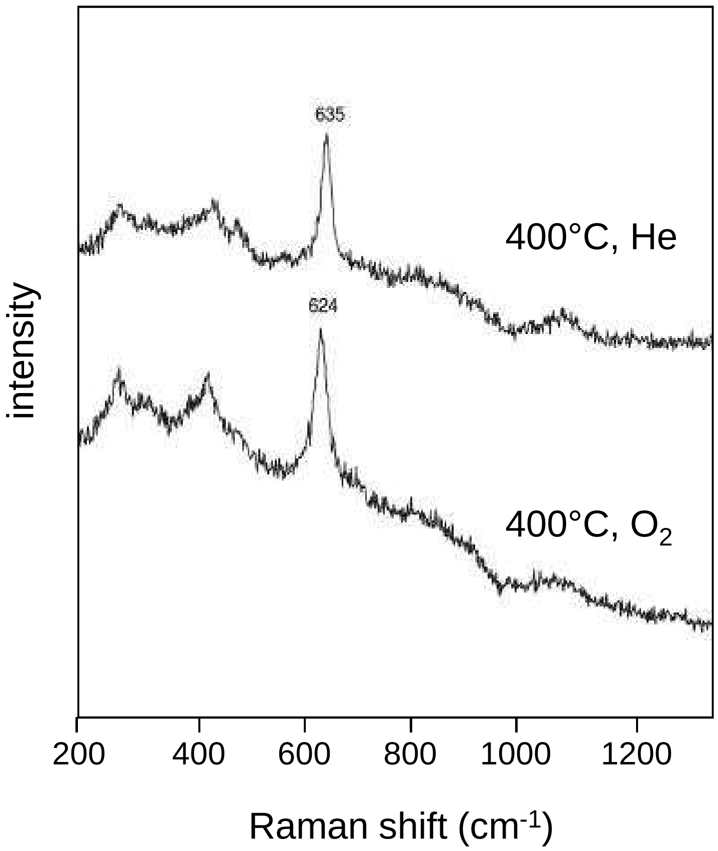
Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

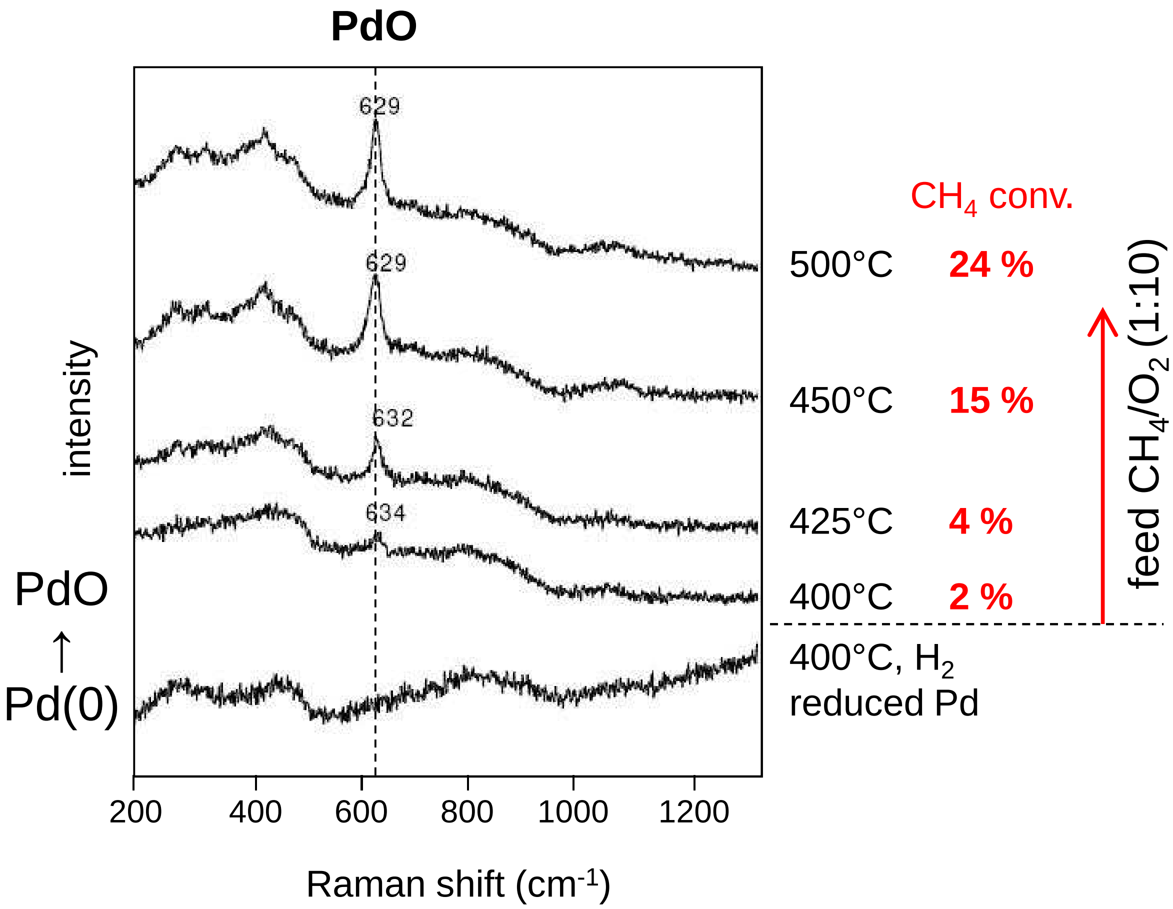


Demoulin et al., *PCCP* **5** (2003) 4394

Applications

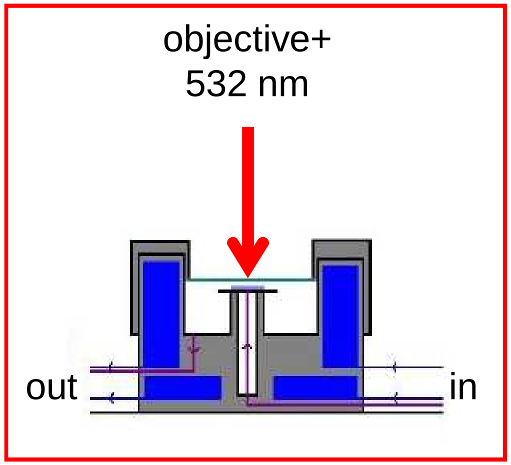
- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



	CH_4 conv.
500°C	**24 %**
450°C	**15 %**
425°C	**4 %**
400°C	**2 %**
400°C, H_2 reduced Pd	

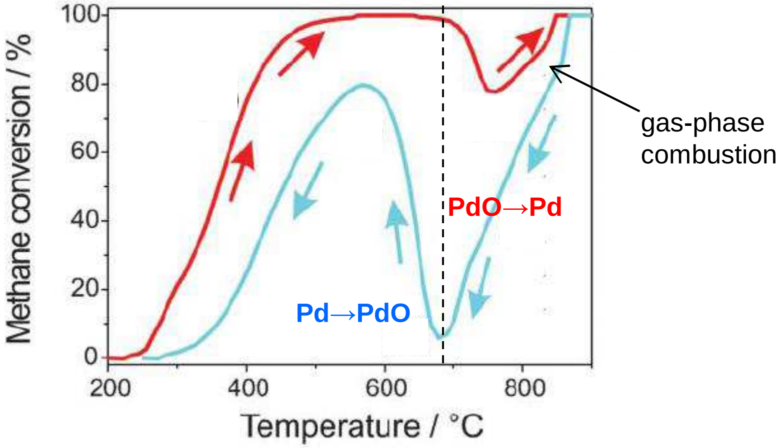
near PdO mode

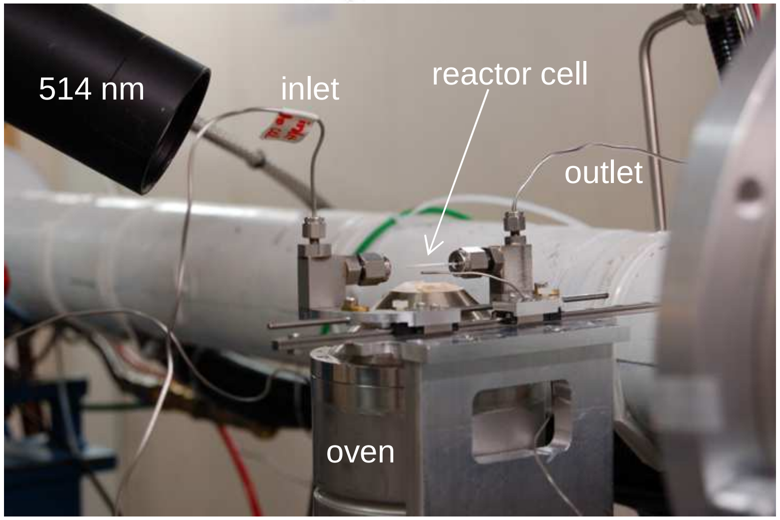


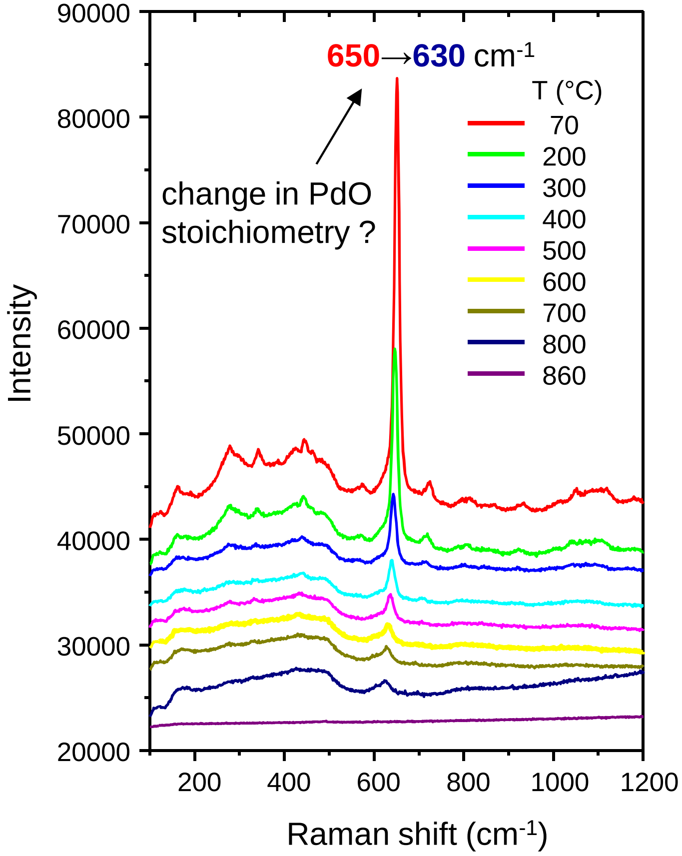
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

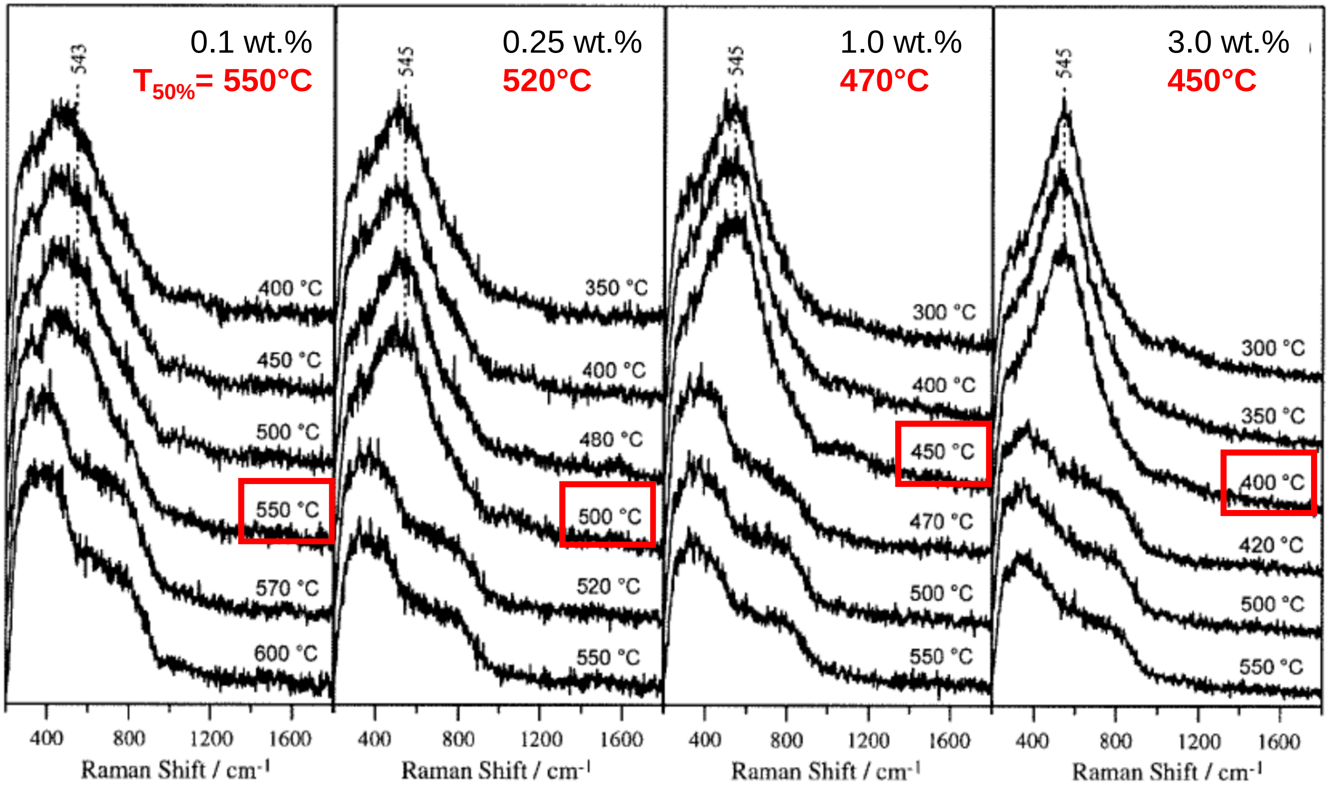
Applications

- Methane partial oxidation over Rh/Al_2O_3

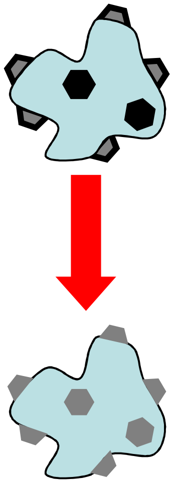
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content →
Activity →



RhO_x
↓
Rh(0)



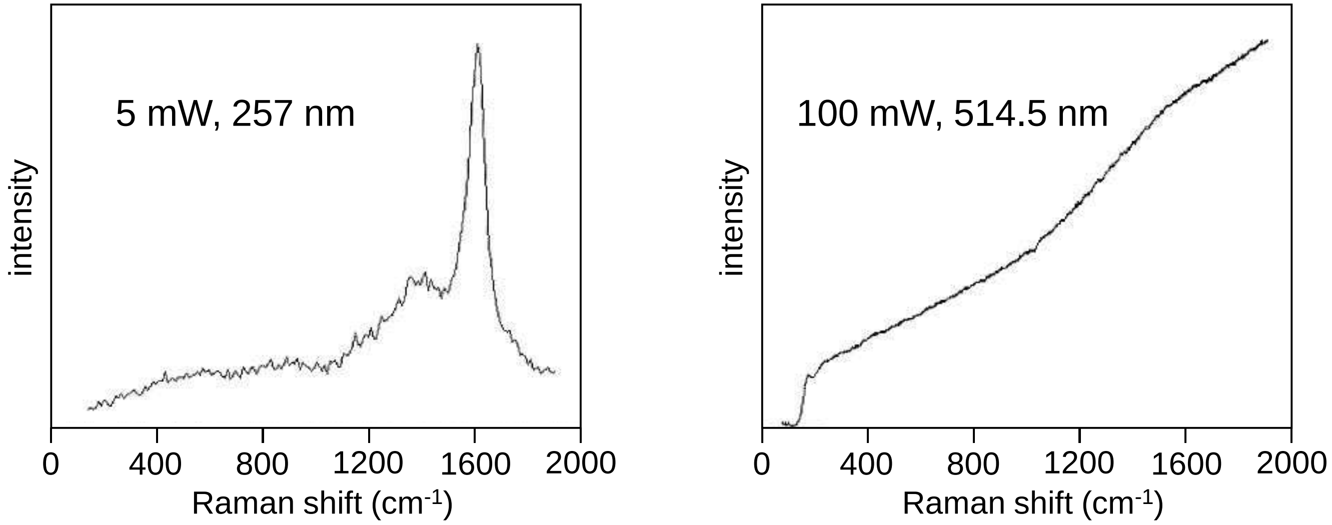
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

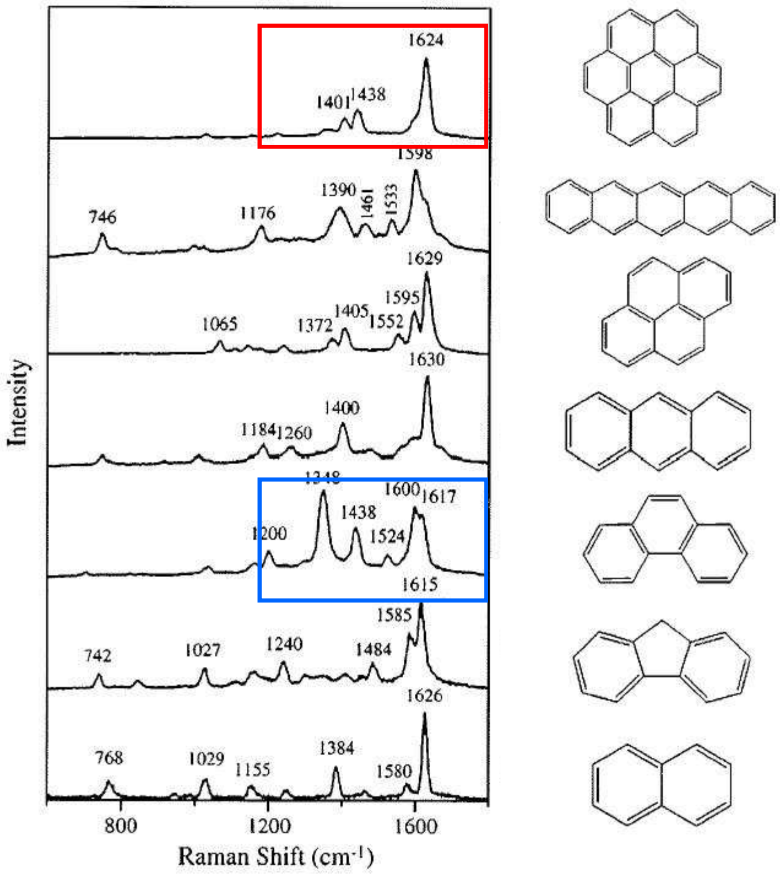
Rh/Al_2O_3, coked 500°C in naphtha

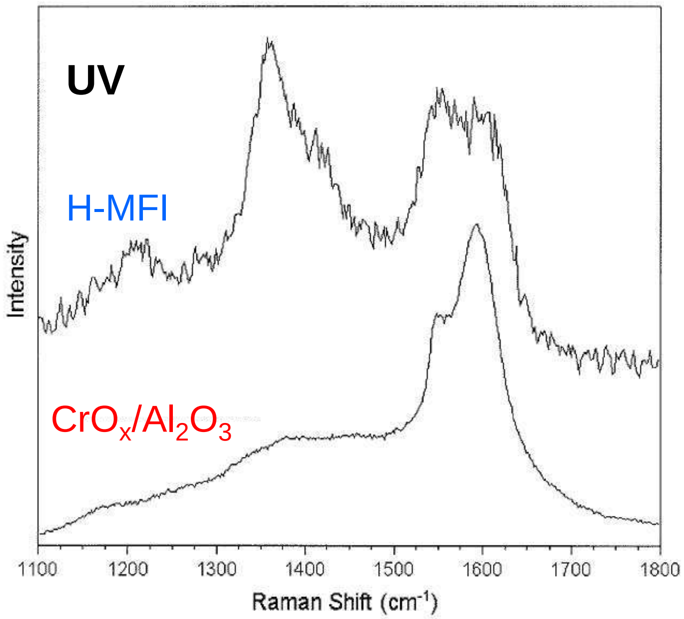


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





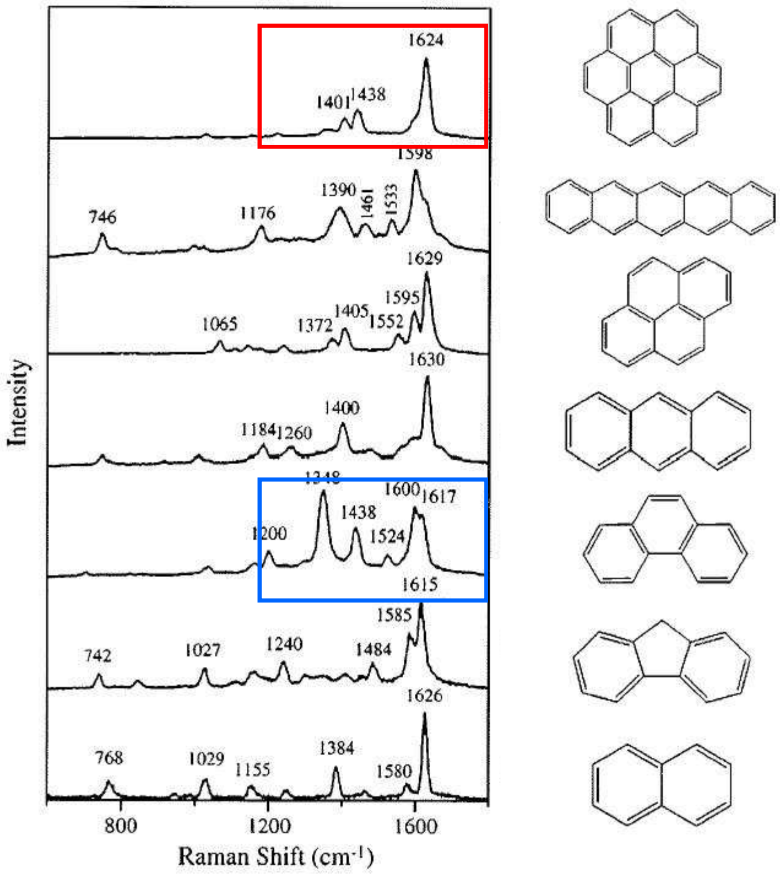
Coke classification
1D topology, chain-like
2D topology, sheet-like

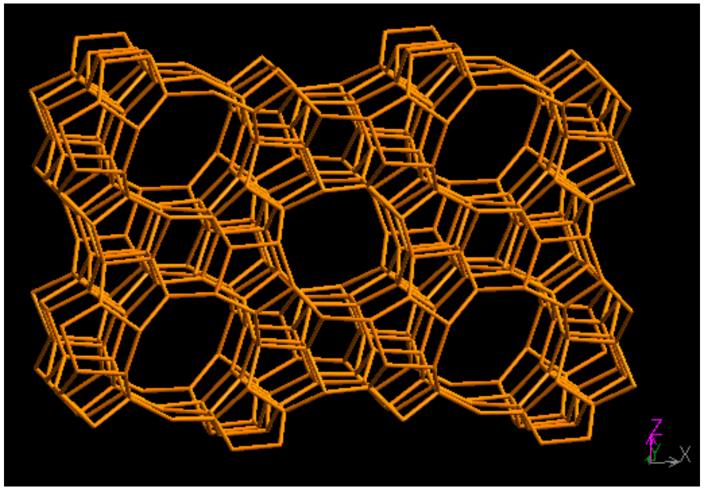
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





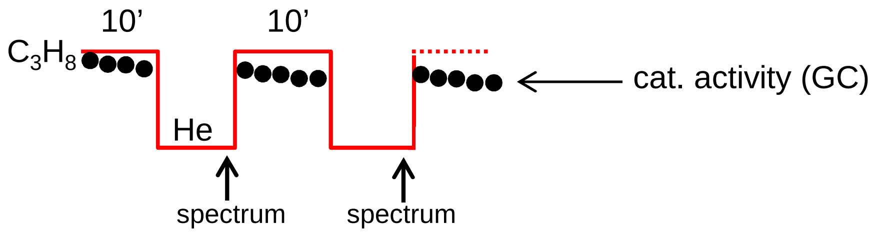
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- Propane dehydrogenation



10’ 10’

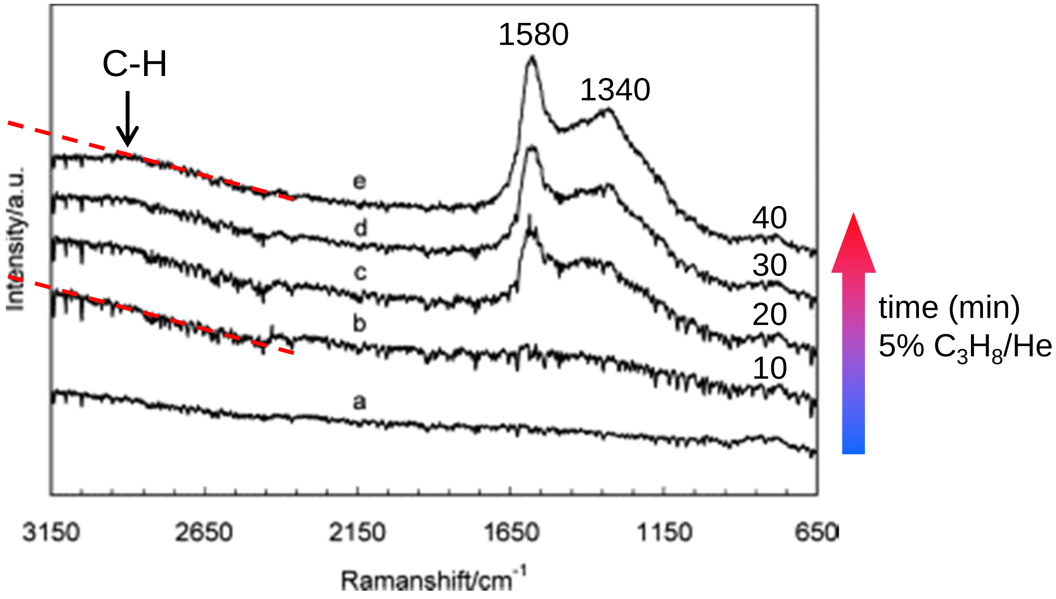
C_3H_8

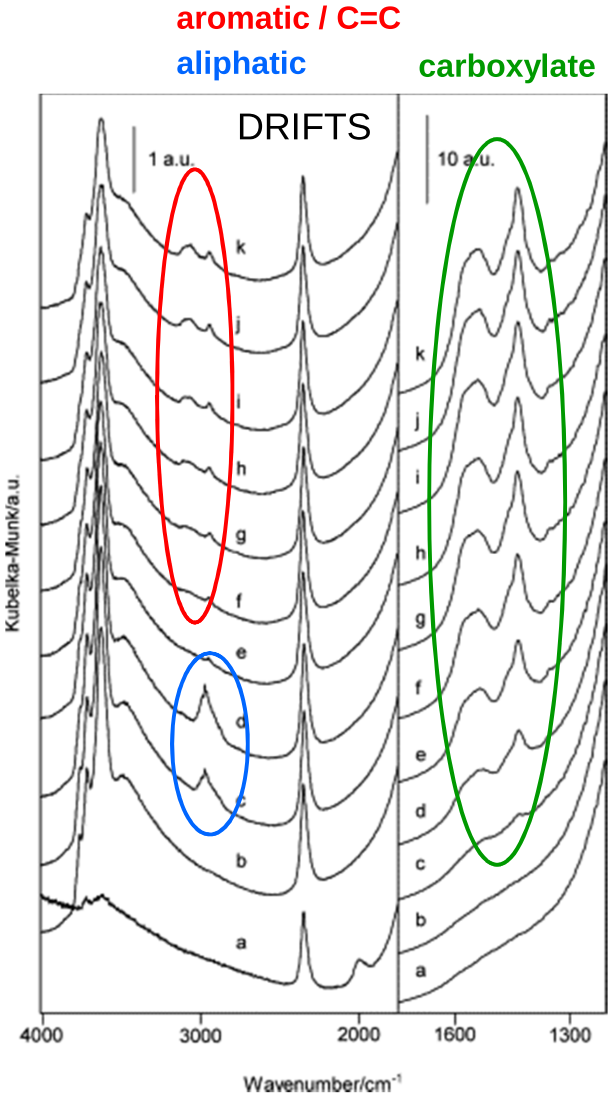
He

spectrum spectrum

cat. activity (GC)

Cr_2O_3/Al_2O_3, 580°C, 514 nm

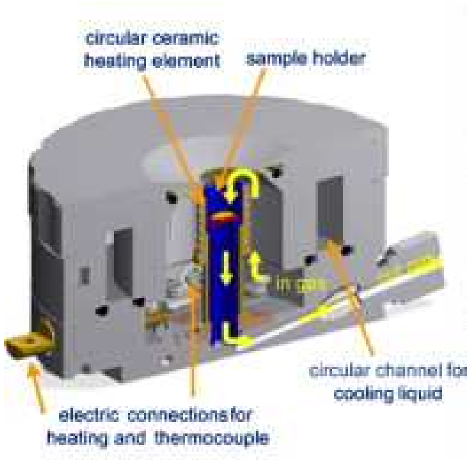


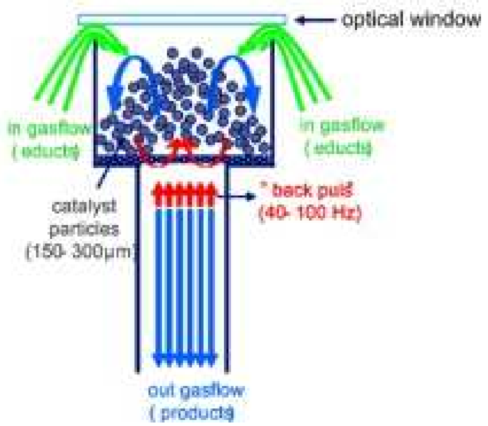


Airaksinen et al., *J. Catal.* **230** (2005) 507

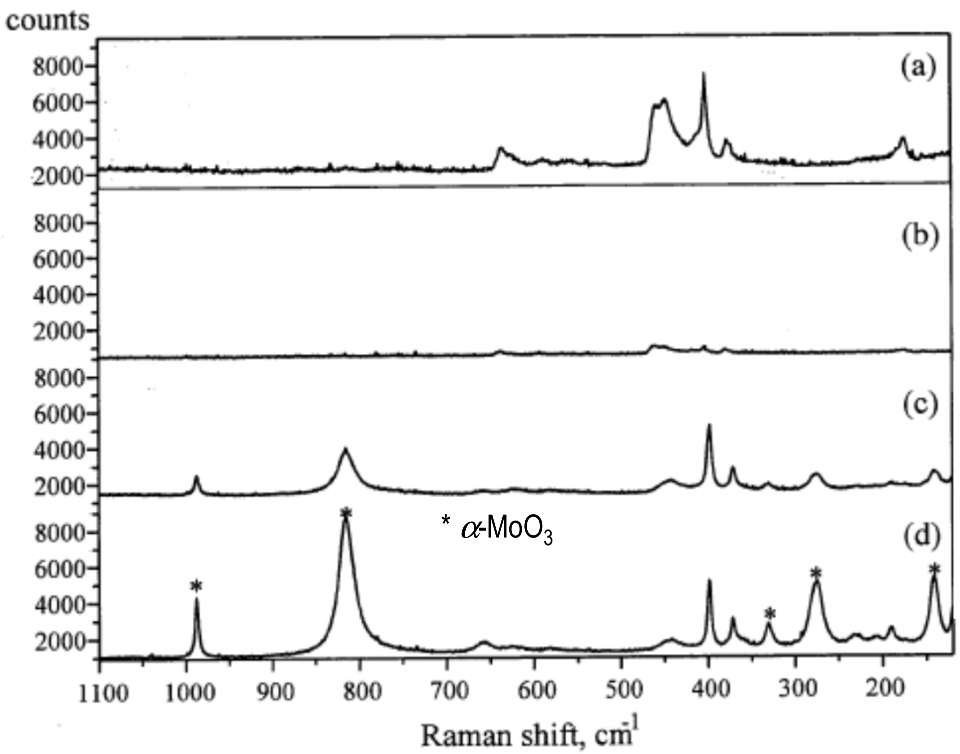
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min full power, FB

MoS_2, 6 min 1/8 power

MoS_2, 1 min full power

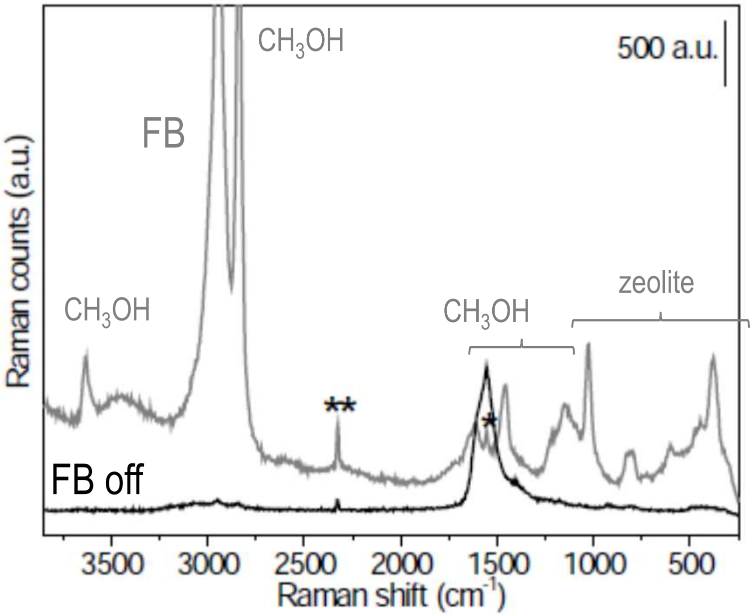
MoS_2, 6 min full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

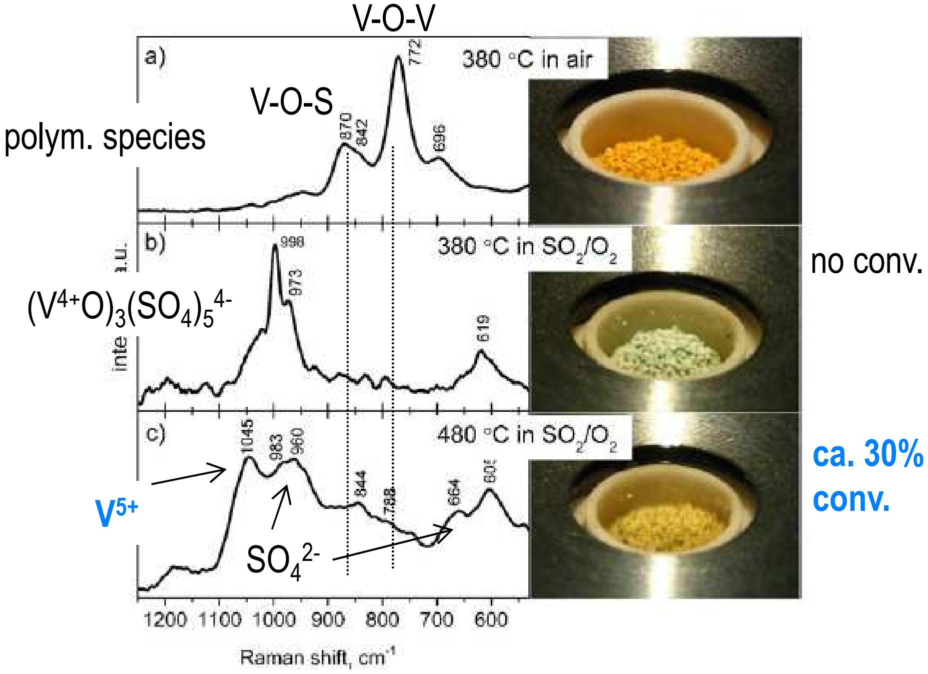
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

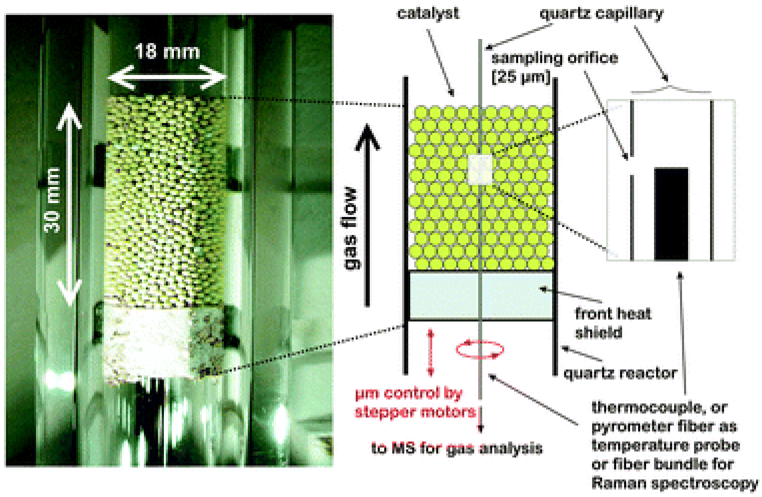


active species: mono- & dimeric V^{5+} oxosulfate species

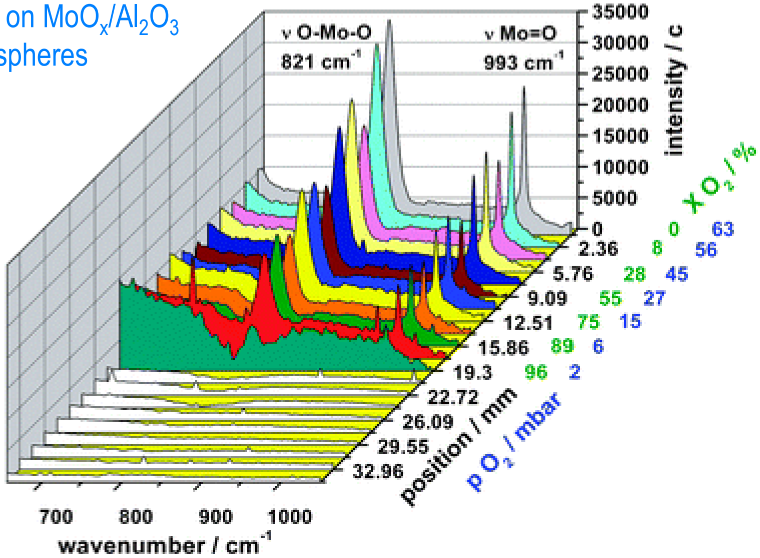
Beato et al., *Catal. Today* 205 (2013) 128

Applications

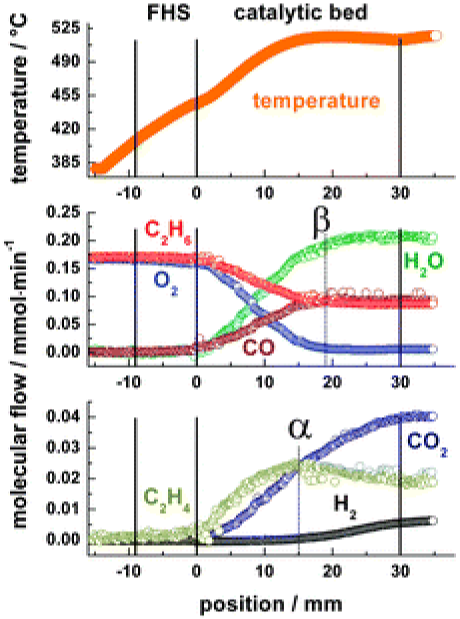
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

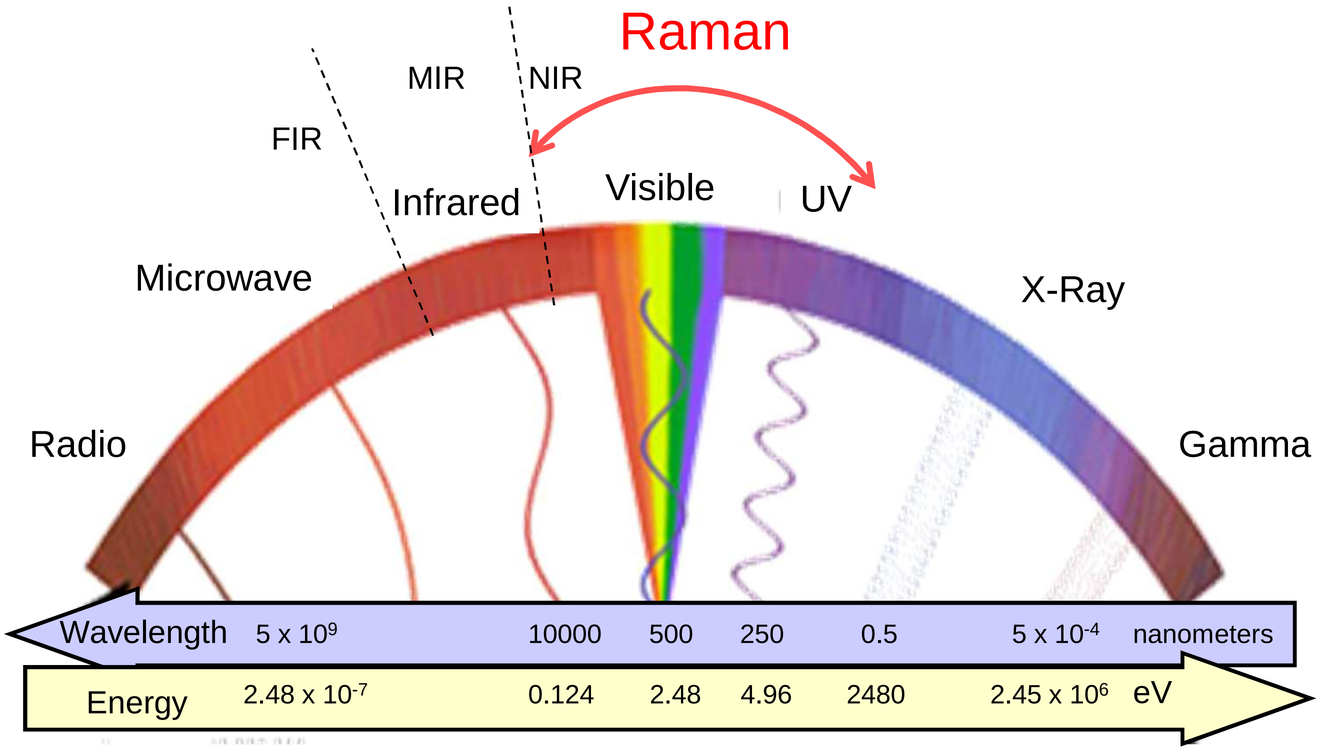
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

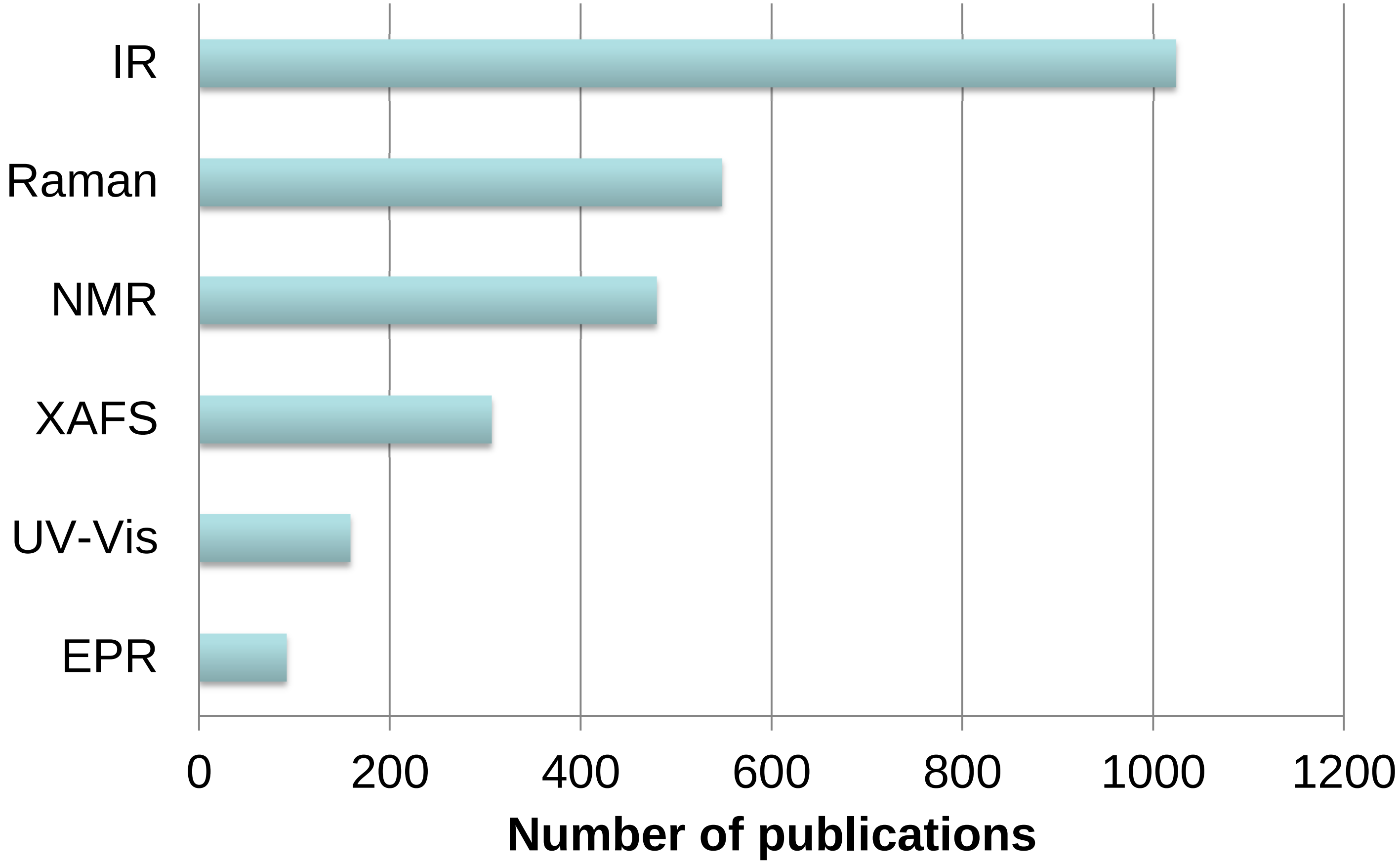
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

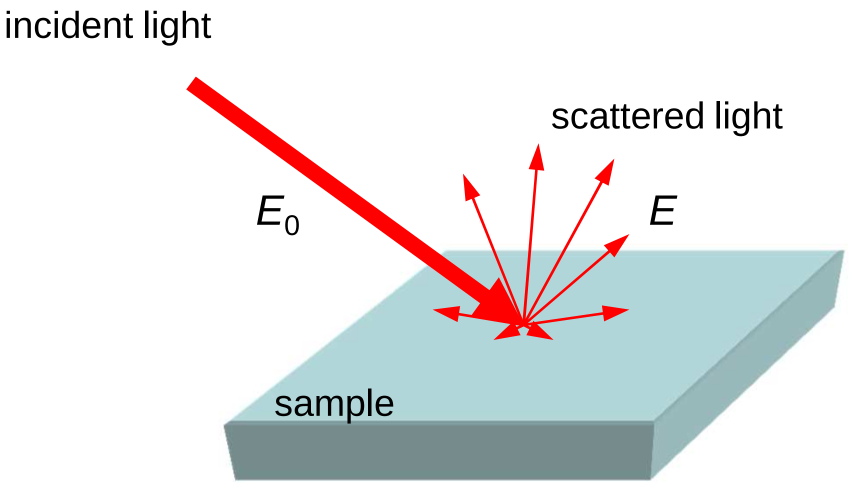


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
    - ☐ Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

- ☐ E_0 = incident beam irradiance
- ☐ α = polarizability of the particle (ease of distortion of the electron cloud)
- ☐ λ = wavelength of the incident radiation
- ☐ θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

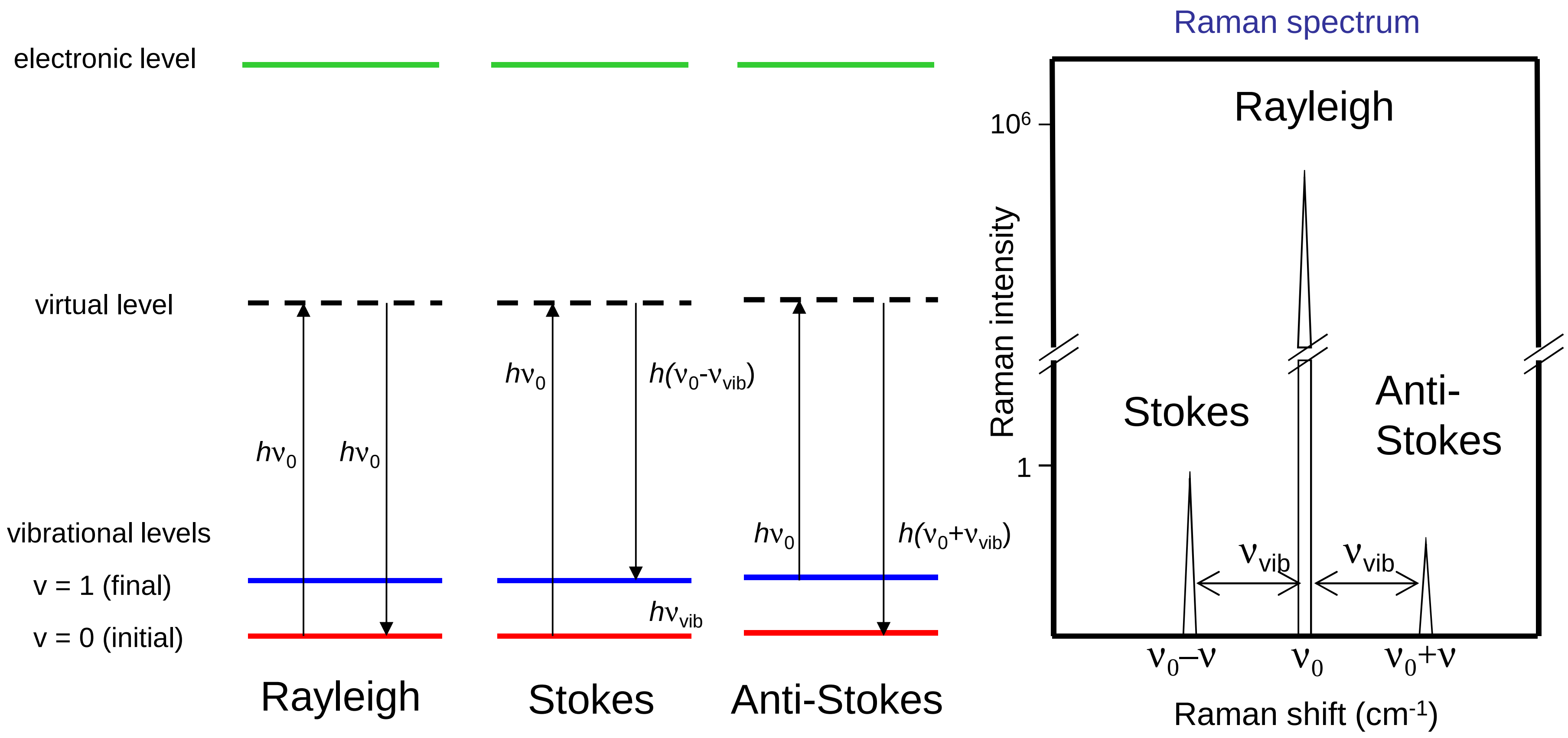
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\ (\text{Anti-Stokes})}{I\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

- 4th power of ν (4th power law)
- 2nd power of $\Delta\alpha$
  - properties of molecules
  - strength of bonds

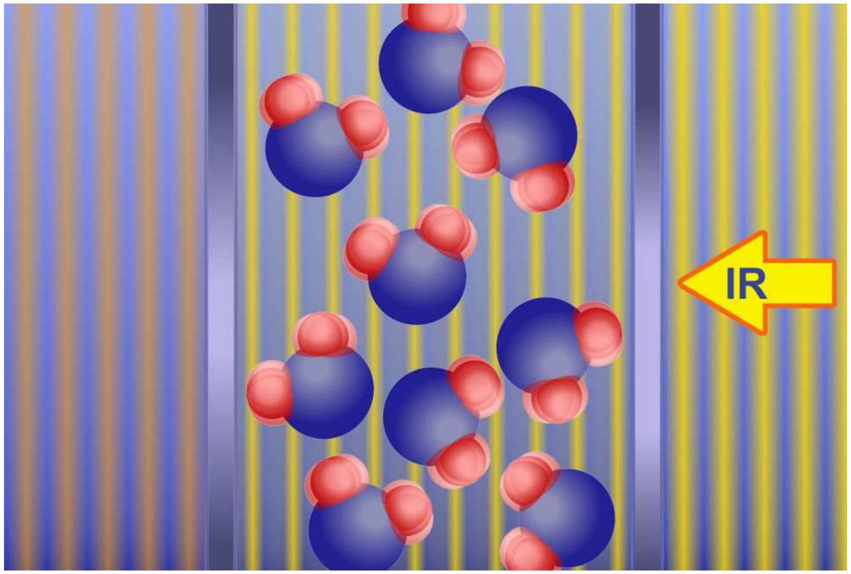
↓

covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

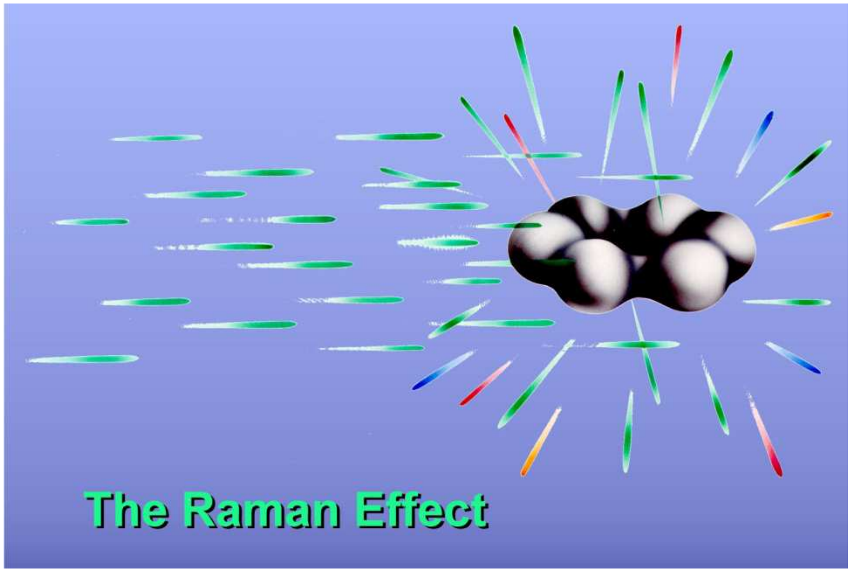
Raman *vs.* Infrared

Infrared



Absorption of IR light

Raman



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

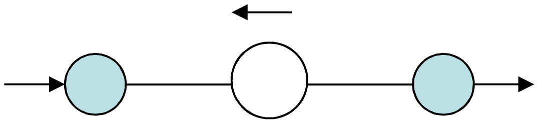
- high absorption for polar bonds ($C=O$, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - ❑ large electron clouds
  - ❑ not polar
- H_2O is a very weak Raman scatterer
- $C=C$ double bonds strong Raman scatterers

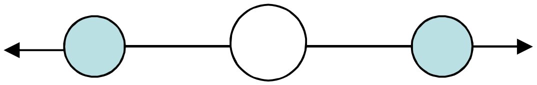
Raman *vs.* Infrared

CO_2



ν_{as}

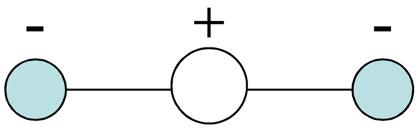
2349 cm^{-1}



ν_s

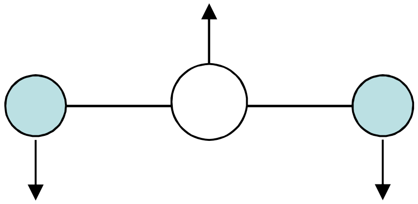
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



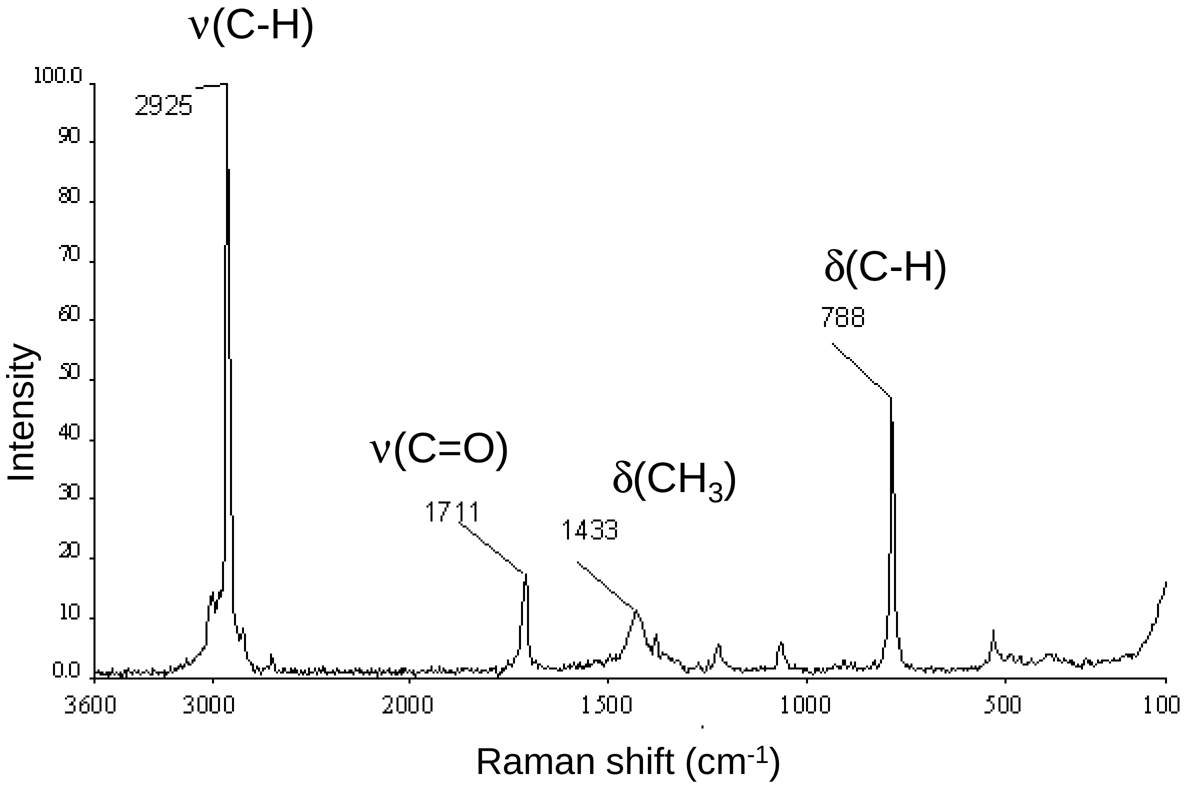
δ

667 cm^{-1}

degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared

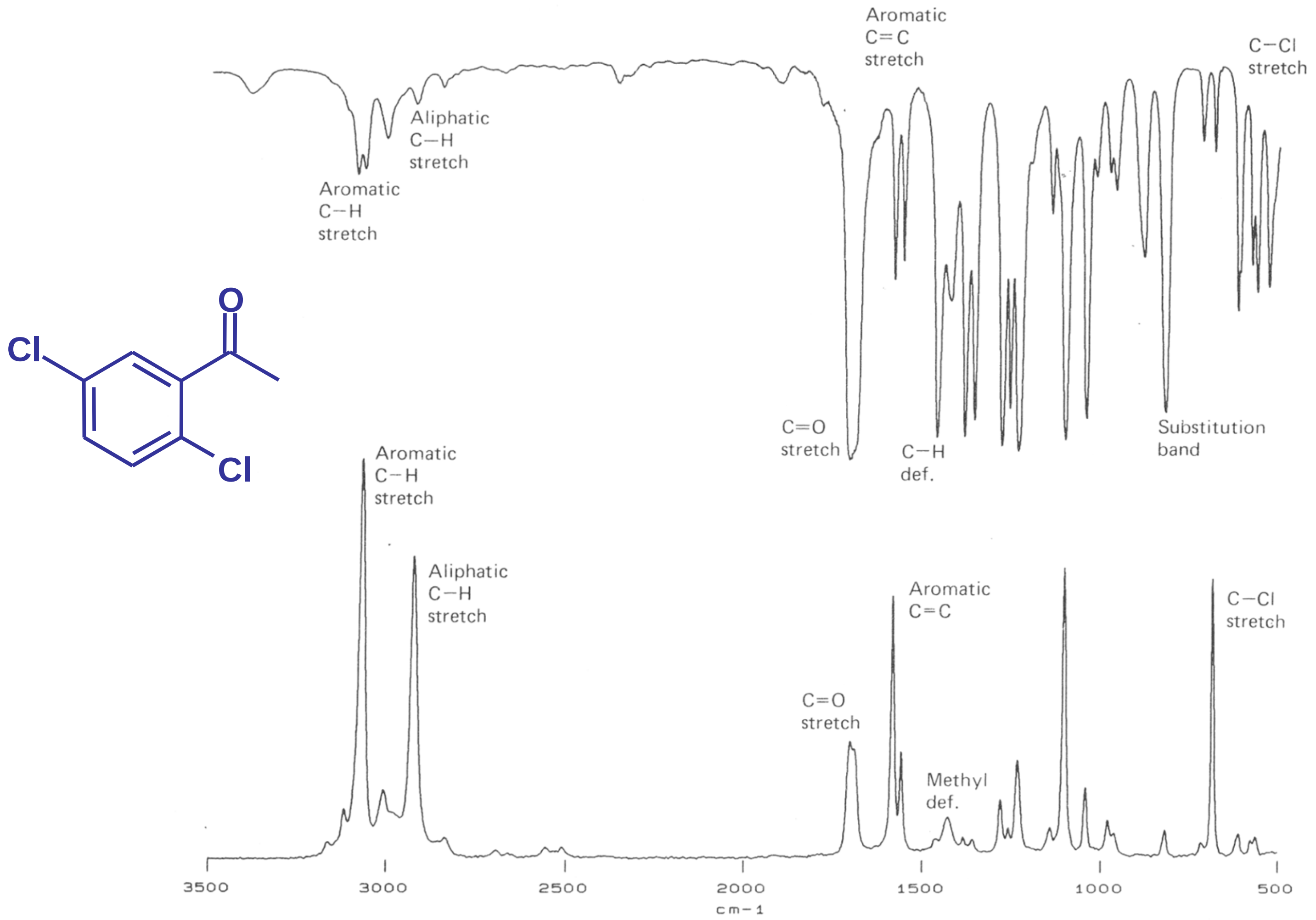


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

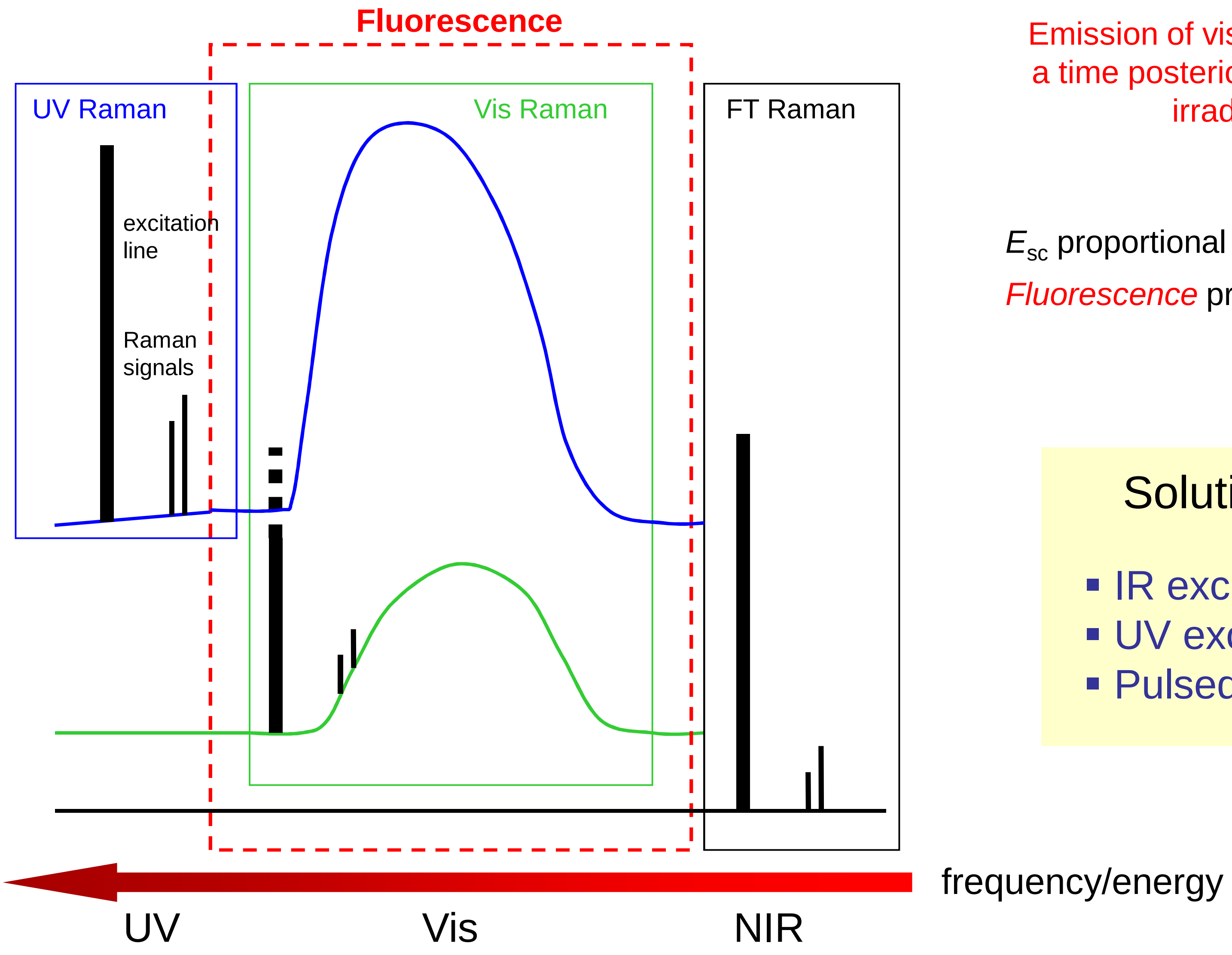
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 μm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

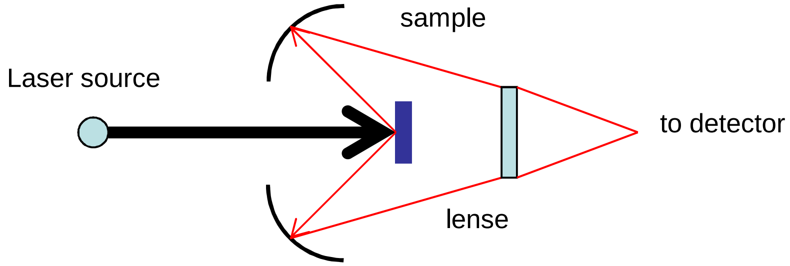
Fluorescence proportional to ν

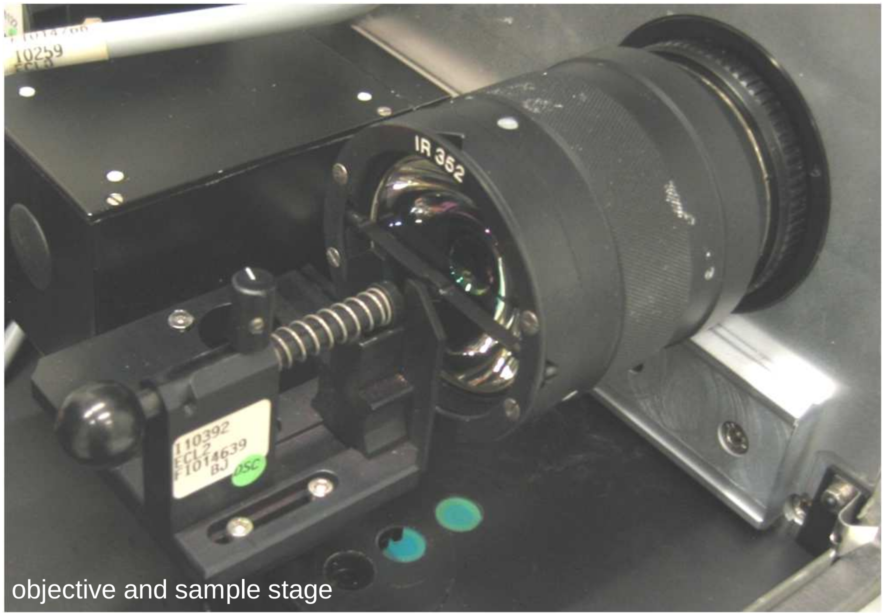
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

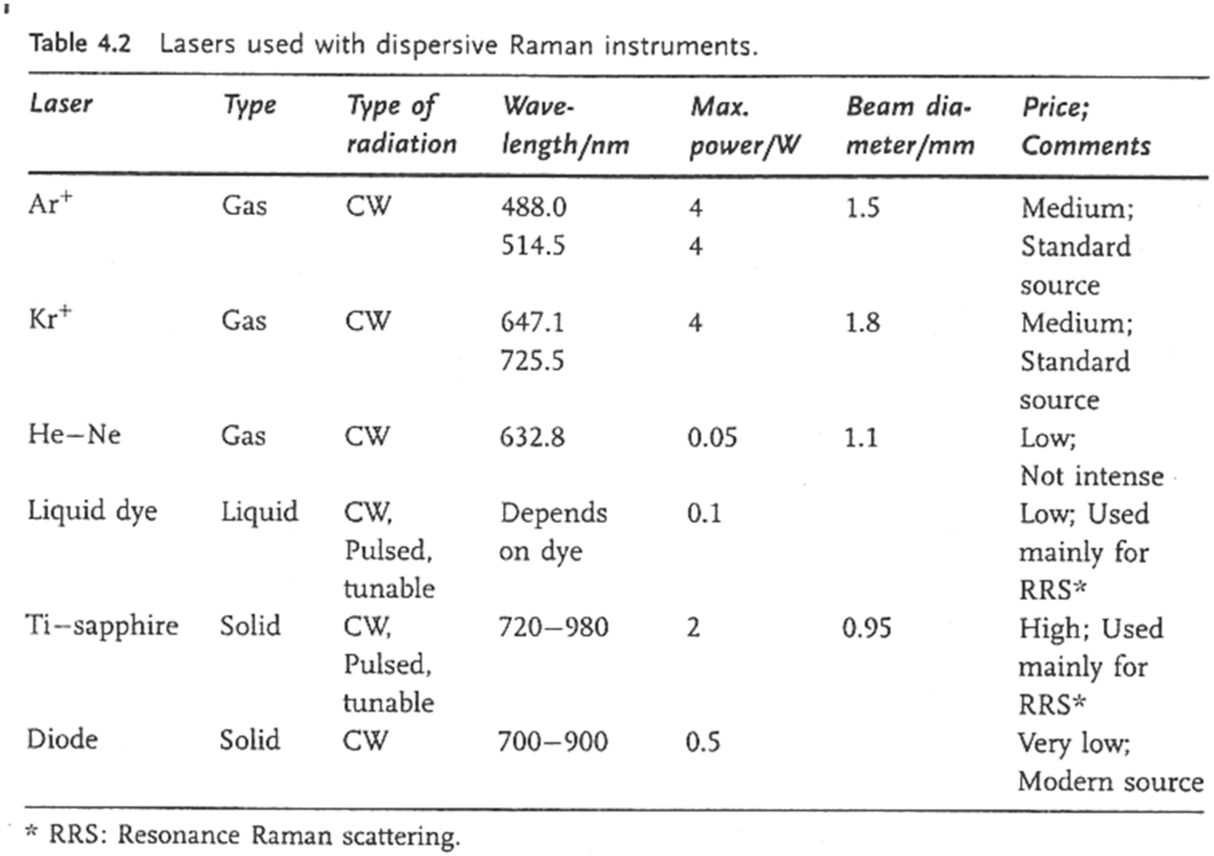


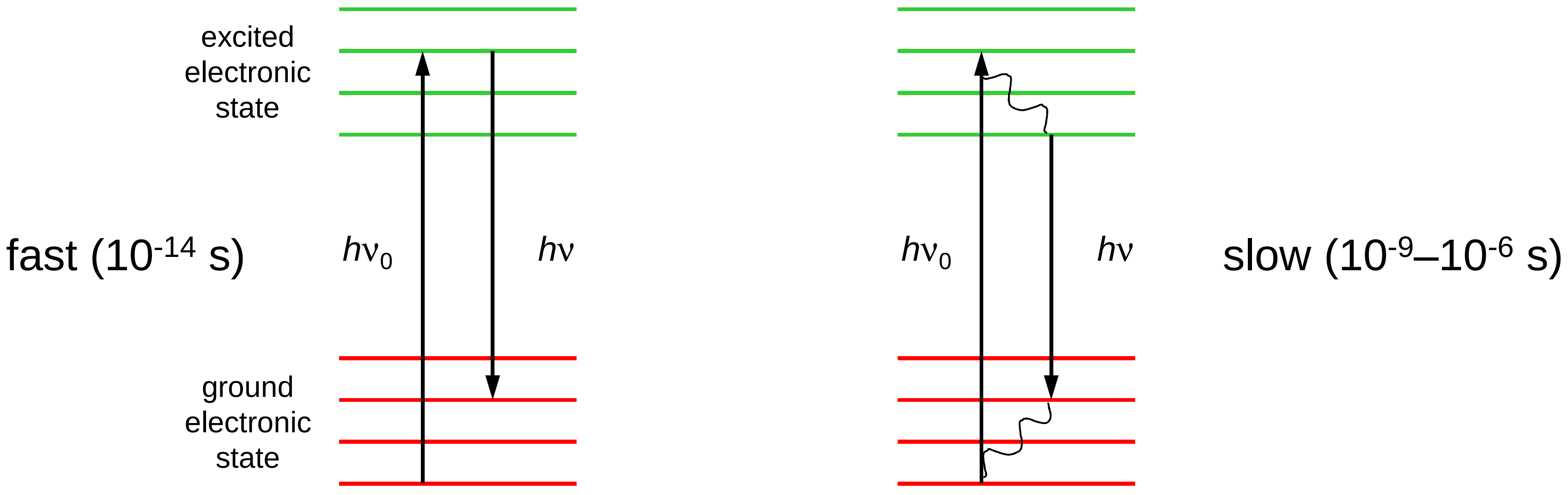
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



Resonance Raman scattering

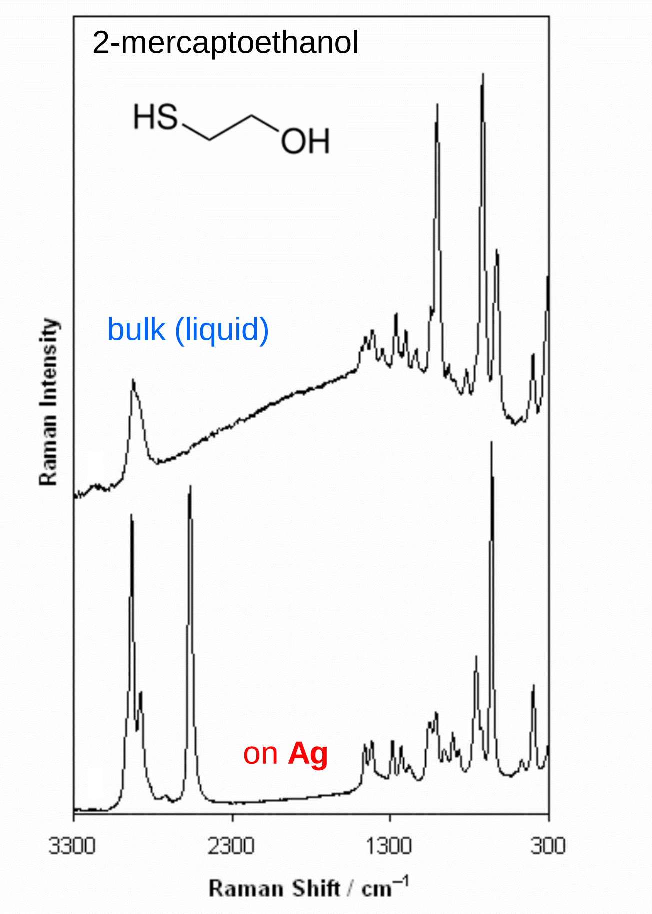
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu
- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

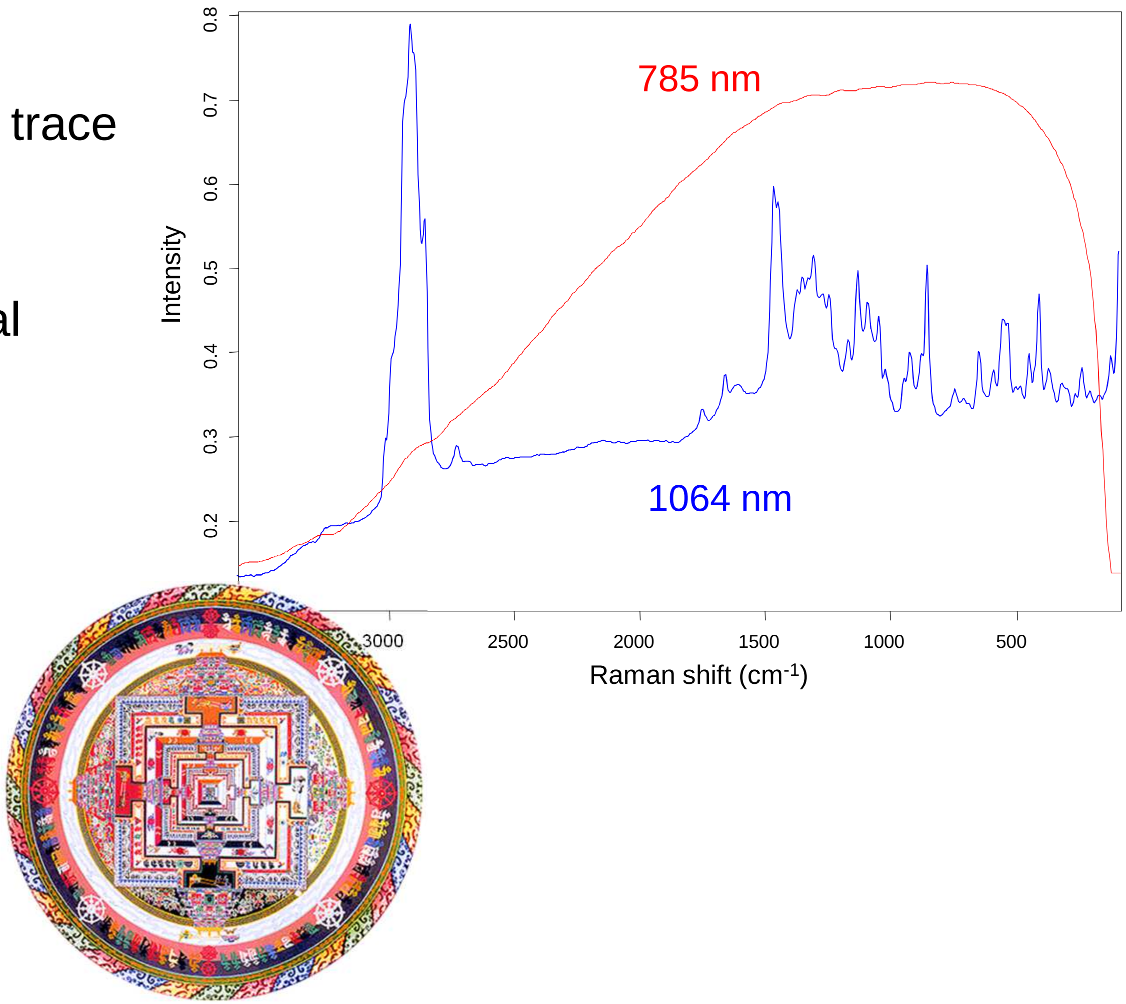
- Remarks:

❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



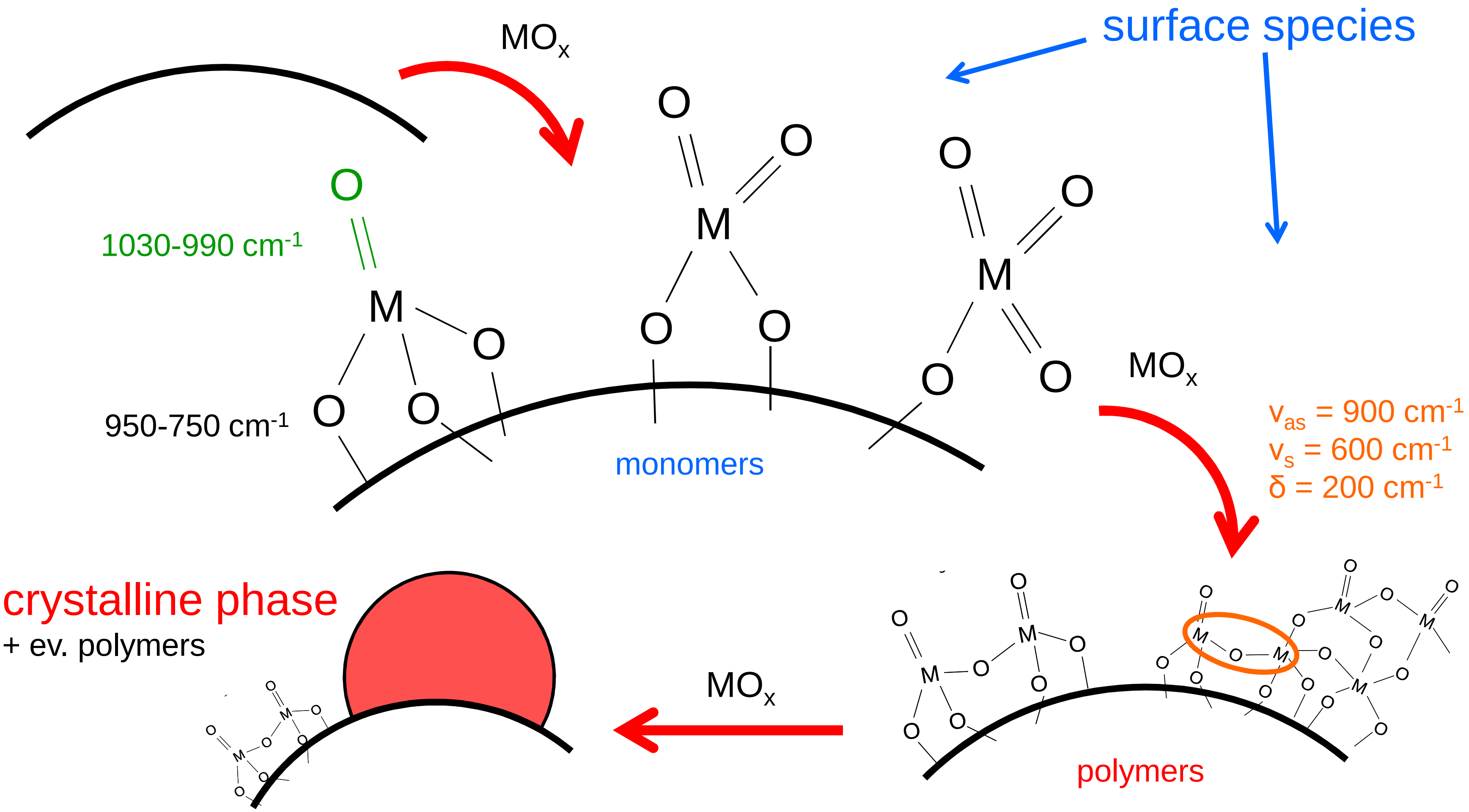
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species

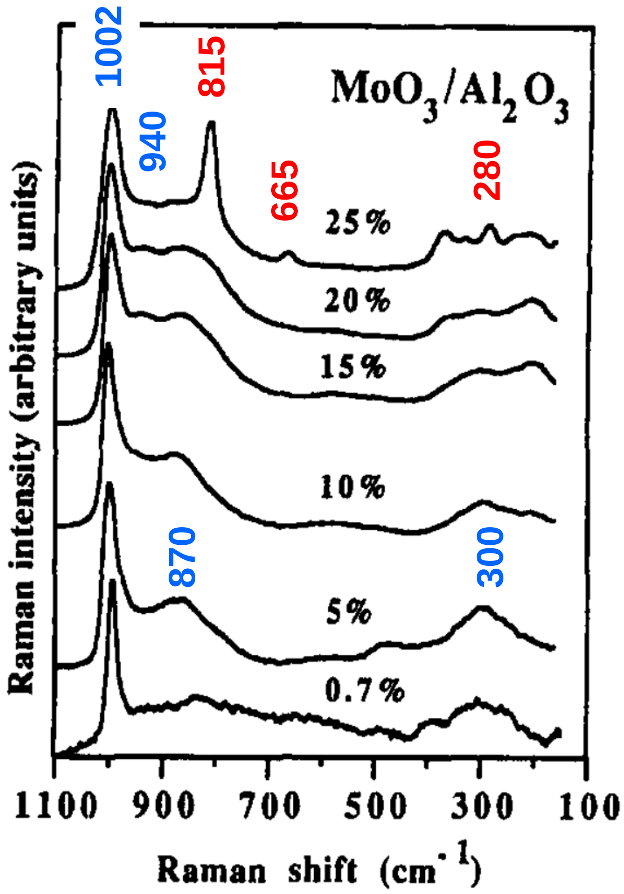


Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



surface MoO_3

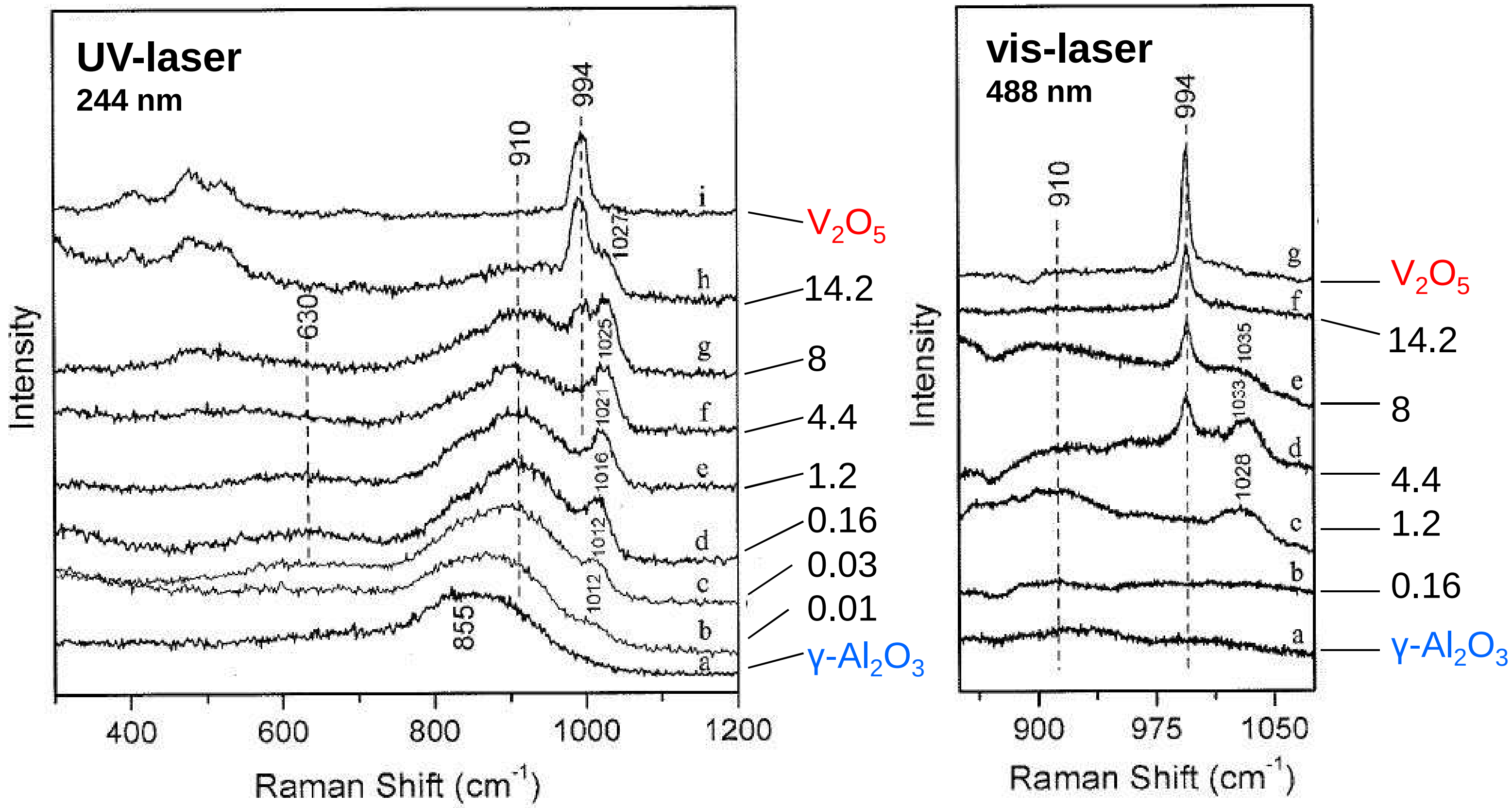
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

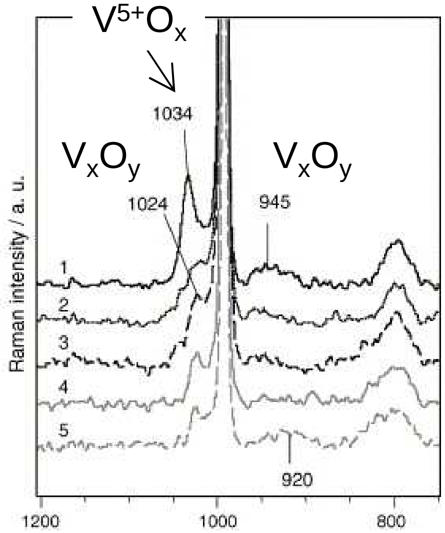
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

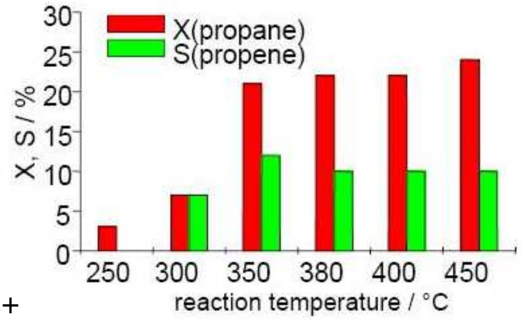
Applications

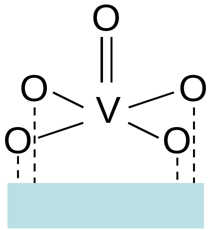
- Reactivity of V/TiO_2 after oxidative treatment

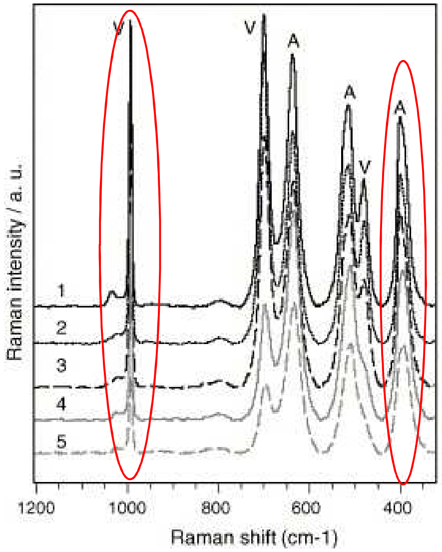


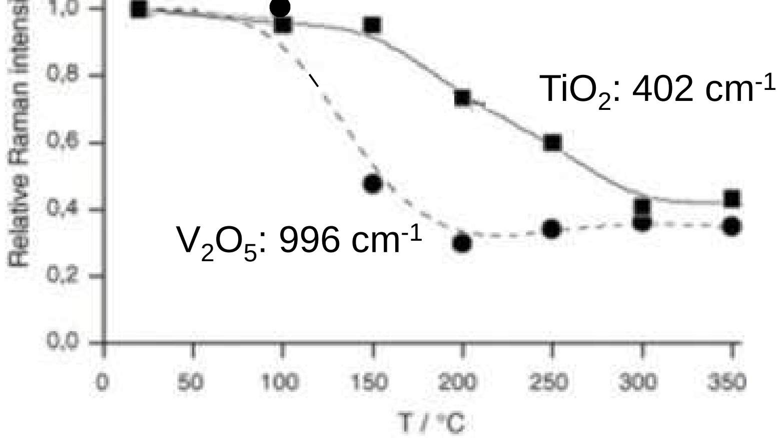
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

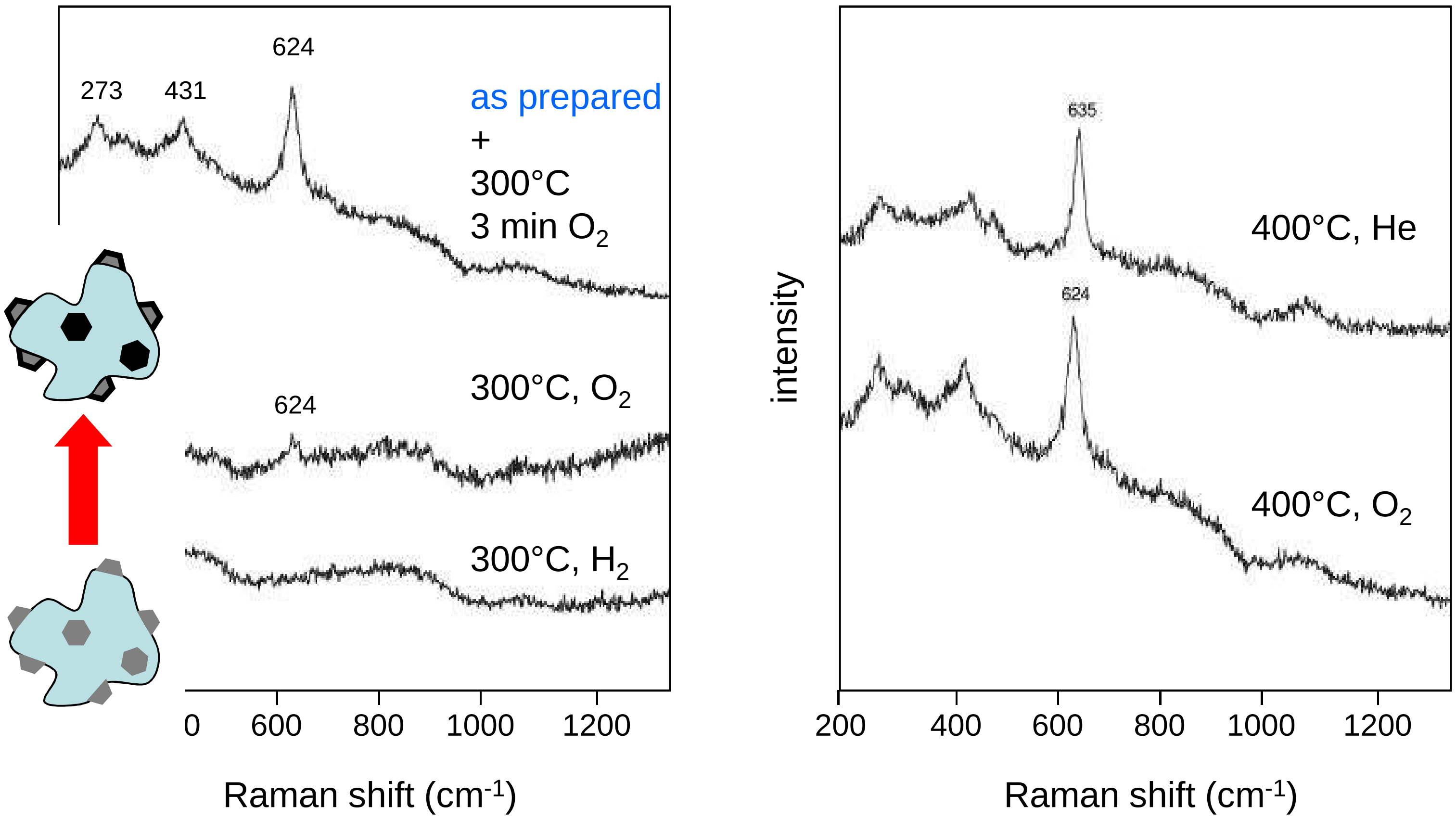
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



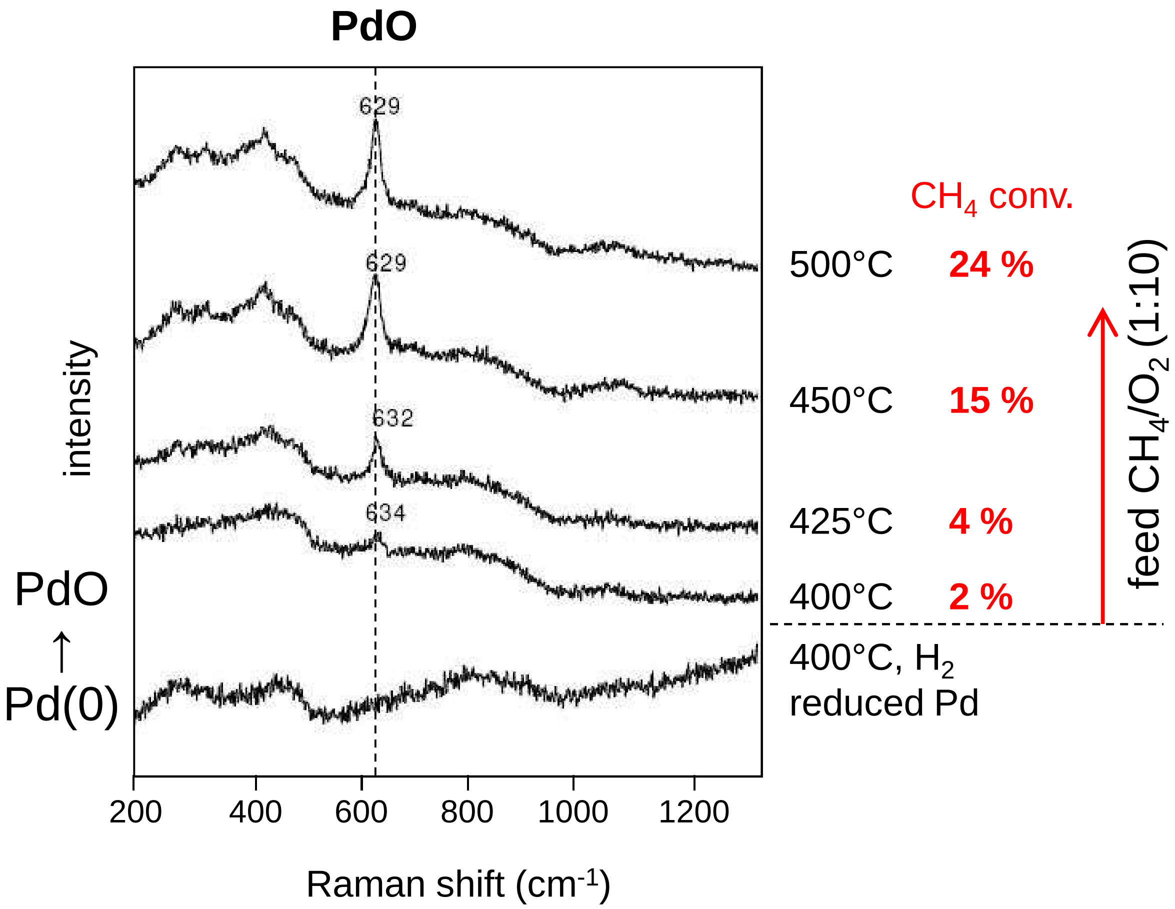
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

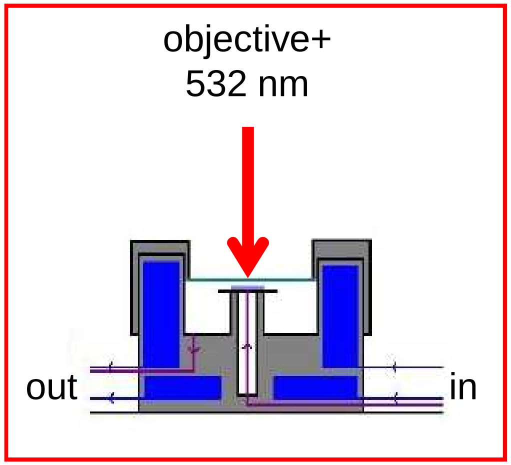
Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



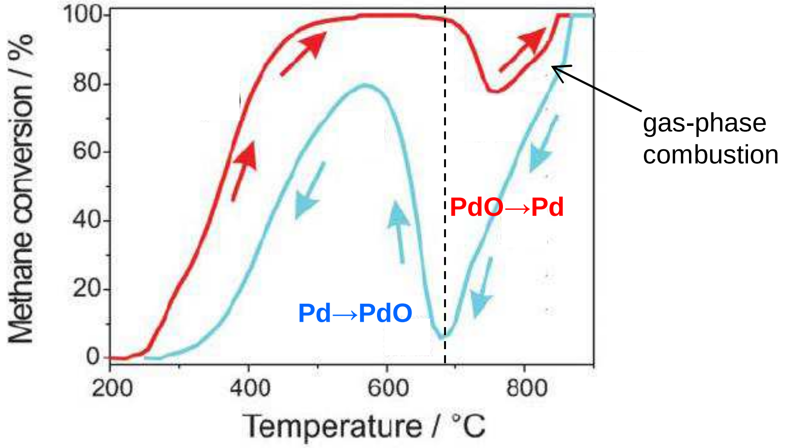
near PdO mode

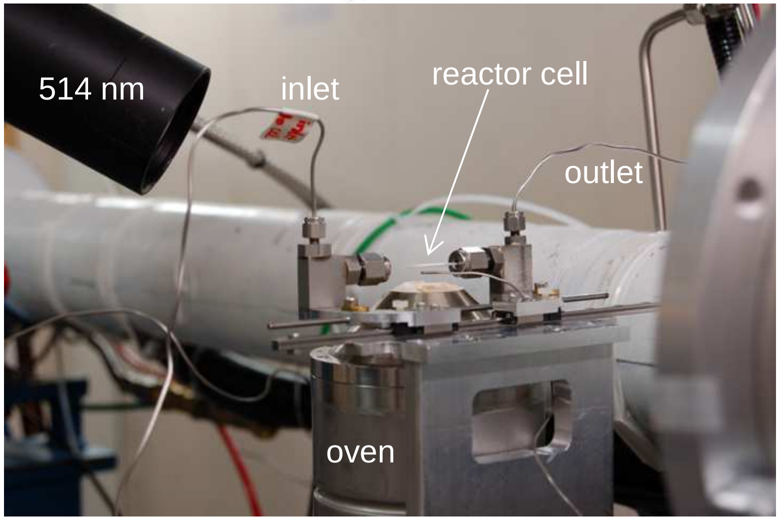


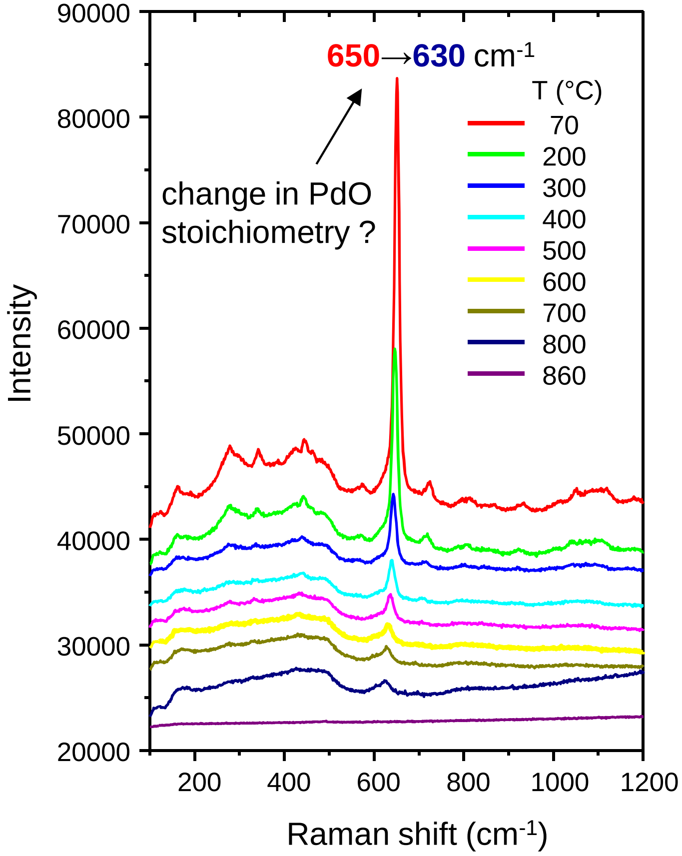
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

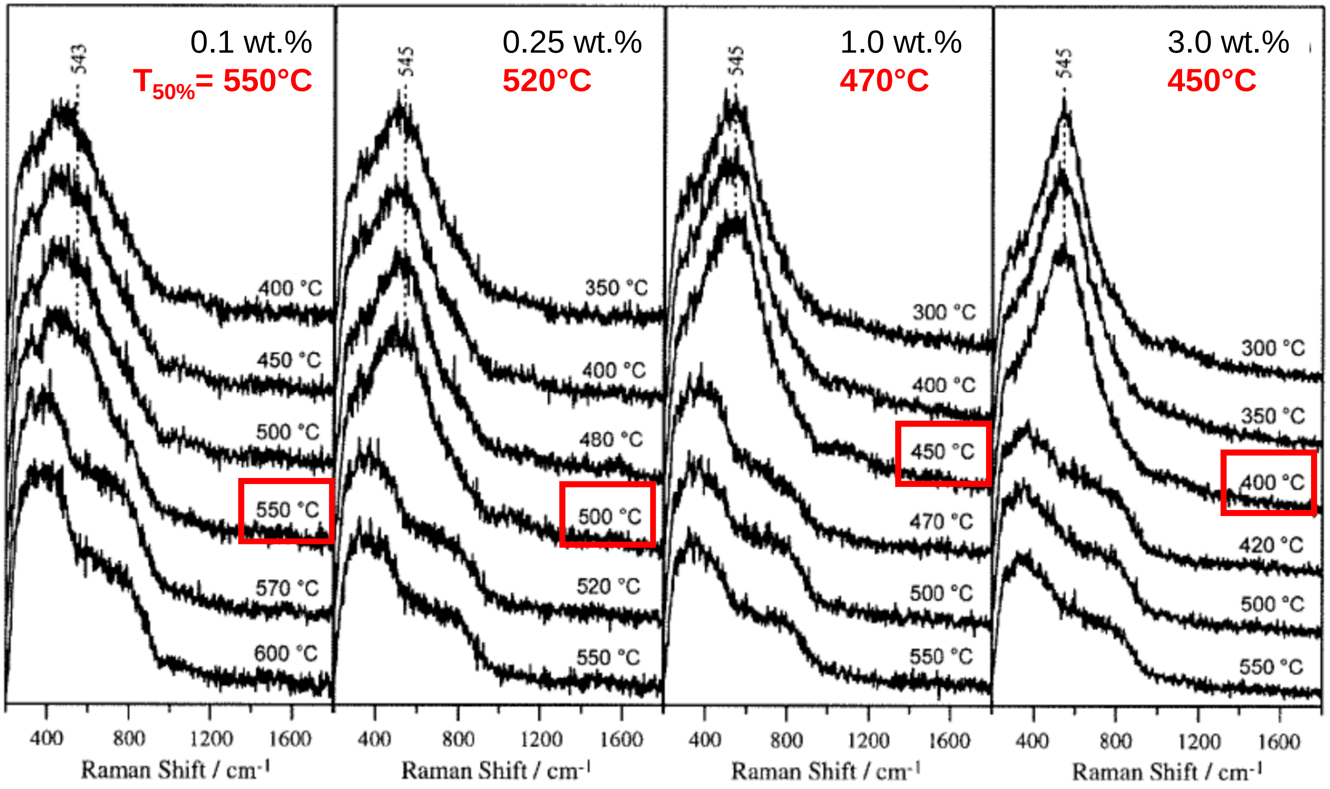
Applications

- Methane partial oxidation over Rh/Al_2O_3

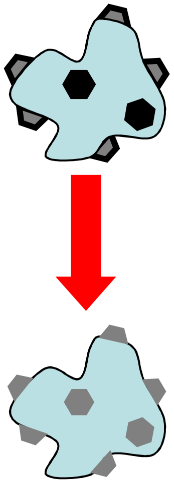
3 mW, 325 nm
$CH_4/O_2/Ar$ = 2/1/45

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content
Activity



RhO_x
↓
Rh(0)



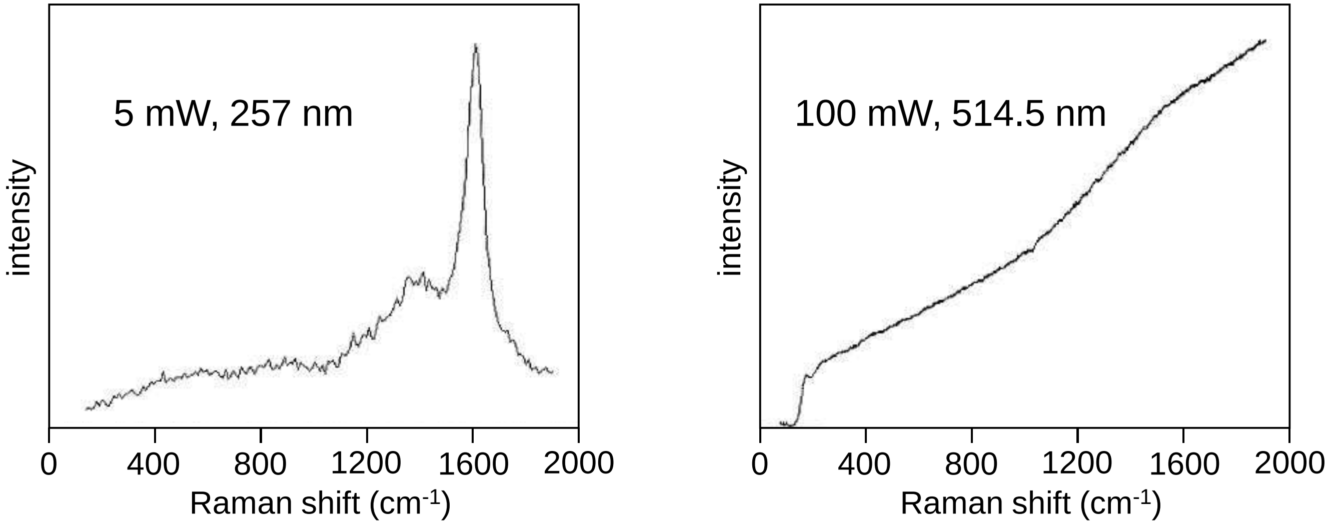
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - ❑ No fluorescence

  (only few molecules fluoresce below 260 nm)

