Kalachakra Mandala of Tibetian Buddhism

Raman Spectroscopy

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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:

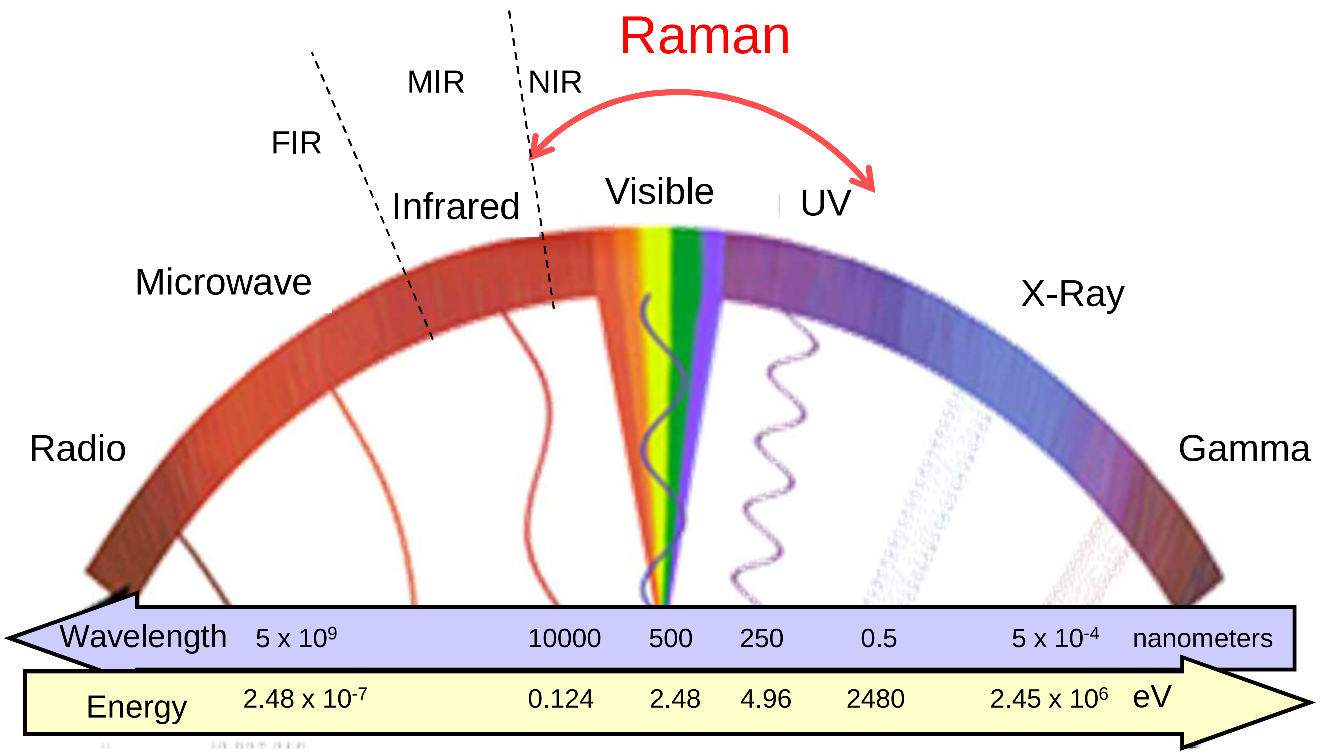
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