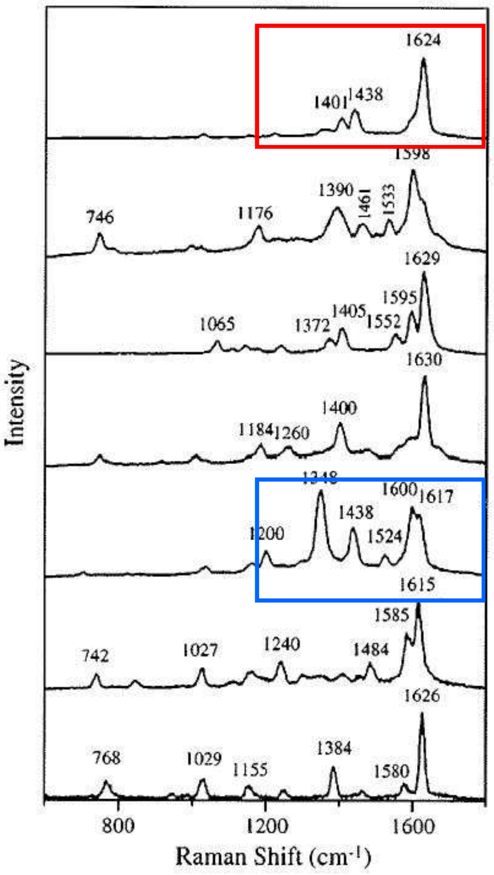
Rh/Al_2O_3, coked 500°C in naphtha

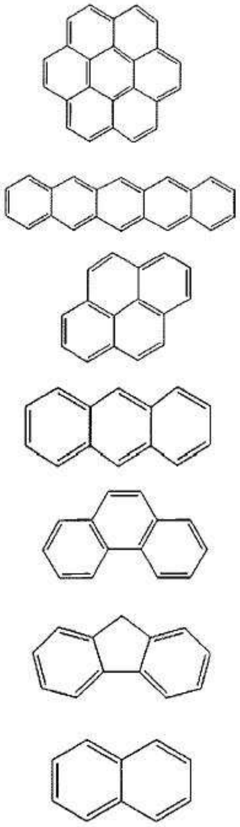


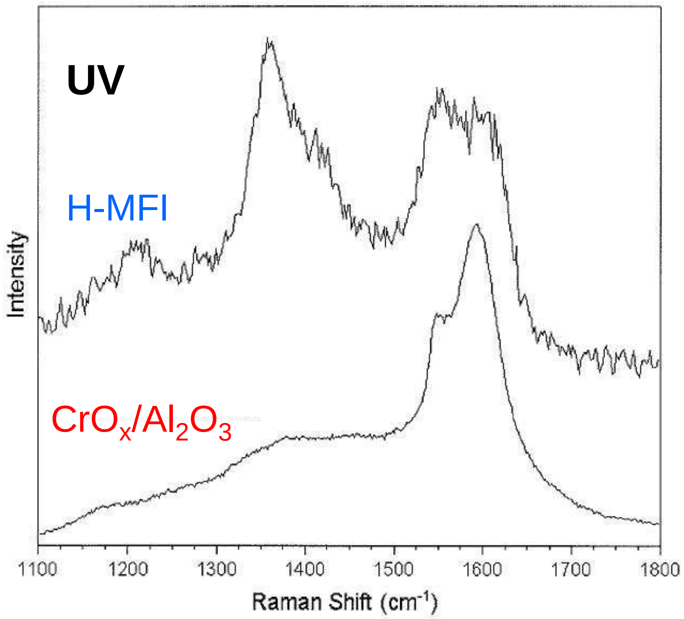
Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization







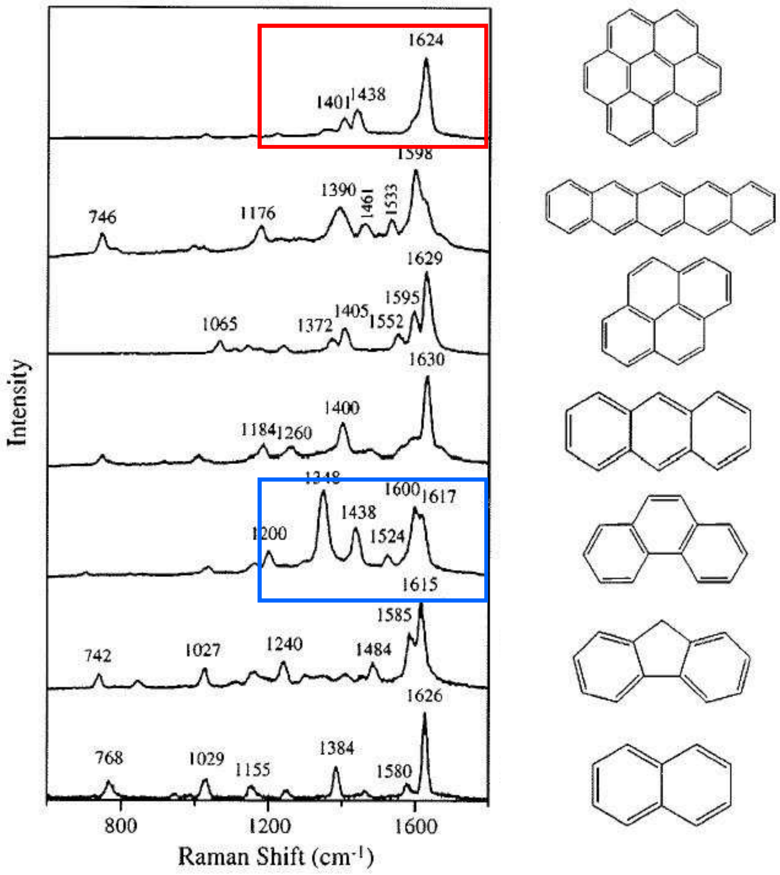
Coke classification
1D topology, chain-like
2D topology, sheet-like

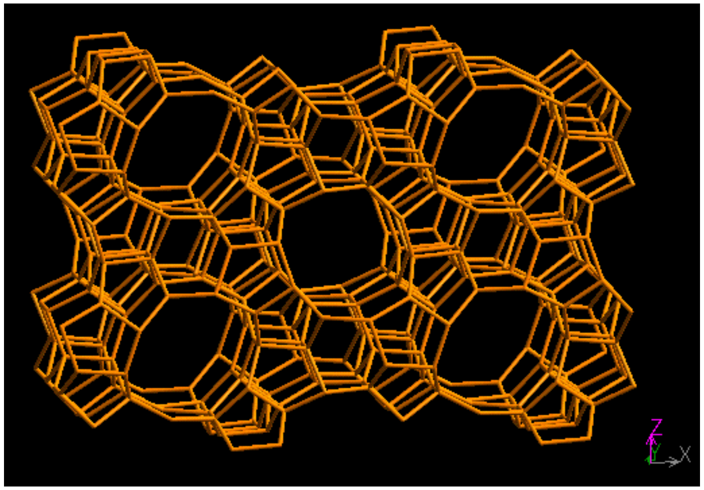
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





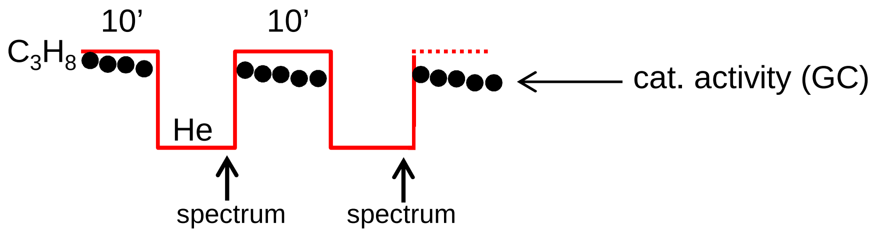
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

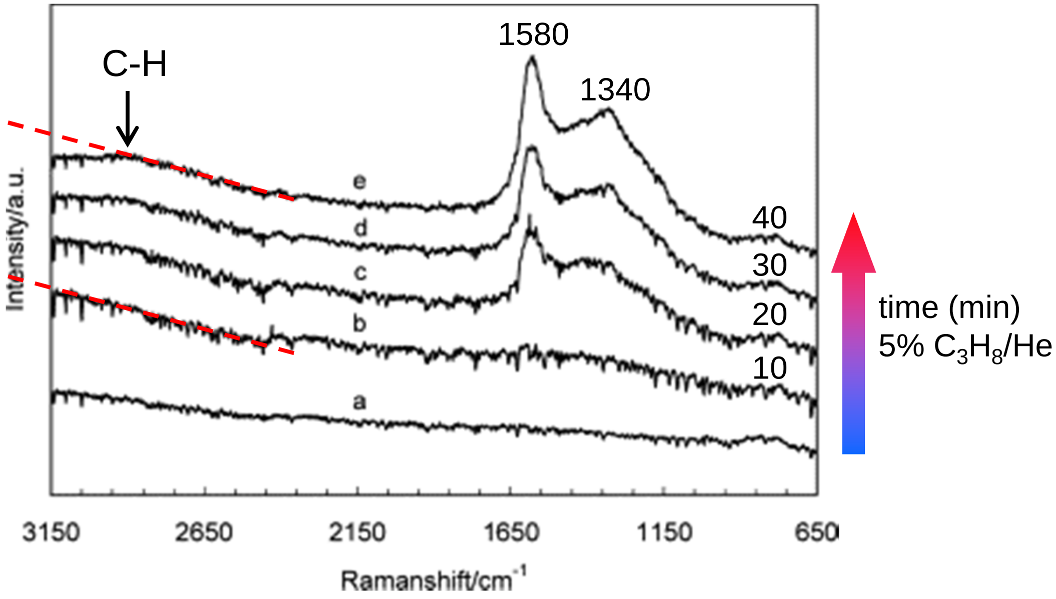
Stair, *Adv. Catal.* **51** (2007) 75

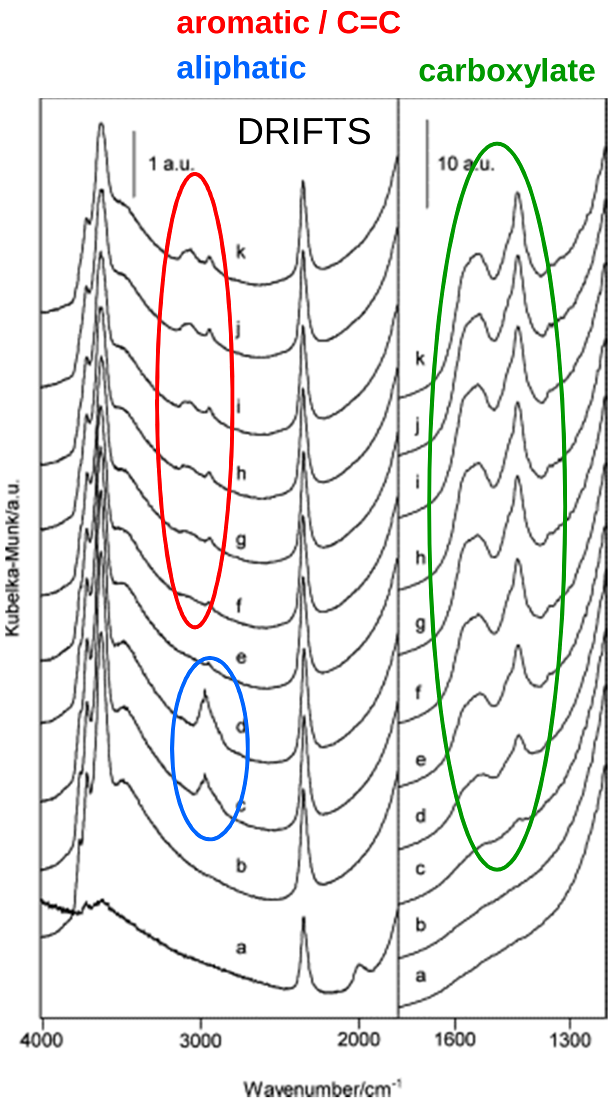
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

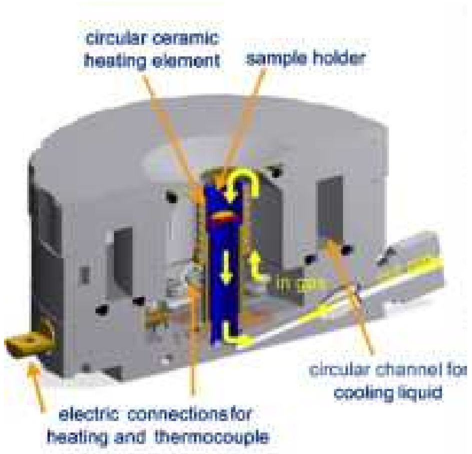


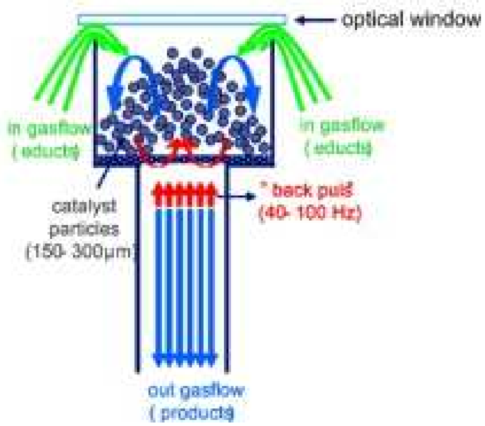


Airaksinen et al., *J. Catal.* **230** (2005) 507

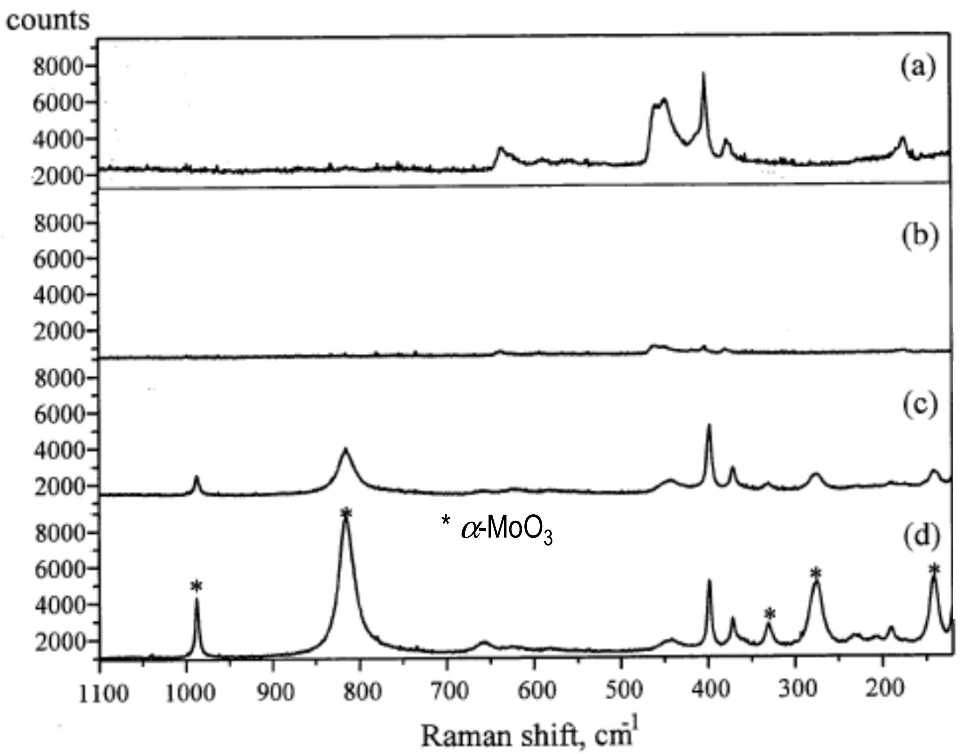
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min
full power, FB

MoS_2, 6 min
1/8 power

MoS_2, 1 min
full power

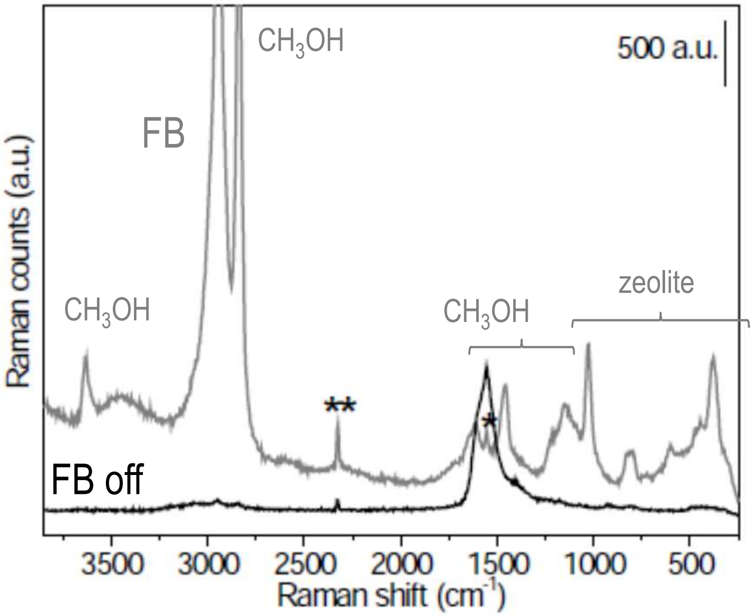
MoS_2, 6 min
full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

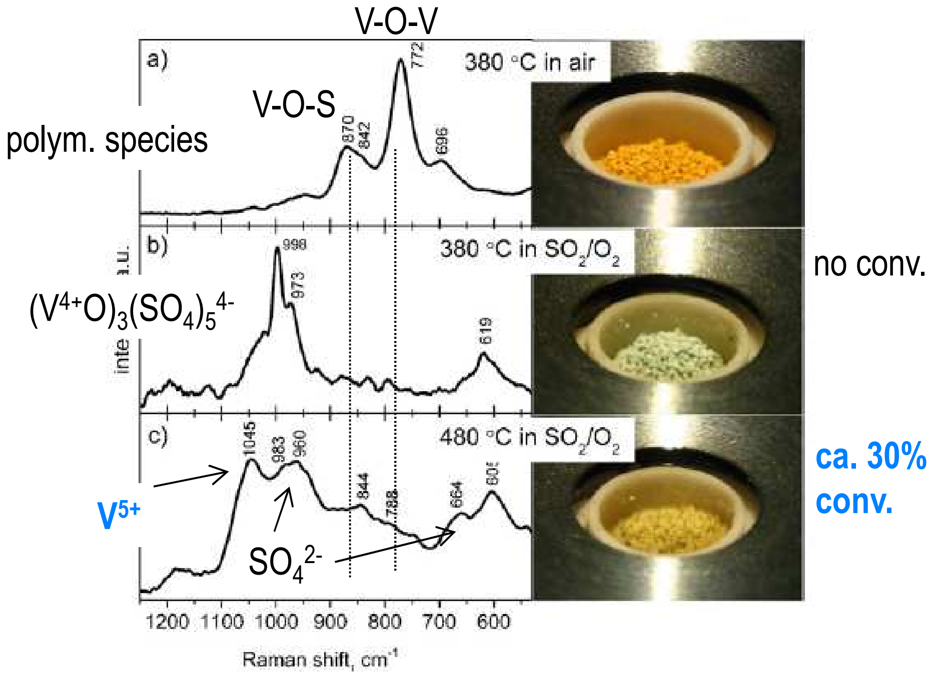
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

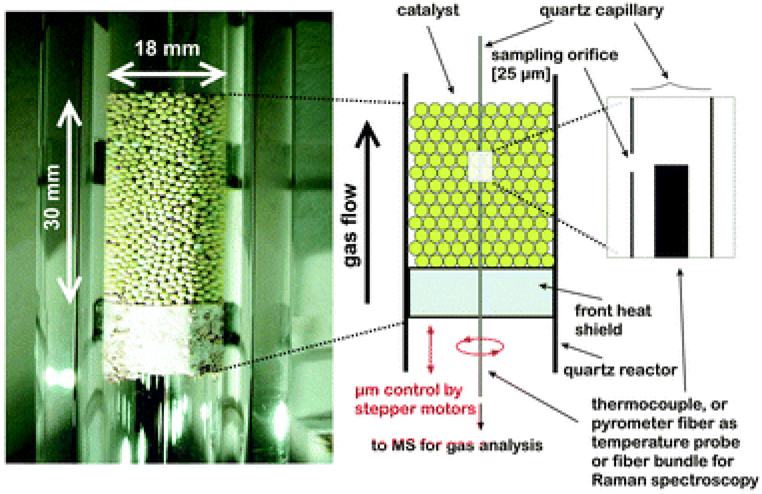


active species: mono- & dimeric V^{5+} oxosulfate species

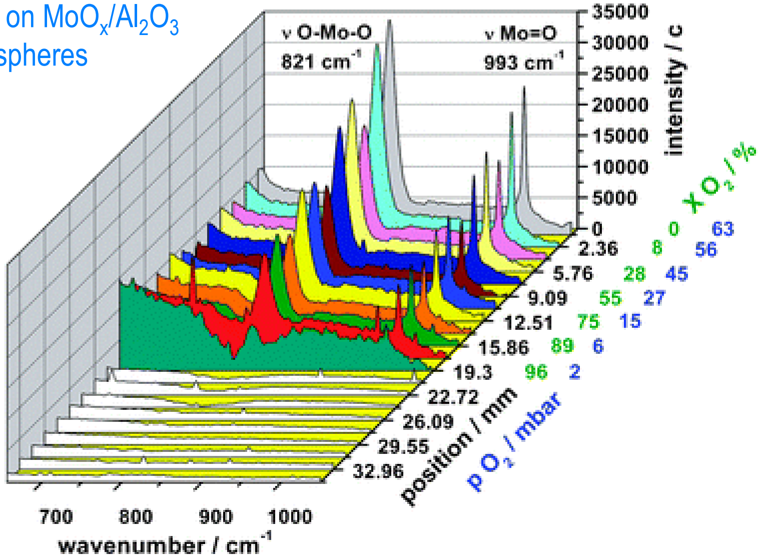
Beato et al., *Catal. Today* 205 (2013) 128

Applications

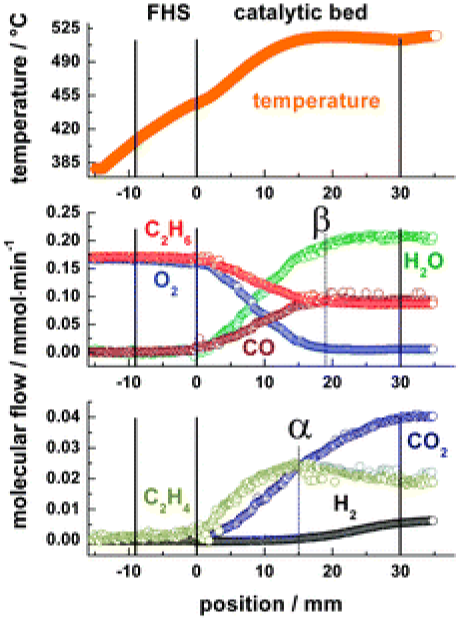
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 "*for his work on the scattering of light and for the discovery of the effect named after him*"

Literature:

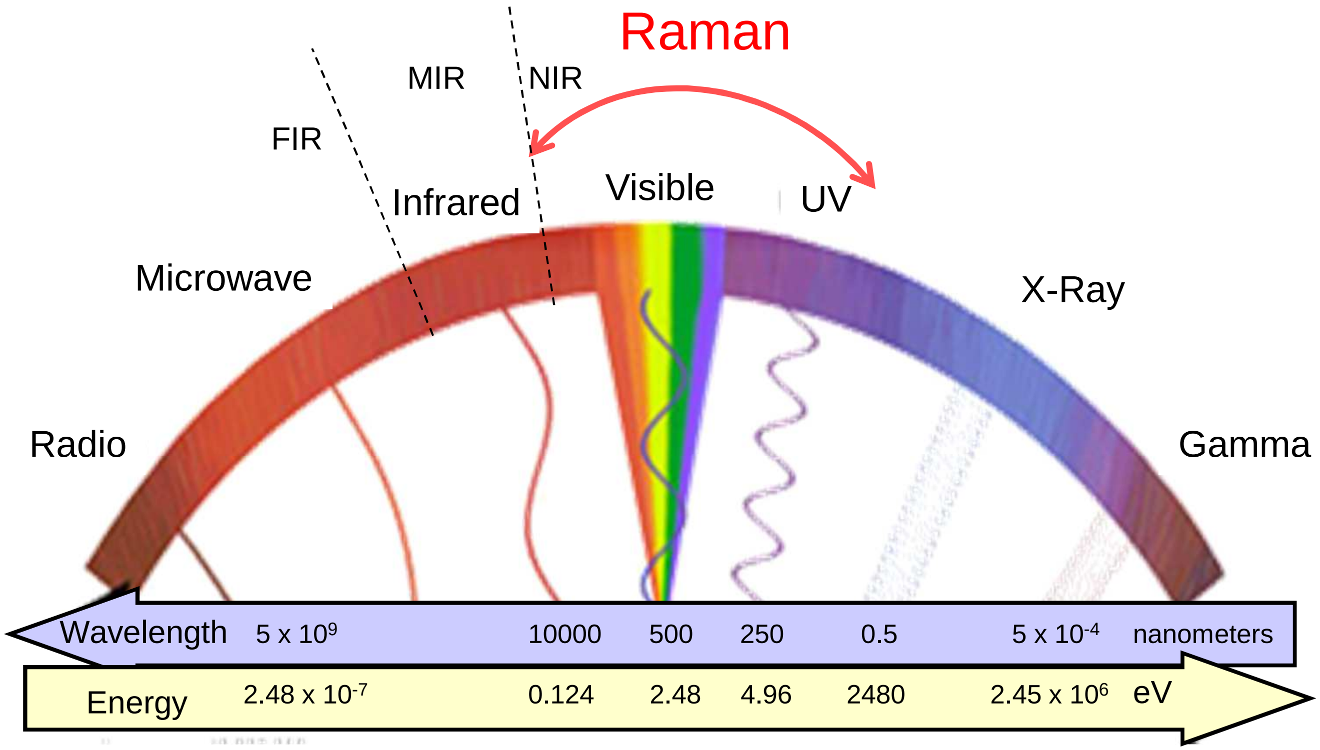
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

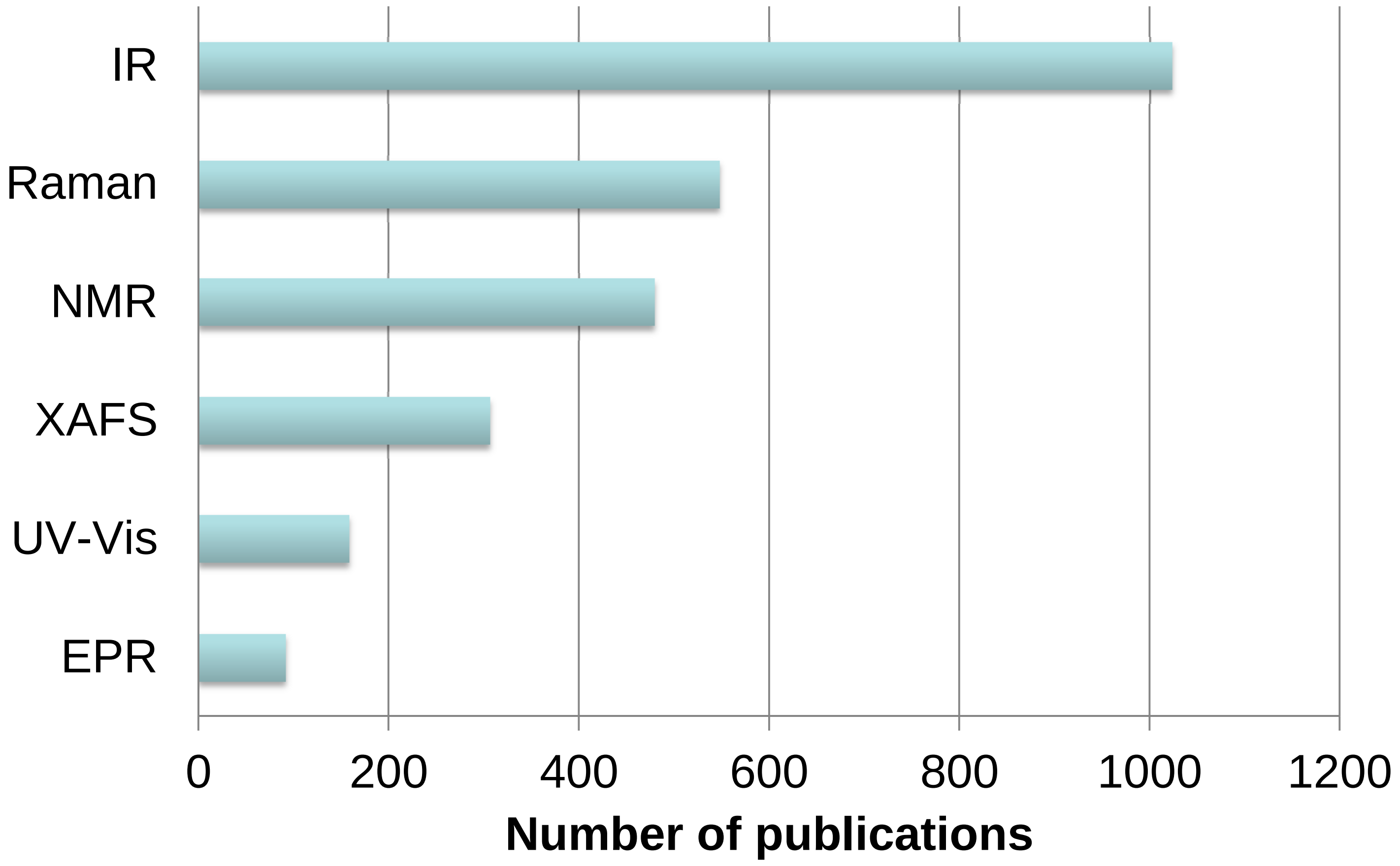
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

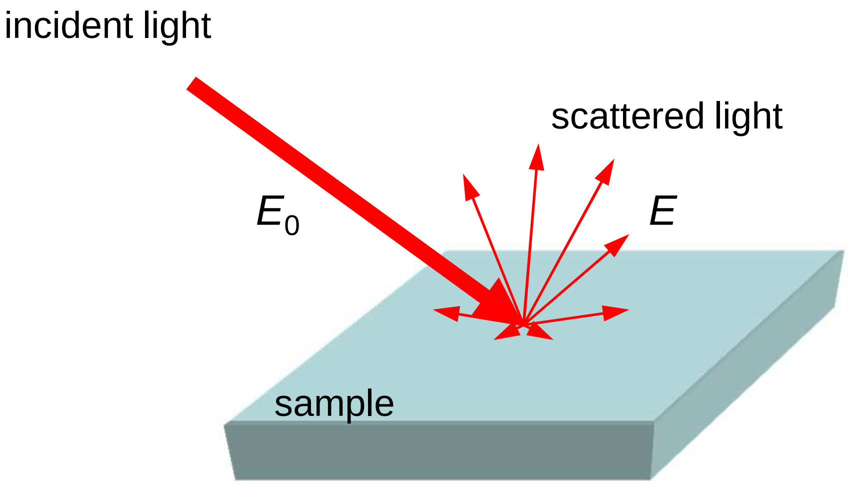


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{\mathrm{vib}} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

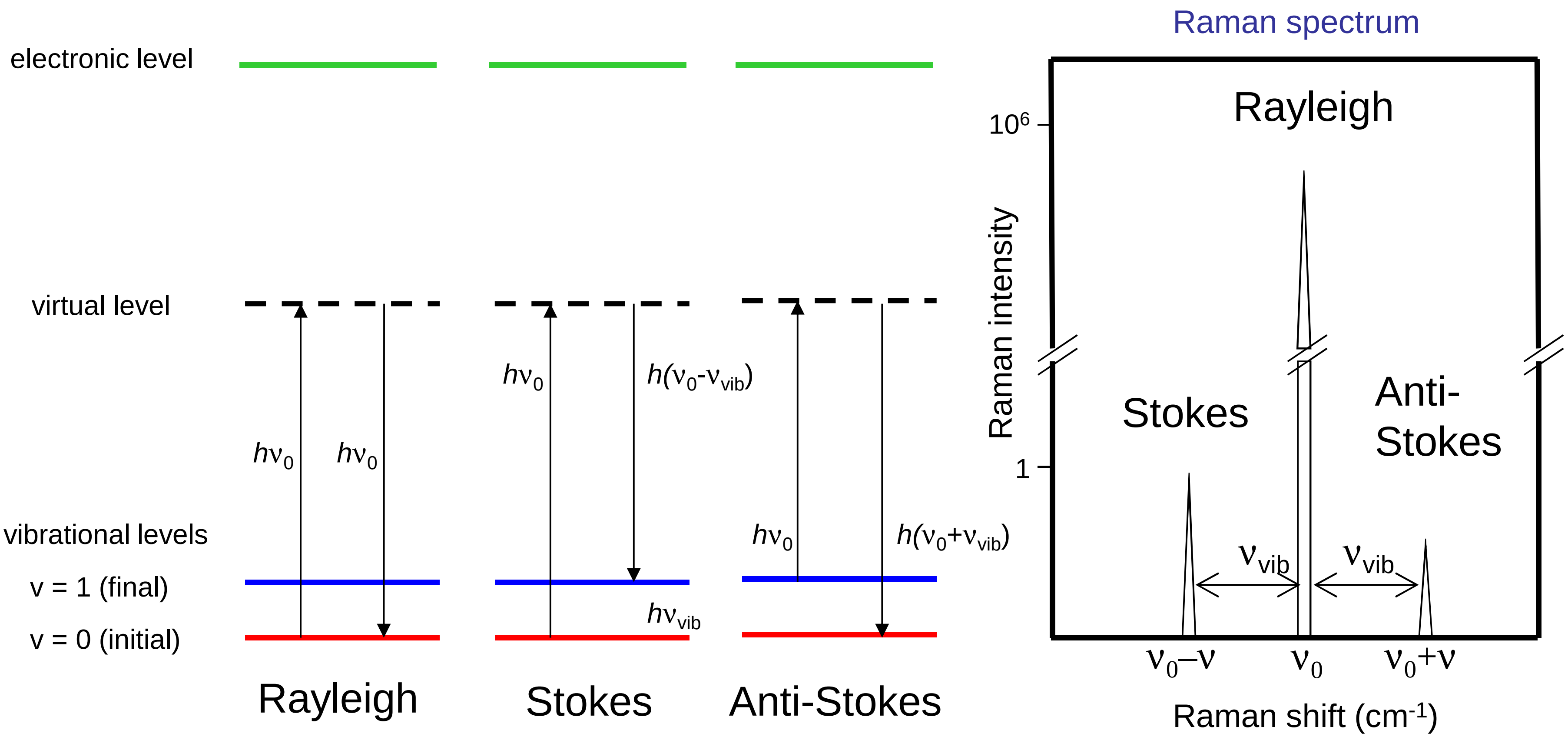
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]}_{\text{Stokes}}\}}$$

$\cos x\cdot\cos y = 1/2\ [\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\ (\text{Anti-Stokes})}{I\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

- 4th power of ν (4th power law)
- 2nd power of $\Delta\alpha$
  - properties of molecules
  - strength of bonds

↓

covalent bond STRONG bands (catalysis!)

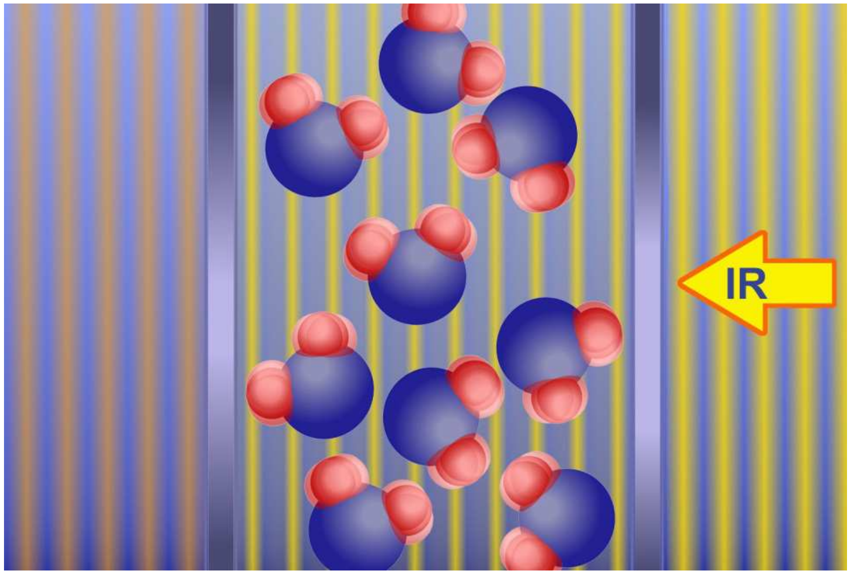
ionic bond WEAK bands

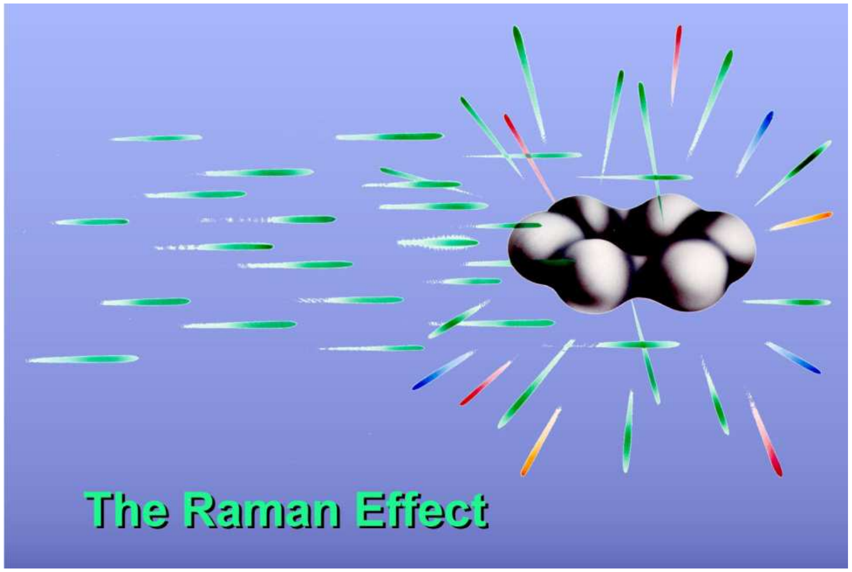
- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

Raman *vs.* Infrared

Infrared

Raman





Absorption of IR light

Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial\mu}{\partial Q}\right)^2 \neq 0$$

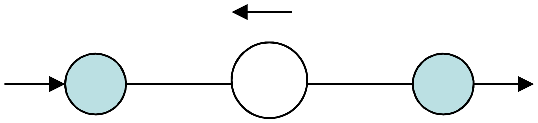
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial\alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - ❑ large electron clouds
  - ❑ not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

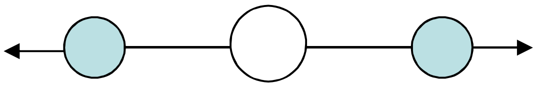
Raman *vs.* Infrared

CO_2



ν_{as}

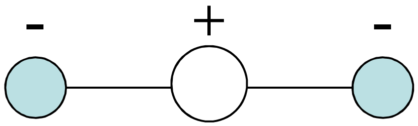
2349 cm^{-1}



ν_s

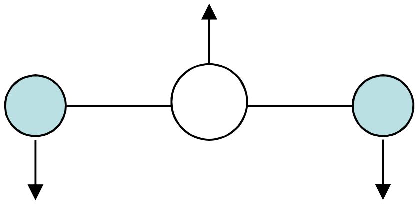
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



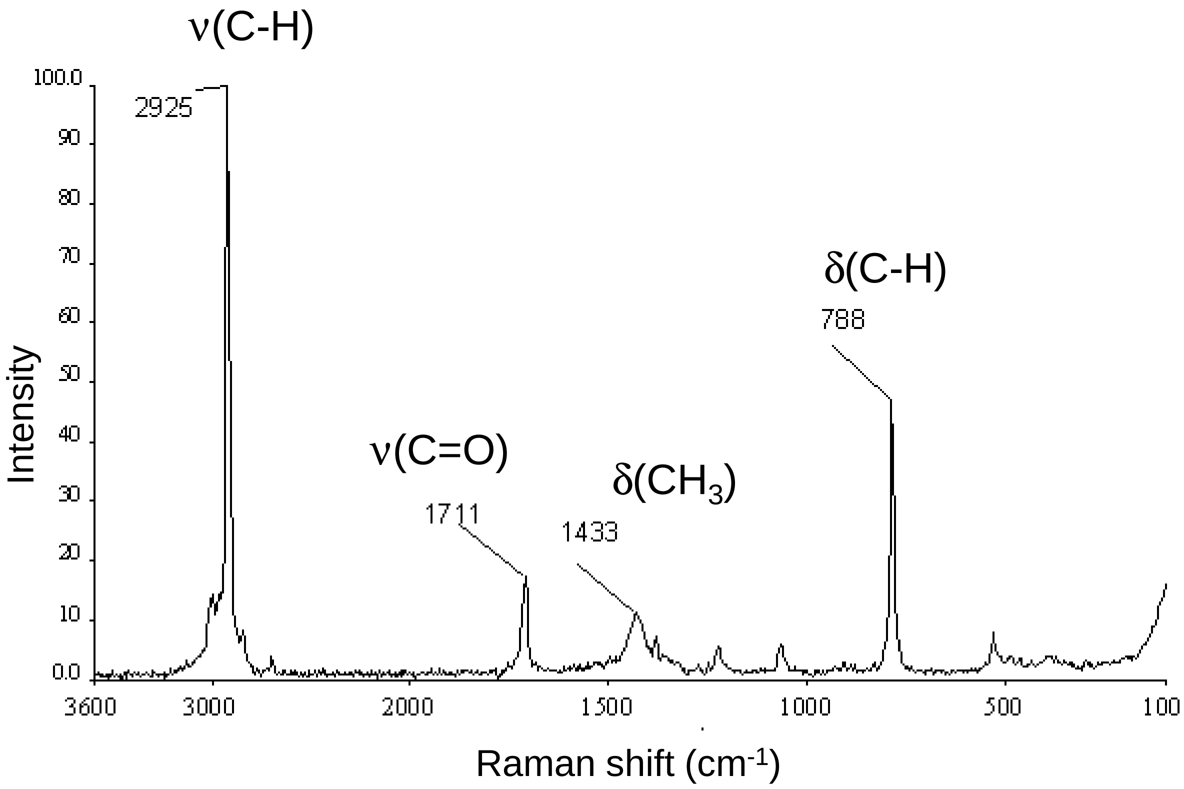
δ

667 cm^{-1}

degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared

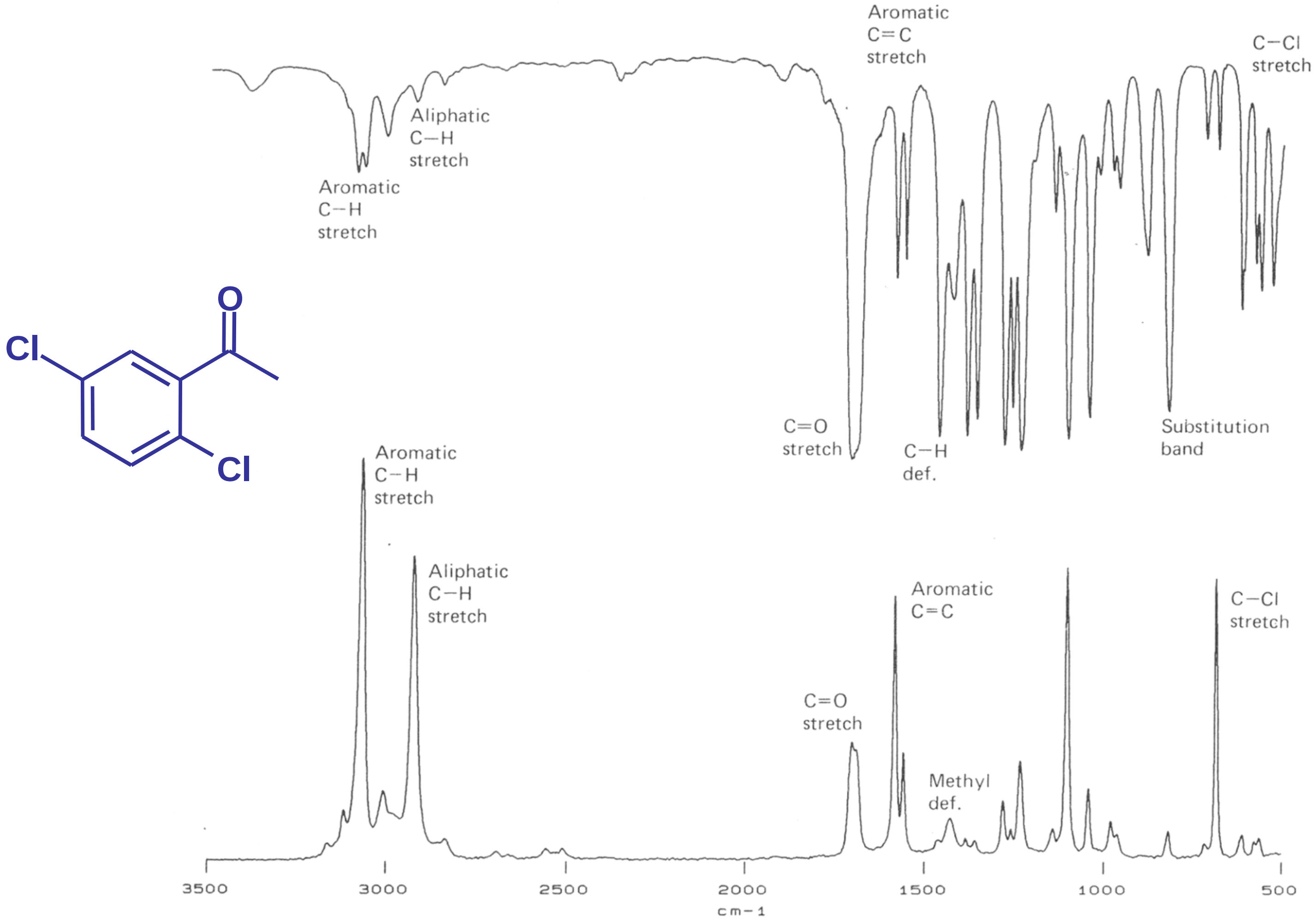


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

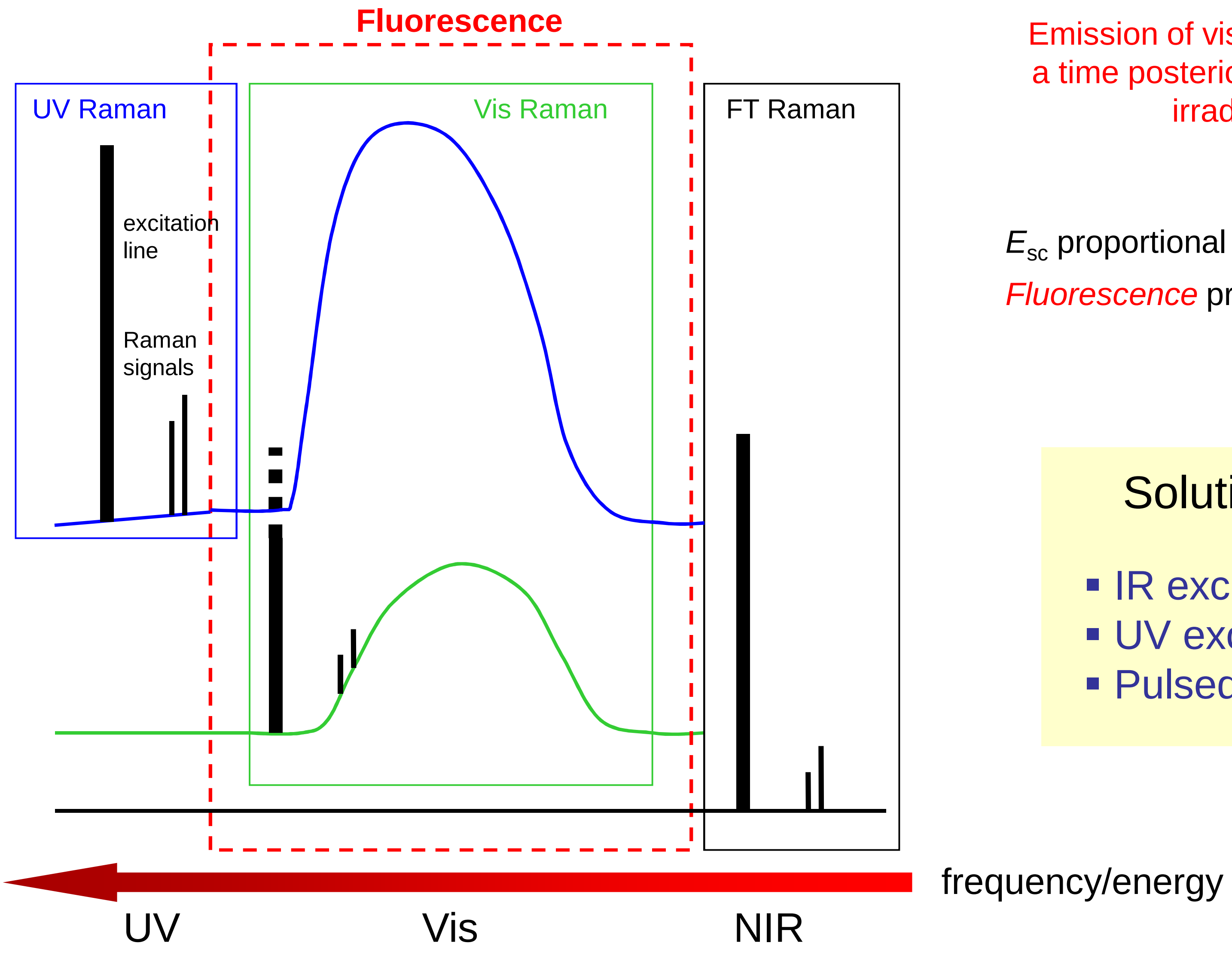
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 μm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during
a time posterior to the sample
irradiation

E_{sc} proportional to ν^4

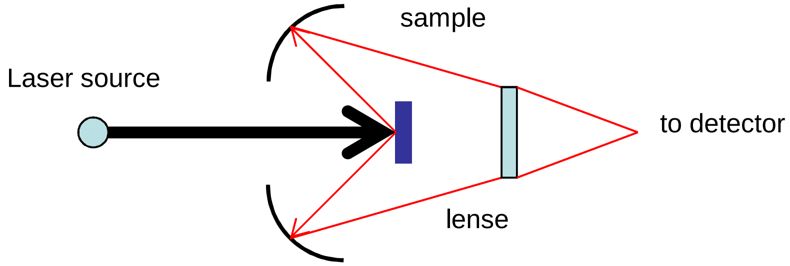
Fluorescence proportional to ν

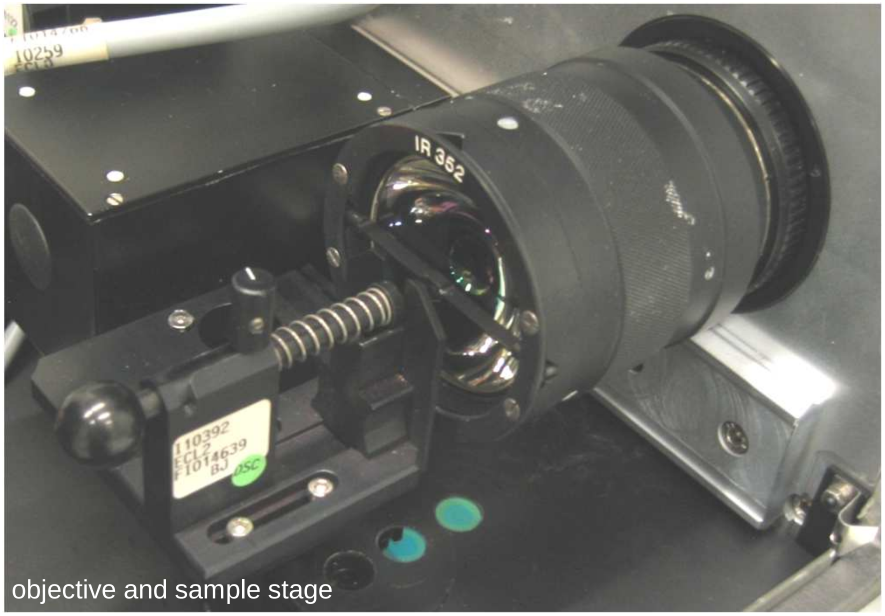
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation




objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

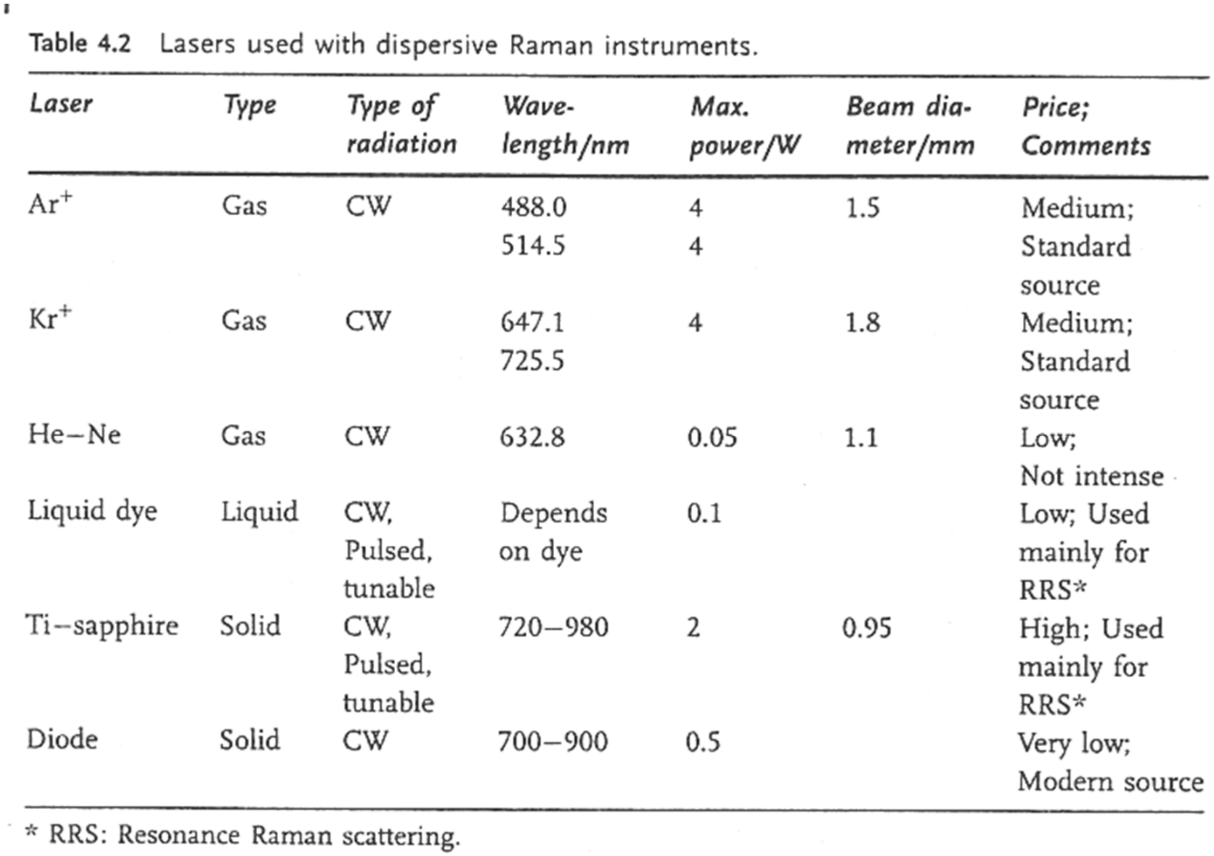


Table 4.2 Lasers used with dispersive Raman instruments.

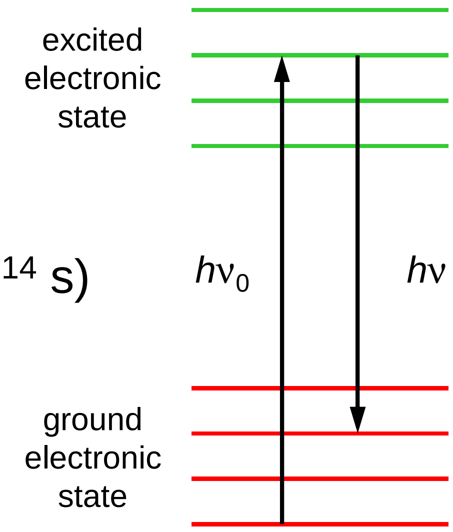
Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

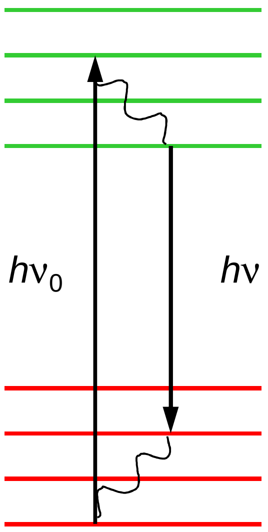
Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited

fast (10^{-14} s)



Resonance Raman scattering



Fluorescence

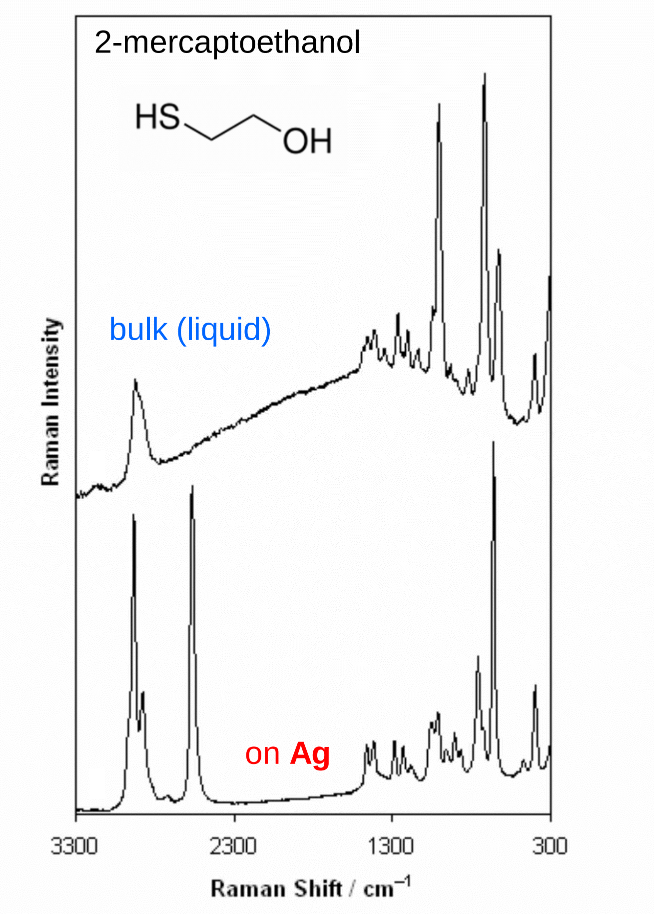
slow (10^{-9}–10^{-6} s)

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

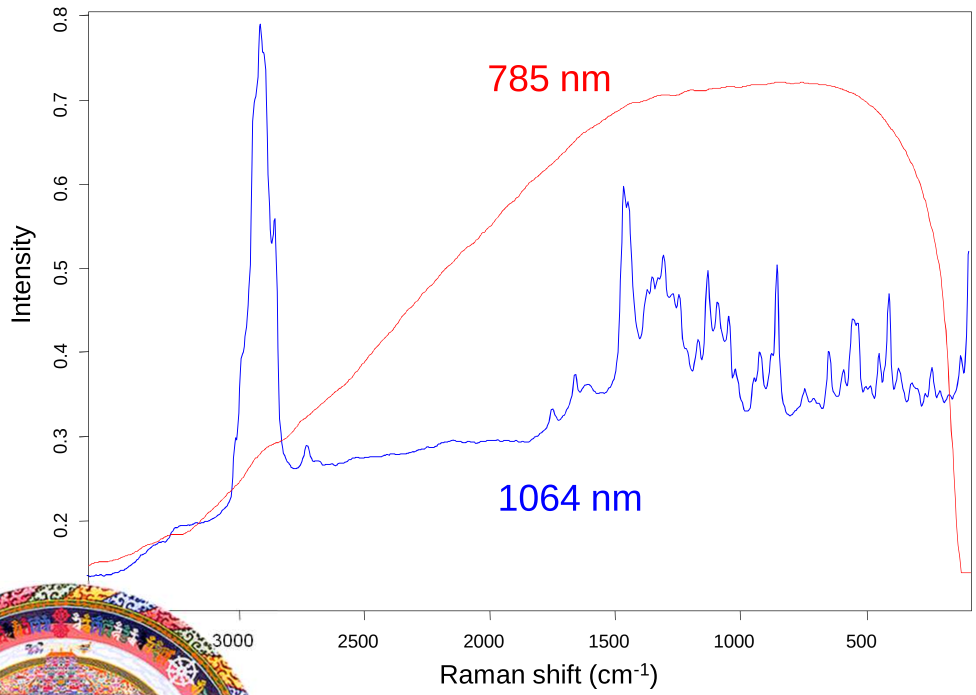
- Remarks:

  - rough surface; nanoparticles (10–100 nm) or kinks, steps etc. (E always perpendicular to surface, locally)
  - vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



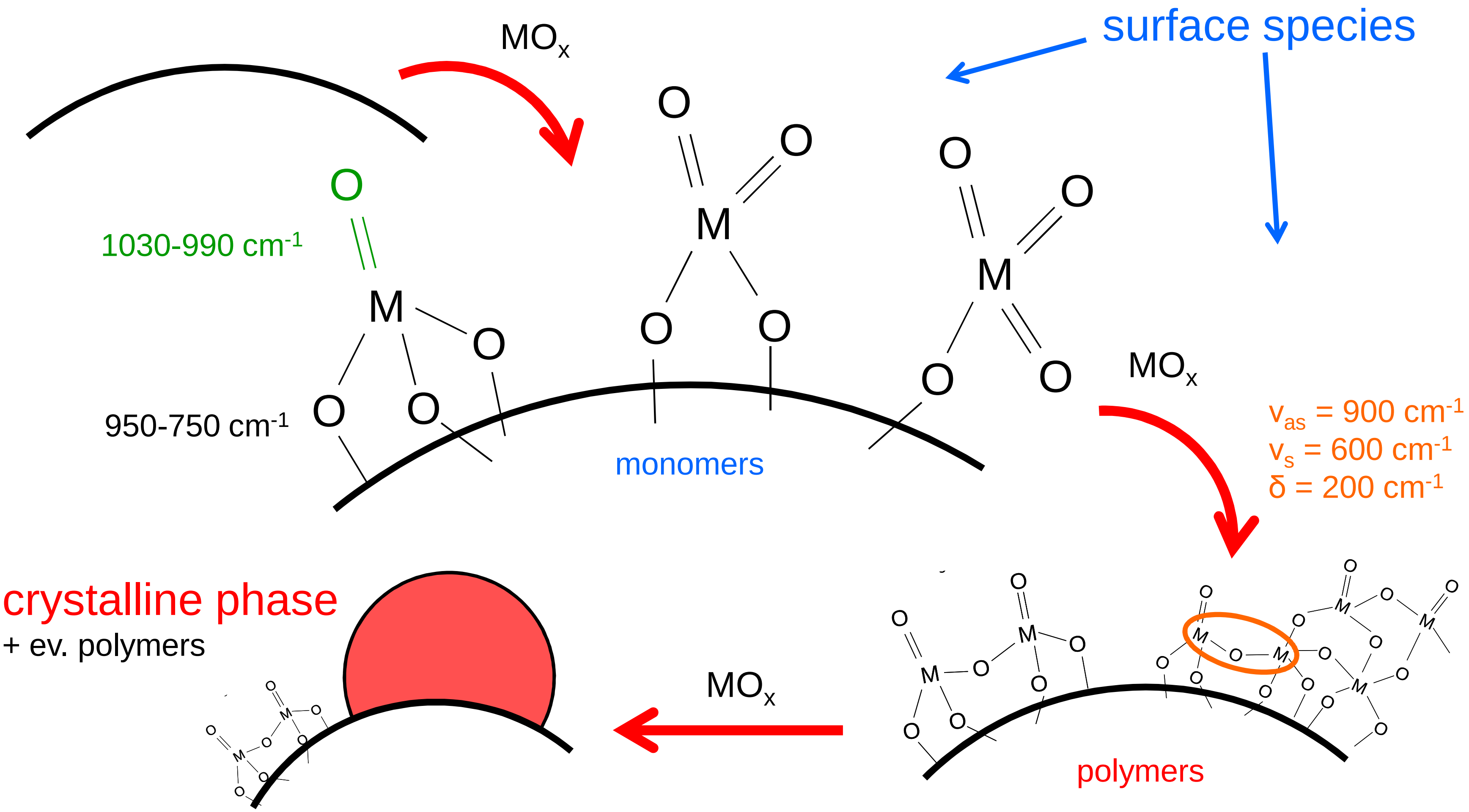
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



surface species

MO_x

1030-990 cm^{-1}

950-750 cm^{-1}

monomers

MO_x

ν_{as} = 900 cm^{-1}
ν_s = 600 cm^{-1}
δ = 200 cm^{-1}

polymers

MO_x

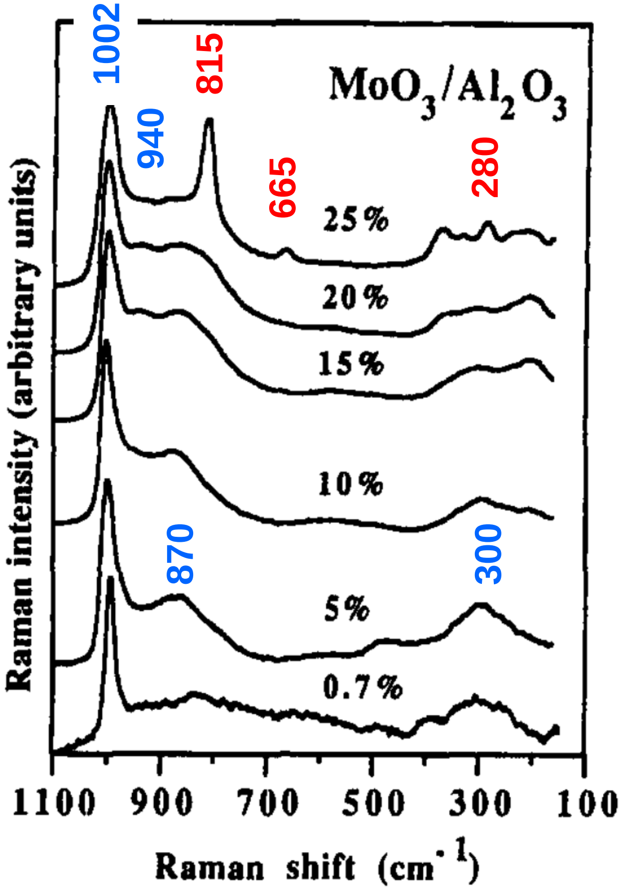
crystalline phase
+ ev. polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



surface MoO_3

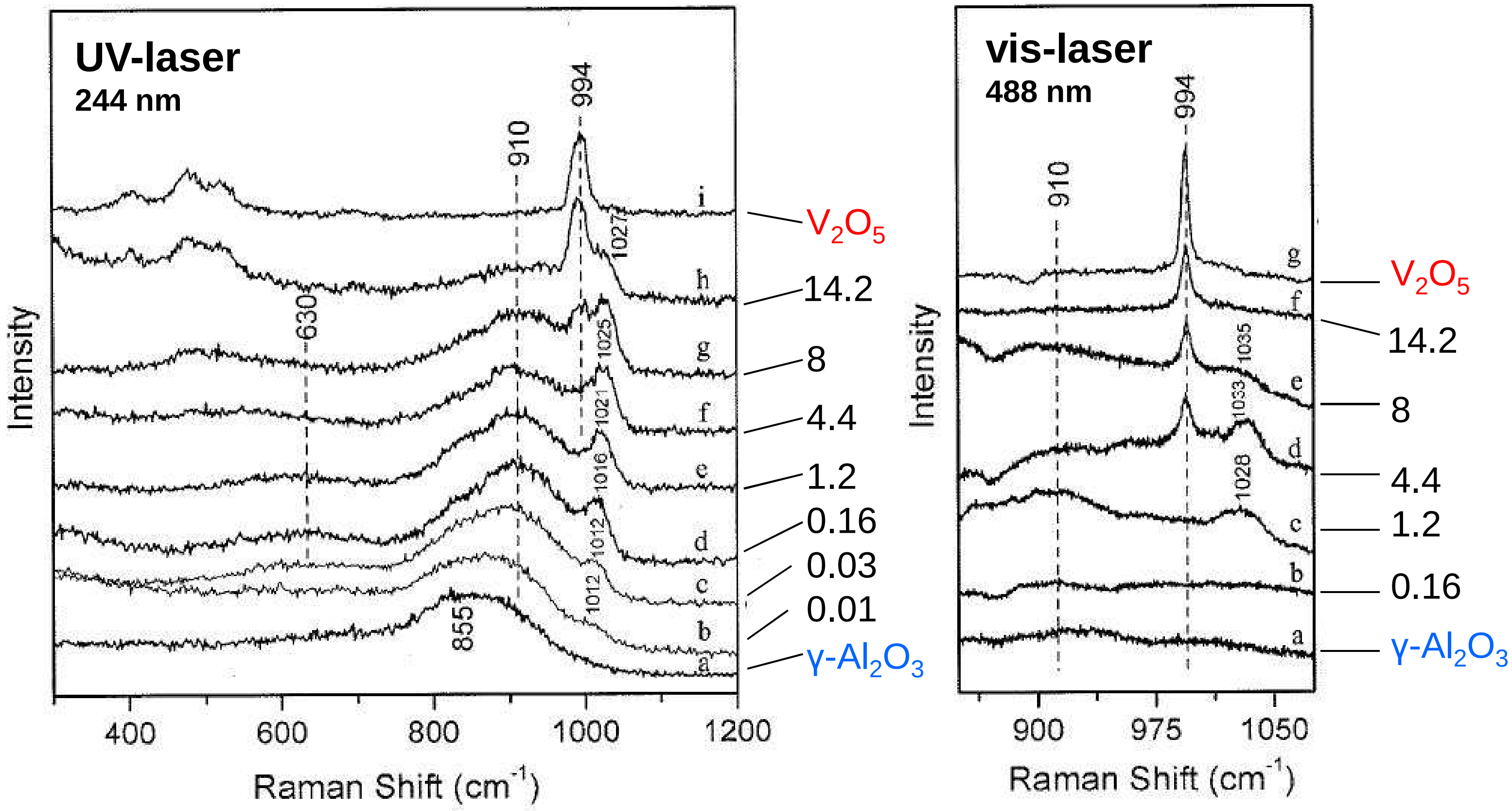
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

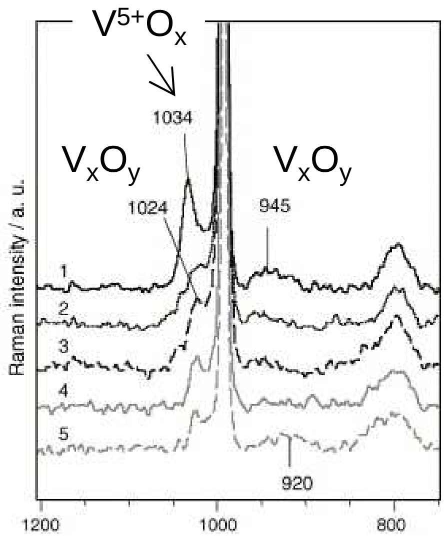
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

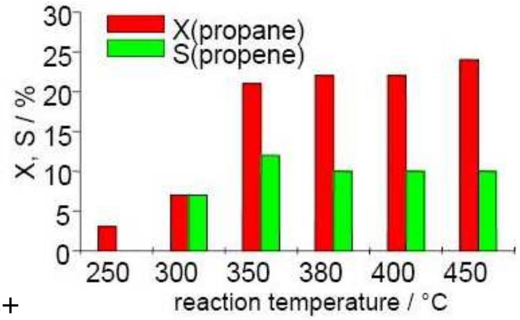
Applications

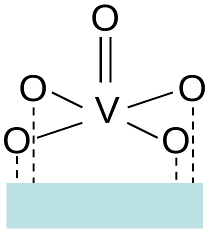
- Reactivity of V/TiO_2 after oxidative treatment

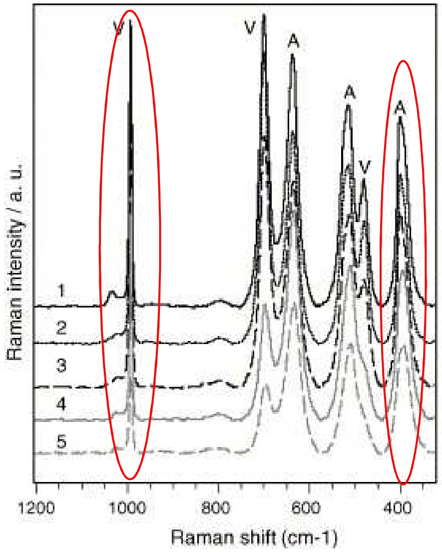


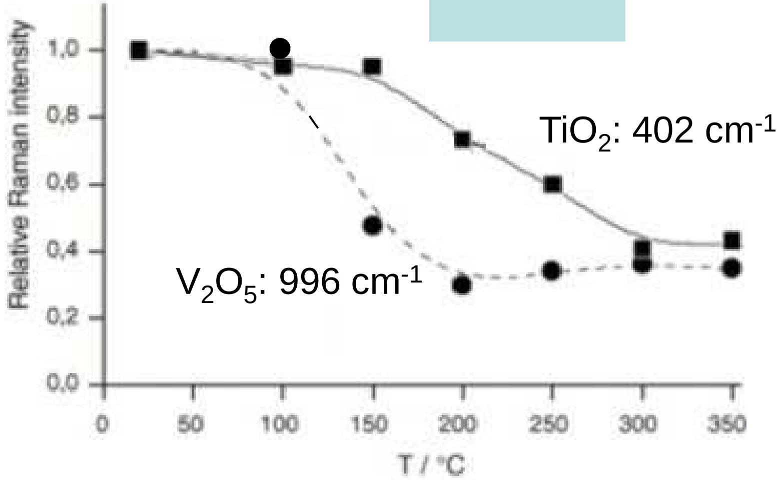
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

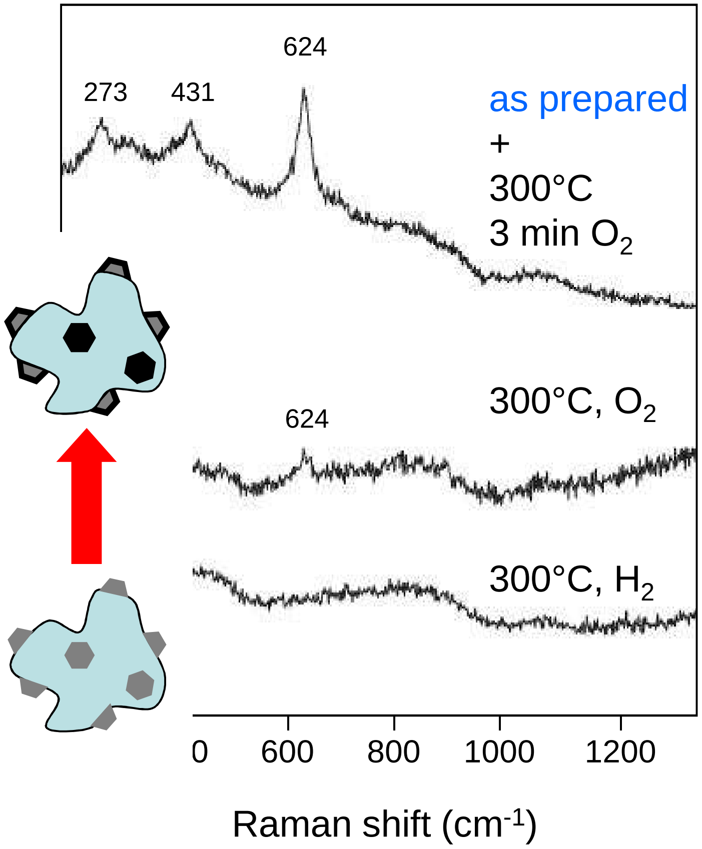
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

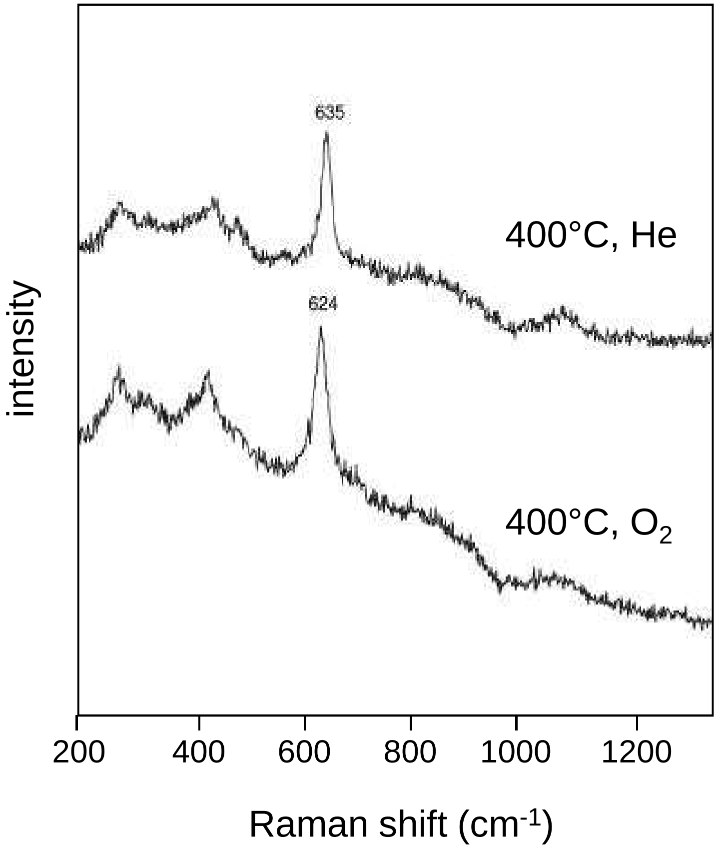
Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



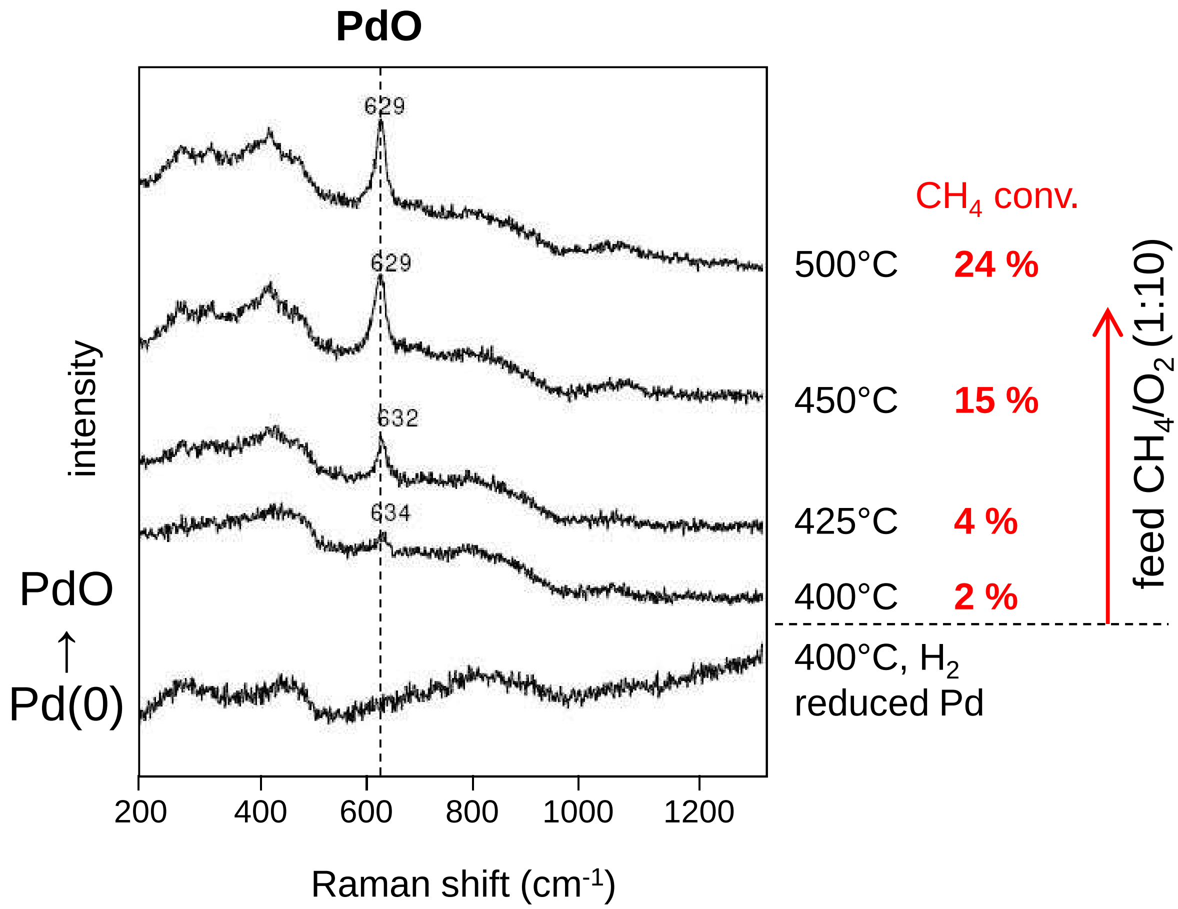


2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

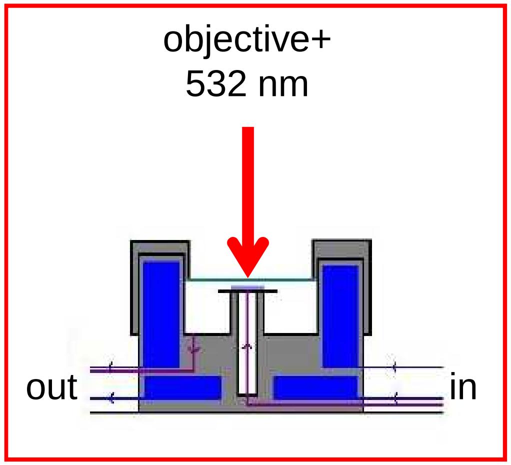
Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3



$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

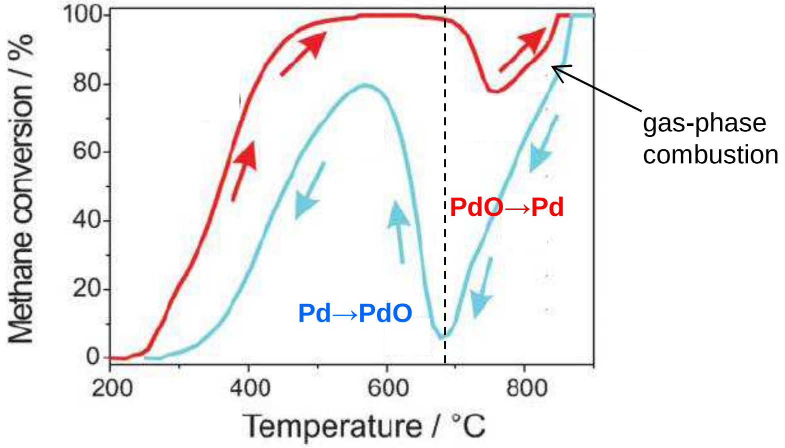
near PdO mode



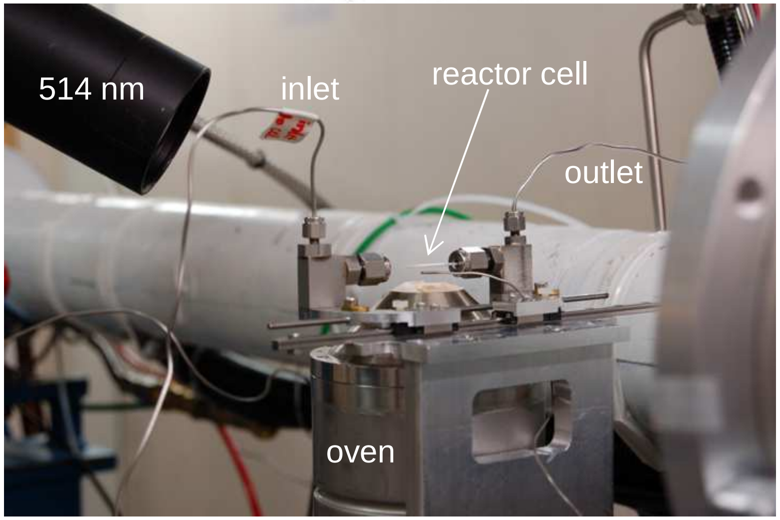
Demoulin et al., *PCCP* **5** (2003) 4394

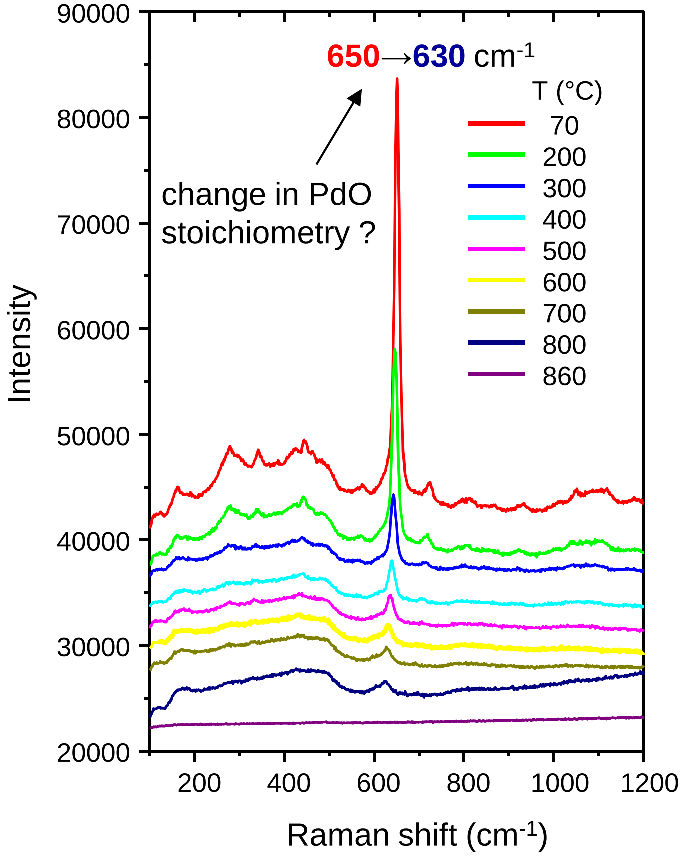
Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2



gas-phase combustion





650→630 cm^{-1}

change in PdO stoichiometry ?

1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

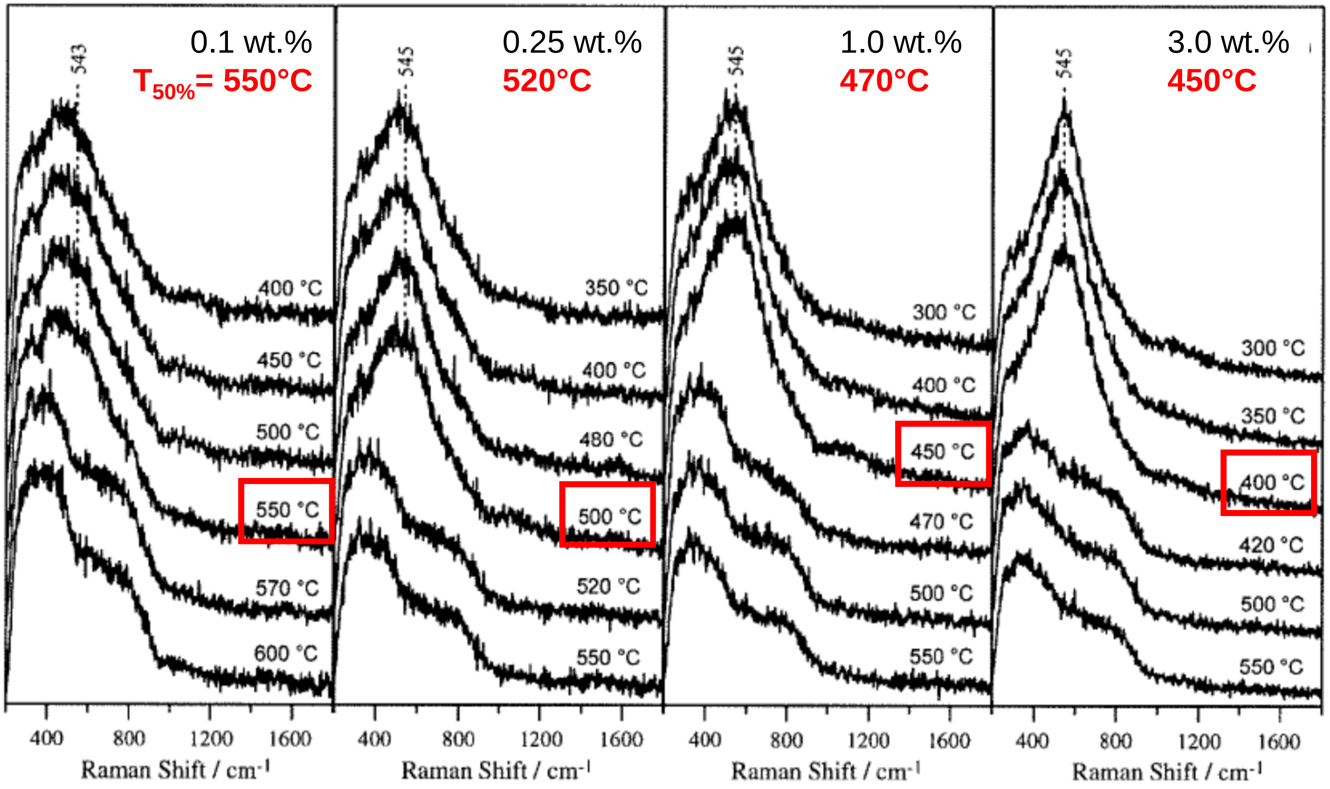
- Methane partial oxidation over Rh/Al_2O_3

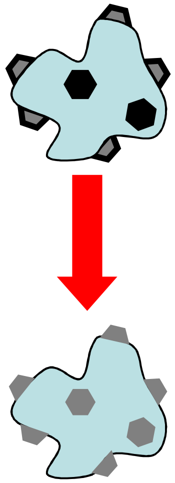
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content
Activity

RhOx
↓
Rh(0)



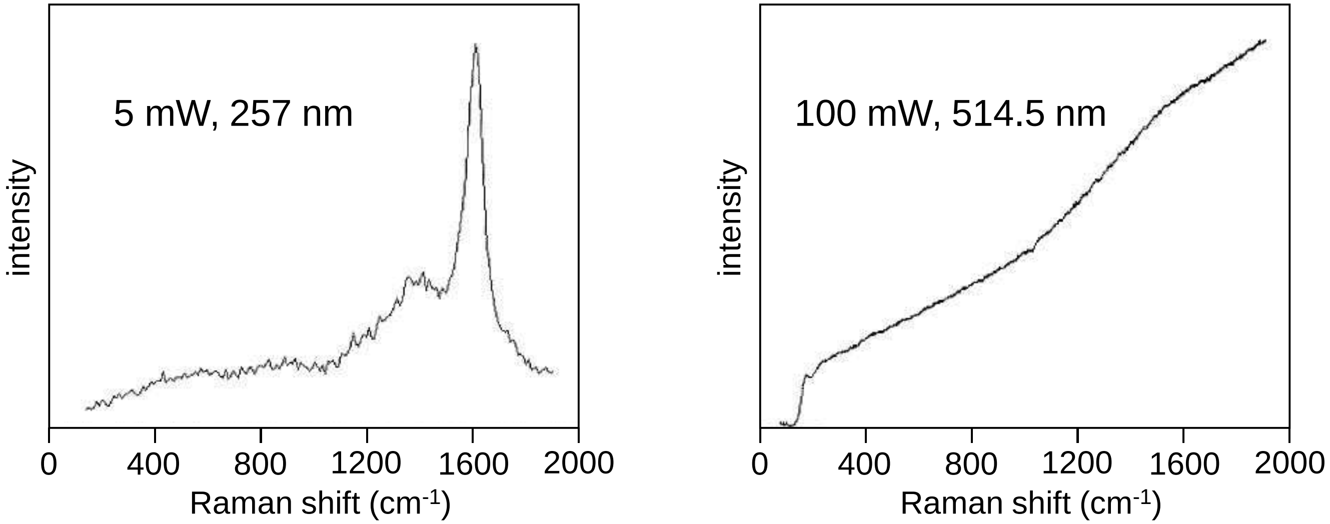


Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

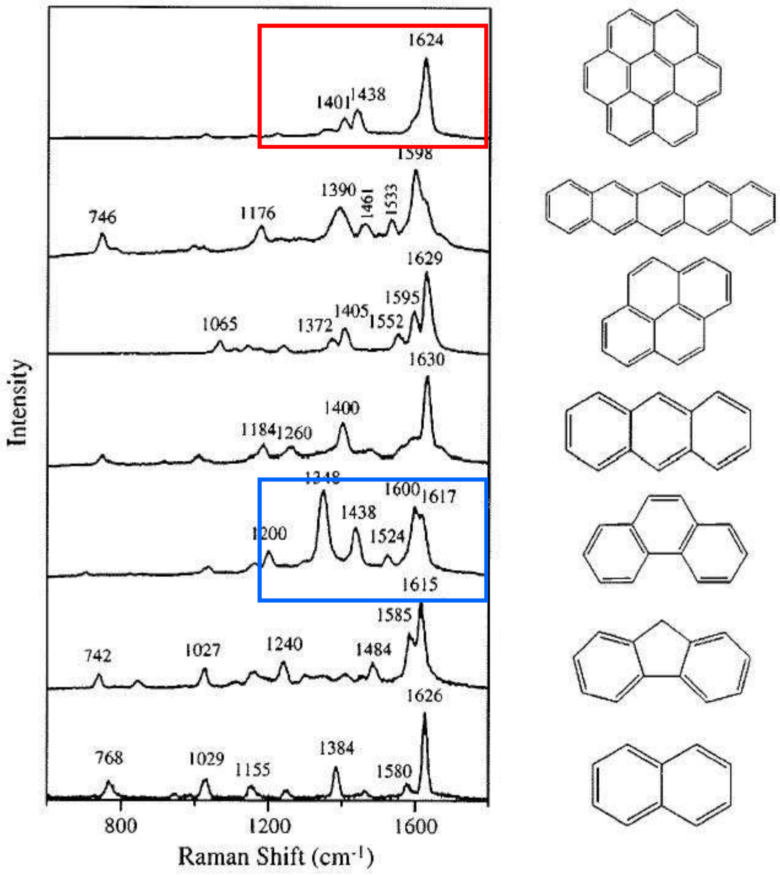


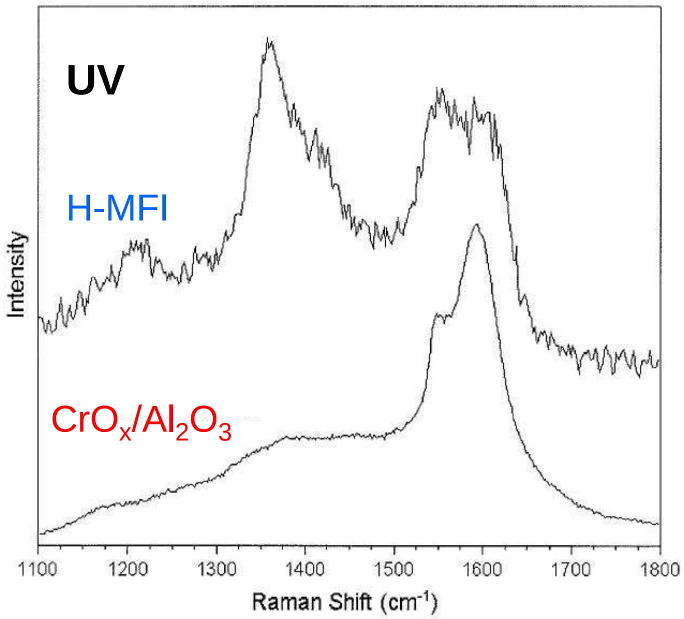
Rh/Al_2O_3, coked 500°C in naphtha

Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





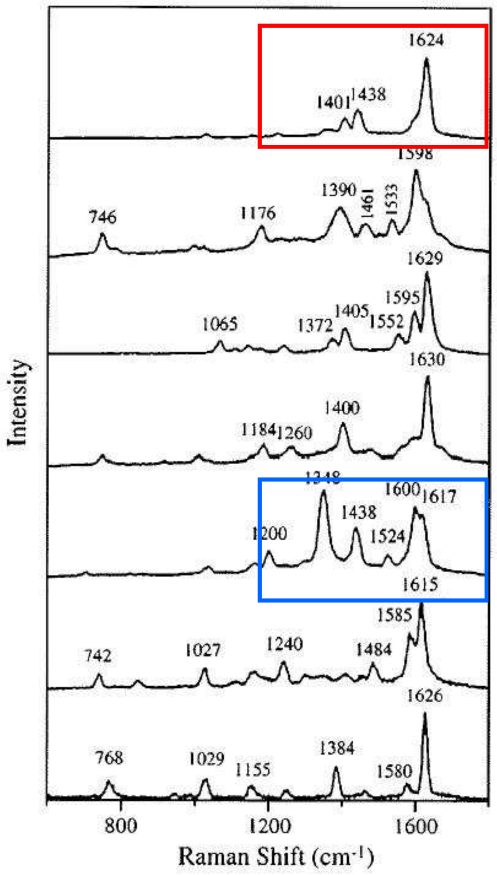
Coke classification
1D topology, chain-like
2D topology, sheet-like

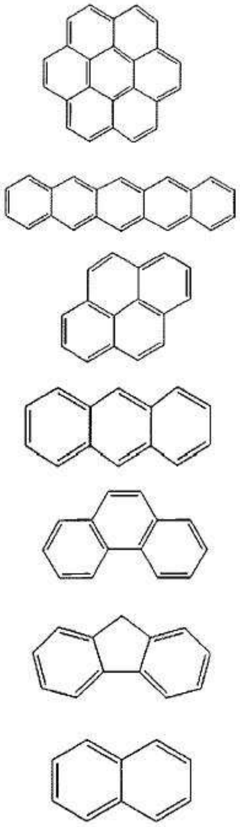
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

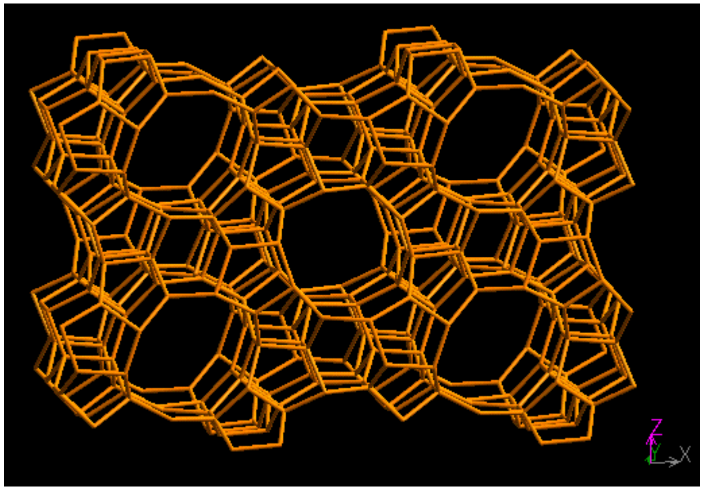
Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization







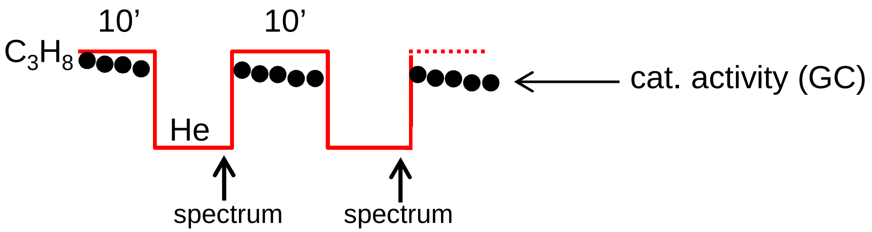
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- Propane dehydrogenation



10’

10’

C_3H_8

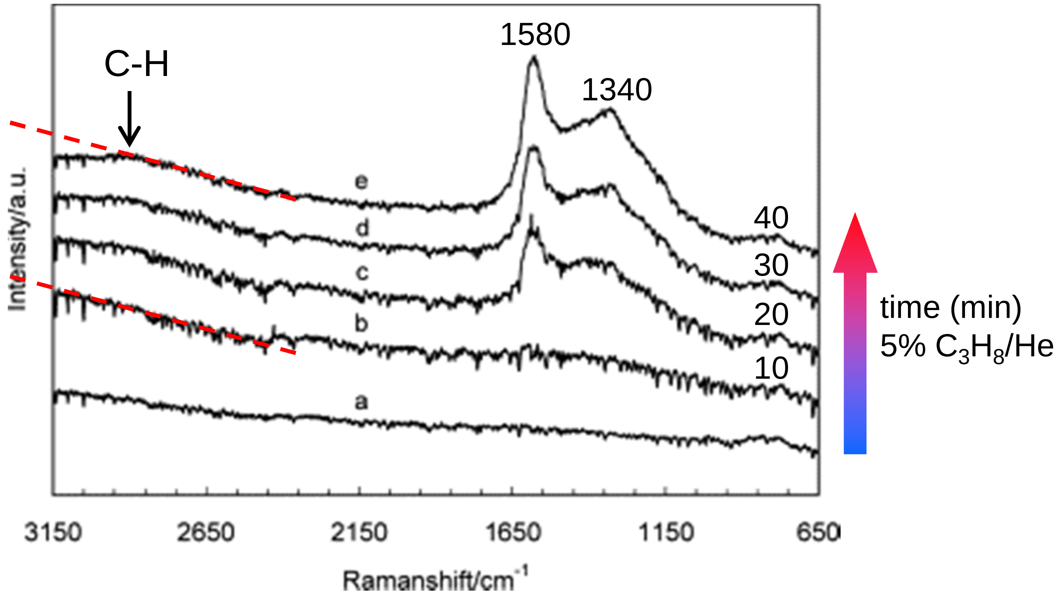
He

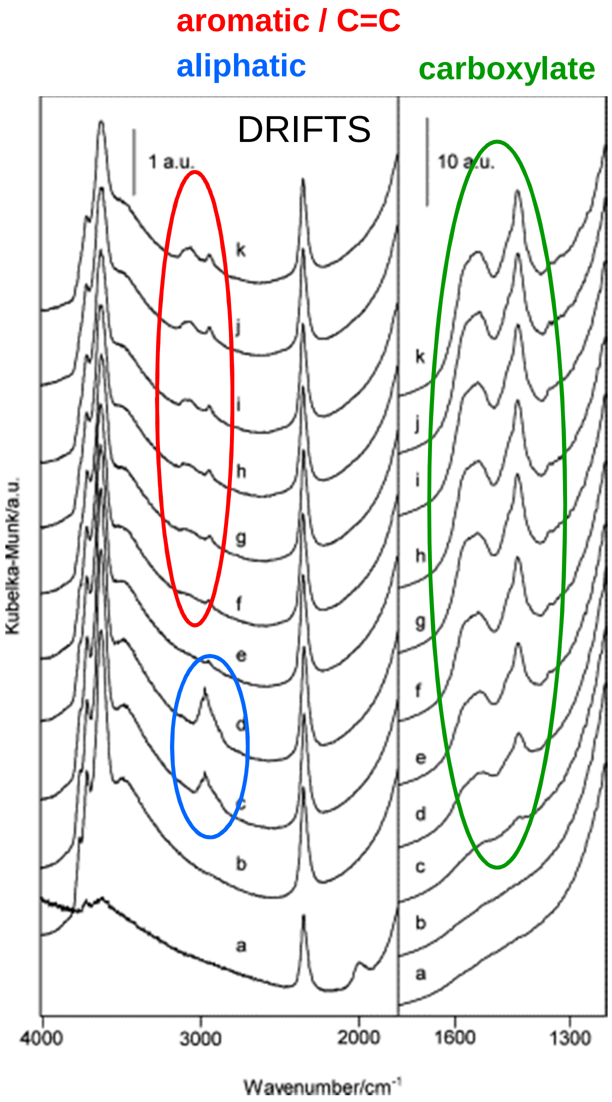
spectrum

spectrum

cat. activity (GC)

Cr_2O_3/Al_2O_3, 580°C, 514 nm

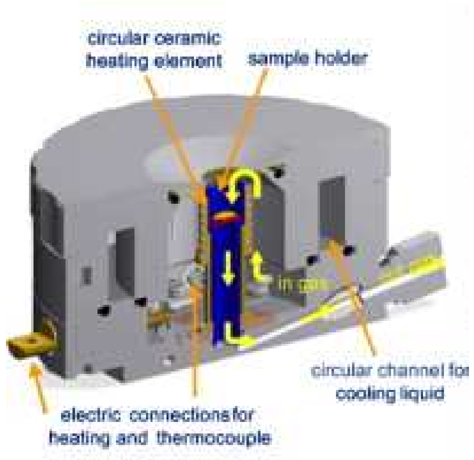


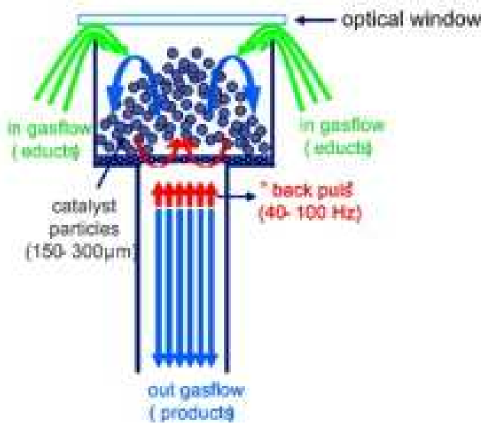


Airaksinen et al., *J. Catal.* **230** (2005) 507

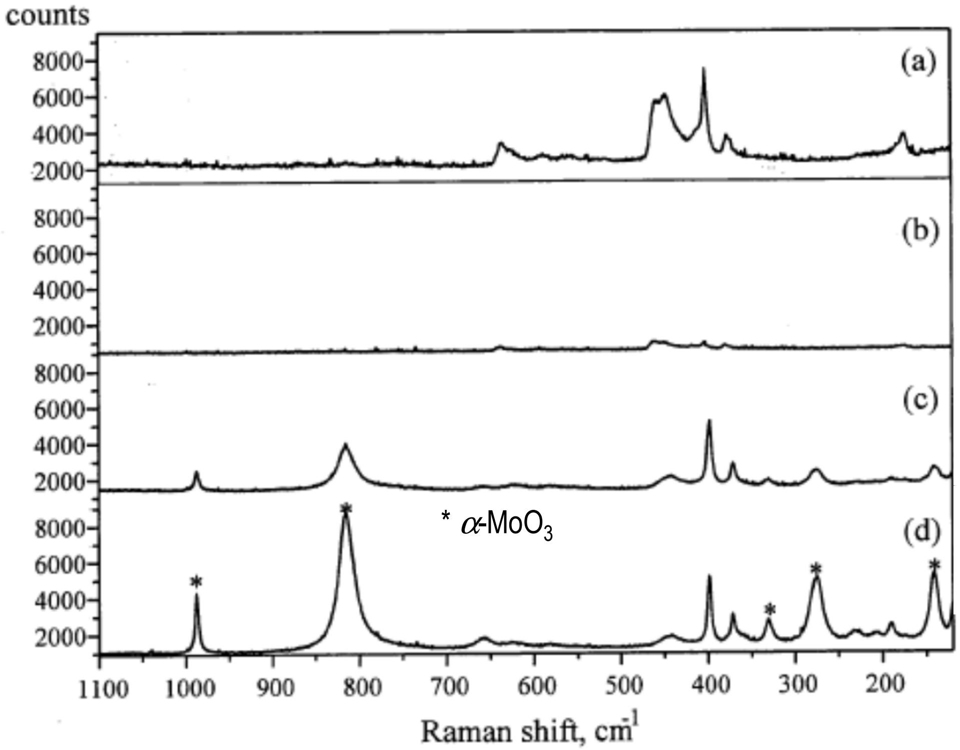
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min
full power, FB

MoS_2, 6 min
1/8 power

MoS_2, 1 min
full power

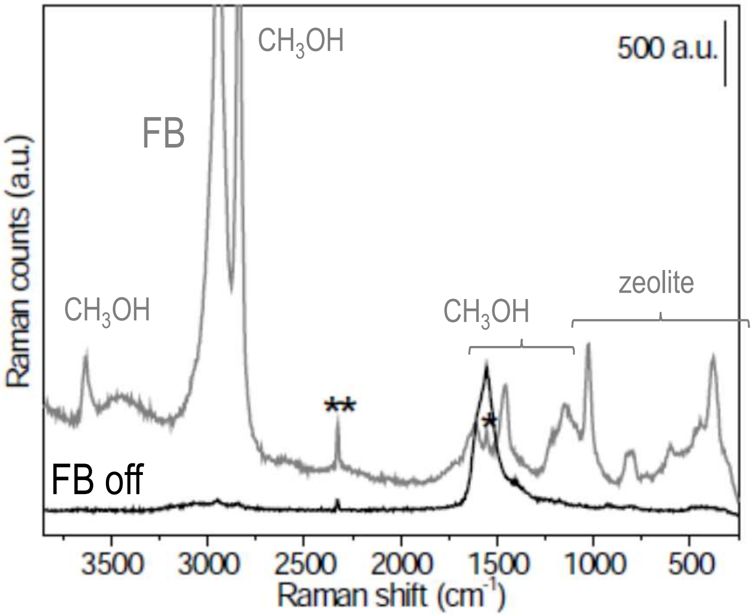
MoS_2, 6 min
full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

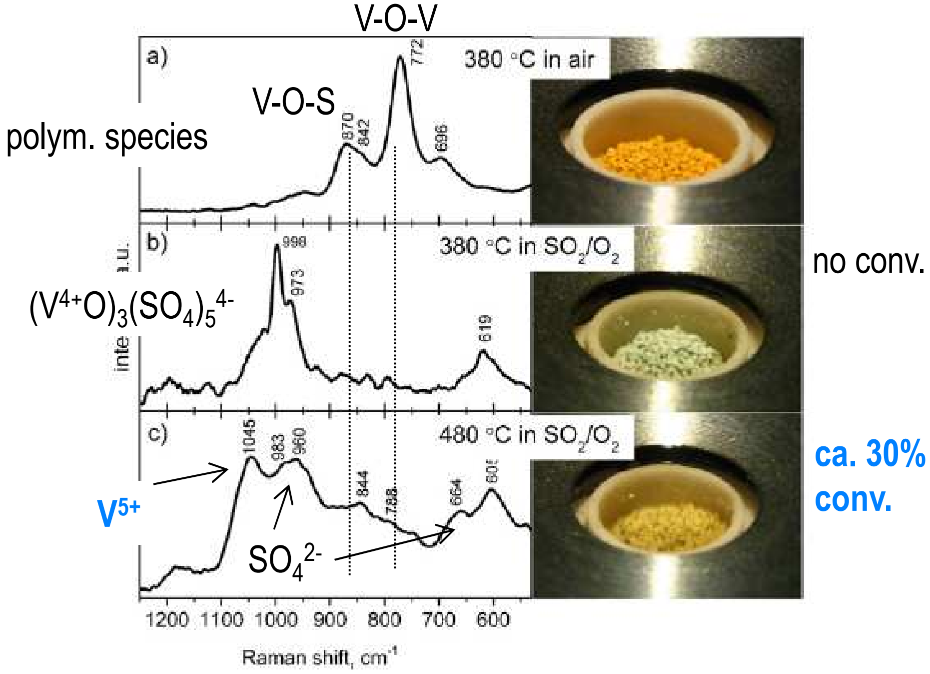
- Fluidized bed reactor cell

CH$_3$OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH$_3$OH decomposition

Sulfuric acid V$_2$O$_5$/pyrosulfate catalyst
λ= 514 nm

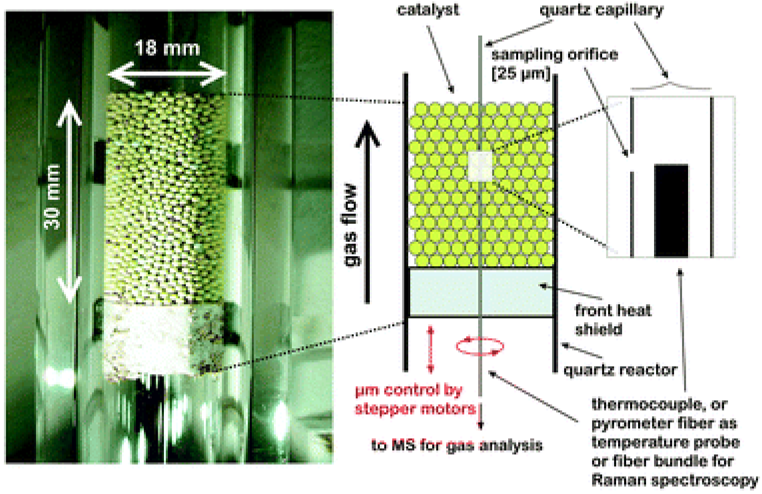


active species: mono- & dimeric V^{5+} oxosulfate species

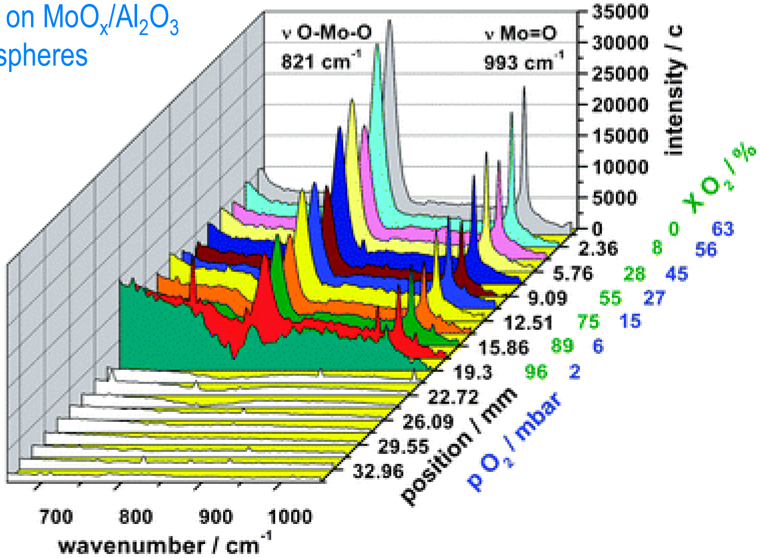
Beato et al., *Catal. Today* 205 (2013) 128

Applications

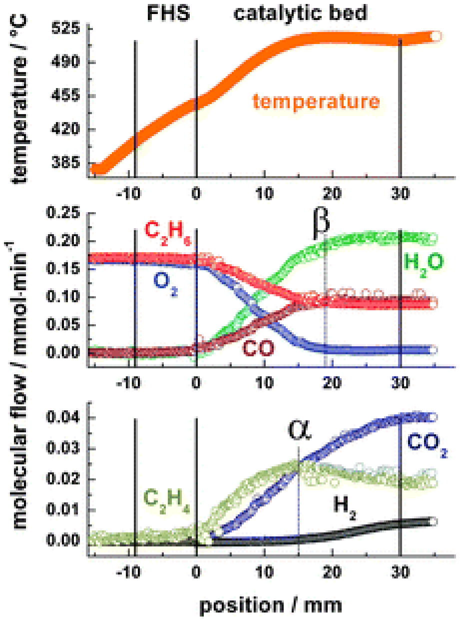
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

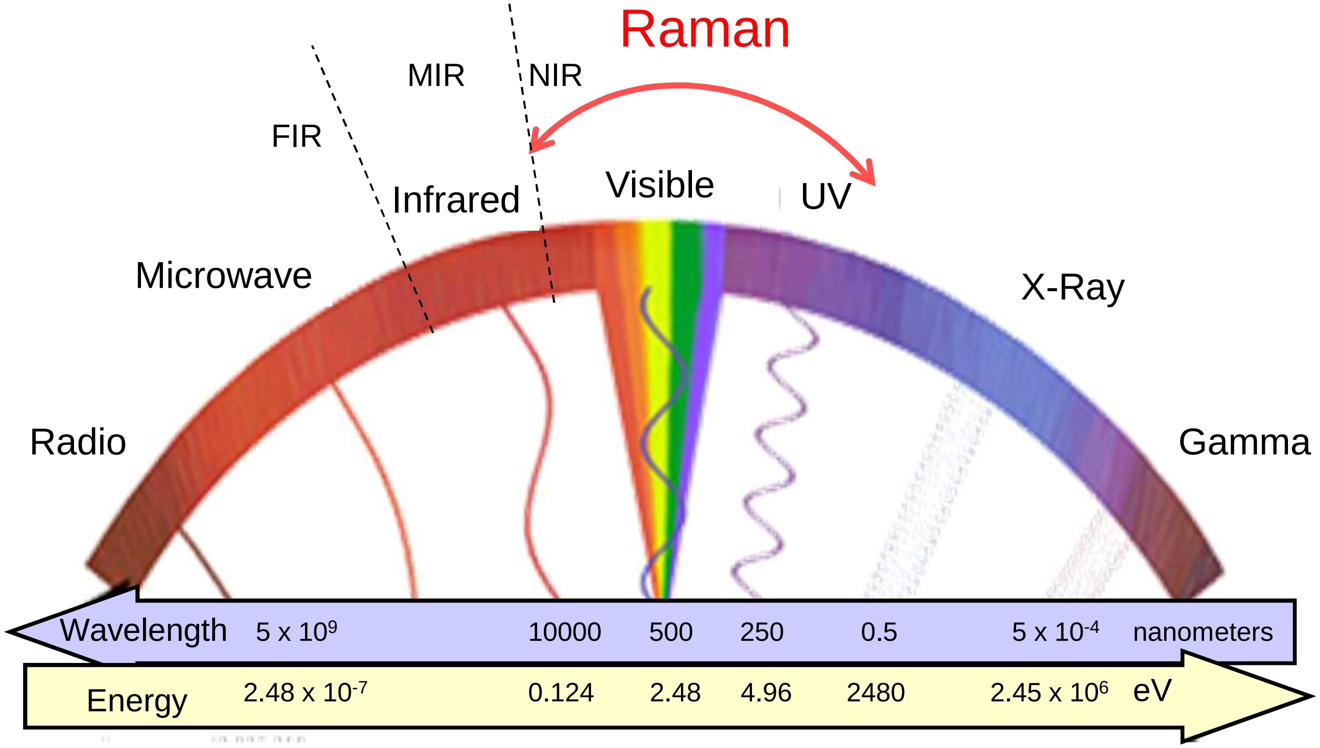
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

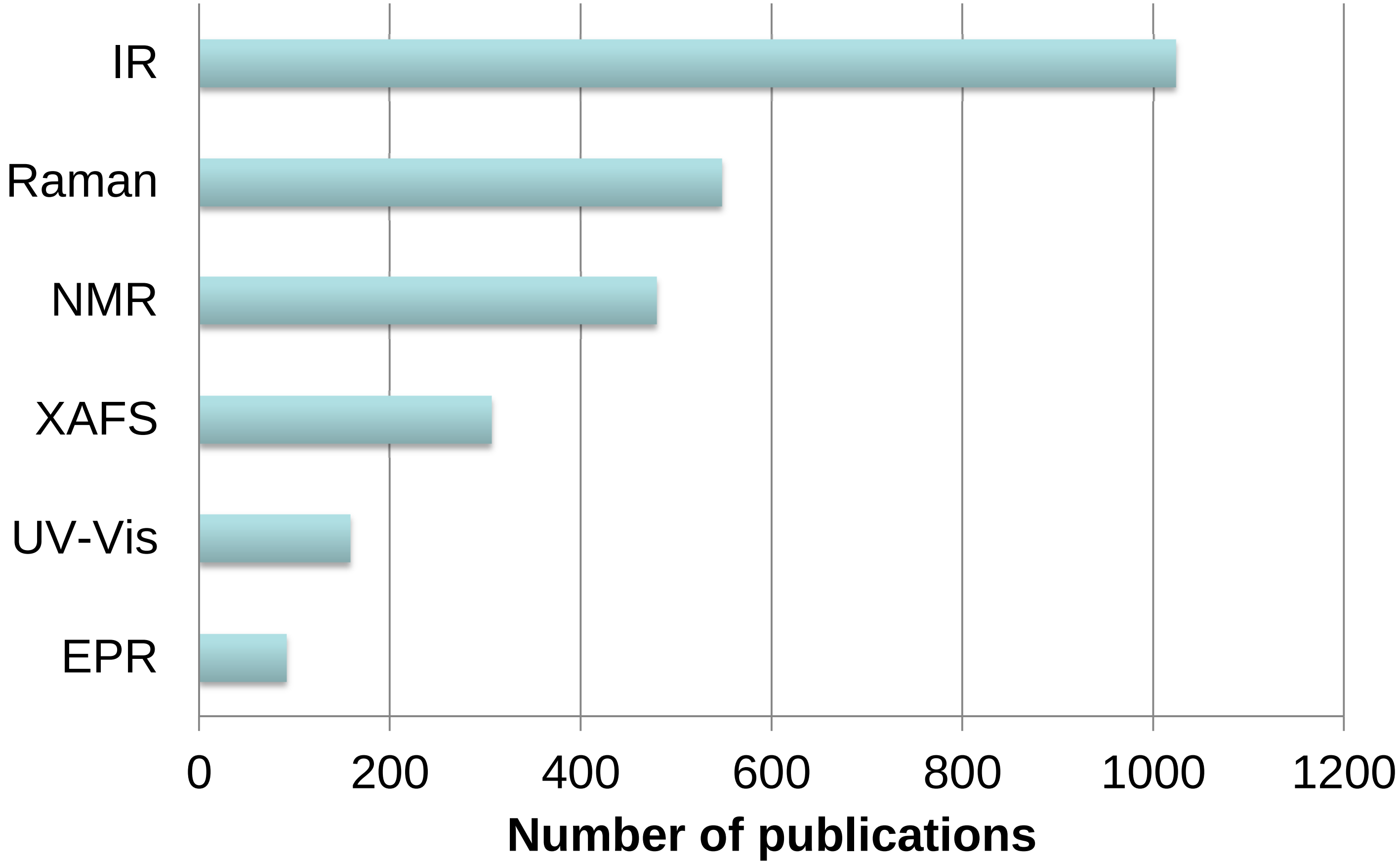
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

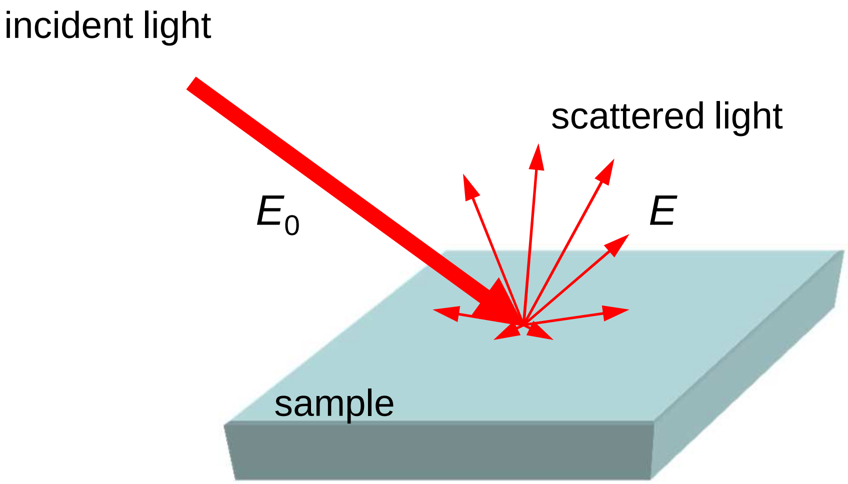


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{\mathrm{vib}} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib}t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib}t)]E_0\cos(2\pi\nu_0 t)$$

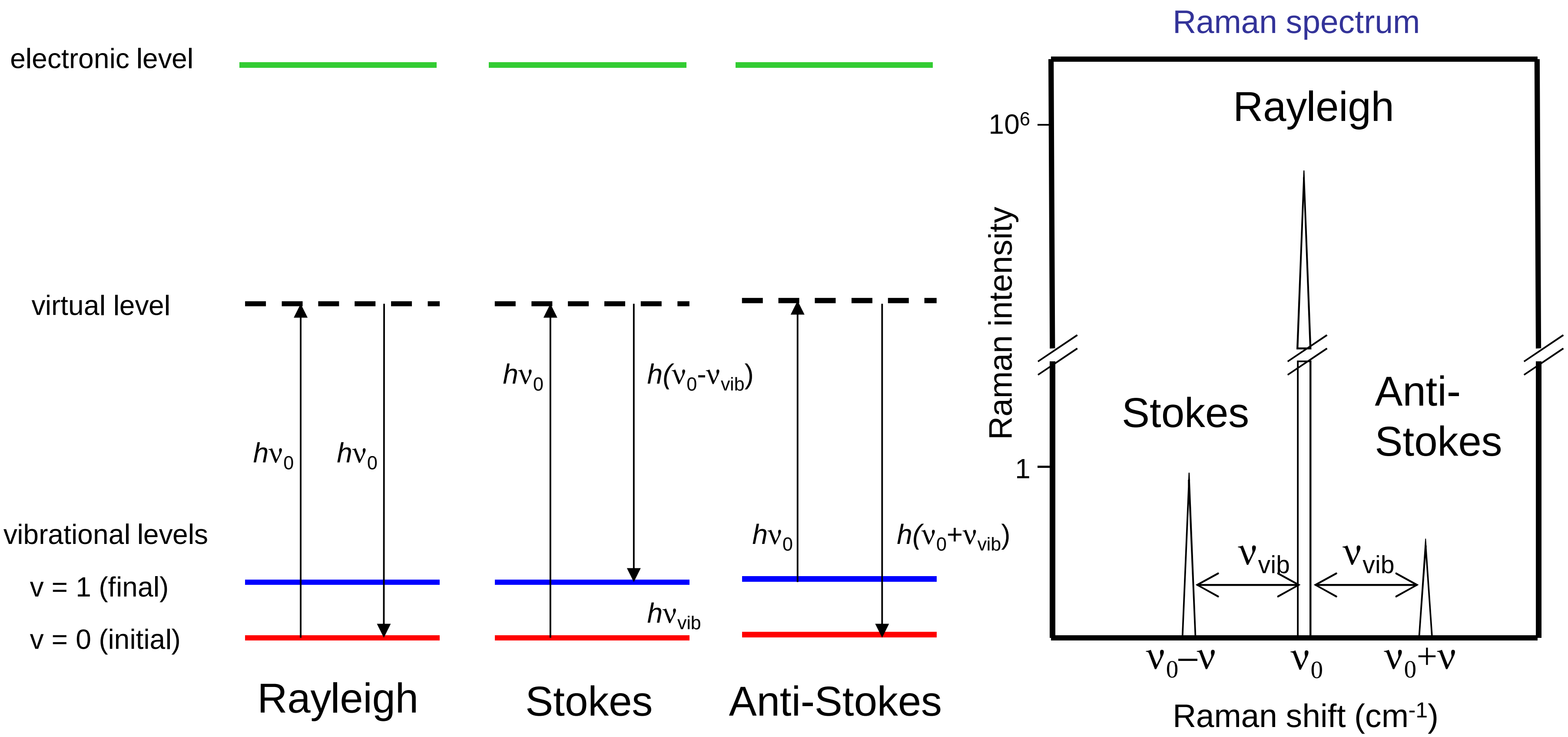
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib}t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\ (\text{Anti-Stokes})}{I\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:
  - 4th power of ν (4th power law)
  - 2nd power of $\Delta\alpha$
    - properties of molecules
    - strength of bonds

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

↓

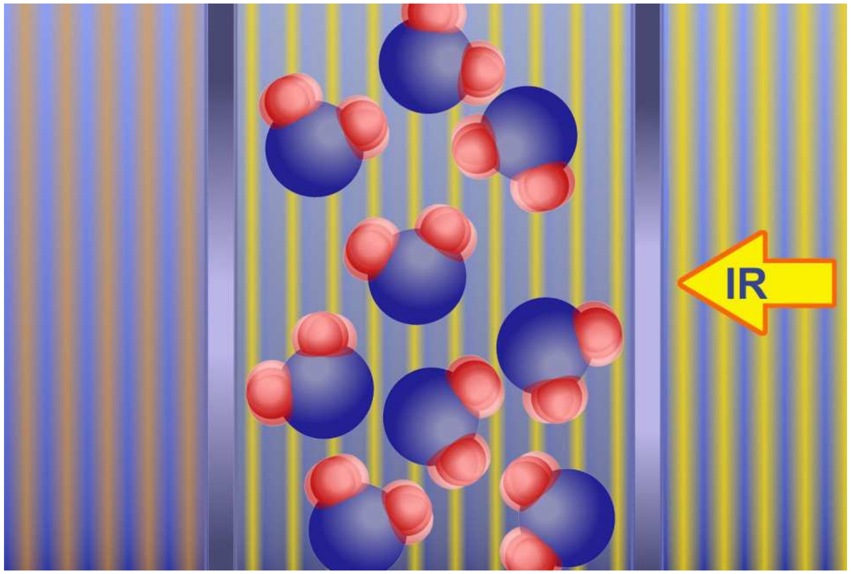
covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

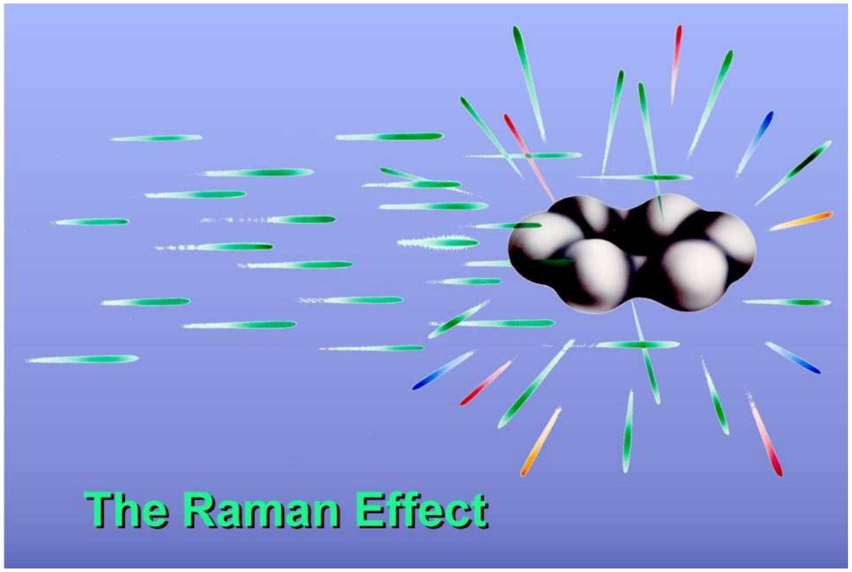
- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

Raman *vs.* Infrared

Infrared

Raman





Absorption of IR light

Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

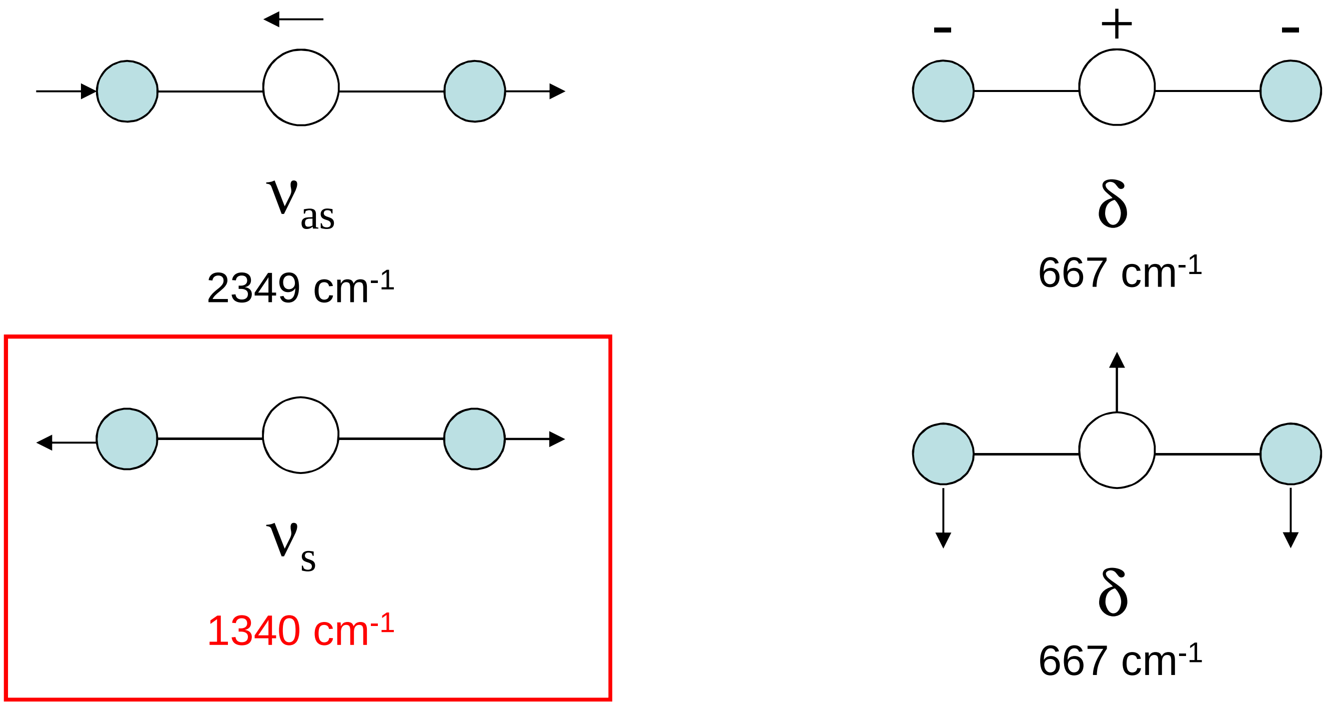
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - large electron clouds
  - not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

Raman *vs.* Infrared

CO_2



ν_{as}

2349 cm^{-1}

ν_s

1340 cm^{-1}

Raman active

- + -

δ

667 cm^{-1}

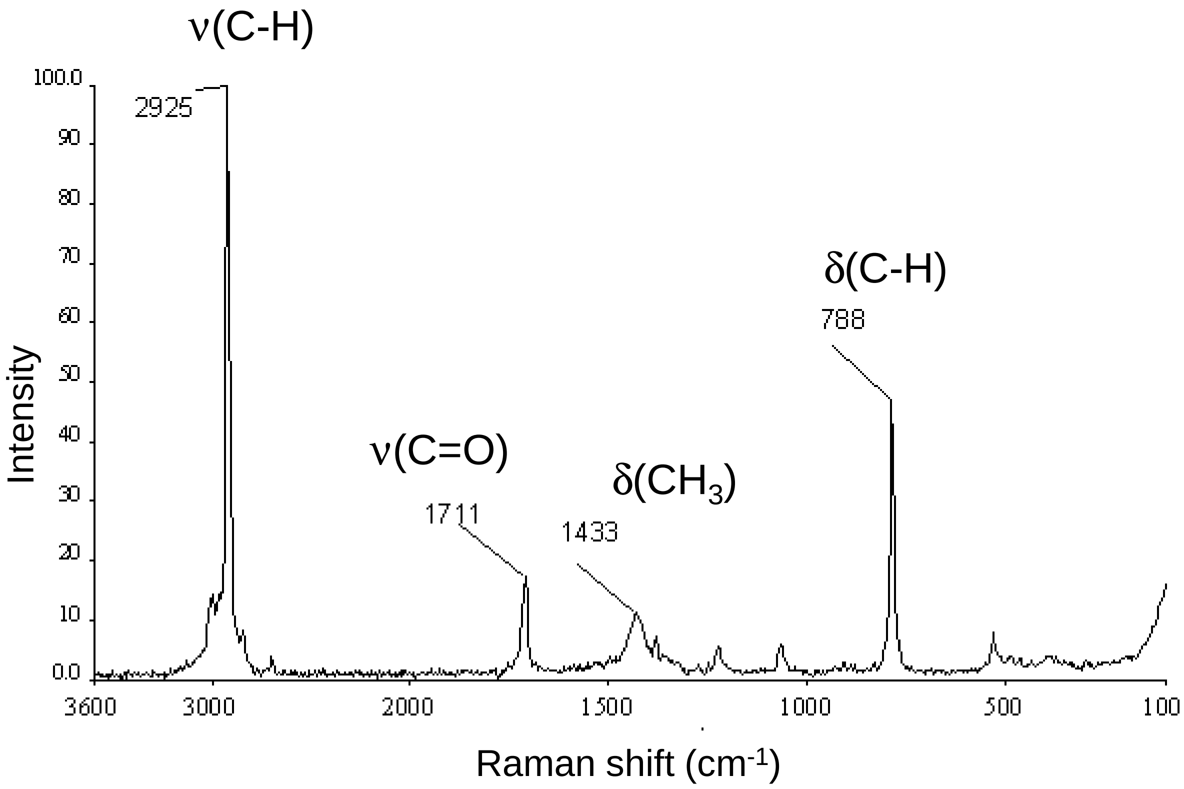
δ

667 cm^{-1}

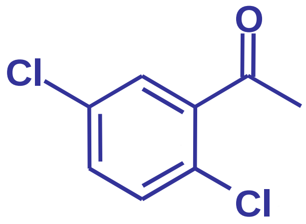
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



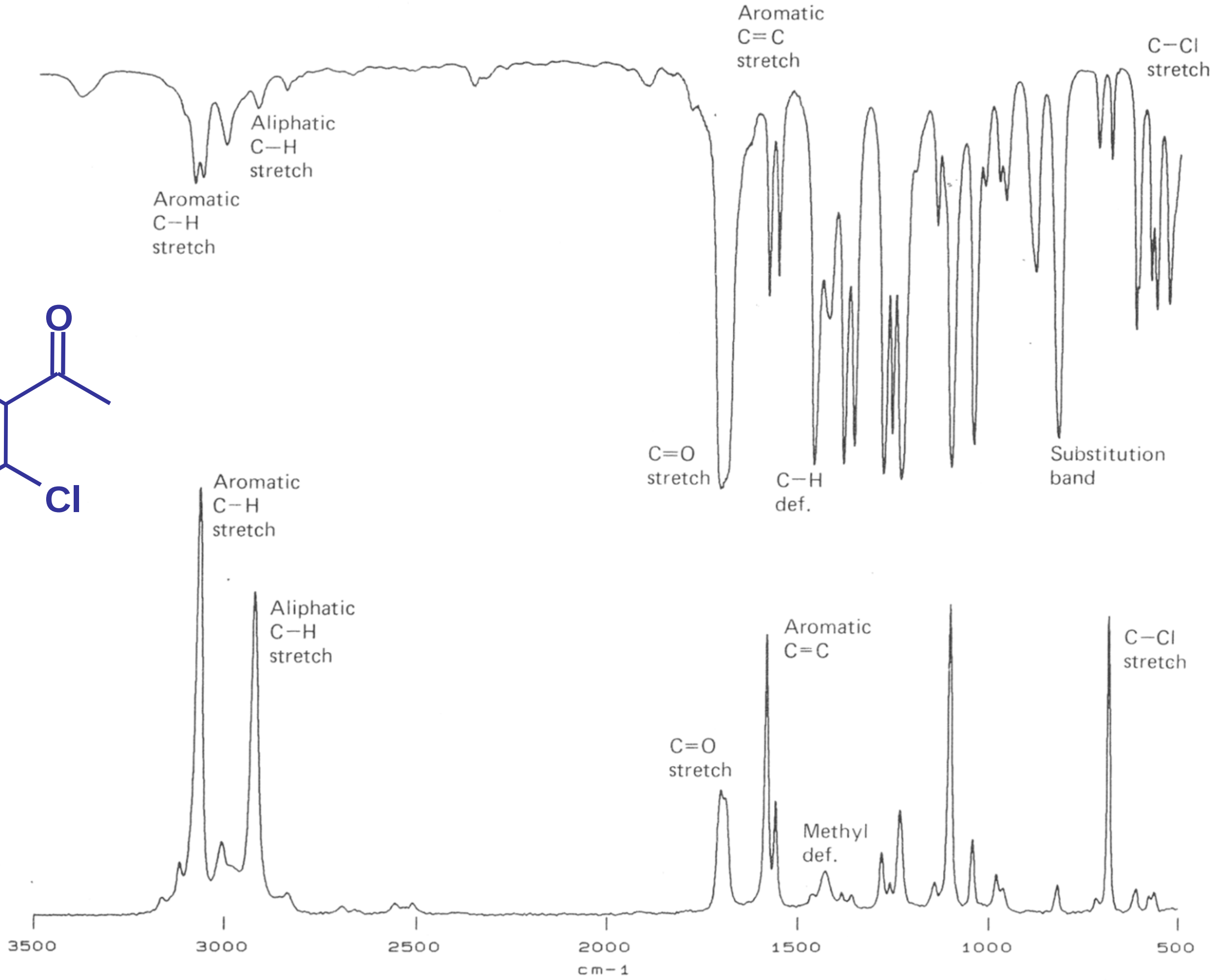


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

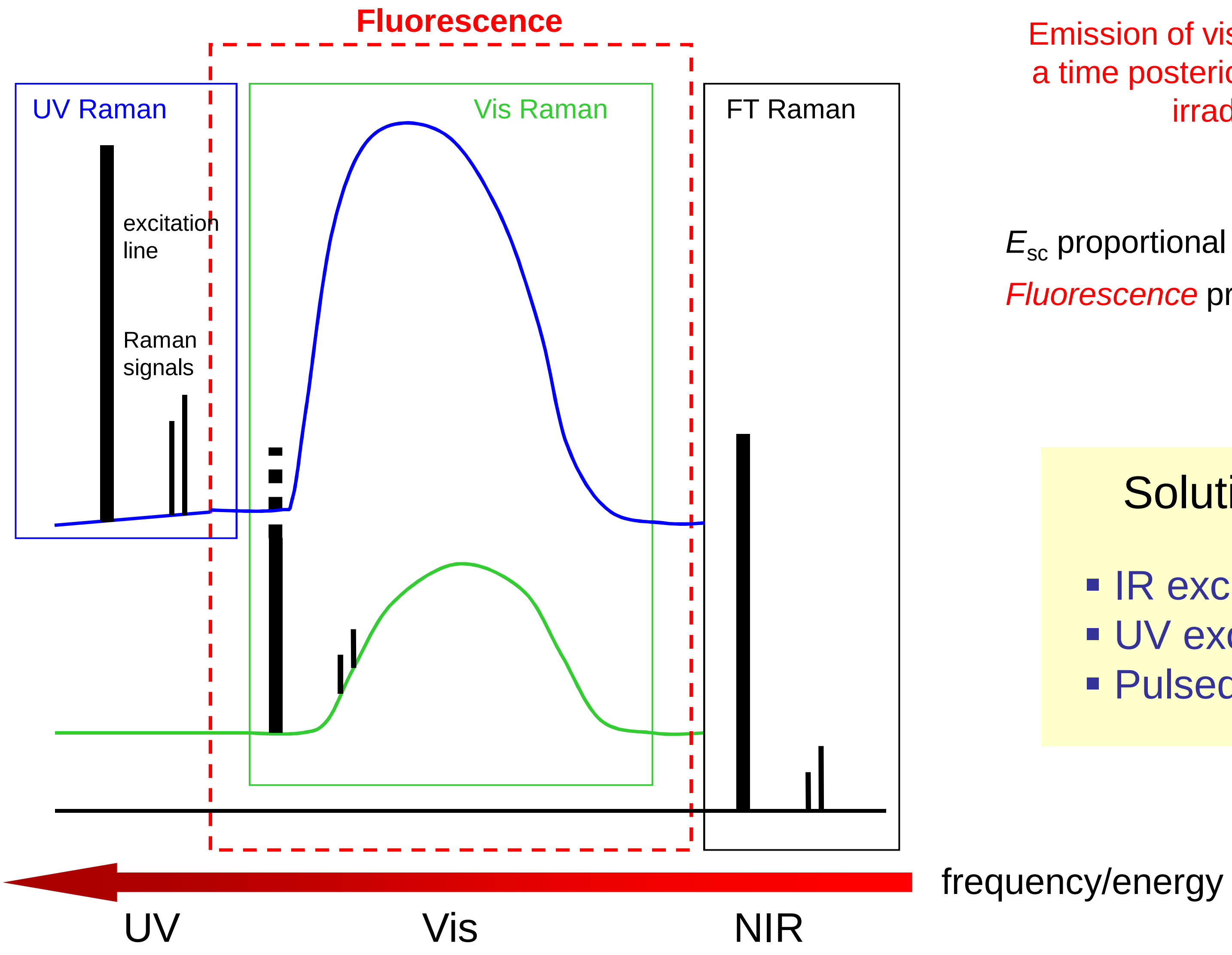
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 μm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

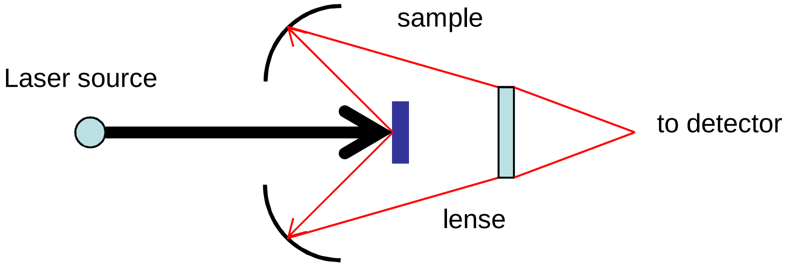
Fluorescence proportional to ν

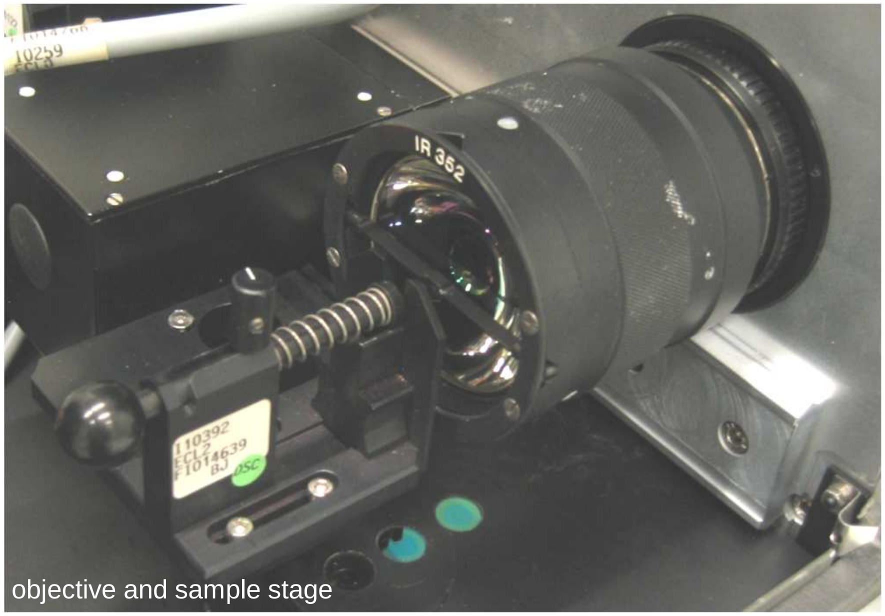
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation




objective and sample stage

Lasers
Excitation wavelengths

UV	250 nm
Vis (green)	514 nm
Vis (red)	633 nm
NIR	780 nm
IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

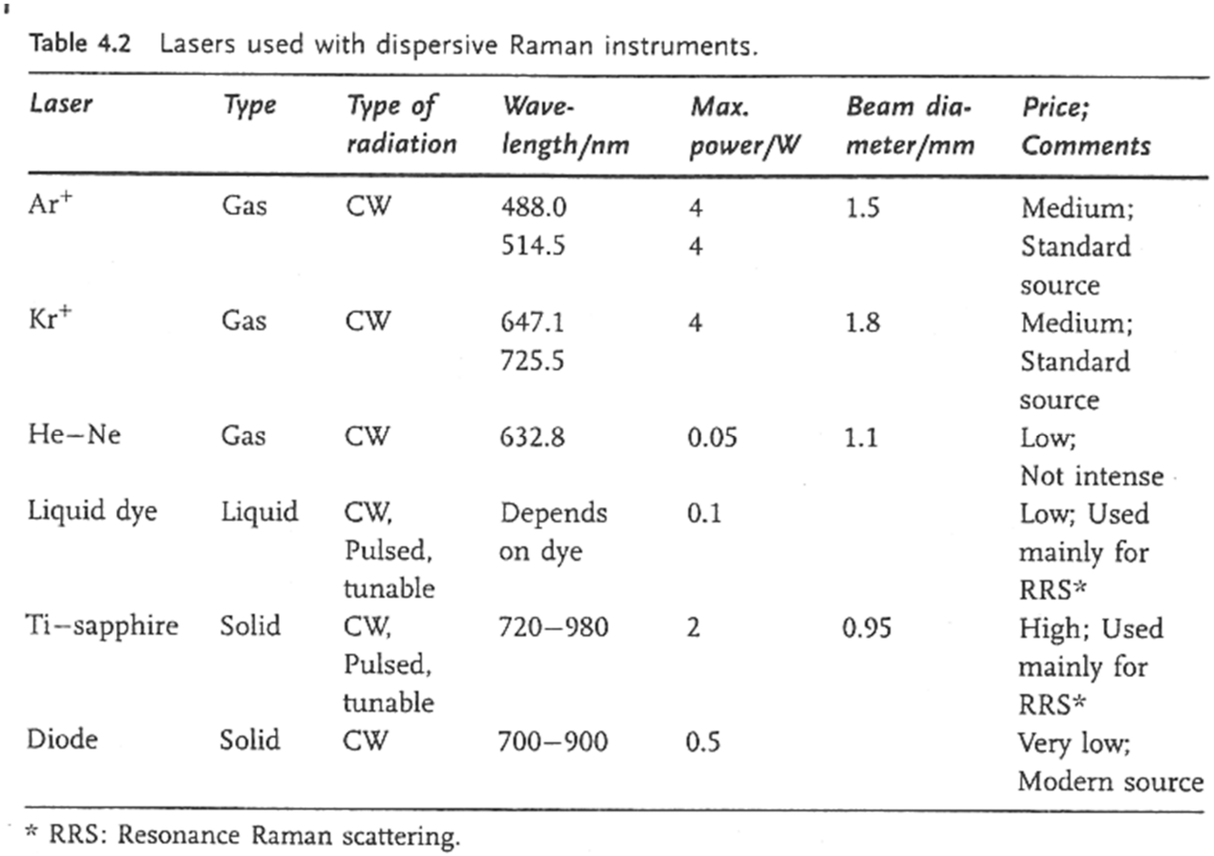


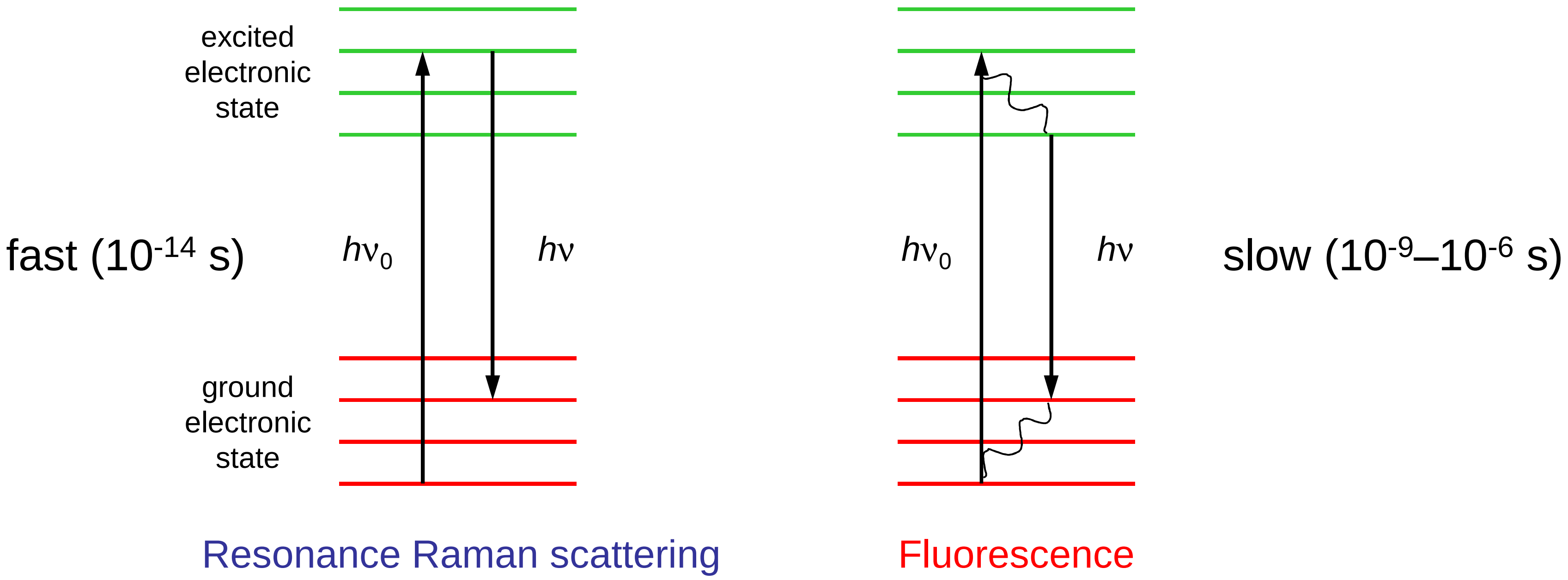
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited

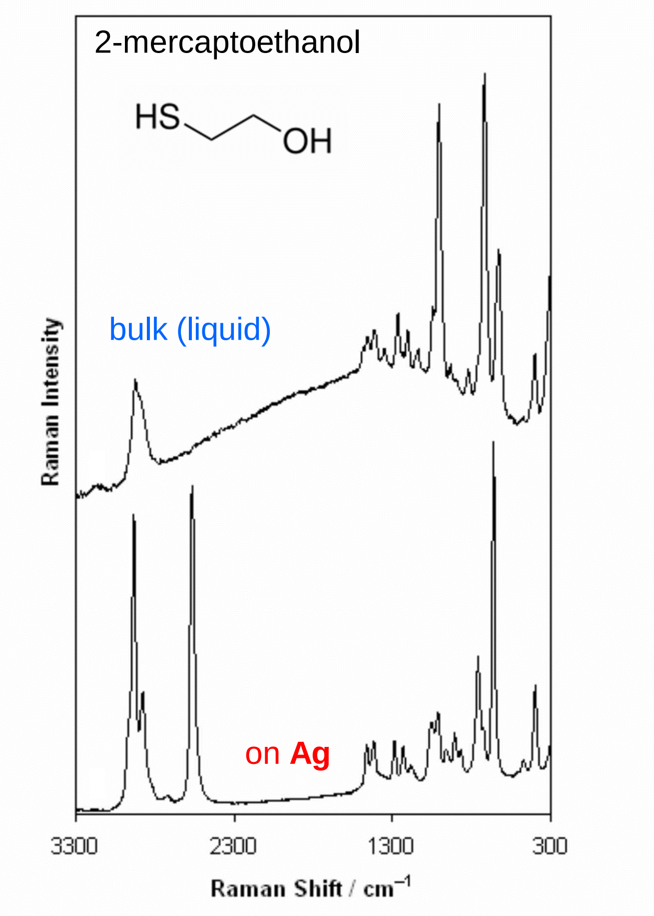


Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

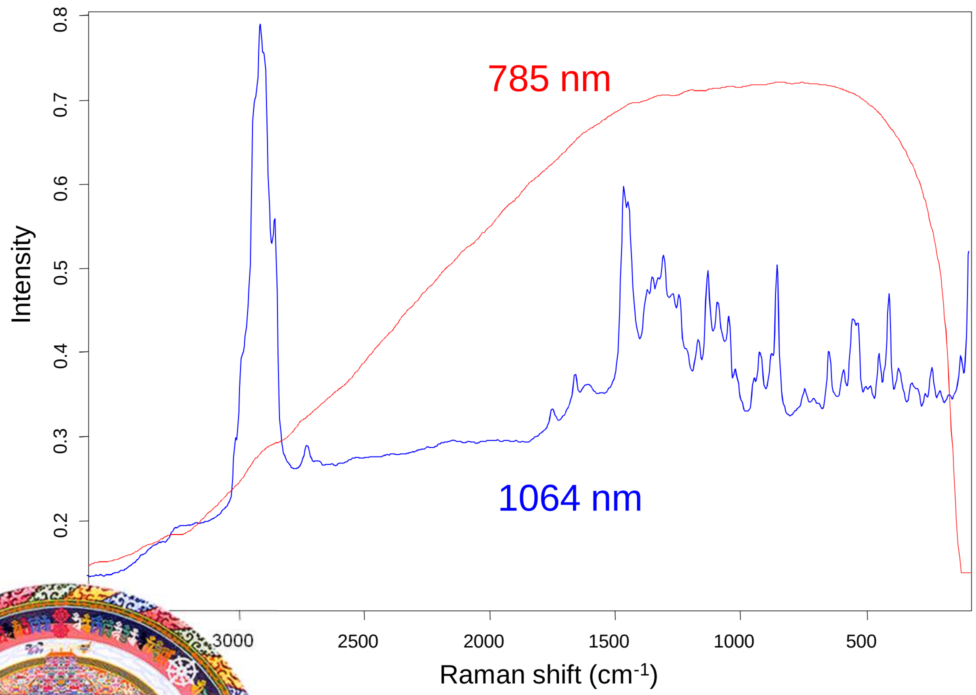
- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

- Remarks:
  - rough surface; nanoparticles (10–100 nm) or kinks, steps etc. (E always perpendicular to surface, locally)
  - vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



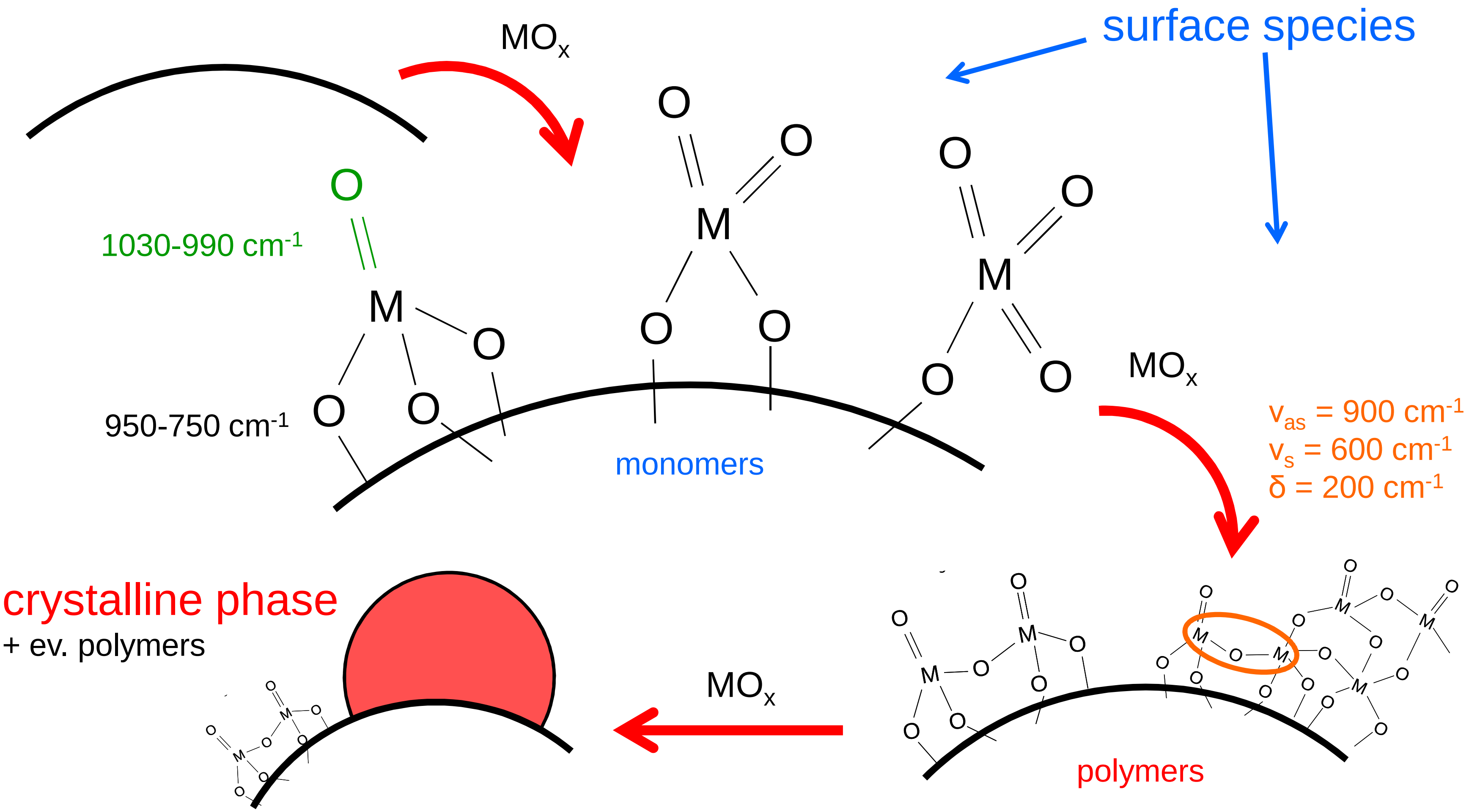
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



MO$_x$

surface species

1030-990 cm^{-1}

950-750 cm^{-1}

monomers

MO$_x$

$\nu_{as} = 900\ \mathrm{cm}^{-1}$
$\nu_{s} = 600\ \mathrm{cm}^{-1}$
$\delta = 200\ \mathrm{cm}^{-1}$

polymers

MO$_x$

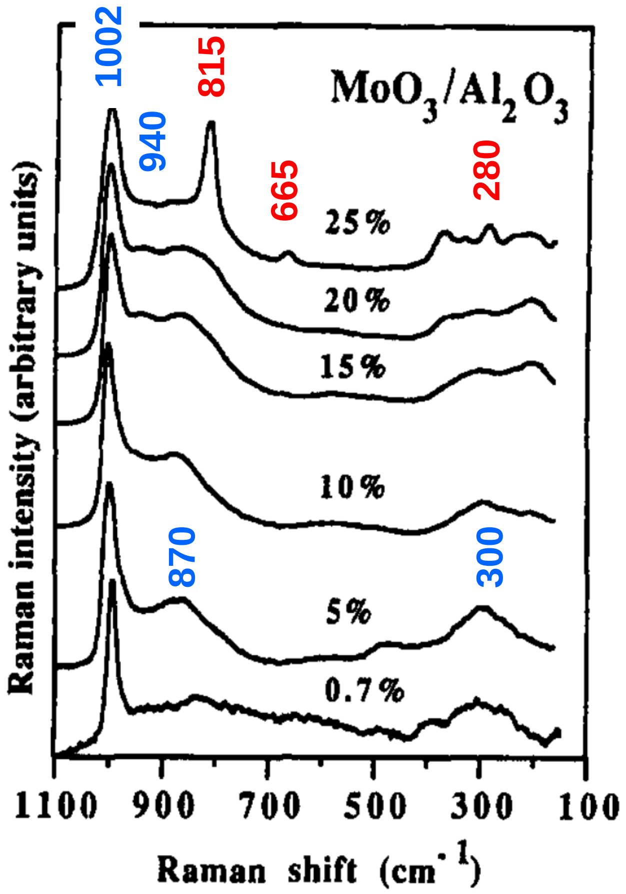
crystalline phase
+ ev. polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



surface MoO_3

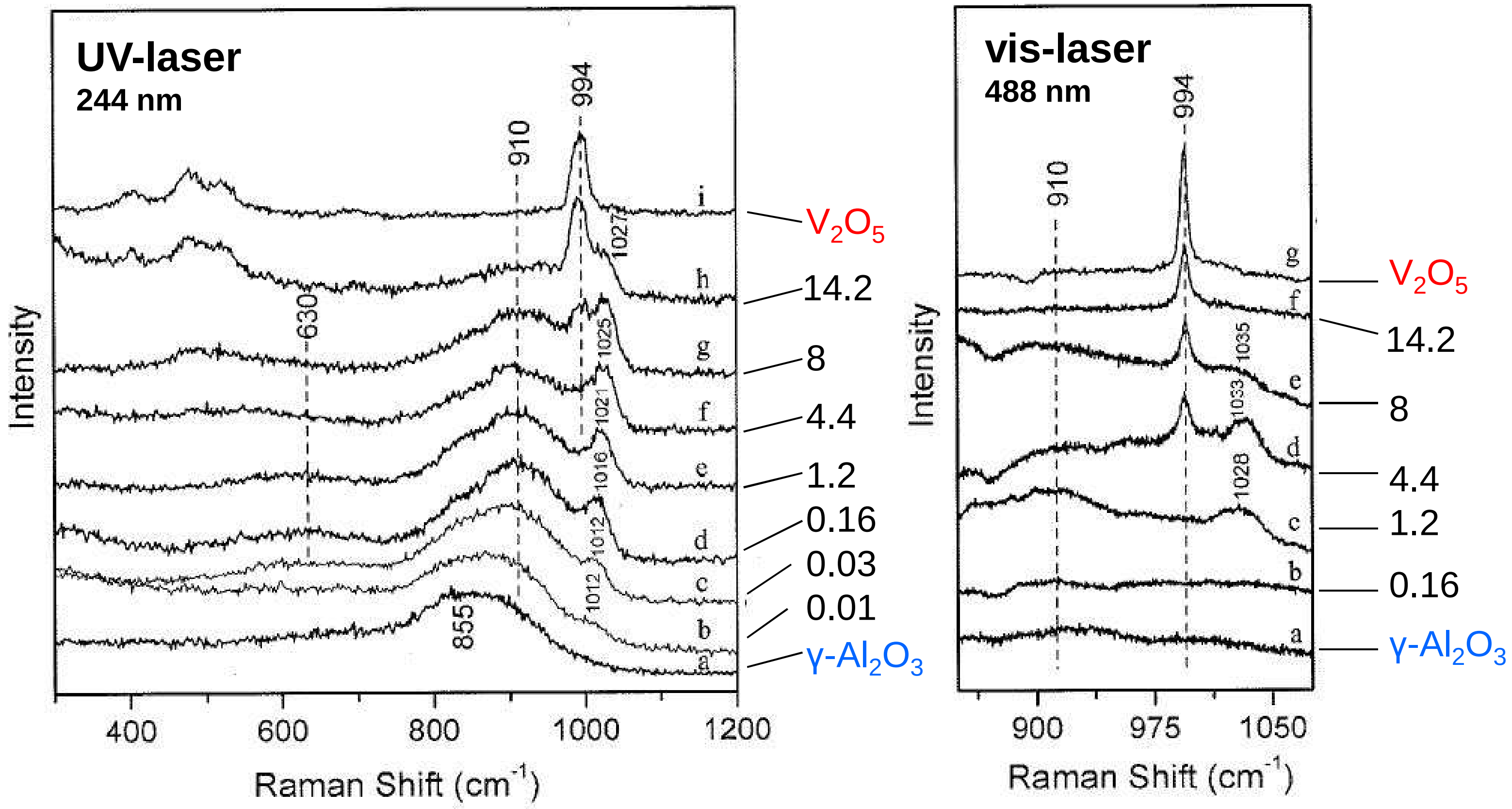
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

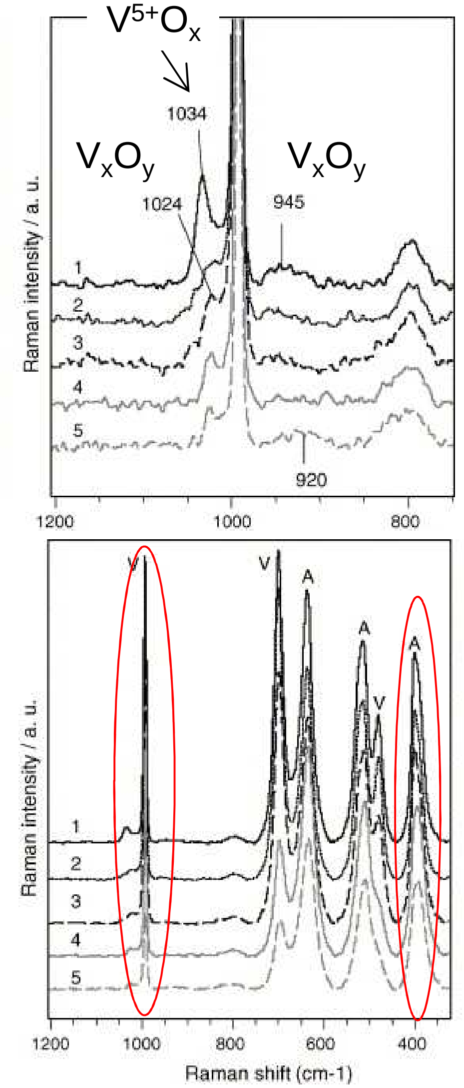
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

Applications

- Reactivity of V/TiO_2 after oxidative treatment



air flow @ 450°C

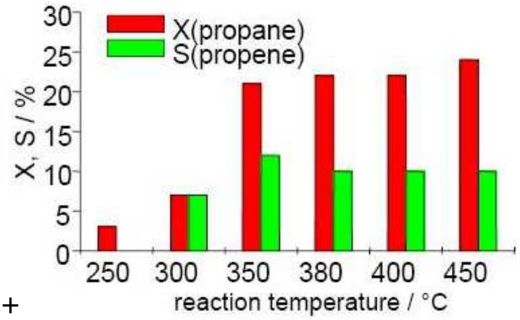
O_2/C_3H_8 @ 20°C

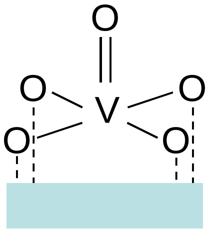
@ 100°C

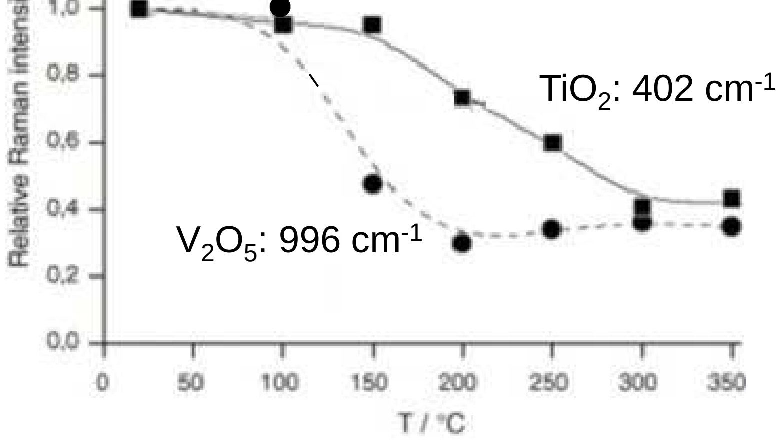
@ 150°C

@ 200°C

$V^{5+} \longrightarrow V^{4+}$







TiO_2: 402 cm^{-1}

V_2O_5: 996 cm^{-1}

Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

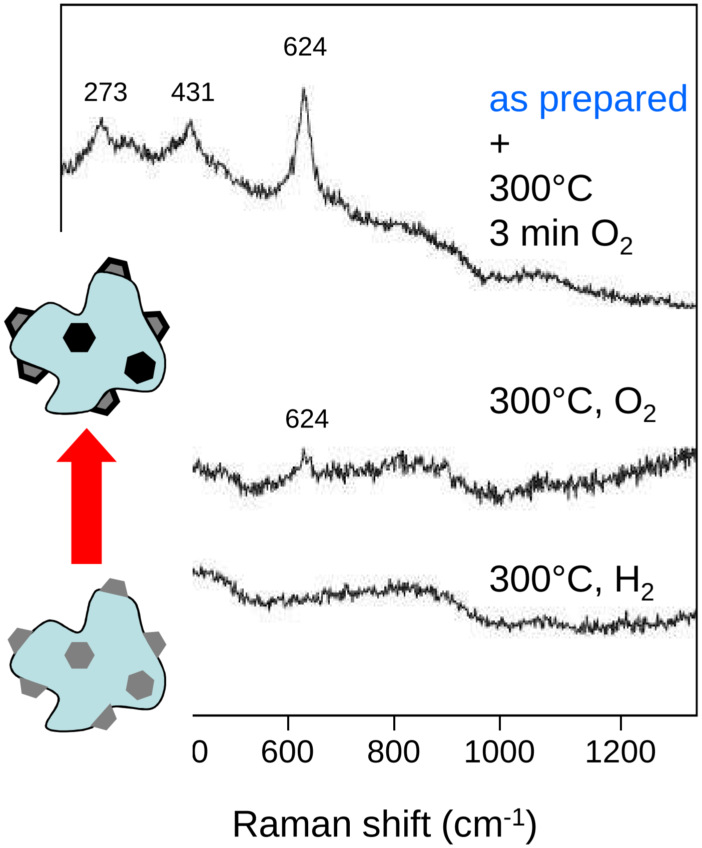
M/MO$_X$ (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

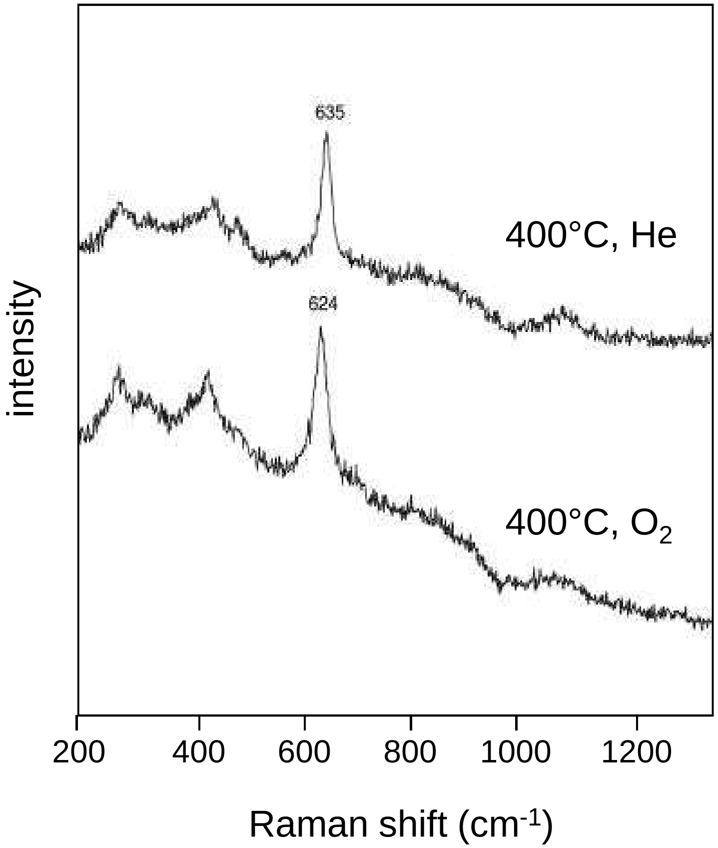
Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3





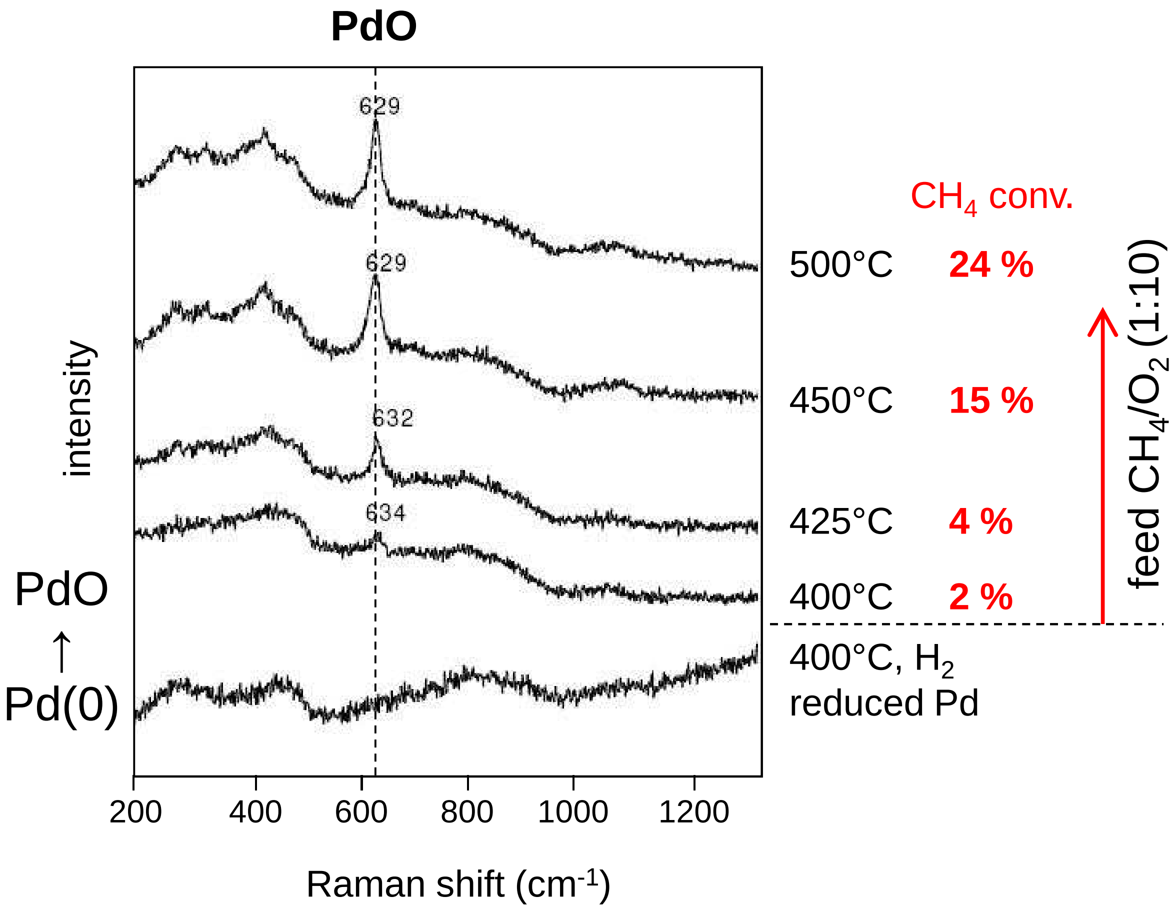
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

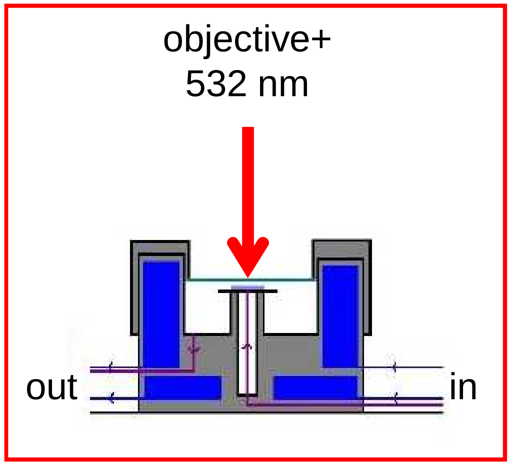
Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$$\mathbf{CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O}$$



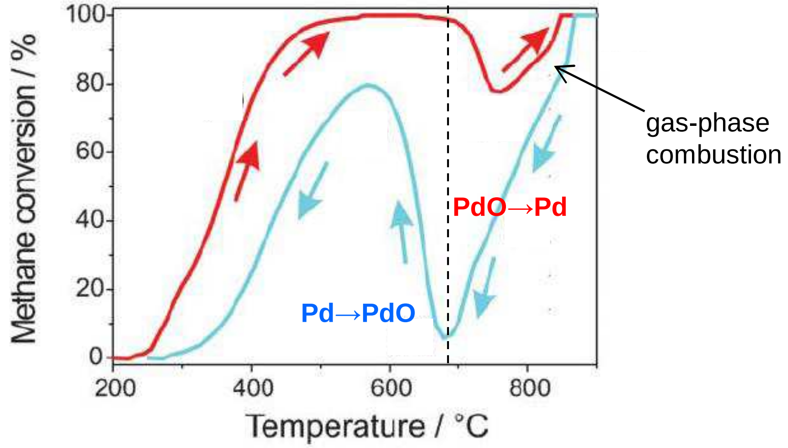
near PdO mode

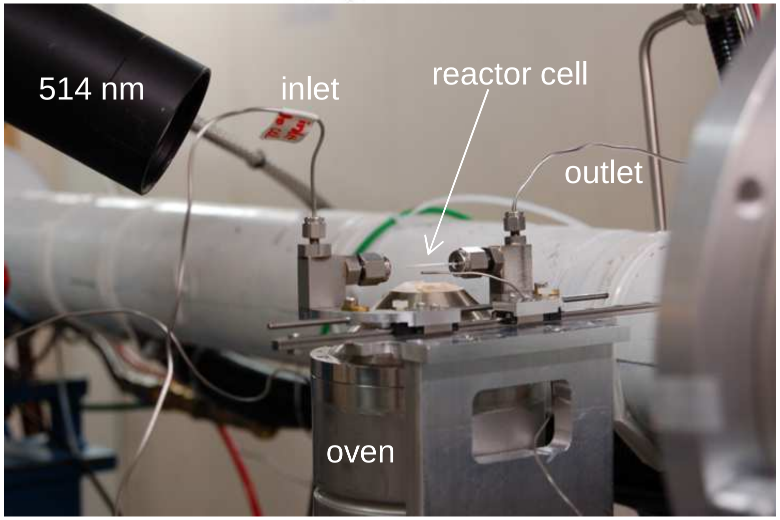


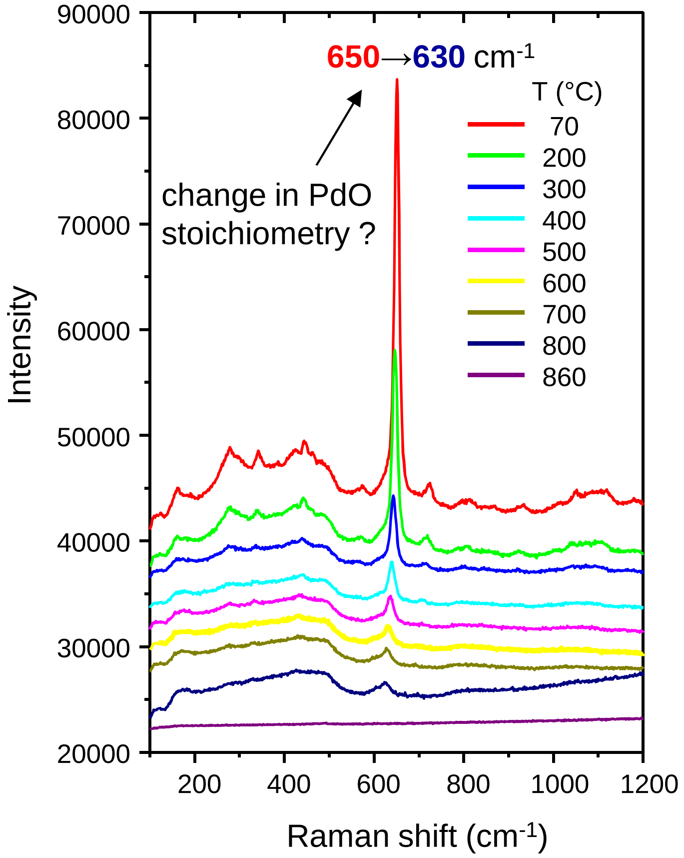
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

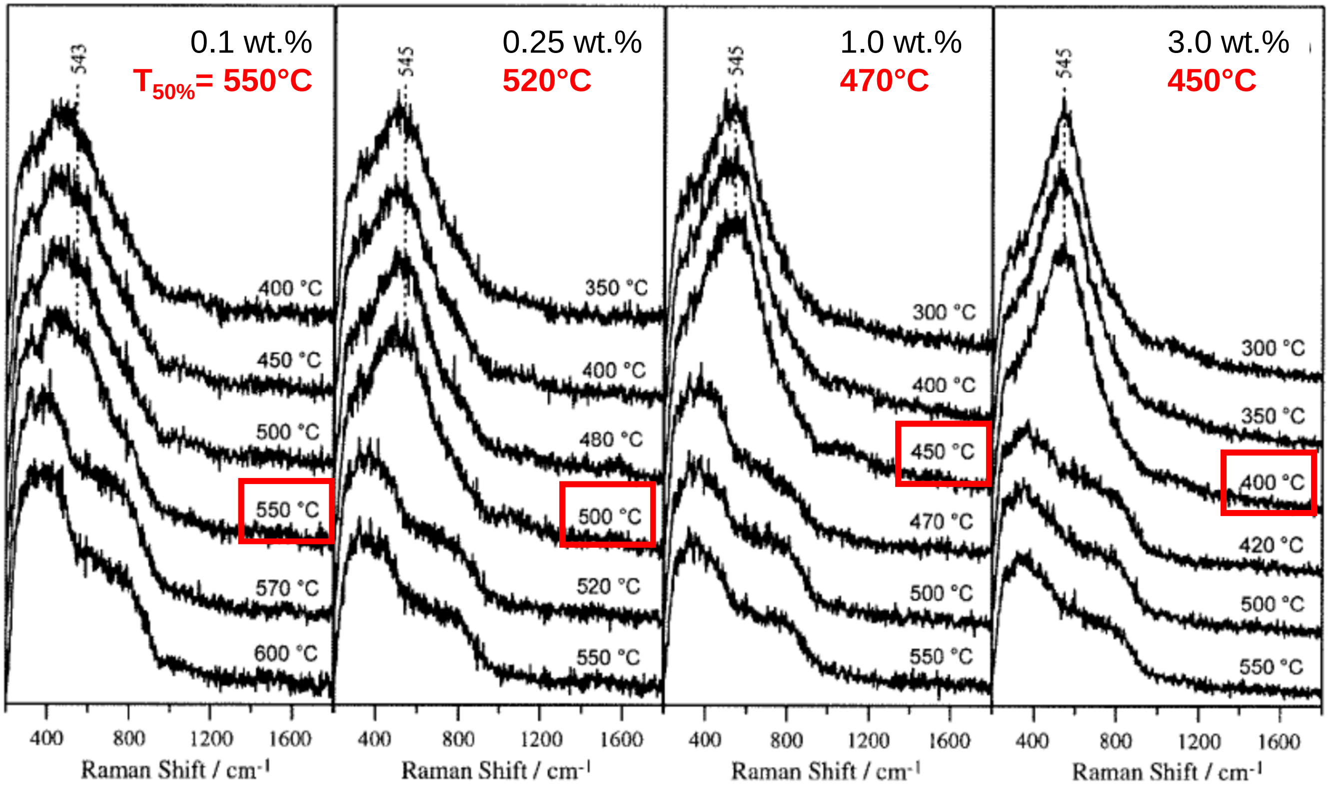
Applications

- Methane partial oxidation over Rh/Al_2O_3

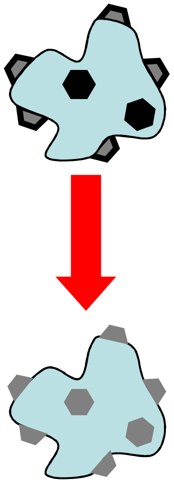
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content
Activity



RhO_x
↓
Rh(0)



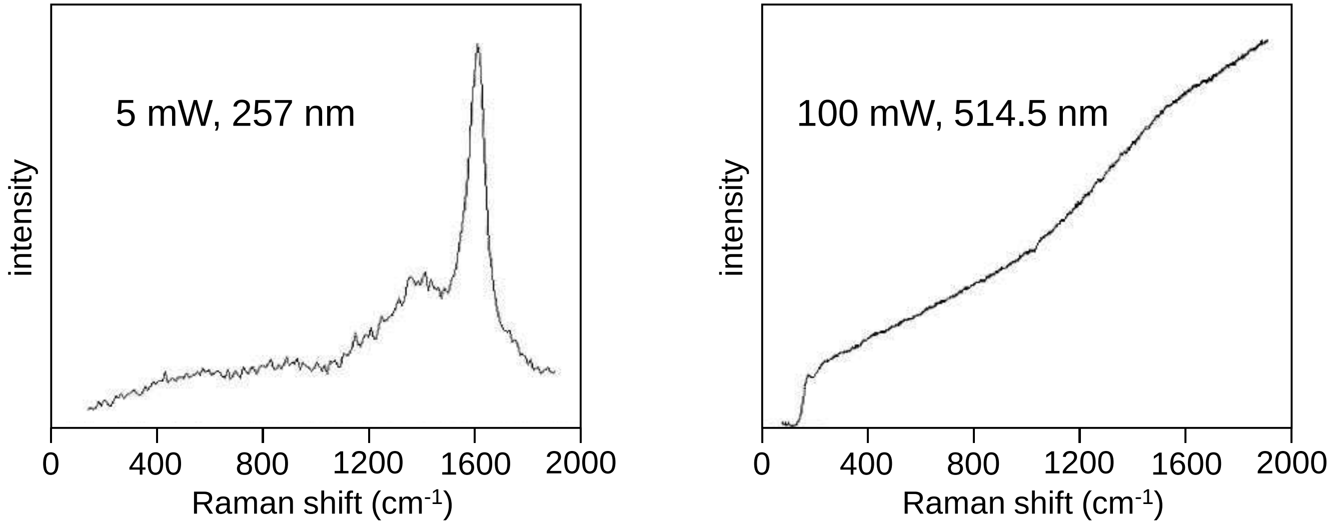
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - ☐ No fluorescence

  (only few molecules fluoresce below 260 nm)

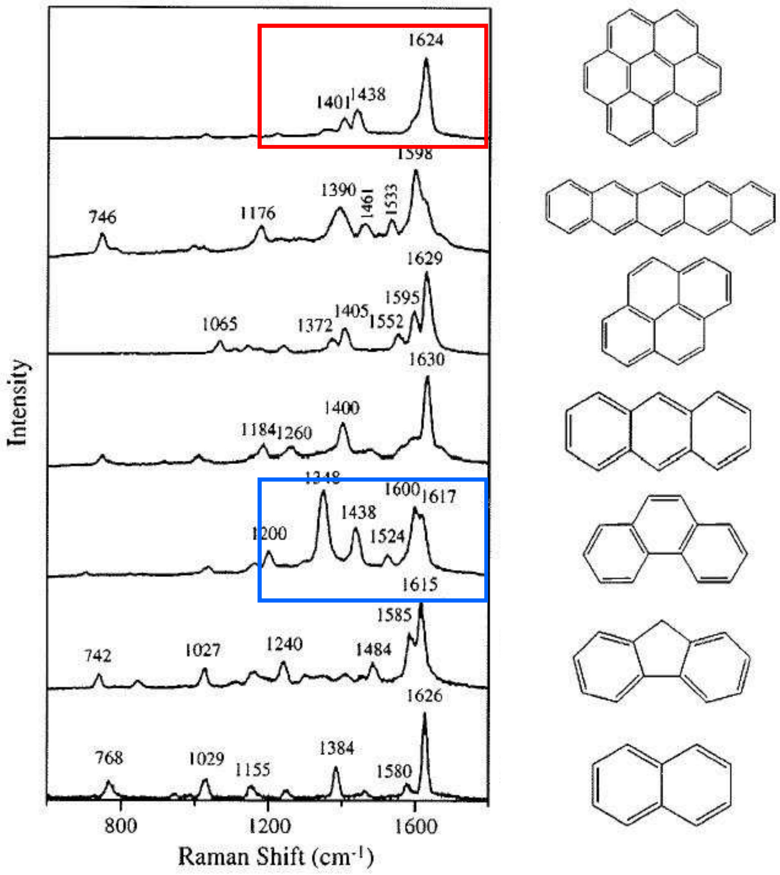
Rh/Al_2O_3, coked 500°C in naphtha

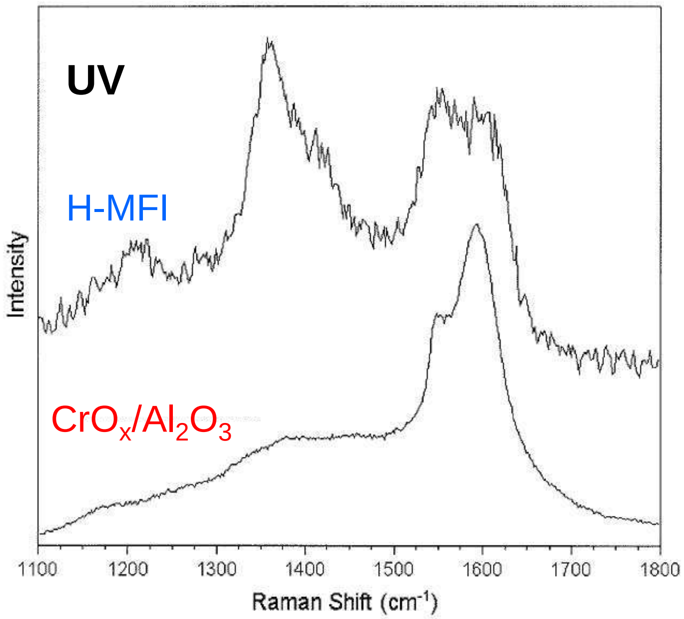


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





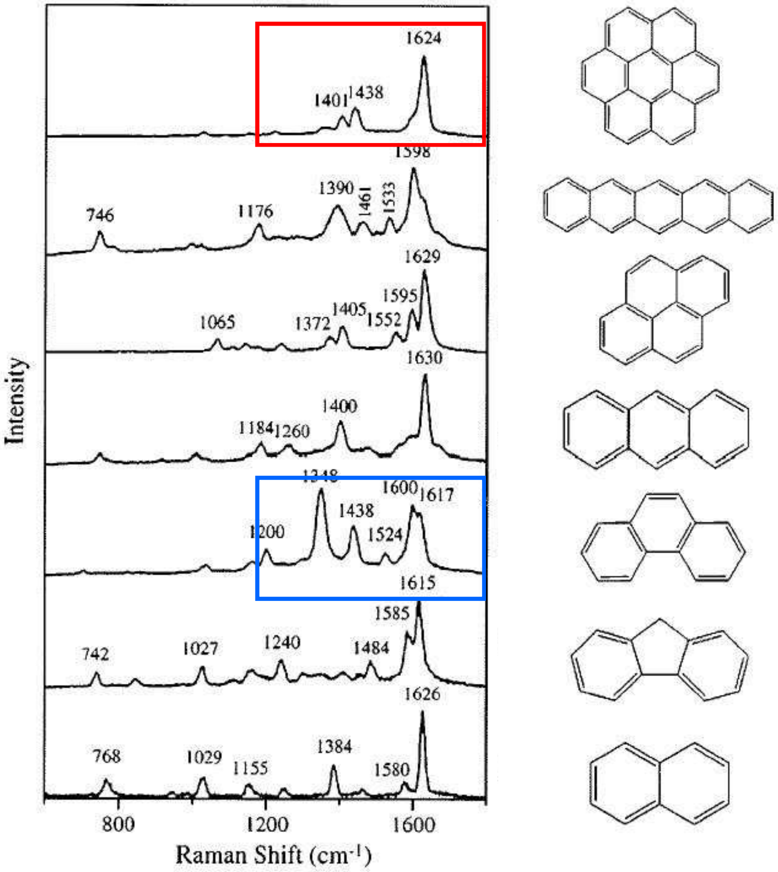
Coke classification
1D topology, chain-like
2D topology, sheet-like

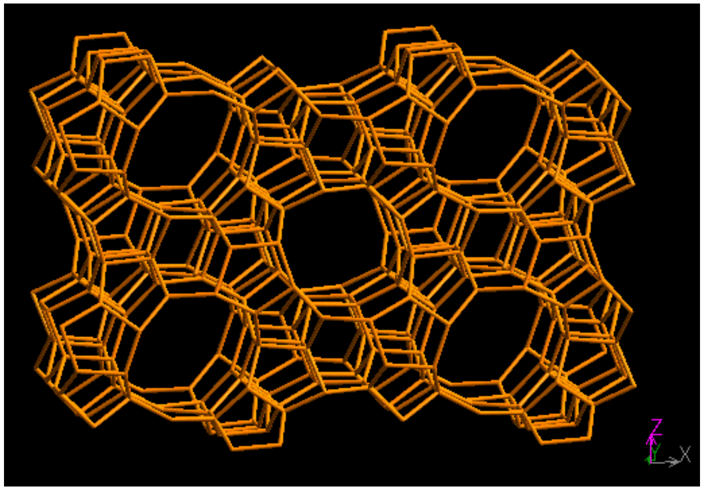
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





Coke classification

1D topology, chain-like

2D topology, sheet-like

Coke from:

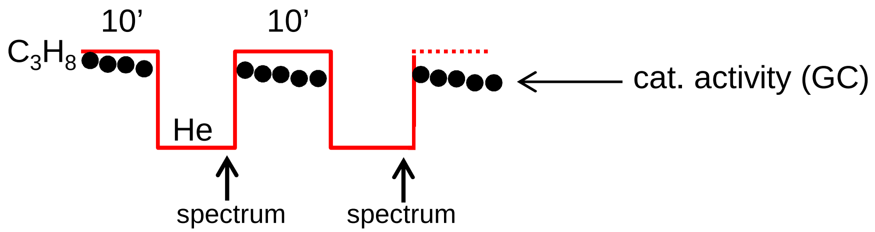
H-MFI: methanol-to-hydrocarbons (MTH)

CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

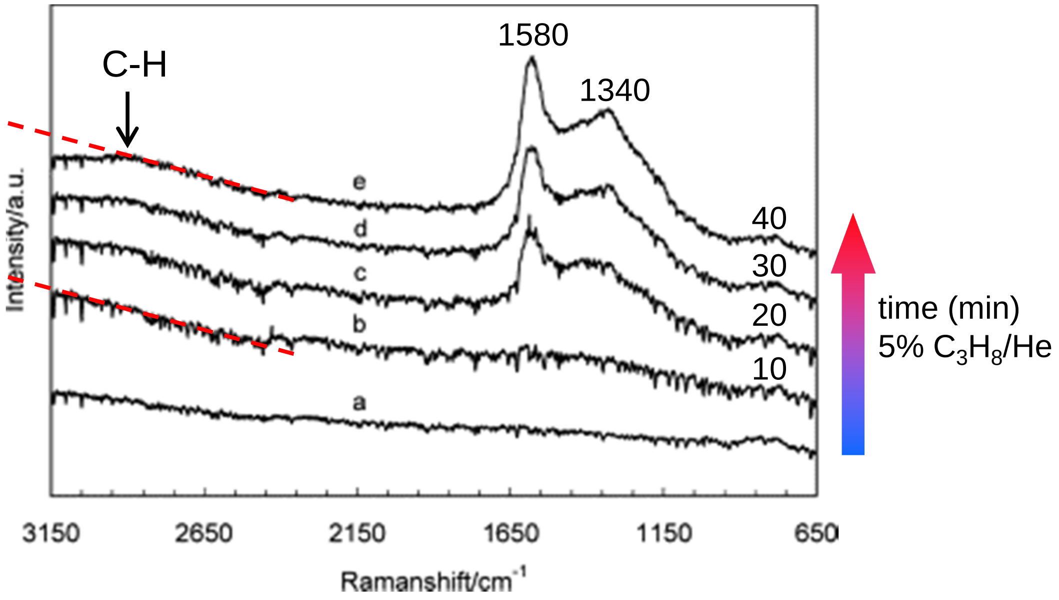
Stair, *Adv. Catal.* **51** (2007) 75

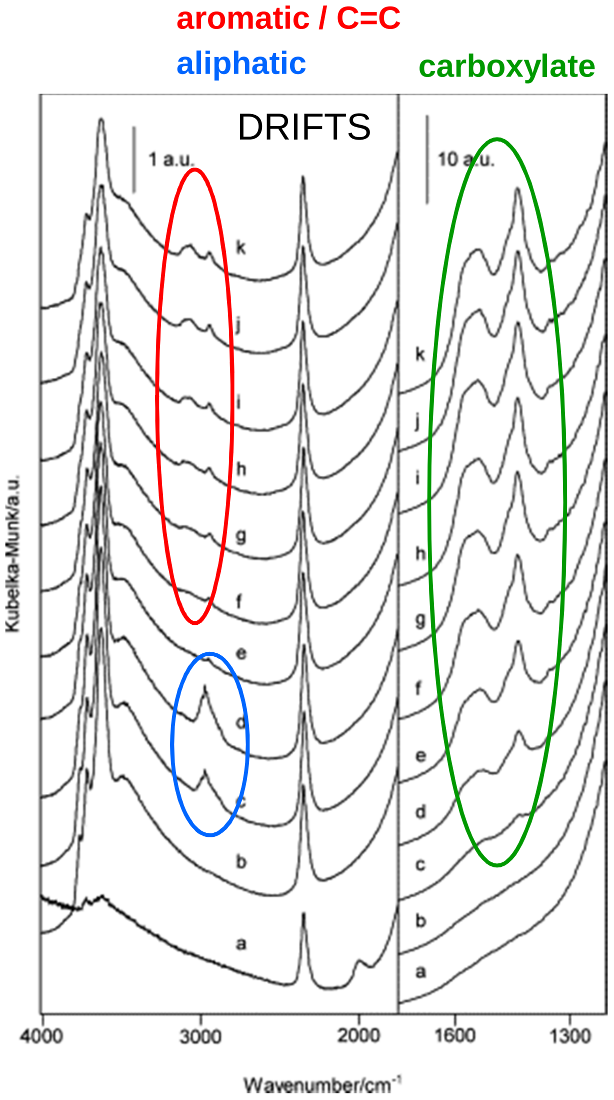
Applications

- Propane dehydrogenation



Cr$_2$O$_3$/Al$_2$O$_3$, 580°C, 514 nm

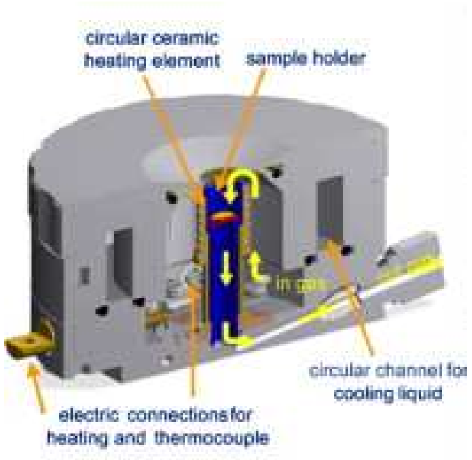


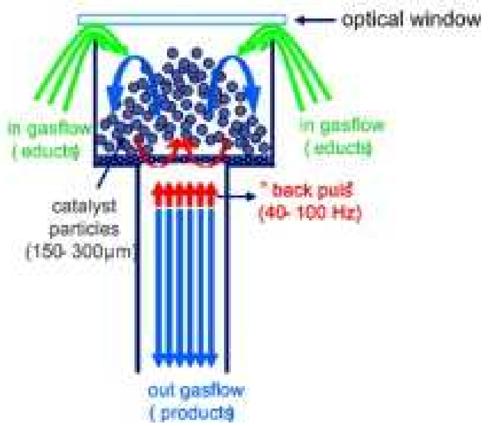


Airaksinen et al., *J. Catal.* **230** (2005) 507

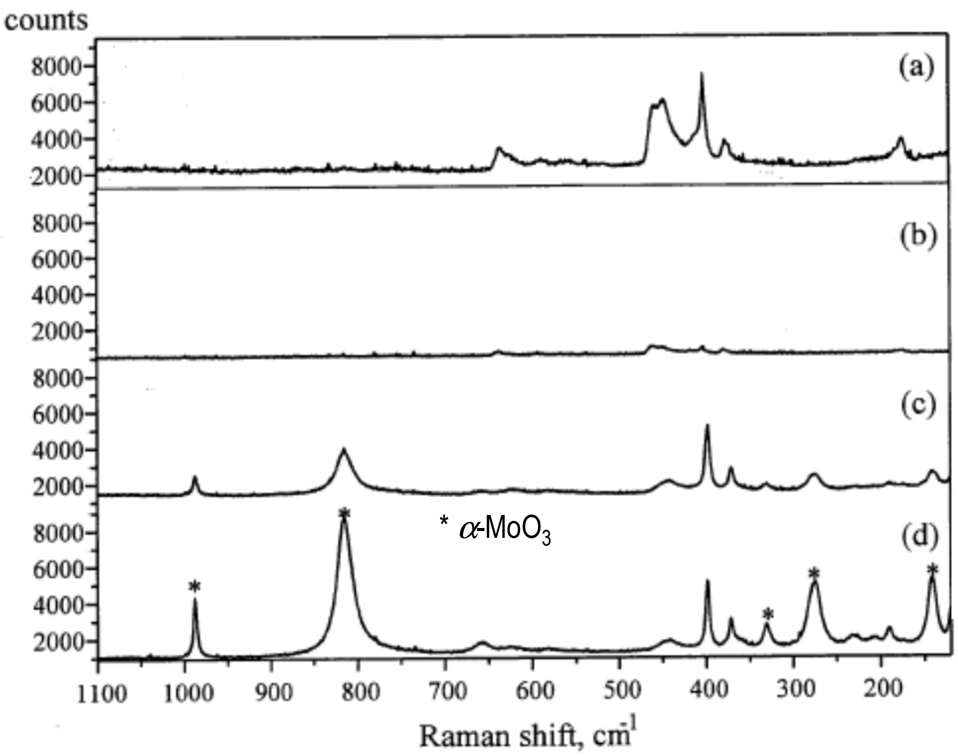
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min full power, FB

MoS_2, 6 min 1/8 power

MoS_2, 1 min full power

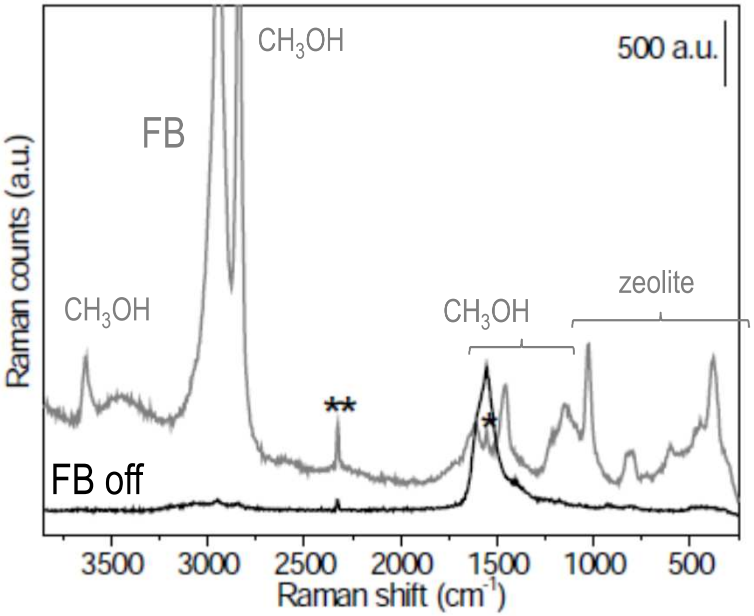
MoS_2, 6 min full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

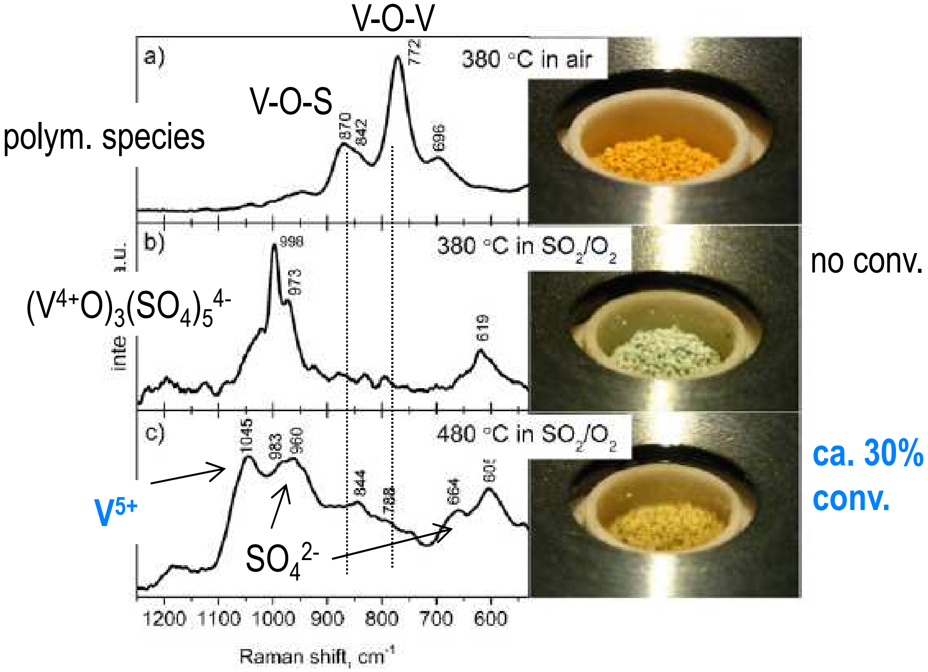
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

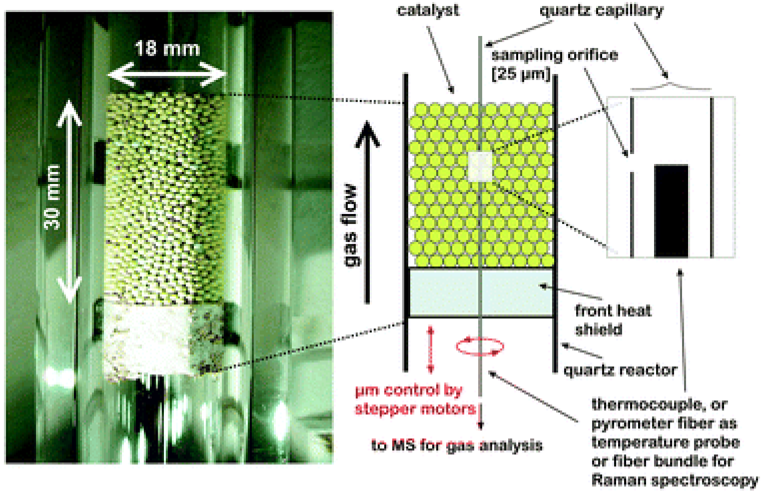


active species: mono- & dimeric V^{5+} oxosulfate species

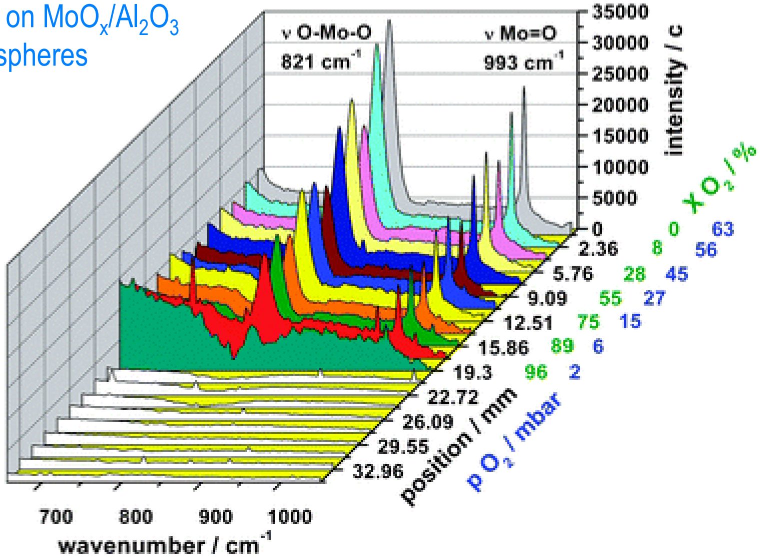
Beato et al., *Catal. Today* 205 (2013) 128

Applications

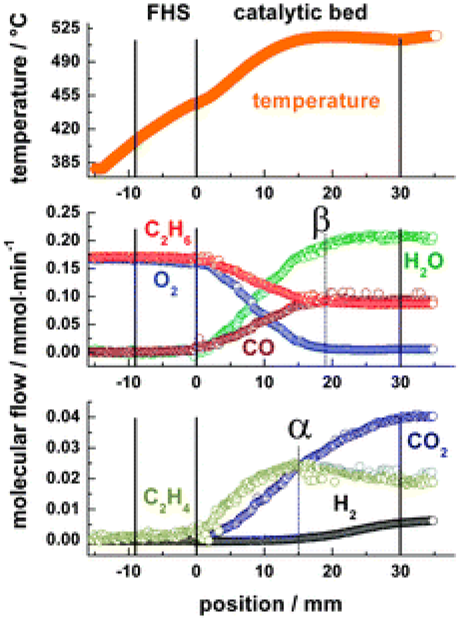
- Fixed bed reactor

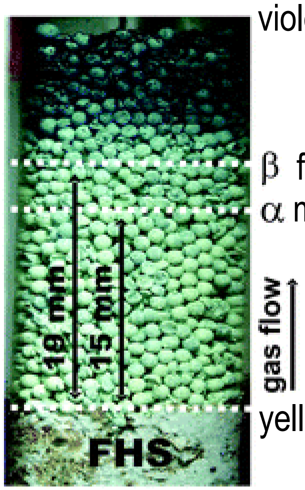


ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm





violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

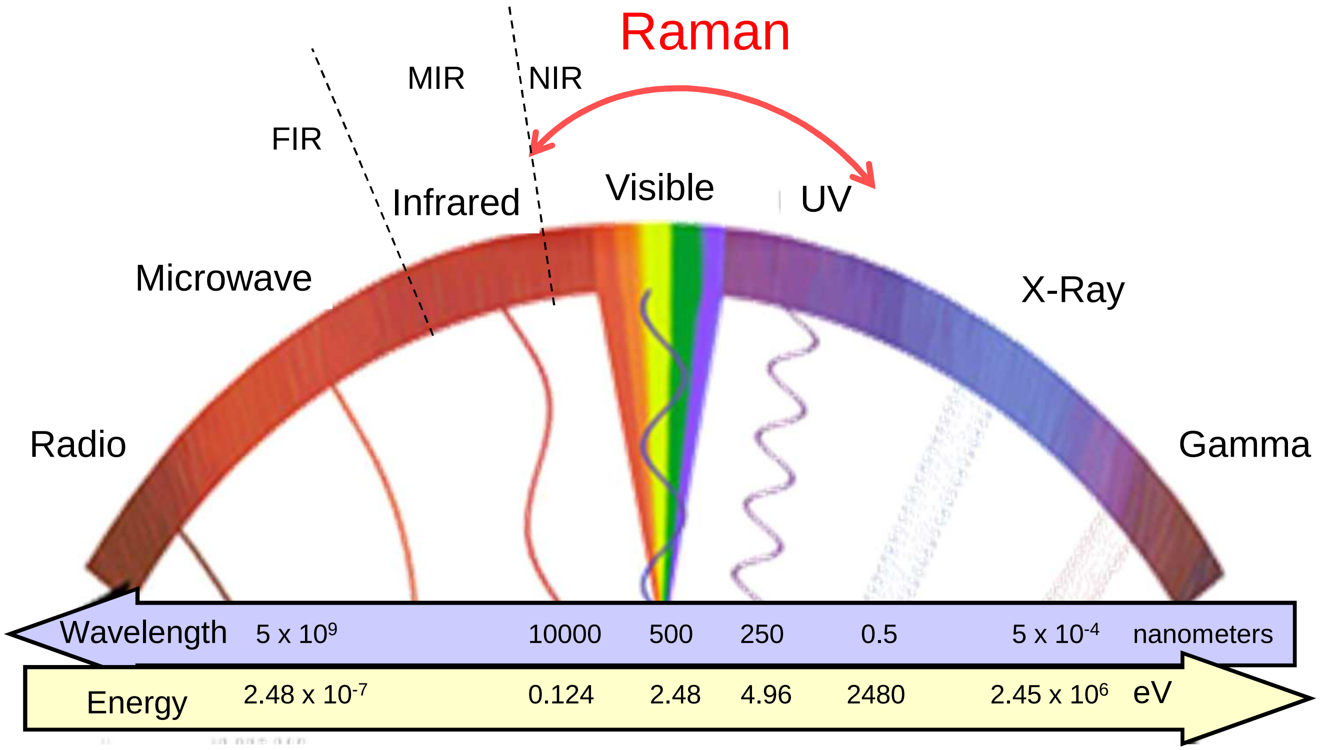
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

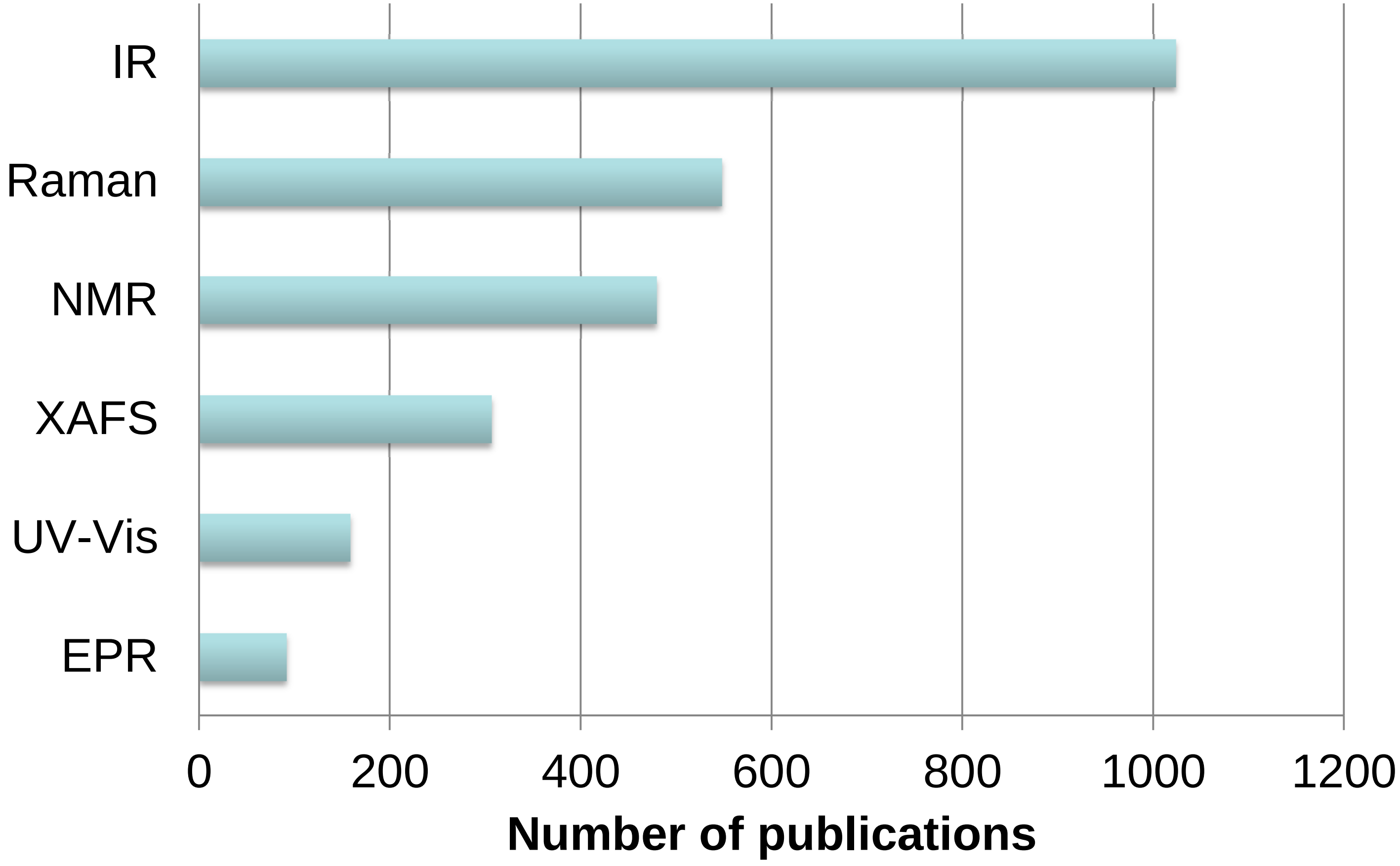
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

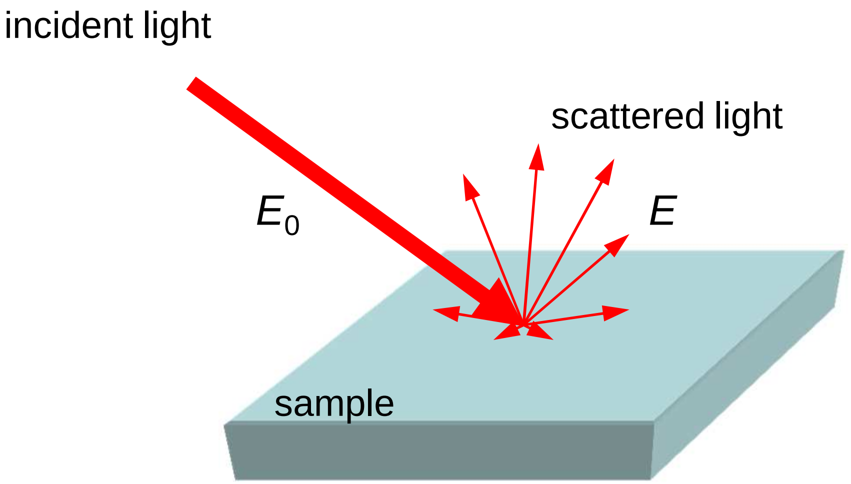


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib}t)]E_0\cos(2\pi\nu_0 t)$$

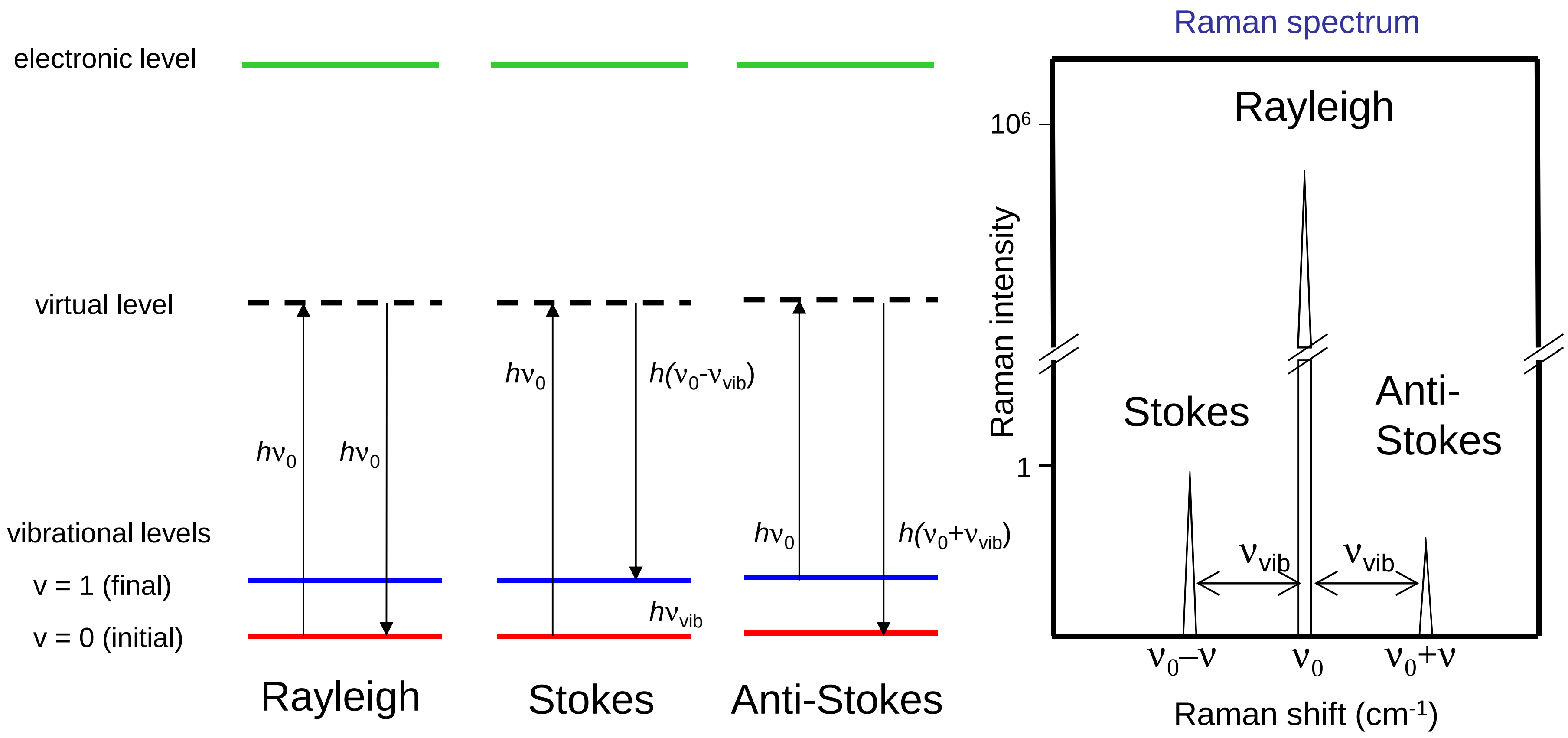
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib}t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\text{ (Anti-Stokes)}}{I\text{ (Stokes)}} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

- 4th power of ν (4th power law)
- 2nd power of $\Delta\alpha$
  - properties of molecules
  - strength of bonds

↓

covalent bond STRONG bands (catalysis!)

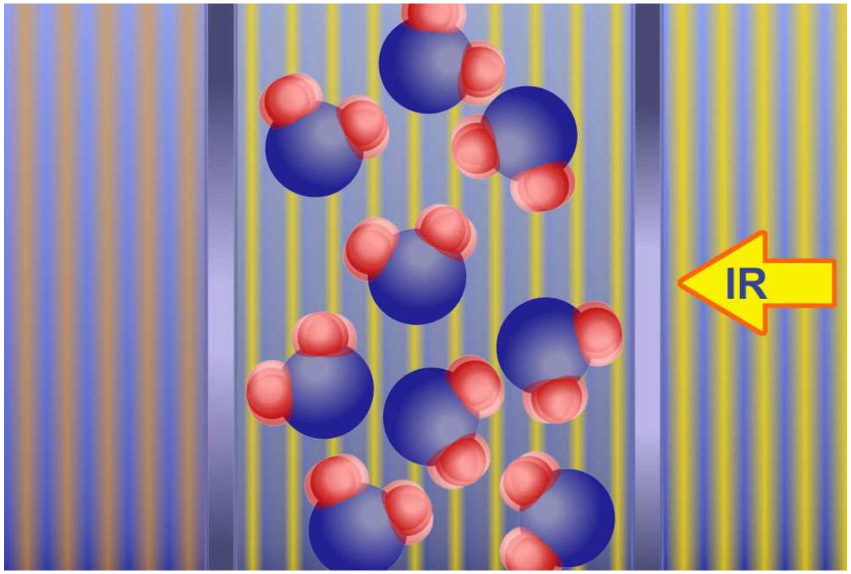
ionic bond WEAK bands

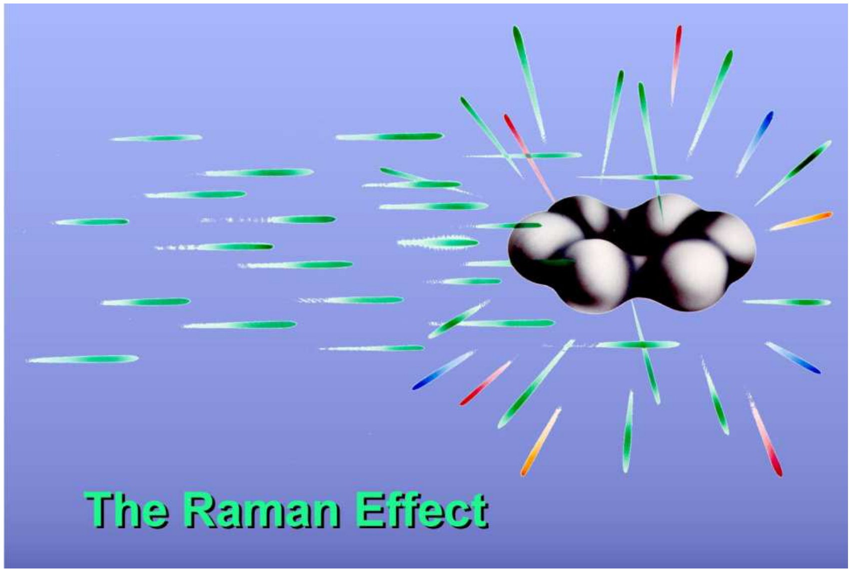
- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

Raman *vs.* Infrared

Infrared

Raman





Absorption of IR light

Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

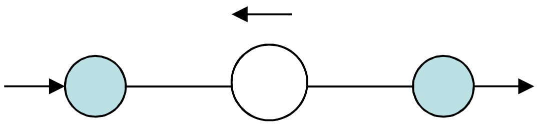
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - large electron clouds
  - not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

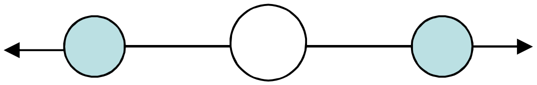
Raman *vs.* Infrared

CO_2



ν_{as}

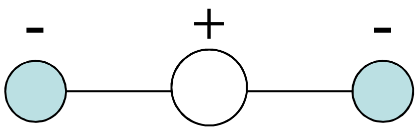
2349 cm^{-1}



ν_s

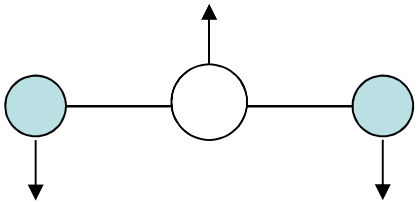
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



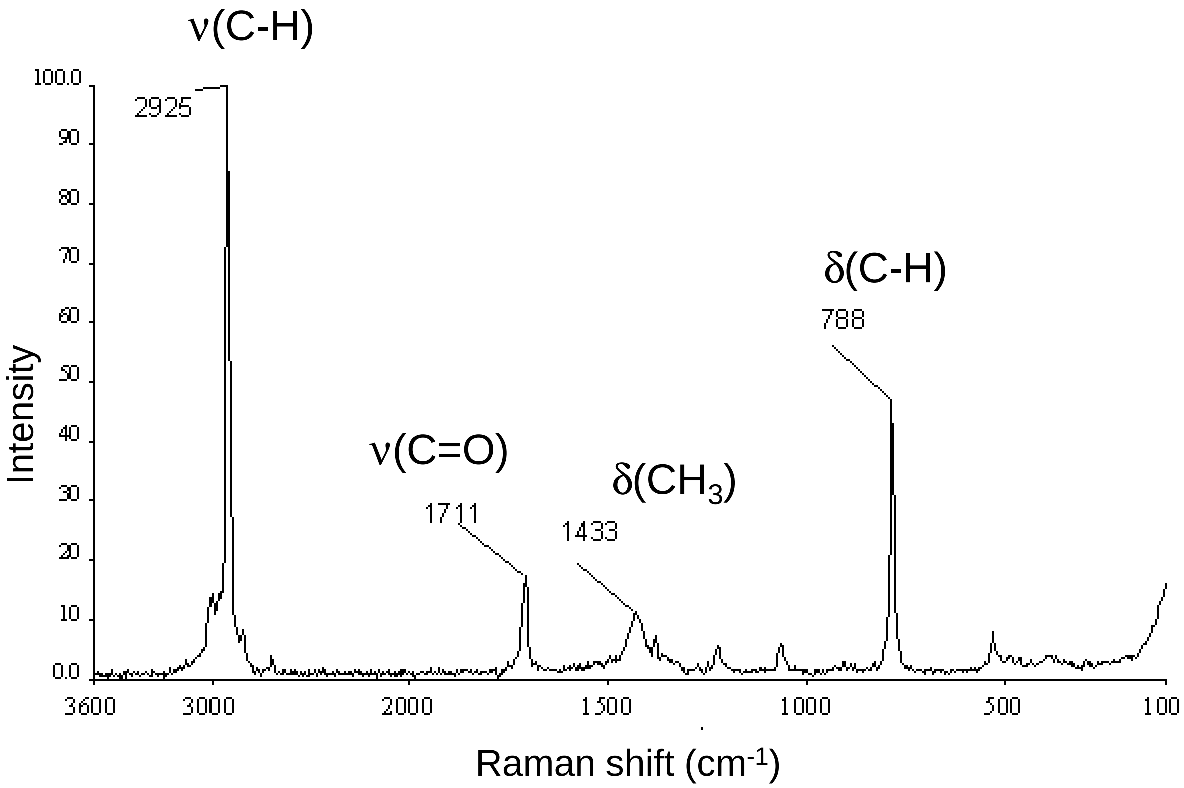
δ

667 cm^{-1}

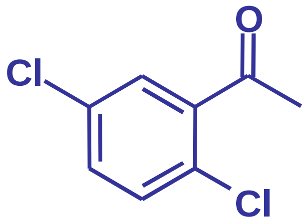
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



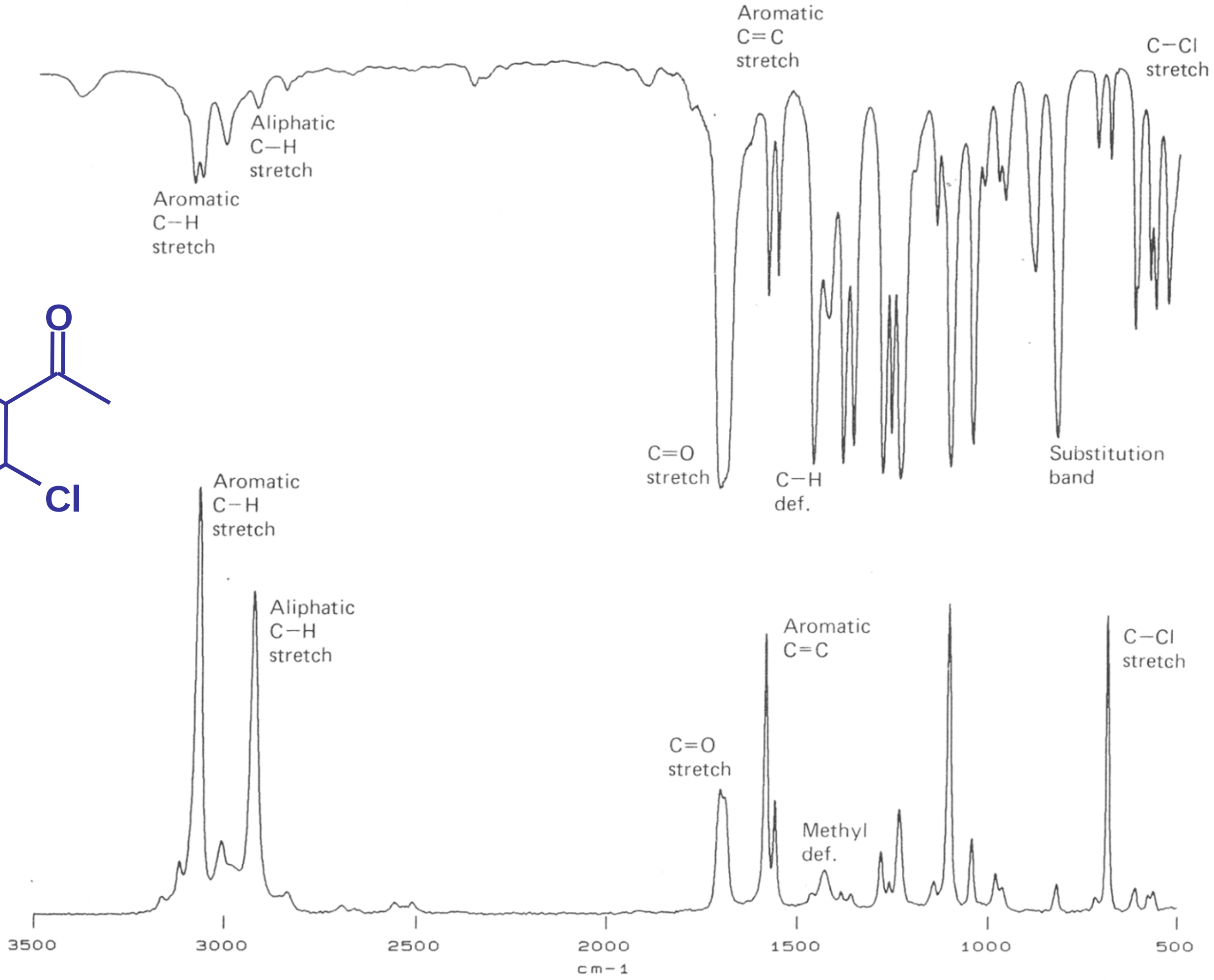


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

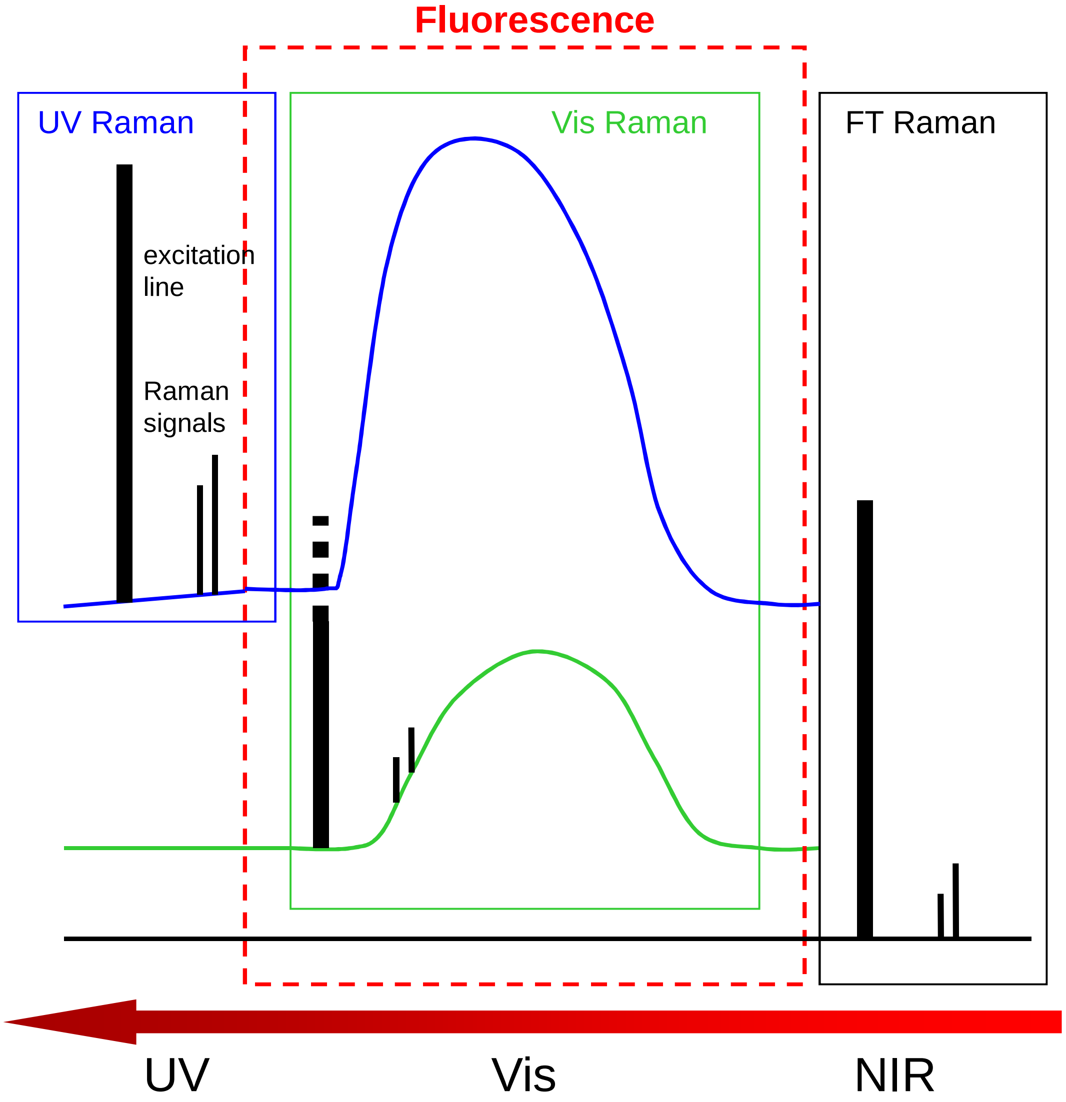
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 µm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

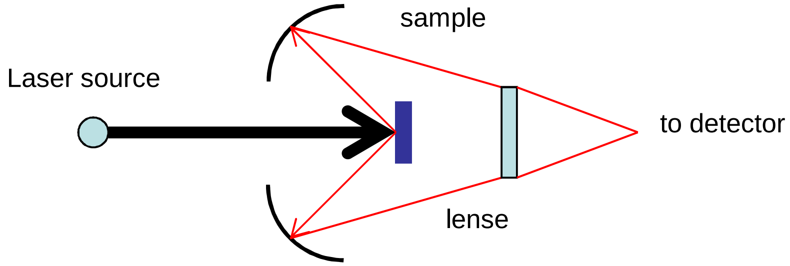
Fluorescence proportional to ν

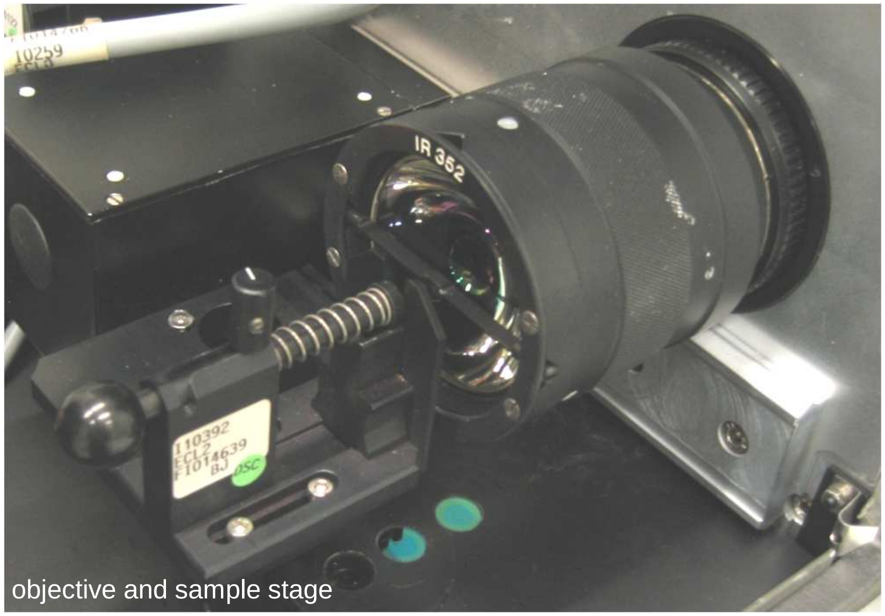
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

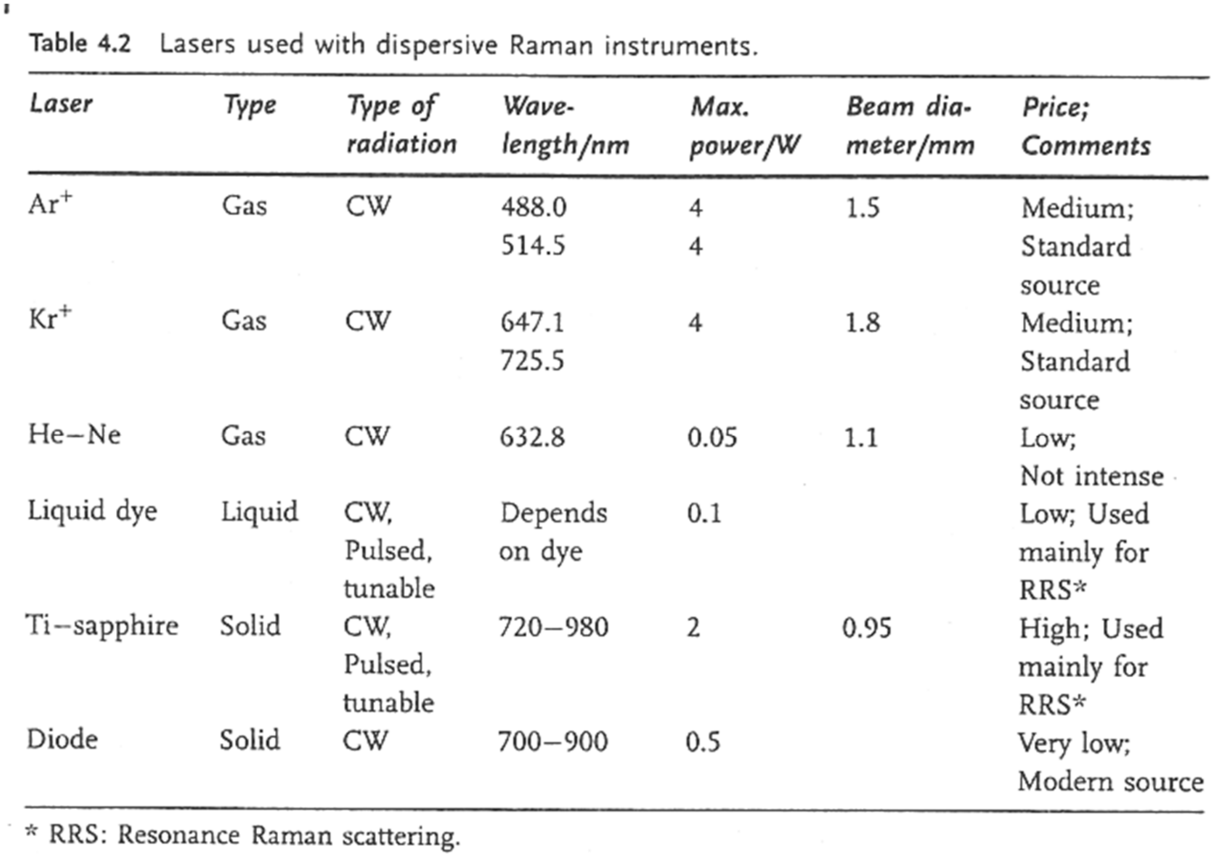


Table 4.2 Lasers used with dispersive Raman instruments.

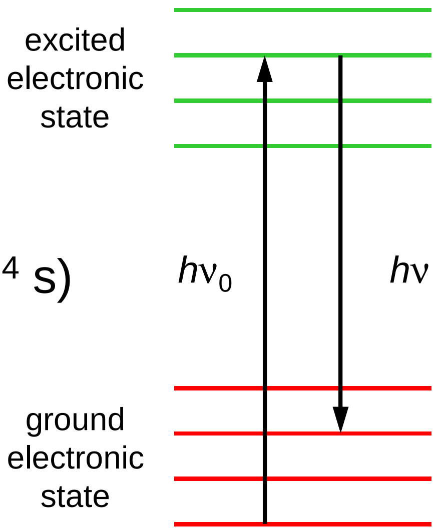
Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

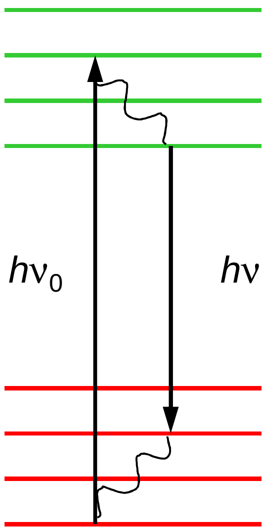
Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited

fast (10^{-14} s)



Resonance Raman scattering



Fluorescence

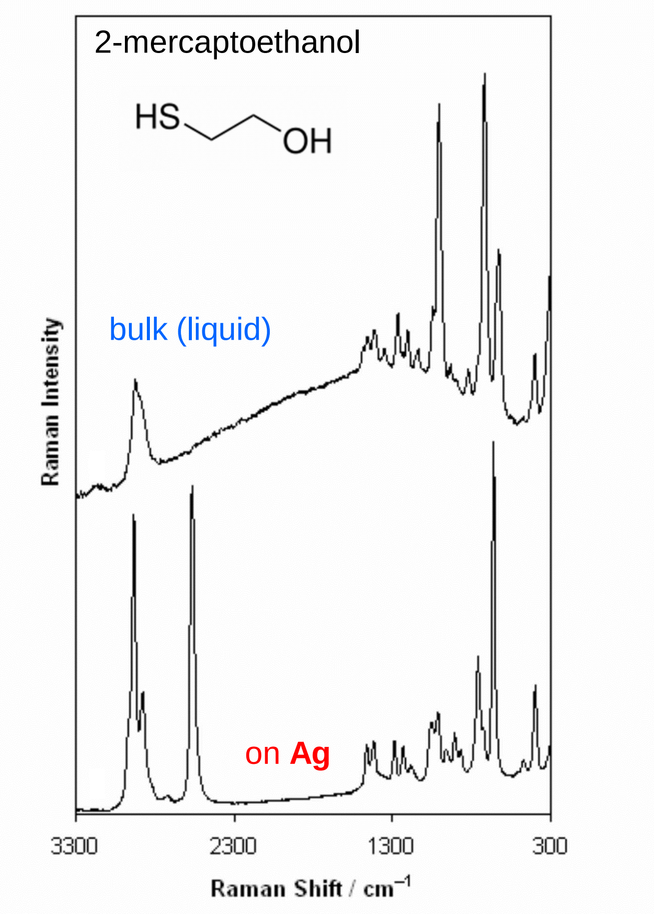
slow (10^{-9}–10^{-6} s)

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

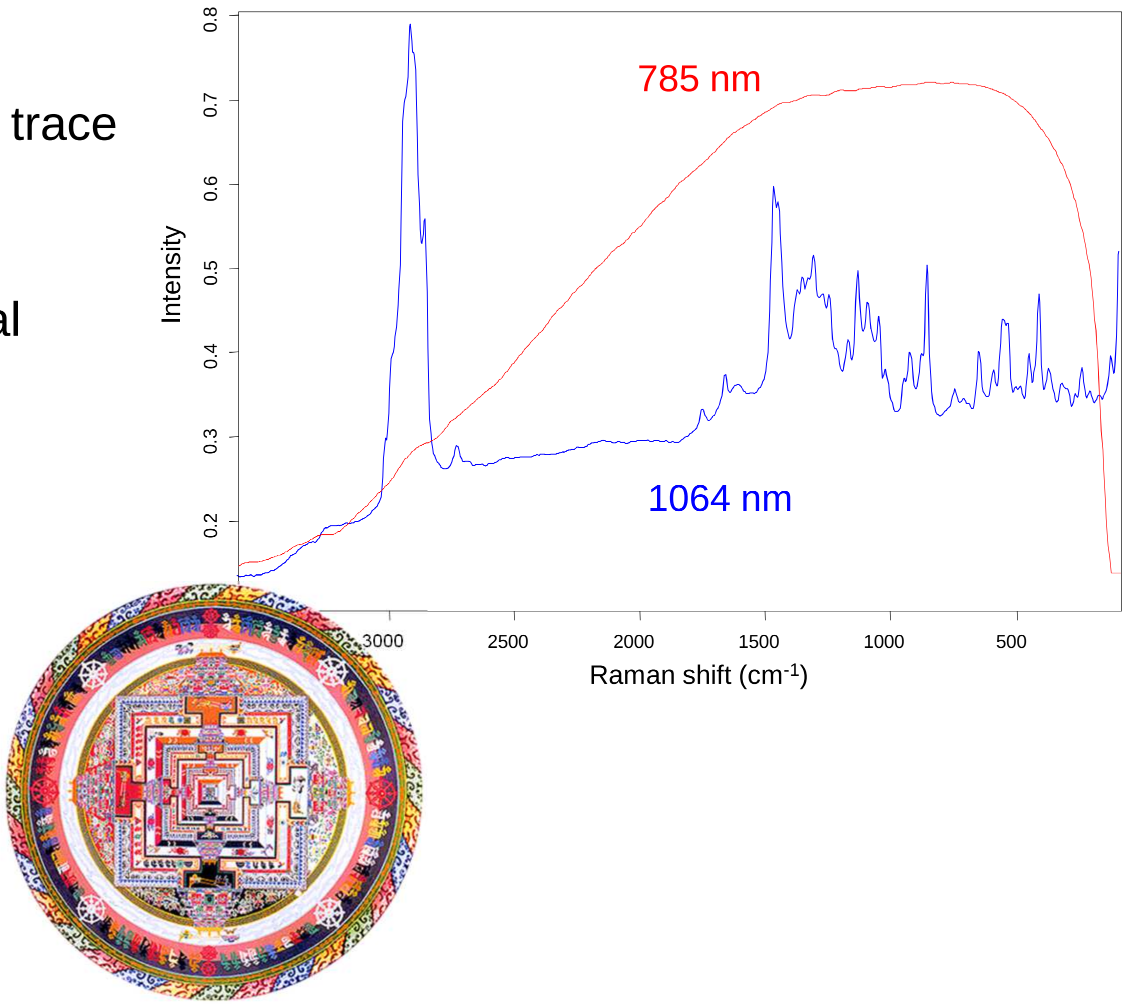
- Remarks:

❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



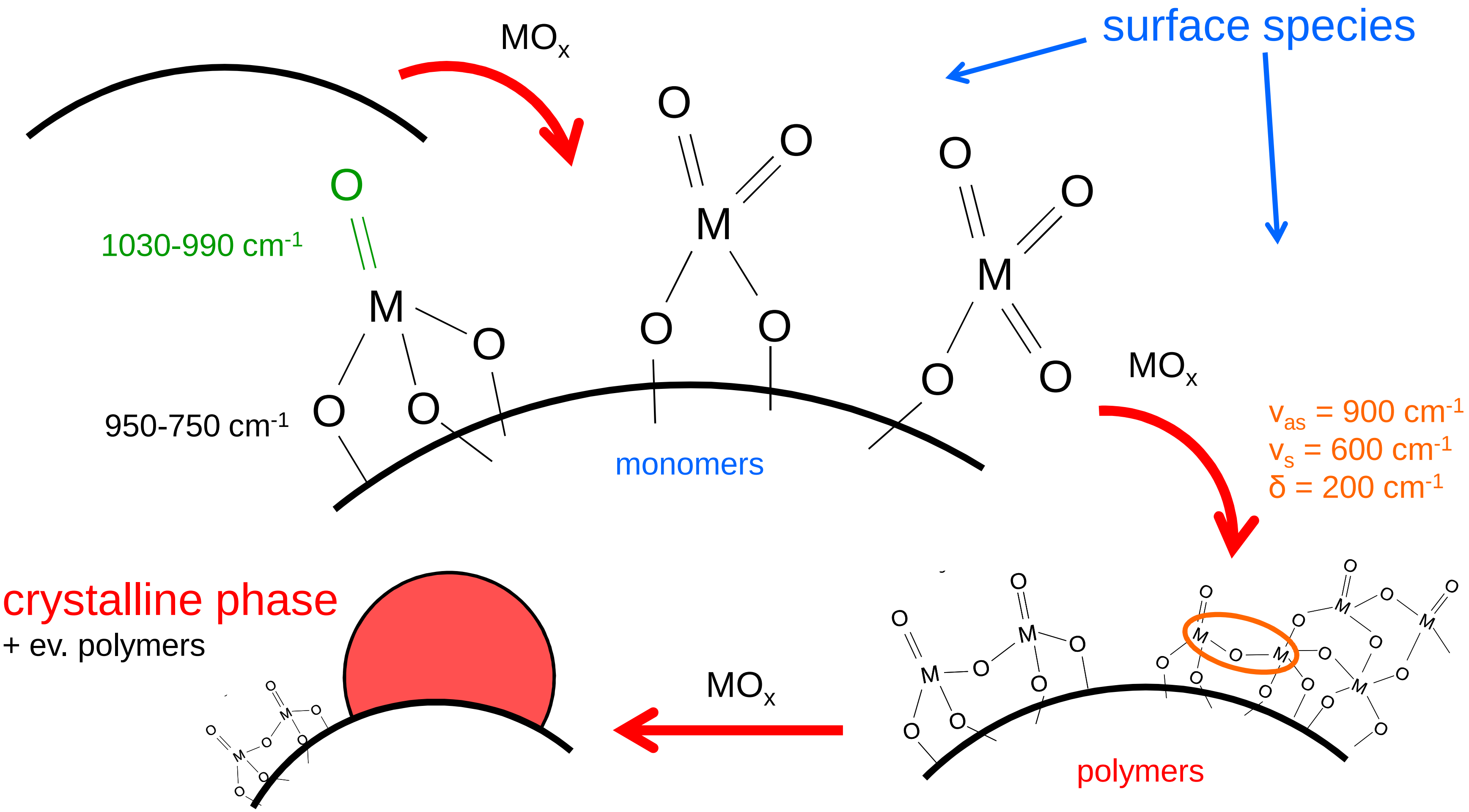
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



surface species

MO_x

1030-990 cm^{-1}

950-750 cm^{-1}

monomers

MO_x

$\nu_{as} = 900\ cm^{-1}$
$\nu_s = 600\ cm^{-1}$
$\delta = 200\ cm^{-1}$

polymers

MO_x

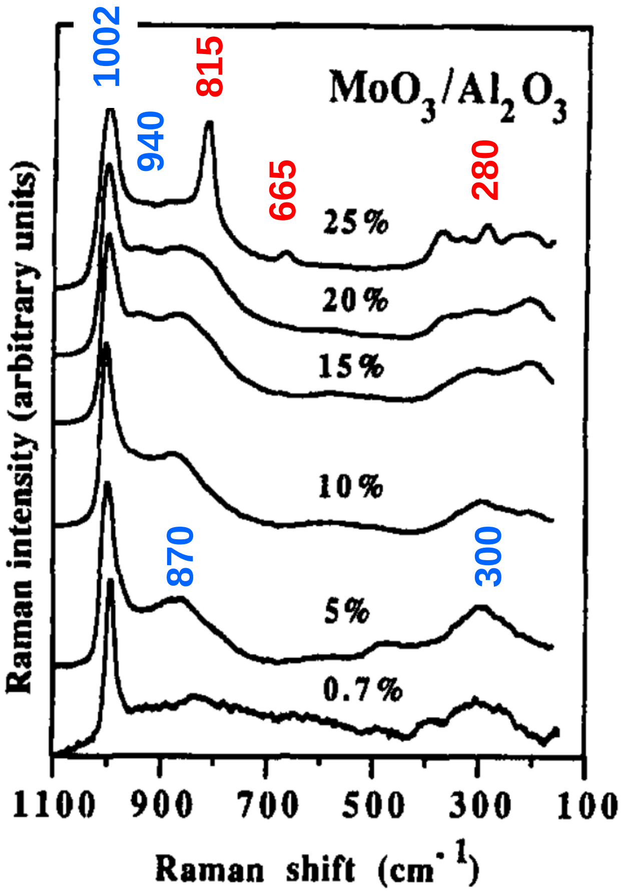
crystalline phase
+ ev. polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



surface MoO_3

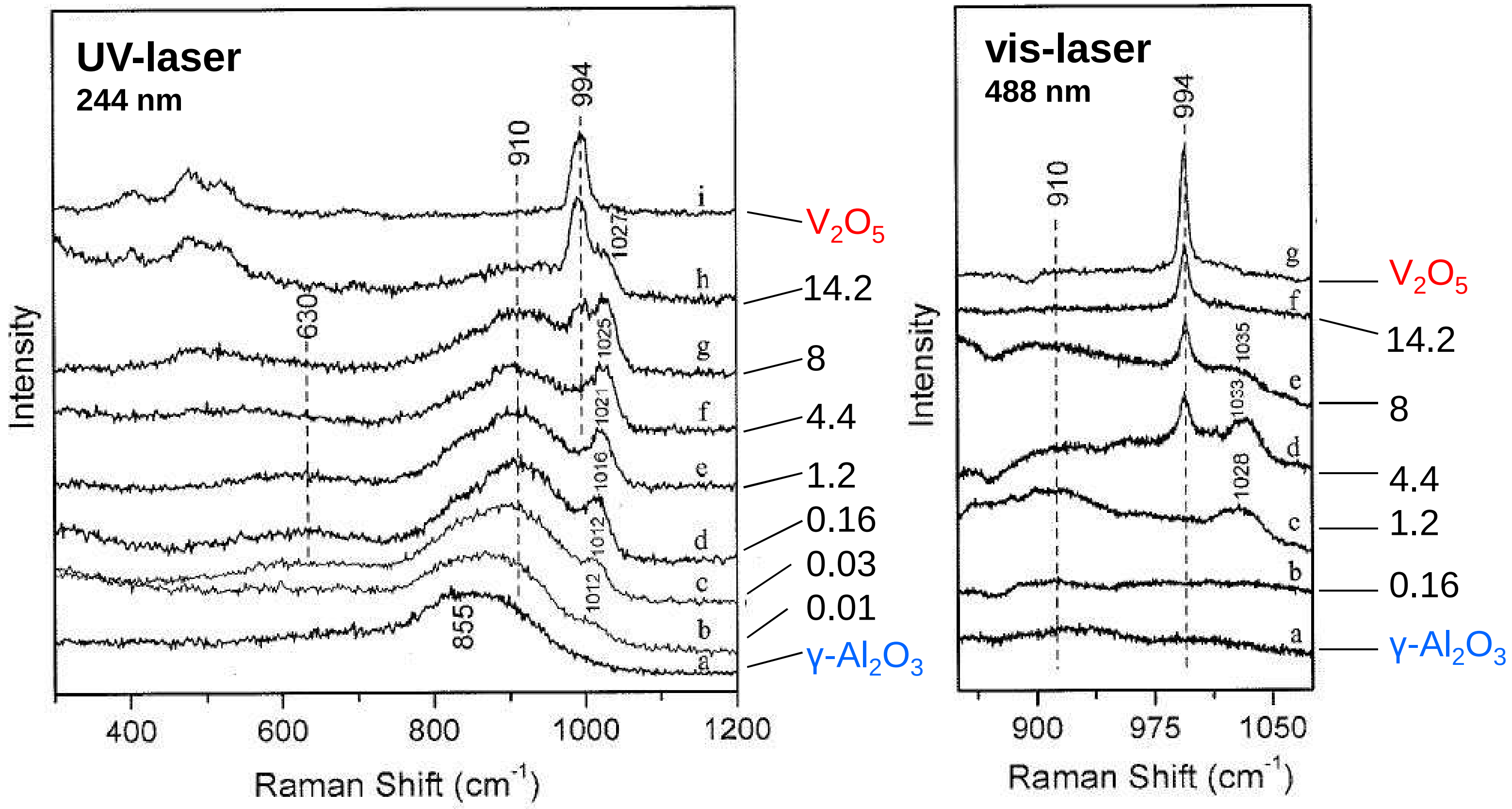
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

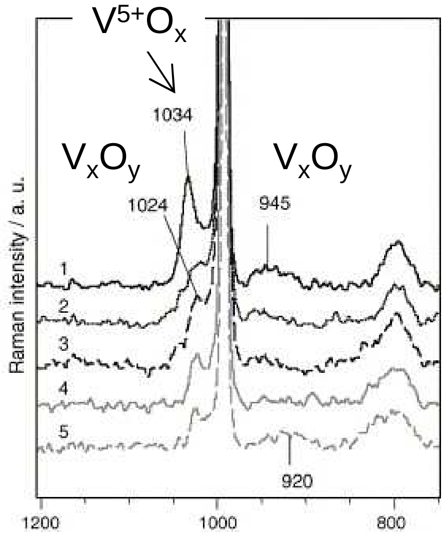
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

Applications

- Reactivity of V/TiO_2 after oxidative treatment



$V^{5+}O_x$

V_xO_y

V_xO_y

air flow @ 450°C

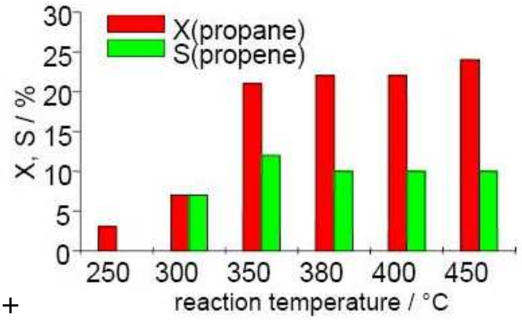
O_2/C_3H_8 @ 20°C

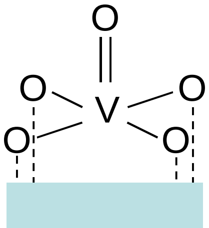
@ 100°C

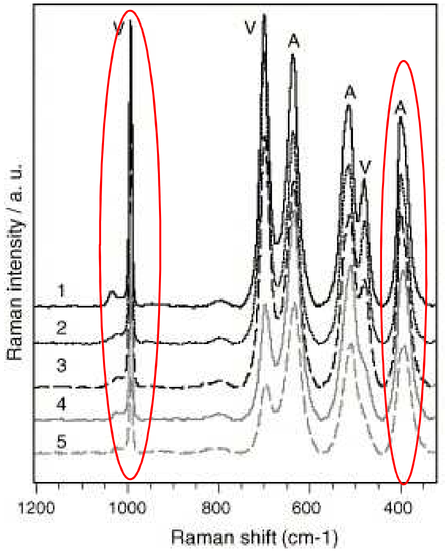
@ 150°C

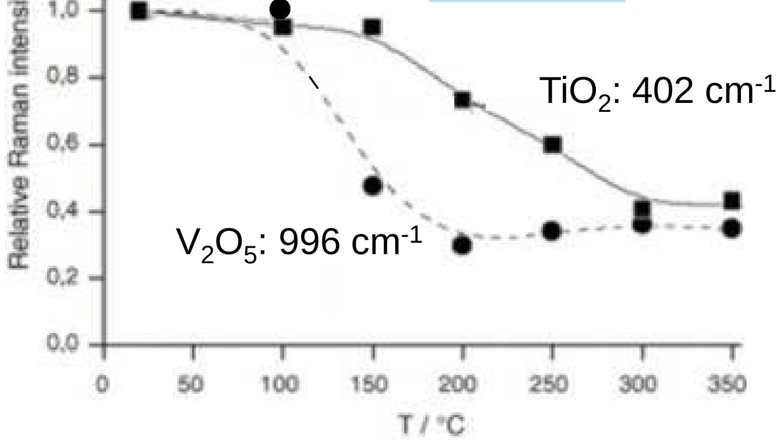
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









TiO_2: 402 cm^{-1}

V_2O_5: 996 cm^{-1}

Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

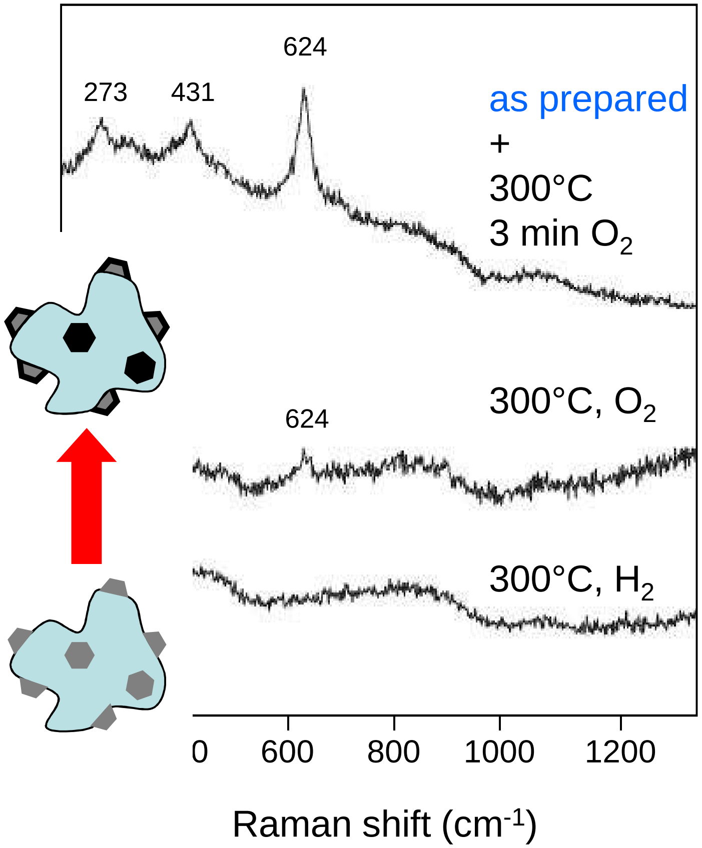
M/MO$_X$ (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

Question: what is the state of Pd during reaction?

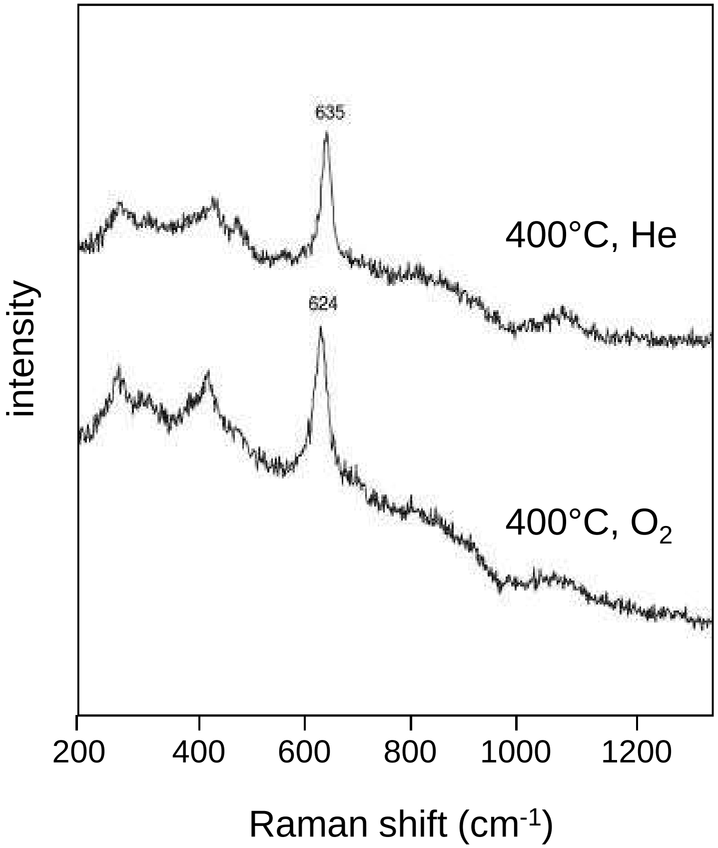
Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

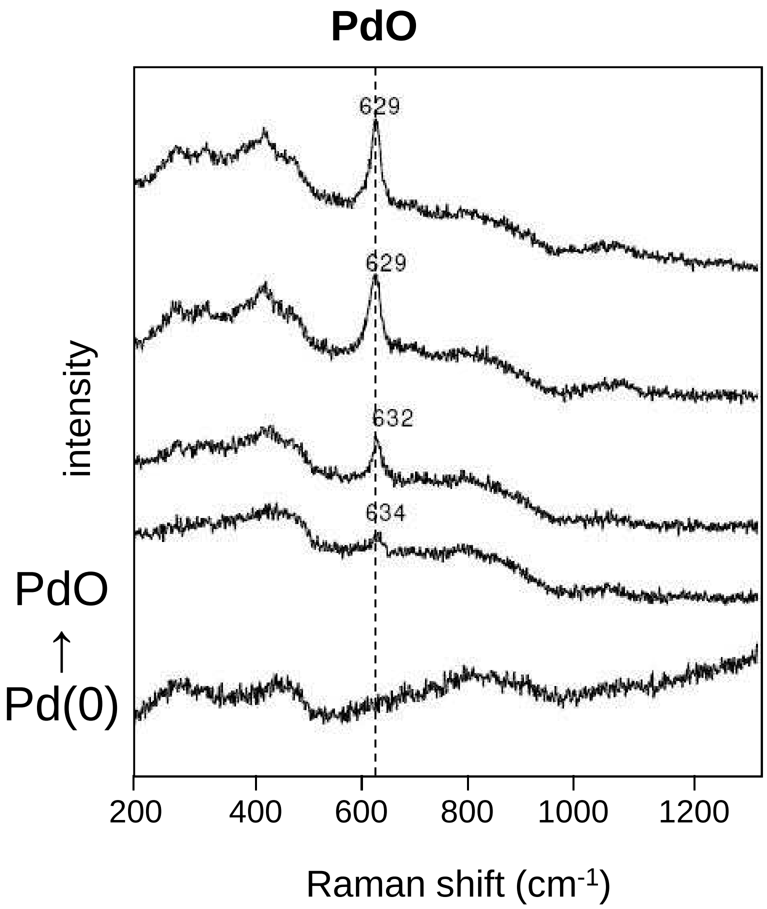


Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

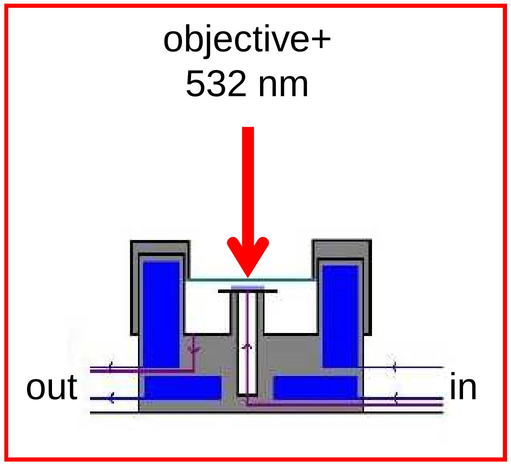
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



	CH_4 conv.
500°C	**24 %**
450°C	**15 %**
425°C	**4 %**
400°C	**2 %**
400°C, H_2 reduced Pd	

↑ feed CH_4/O_2 (1:10)

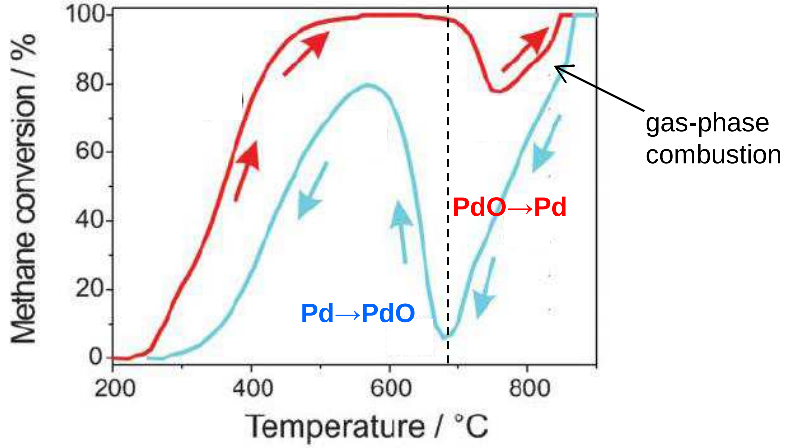
near PdO mode

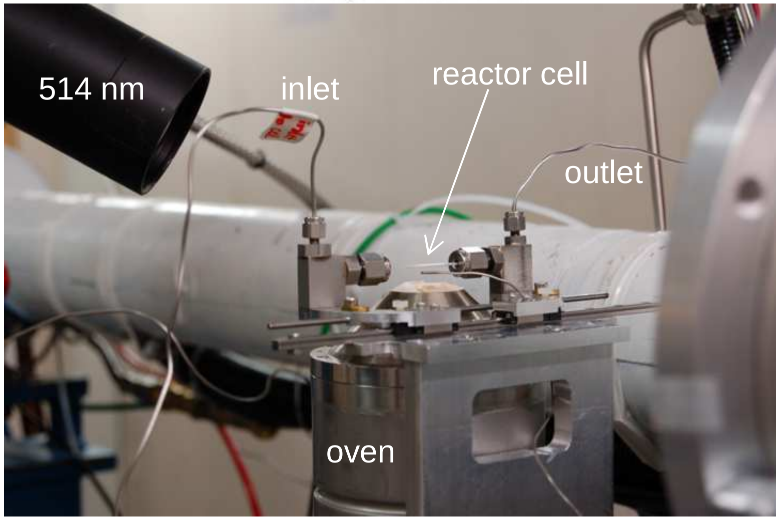


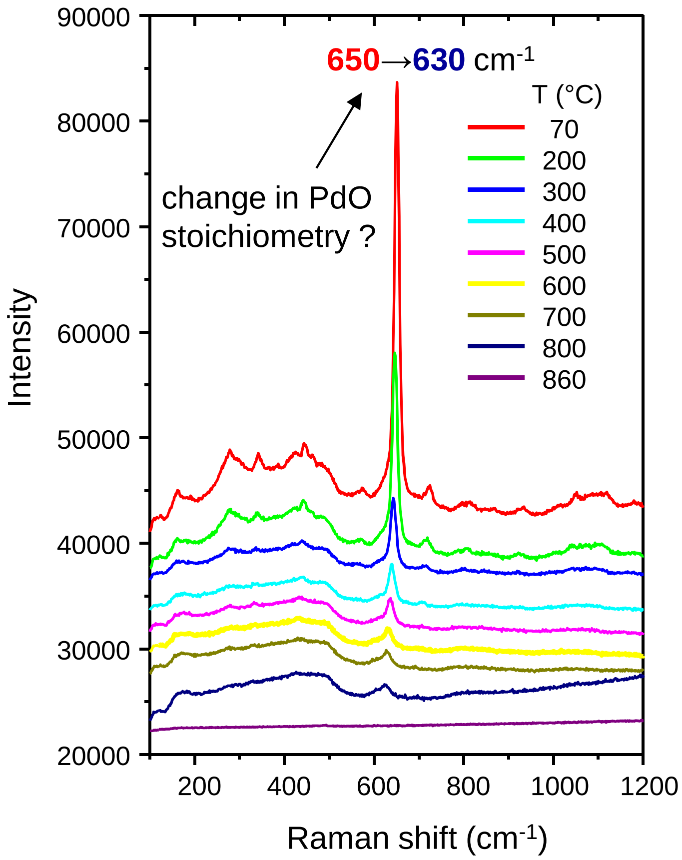
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

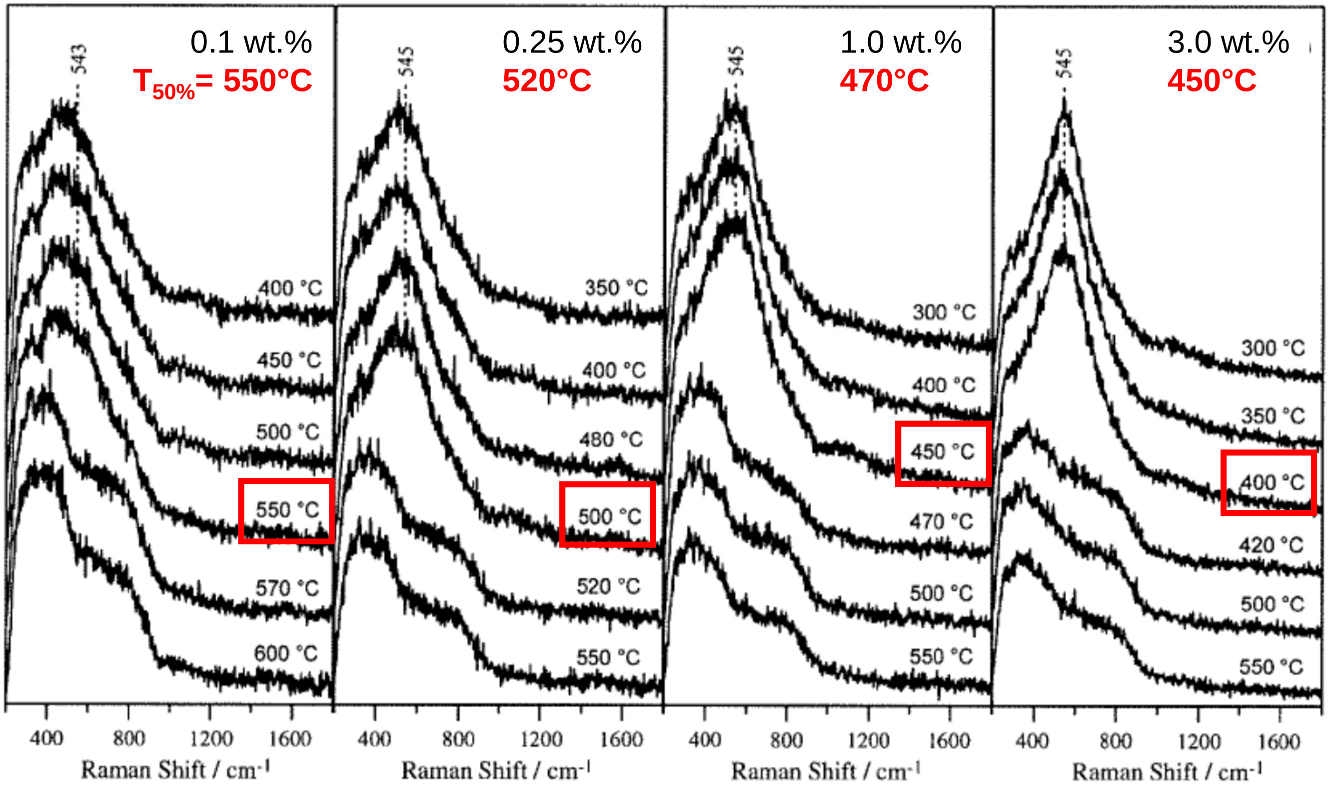
Applications

- Methane partial oxidation over Rh/Al_2O_3

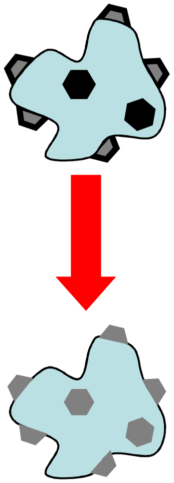
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content
Activity



RhO_x
↓
Rh(0)



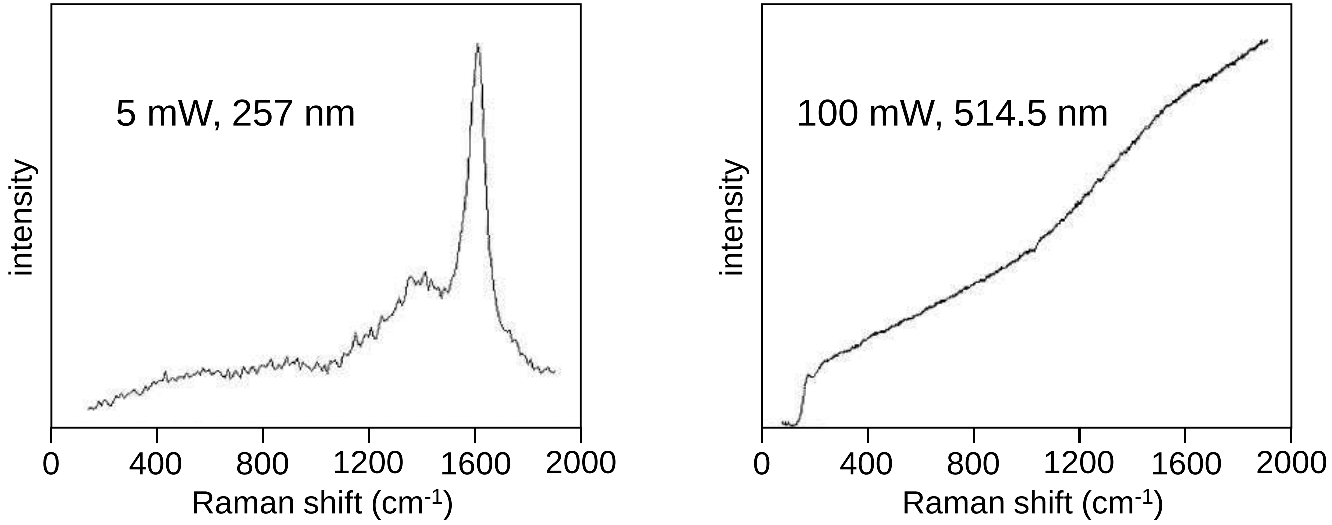
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

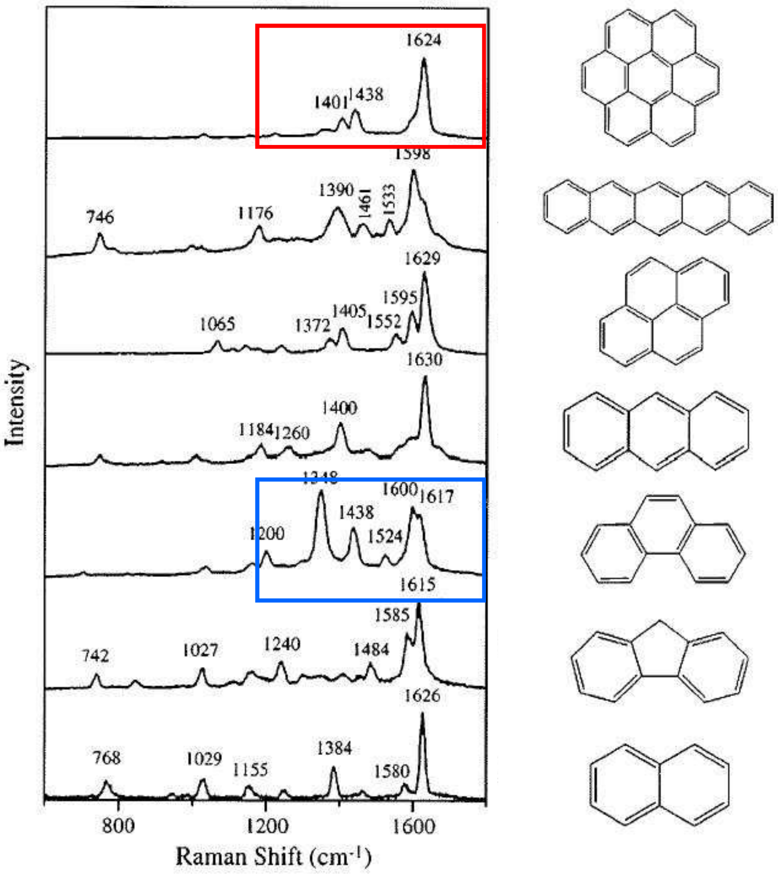
Rh/Al_2O_3, coked 500°C in naphtha

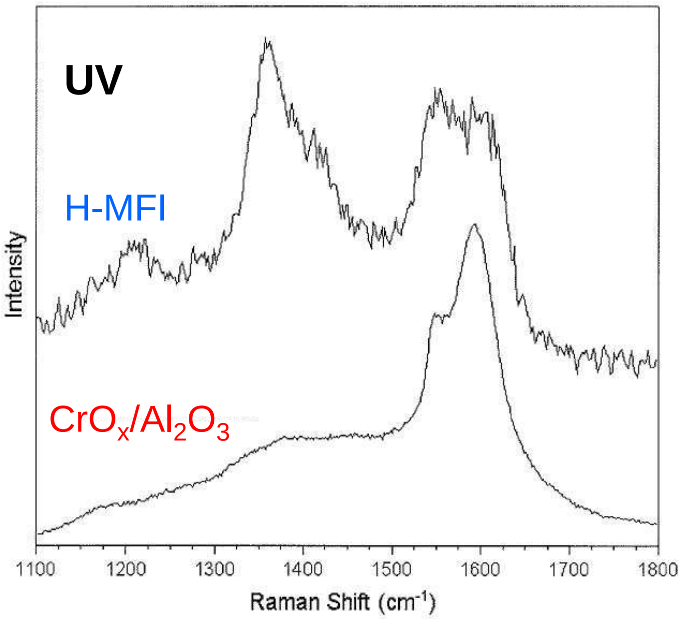


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





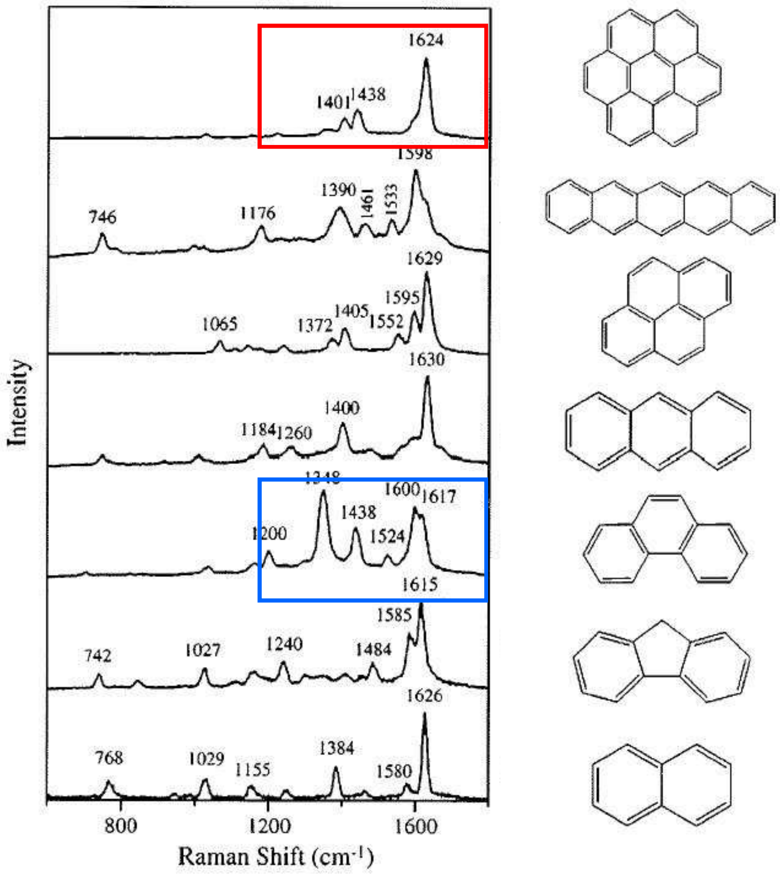
Coke classification
1D topology, chain-like
2D topology, sheet-like

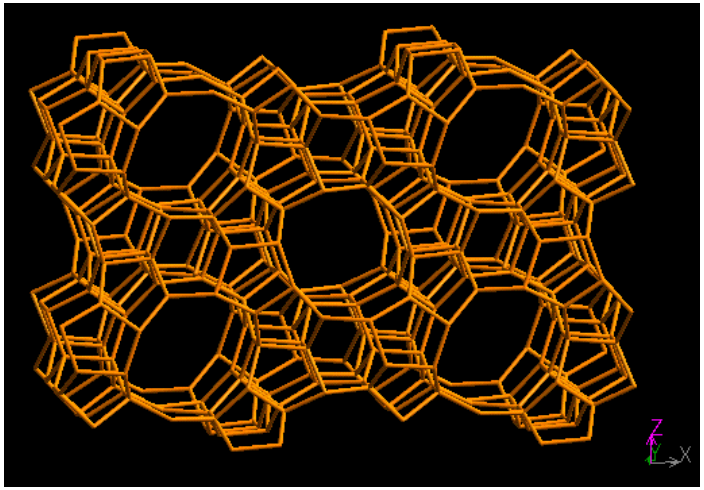
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





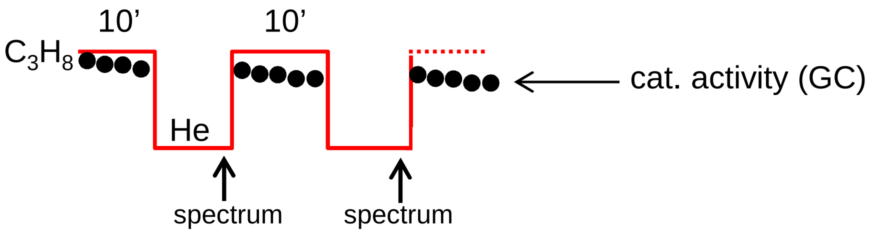
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- Propane dehydrogenation



10’

10’

C_3H_8

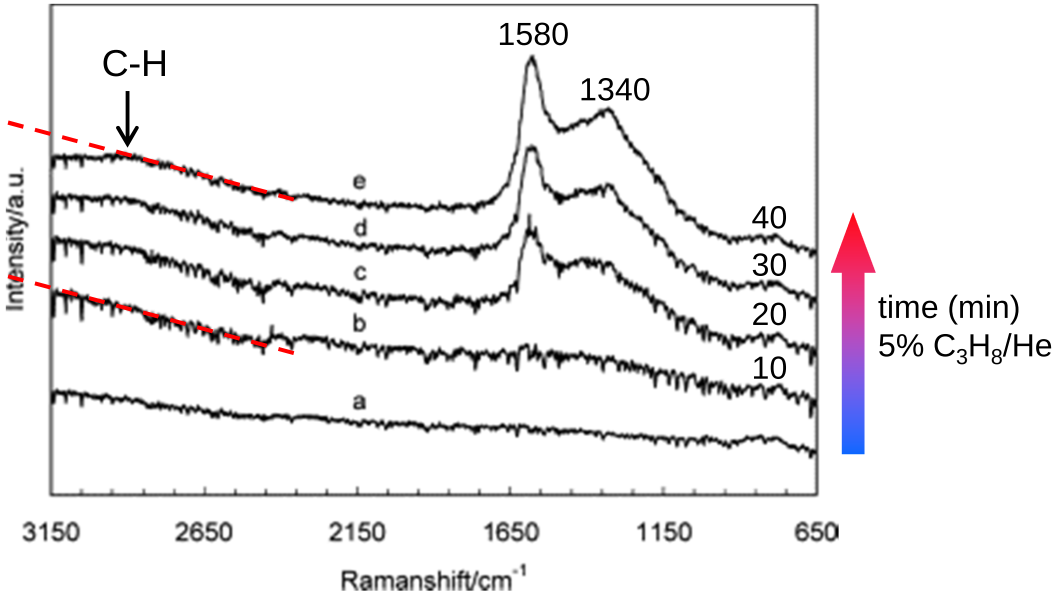
He

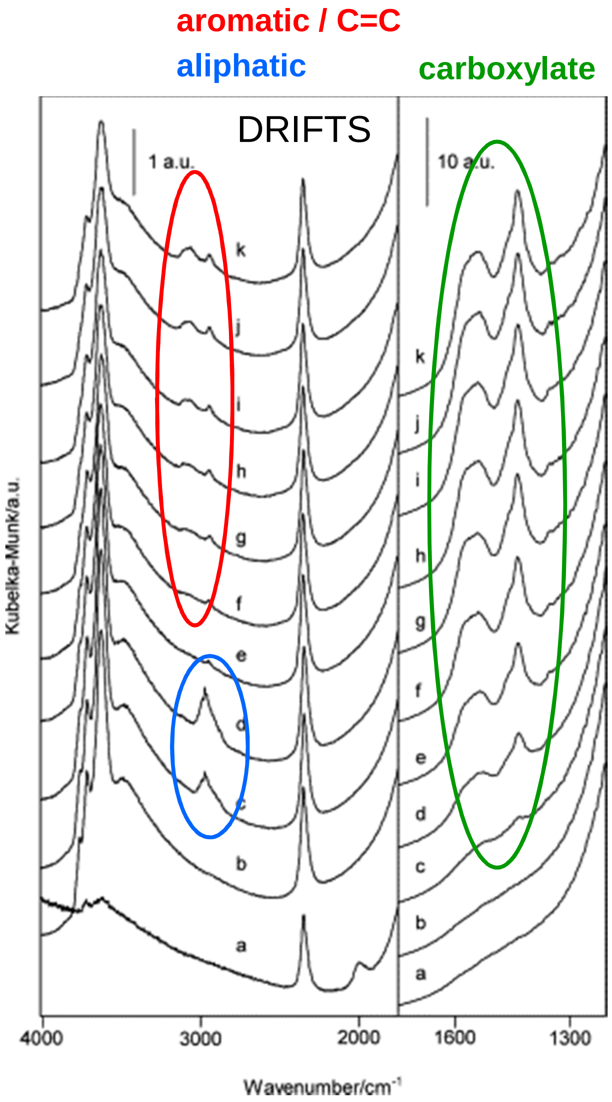
cat. activity (GC)

spectrum

spectrum

Cr_2O_3/Al_2O_3, 580°C, 514 nm

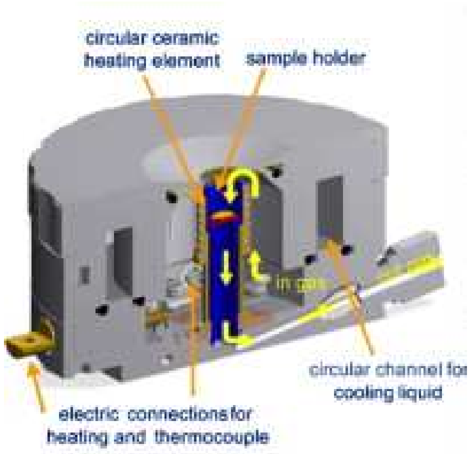


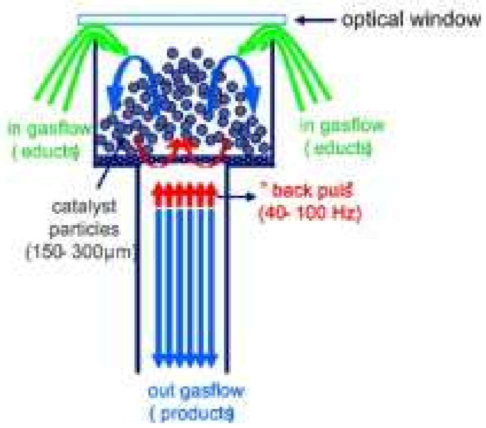


Airaksinen et al., *J. Catal.* **230** (2005) 507

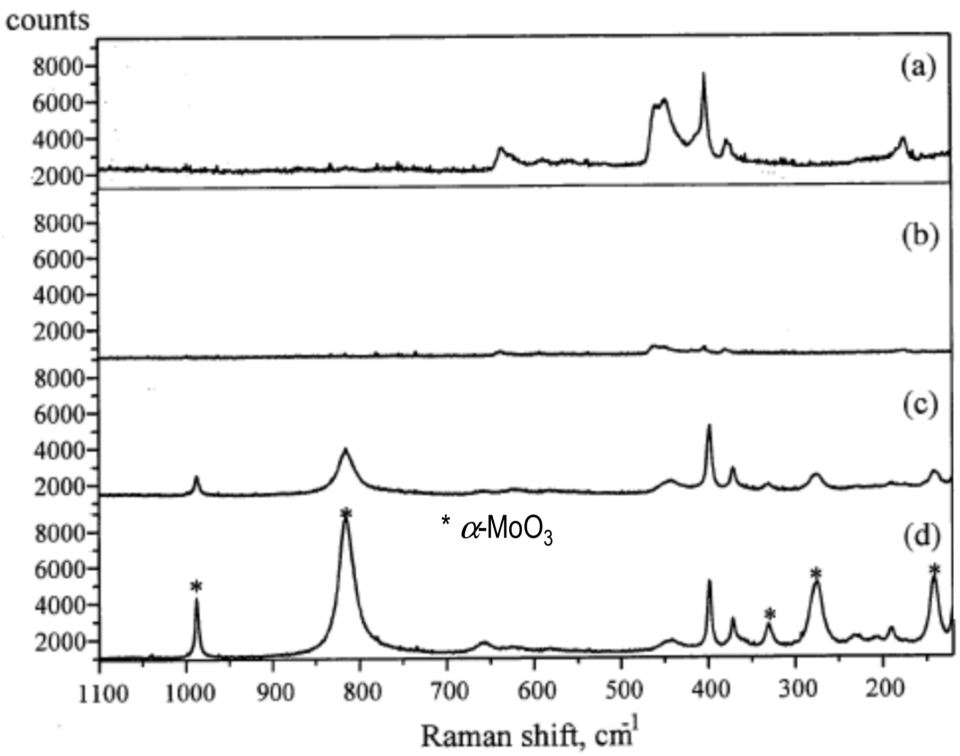
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min full power, FB

MoS_2, 6 min 1/8 power

MoS_2, 1 min full power

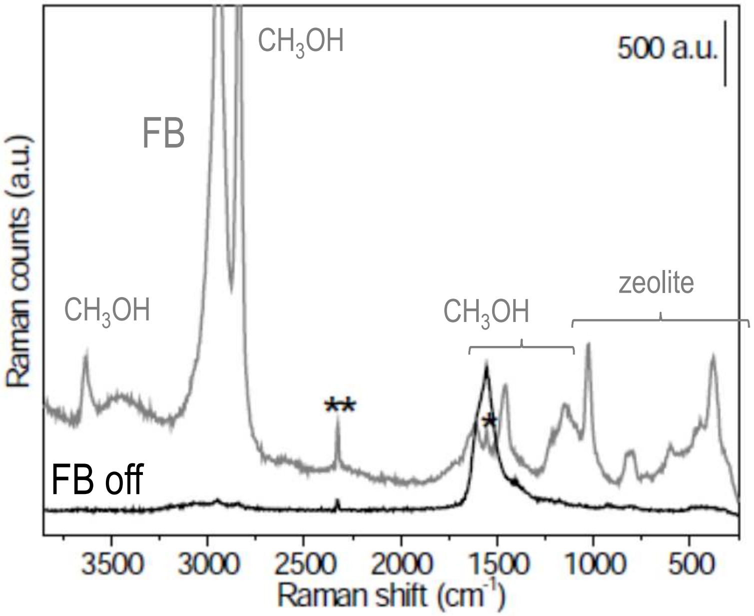
MoS_2, 6 min full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

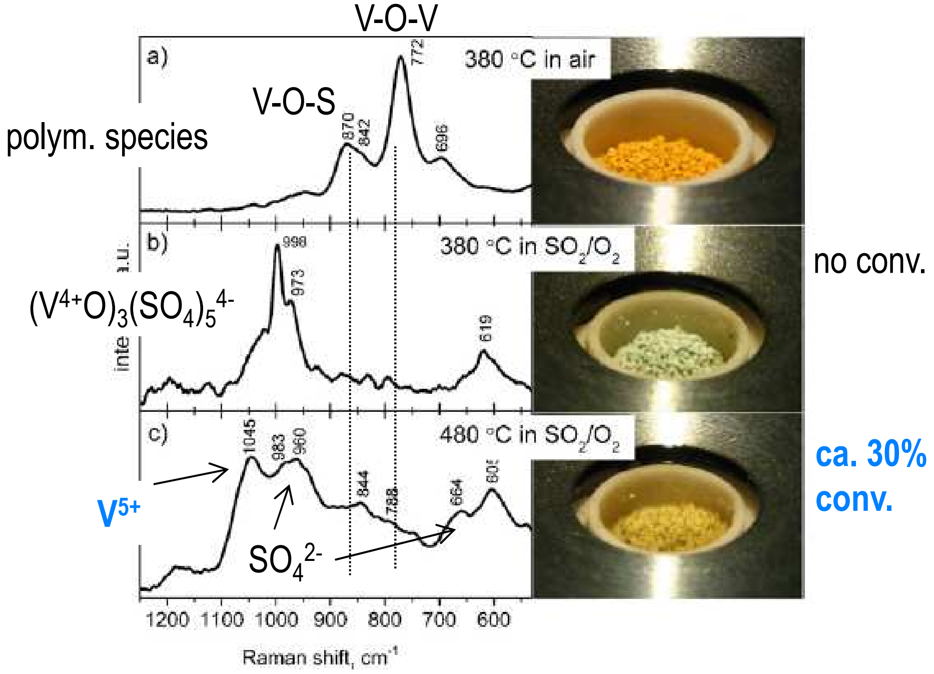
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

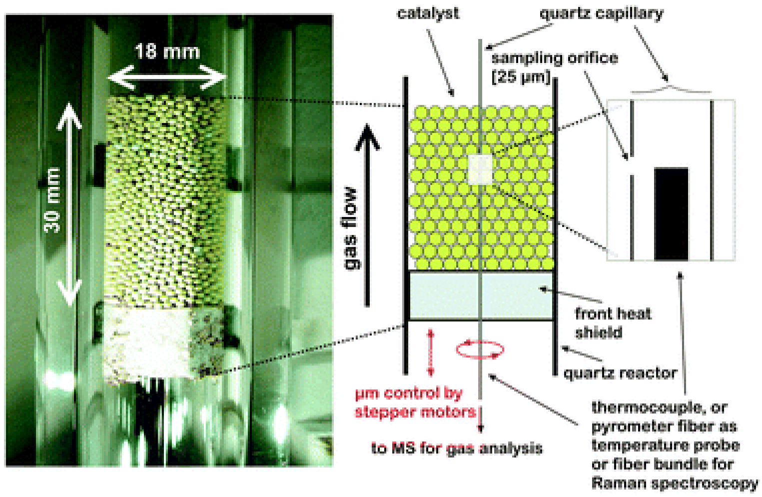


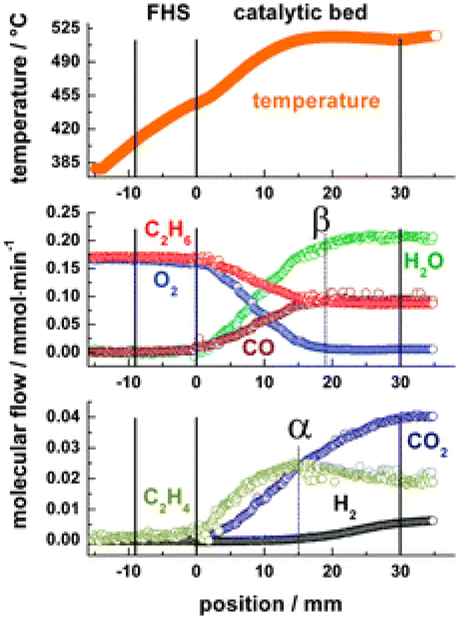
active species: mono- & dimeric V^{5+} oxosulfate species

Beato et al., *Catal. Today* 205 (2013) 128

Applications

- Fixed bed reactor





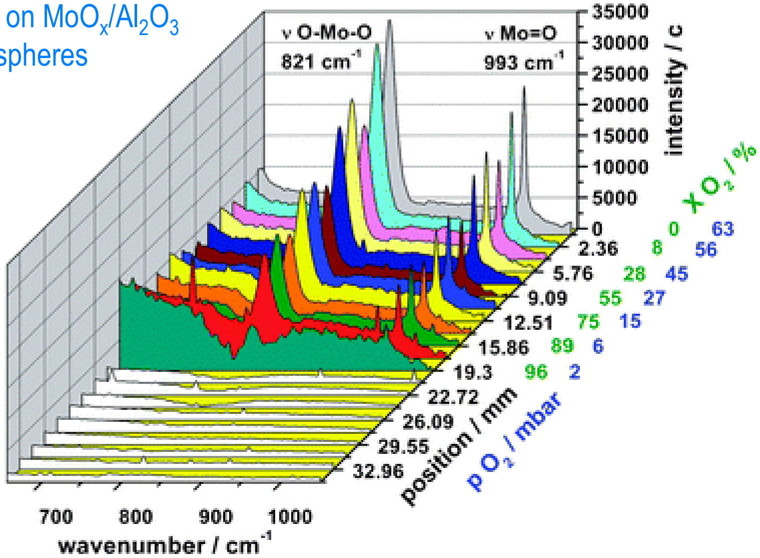
violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

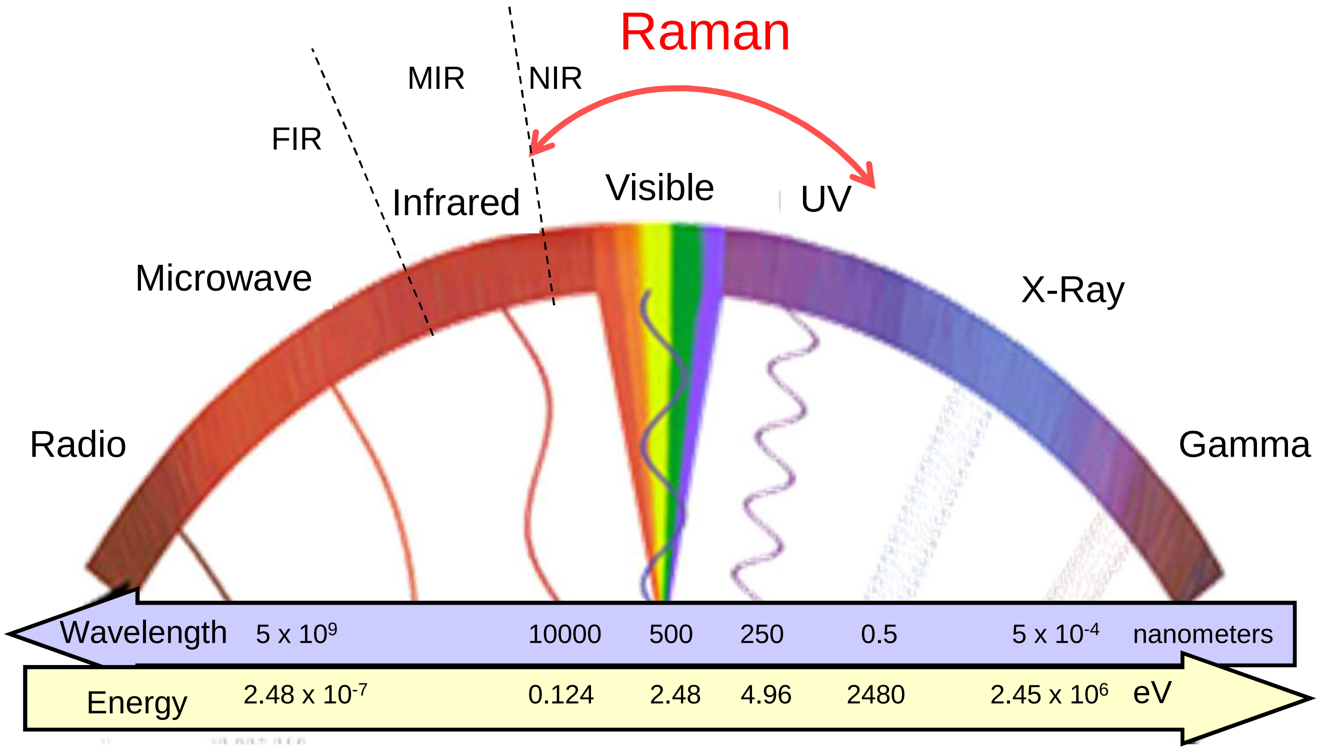
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

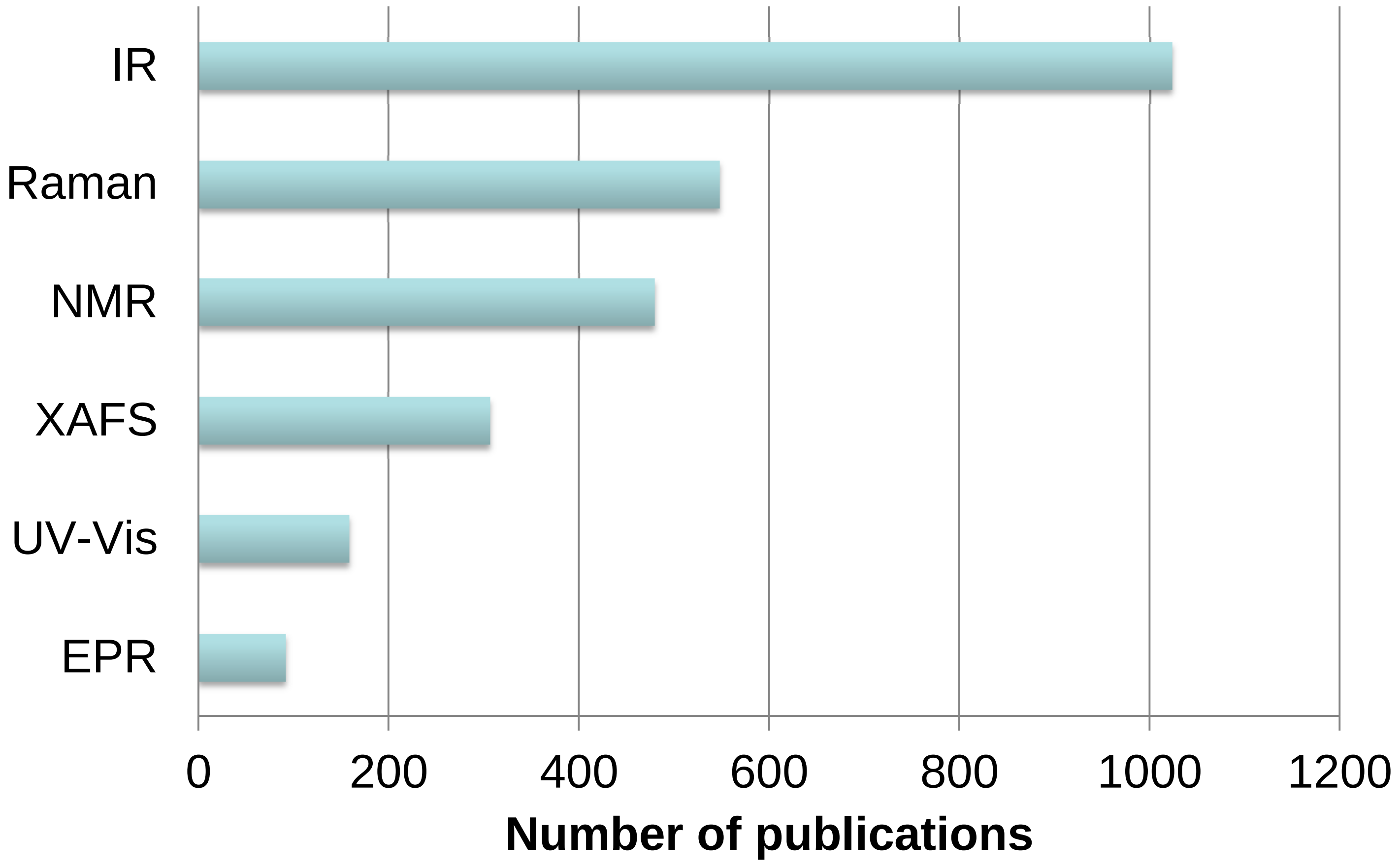
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

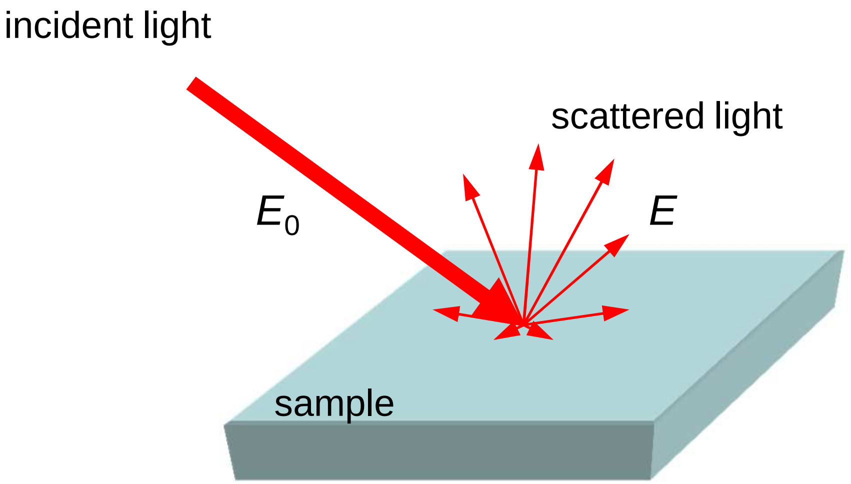


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
    - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

- E_0 = incident beam irradiance
- α = polarizability of the particle (ease of distortion of the electron cloud)
- λ = wavelength of the incident radiation
- θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

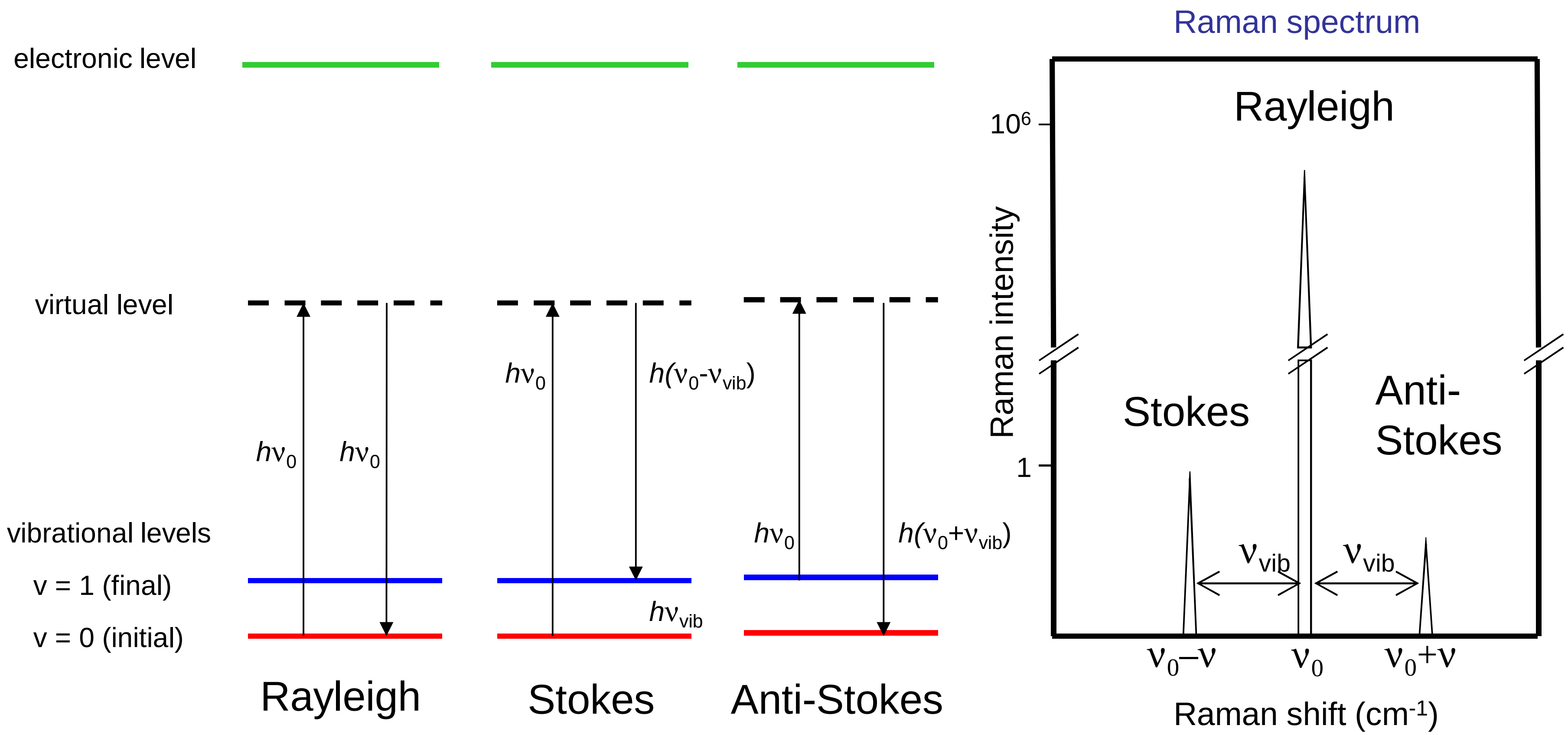
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\text{ (Anti-Stokes)}}{I\text{ (Stokes)}} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

  - 4th power of ν (4th power law)
  - 2nd power of $\Delta\alpha$
    - properties of molecules
    - strength of bonds

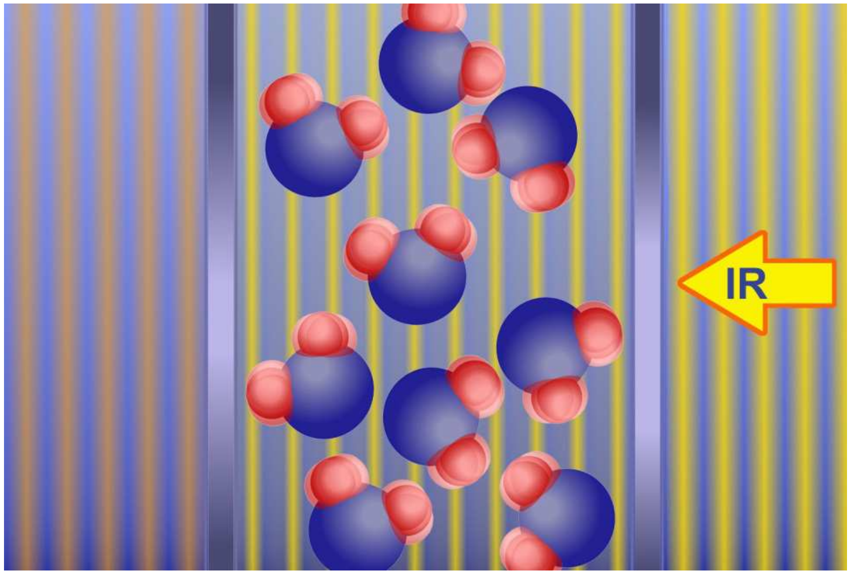
covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

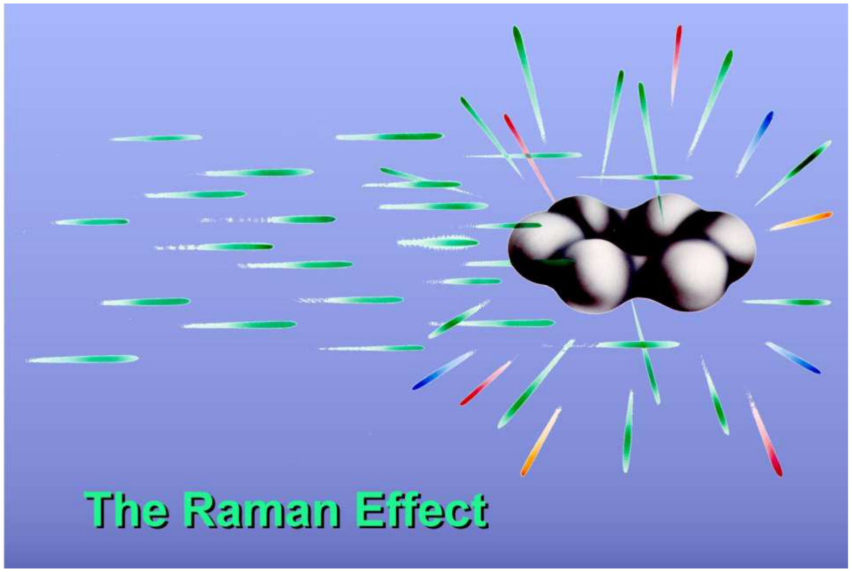
- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

Raman *vs.* Infrared

Infrared

Raman





Absorption of IR light

Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial\mu}{\partial Q}\right)^2 \neq 0$$

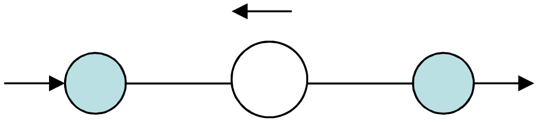
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial\alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - large electron clouds
  - not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

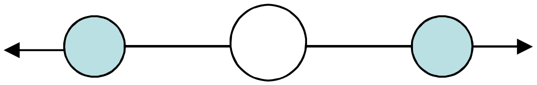
Raman *vs.* Infrared

CO_2



ν_{as}

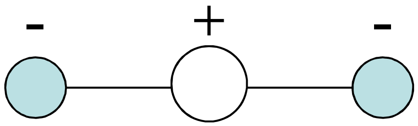
2349 cm^{-1}



ν_s

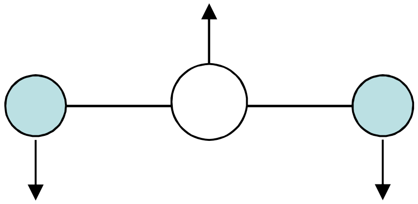
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



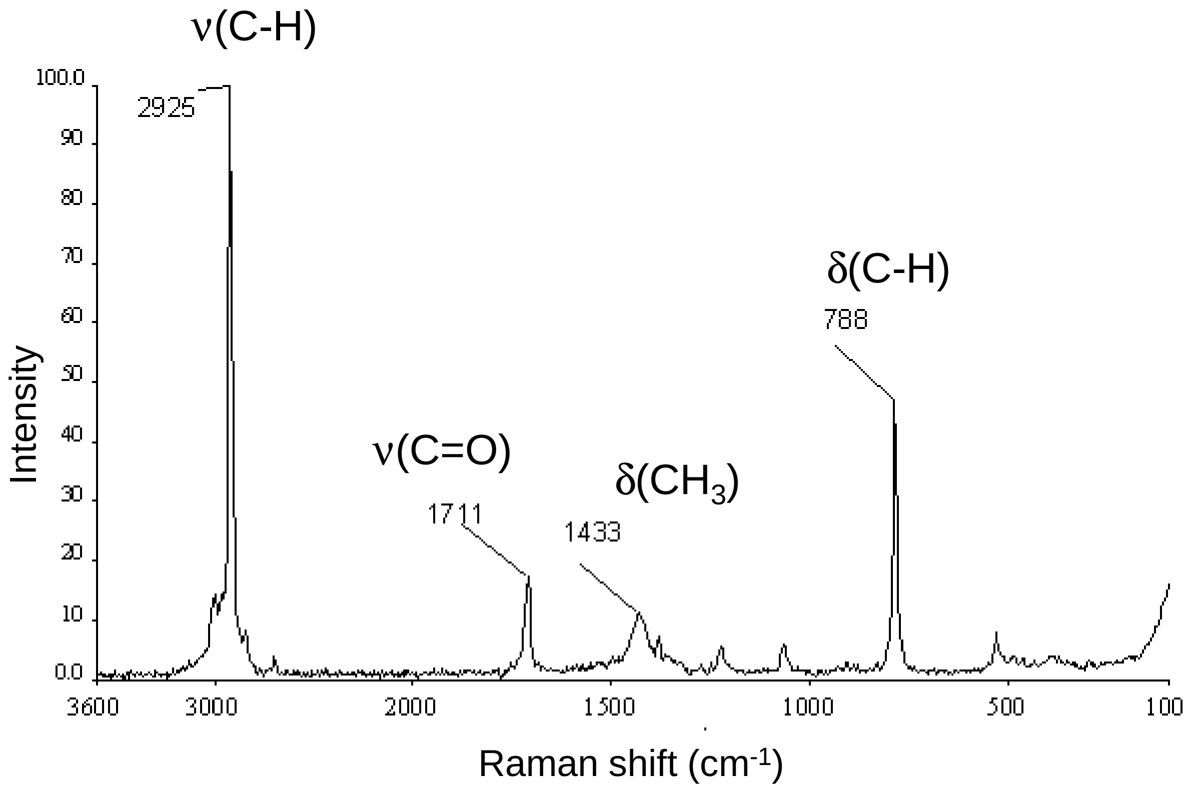
δ

667 cm^{-1}

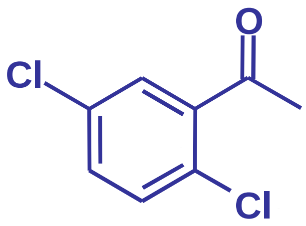
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



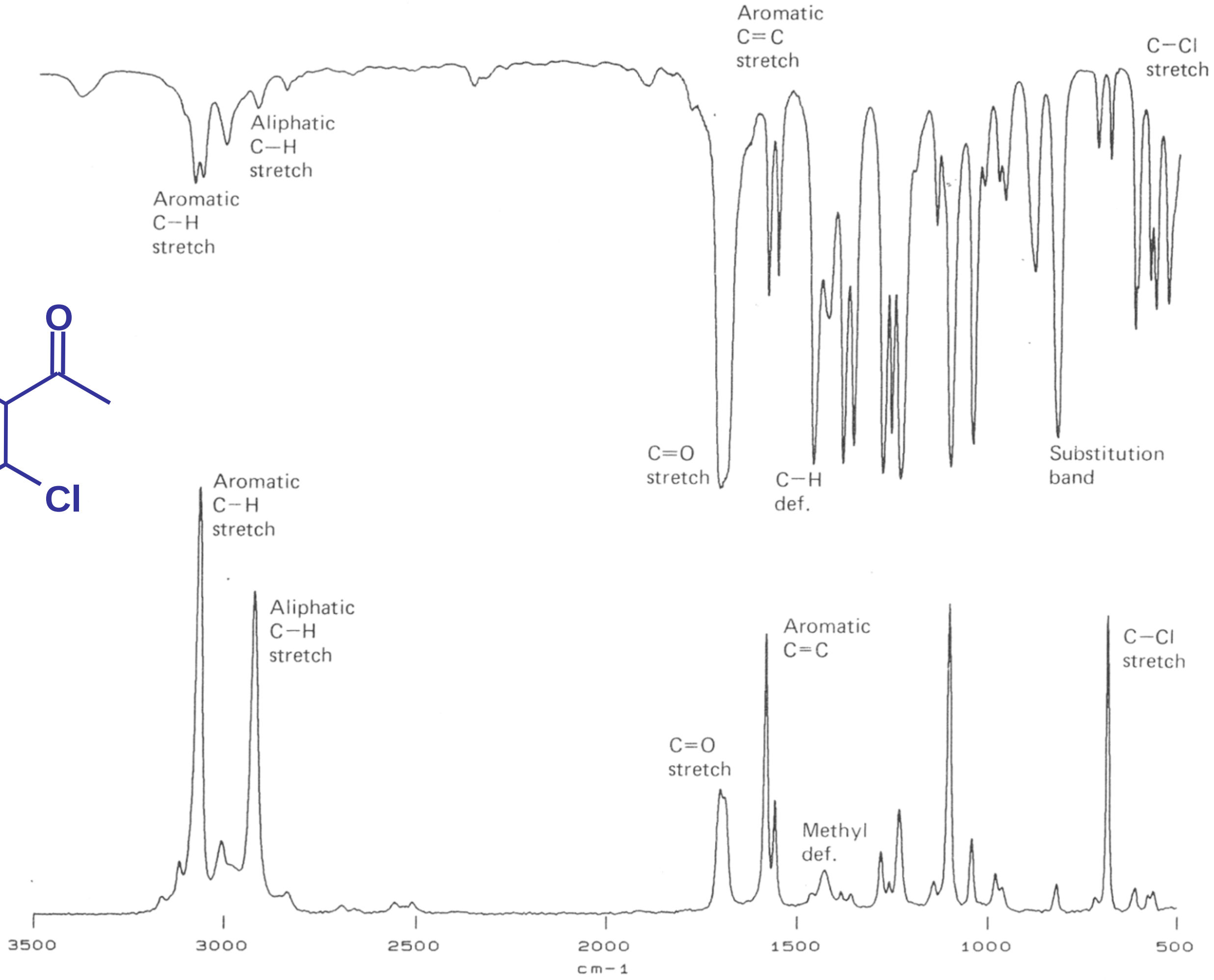


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

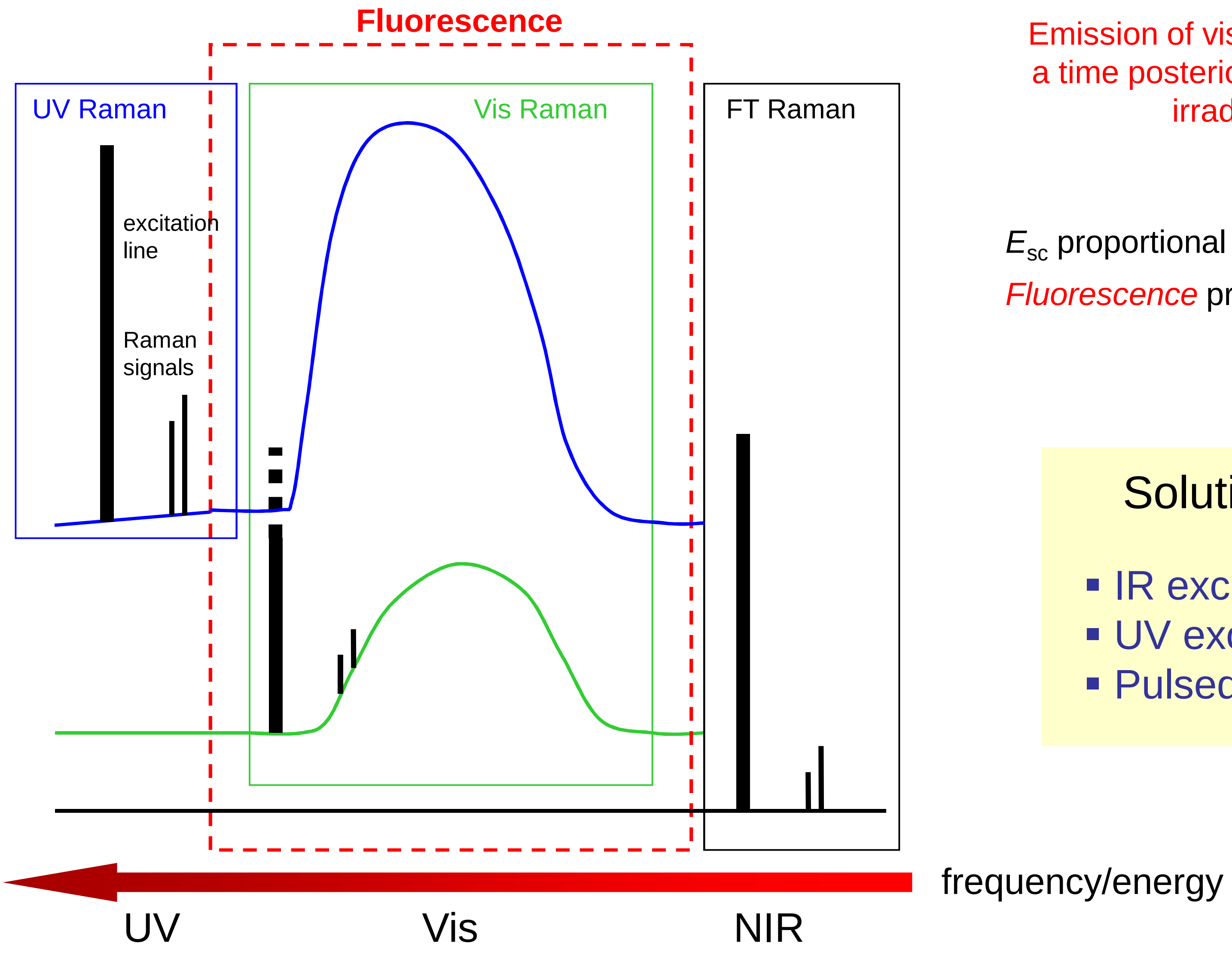
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 μm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

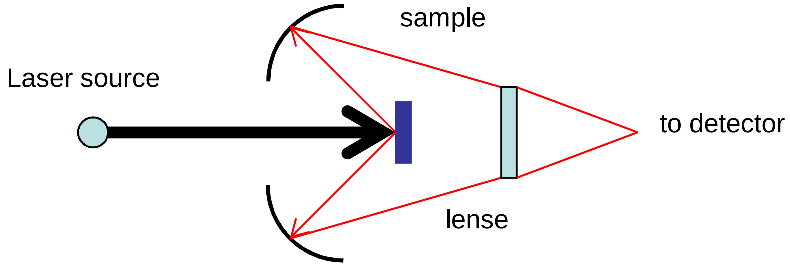
Fluorescence proportional to ν

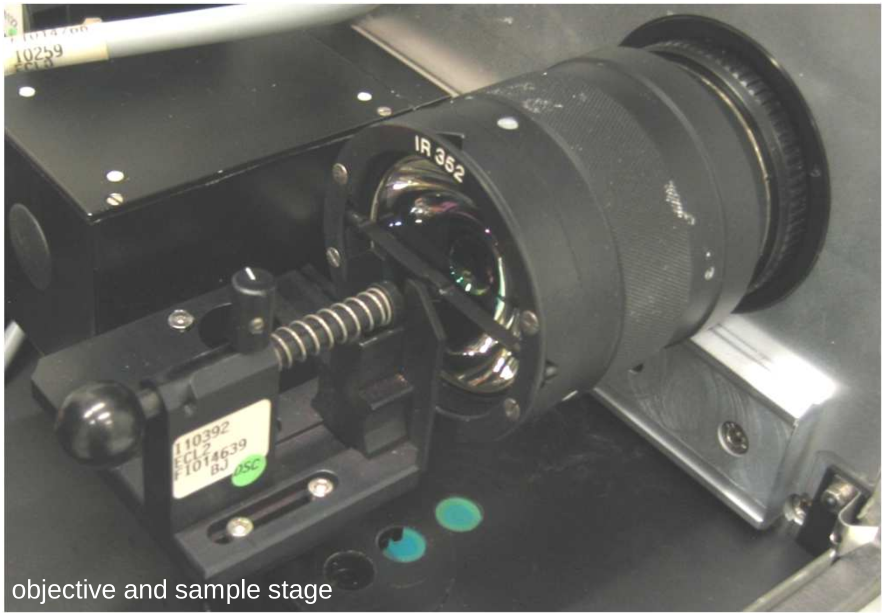
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

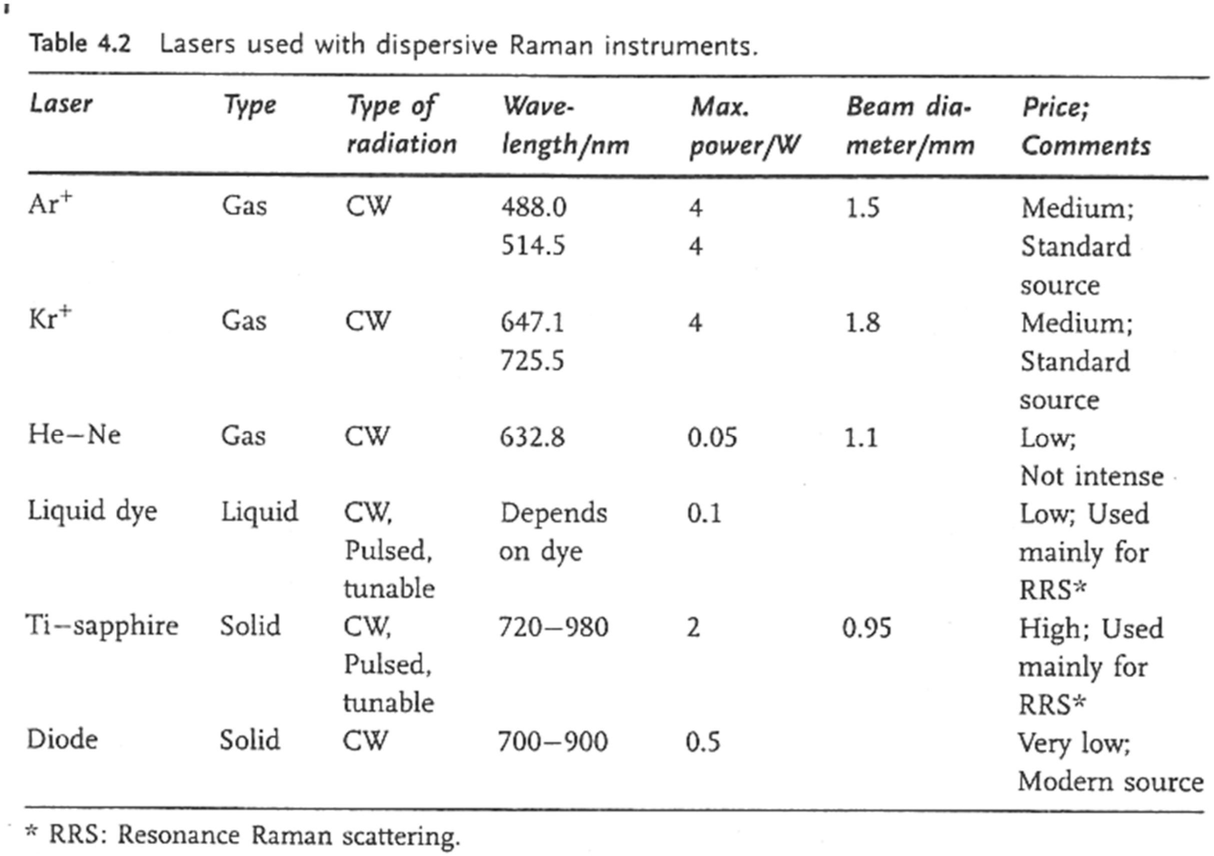


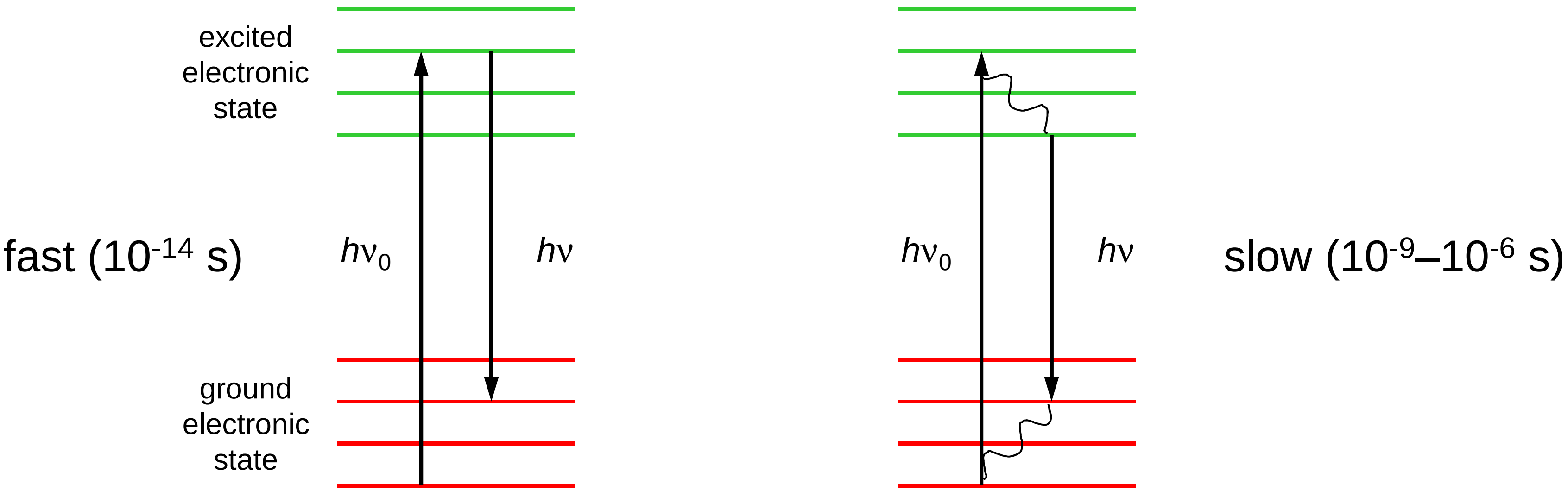
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



fast (10^{-14} s)

slow (10^{-9}–10^{-6} s)

Resonance Raman scattering

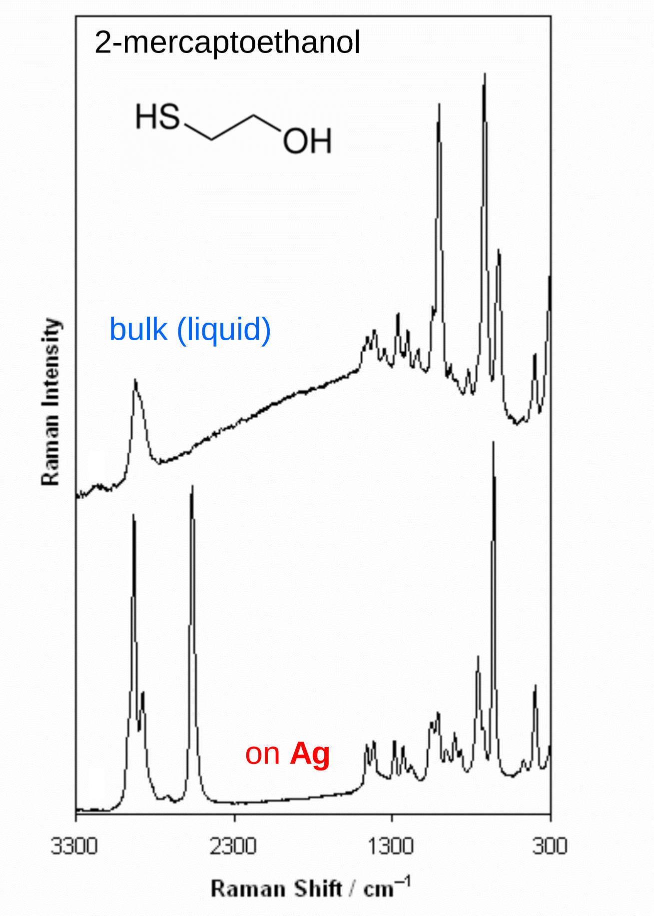
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

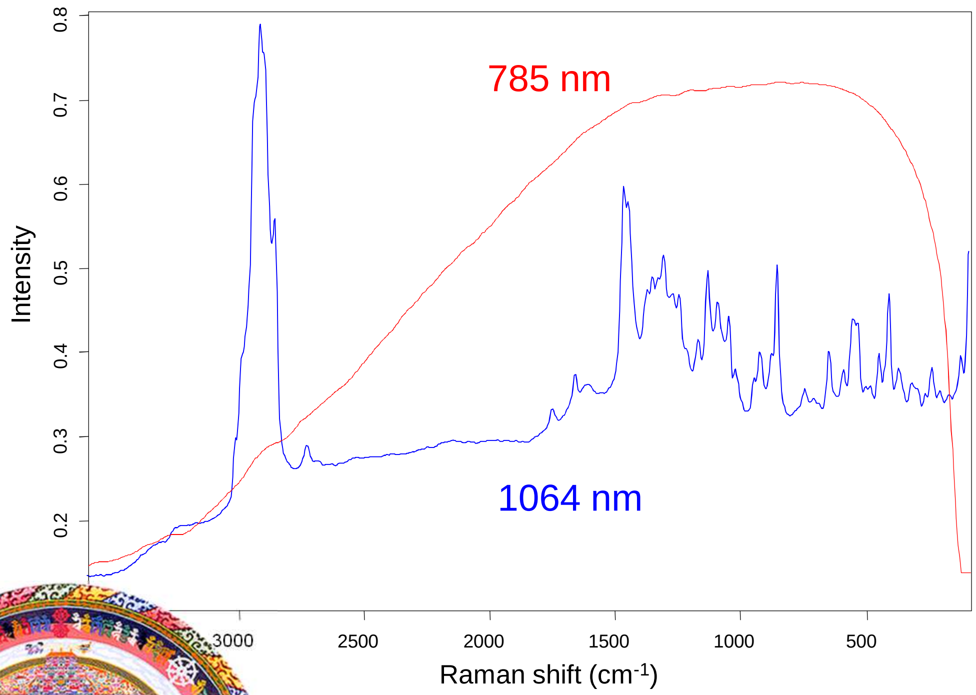
- Remarks:

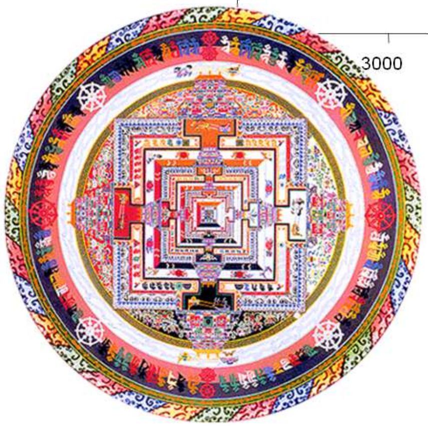
❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring





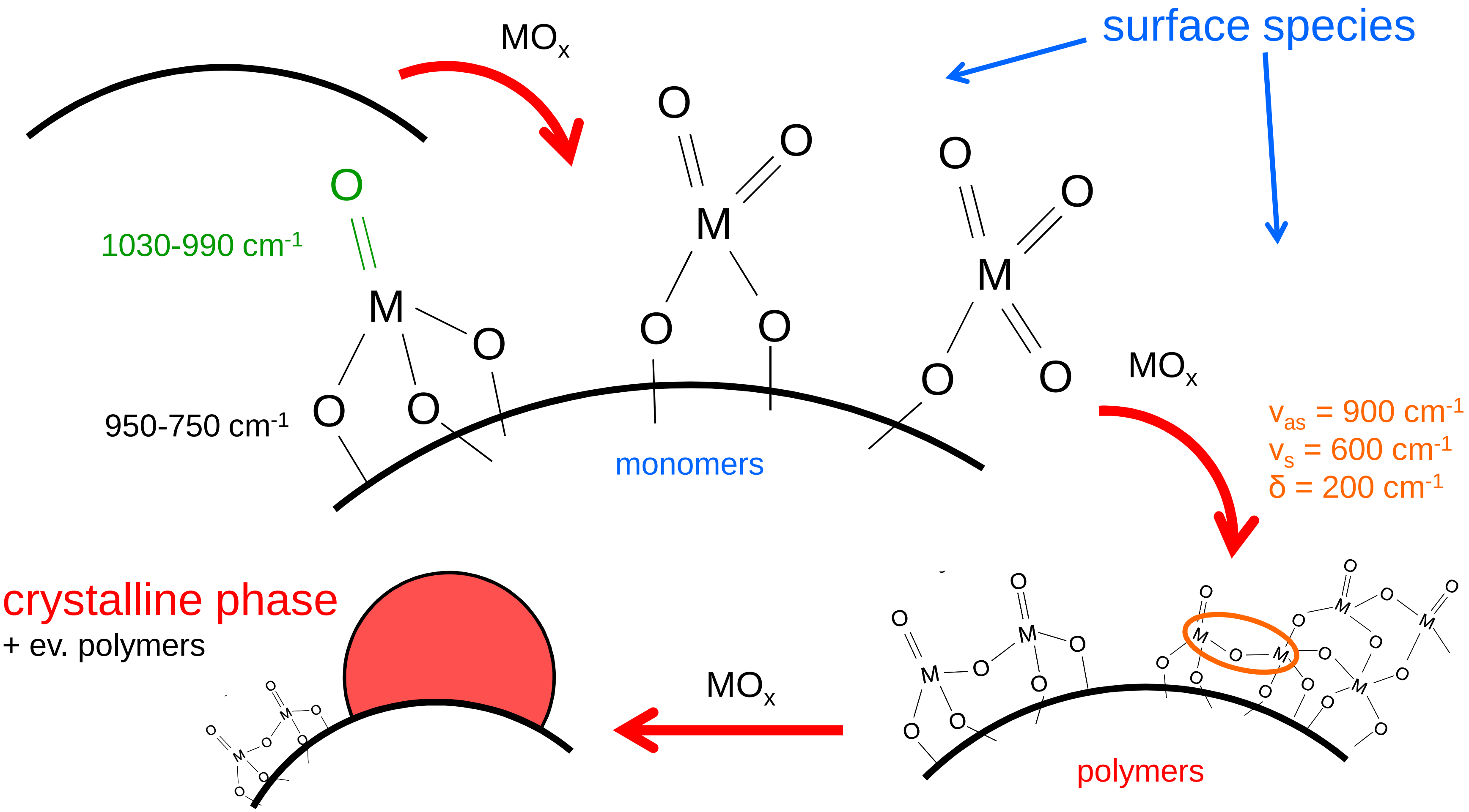
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



surface species

MO_x

1030-990 cm^{-1}

950-750 cm^{-1}

monomers

MO_x

ν_{as} = 900 cm^{-1}
ν_s = 600 cm^{-1}
δ = 200 cm^{-1}

polymers

MO_x

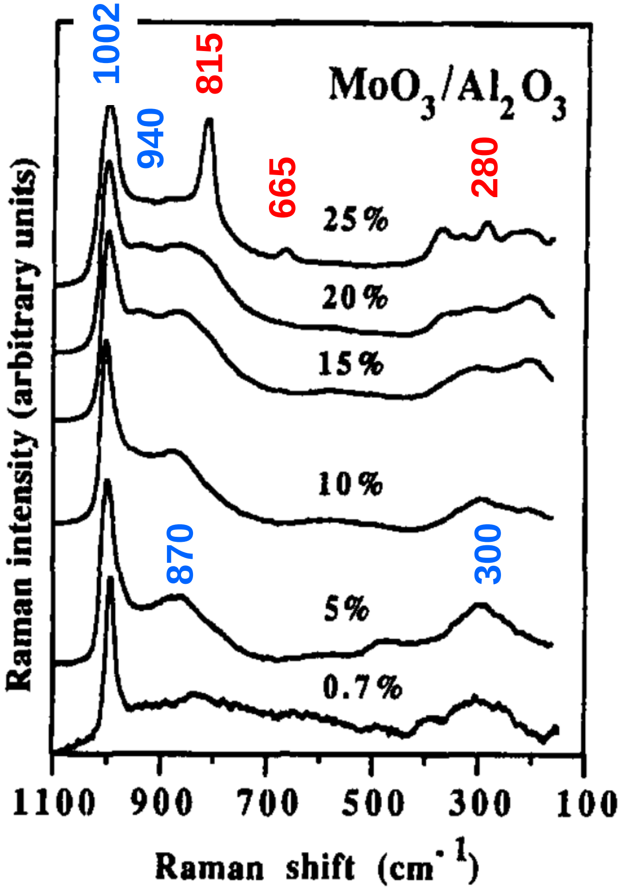
crystalline phase
+ ev. polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



surface MoO_3

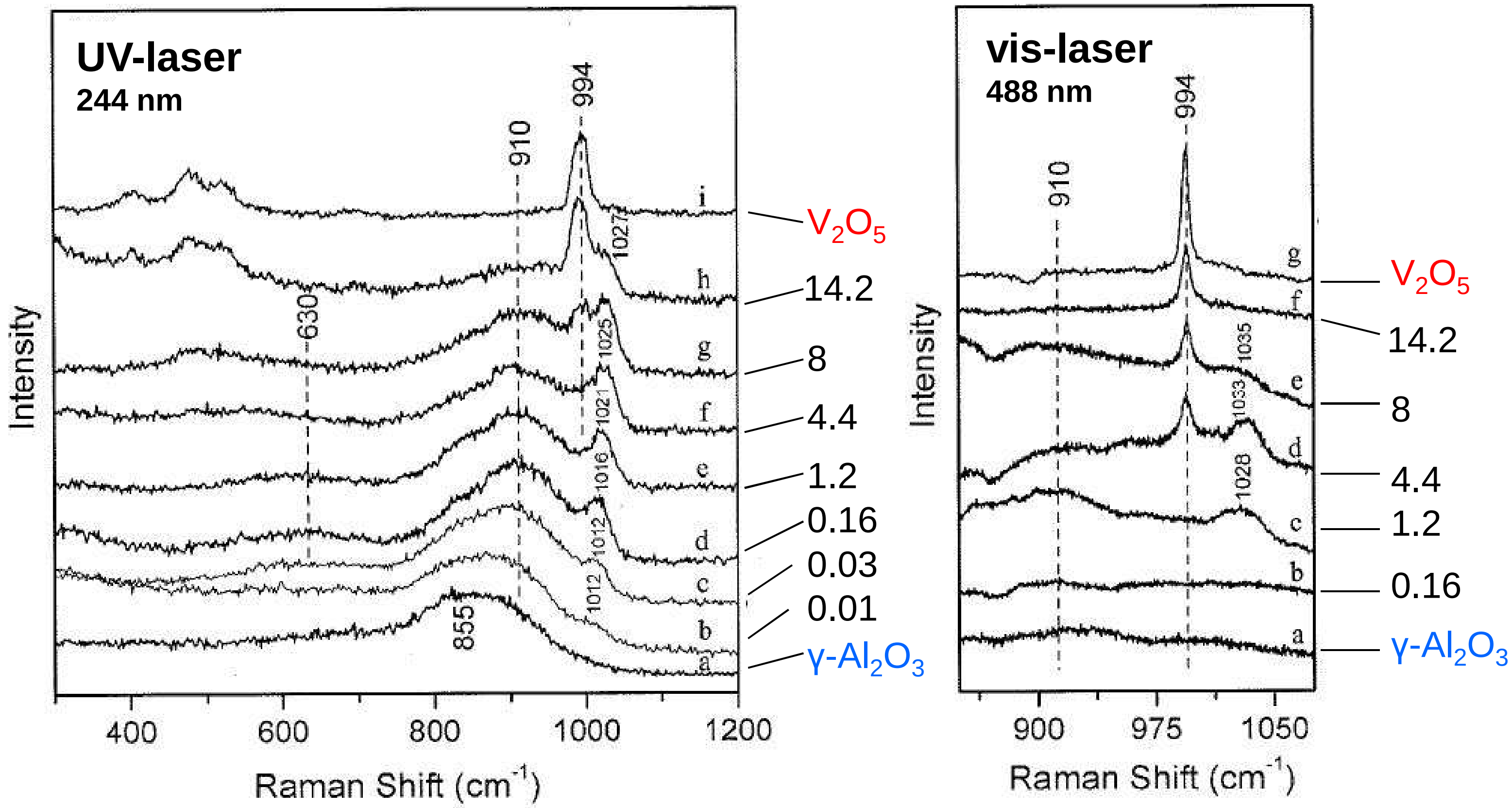
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

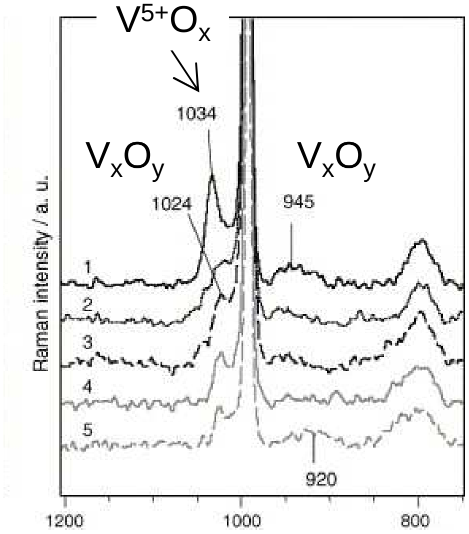
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

Applications

- Reactivity of V/TiO$_2$ after oxidative treatment



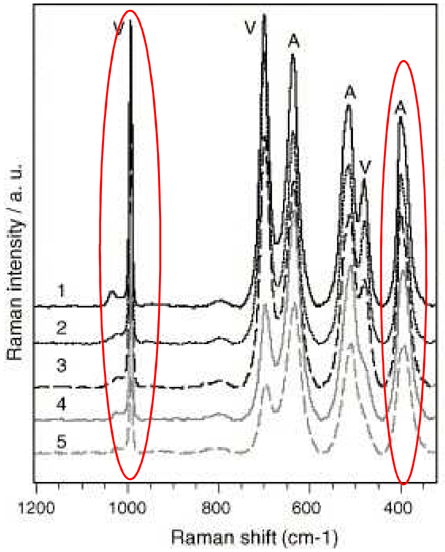
air flow @ 450°C

O_2/C_3H_8 @ 20°C

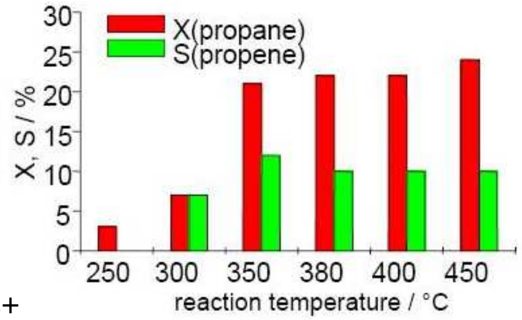
@ 100°C

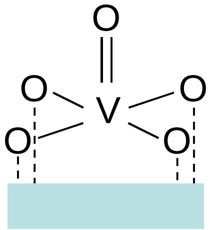
@ 150°C

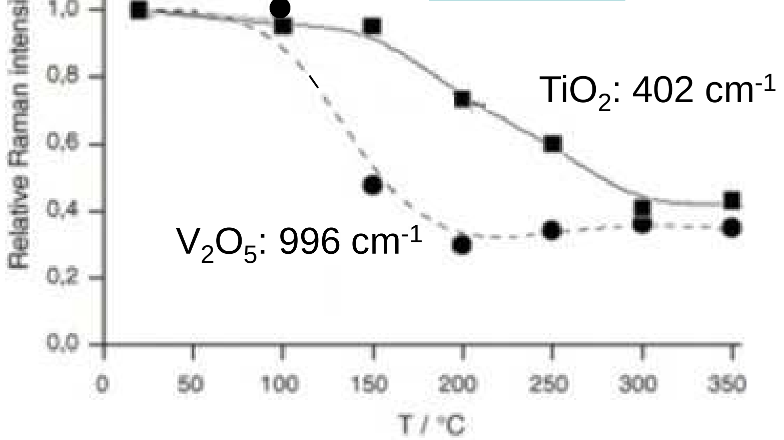
@ 200°C



$V^{5+} \longrightarrow V^{4+}$







Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

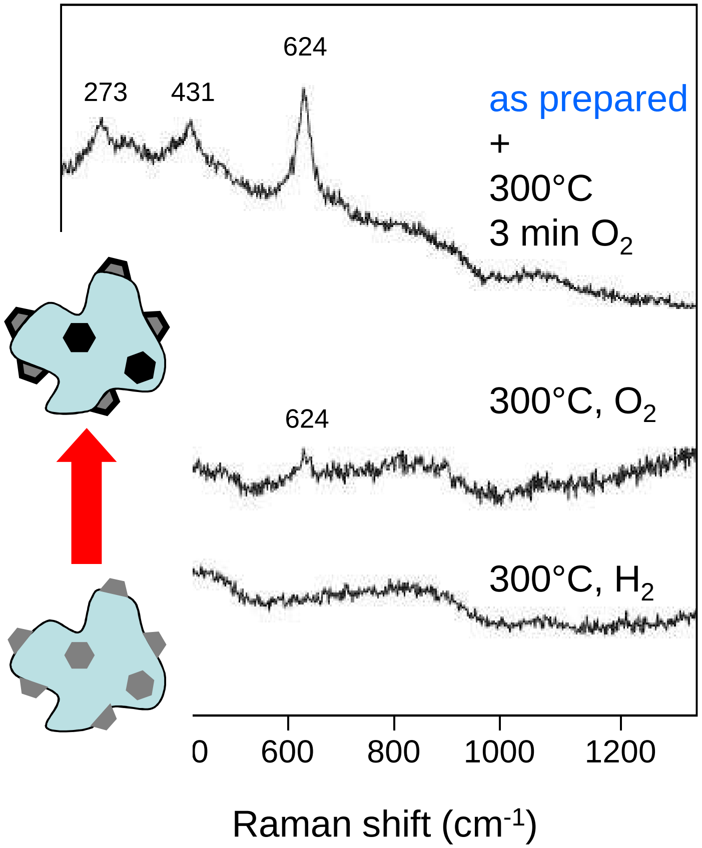
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

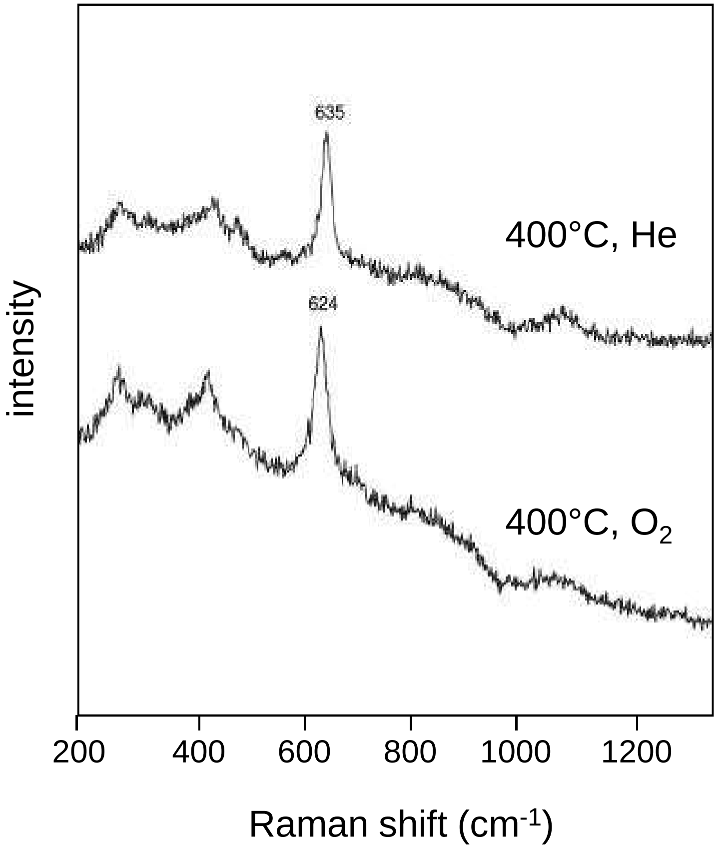
Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



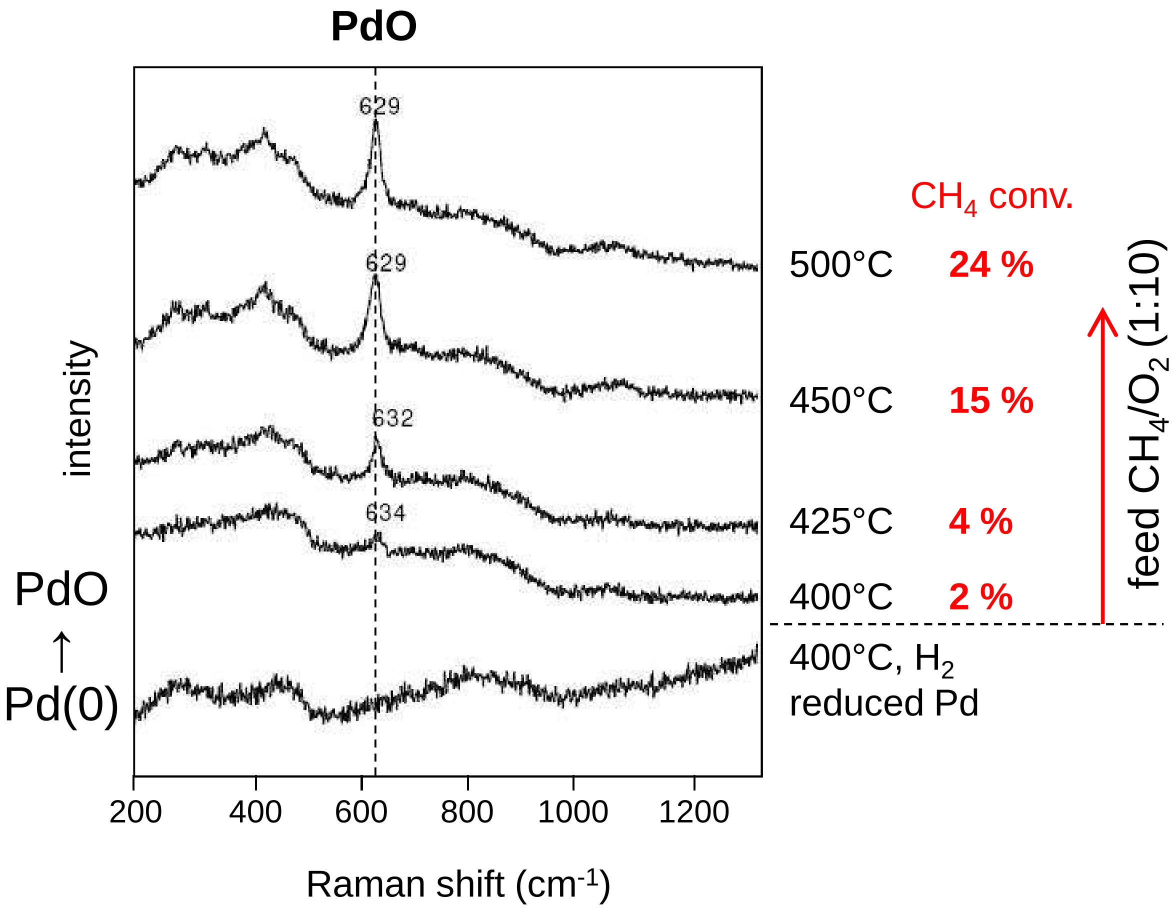


2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

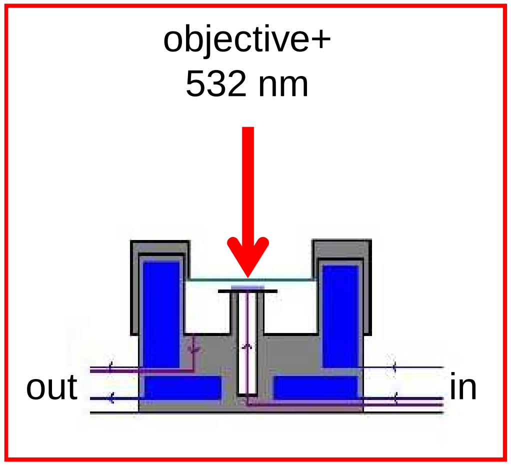
Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3



$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

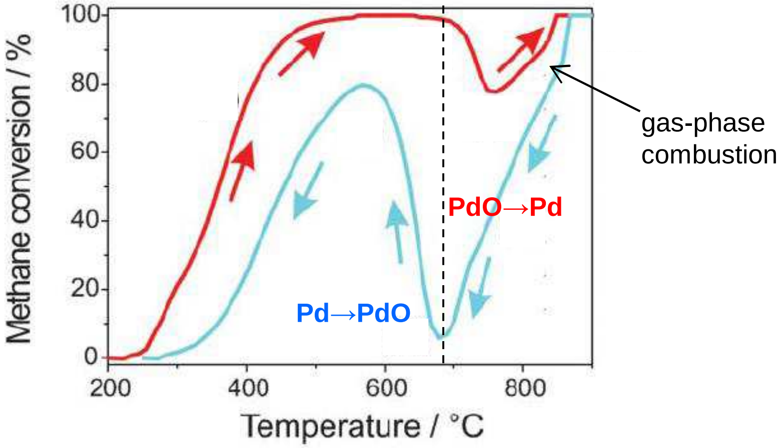
near PdO mode

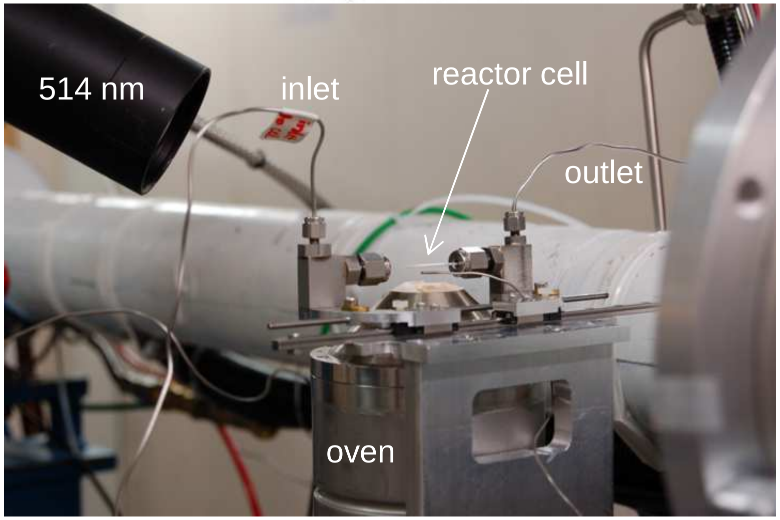


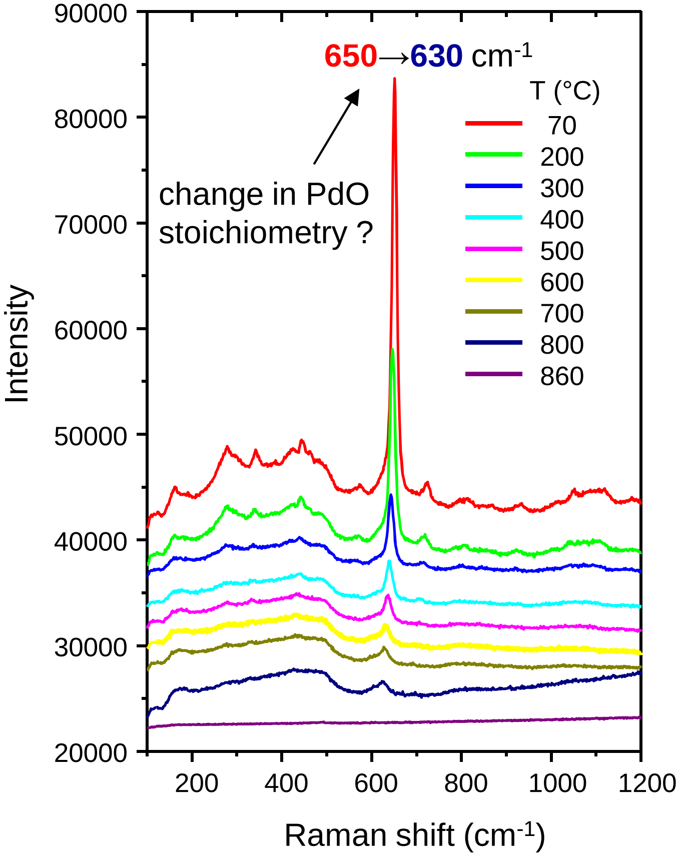
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

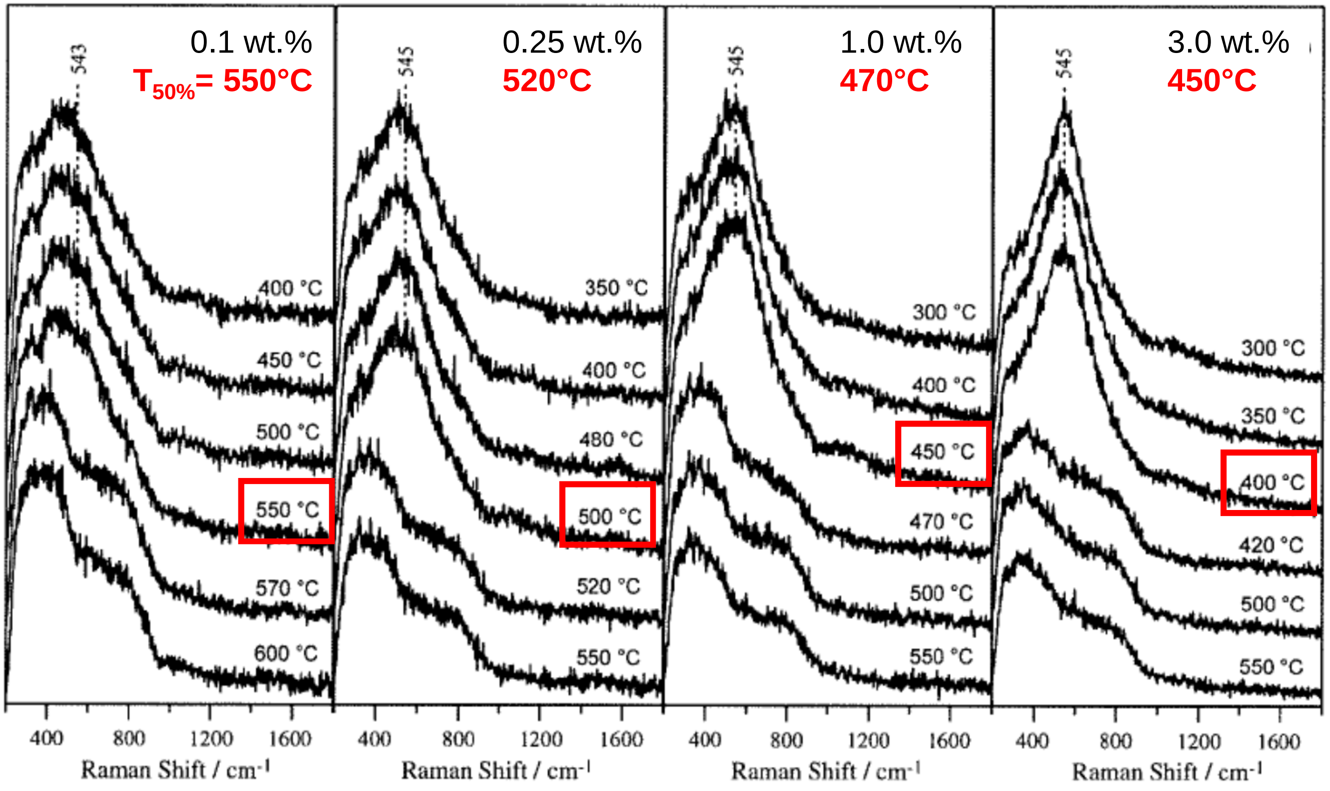
Applications

- Methane partial oxidation over Rh/Al_2O_3

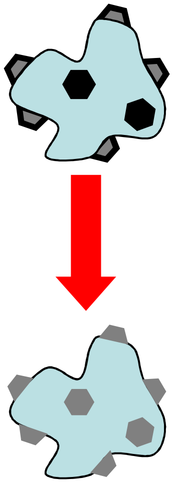
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$$


Rh content
Activity



RhO_x
↓
Rh(0)



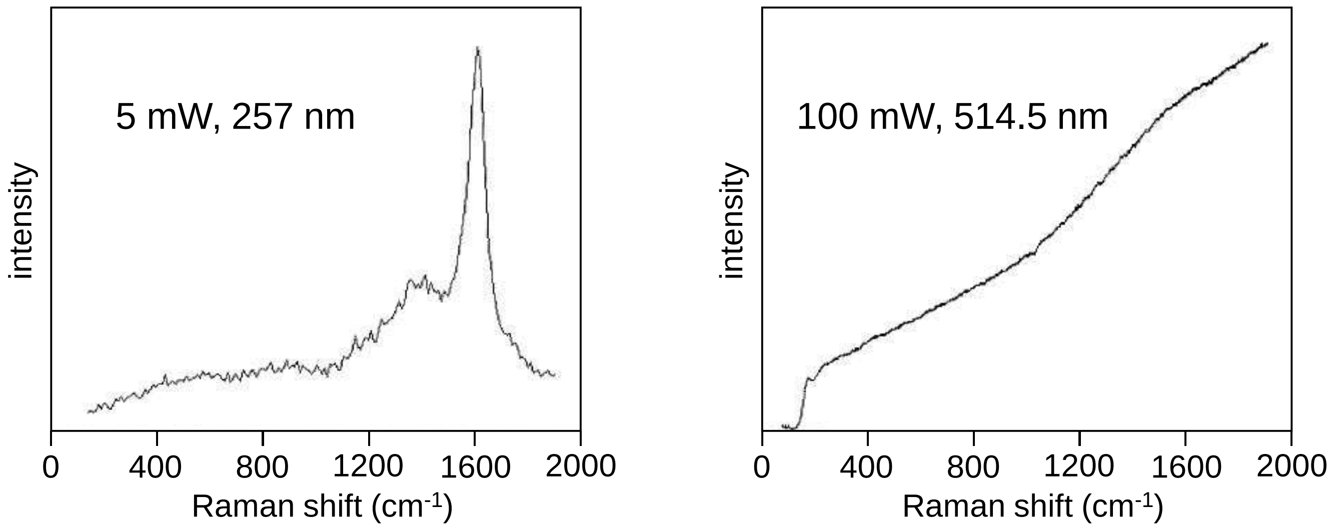
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

    (only few molecules fluoresce below 260 nm)

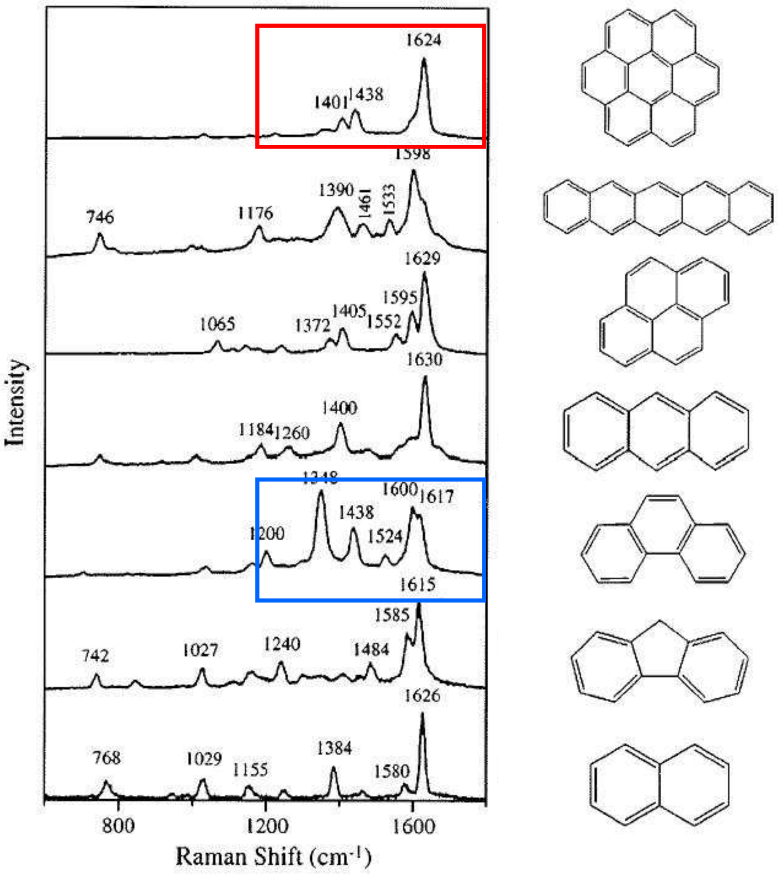
Rh/Al_2O_3, coked 500°C in naphtha

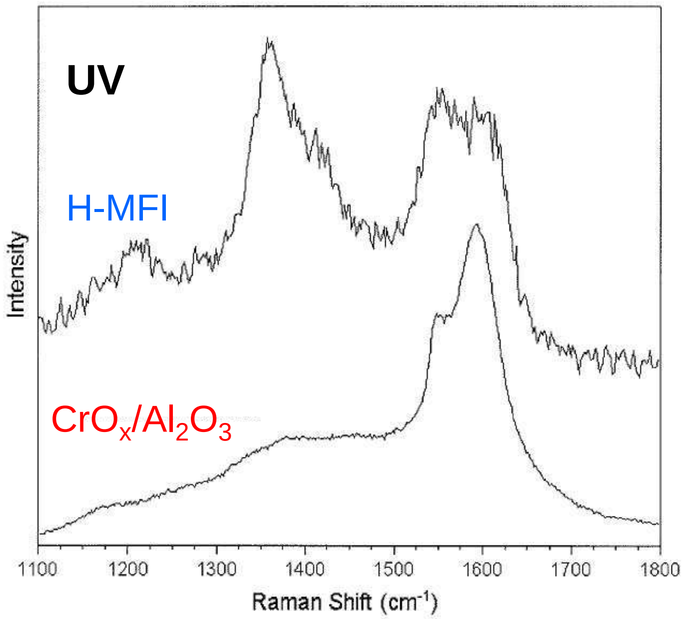


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





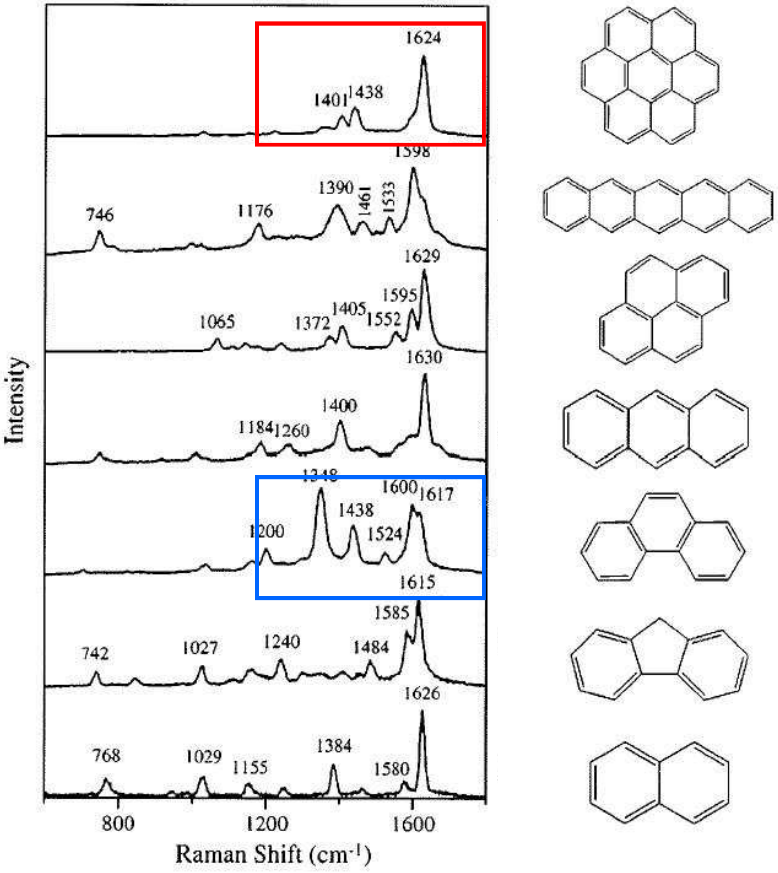
Coke classification
1D topology, chain-like
2D topology, sheet-like

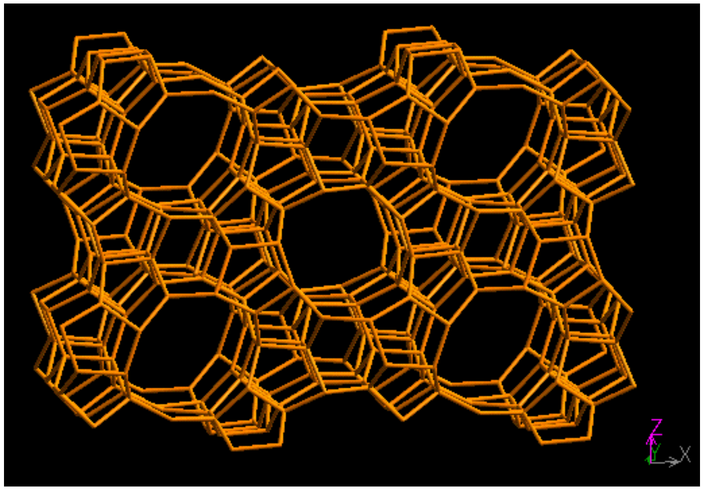
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





Coke classification

1D topology, chain-like

2D topology, sheet-like

Coke from:

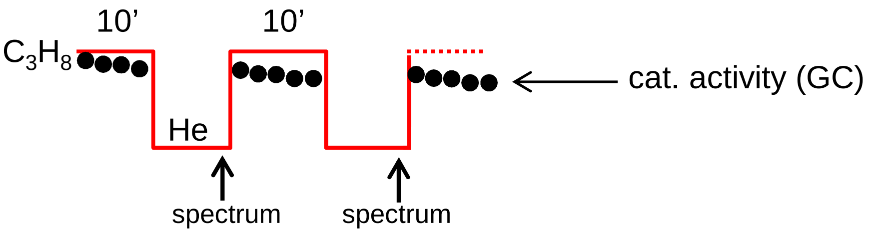
H-MFI: methanol-to-hydrocarbons (MTH)

CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

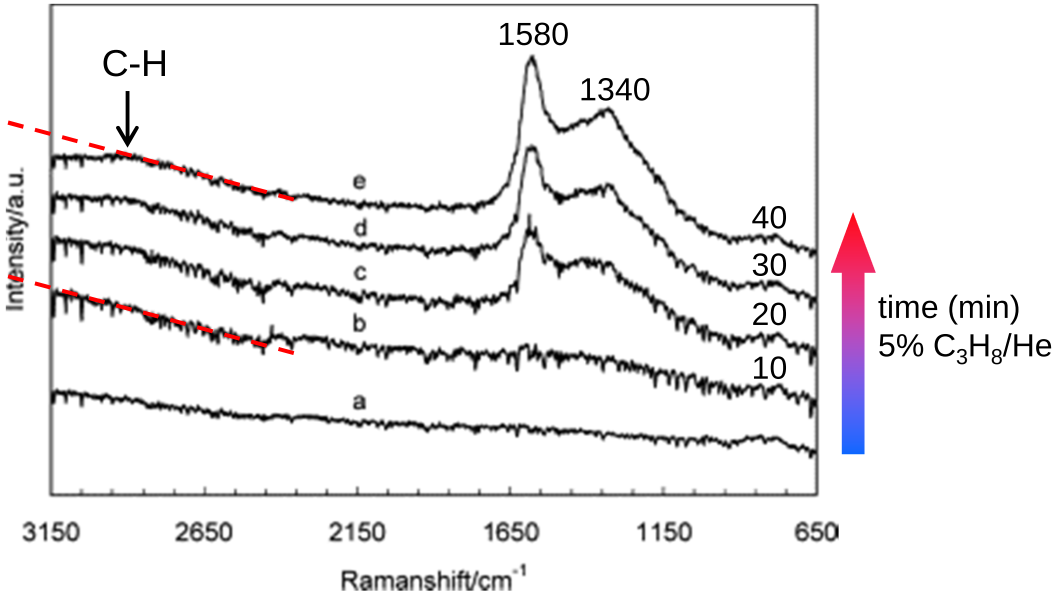
Stair, *Adv. Catal.* **51** (2007) 75

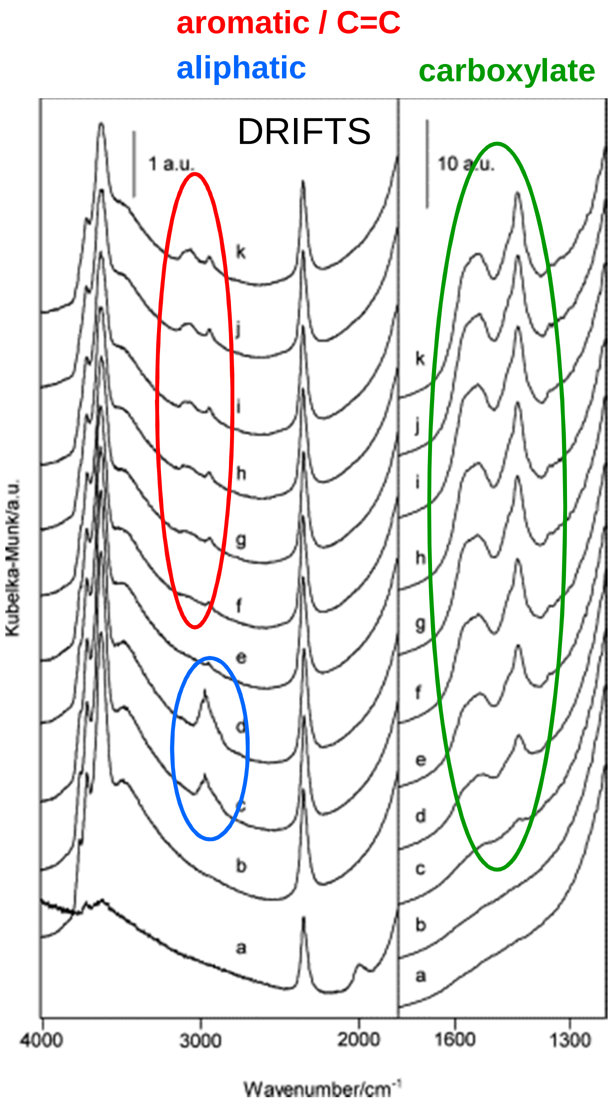
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

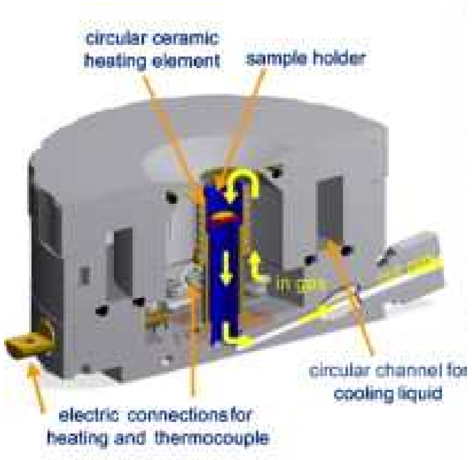


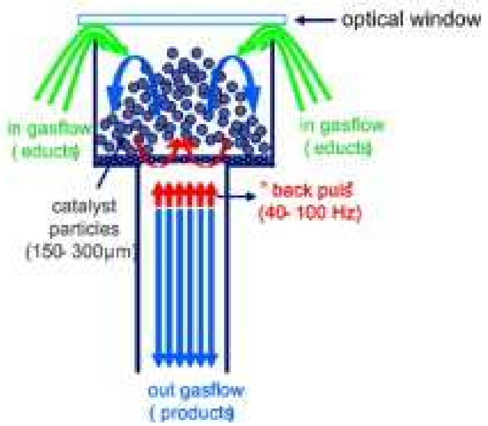


Airaksinen et al., *J. Catal.* **230** (2005) 507

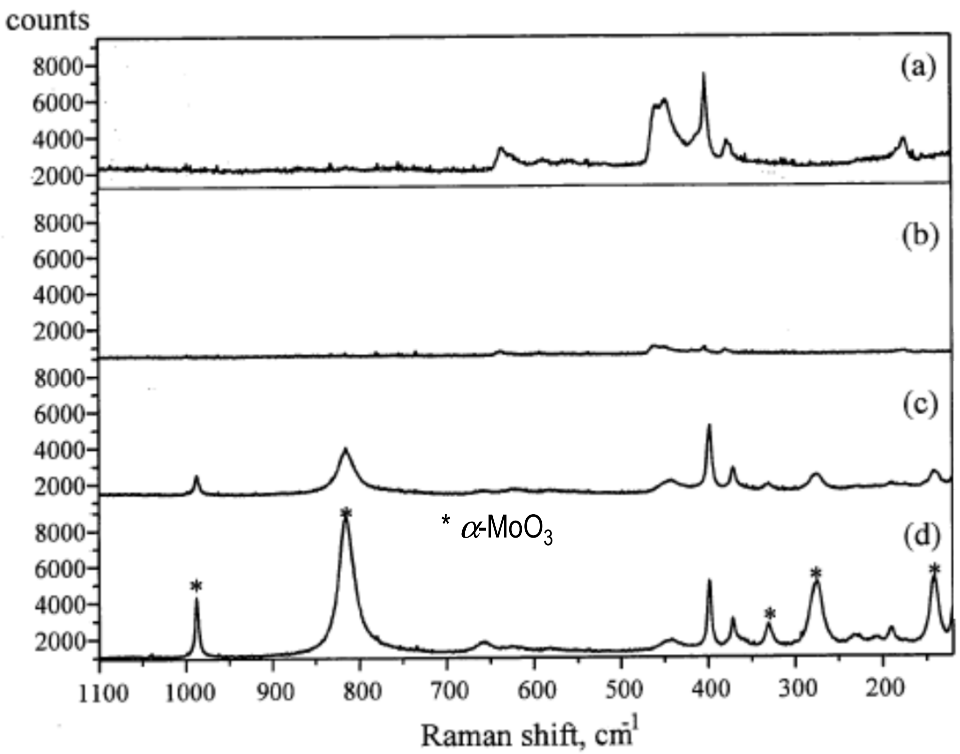
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min full power, FB

MoS_2, 6 min 1/8 power

MoS_2, 1 min full power

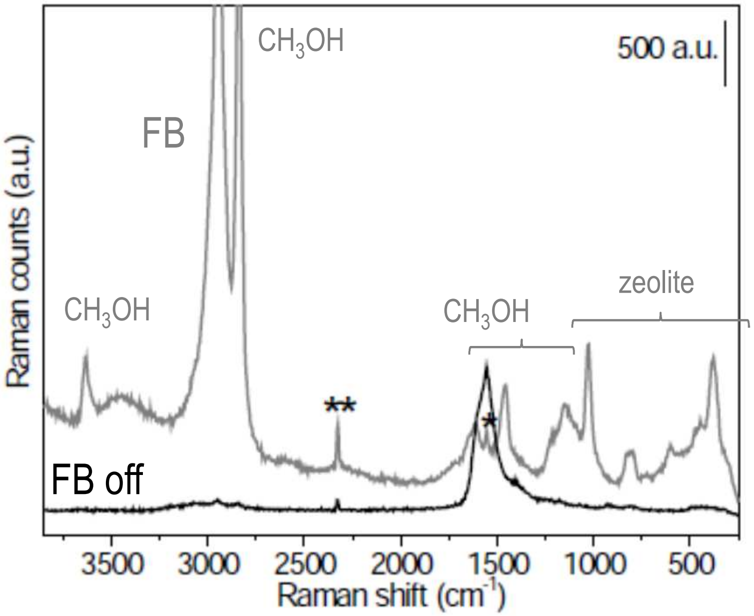
MoS_2, 6 min full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

- Fluidized bed reactor cell

CH$_3$OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



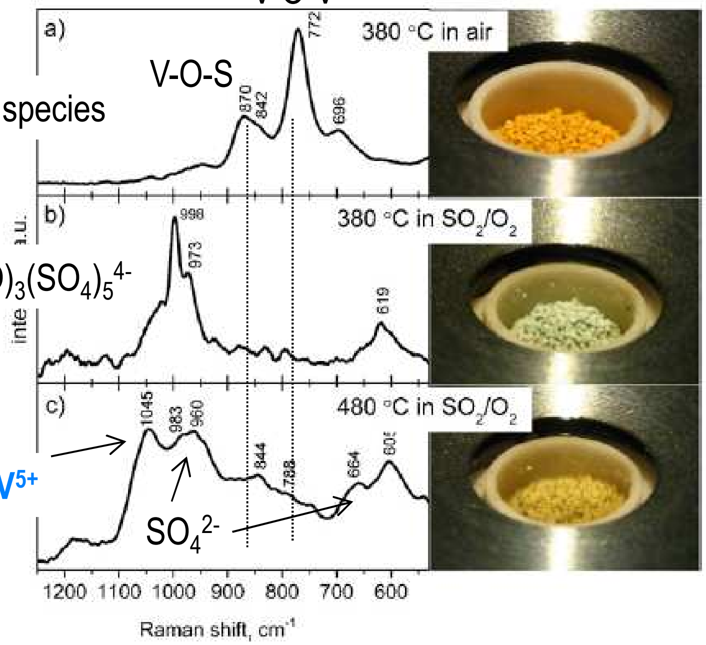
Laser induced CH$_3$OH decomposition

Sulfuric acid V$_2$O$_5$/pyrosulfate catalyst
λ= 514 nm

V-O-V

V-O-S

polym. species



(V^{4+}O)$_3$(SO$_4$)$_5$$^{4-}$

no conv.

V^{5+}

SO$_4$$^{2-}$

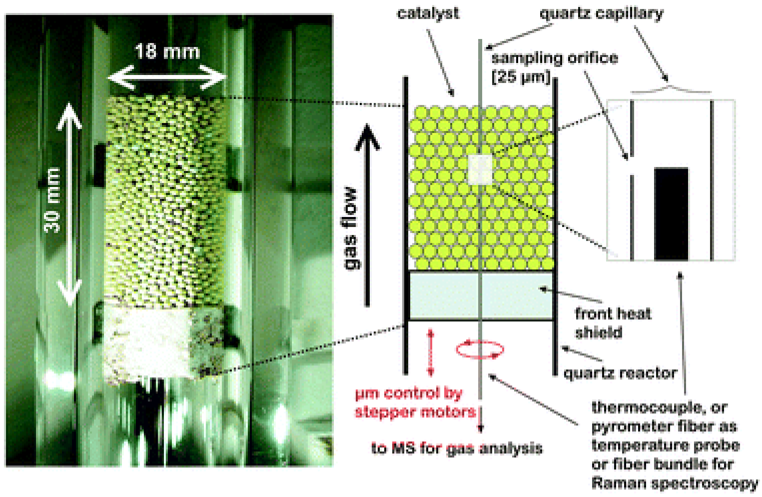
ca. 30% conv.

active species: mono- & dimeric V^{5+} oxosulfate species

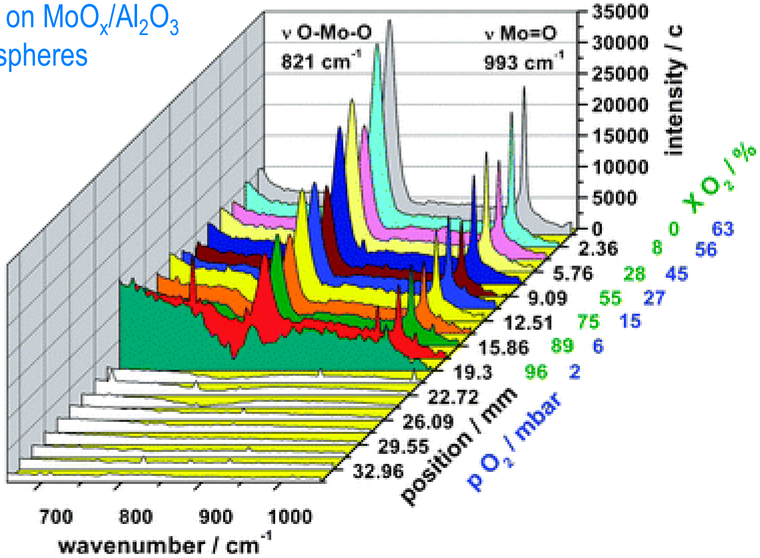
Beato et al., *Catal. Today* 205 (2013) 128

Applications

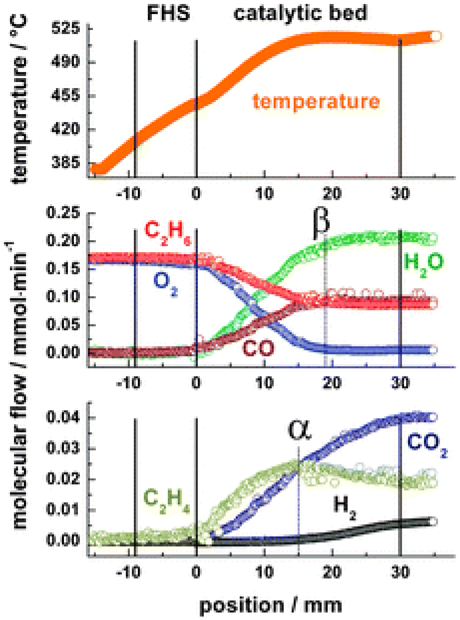
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

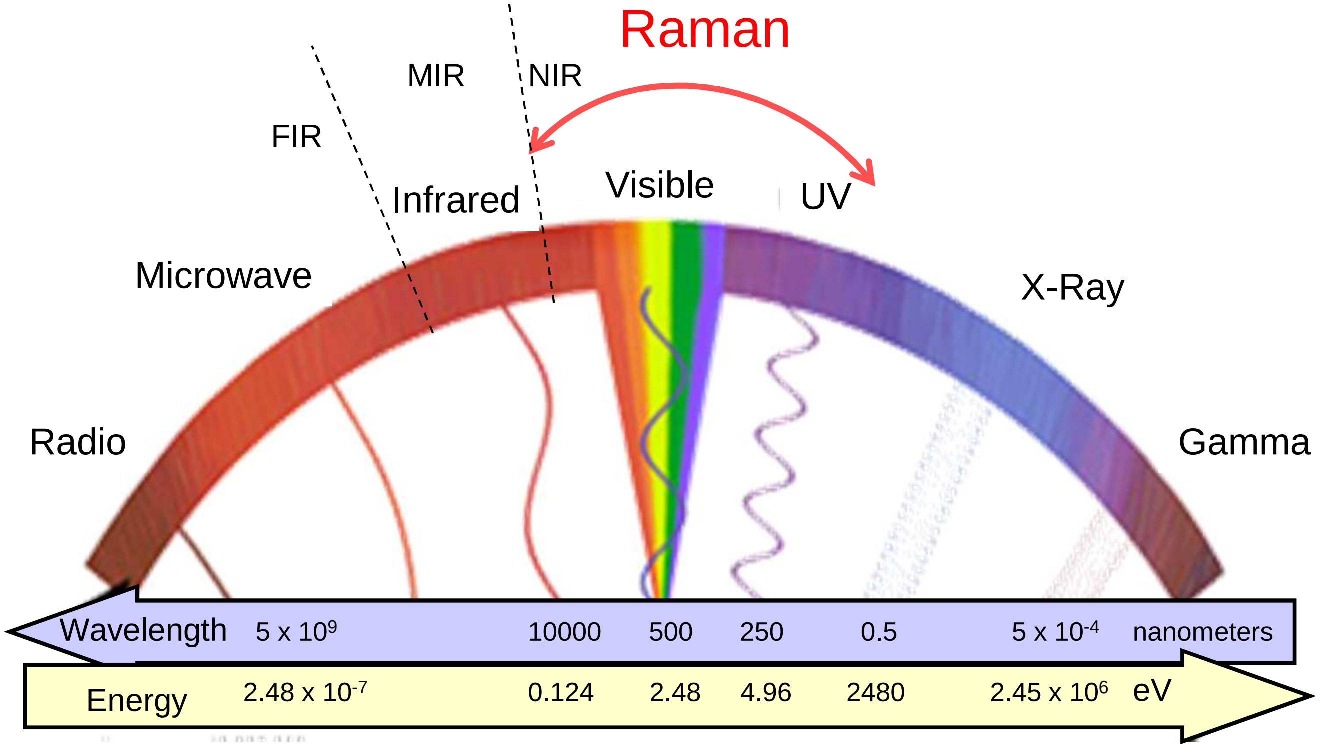
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy



Raman

FIR

MIR

NIR

Infrared

Visible

UV

Microwave

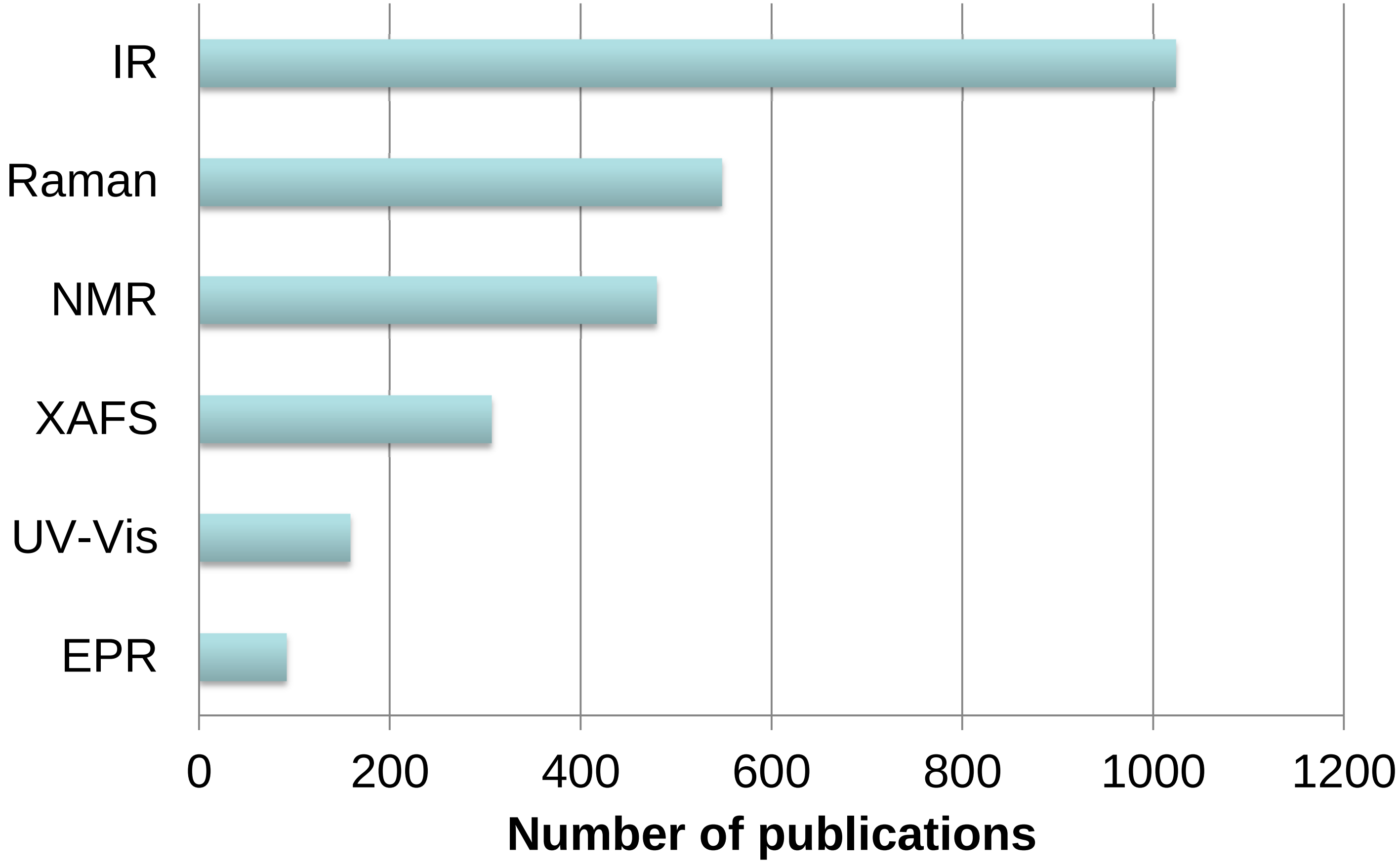
X-Ray

Radio

Gamma

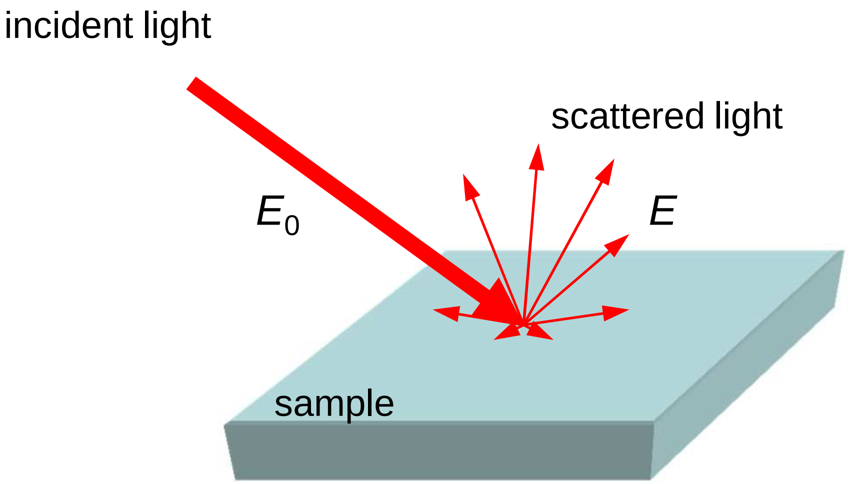
Wavelength	5 x 10^{9}	10000	500	250	0.5	5 x 10^{-4}	nanometers
Energy	2.48 x 10^{-7}	0.124	2.48	4.96	2480	2.45 x 10^{6}	eV

Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

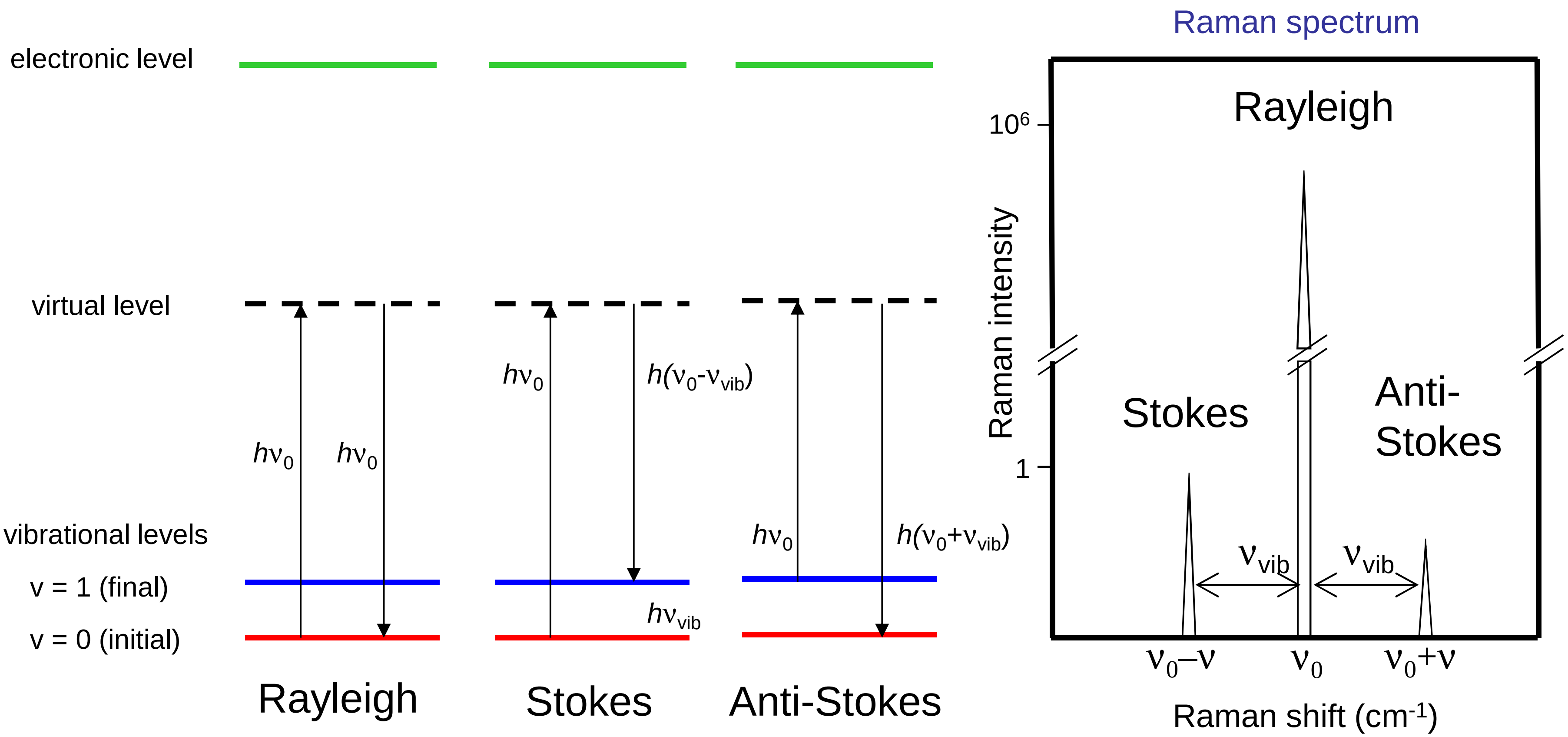
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/\mathrm{k}T}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{\mathrm{I}\ (\text{Anti-Stokes})}{\mathrm{I}\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/\mathrm{k}T}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

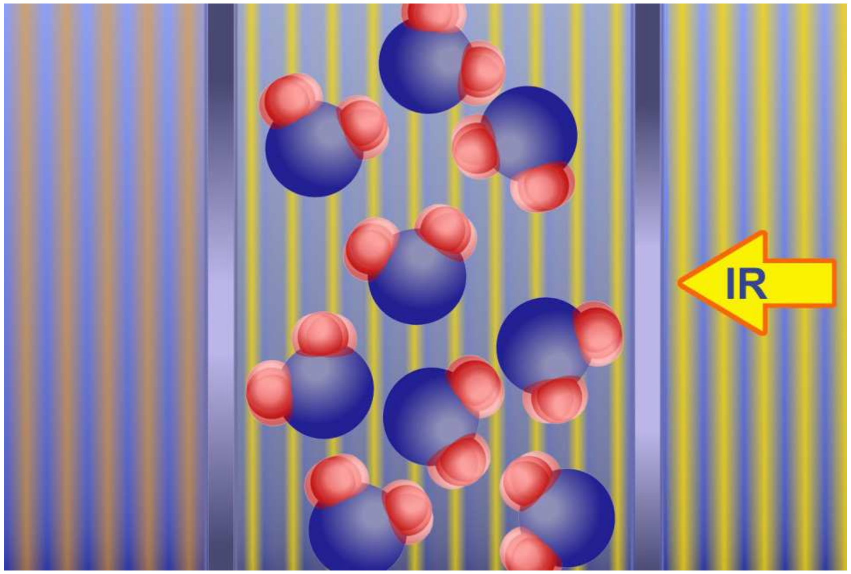
  - 4th power of ν (4th power law)
  - 2nd power of $\Delta\alpha$
    - properties of molecules
    - strength of bonds

covalent bond	STRONG bands (catalysis!)
ionic bond	WEAK bands

- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

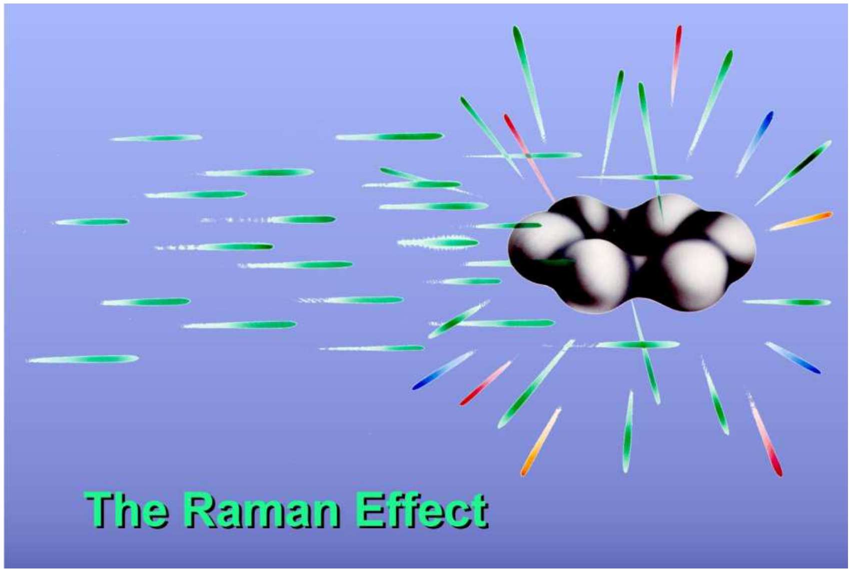
Raman *vs.* Infrared

Infrared



Absorption of IR light

Raman



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

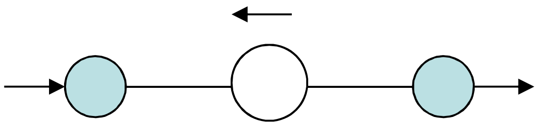
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - large electron clouds
  - not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

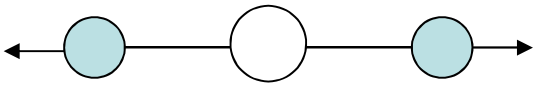
Raman *vs.* Infrared

CO_2



ν_{as}

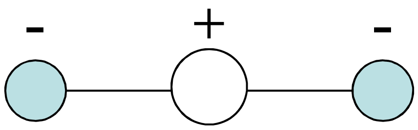
2349 cm^{-1}



ν_s

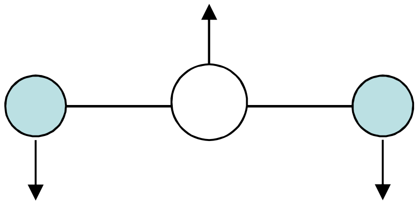
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



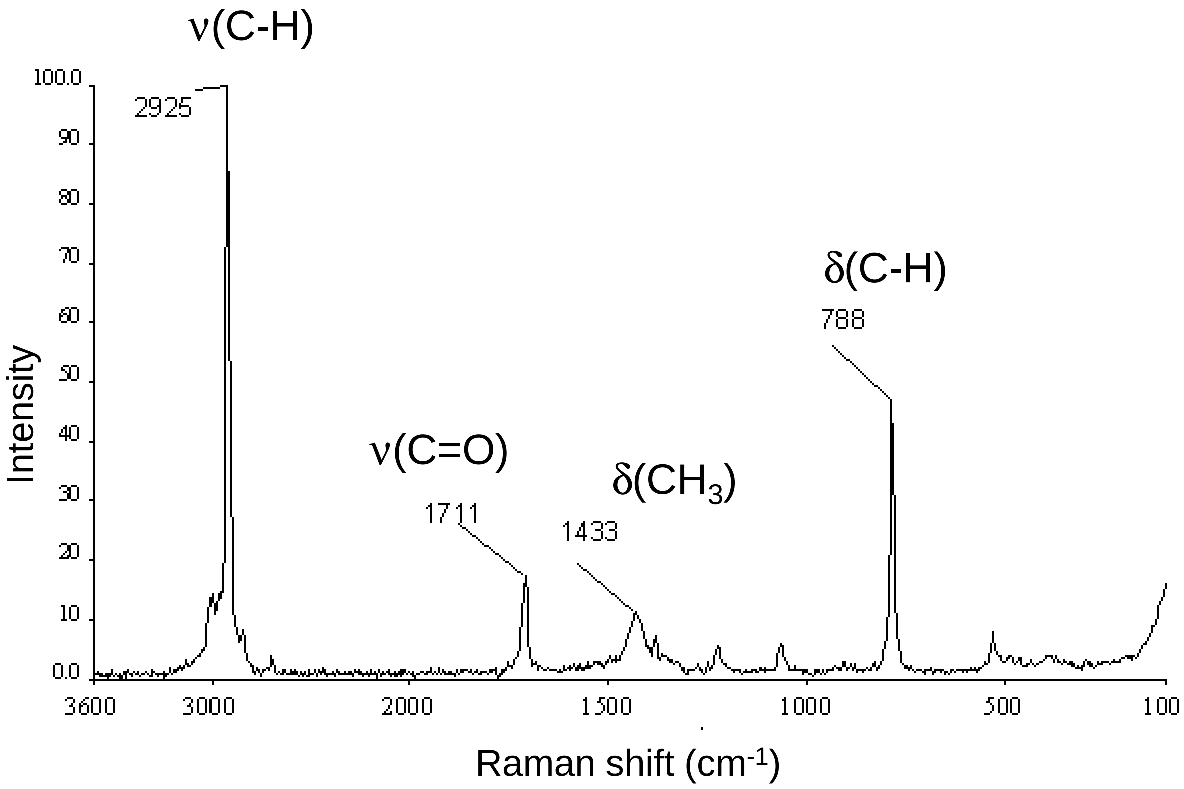
δ

667 cm^{-1}

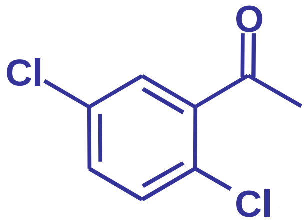
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



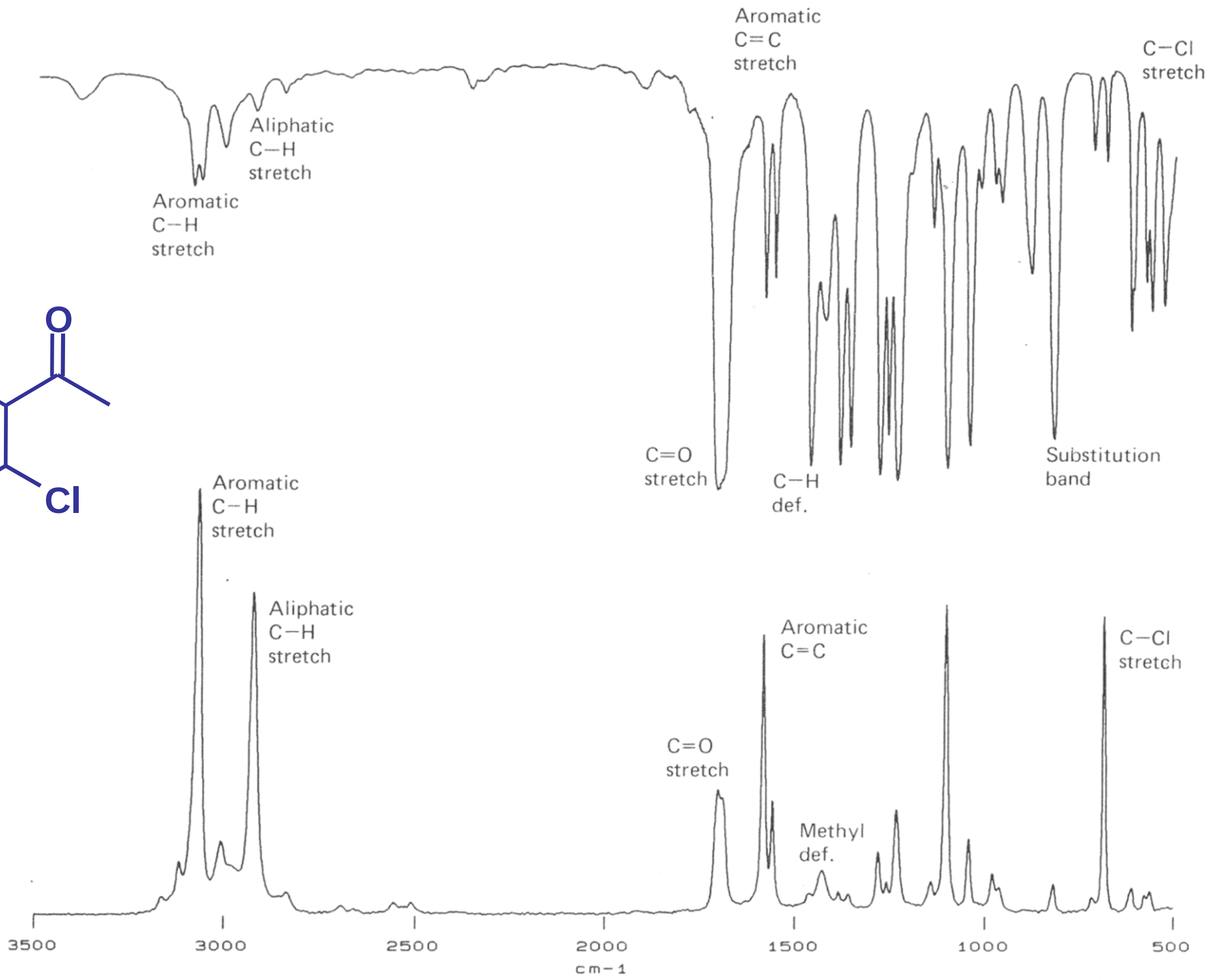


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

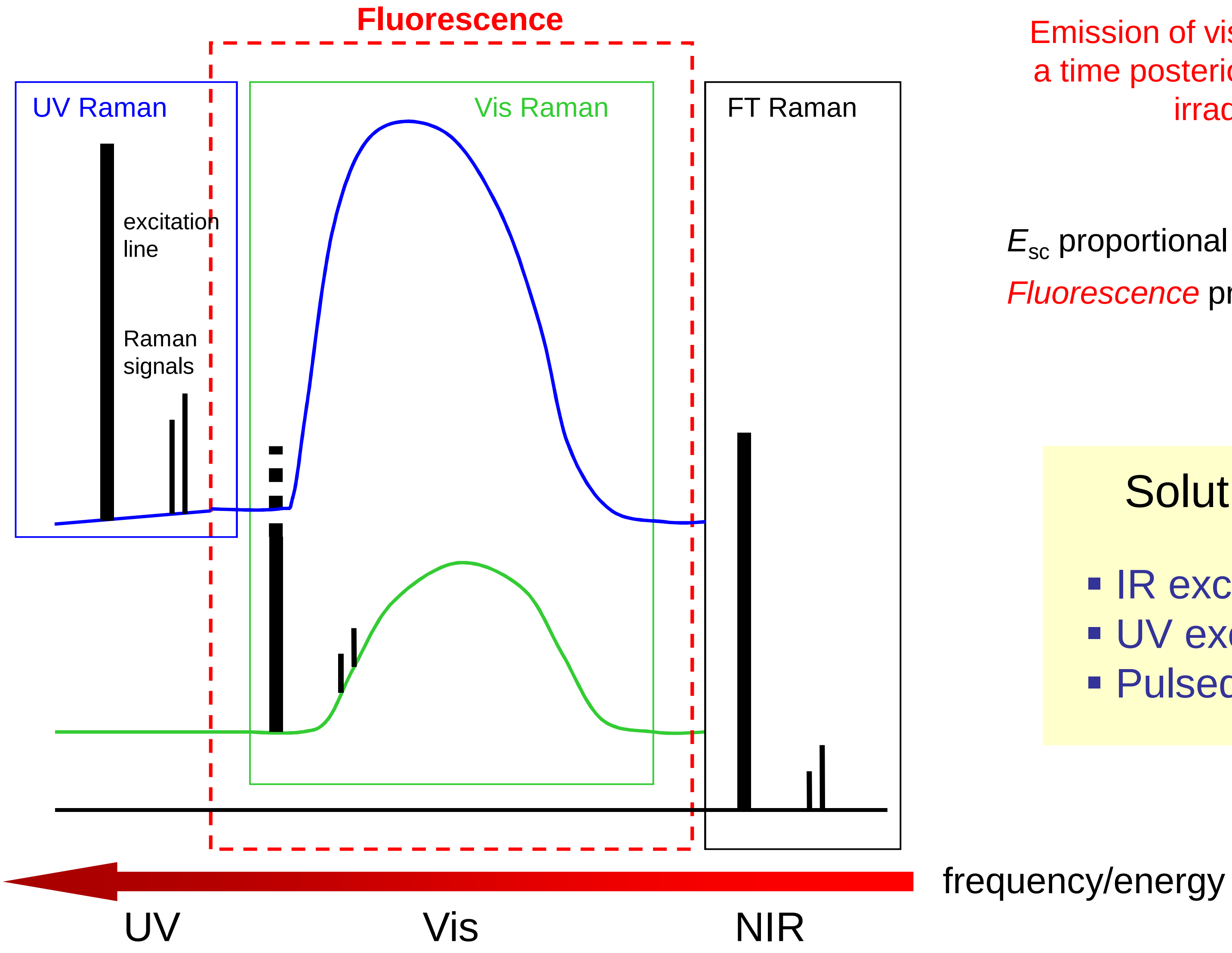
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 µm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

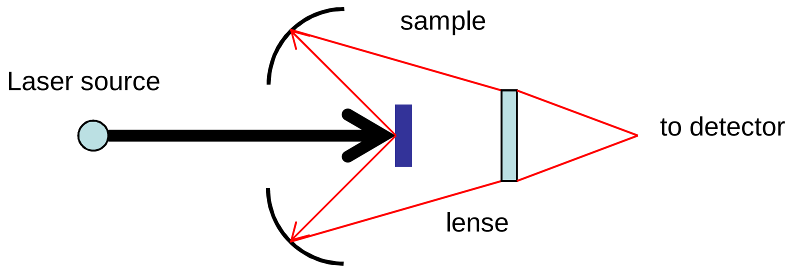
Fluorescence proportional to ν

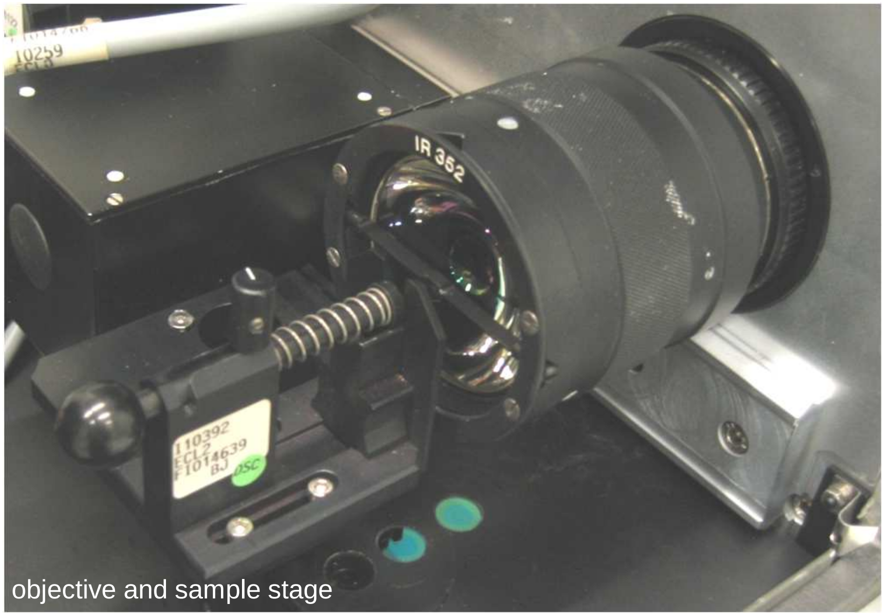
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation




objective and sample stage

Lasers

Excitation wavelengths

UV	250 nm
Vis (green)	514 nm
Vis (red)	633 nm
NIR	780 nm
IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

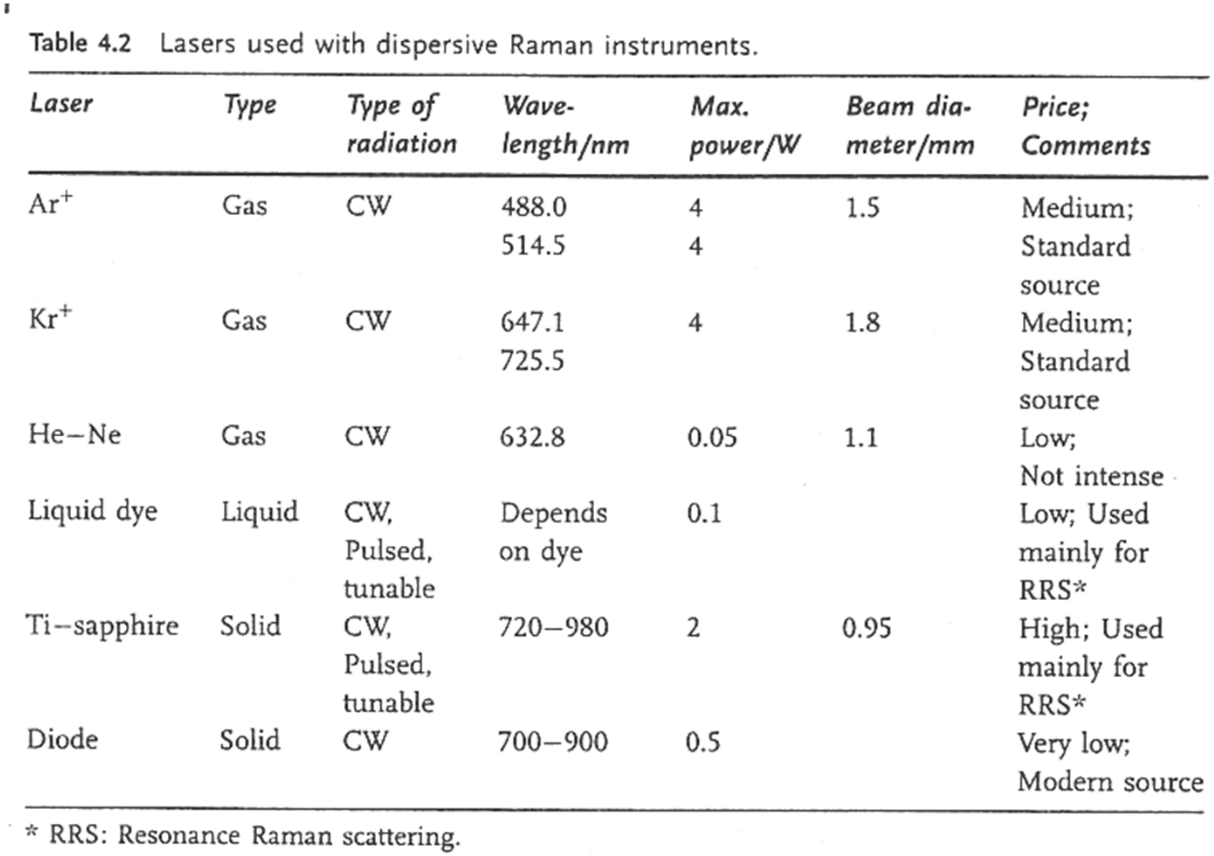


Table 4.2 Lasers used with dispersive Raman instruments.

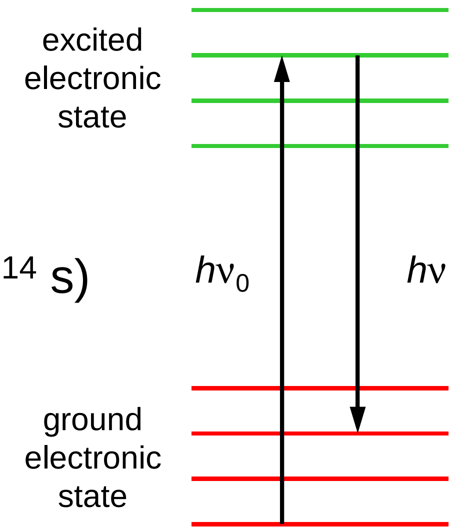
Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

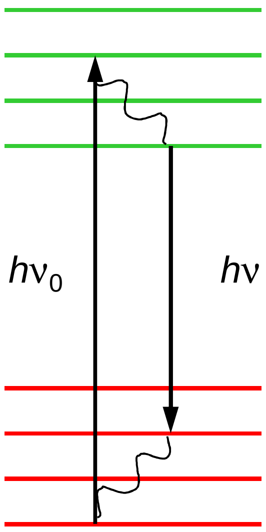
Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited

fast (10^{-14} s)



Resonance Raman scattering



slow (10^{-9}–10^{-6} s)

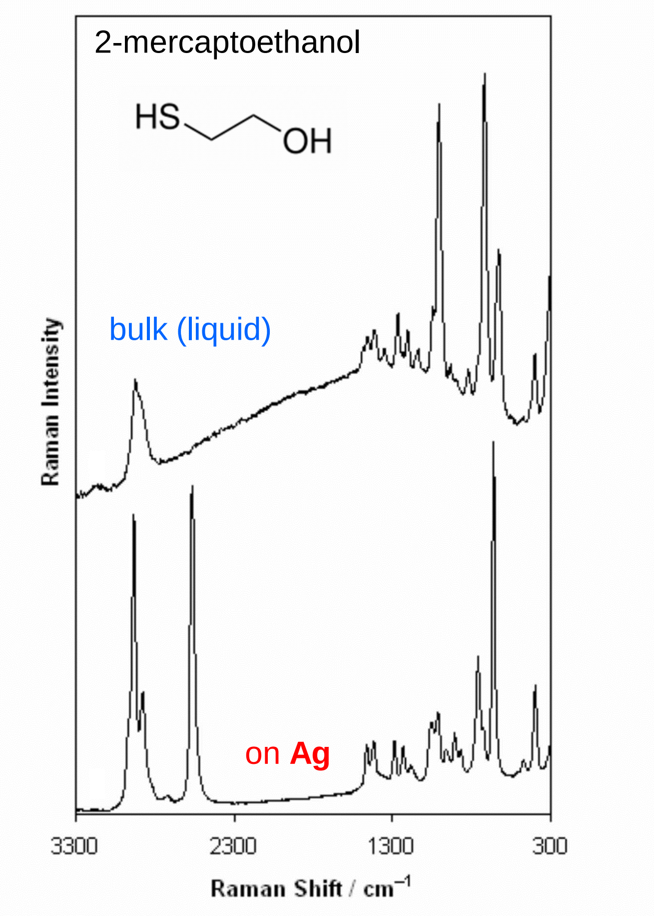
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu
- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

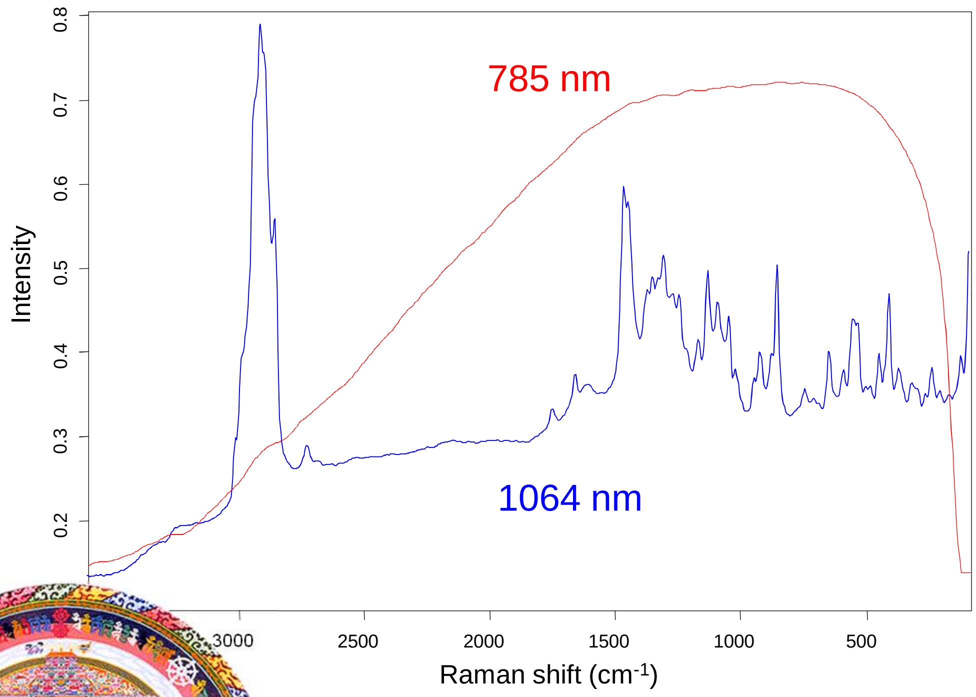
- Remarks:

☐ rough surface; nanoparticles (10–100 nm) or kinks, steps etc. (E always perpendicular to surface, locally)
☐ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



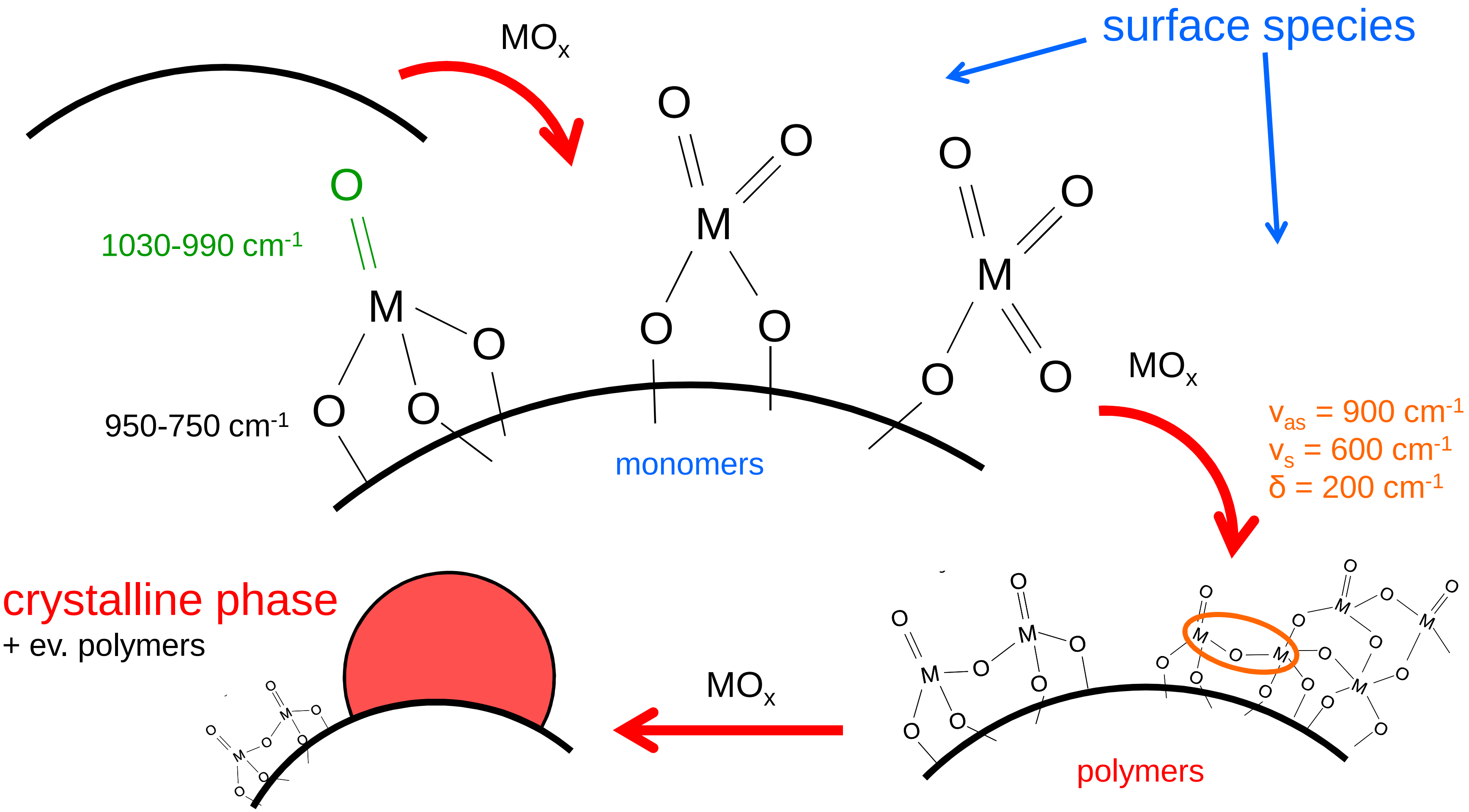
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



surface species

MO_x

1030-990 cm^{-1}

950-750 cm^{-1}

monomers

MO_x

ν_{as} = 900 cm^{-1}
ν_s = 600 cm^{-1}
δ = 200 cm^{-1}

polymers

MO_x

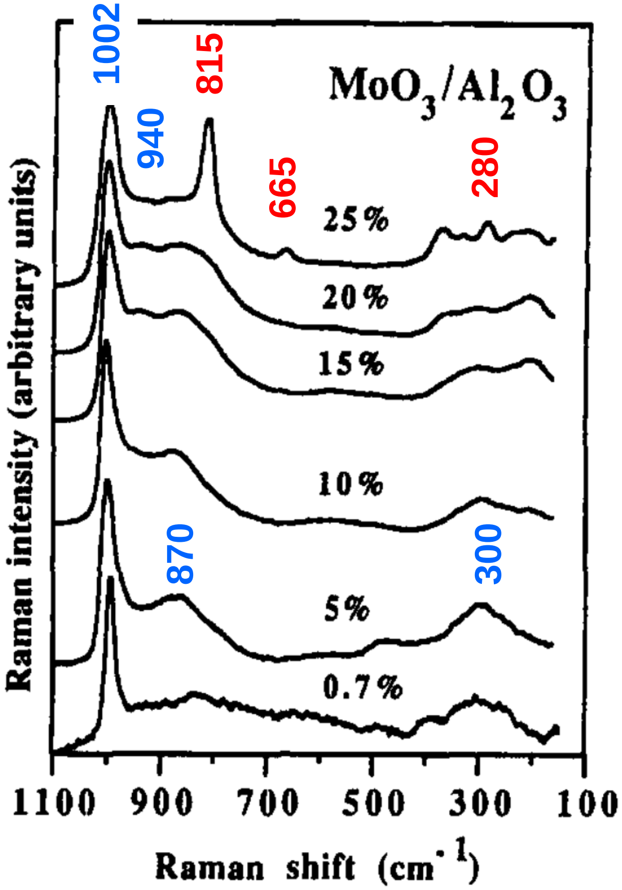
crystalline phase
+ ev. polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



surface MoO_3

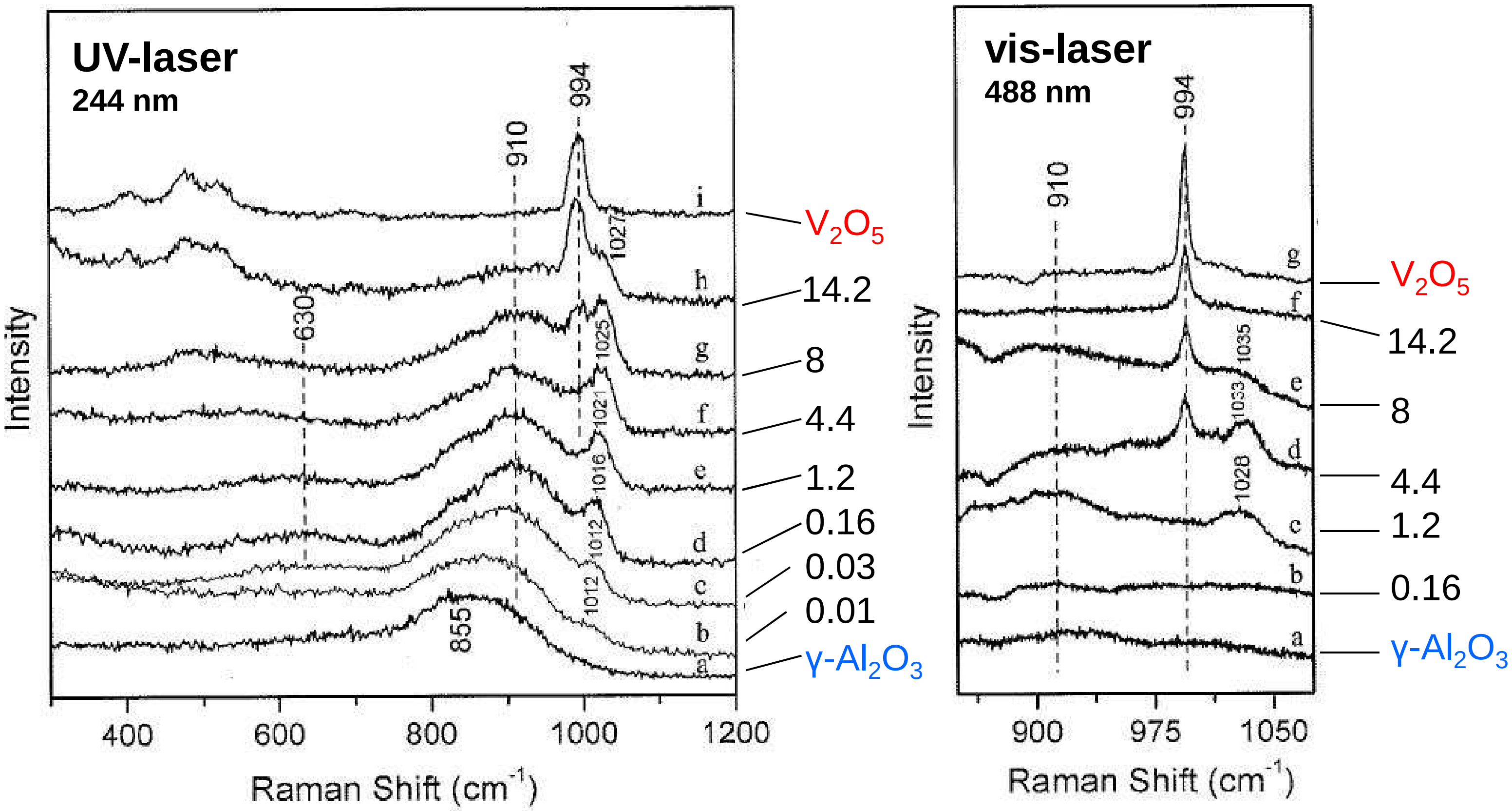
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

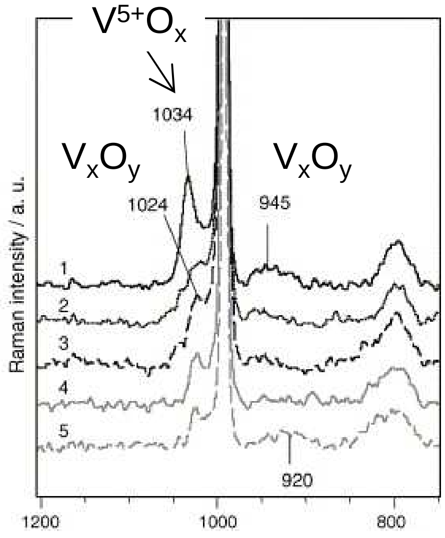
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

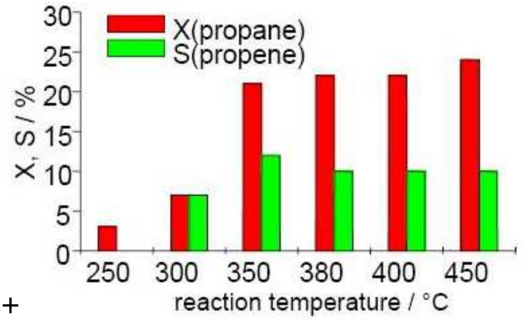
Applications

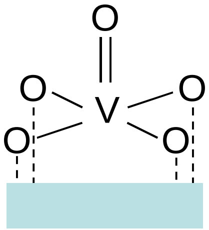
- Reactivity of V/TiO_2 after oxidative treatment

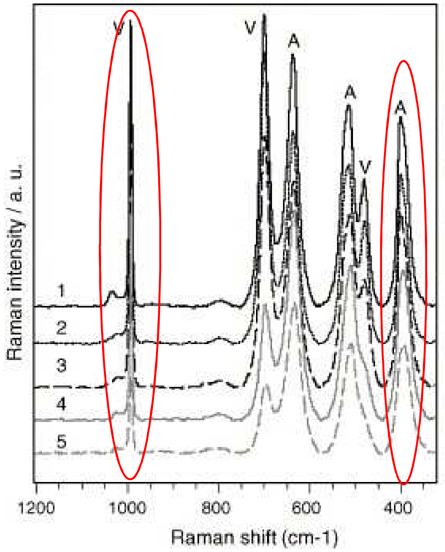


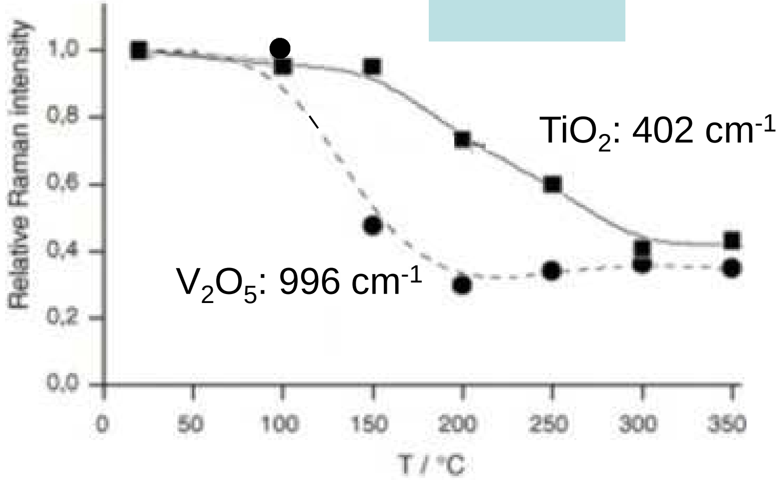
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









TiO_2: 402 cm^{-1}

V_2O_5: 996 cm^{-1}

Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

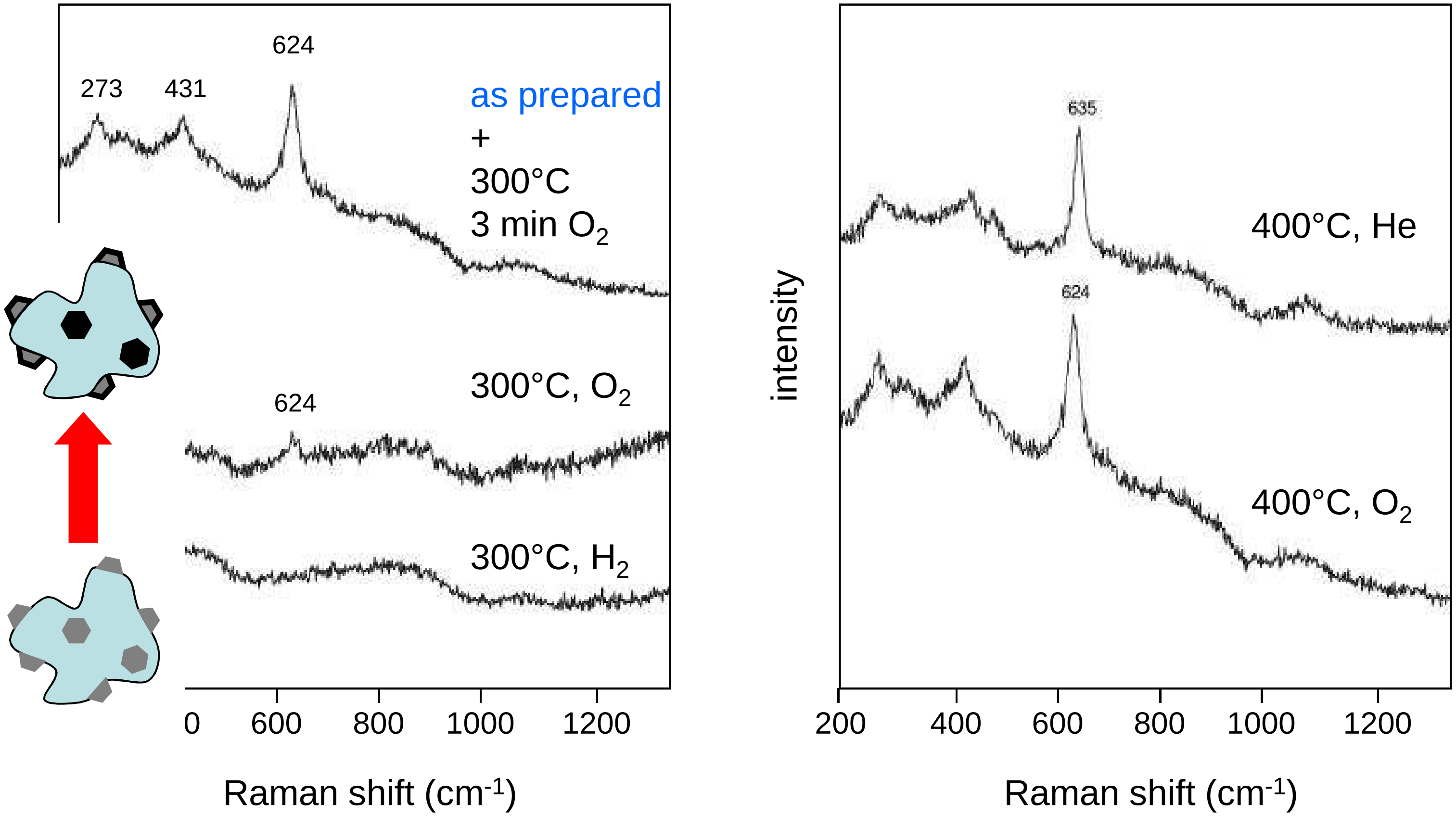
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…) used for total and partial oxidation reactions

Question: what is the state of Pd during reaction?

Examples:	Pd for CH_4 combustion
	Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3



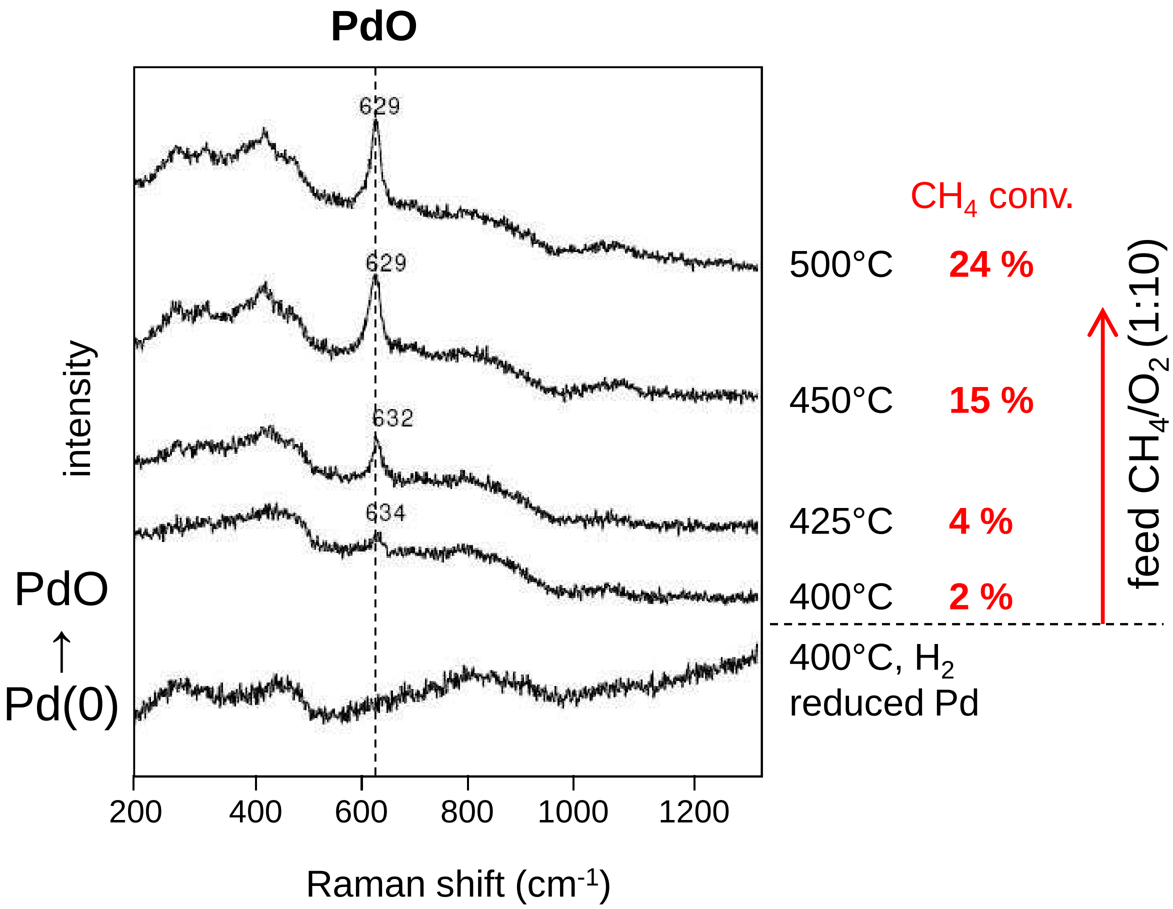
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

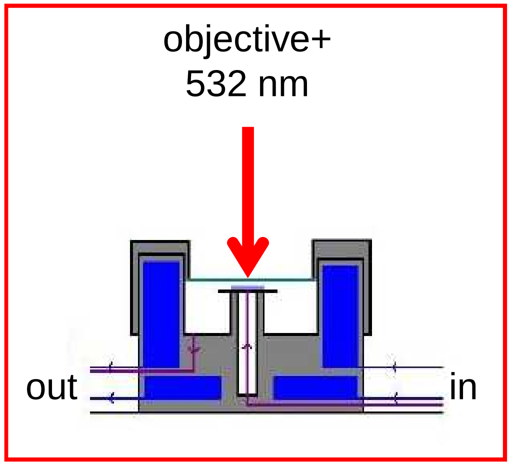
Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



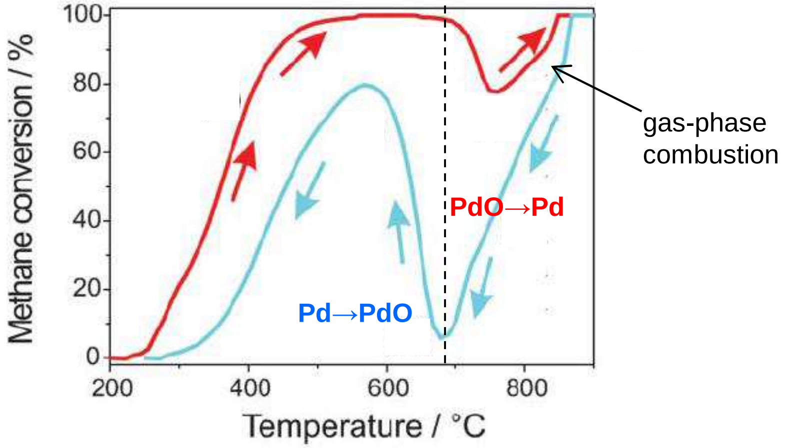
near PdO mode

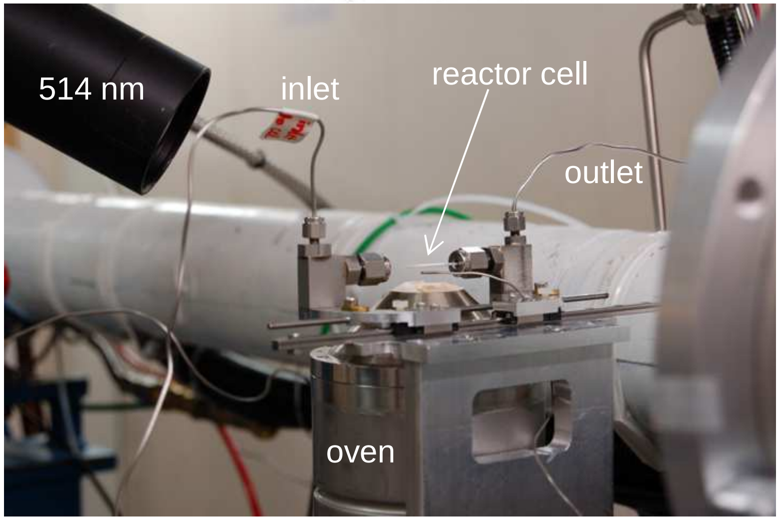


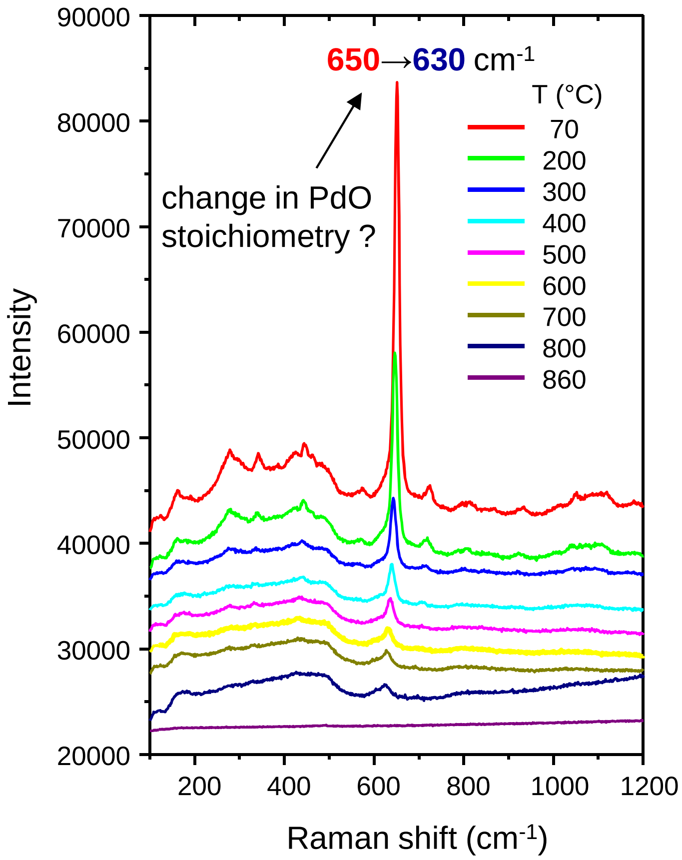
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

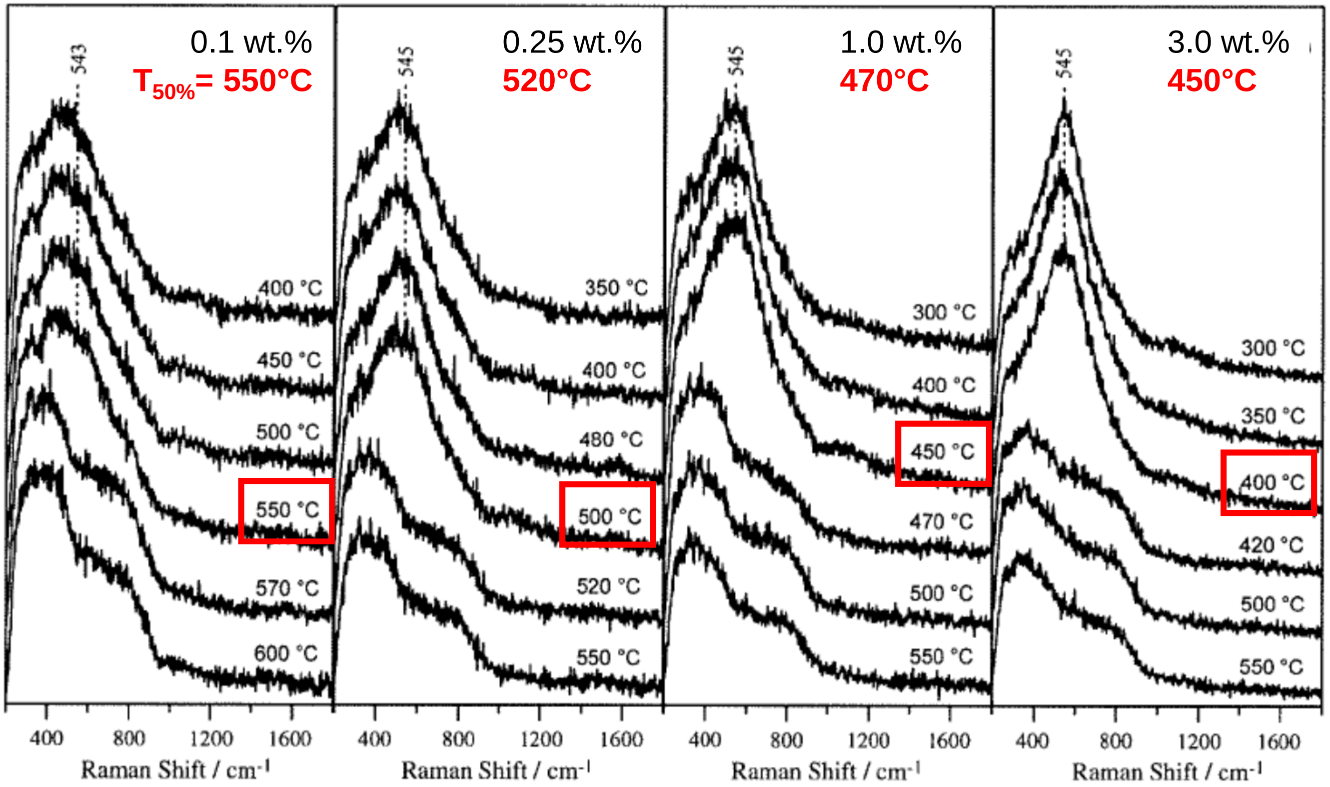
Applications

- Methane partial oxidation over Rh/Al_2O_3

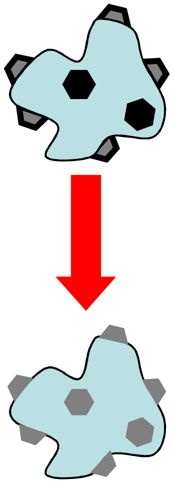
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content →
Activity →



RhO_x
↓
Rh(0)



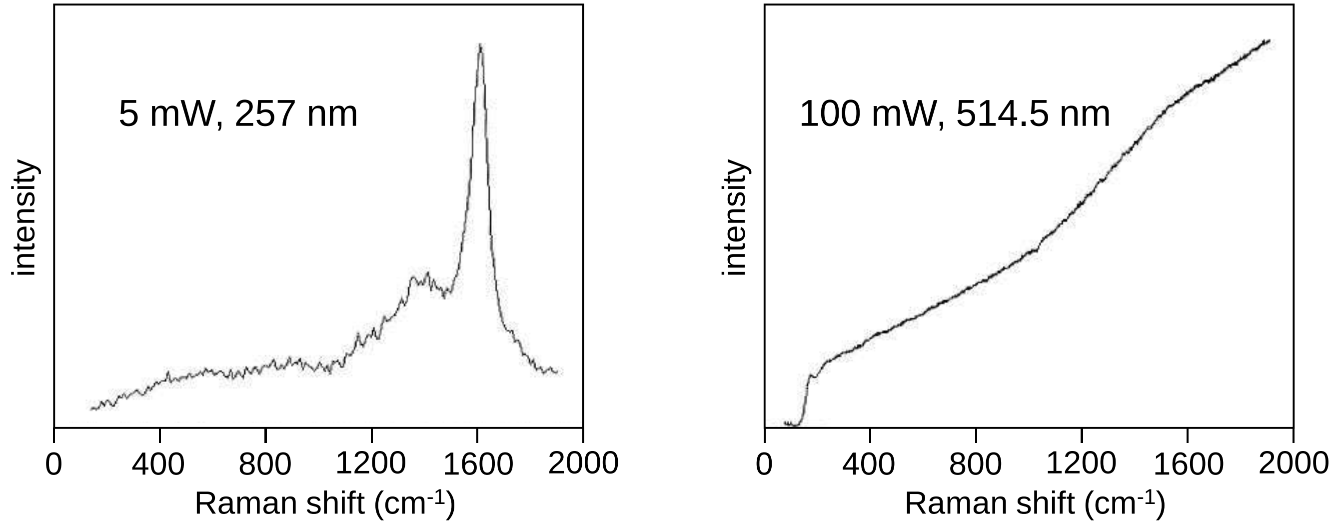
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

(only few molecules fluoresce below 260 nm)

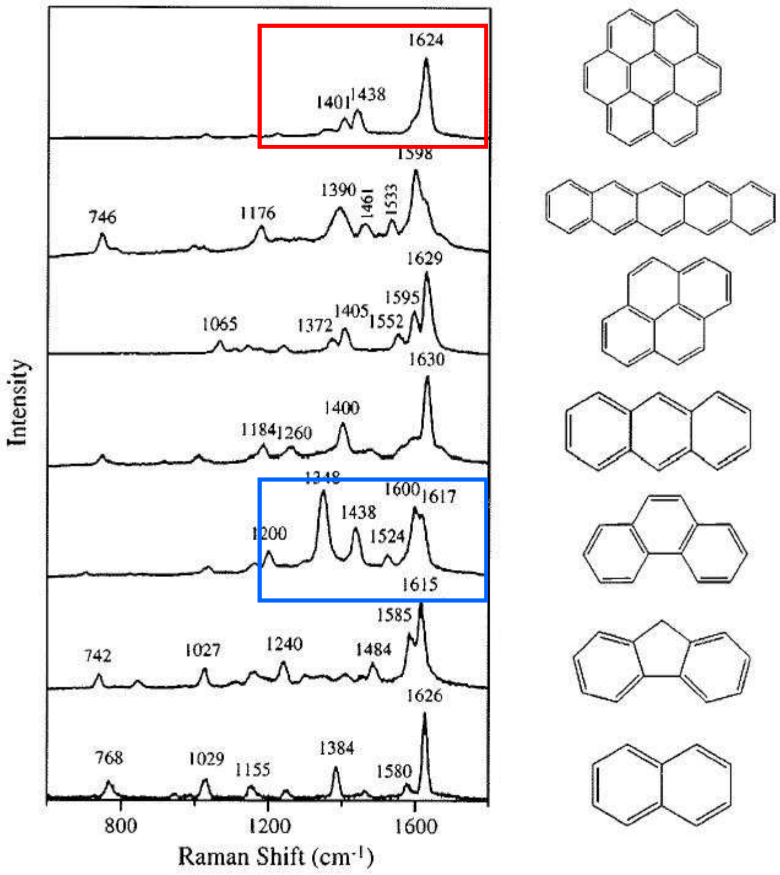
Rh/Al_2O_3, coked 500°C in naphtha

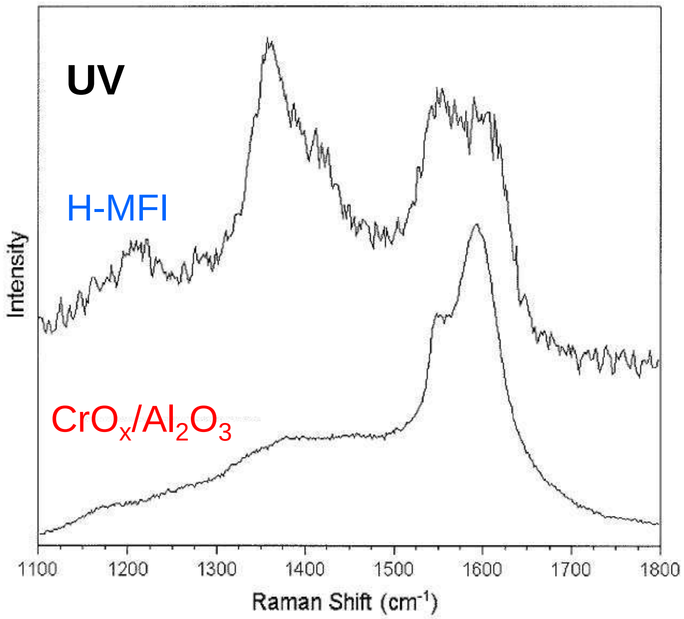


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





Coke classification

1D topology, chain-like

2D topology, sheet-like

Coke from:

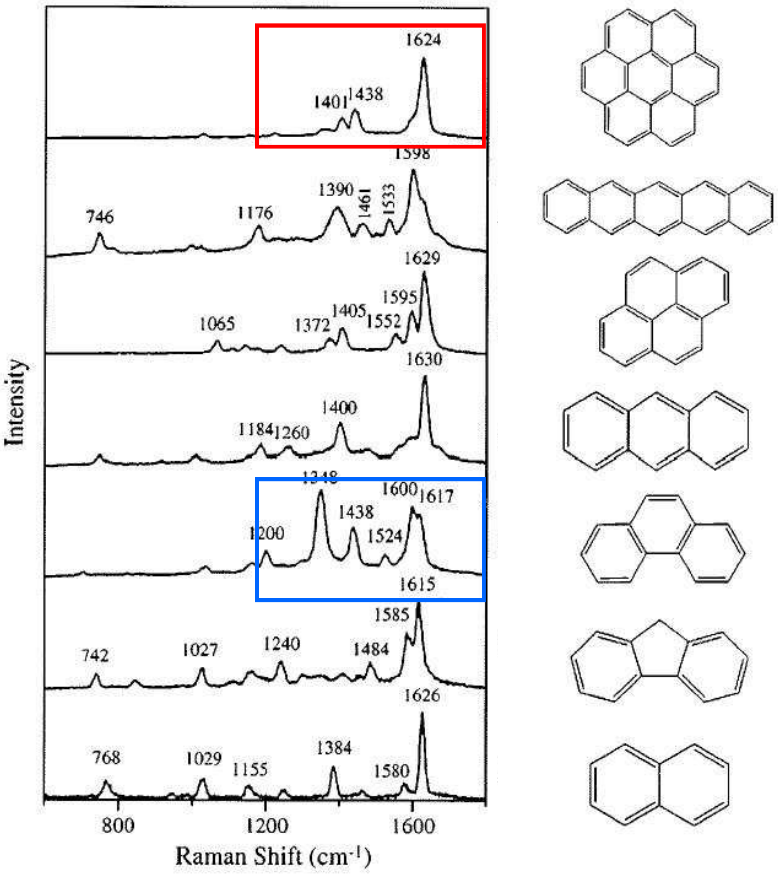
H-MFI: methanol-to-hydrocarbons (MTH)

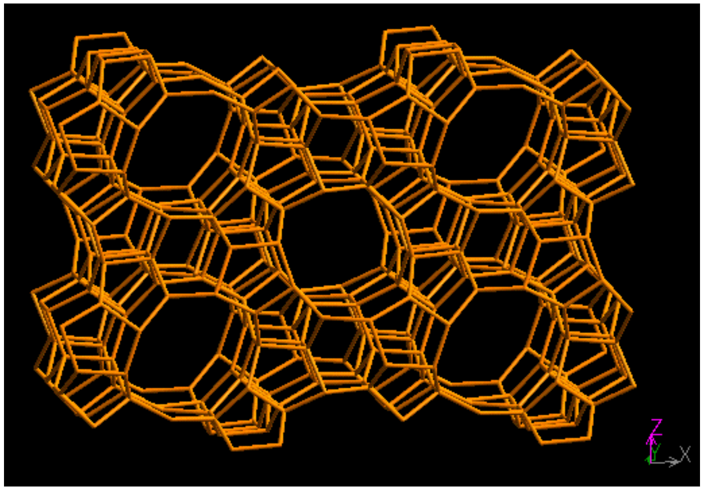
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





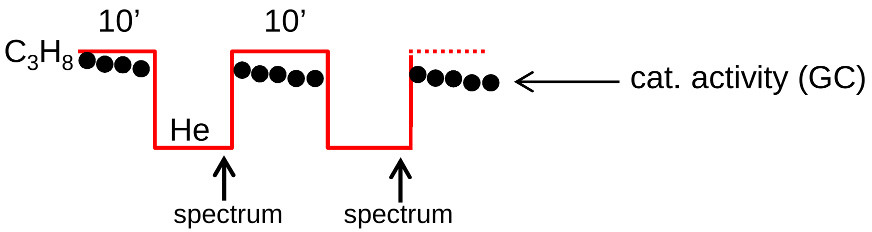
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- Propane dehydrogenation



10’

10’

C_3H_8

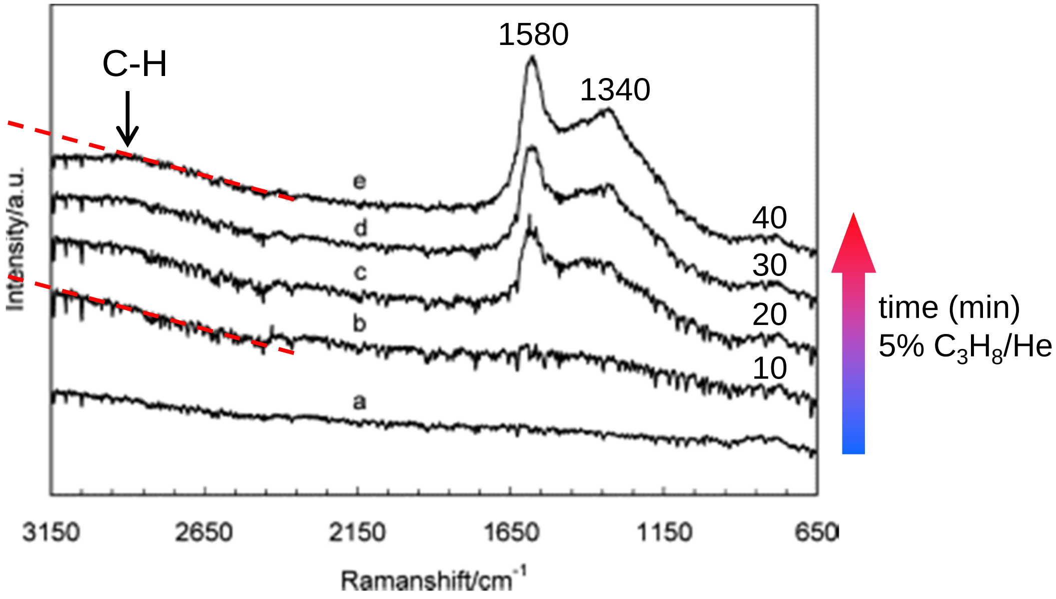
He

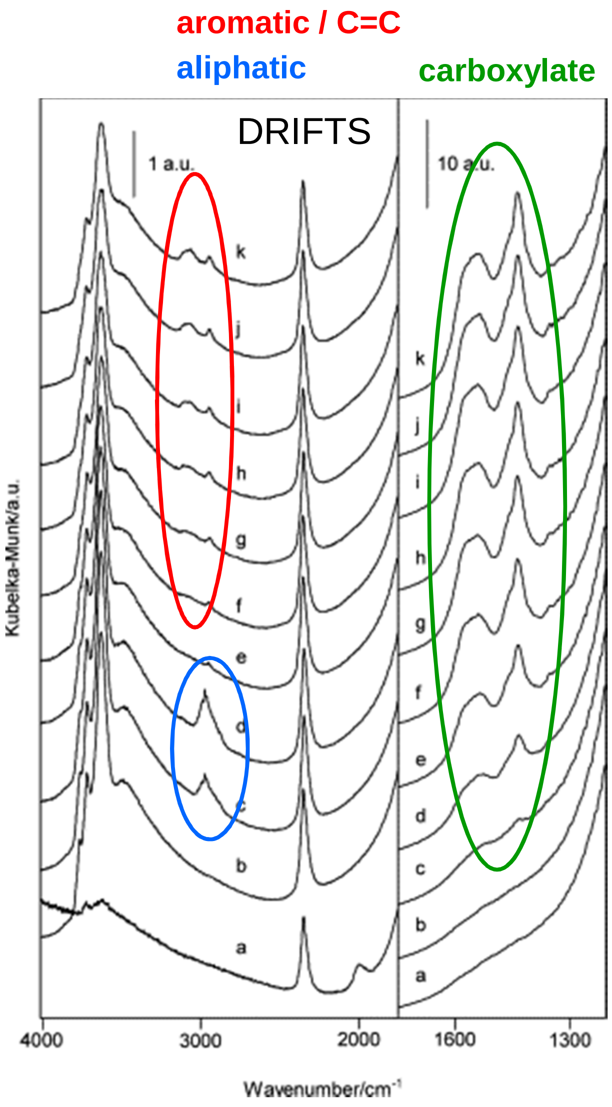
← cat. activity (GC)

spectrum

spectrum

Cr_2O_3/Al_2O_3, 580°C, 514 nm

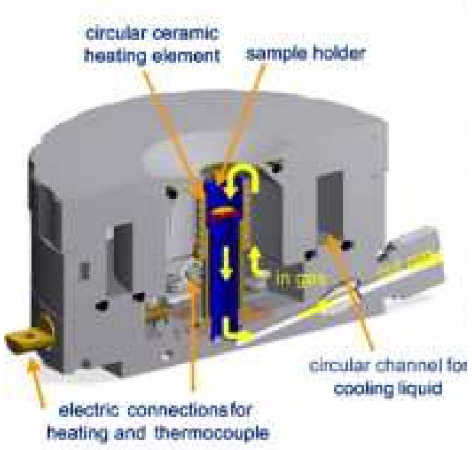


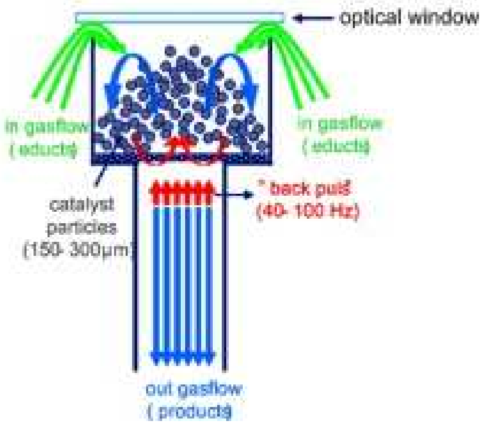


Airaksinen et al., *J. Catal.* **230** (2005) 507

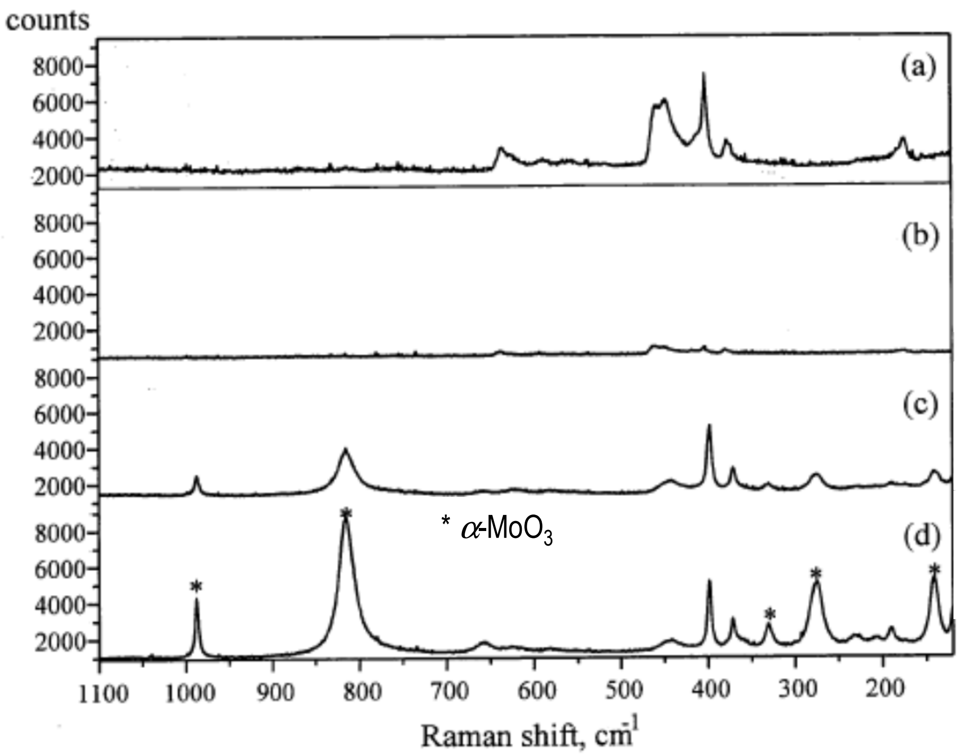
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min
full power, FB

MoS_2, 6 min
1/8 power

MoS_2, 1 min
full power

MoS_2, 6 min
full power

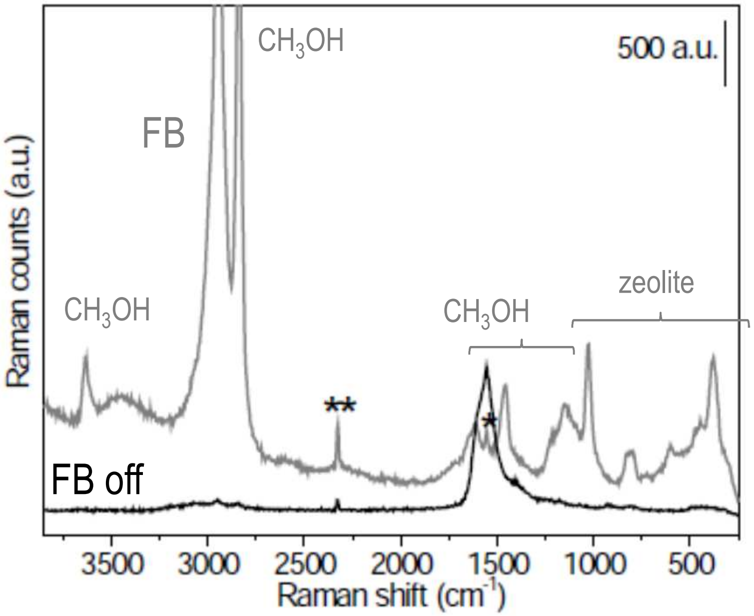
Beato et al., *Catal. Today* 205 (2013) 128

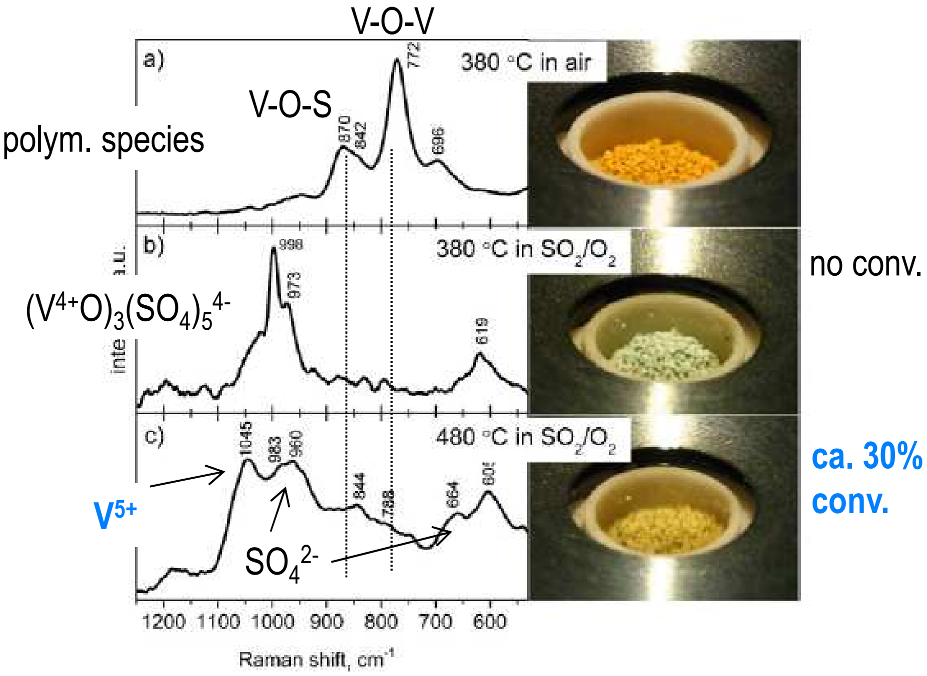
Applications

- Fluidized bed reactor cell

CH$_3$OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm

Sulfuric acid V$_2$O$_5$/pyrosulfate catalyst
λ= 514 nm





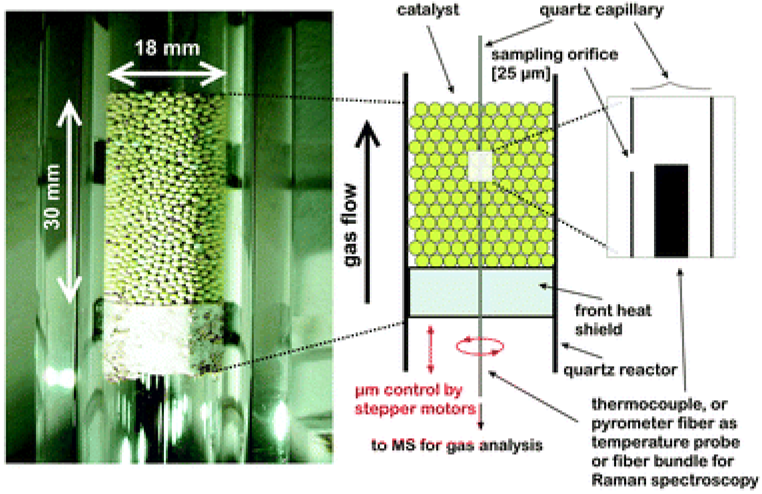
Laser induced CH$_3$OH decomposition

active species: mono- & dimeric V^{5+} oxosulfate species

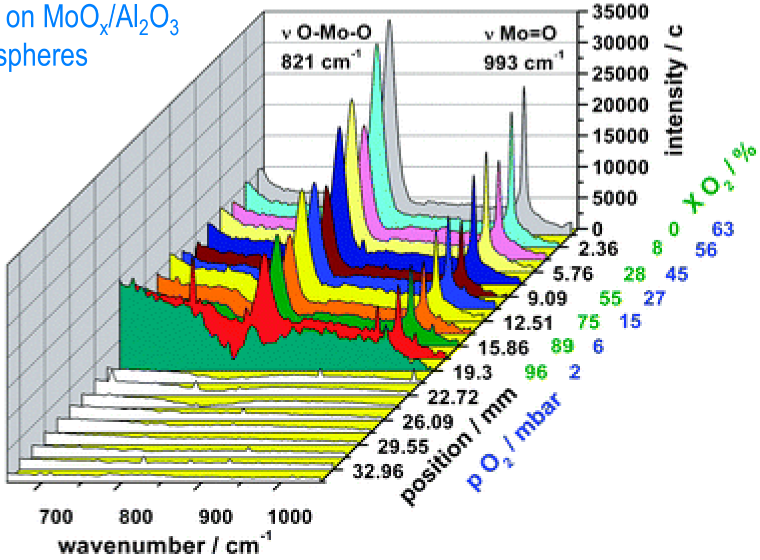
Beato et al., *Catal. Today* 205 (2013) 128

Applications

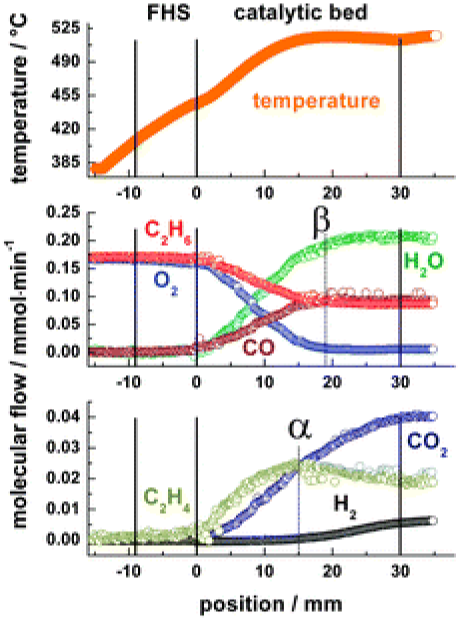
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

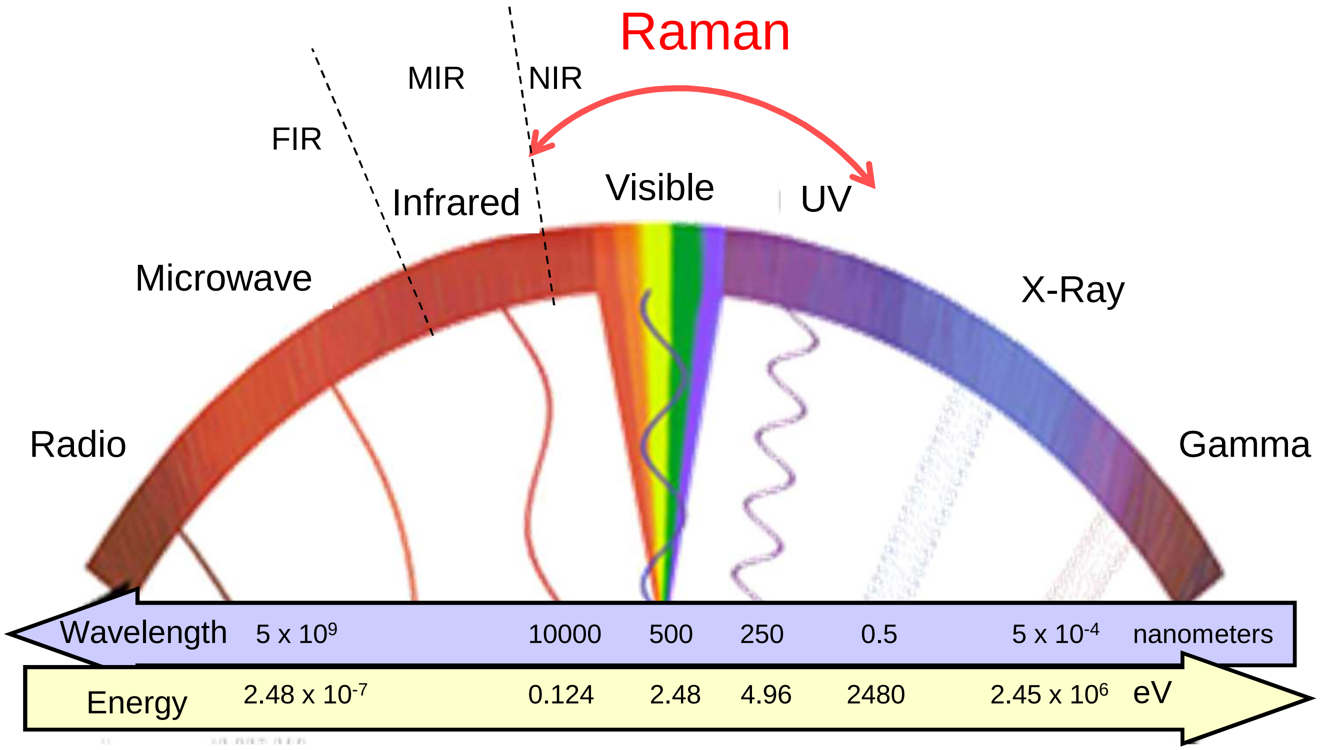
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

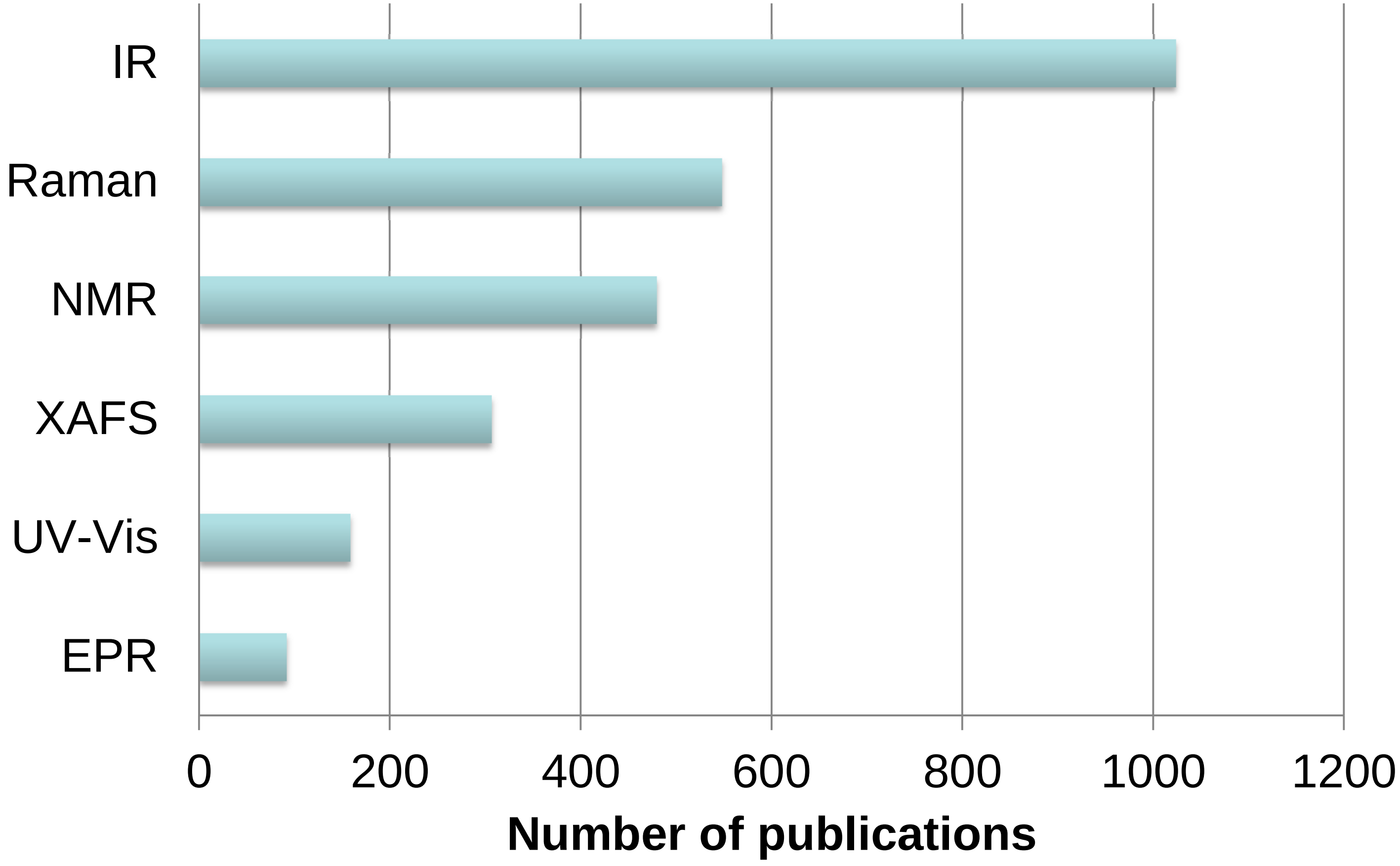
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

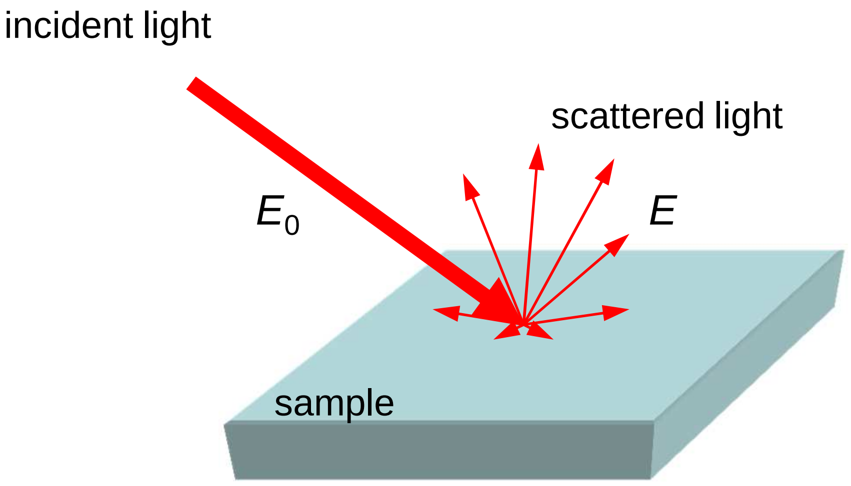


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering

inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - ❑ Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

- ❑ E_0 = incident beam irradiance
- ❑ α = polarizability of the particle (ease of distortion of the electron cloud)
- ❑ λ = wavelength of the incident radiation
- ❑ θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

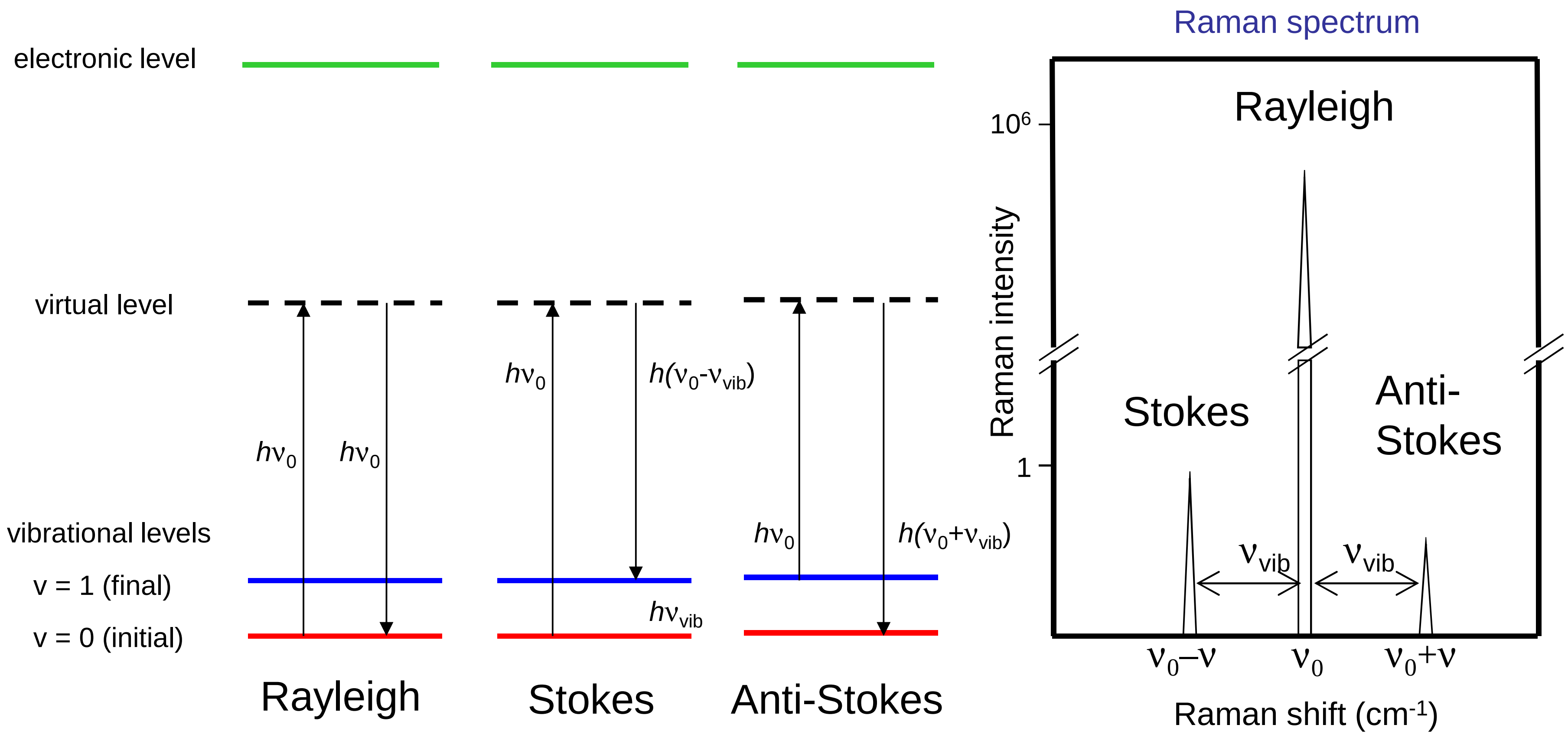
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\ [\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\ \text{(Anti-Stokes)}}{I\ \text{(Stokes)}} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

  - 4th power of ν (4th power law)
  - 2nd power of $\Delta\alpha$

    - properties of molecules
    - strength of bonds

↓

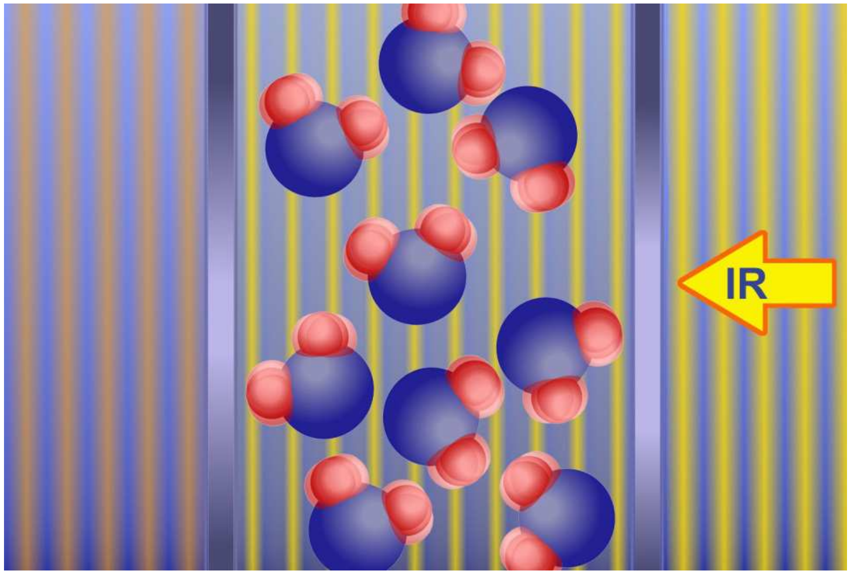
covalent bond STRONG bands (catalysis!)

ionic bond WEAK bands

- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

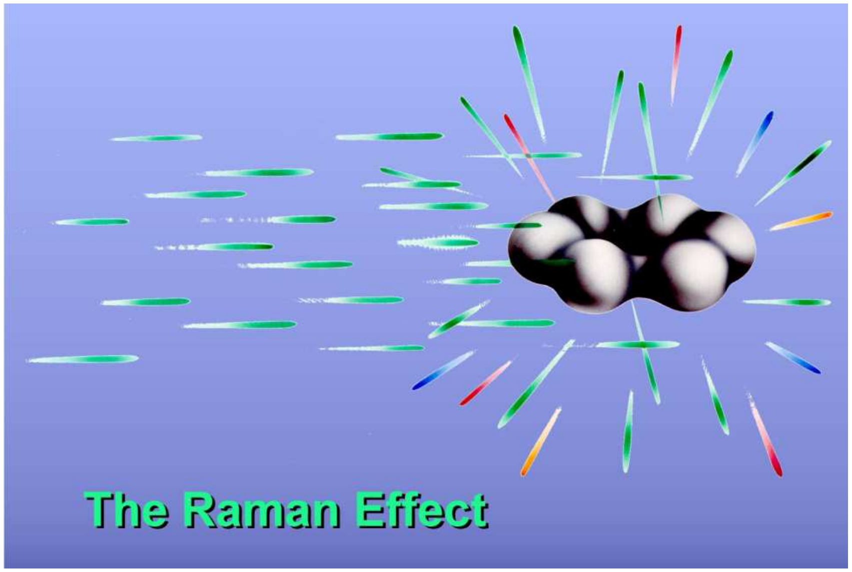
Raman *vs.* Infrared

Infrared



Absorption of IR light

Raman



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial\mu}{\partial Q}\right)^2 \neq 0$$

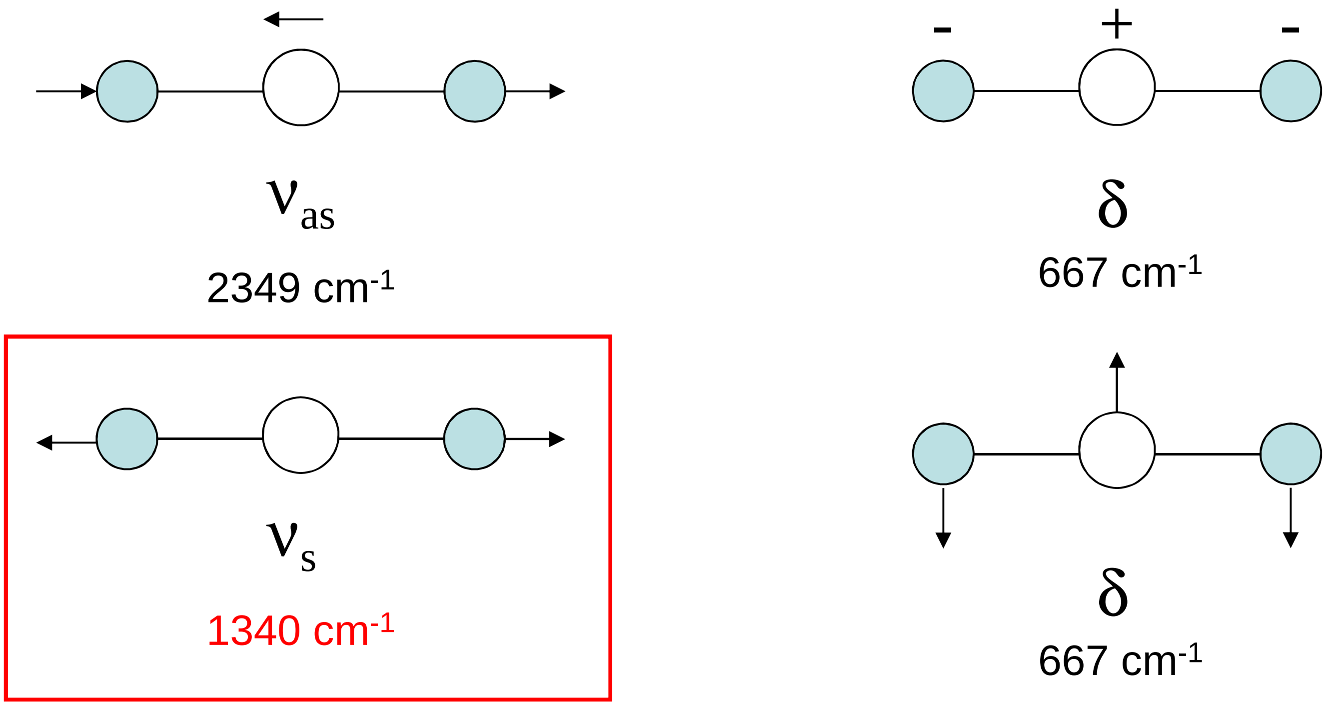
- high absorption for polar bonds ($C{=}O$, H_2O, NH, etc.)

$$\left(\frac{\partial\alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - large electron clouds
  - not polar
- H_2O is a very weak Raman scatterer
- $C{=}C$ double bonds strong Raman scatterers

Raman *vs.* Infrared

CO_2



ν_{as}

2349 cm^{-1}

ν_s

1340 cm^{-1}

Raman active

δ

667 cm^{-1}

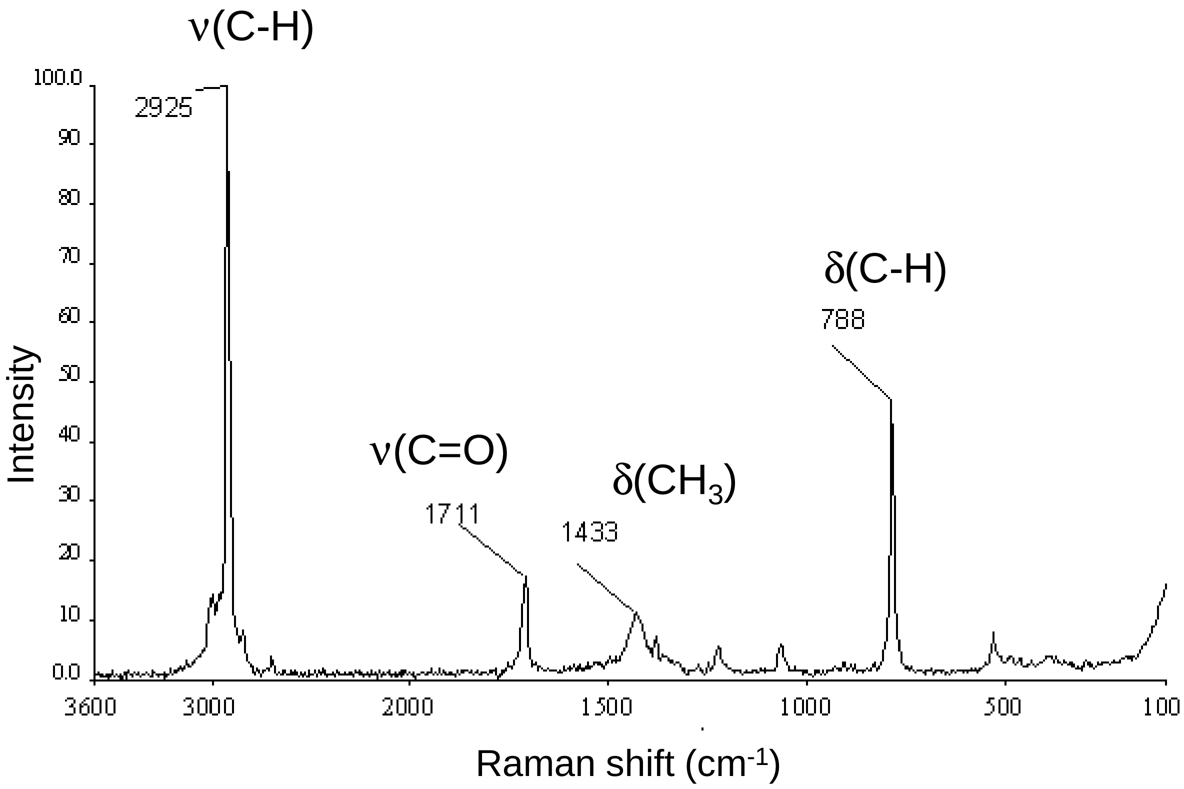
δ

667 cm^{-1}

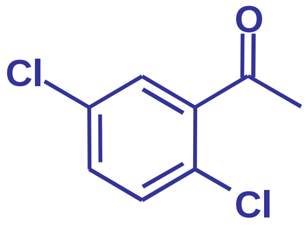
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



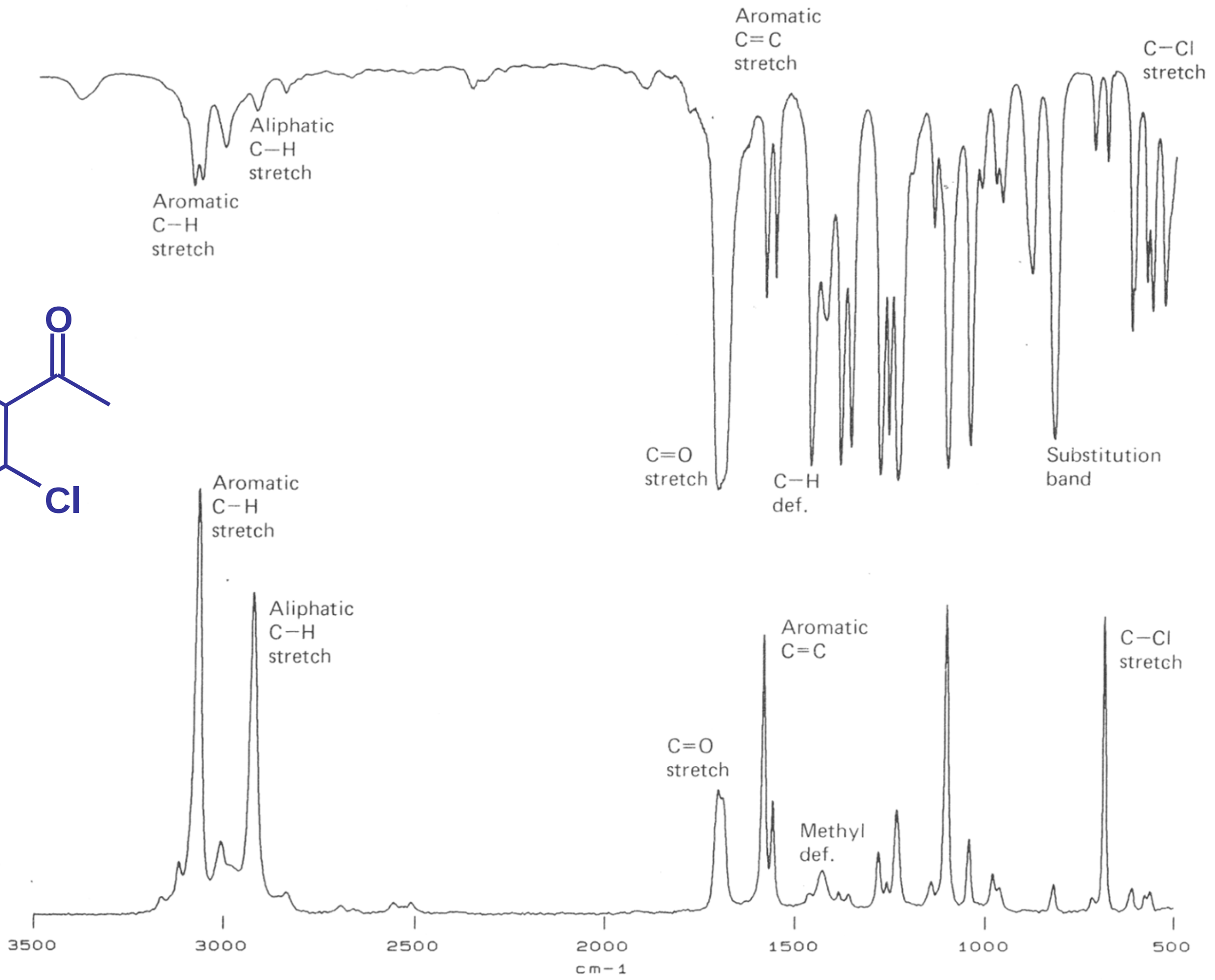


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

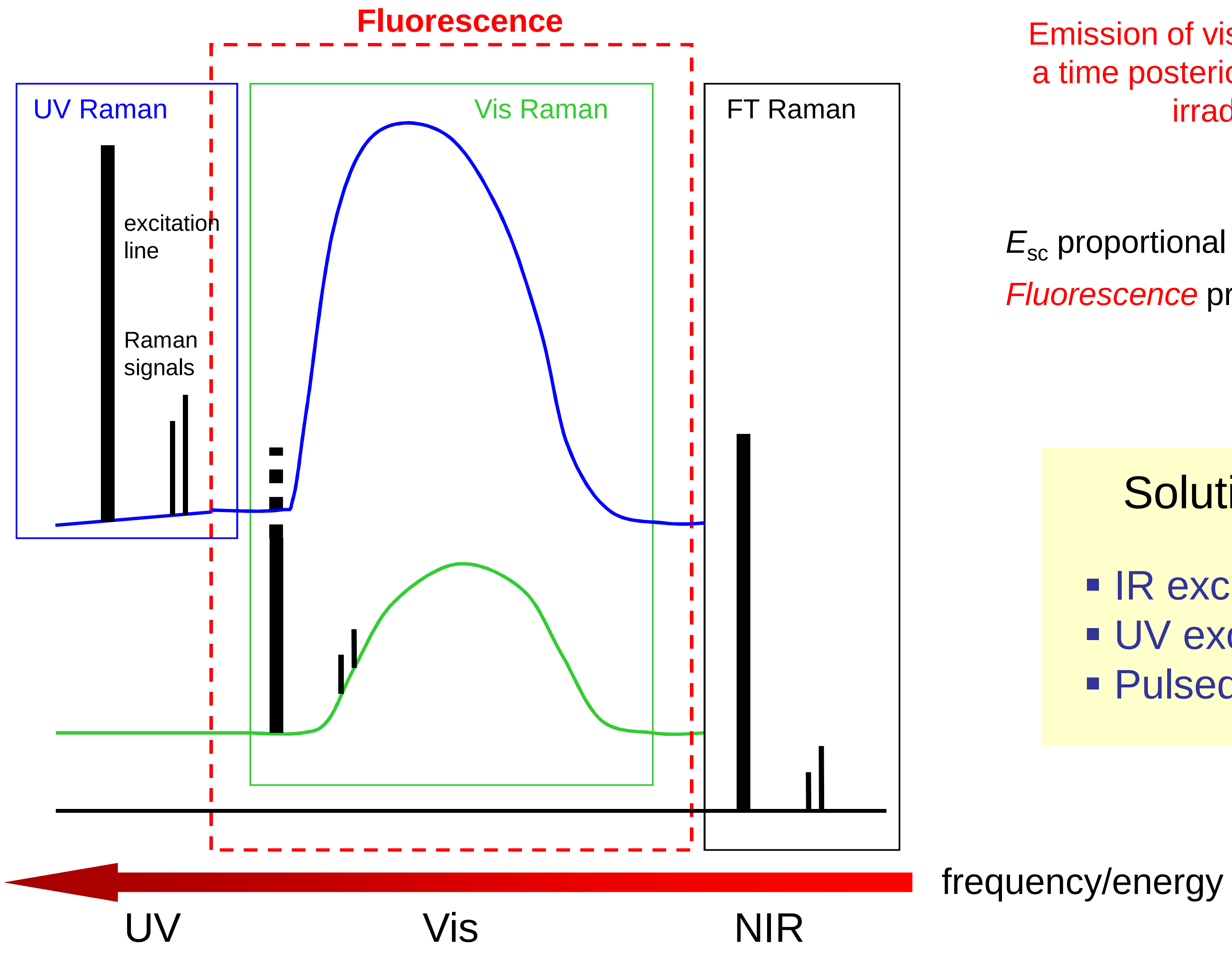
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 μm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

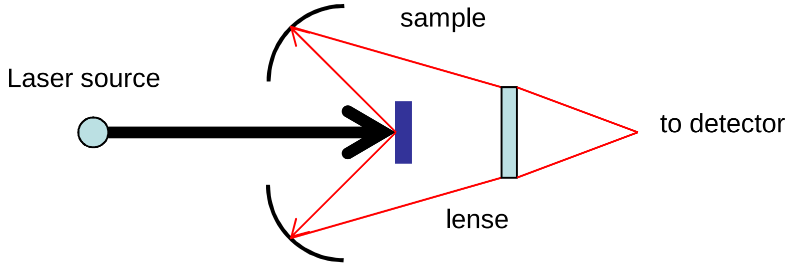
Fluorescence proportional to ν

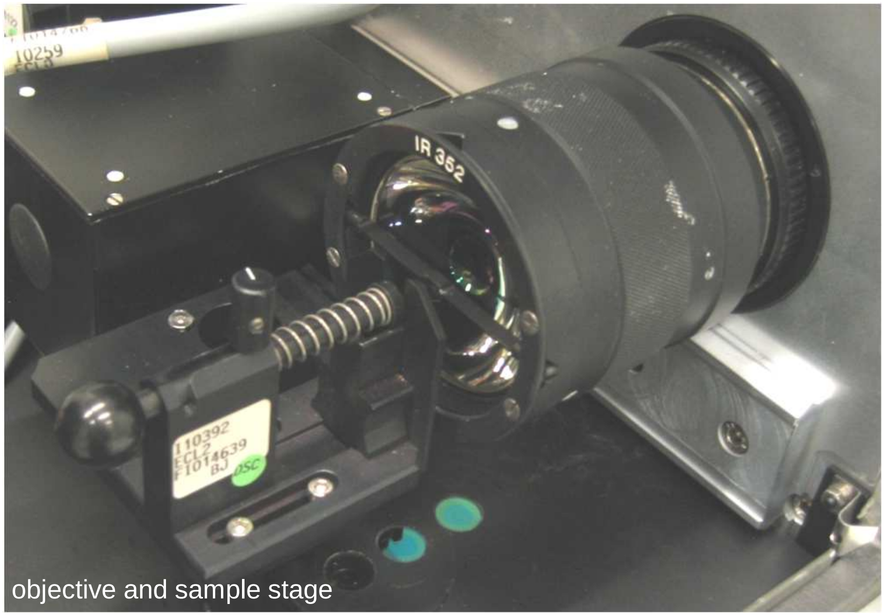
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

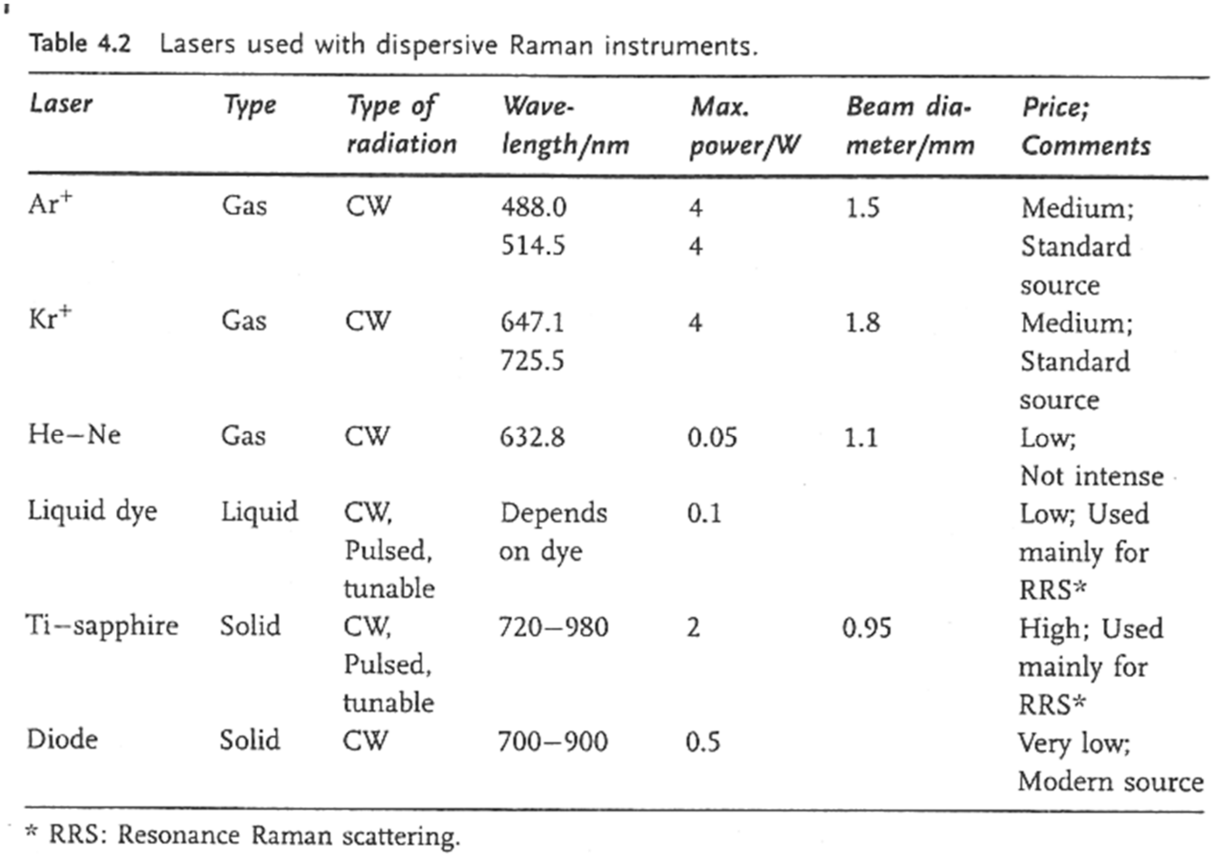


Table 4.2 Lasers used with dispersive Raman instruments.

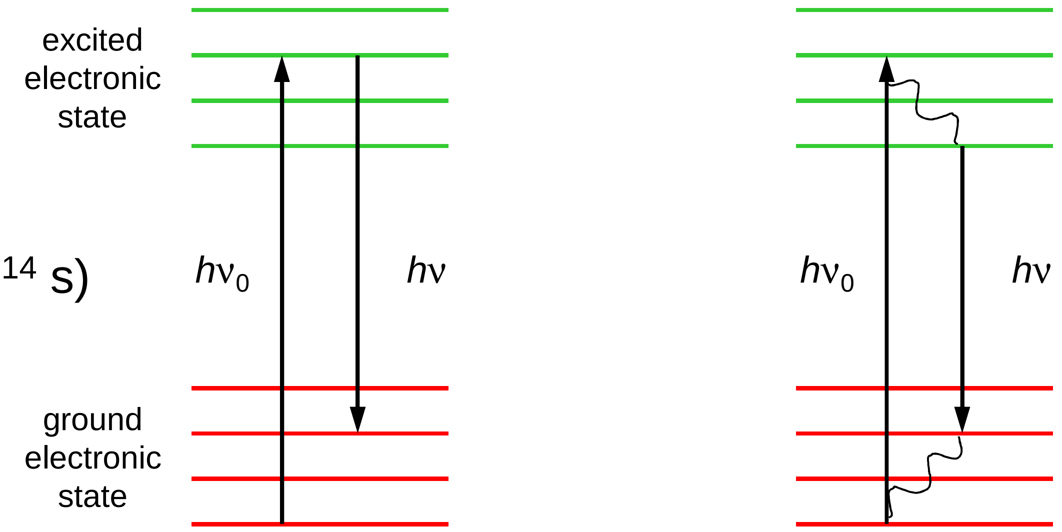
Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited

fast (10^{-14} s)



slow (10^{-9}–10^{-6} s)

Resonance Raman scattering

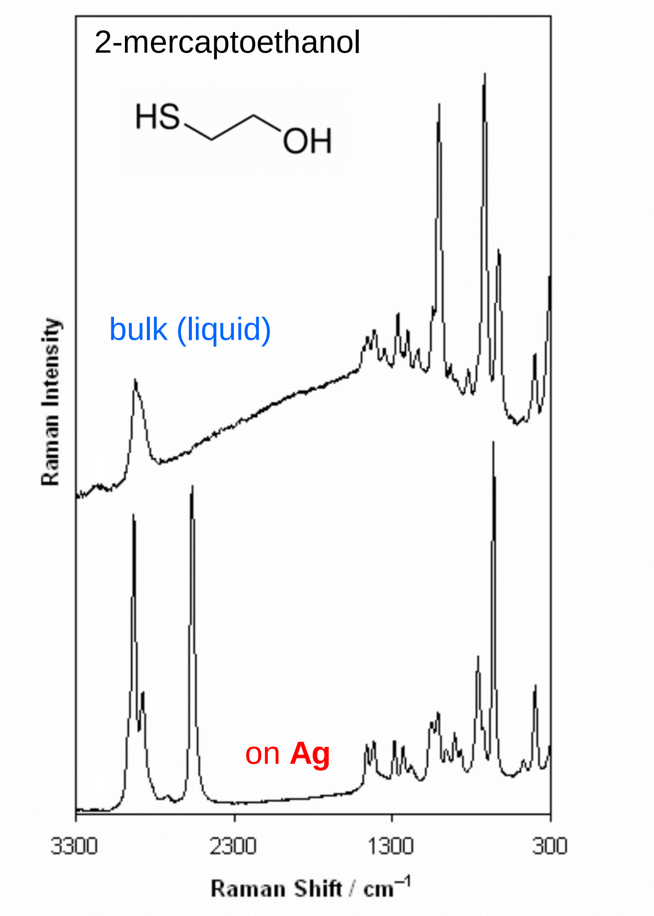
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

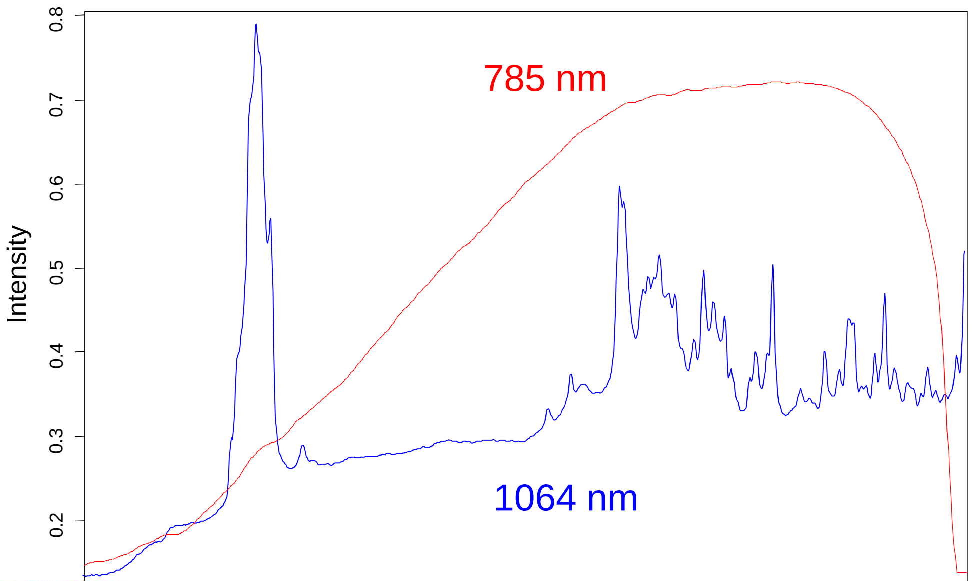
- Remarks:

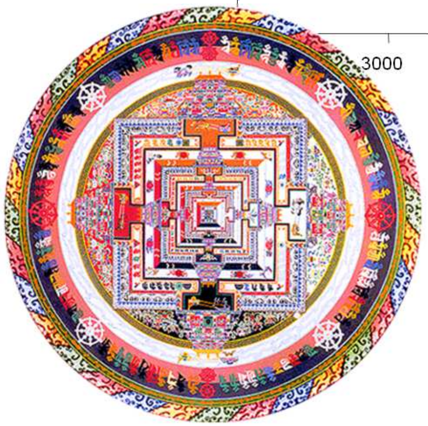
❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring





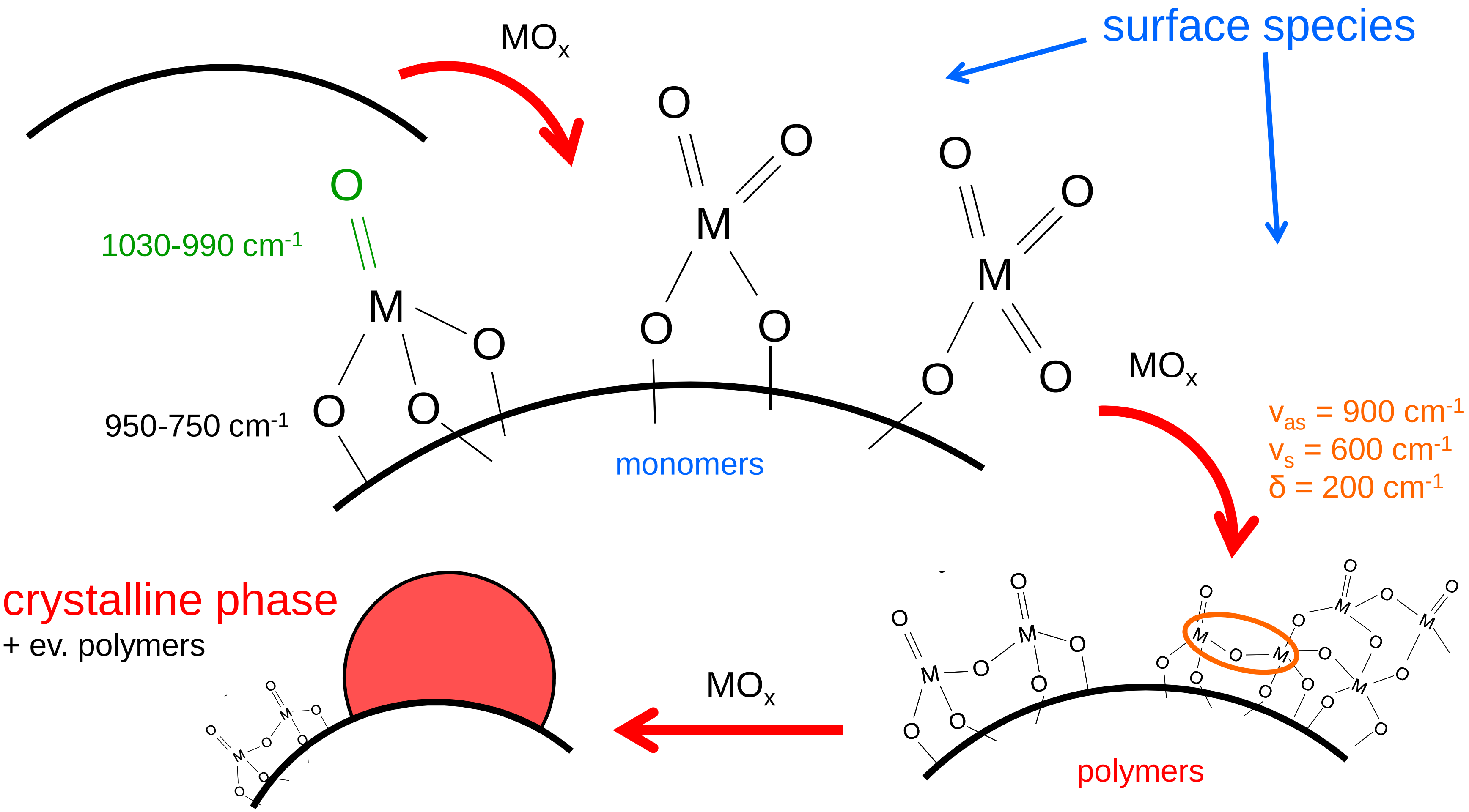
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



surface species

MO_x

$1030\text{-}990\ cm^{-1}$

$950\text{-}750\ cm^{-1}$

monomers

MO_x

$\nu_{as} = 900\ cm^{-1}$
$\nu_s = 600\ cm^{-1}$
$\delta = 200\ cm^{-1}$

polymers

MO_x

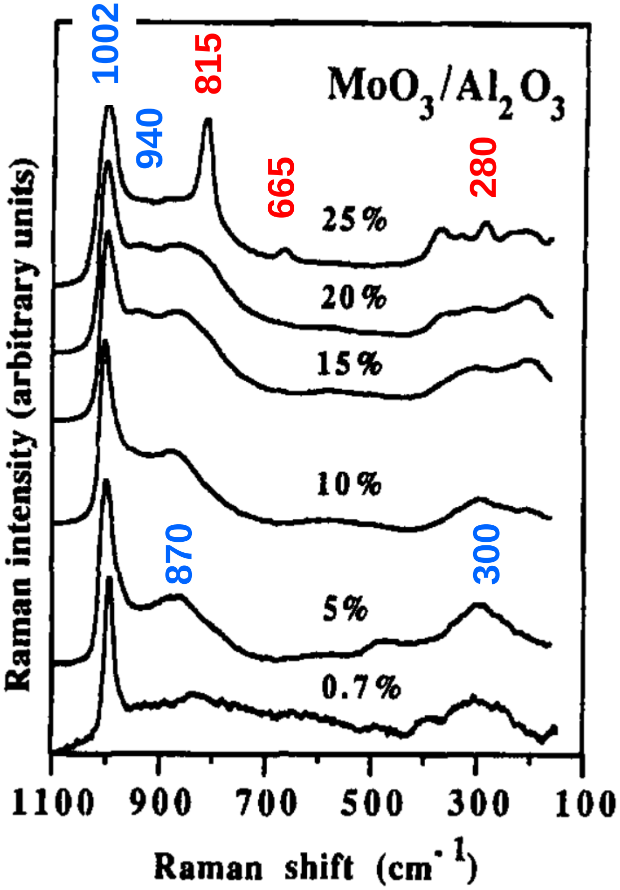
crystalline phase
+ ev. polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



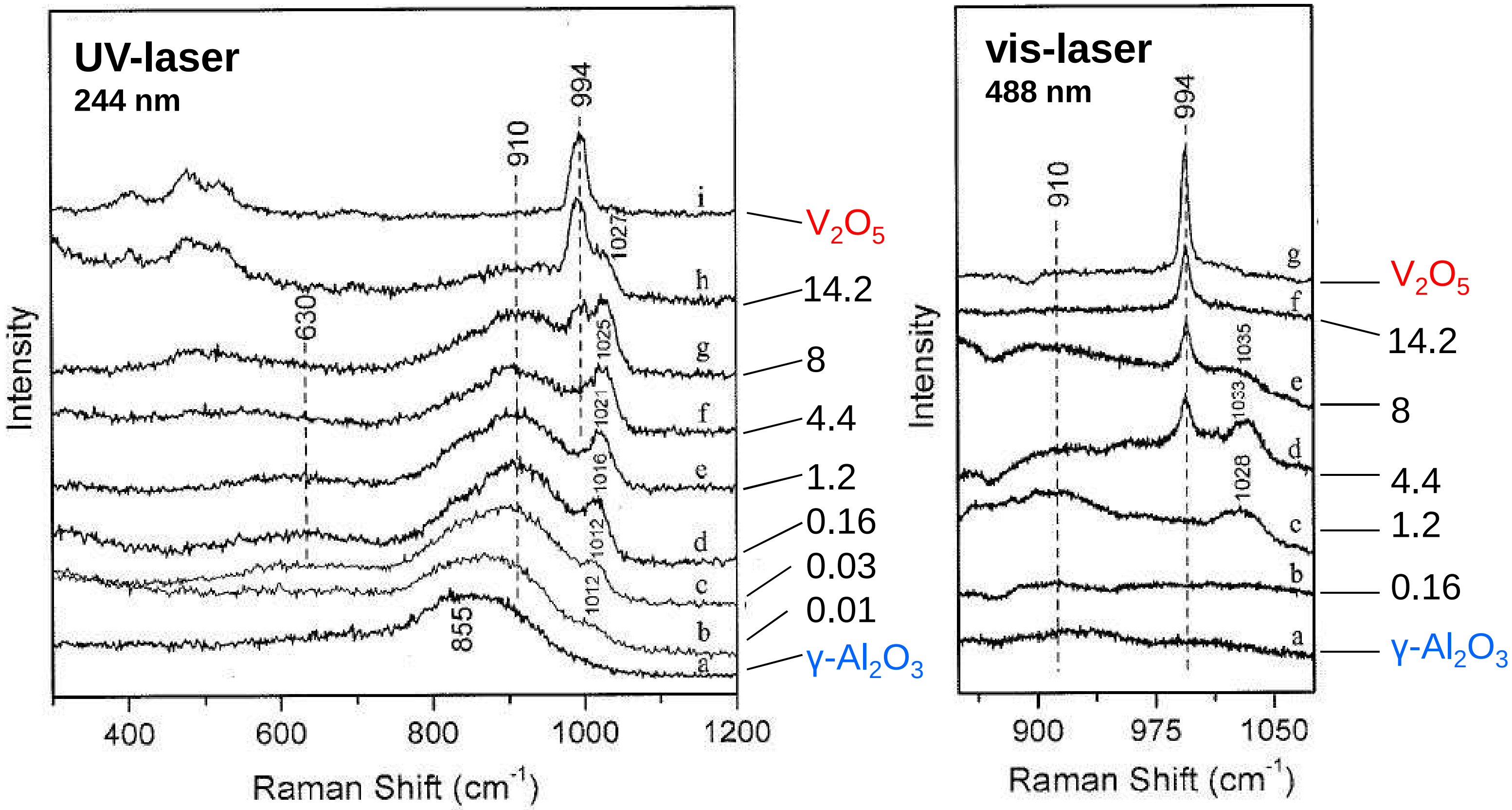
surface MoO_3
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

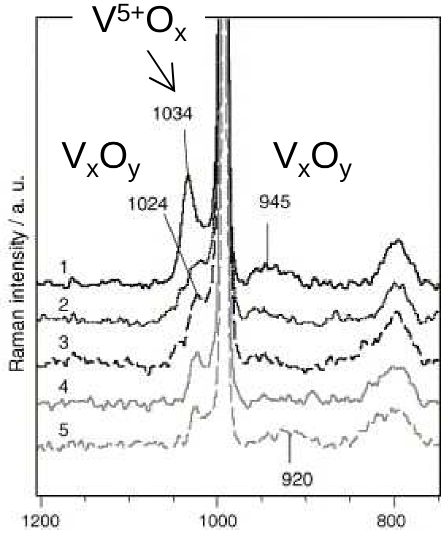
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

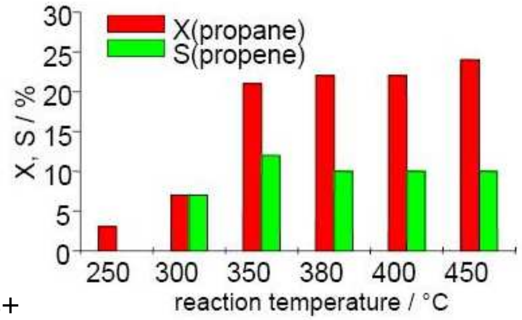
Applications

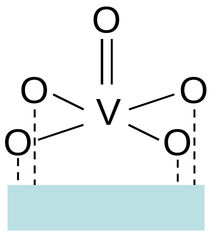
- Reactivity of V/TiO_2 after oxidative treatment

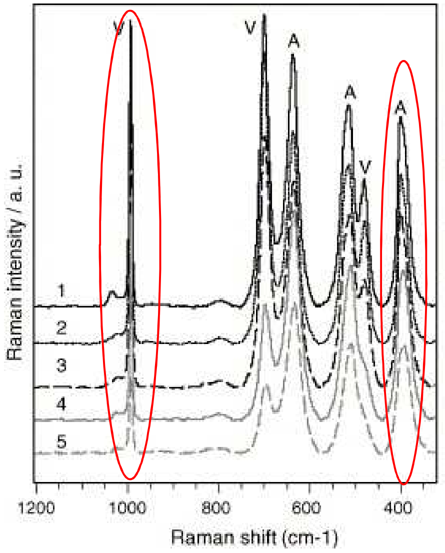


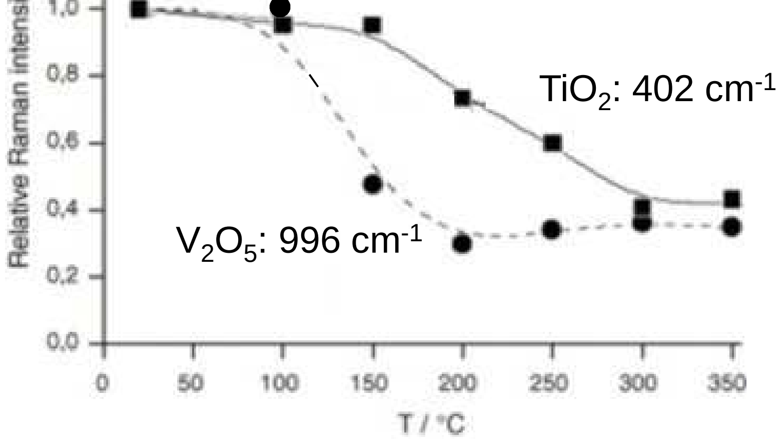
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









TiO_2: 402 cm^{-1}

V_2O_5: 996 cm^{-1}

Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

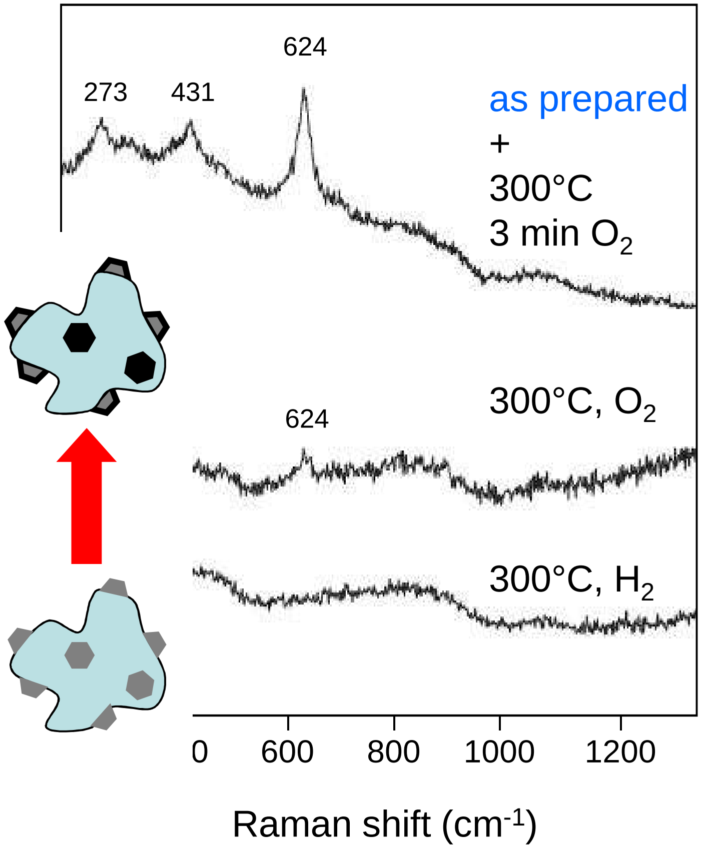
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

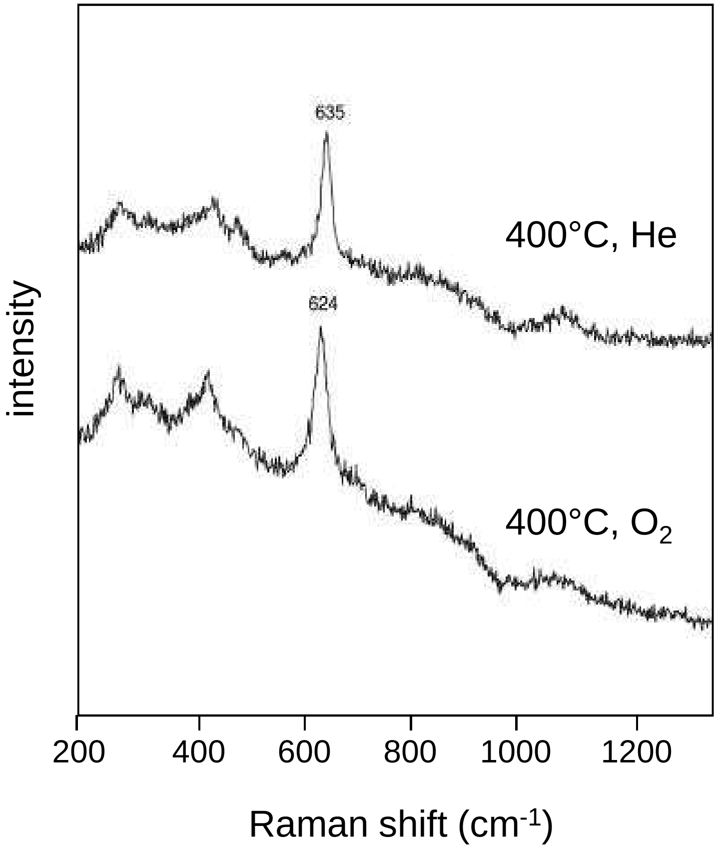
Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3





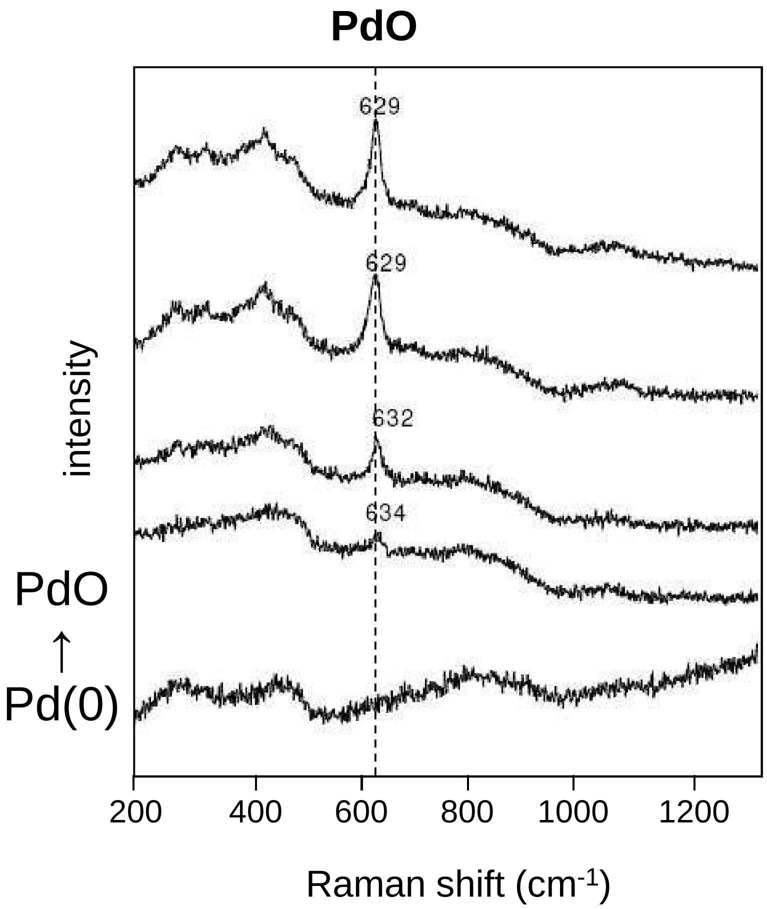
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

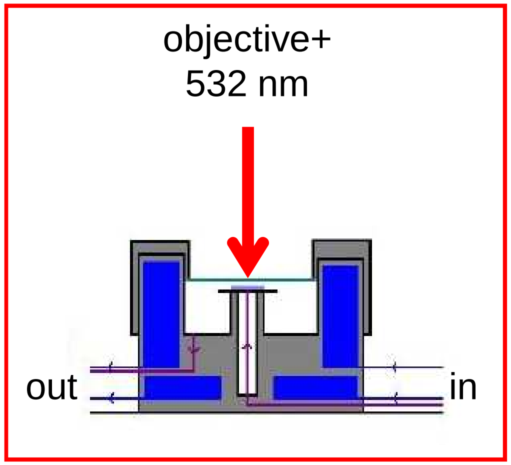
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$



	CH_4 conv.
500°C	**24 %**
450°C	**15 %**
425°C	**4 %**
400°C	**2 %**
400°C, H_2 reduced Pd	

↑ feed CH_4/O_2 (1:10)

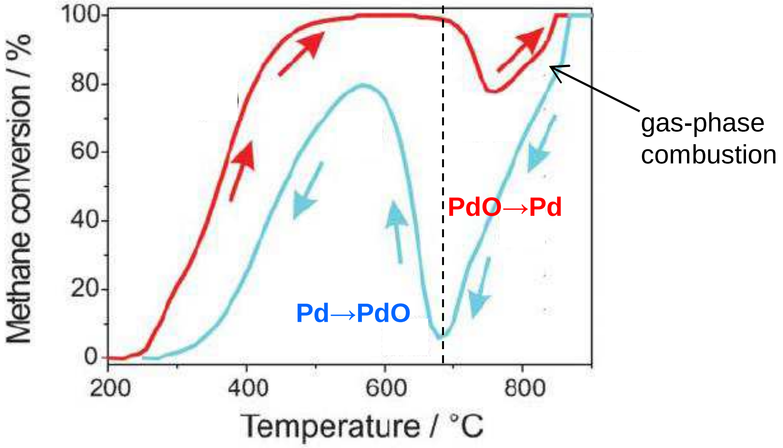
near PdO mode

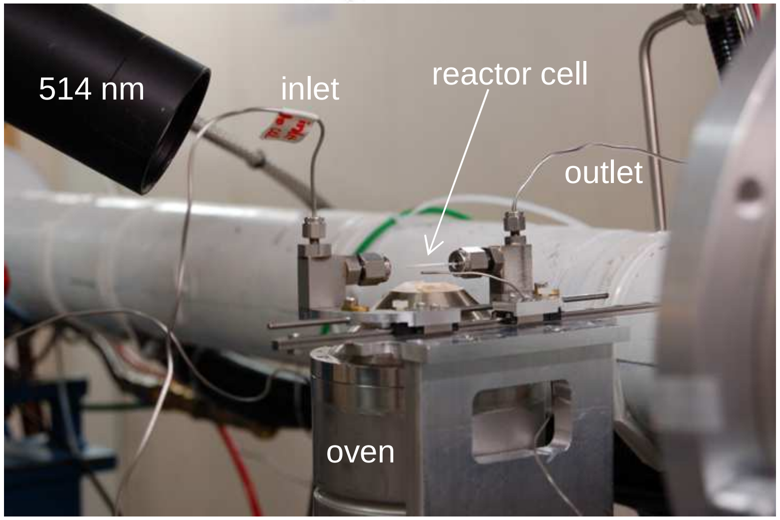


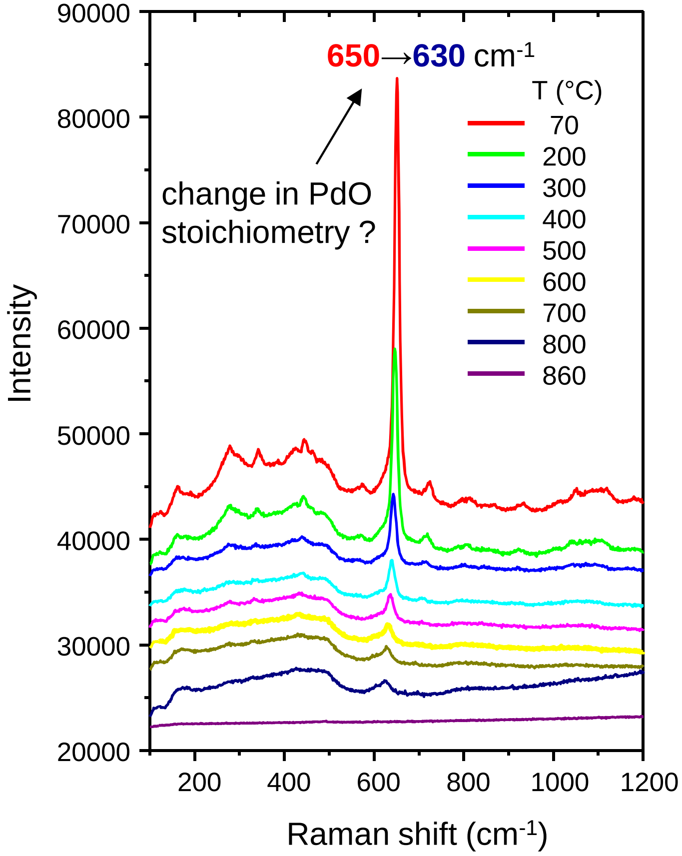
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

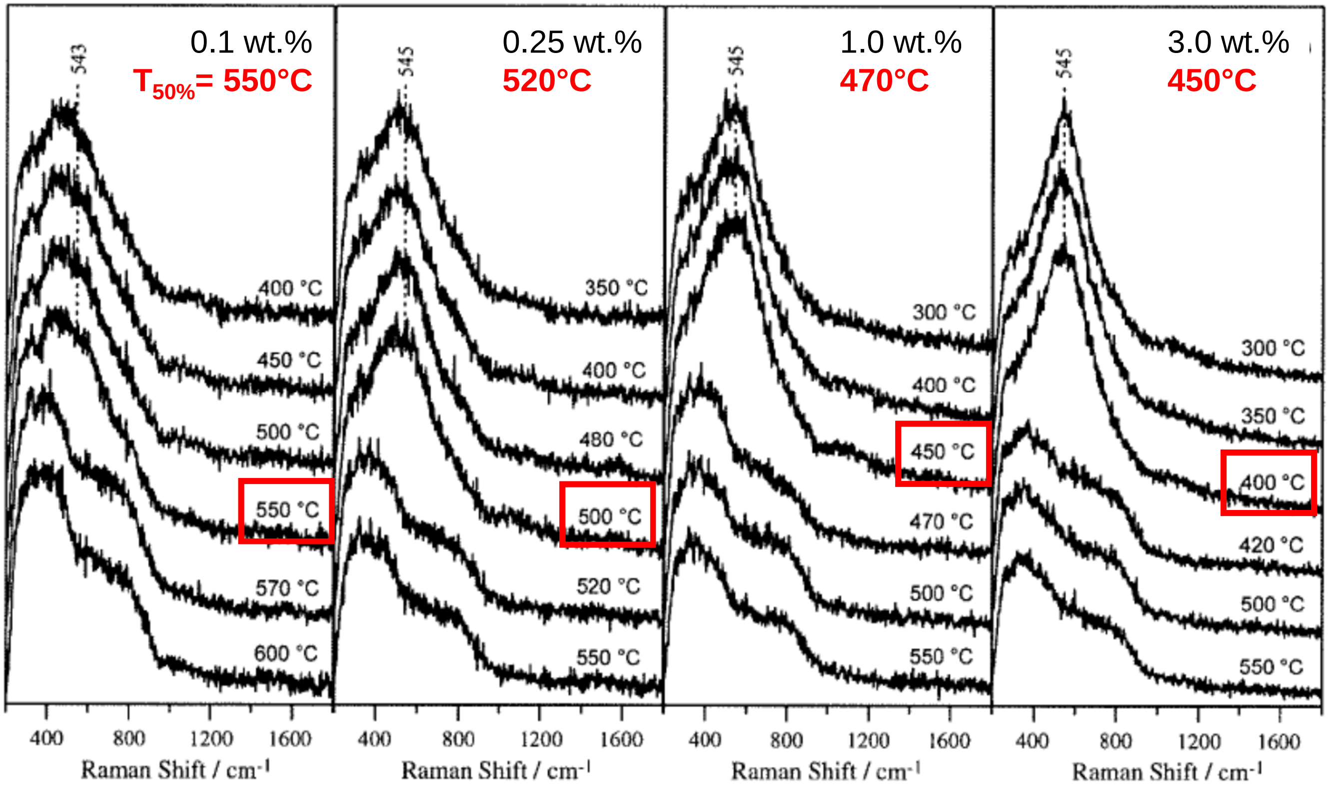
- Methane partial oxidation over Rh/Al_2O_3

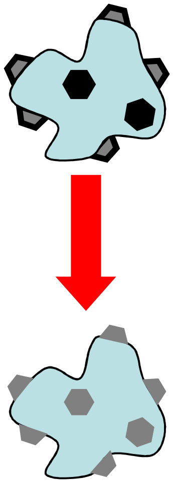
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$$

Rh content →
Activity →

RhO_x
↓
Rh(0)





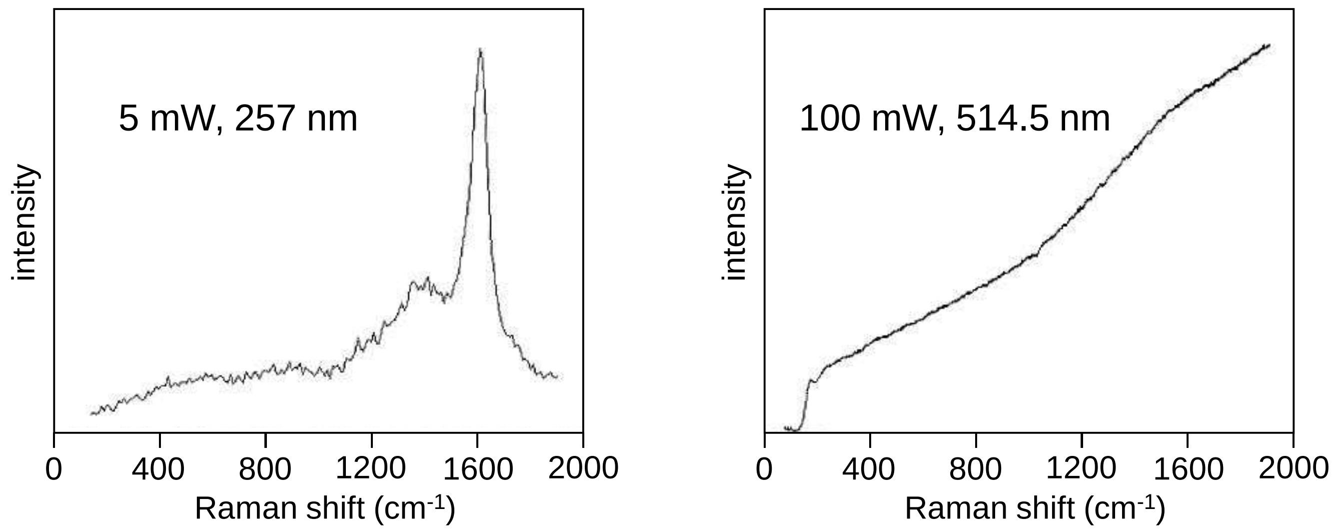
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

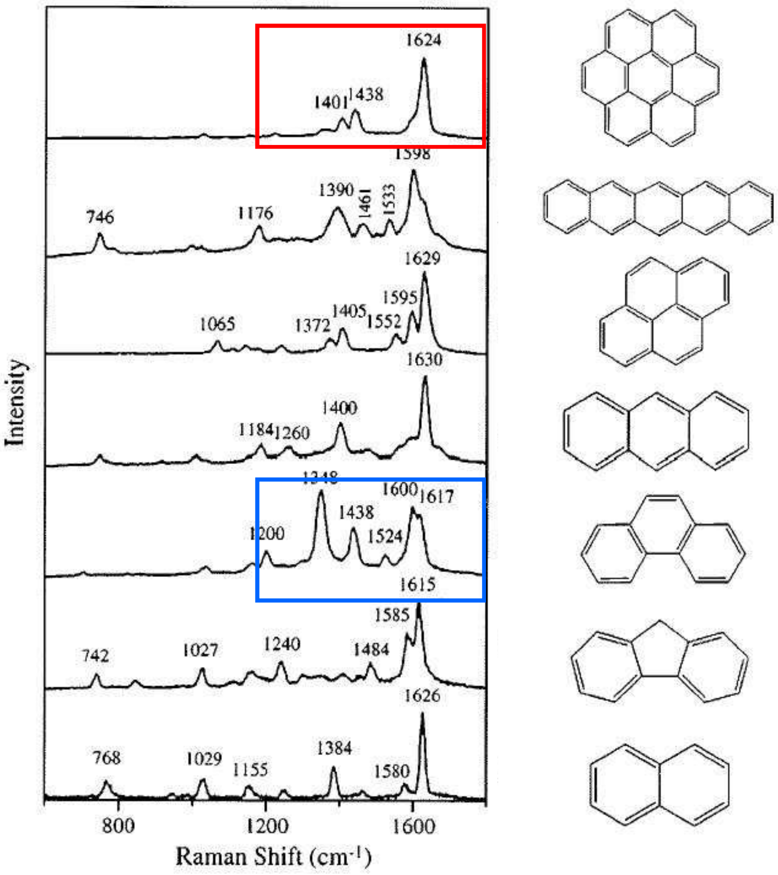
Rh/Al_2O_3, coked 500°C in naphtha

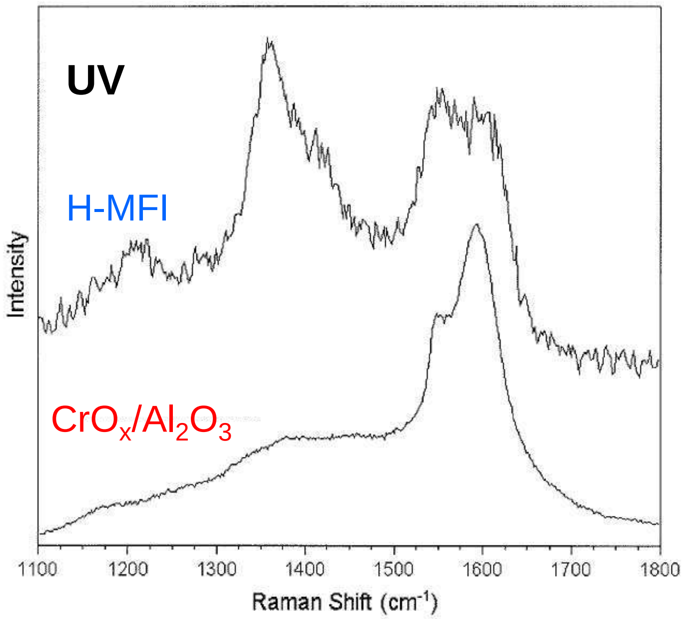


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





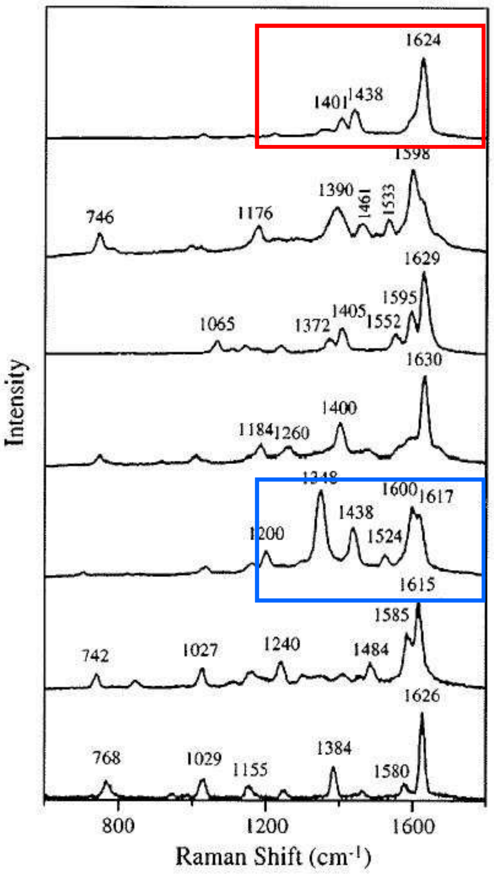
Coke classification
1D topology, chain-like
2D topology, sheet-like

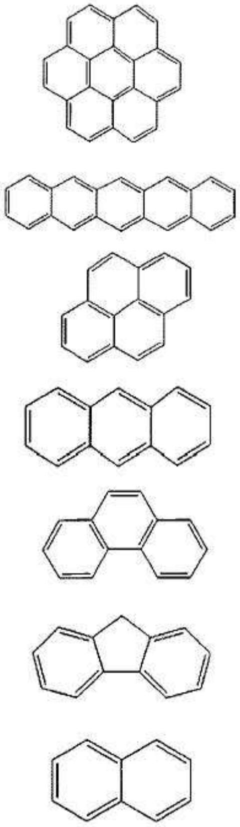
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

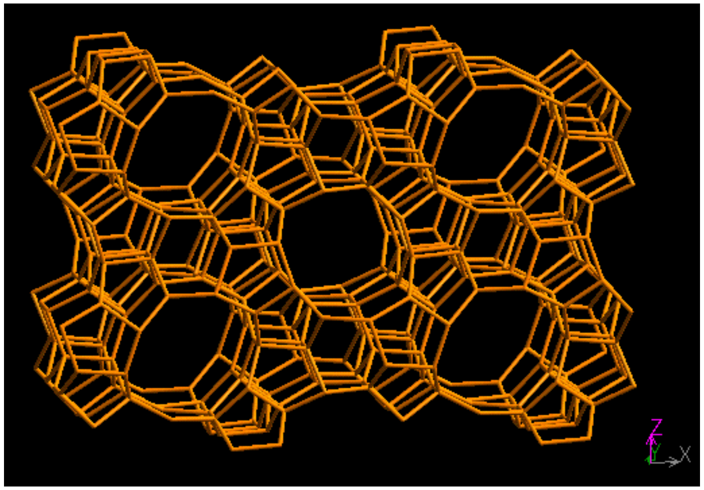
Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization







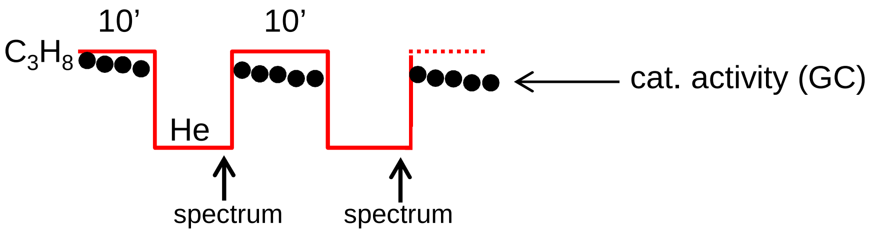
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

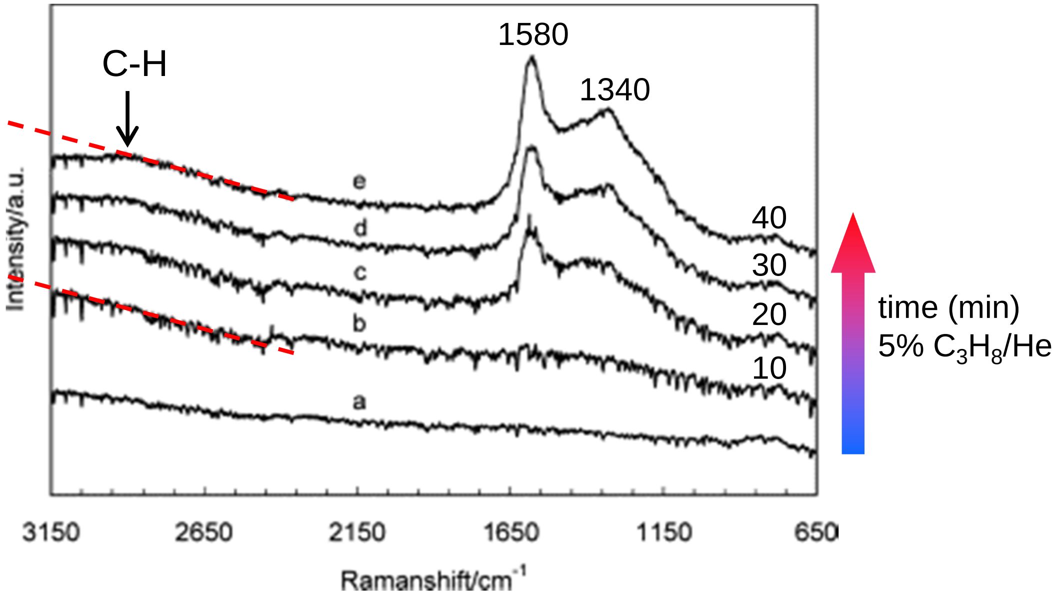
Stair, *Adv. Catal.* **51** (2007) 75

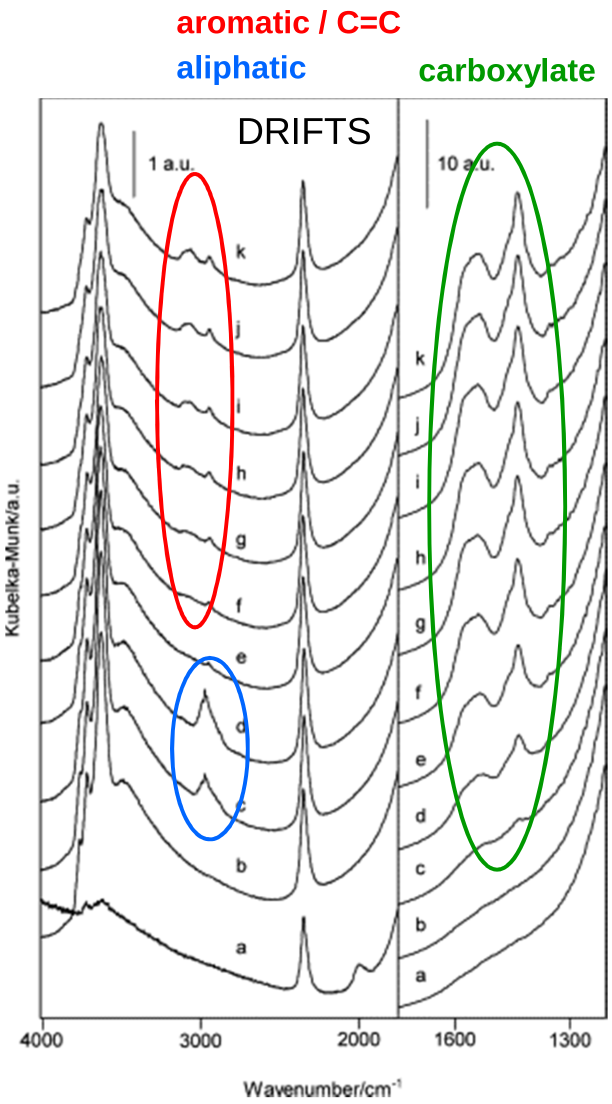
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

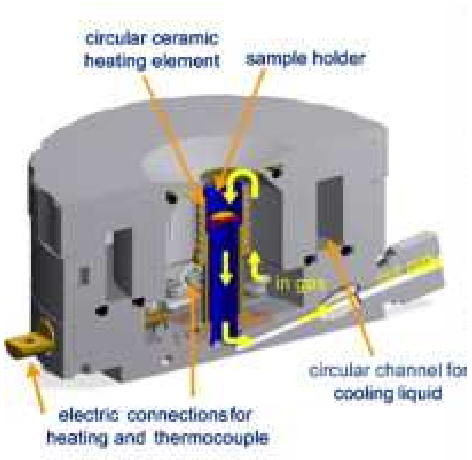


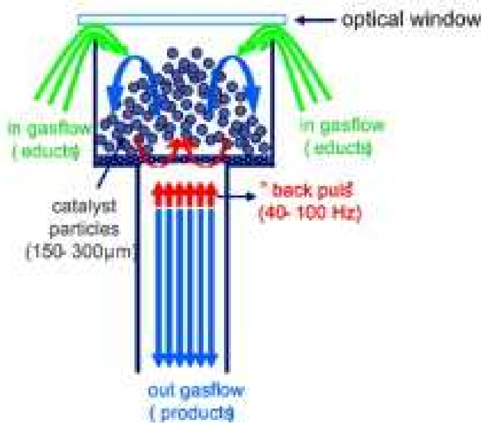


Airaksinen et al., *J. Catal.* **230** (2005) 507

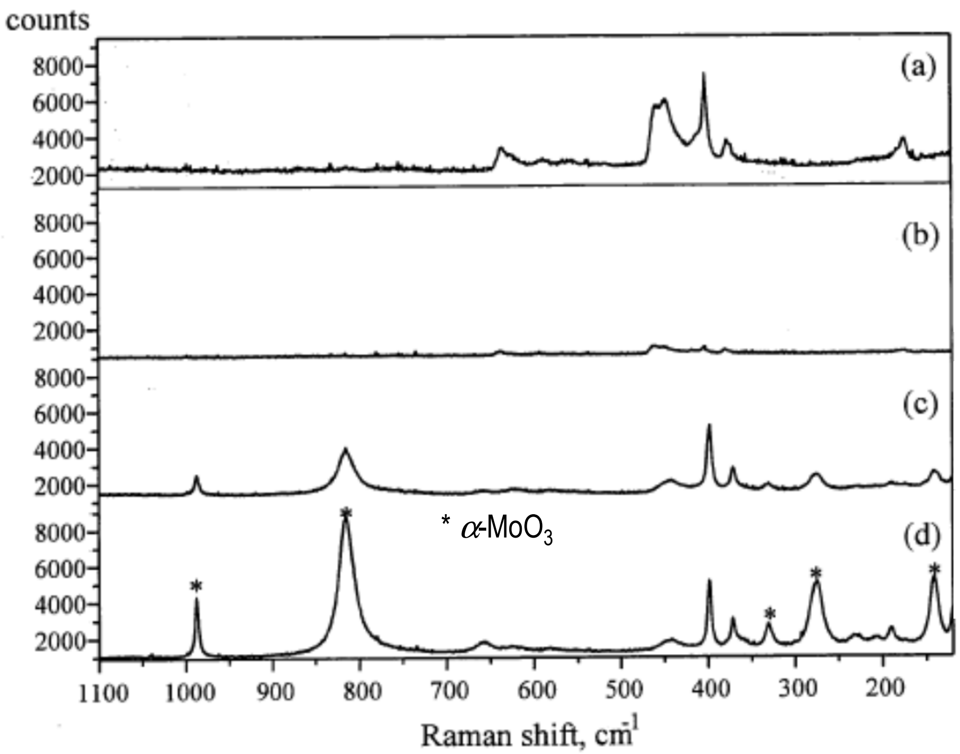
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min full power, FB

MoS_2, 6 min 1/8 power

MoS_2, 1 min full power

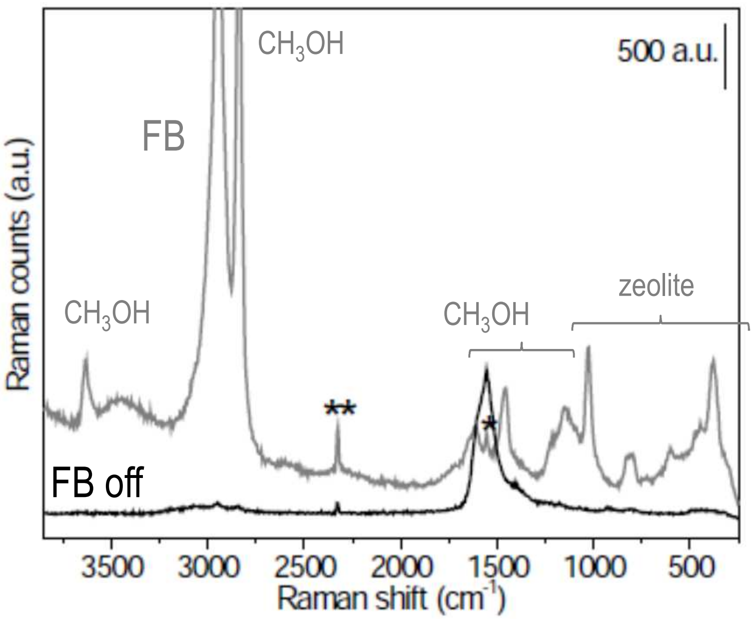
MoS_2, 6 min full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

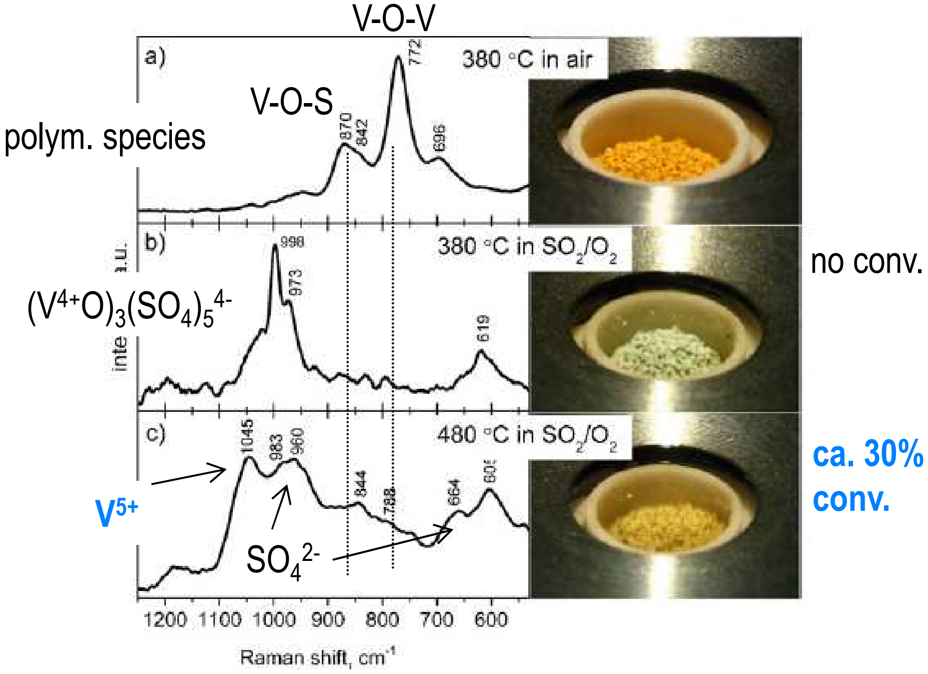
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

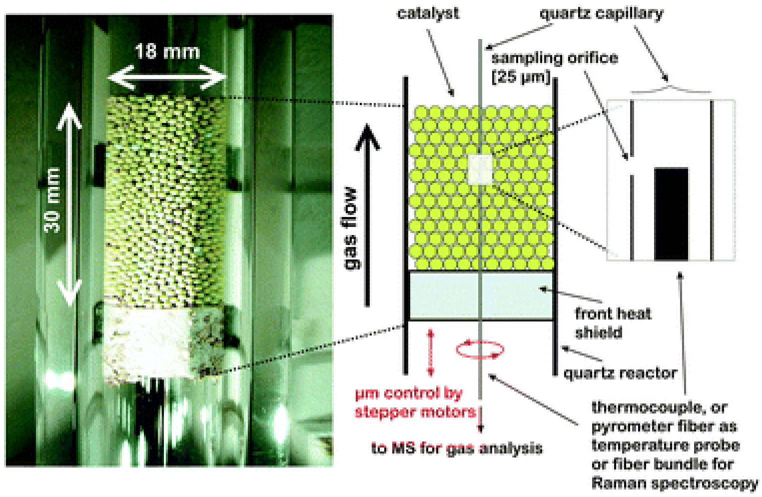


active species: mono- & dimeric V^{5+} oxosulfate species

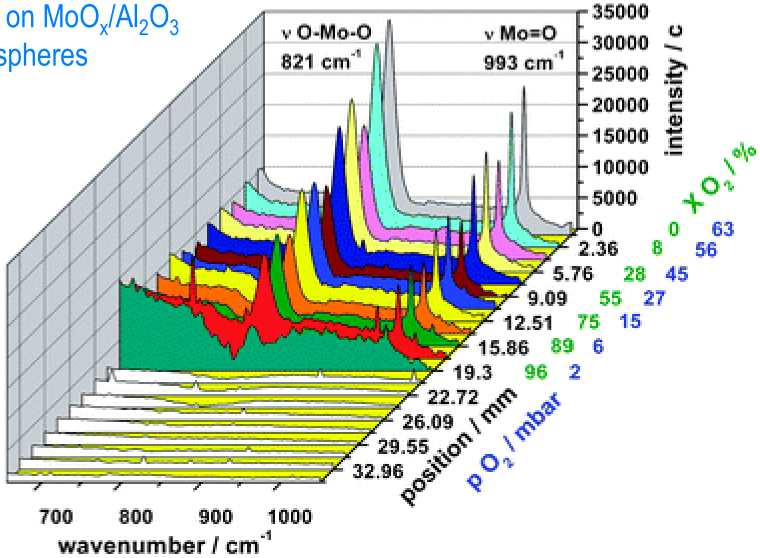
Beato et al., *Catal. Today* 205 (2013) 128

Applications

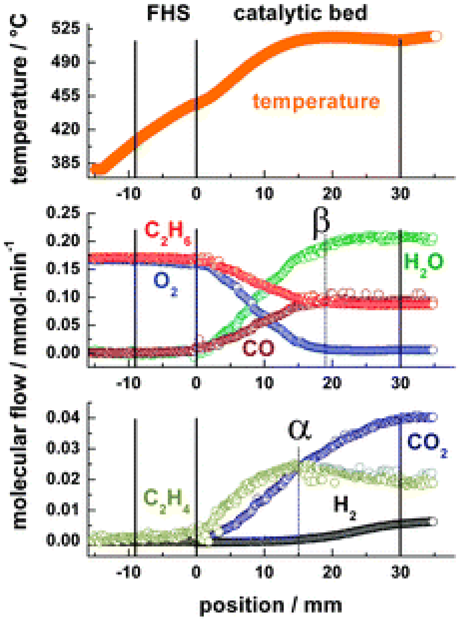
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 “*for his work on the scattering of light and for the discovery of the effect named after him*”

Literature:

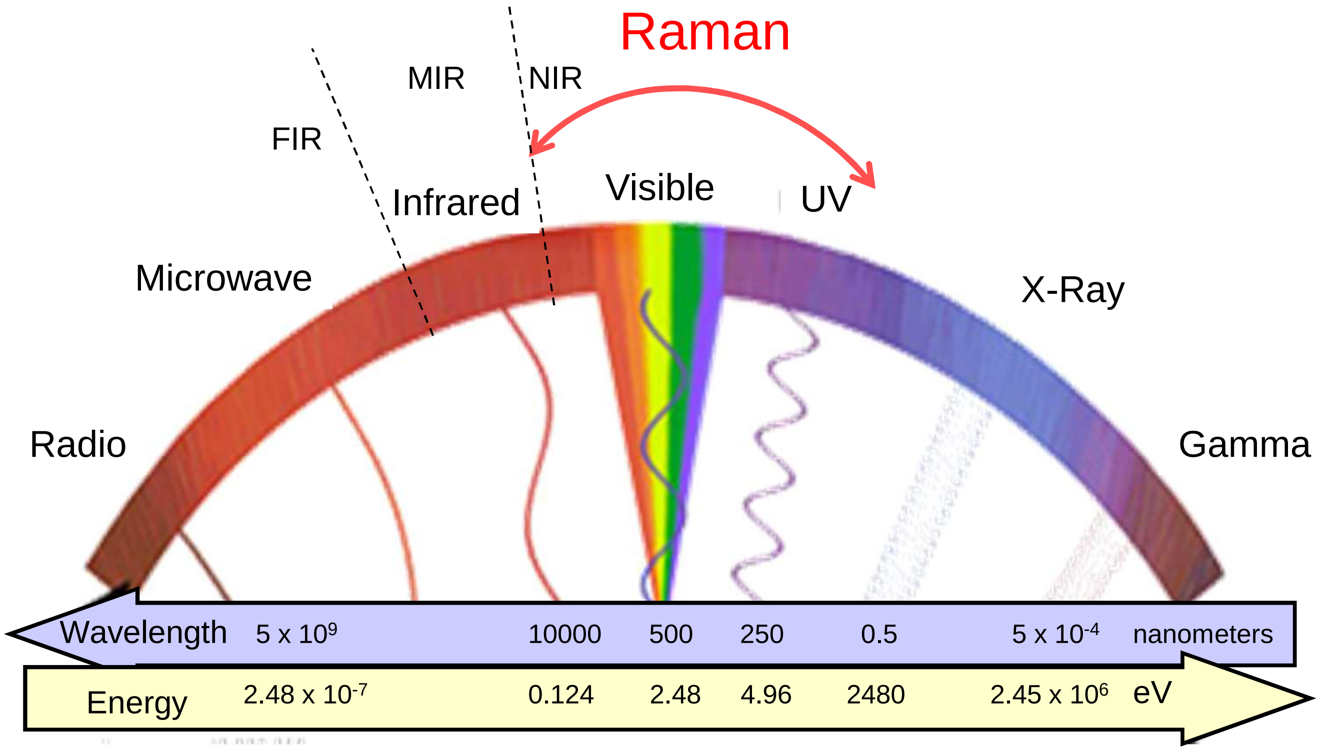
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

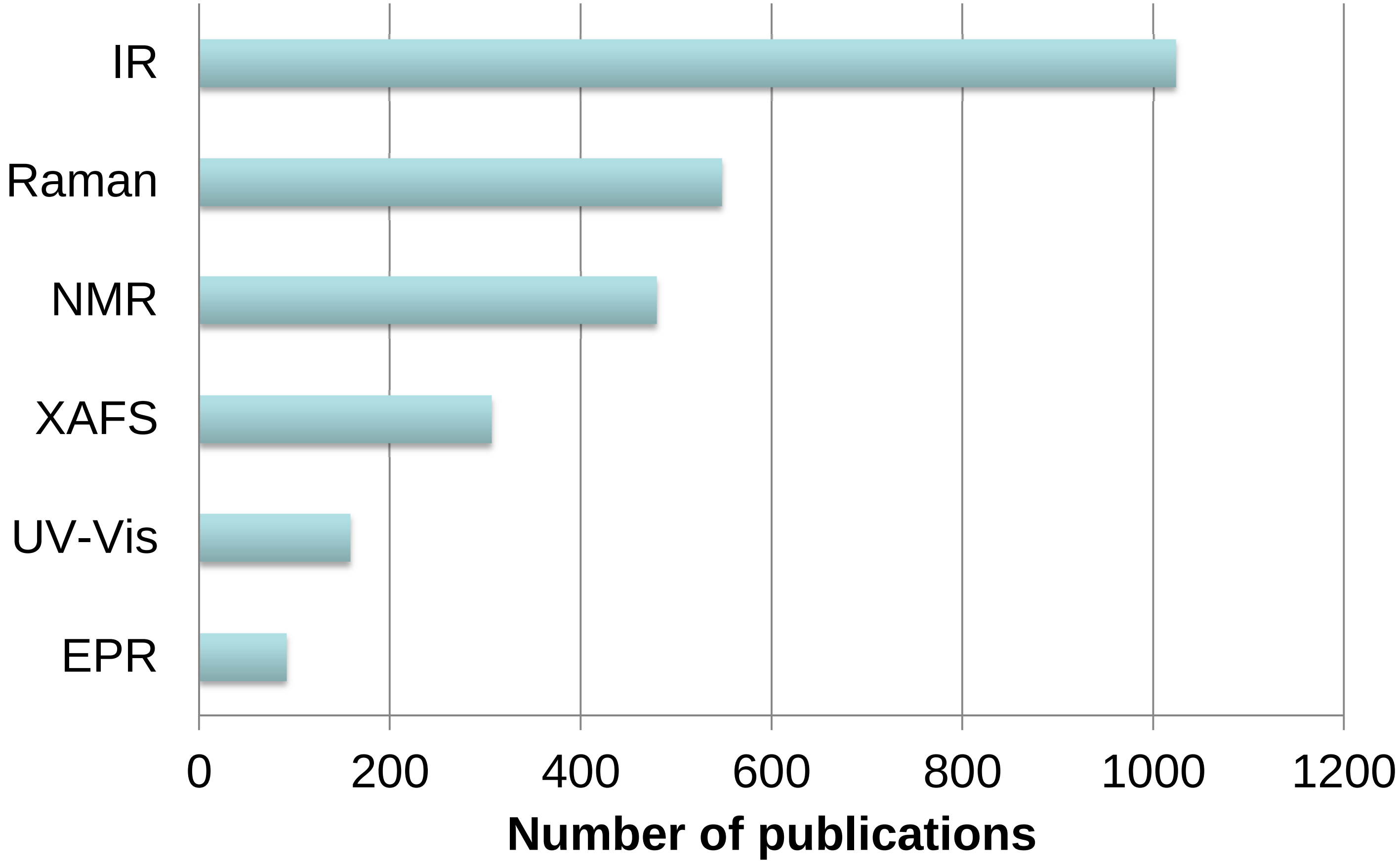
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

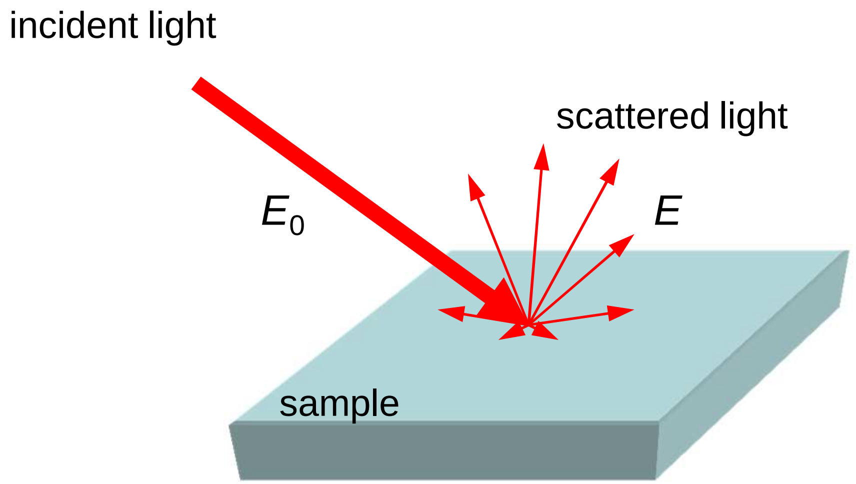


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α : $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

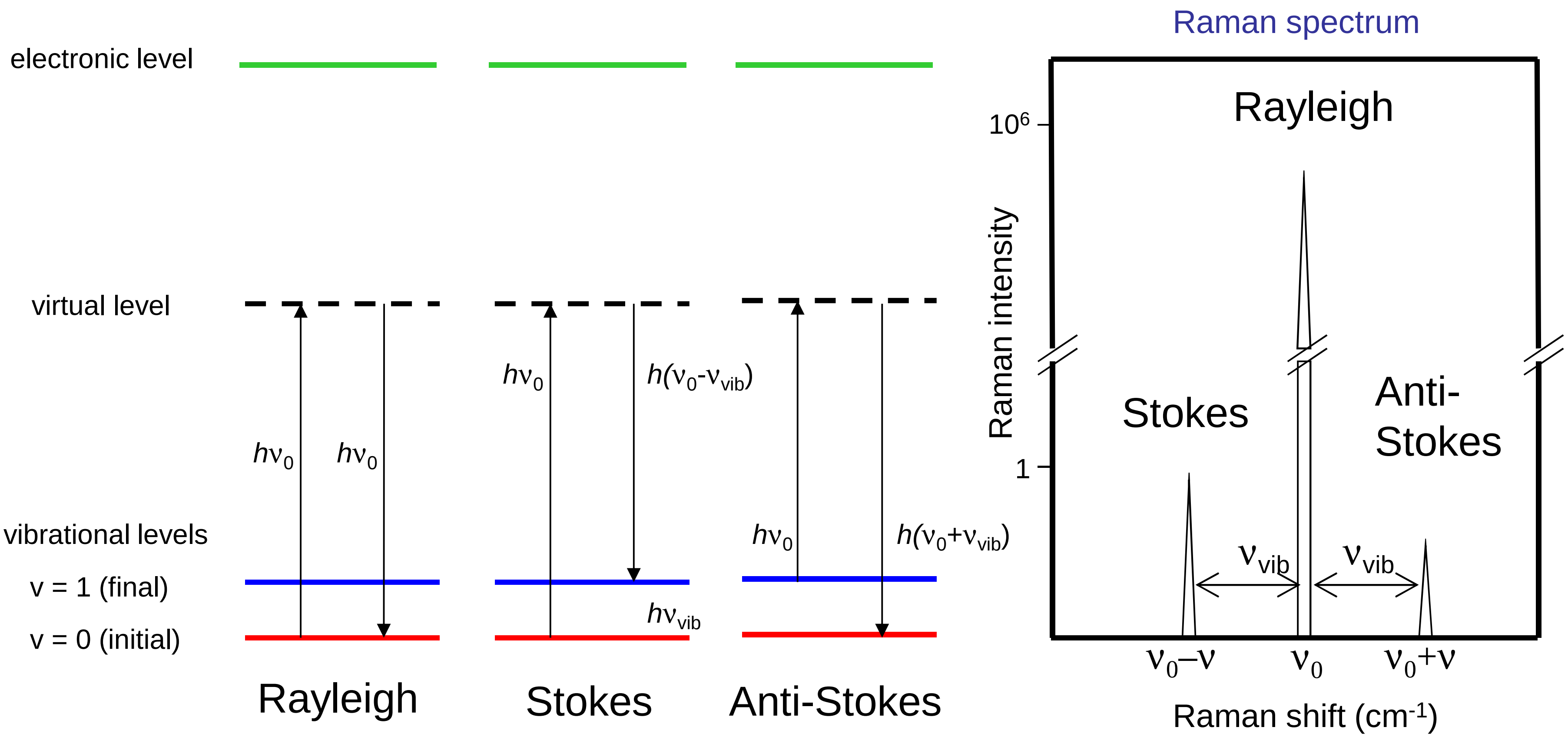
$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

and

$$\boxed{\mu_{in} = \underbrace{\alpha_0 E_0\cos(2\pi\nu_0 t)}_{\text{Rayleigh}} + \underbrace{\alpha/2 E_0\cos[2\pi(\nu_0+\nu_{vib})t]}_{\text{Anti-Stokes}} + \underbrace{\alpha/2 E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}_{\text{Stokes}}}$$

$\cos x\cdot\cos y = 1/2\ [\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach



Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{I\ (\text{Anti-Stokes})}{I\ (\text{Stokes})} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

- ❑ 4th power of ν (4th power law)
- ❑ 2nd power of $\Delta\alpha$
  - properties of molecules
  - strength of bonds

↓

covalent bond STRONG bands (catalysis!)

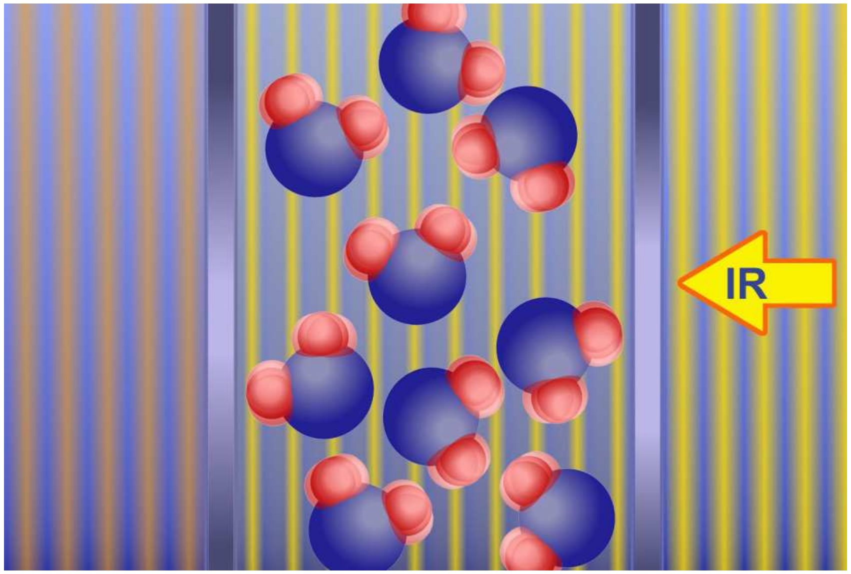
ionic bond WEAK bands

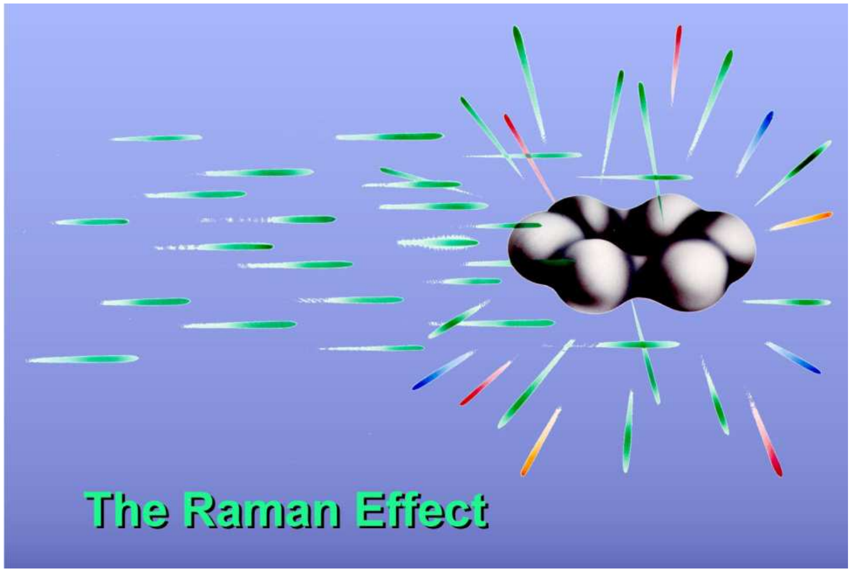
- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

Raman *vs.* Infrared

Infrared

Raman





Absorption of IR light

Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial\mu}{\partial Q}\right)^2 \neq 0$$

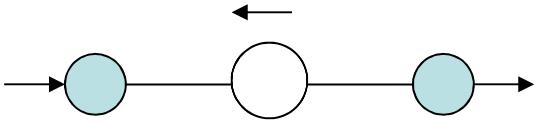
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial\alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - ☐ large electron clouds
  - ☐ not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

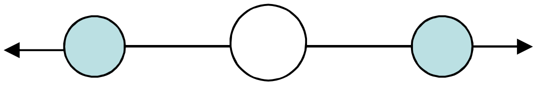
Raman *vs.* Infrared

CO_2



ν_{as}

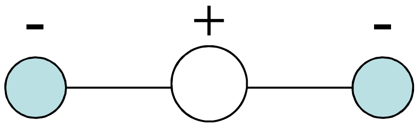
2349 cm^{-1}



ν_s

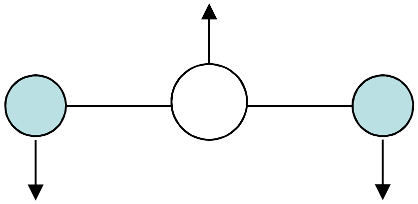
1340 cm^{-1}

Raman active



δ

667 cm^{-1}



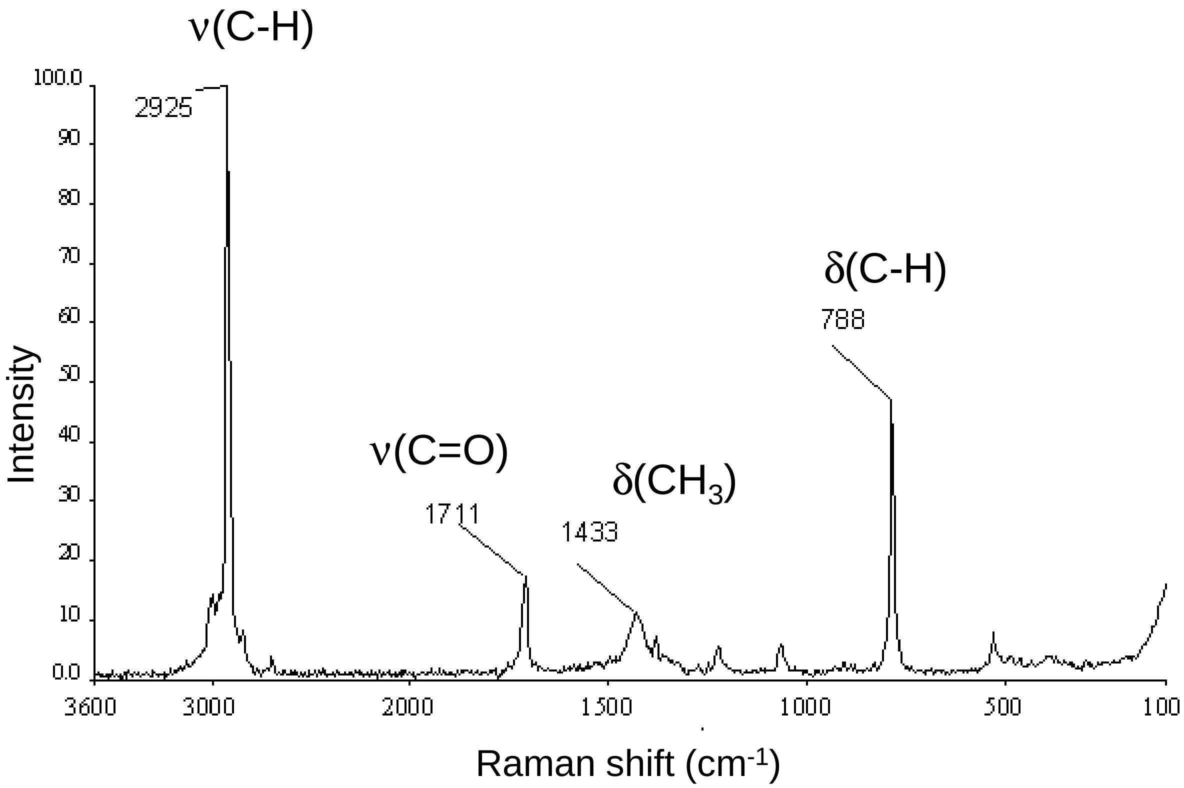
δ

667 cm^{-1}

degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared

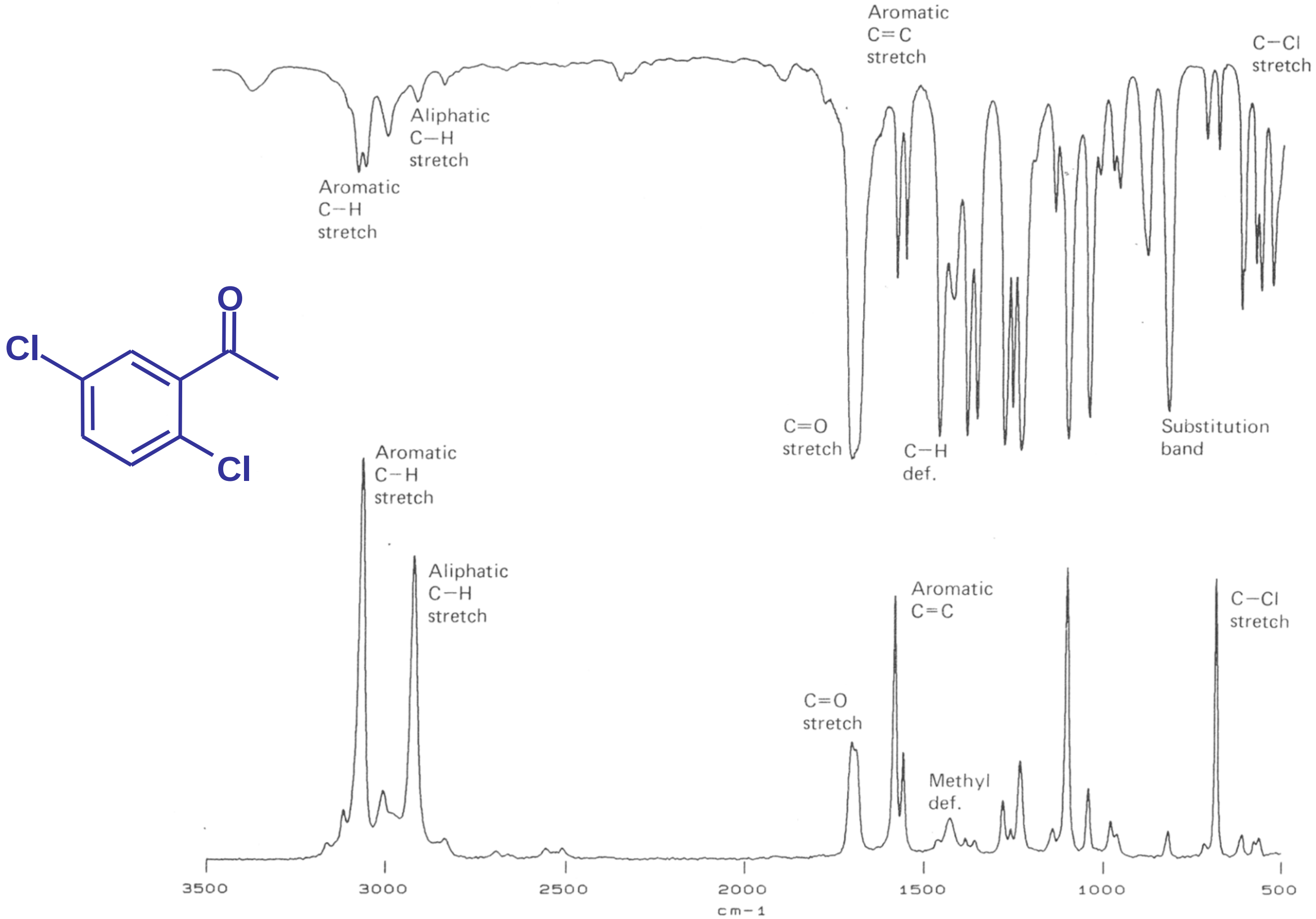


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

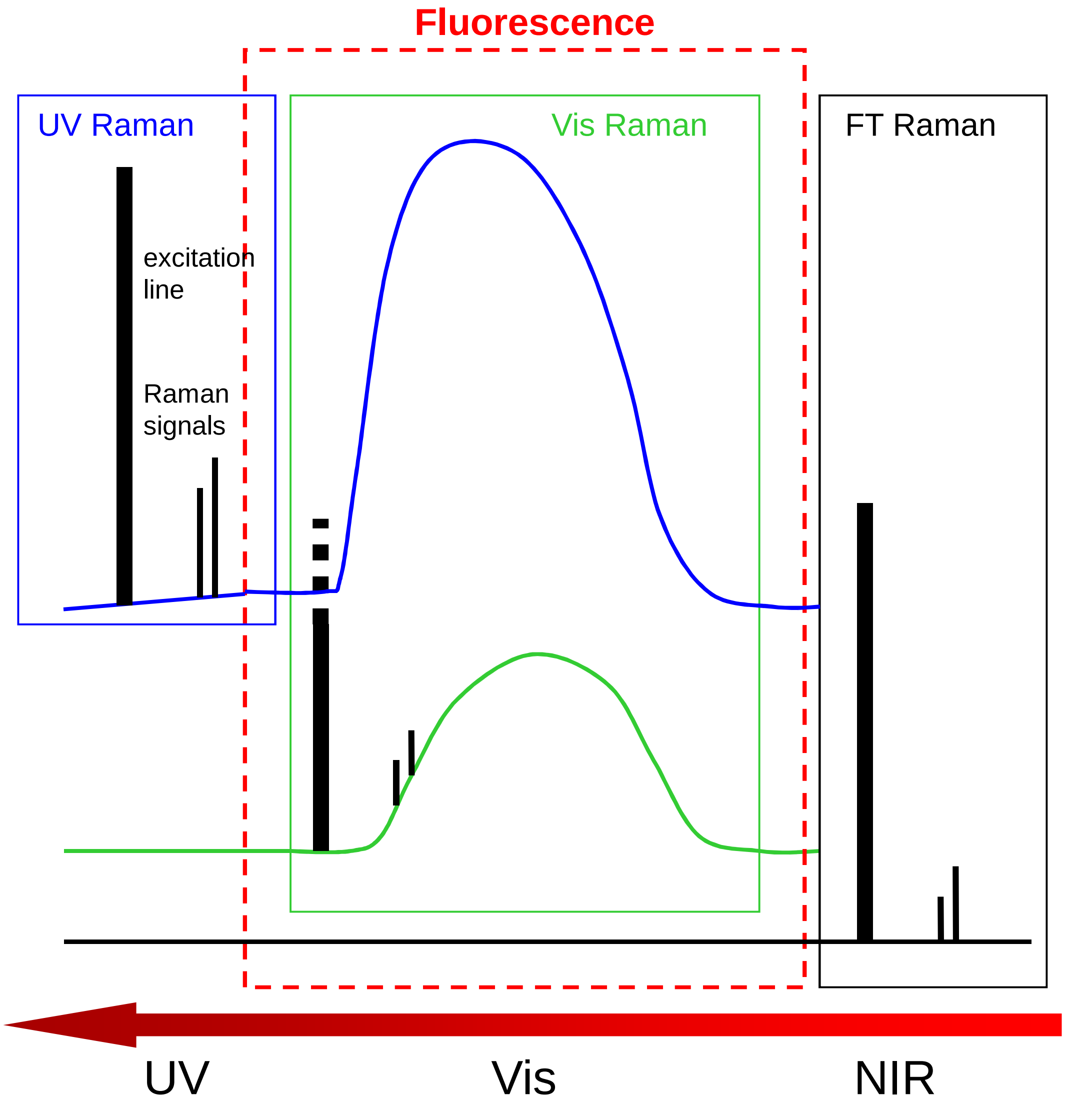
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 μm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

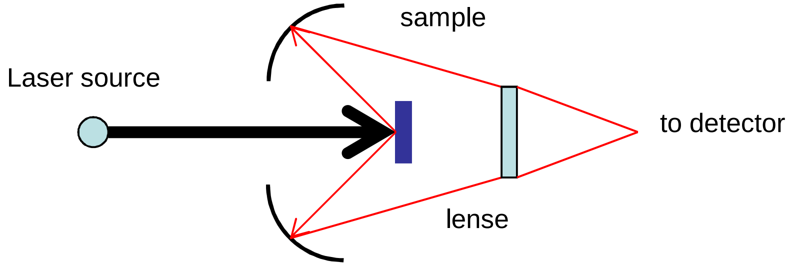
Fluorescence proportional to ν

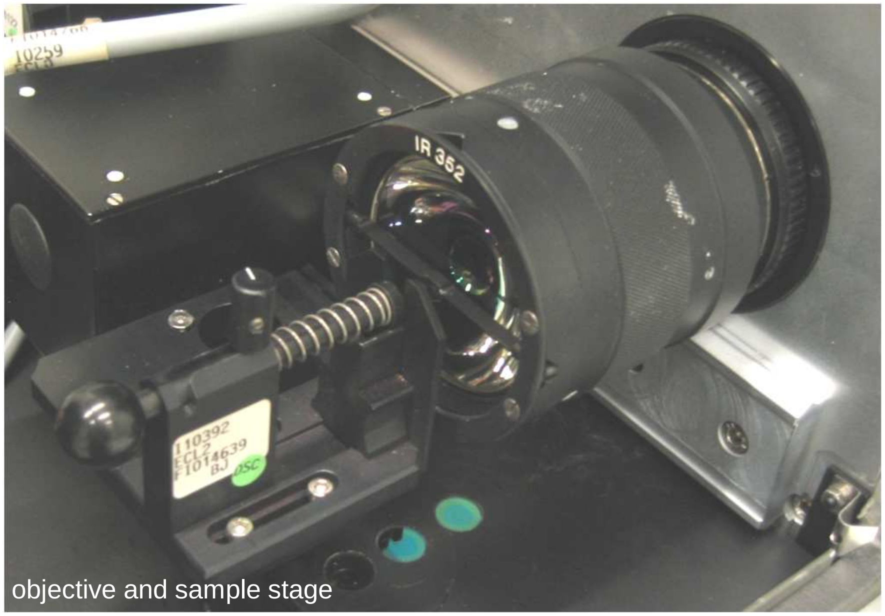
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers
Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

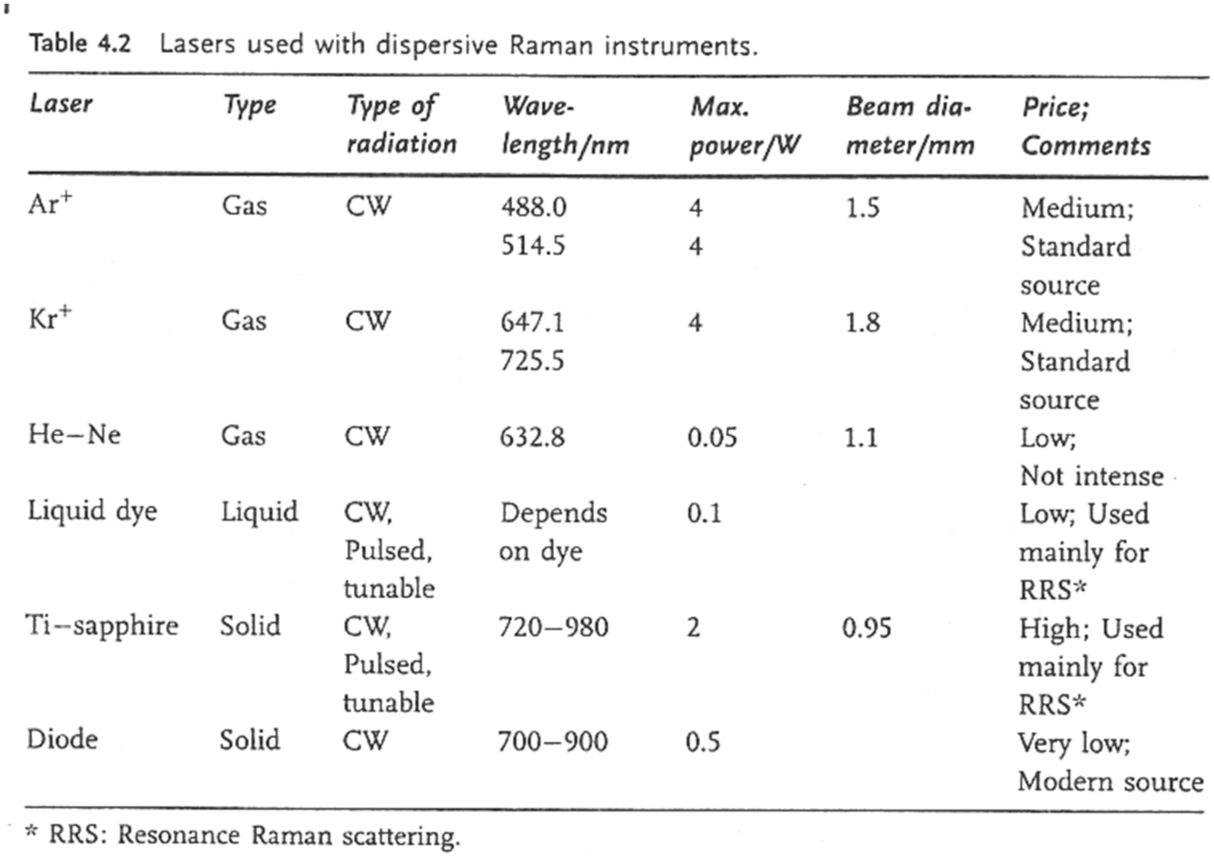


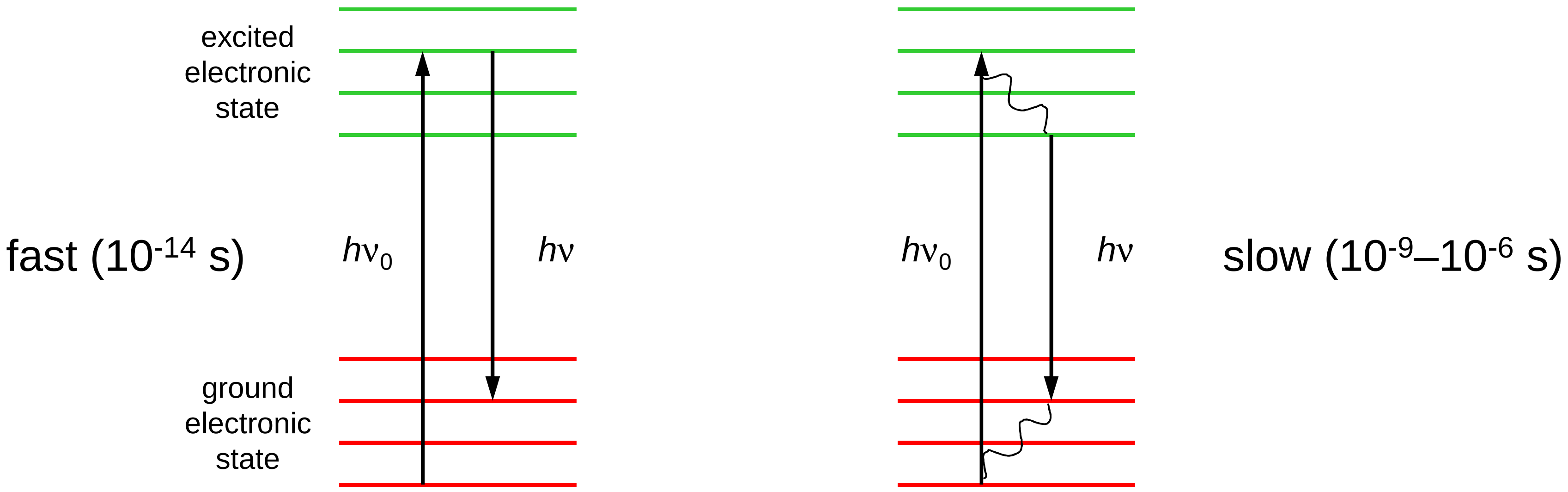
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



excited electronic state

ground electronic state

fast (10^{-14} s)

$h\nu_0$

$h\nu$

$h\nu_0$

$h\nu$

slow (10^{-9}–10^{-6} s)

Resonance Raman scattering

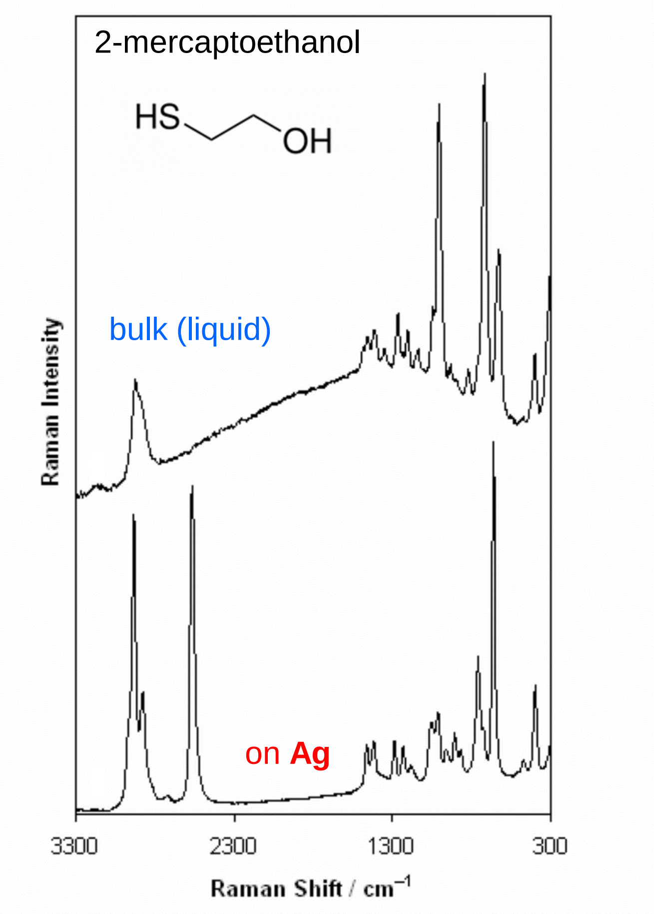
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

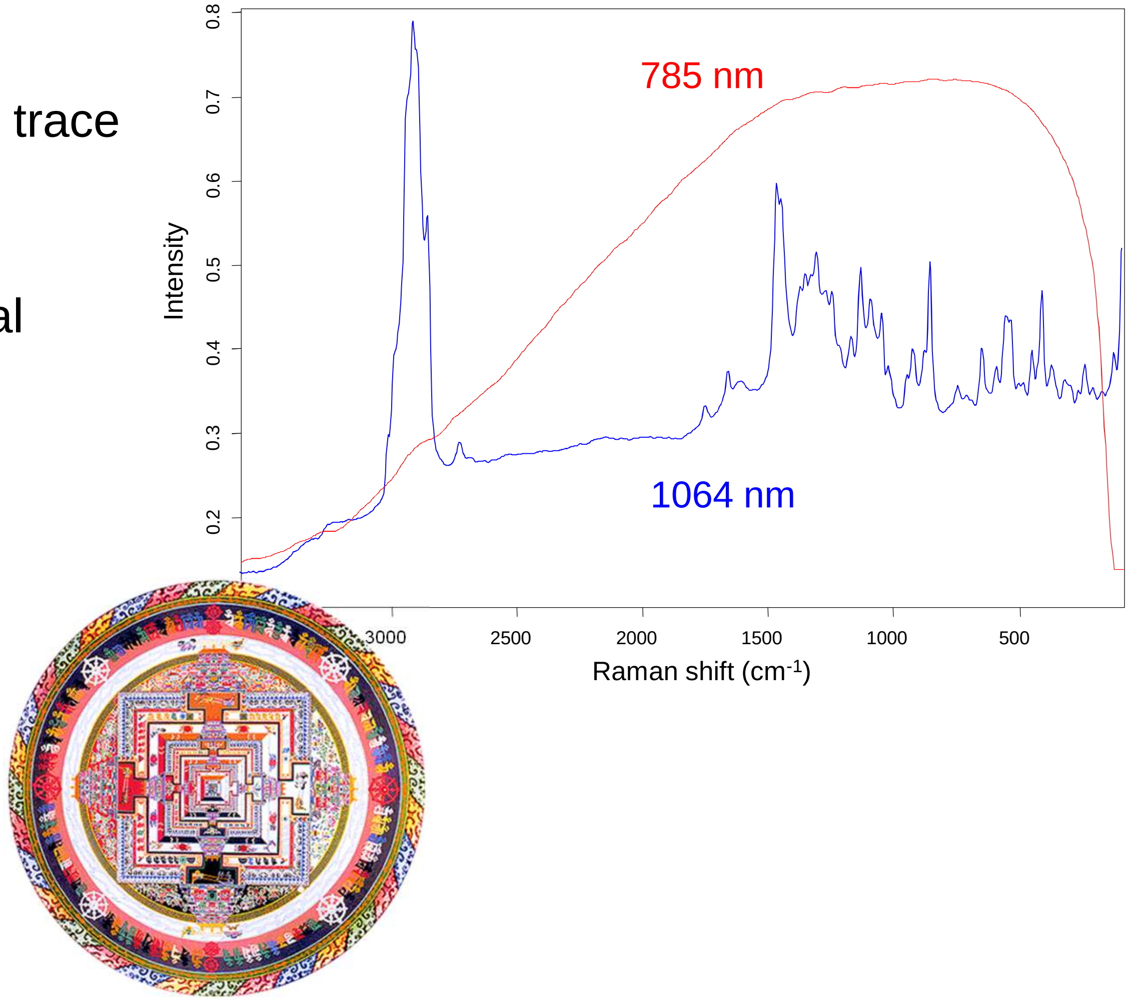
- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

- Remarks:
  - rough surface; nanoparticles (10–100 nm) or kinks, steps etc. (E always perpendicular to surface, locally)
  - vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



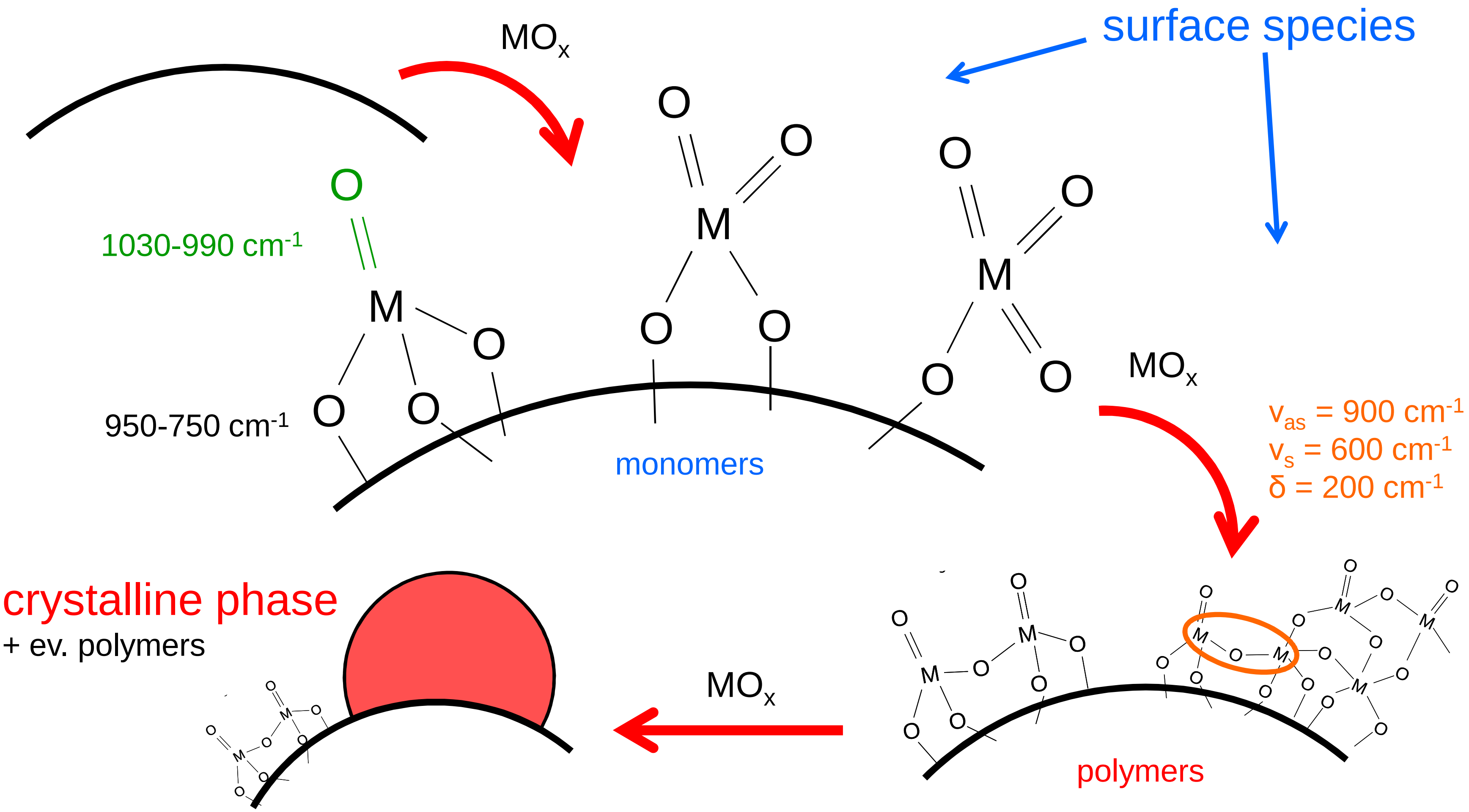
Applications

MO_x/$M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species



surface species

MO_x

$1030\text{-}990\ cm^{-1}$

$950\text{-}750\ cm^{-1}$

monomers

MO_x

$\nu_{as} = 900\ cm^{-1}$
$\nu_s = 600\ cm^{-1}$
$\delta = 200\ cm^{-1}$

polymers

MO_x

crystalline phase

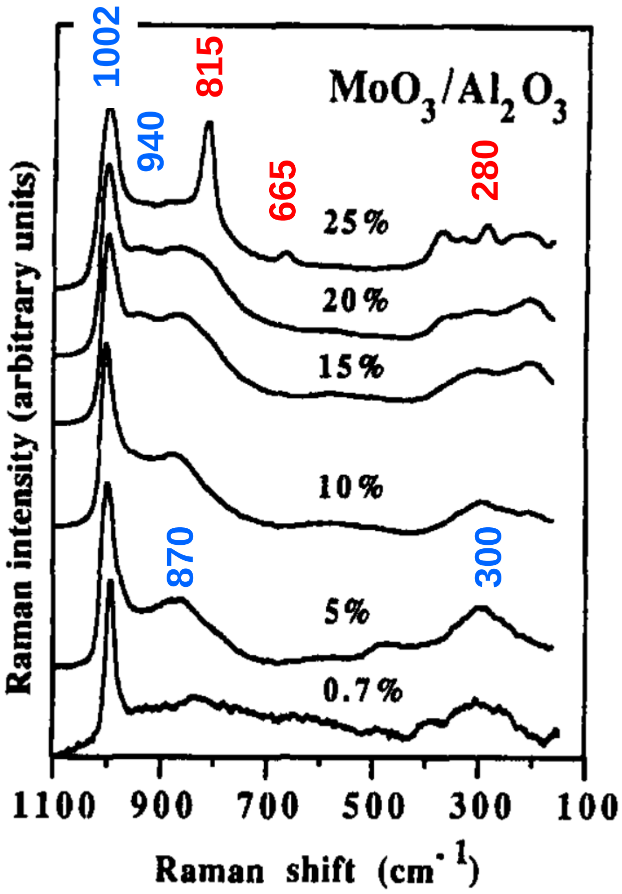
\+ ev. polymers

Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



surface MoO_3

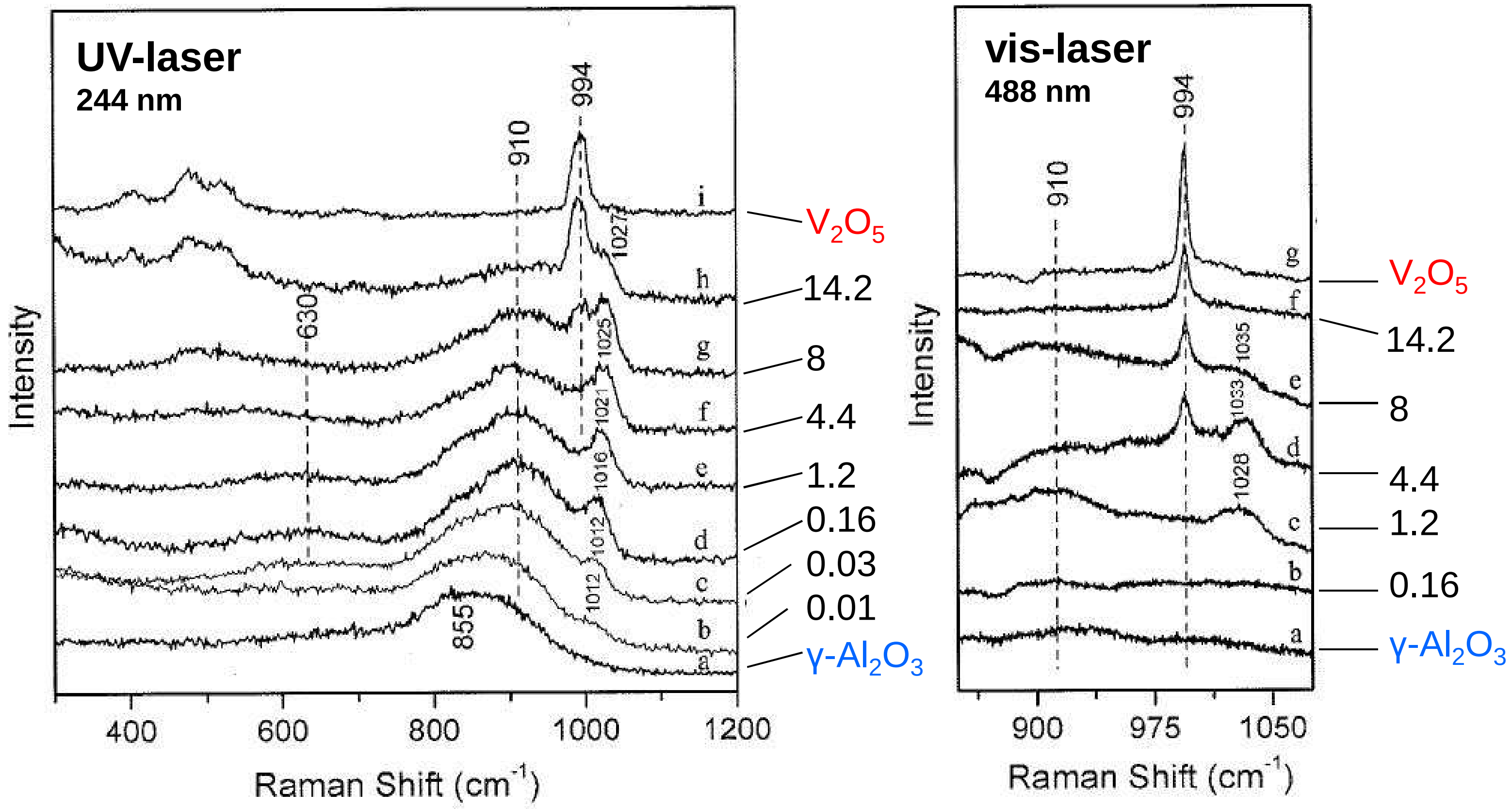
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

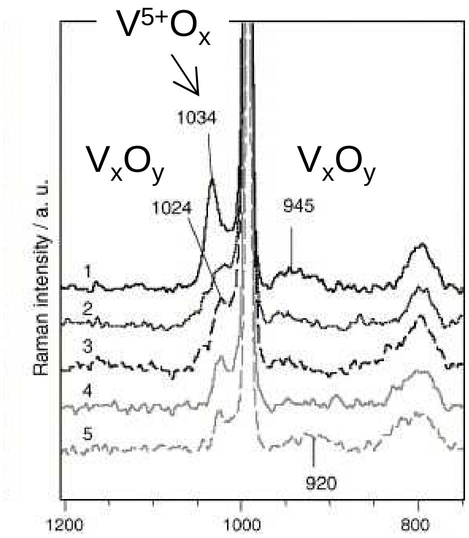
- Monomeric & polymeric species



Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

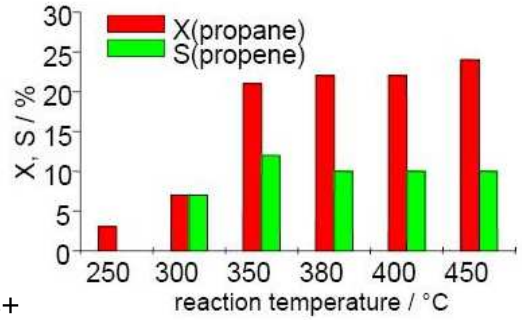
Applications

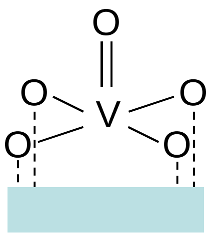
- Reactivity of V/TiO_2 after oxidative treatment

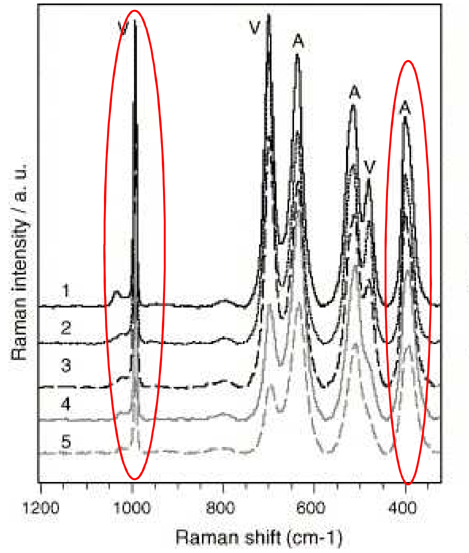


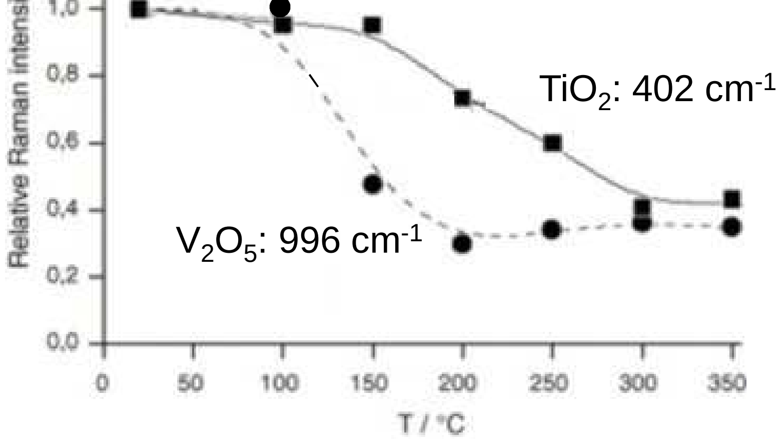
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

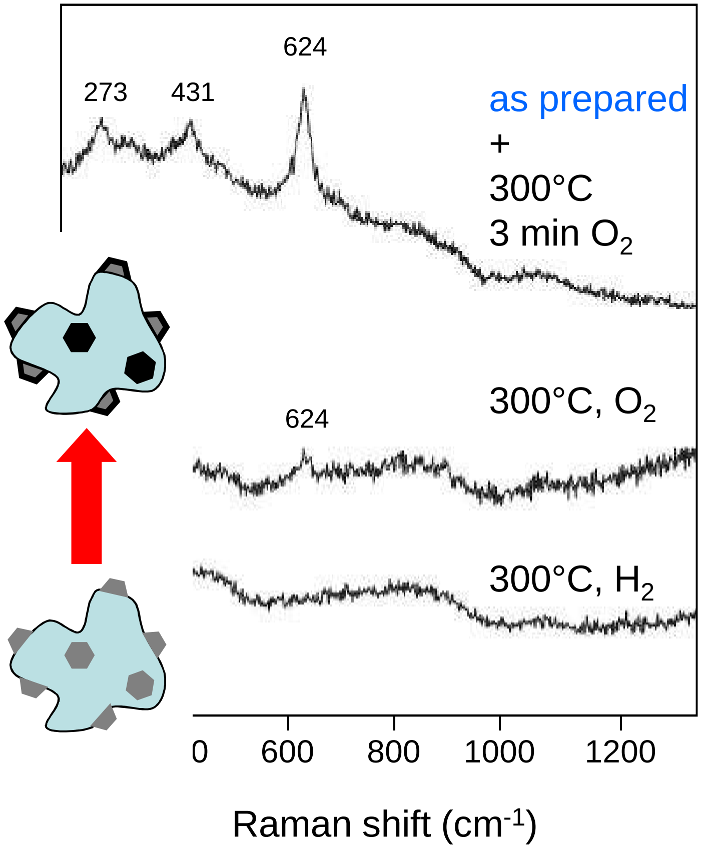
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…)
used for total and partial oxidation reactions

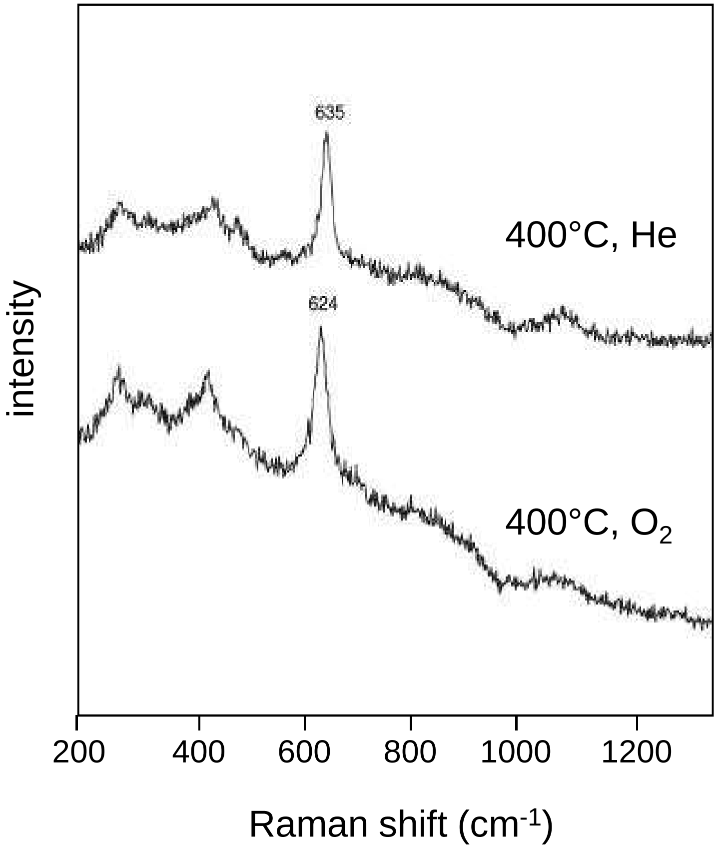
Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3





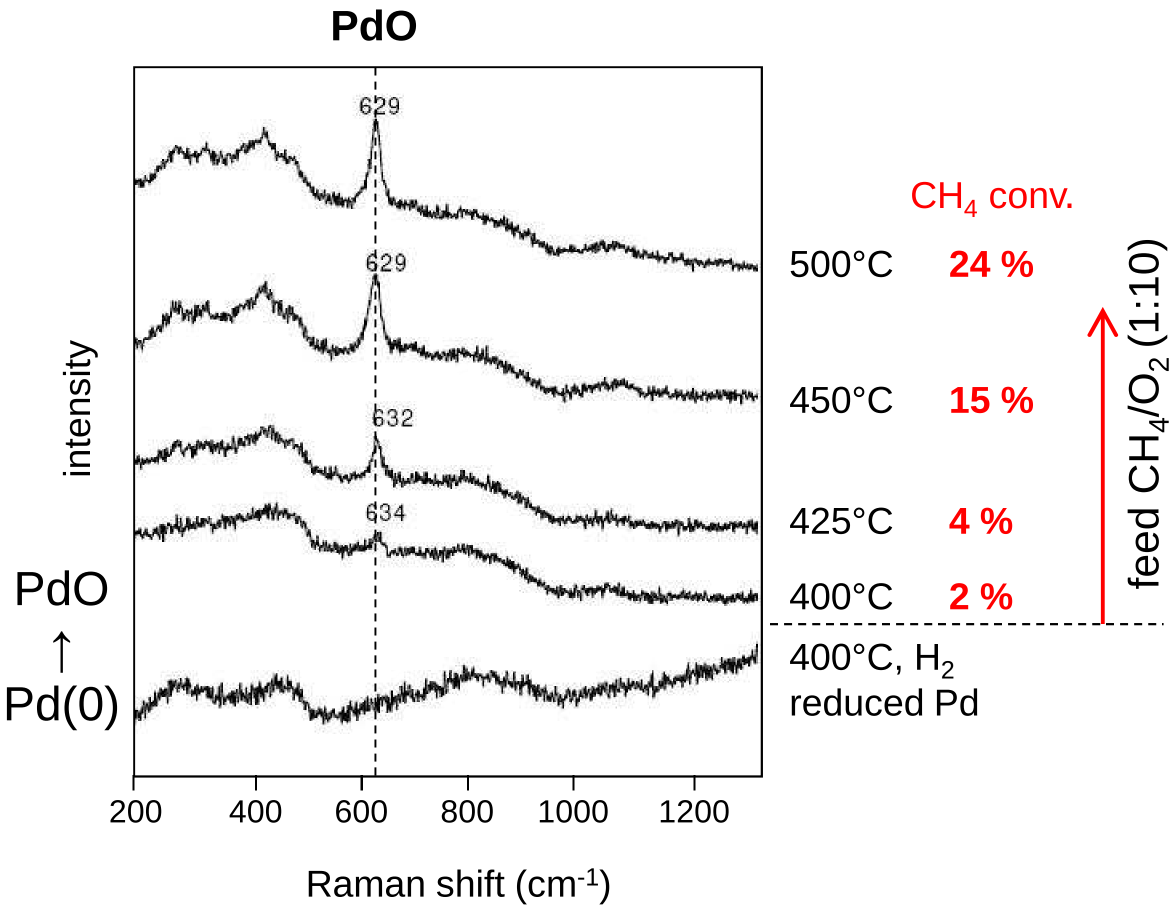
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

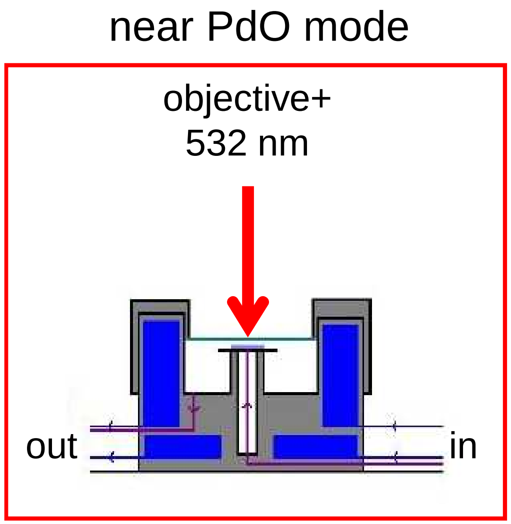
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

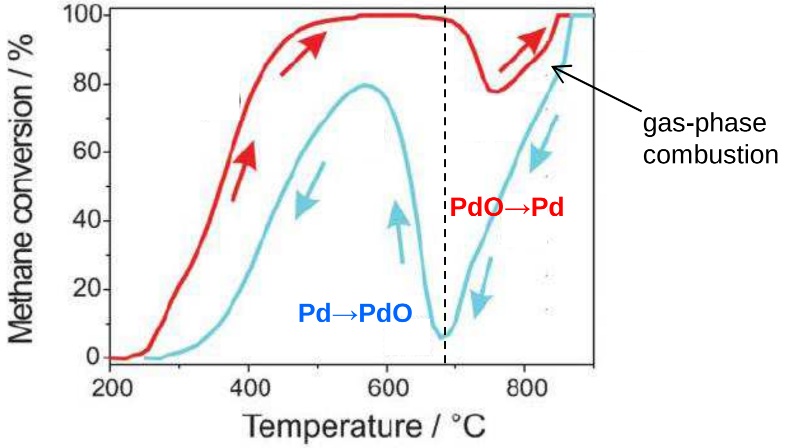


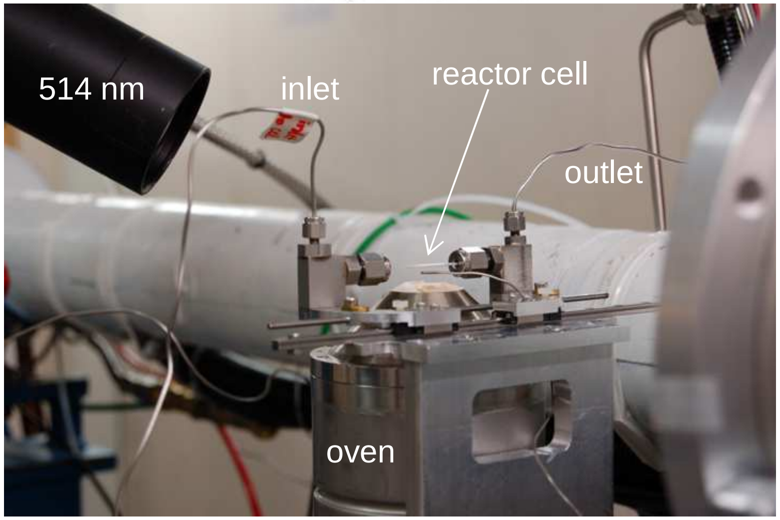


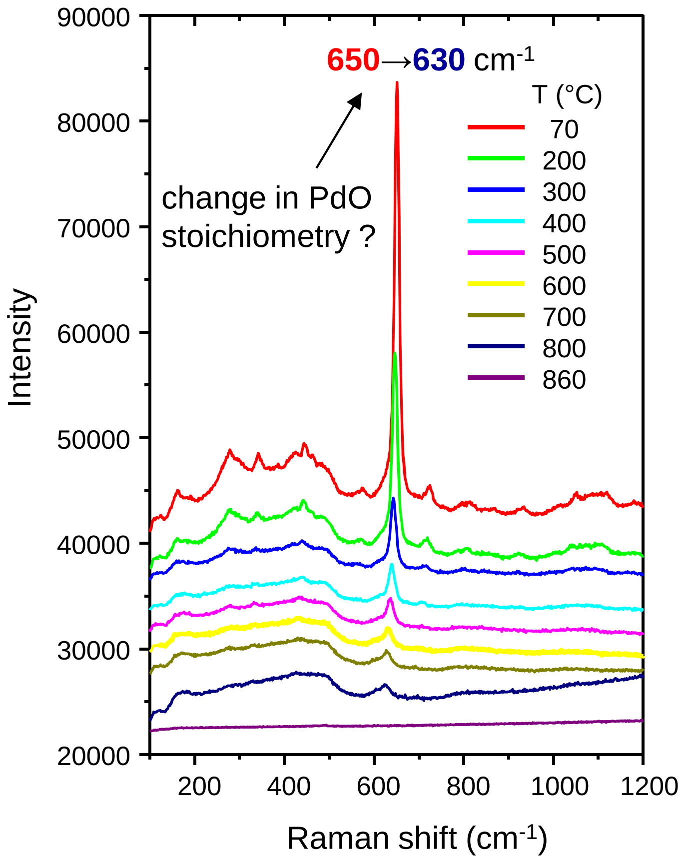
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

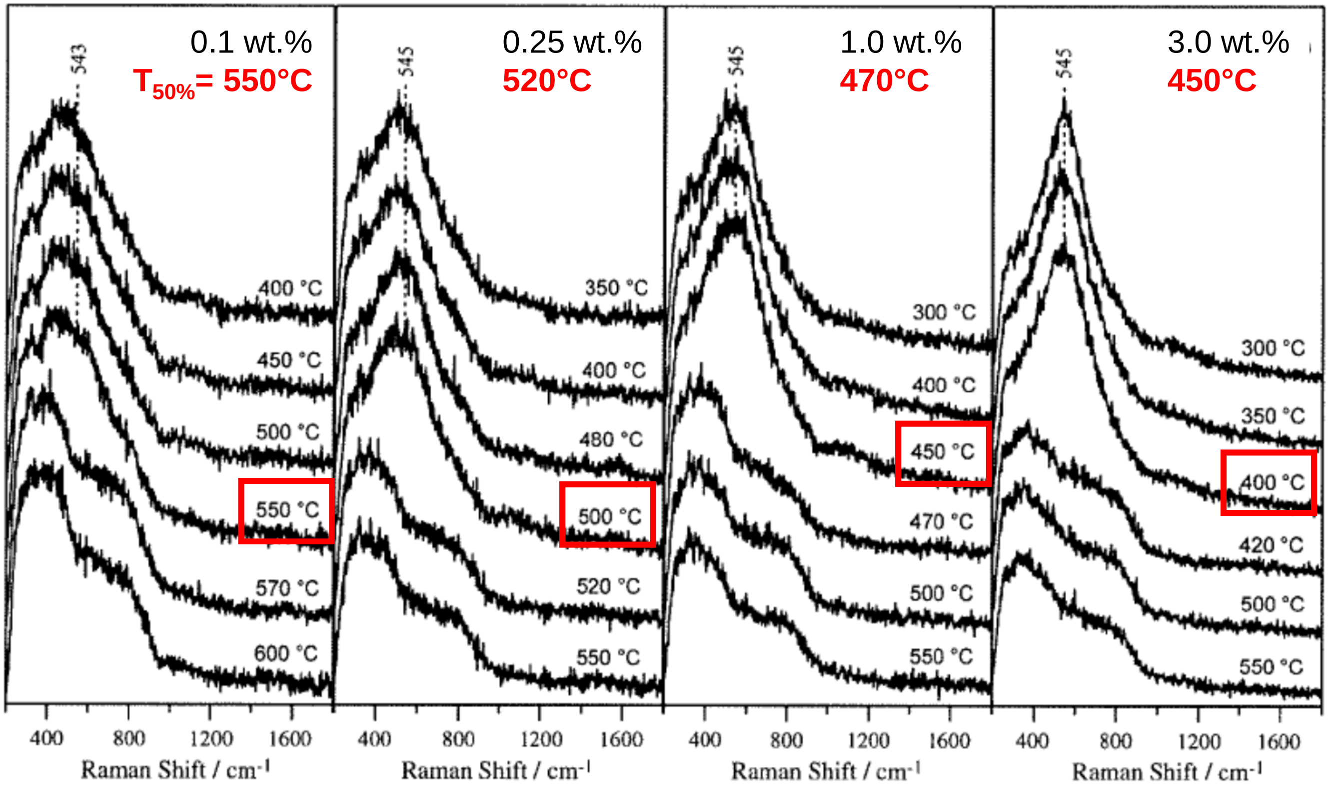
- Methane partial oxidation over Rh/Al_2O_3

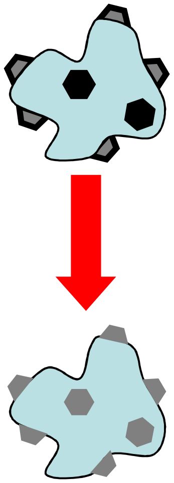
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content →
Activity →

RhO_x
↓
Rh(0)





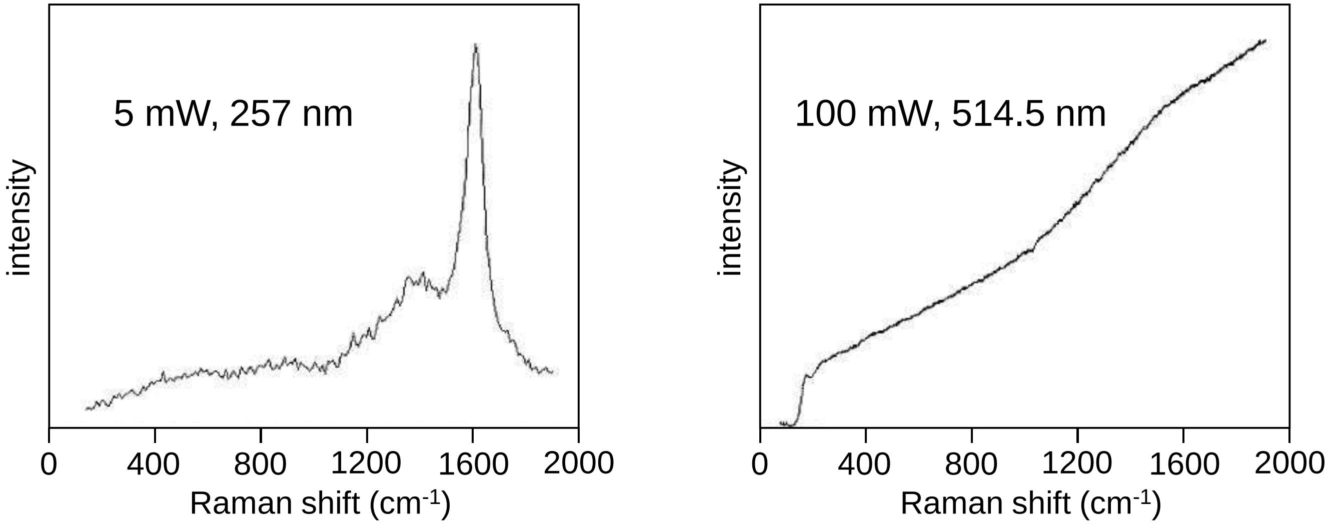
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

    (only few molecules fluoresce below 260 nm)

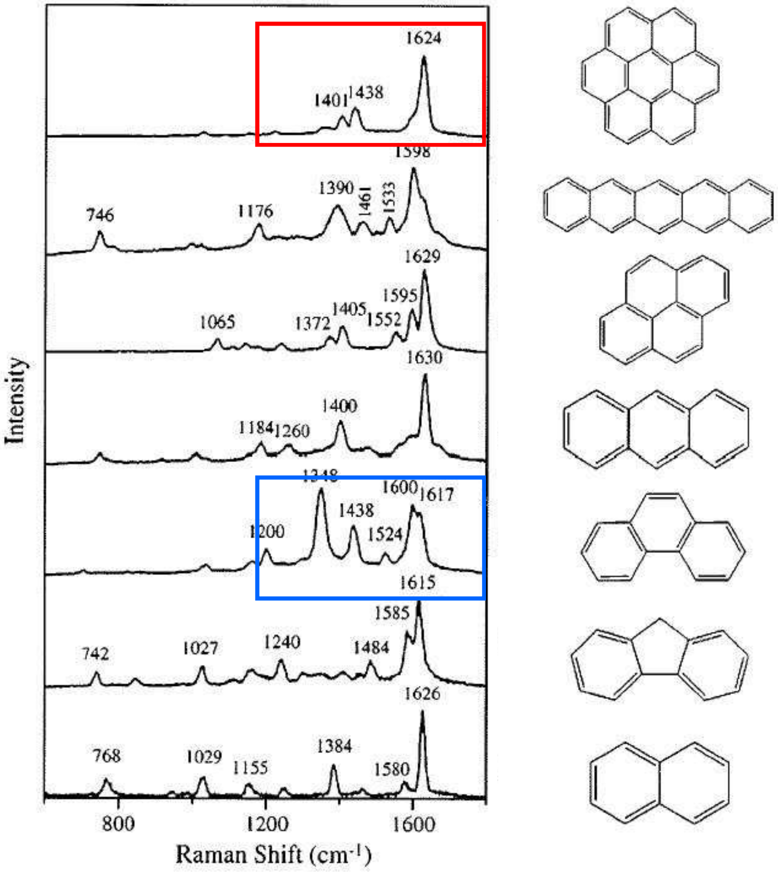
Rh/Al_2O_3, coked 500°C in naphtha

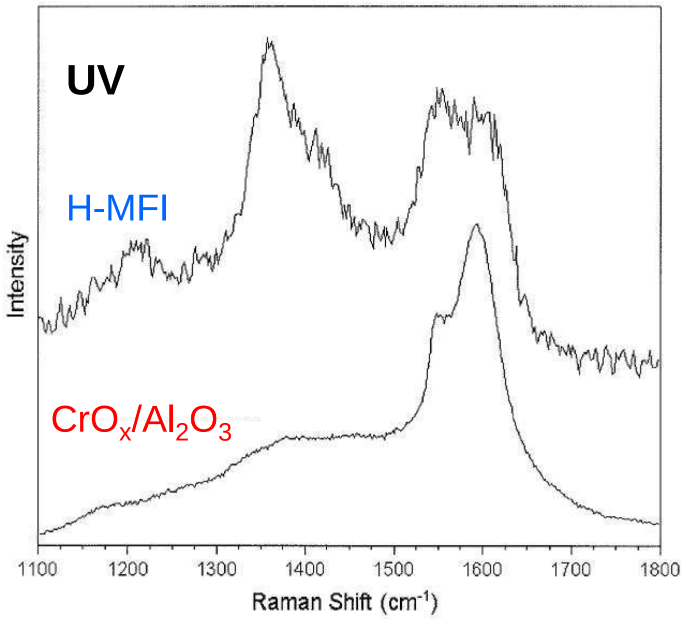


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





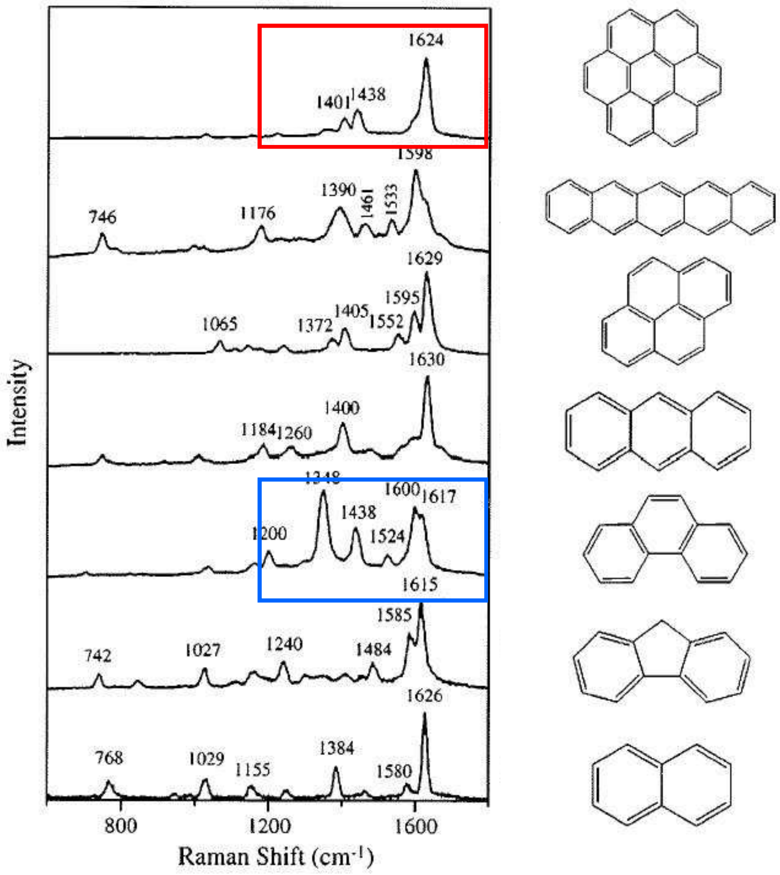
Coke classification
1D topology, chain-like
2D topology, sheet-like

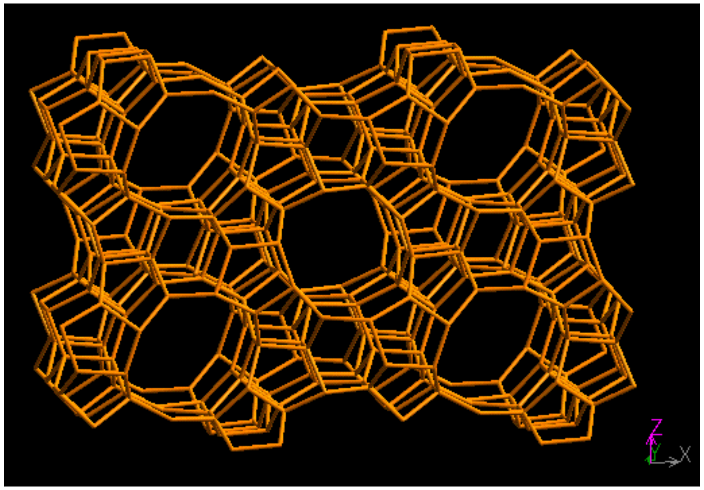
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization





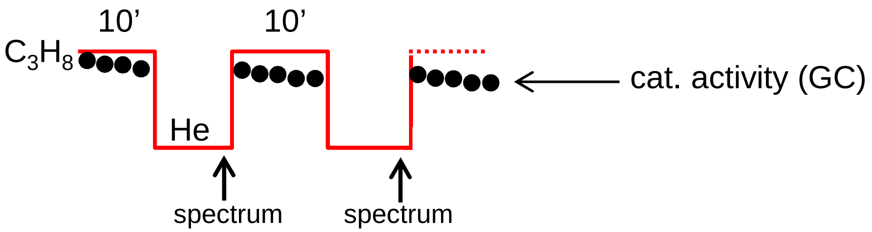
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

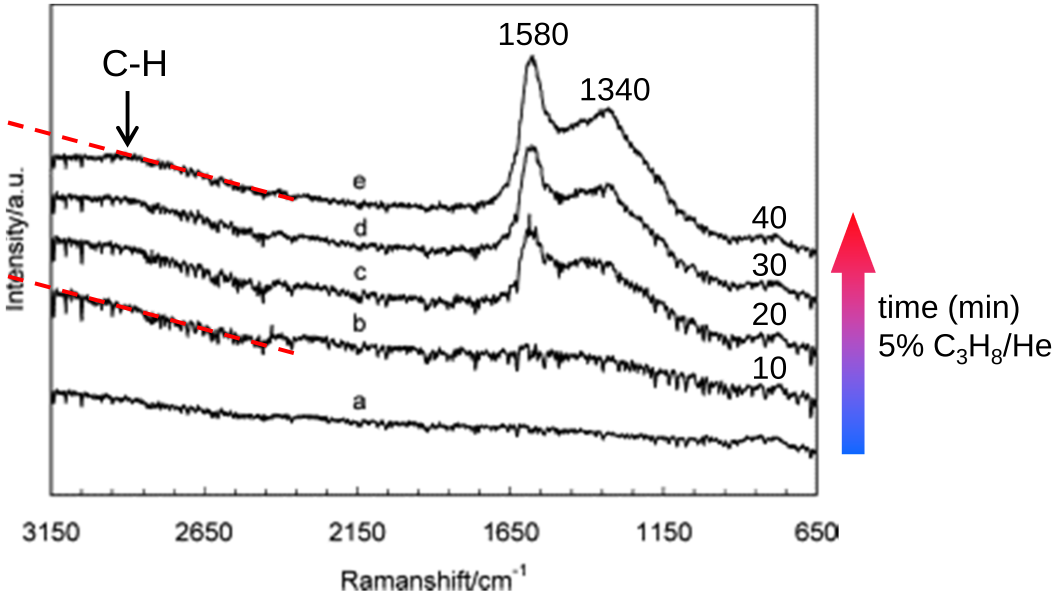
Stair, *Adv. Catal.* **51** (2007) 75

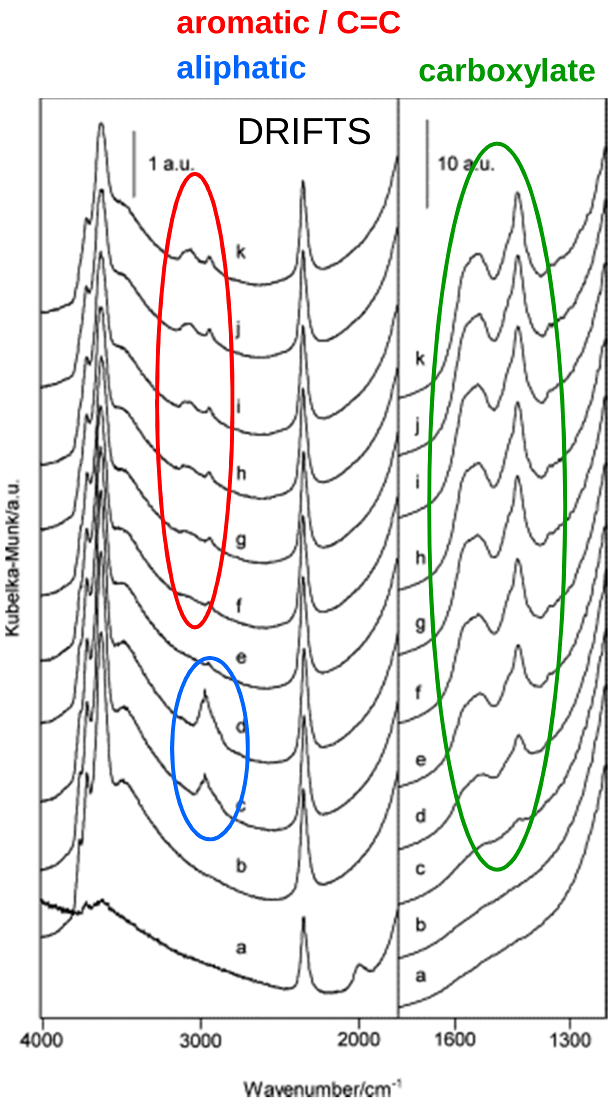
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

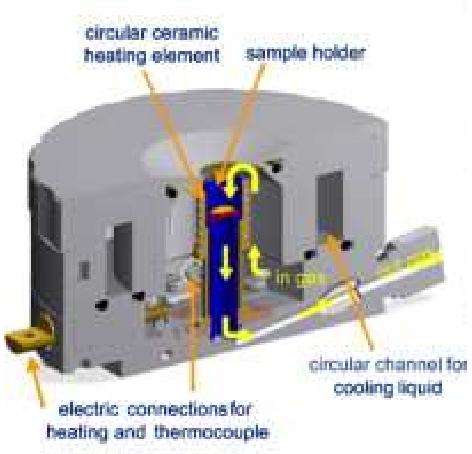


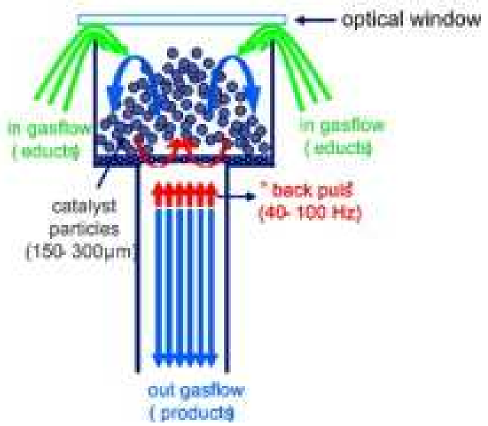


Airaksinen et al., *J. Catal.* **230** (2005) 507

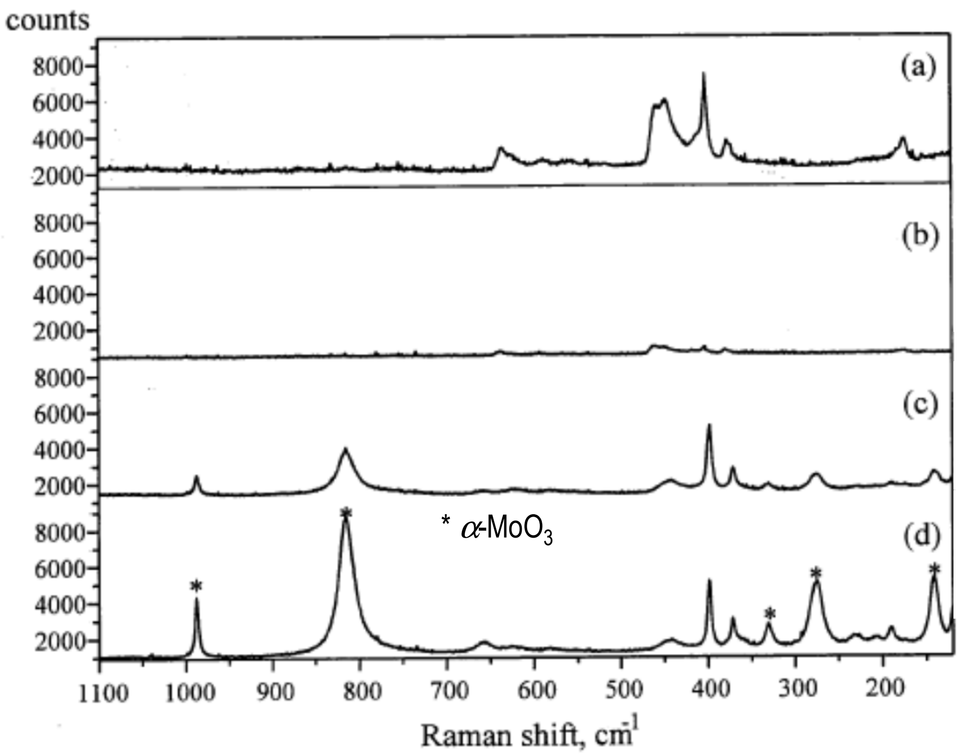
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min full power, FB

MoS_2, 6 min 1/8 power

MoS_2, 1 min full power

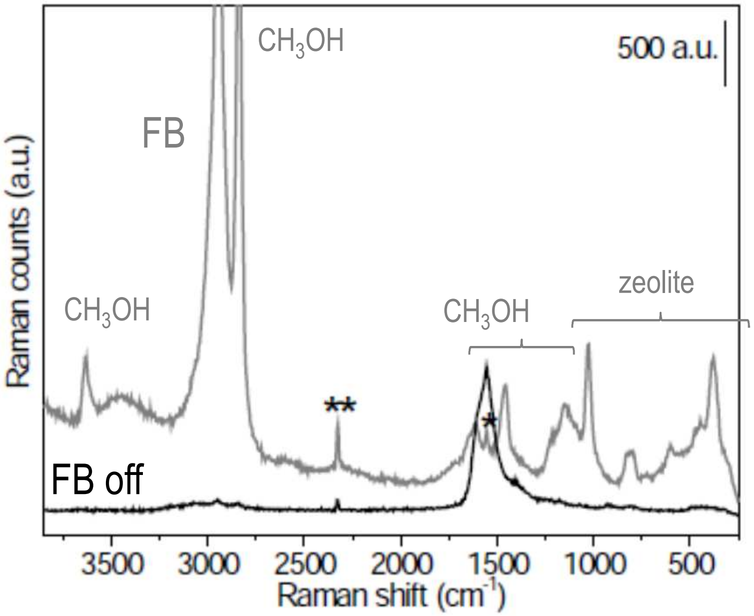
MoS_2, 6 min full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

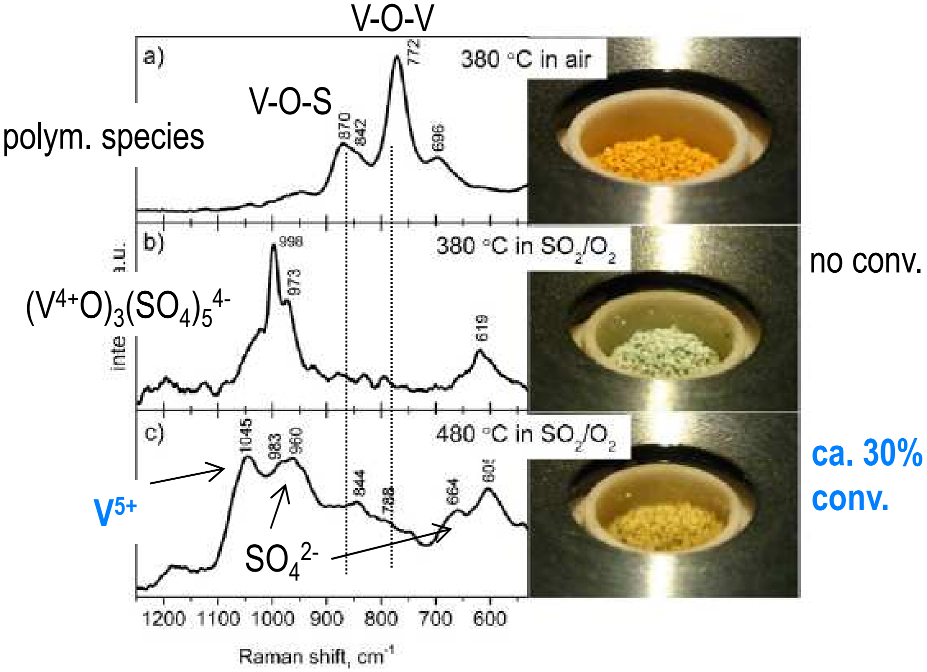
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

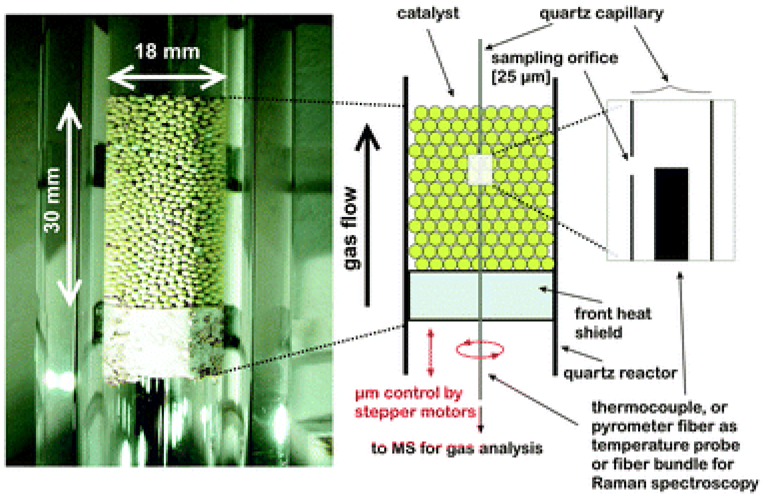


active species: mono- & dimeric V^{5+} oxosulfate species

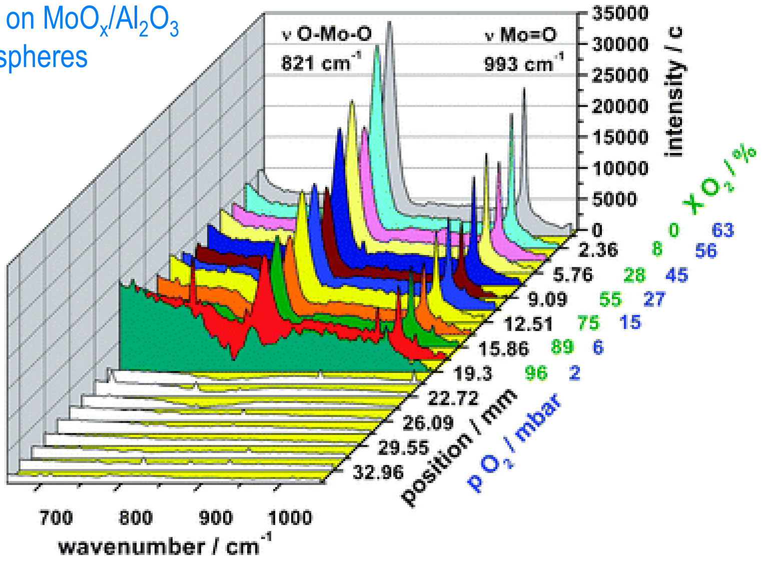
Beato et al., *Catal. Today* 205 (2013) 128

Applications

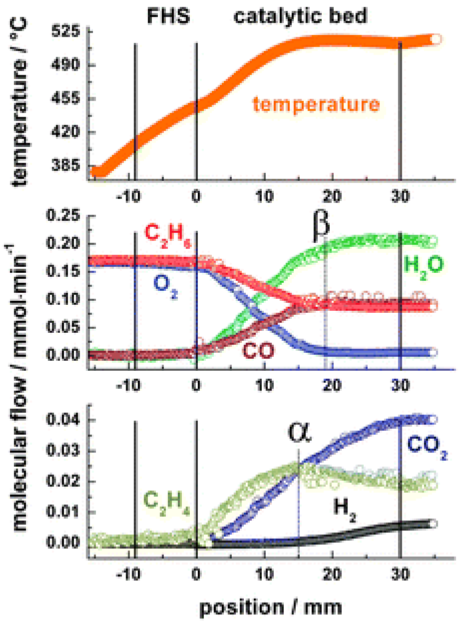
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169

Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
🖃 davide.ferri@psi.ch

Raman spectroscopy

Chandrasekhara Venkata Raman (1888 – 1970)

February 28, 1928: discovery of the Raman effect

Nobel Prize Physics 1930 "*for his work on the scattering of light and for the discovery of the effect named after him*"

Literature:

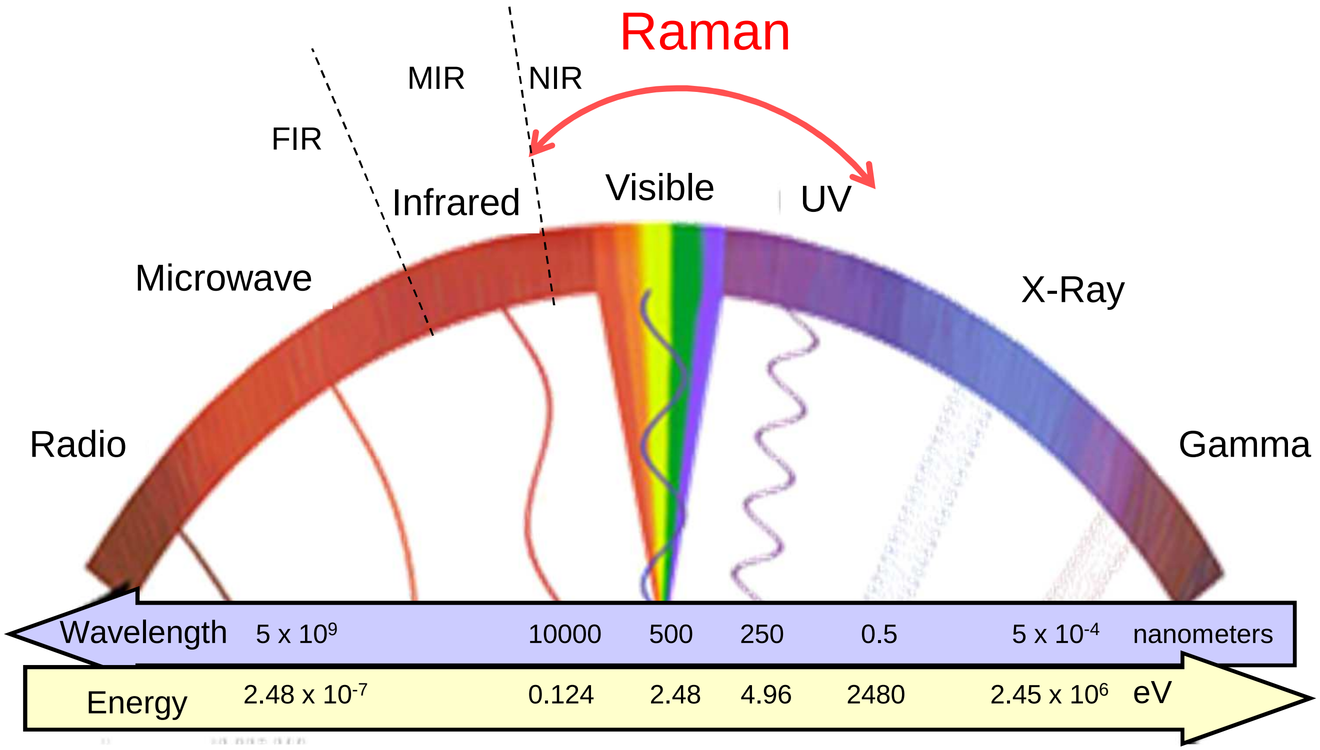
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

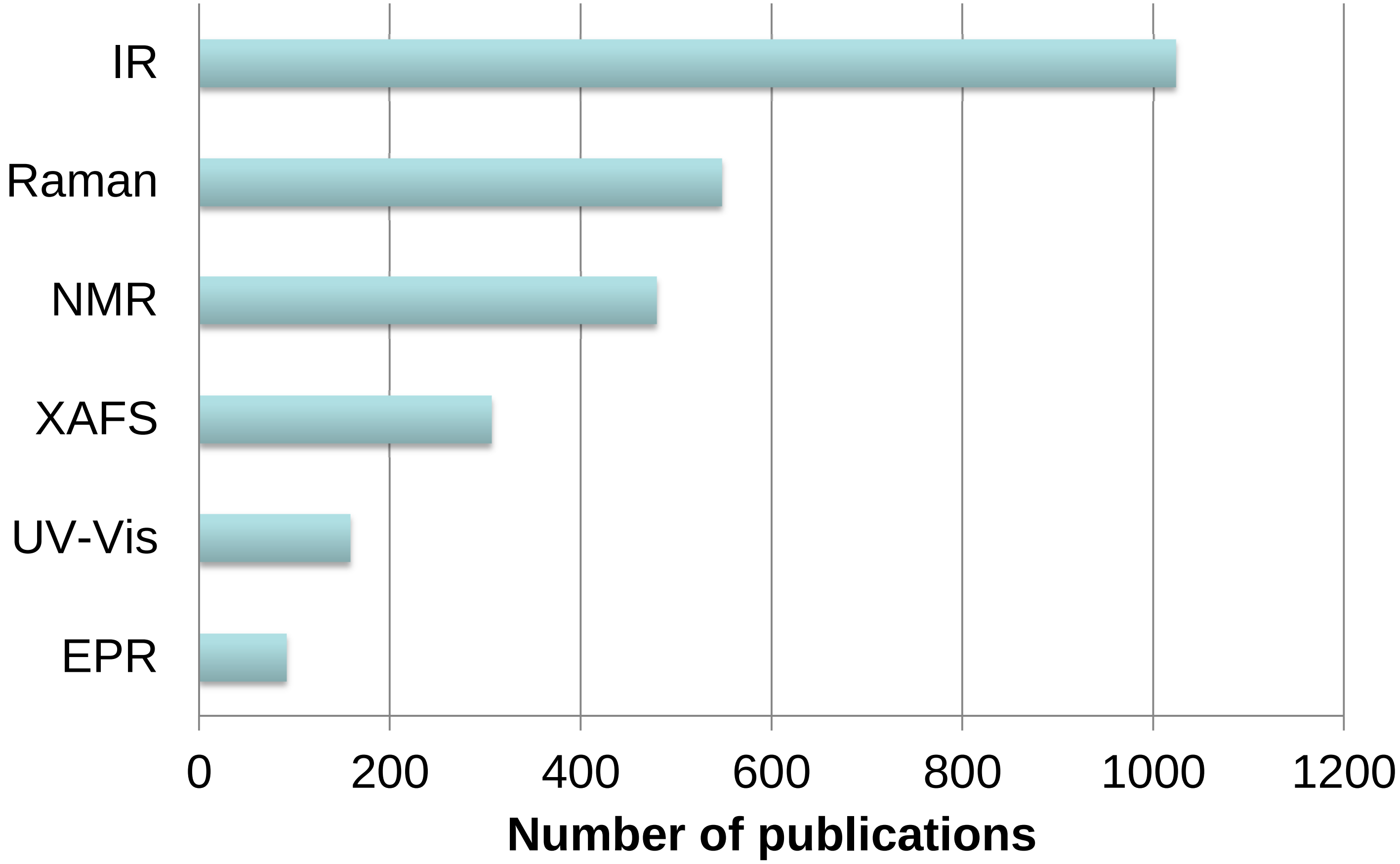
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

http://www.kosi.com/raman/resources/tutorial/index.html

Raman spectroscopy

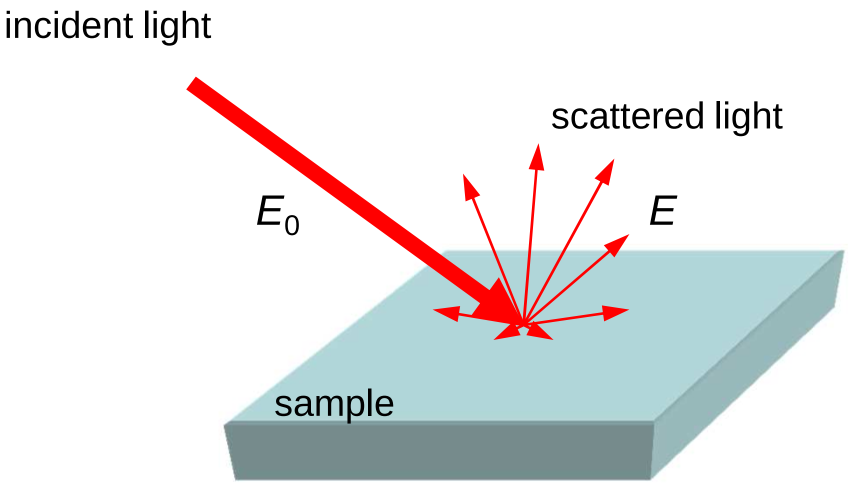


Importance of Raman spec. in catalysis



Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)

Raman spectroscopy



$$E_{vib} = E_0 - E$$

Raman shift

elastic scattering = Rayleigh scattering
inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Raman effect

- Change in **polarizability**, α
- Particle << wavelength: d << λ
  - Particle emits scattered light as a point source

$$\boxed{E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0}$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

- **More scattering at low wavelength** (4th power law)

Classic mechanics approach

Electric field of exciting radiation: $E = E_0\cos(2\pi\nu_0 t)$

Induced dipole: $\mu_{in} = \alpha E = \alpha E_0\cos(2\pi\nu_0 t)$

Induced change of α: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

$$\mu_{in} = \alpha E = [\alpha_0 + \alpha\cos(2\pi\nu_{vib} t)]E_0\cos(2\pi\nu_0 t)$$

$$\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha E_0\cos(2\pi\nu_{vib} t)\cos(2\pi\nu_0 t)$$

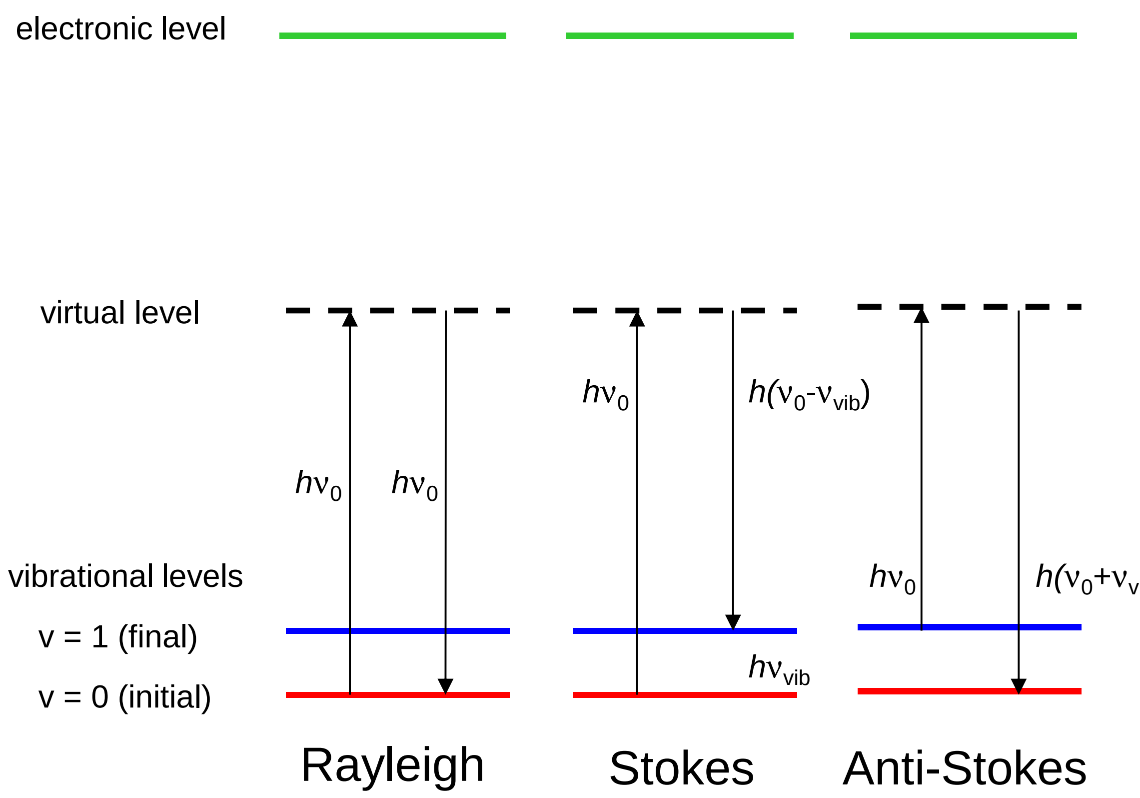
and

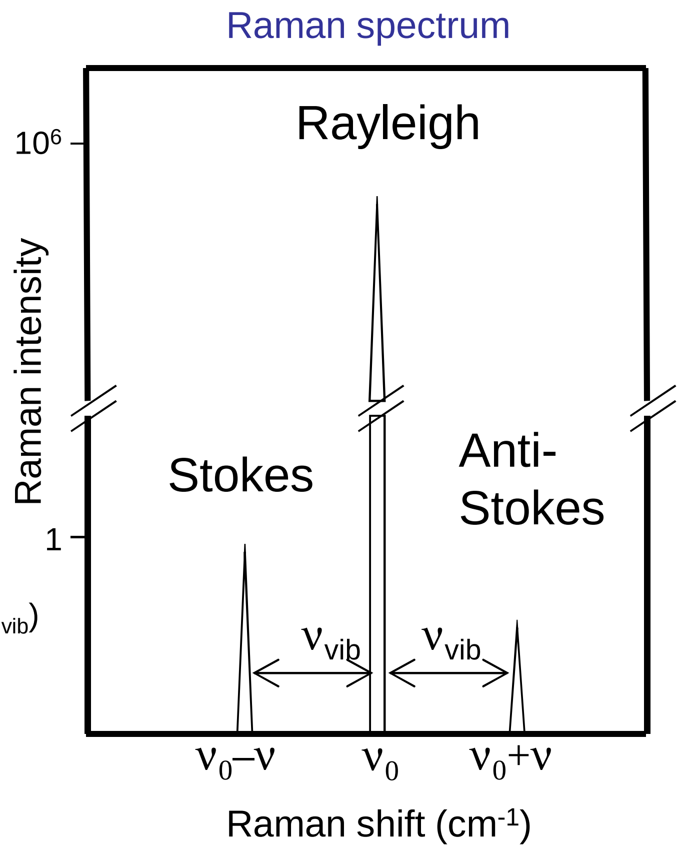
$$\boxed{\mu_{in} = \alpha_0 E_0\cos(2\pi\nu_0 t) + \alpha/2E_0\cos[2\pi(\nu_0+\nu_{vib})t] + \alpha/2E_0\cos[2\pi(\nu_0-\nu_{vib})t]\}}$$

Rayleigh — Anti-Stokes — Stokes

$\cos x\cdot\cos y = 1/2\,[\cos(x+y)+\cos(x-y)]$

Quantum mechanics approach





Quantum mechanics theory

- Classical theory inadequate: same intensity for Anti-Stokes and Stokes lines is predicted

$$\frac{\text{excited population}}{\text{relaxed population}} = e^{-E/kT}$$

Stokes lines more intense than Anti-Stokes lines (factor 100)

- Measure of Temperature:

$$\frac{\mathrm{I}\ \text{(Anti-Stokes)}}{\mathrm{I}\ \text{(Stokes)}} = \left(\frac{\nu_0+\nu_{vib}}{\nu_0-\nu_{vib}}\right)^4 e^{-h\nu_{vib}/kT}$$

Raman signals

- Intensity of Raman signals depends on:

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

  - 4th power of ν (4th power law)
  - 2nd power of $\Delta\alpha$
    - properties of molecules
    - strength of bonds

↓

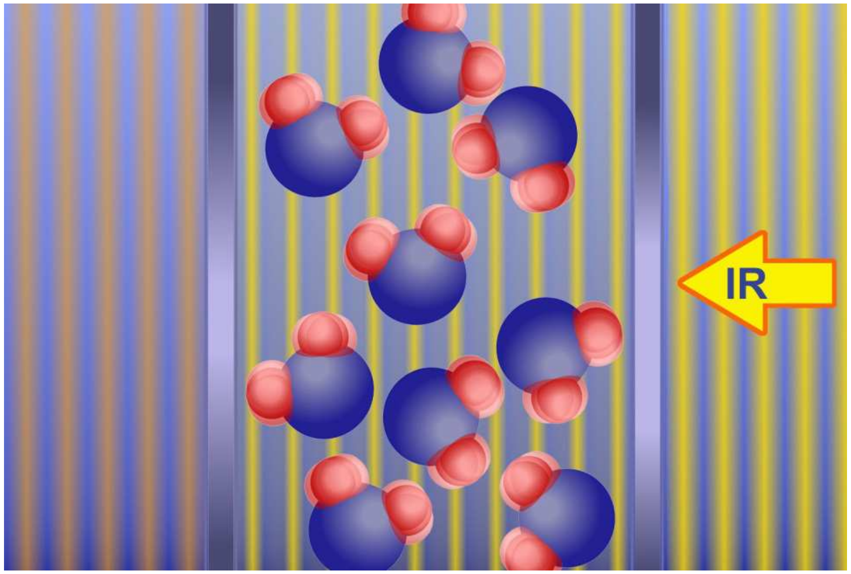
covalent bond STRONG bands (catalysis!)

ionic bond WEAK bands

- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

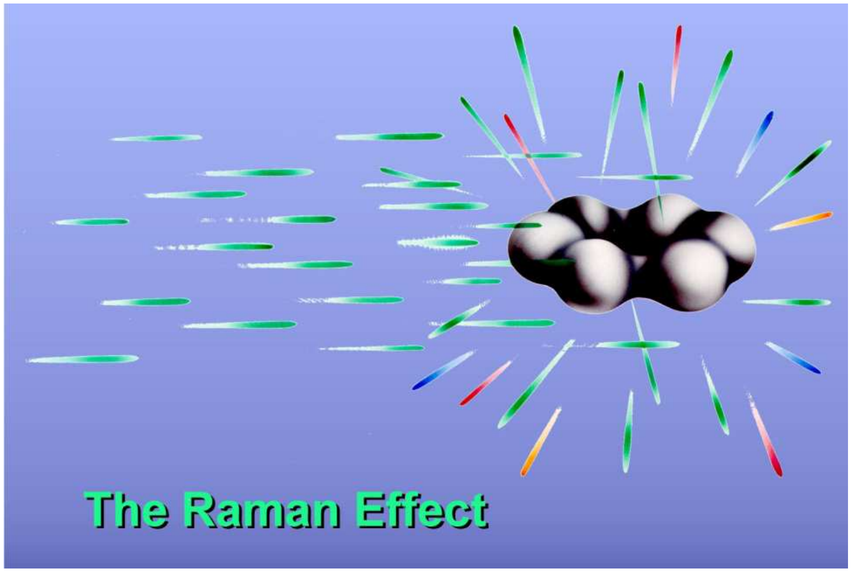
Raman *vs.* Infrared

Infrared



Absorption of IR light

Raman



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

$$\left(\frac{\partial\mu}{\partial Q}\right)^2 \neq 0$$

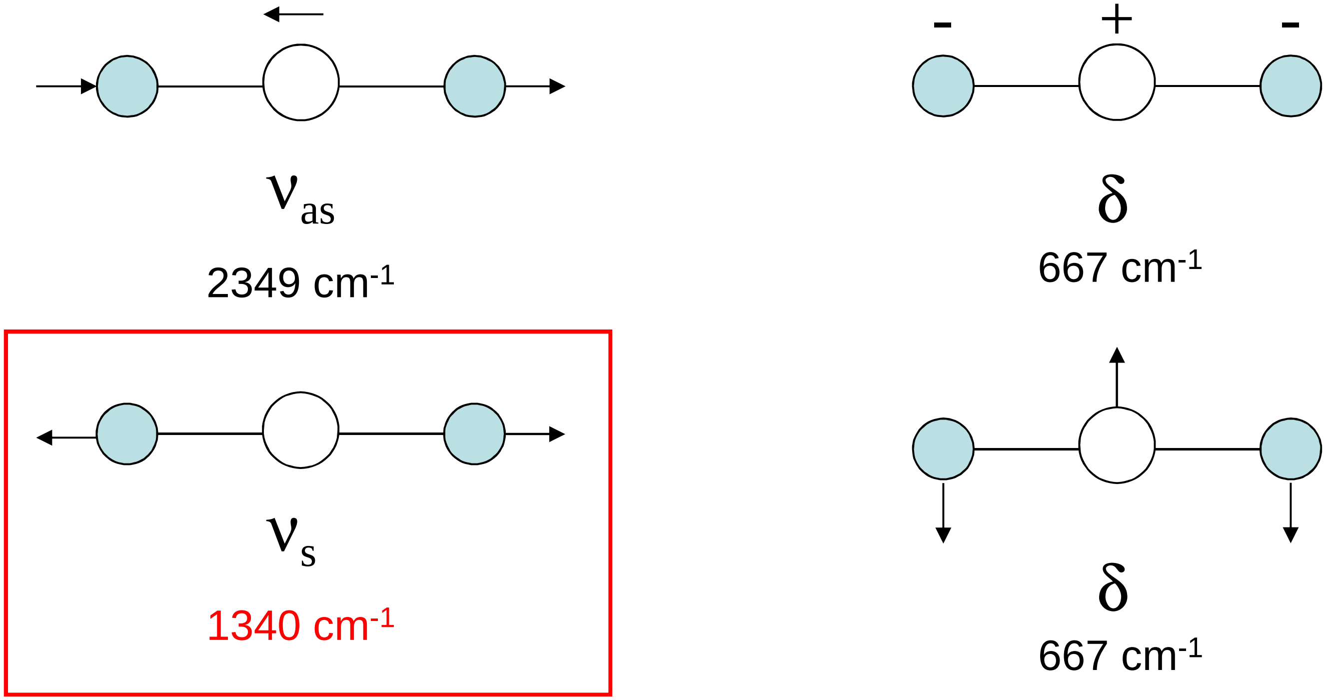
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

$$\left(\frac{\partial\alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - ❑ large electron clouds
  - ❑ not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers

Raman *vs.* Infrared

CO_2



ν_{as}

2349 cm^{-1}

ν_s

1340 cm^{-1}

Raman active

δ

667 cm^{-1}

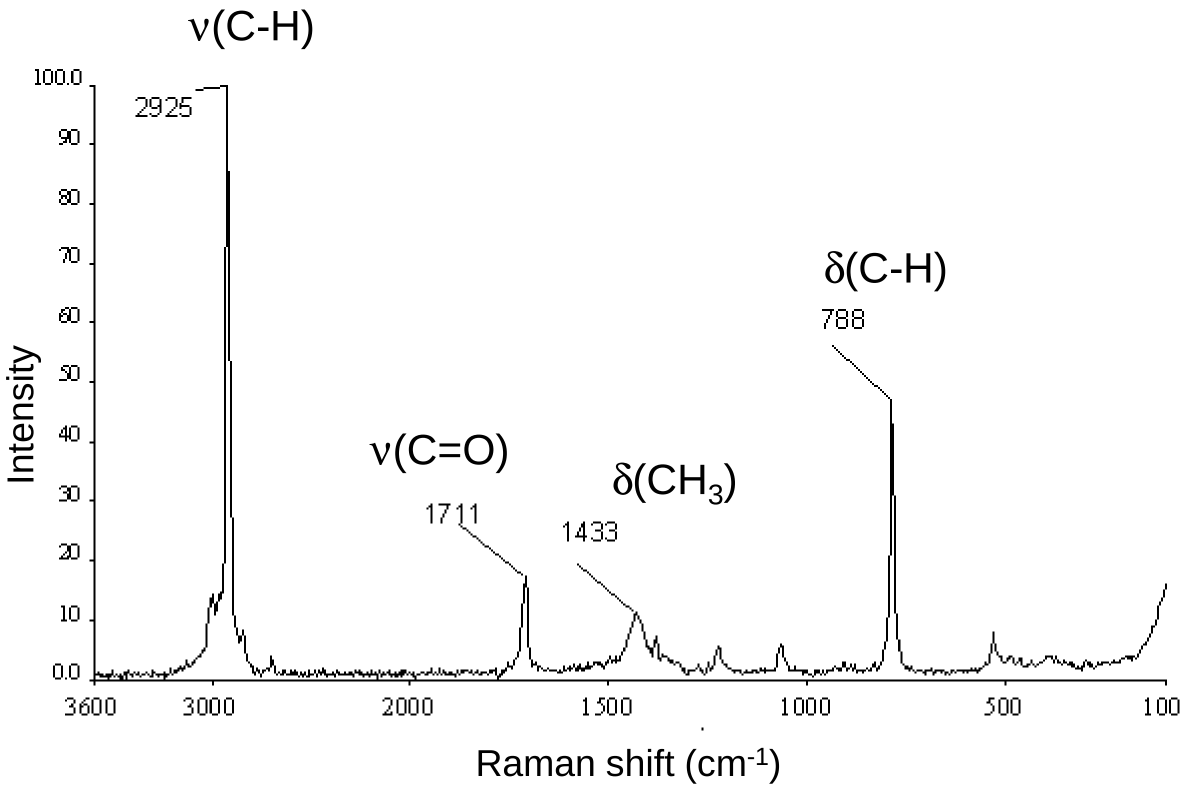
δ

667 cm^{-1}

degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared

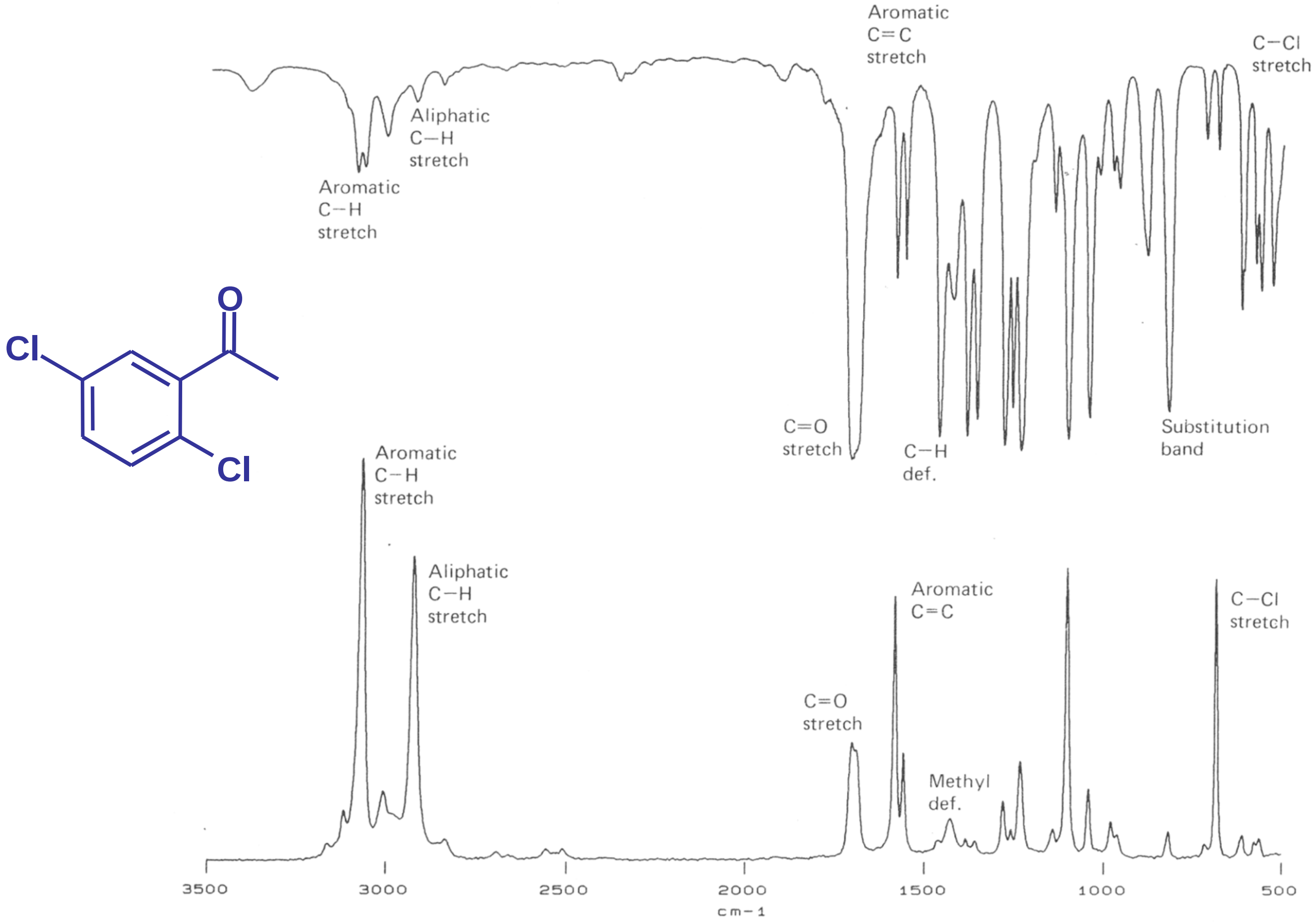


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

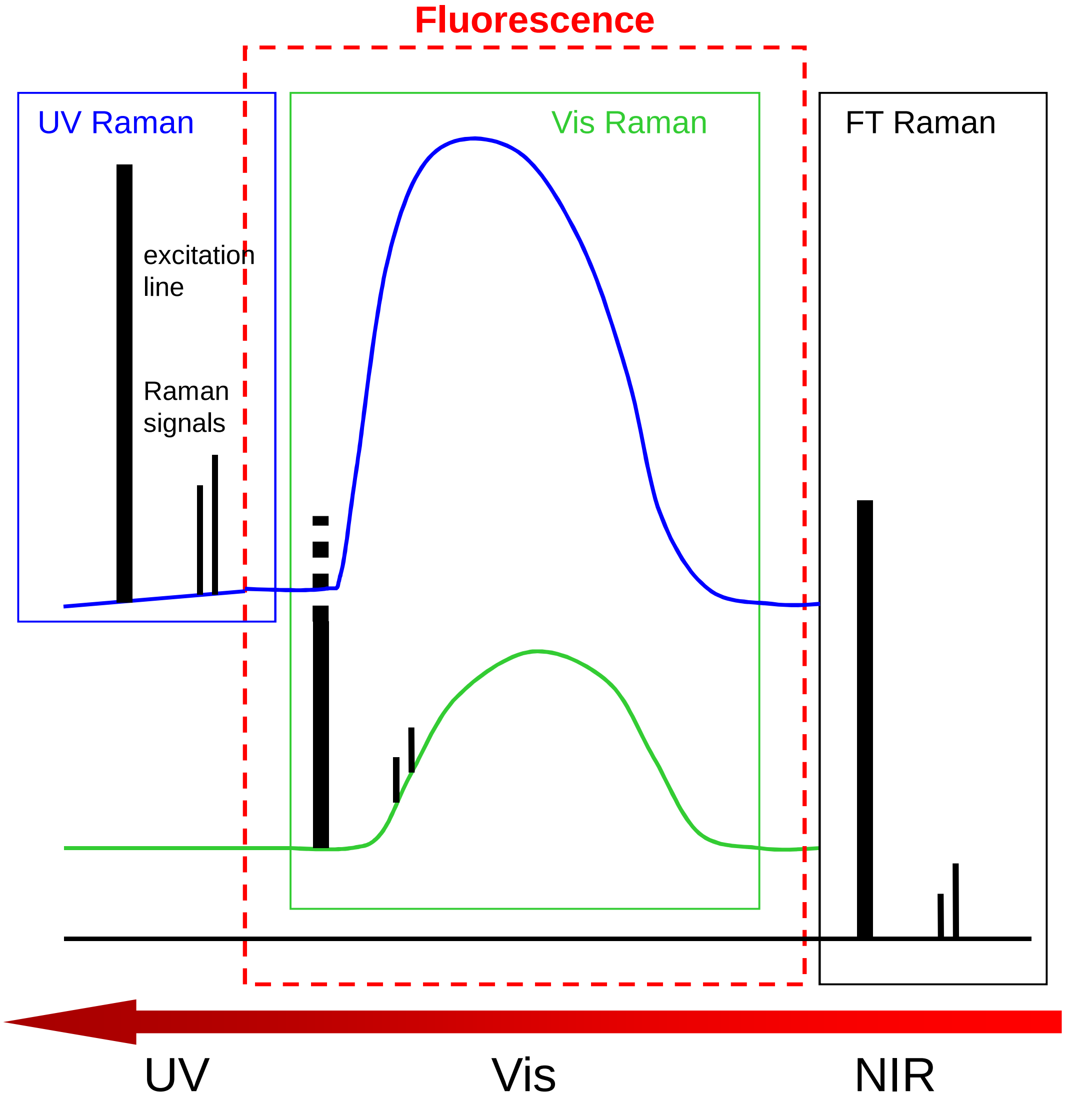
Advantages

- Simple optics
- Versatile design of cells (quartz & glass allowed)
- Fiber optics
- Almost no limitation in temperature
- Very small amount (*pico*g) of sample possible
- Water no problem
- Sensitive to microcrystals (< 4 nm)
- Sample of phase not critical
- Spatial resolution (1 µm)
- No contribution from gas phase

Disadvantages

- Relatively expensive instruments
- Low spectral resolution (UV and Vis)
- Difficult quantification (limited to heterogeneous catalysis)
- Structure of analyte affected by high energy of laser (e.g. UV Raman)
- Fluorescence

Fluorescence and Raman signals



Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

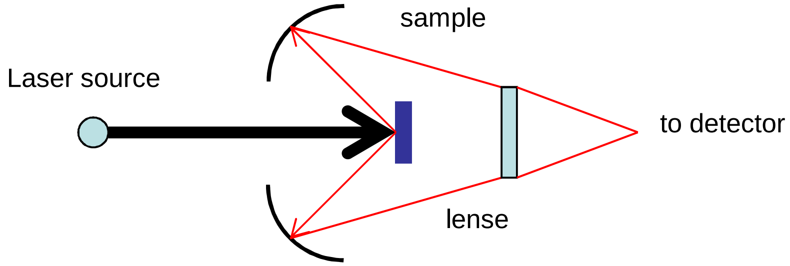
Fluorescence proportional to ν

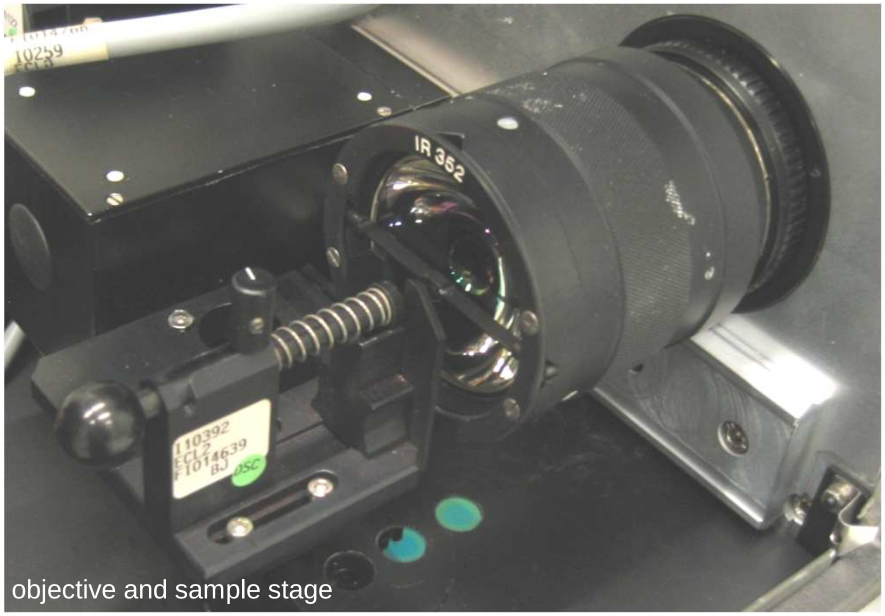
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Instrumentation





objective and sample stage

Lasers

Excitation wavelengths

▪ UV	250 nm
▪ Vis (green)	514 nm
▪ Vis (red)	633 nm
▪ NIR	780 nm
▪ IR	1064 nm (9395 cm^{-1})

Dispersive instruments

Lasers

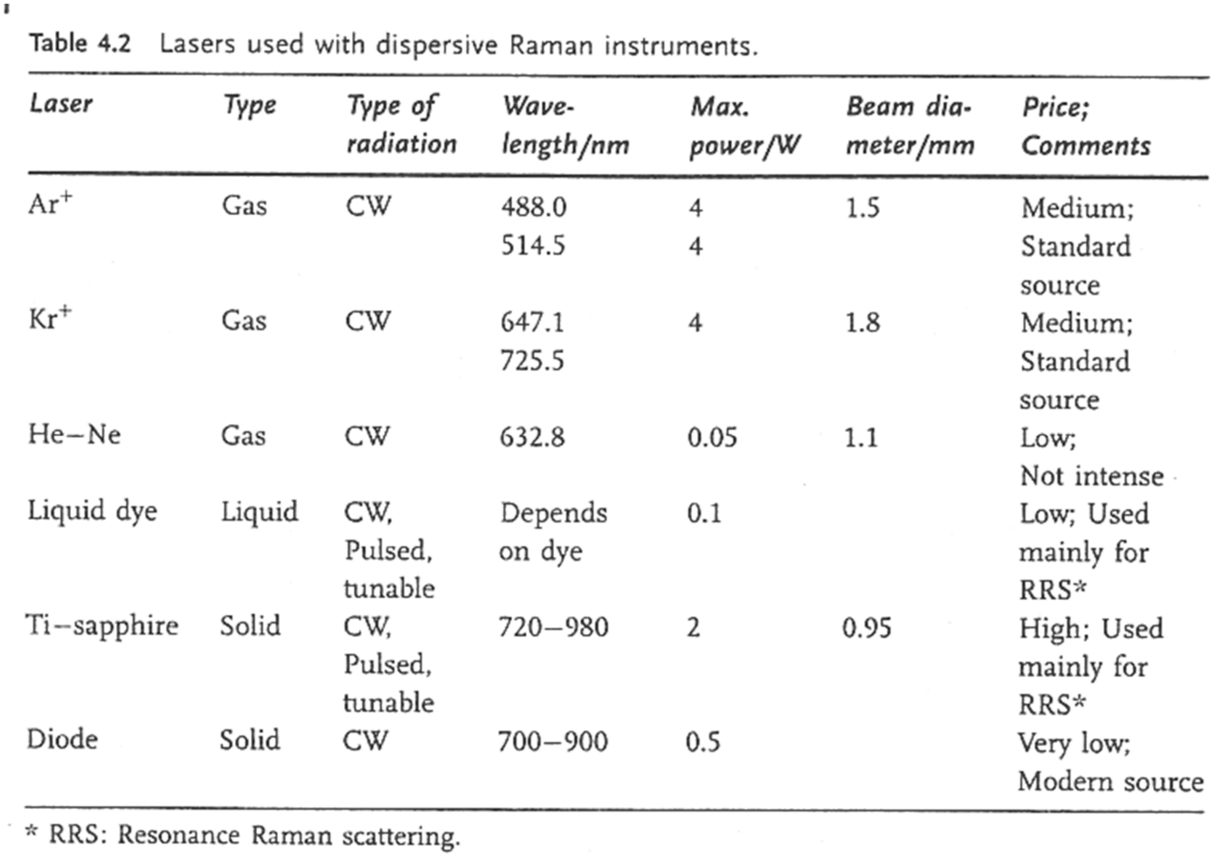


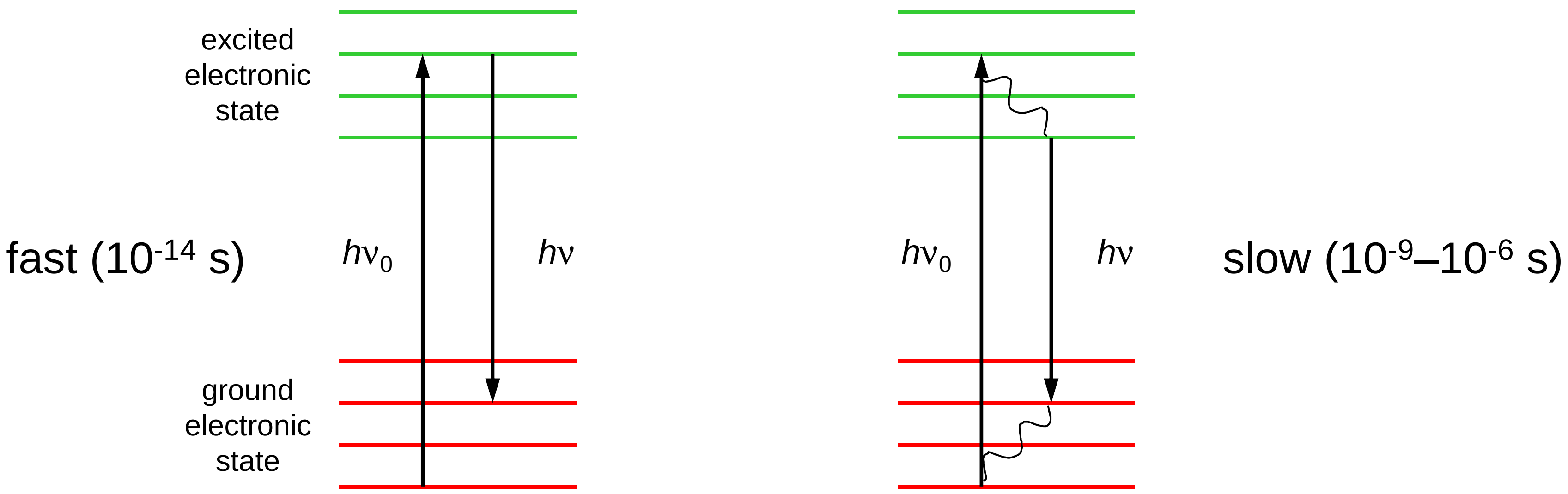
Table 4.2 Lasers used with dispersive Raman instruments.

Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends on dye	0.1		Low; Used mainly for RRS*
Ti–sapphire	Solid	CW, Pulsed, tunable	720–980	2	0.95	High; Used mainly for RRS*
Diode	Solid	CW	700–900	0.5		Very low; Modern source

* RRS: Resonance Raman scattering.

Resonance Raman Spectroscopy

- Raman scattering strongly enhanced if the excited state is not virtual, but an electronically excited state (factor 10^6 !)
- Vibrations related to an electronic transition are excited



Resonance Raman scattering

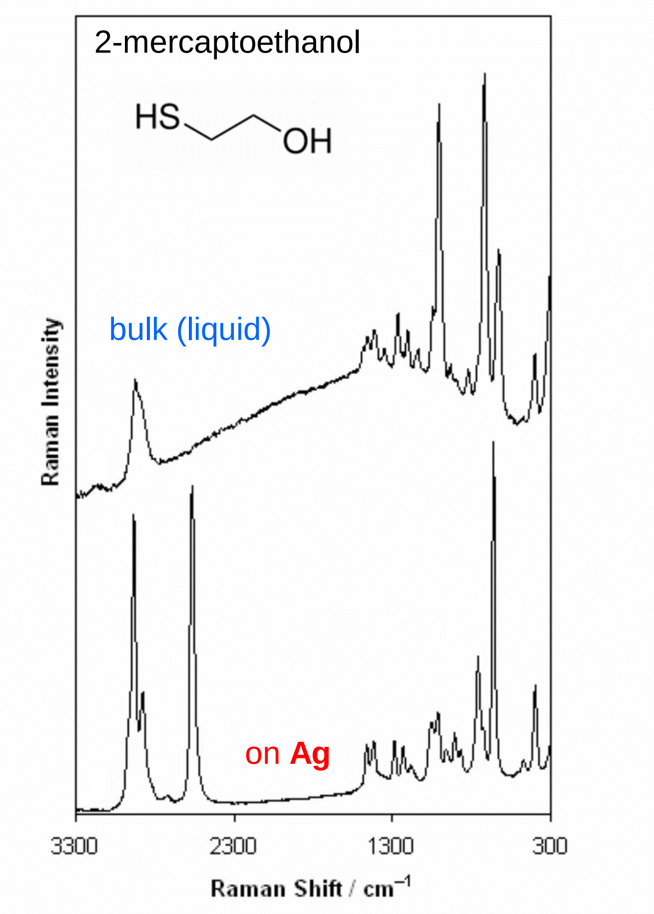
Fluorescence

Pulsed laser used to avoid fluorescence

Surface Enhanced Raman Spectroscopy

- Valid for adsorbates
- Enhanced electric field provided by surface
- Excitation of surface plasmons by light
- Enhancement greater when plasmon frequency in resonance with incident radiation
- Plasmon oscillations perpendicular to surface

The original experiment



Fleischmann, *Chem. Phys. Lett.* **26** (1974) 163

Surface Enhanced Raman Spectroscopy

- Enhancement factor up to **10^6** on substrates like: Ag, Au, Cu

- Less enhancement for other metals (Pt and Pd)

- Dual nature (electromagnetic [surface plasmons] + chemical [charge transfer surface–adsorbate])

- Applications: electrochemistry, corrosion, (bio-)adsorbates, acidity of surfaces, (bio-)sensing

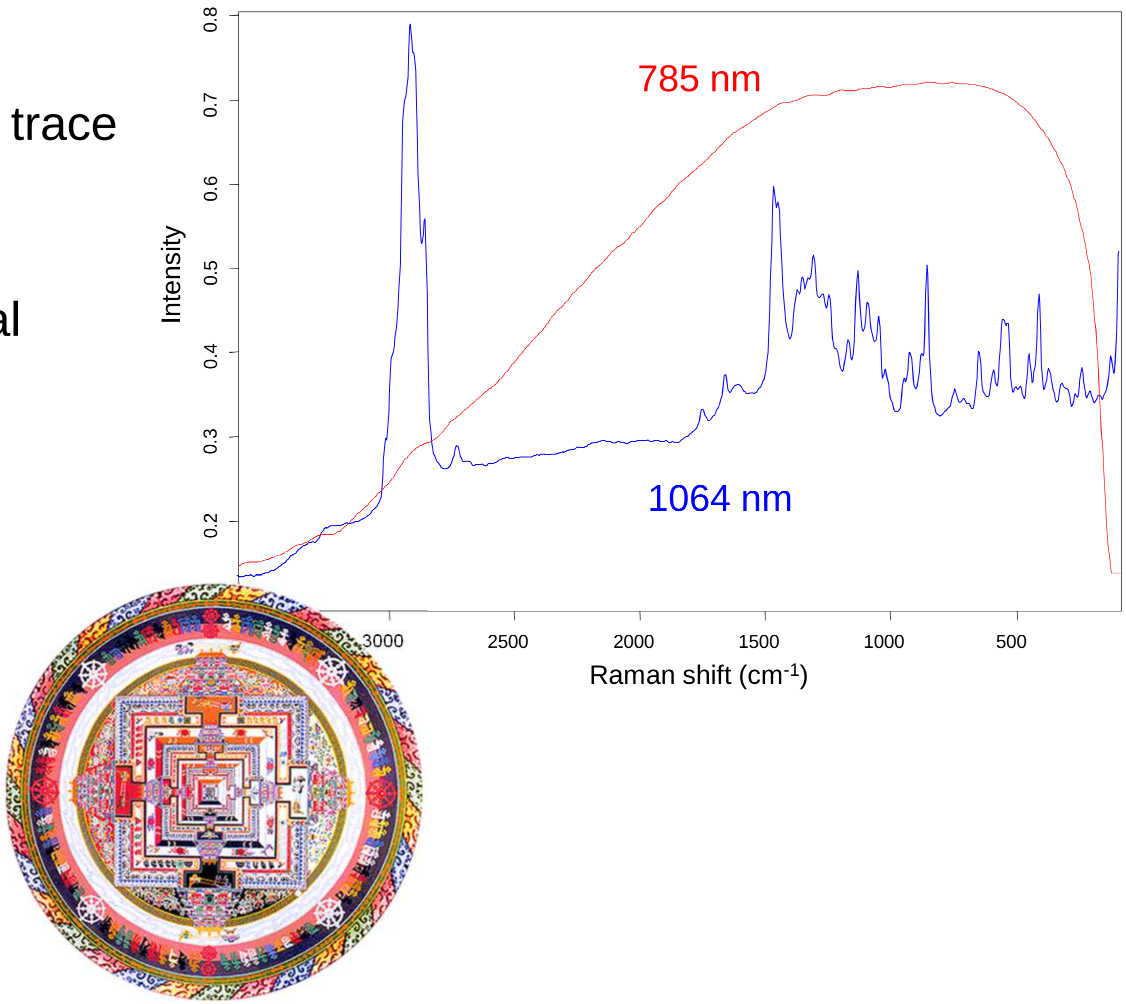
- Remarks:

❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

Njoki et al., *J. Phys. Chem. C* **111** (2007) 14664

Applications

- Aqueous solutions
- Environmental chemistry & trace analysis
- Semiconductor technology
- Biochemical and biomedical
- Pharmaceutical industry
- **Heterogeneous catalysis**
- Forensic science
- Polymer science
- Food science
- Art conservation
- Reaction monitoring



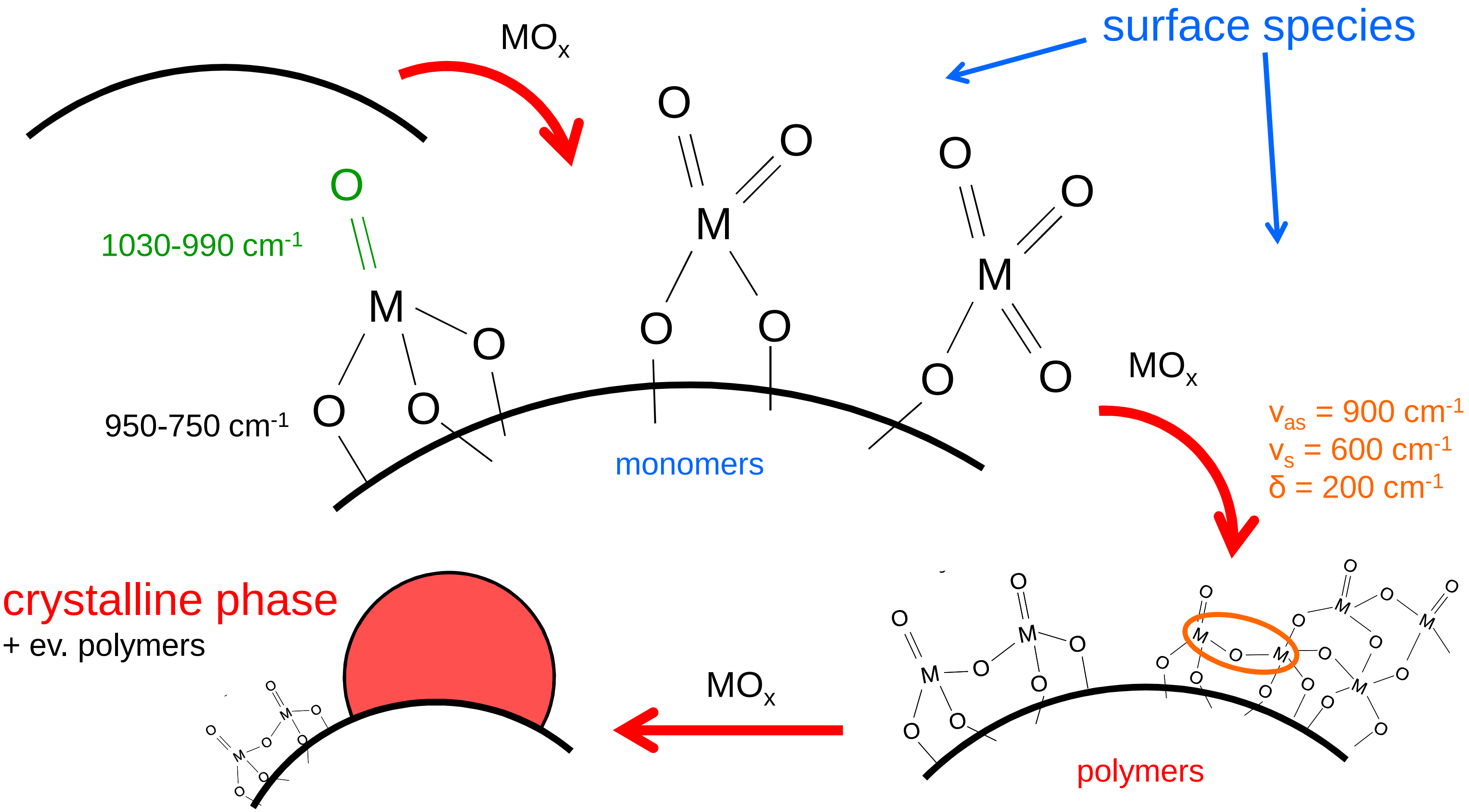
Applications

$MO_x/M'O_X$ used in a number of industrial chemical processes (dehydrogenation, oxidation, amoxidation…)

Question: nature of MO_x and the role in catalysis?

Applications

- Monolayer (monomeric) & polymeric species

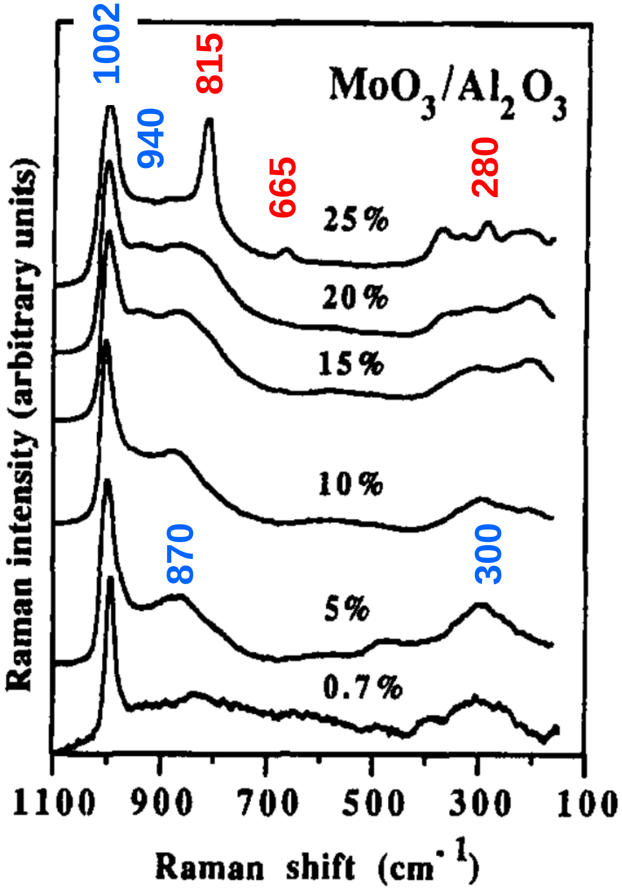


Applications

- Monomeric & polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}



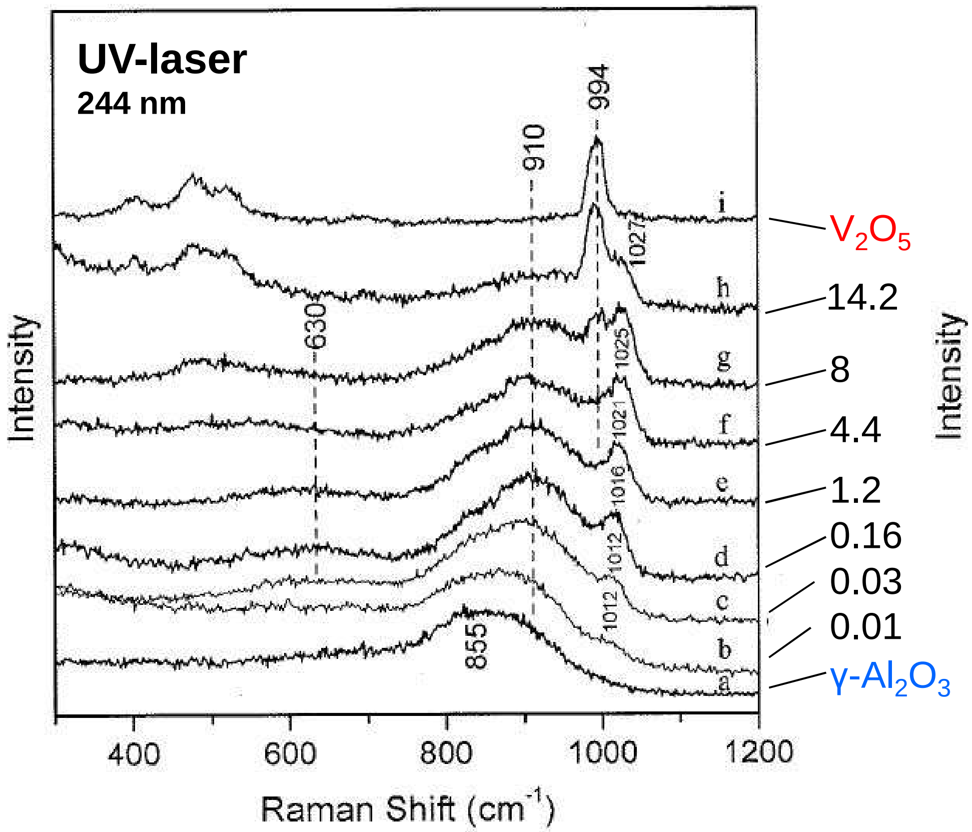
surface MoO_3
crystalline MoO_3

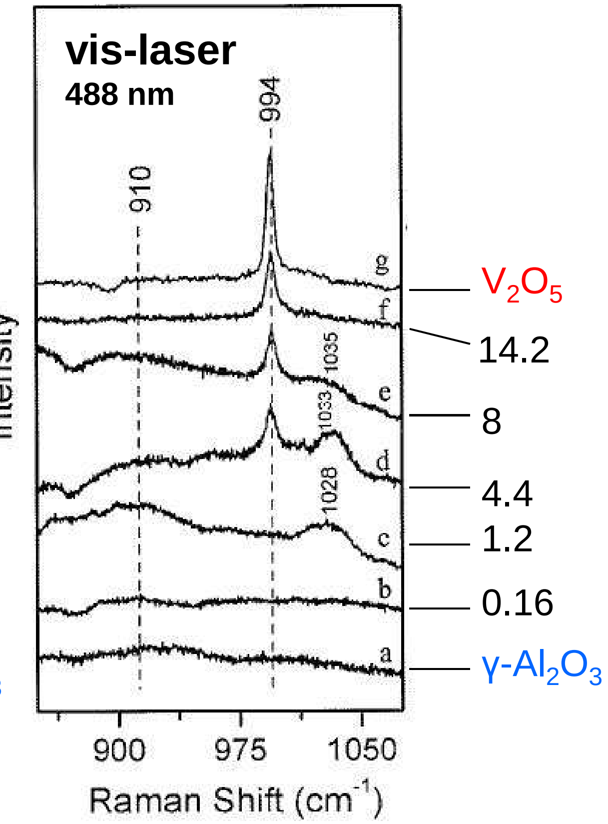
MoO_3/Al_2O_3
dehydrated at 500°C

Wachs, *Catal. Today* **27** (1996) 437

Applications

- Monomeric & polymeric species

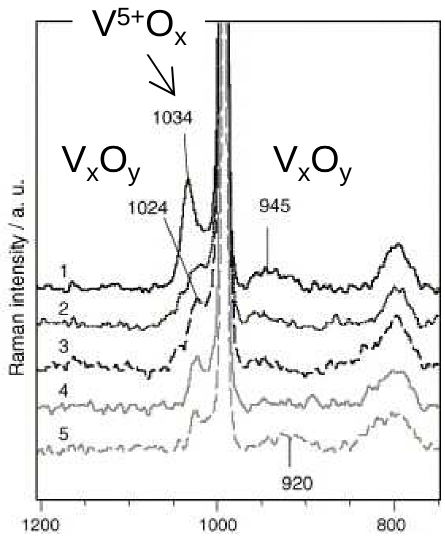




Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

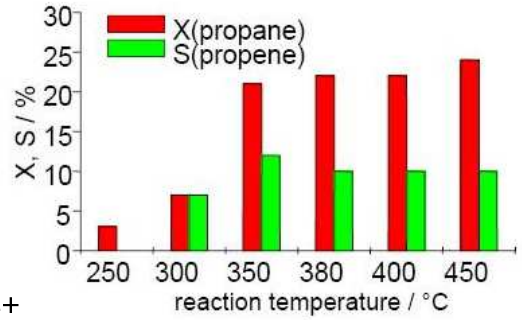
Applications

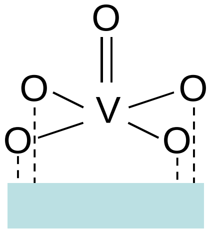
- Reactivity of V/TiO$_2$ after oxidative treatment

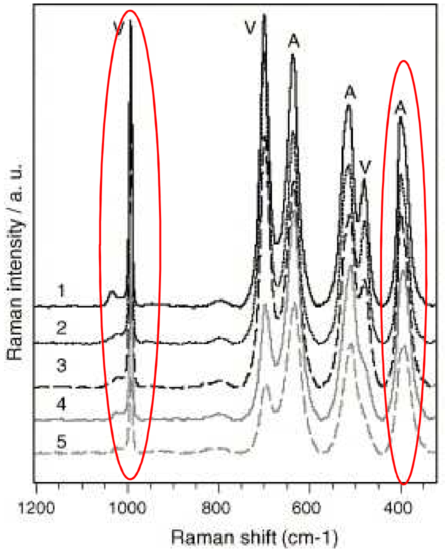


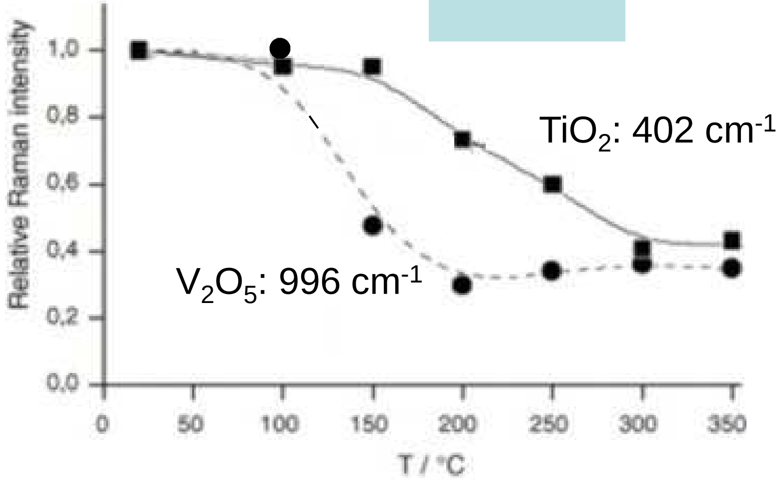
air flow @ 450°C
O_2/C_3H_8 @ 20°C
@ 100°C
@ 150°C
@ 200°C

$V^{5+} \longrightarrow V^{4+}$









Brückner et al., *Catal. Today* **113** (2006) 16

Examples for in situ studies

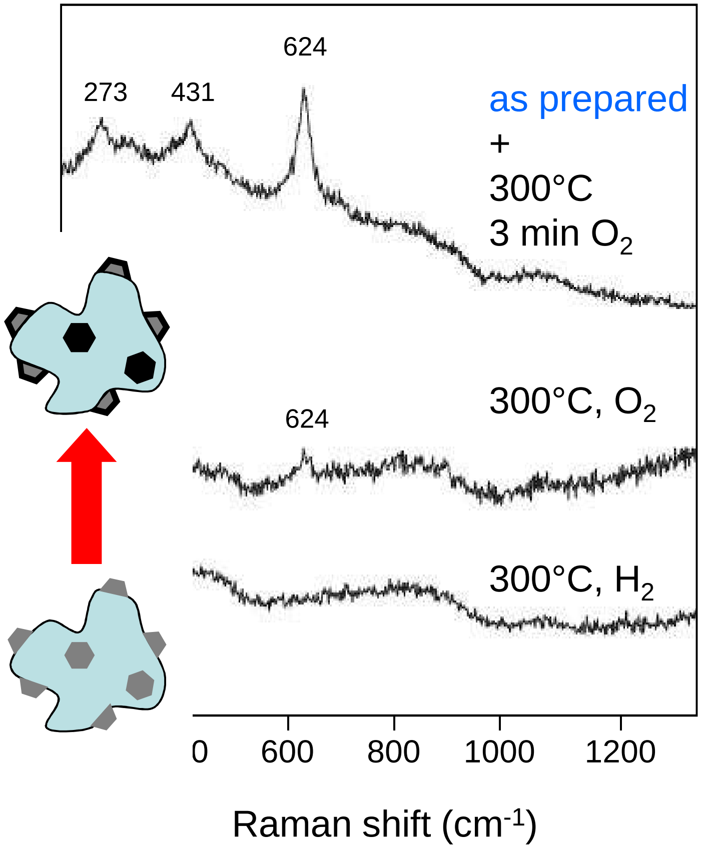
M/MO$_X$ (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…) used for total and partial oxidation reactions

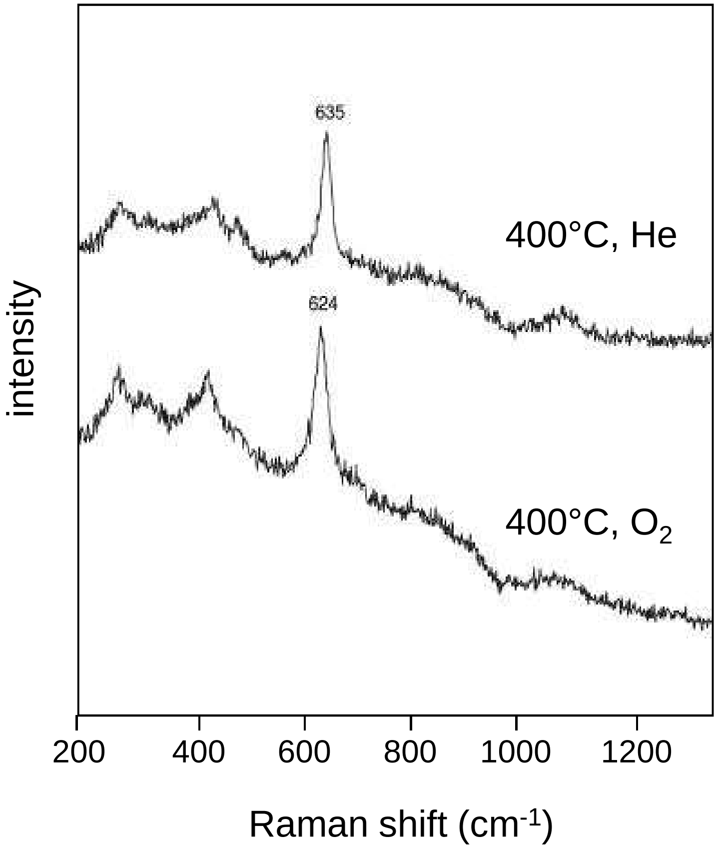
Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

- Resonance Raman – State of the metal in Pd/Al_2O_3





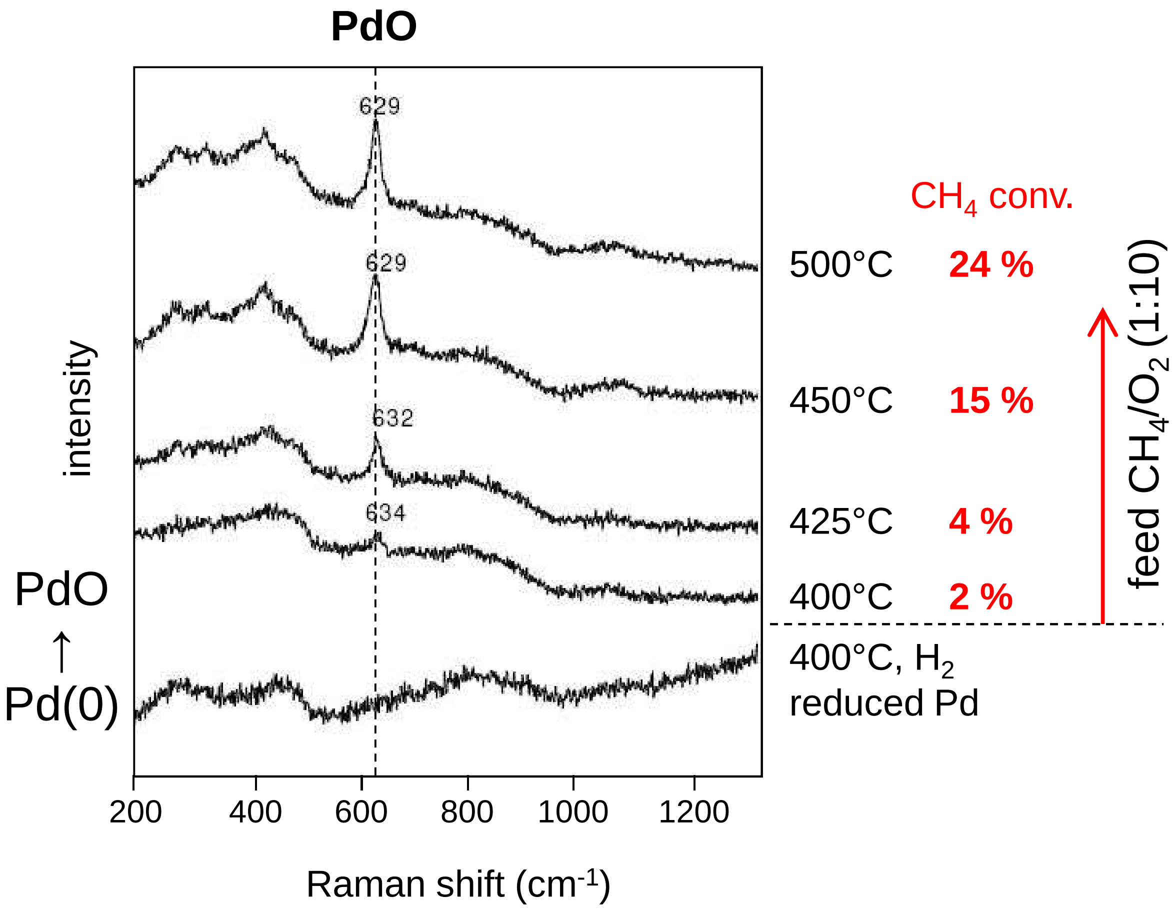
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

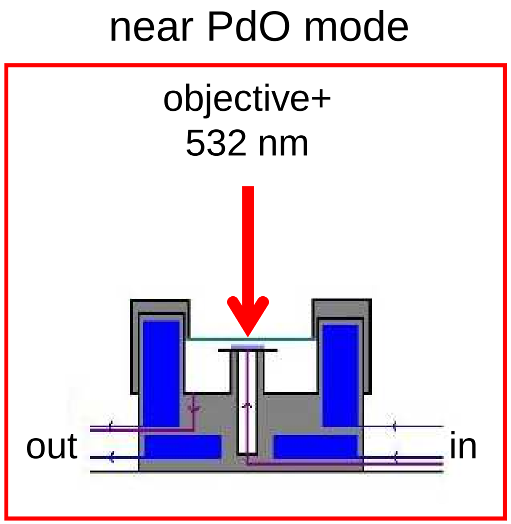
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

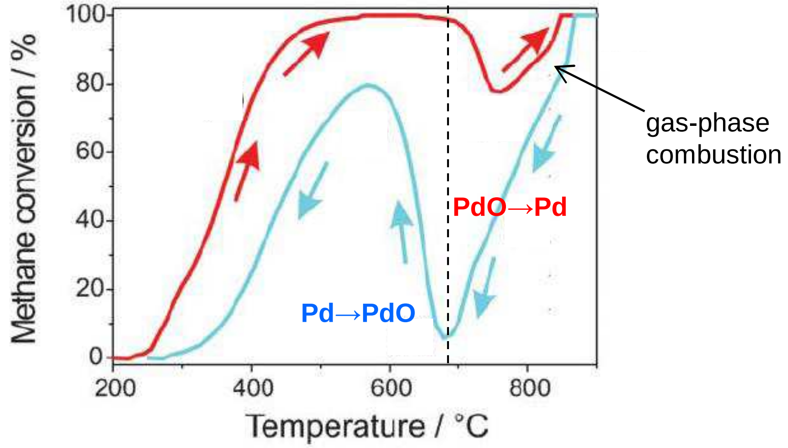


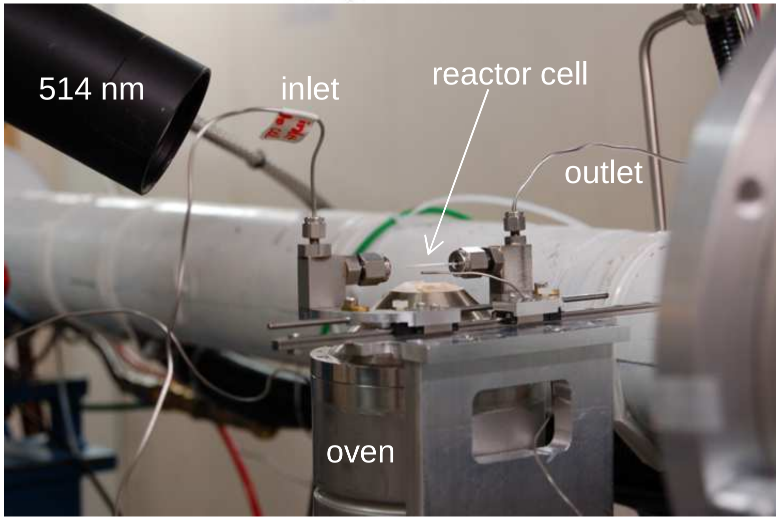


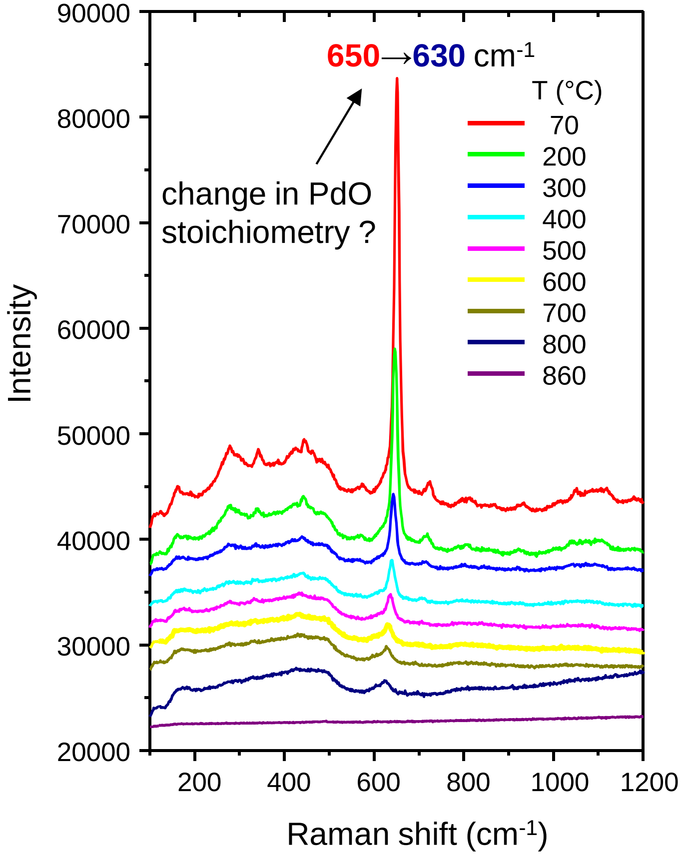
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

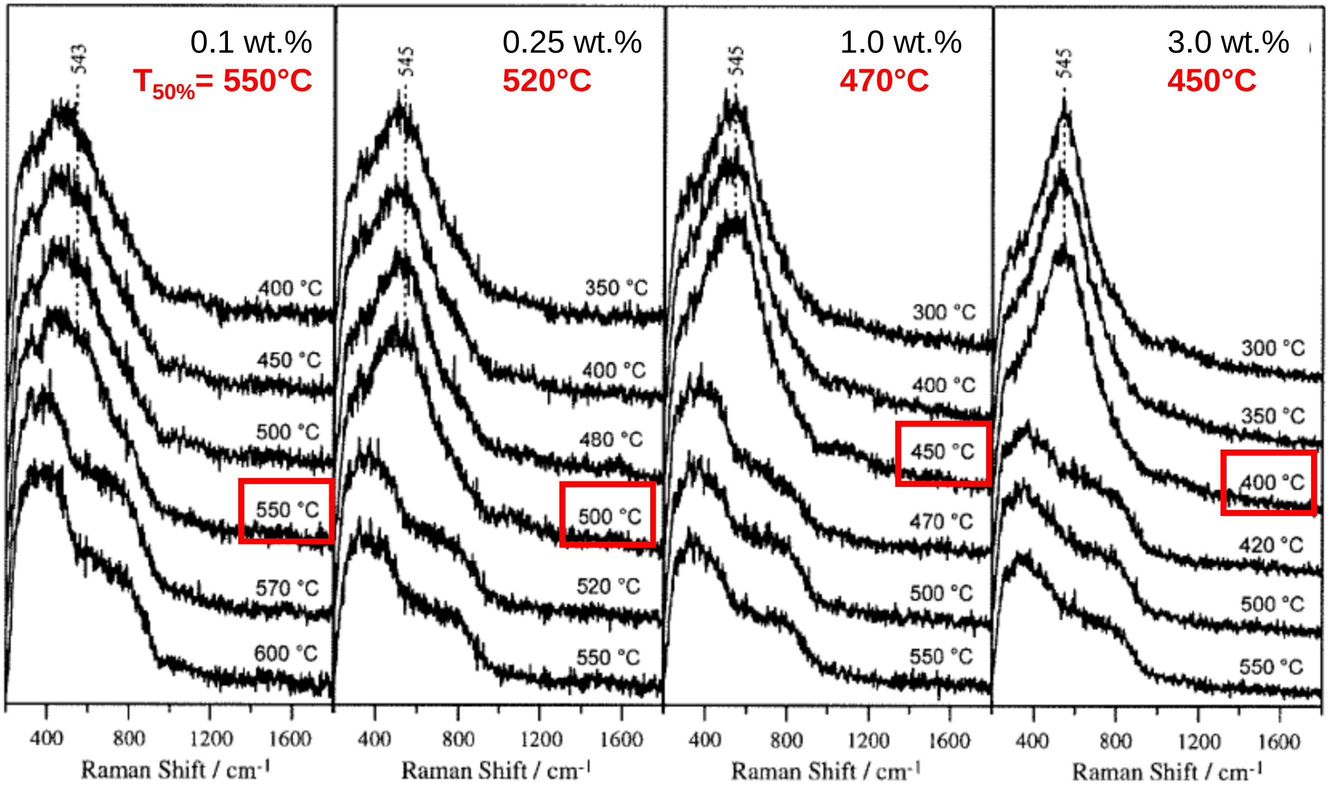
Applications

- Methane partial oxidation over Rh/Al_2O_3

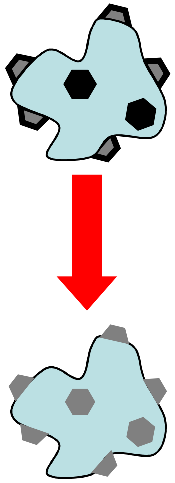
3 mW, 325 nm
$CH_4/O_2/Ar = 2/1/45$

$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$

Rh content
Activity



RhO_x
↓
Rh(0)



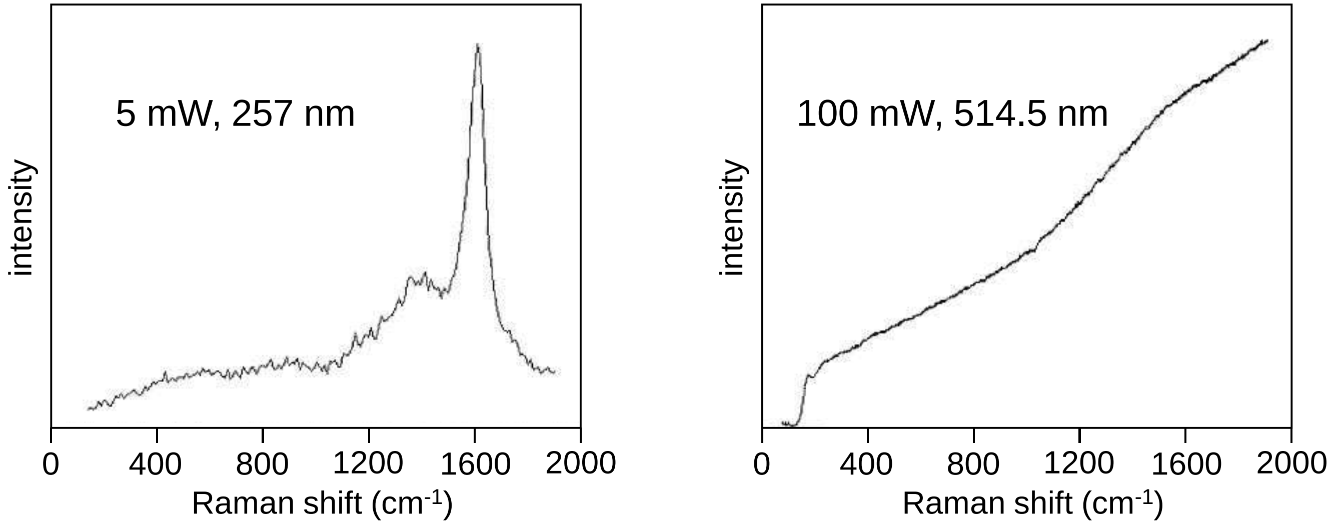
Li et al., *Catal. Today* **131** (2008) 179

Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

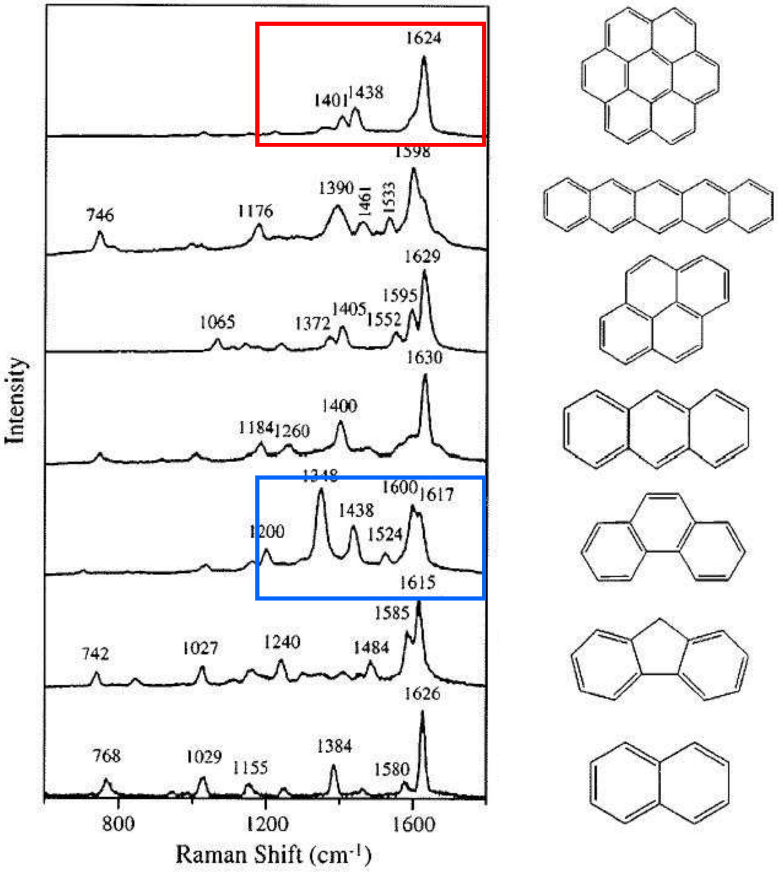
Rh/Al_2O_3, coked 500°C in naphtha

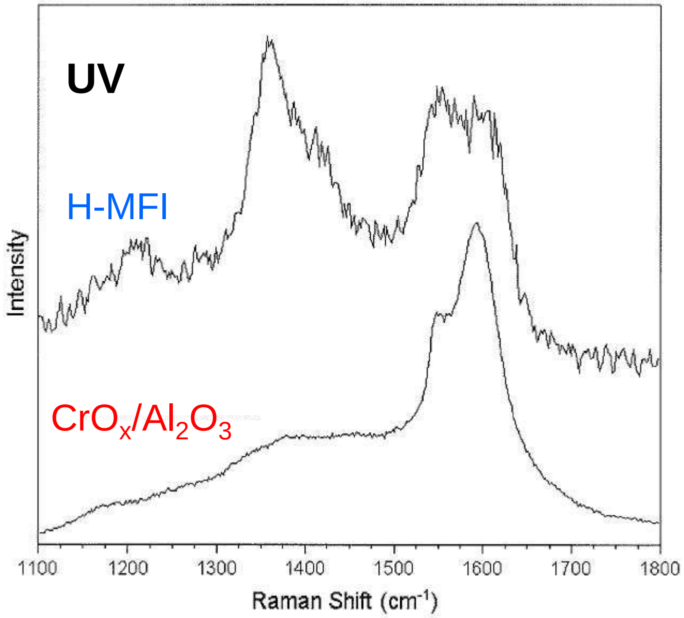


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





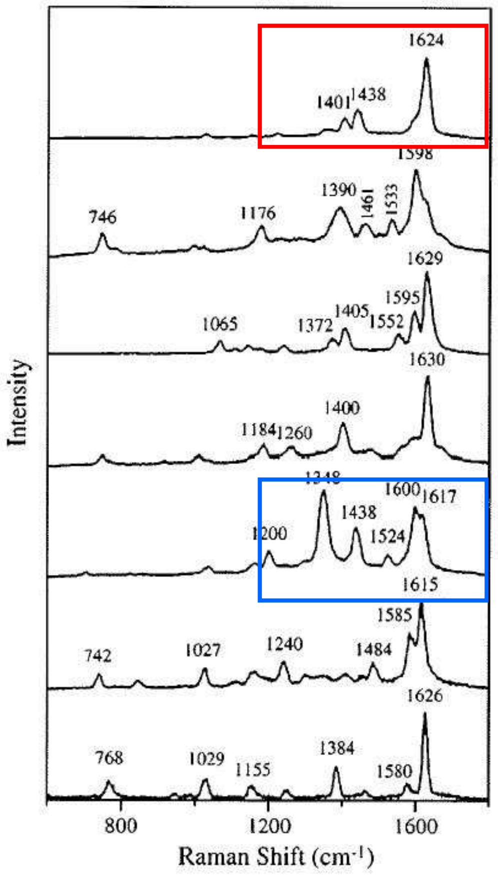
Coke classification
1D topology, chain-like
2D topology, sheet-like

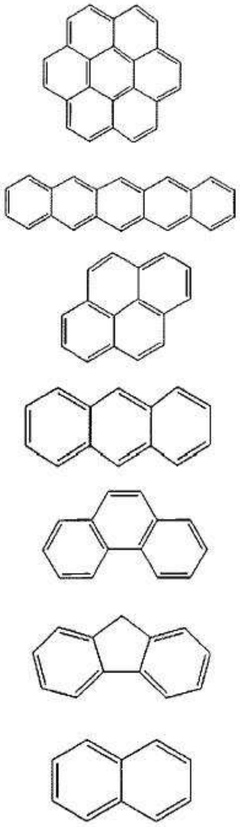
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

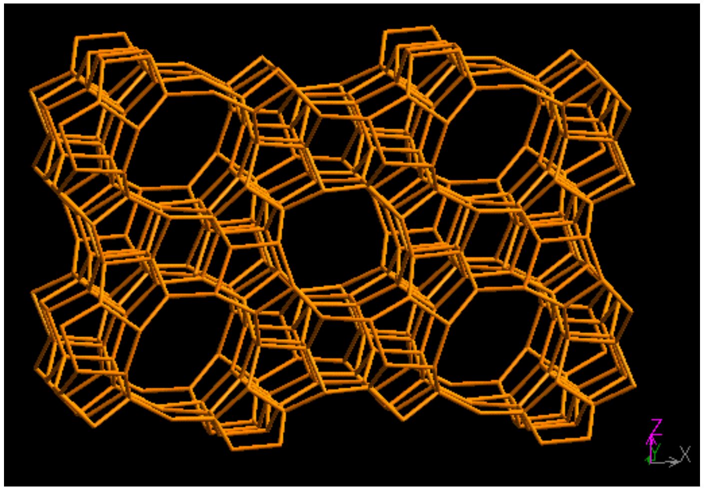
Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization







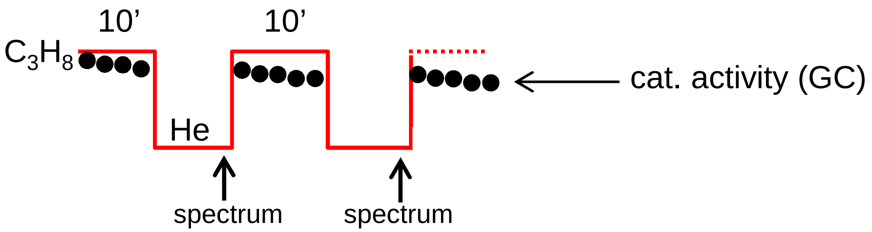
Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

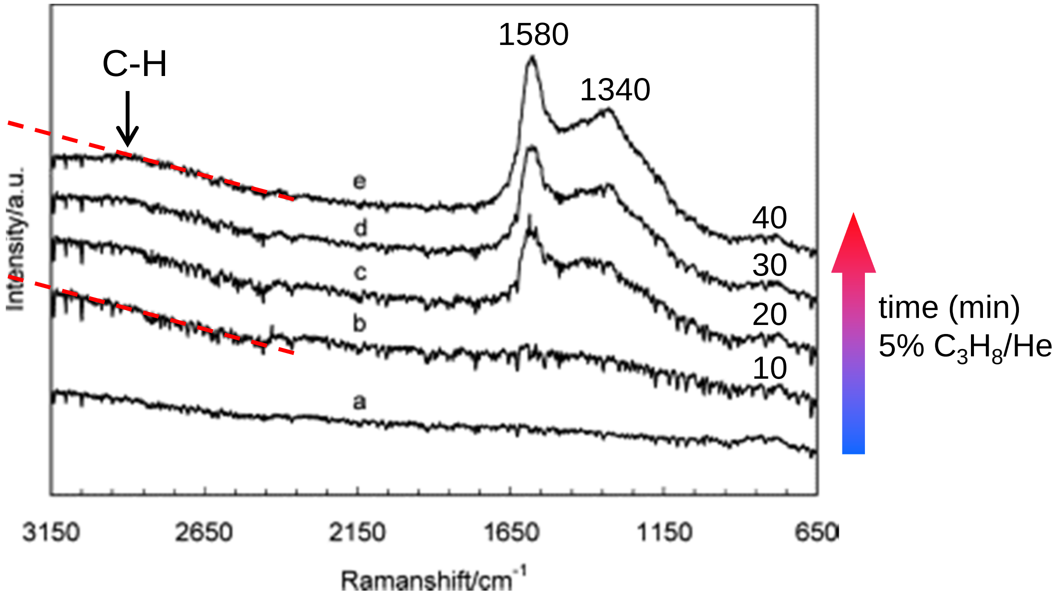
Stair, *Adv. Catal.* **51** (2007) 75

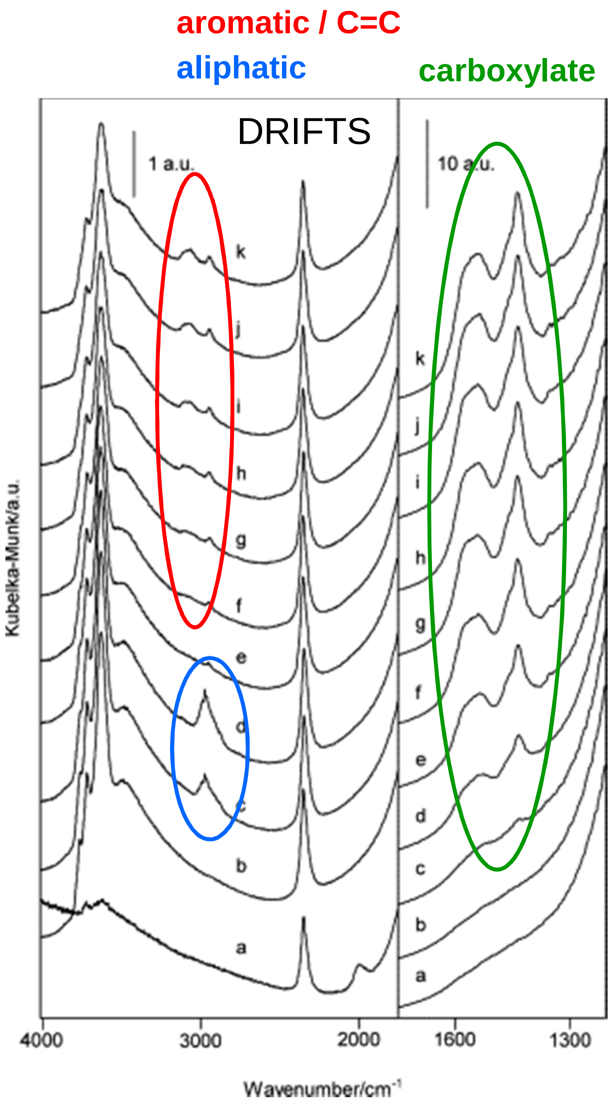
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

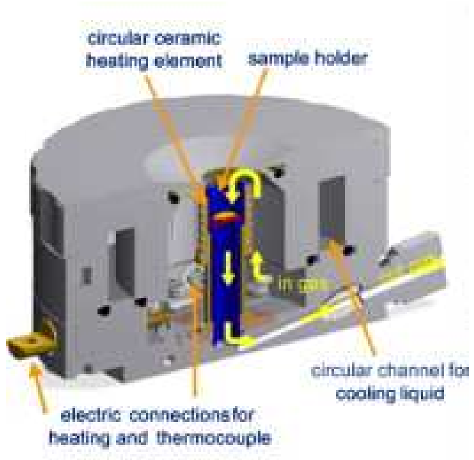


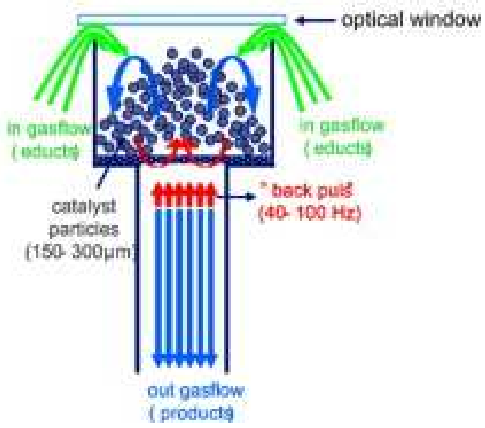


Airaksinen et al., *J. Catal.* **230** (2005) 507

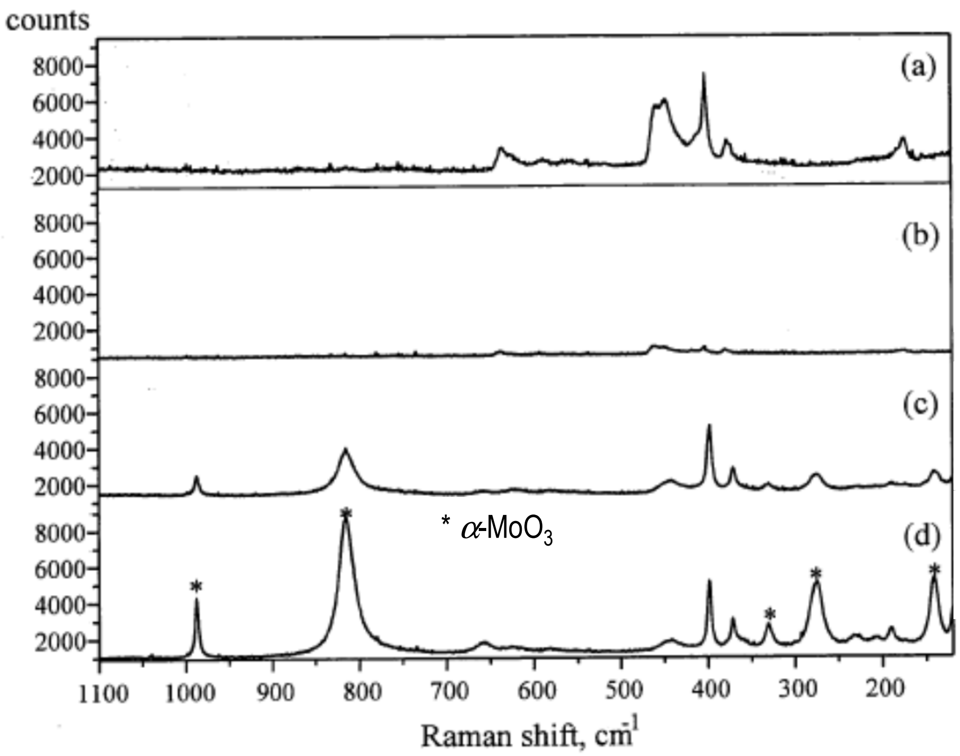
Applications

- Fluidized bed reactor cell





hydrodesulfurization



MoS_2, 6 min full power, FB

MoS_2, 6 min 1/8 power

MoS_2, 1 min full power

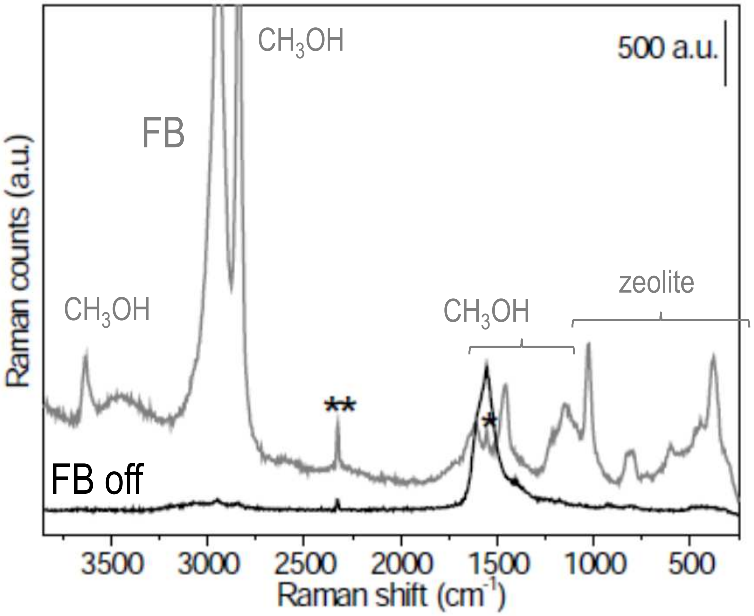
MoS_2, 6 min full power

Beato et al., *Catal. Today* 205 (2013) 128

Applications

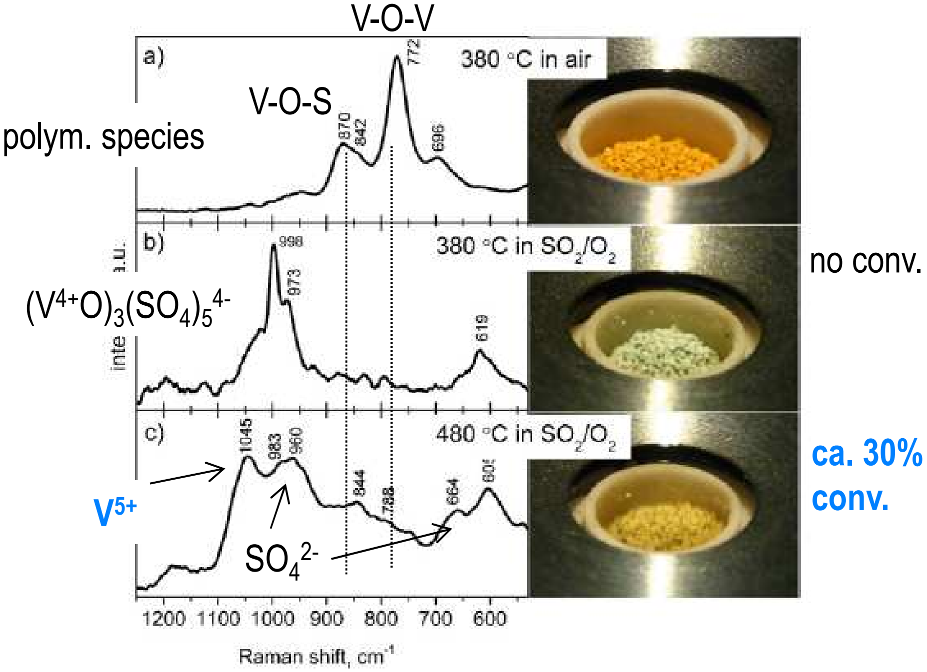
- Fluidized bed reactor cell

CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Sulfuric acid V_2O_5/pyrosulfate catalyst
λ= 514 nm

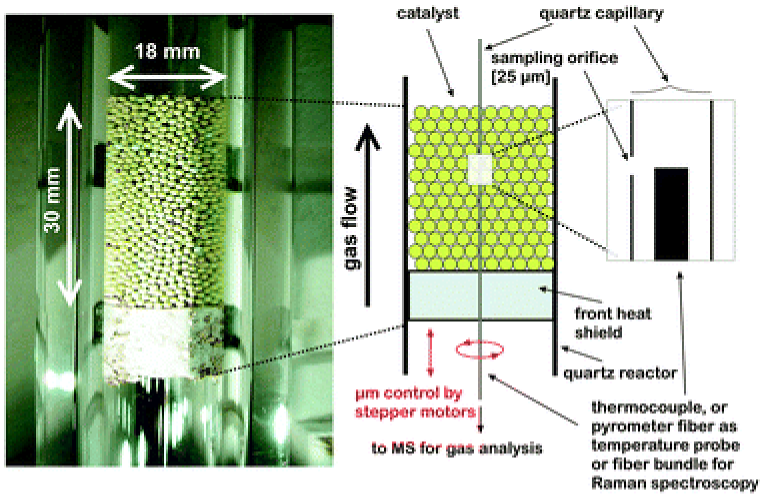


active species: mono- & dimeric V^{5+} oxosulfate species

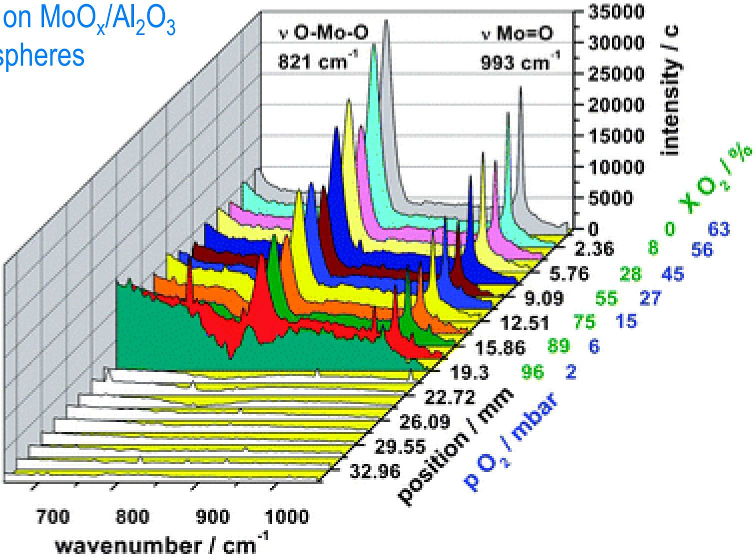
Beato et al., *Catal. Today* 205 (2013) 128

Applications

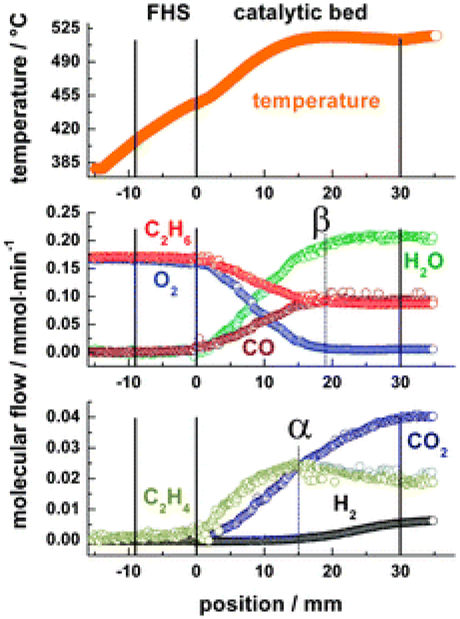
- Fixed bed reactor



ethane ODH on MoO_x/Al_2O_3
1 mm Al_2O_3 spheres



fiber optics; spatial resolution, 1 mm



violet/MoO_2

β full O_2 conv.

α max. C_2H_4 conc.

yellow/MoO_3

- monitoring of reaction in fixed bed reactor (Raman/MS)
- partial reduction $MoO_3 \rightarrow MoO_2$ with decreasing O_2 content
- MoO_3 vanishes when no O_2 is present (point β, 19 mm)

Geske et al., *Catal. Sci. Technol.* 3 (2013) 169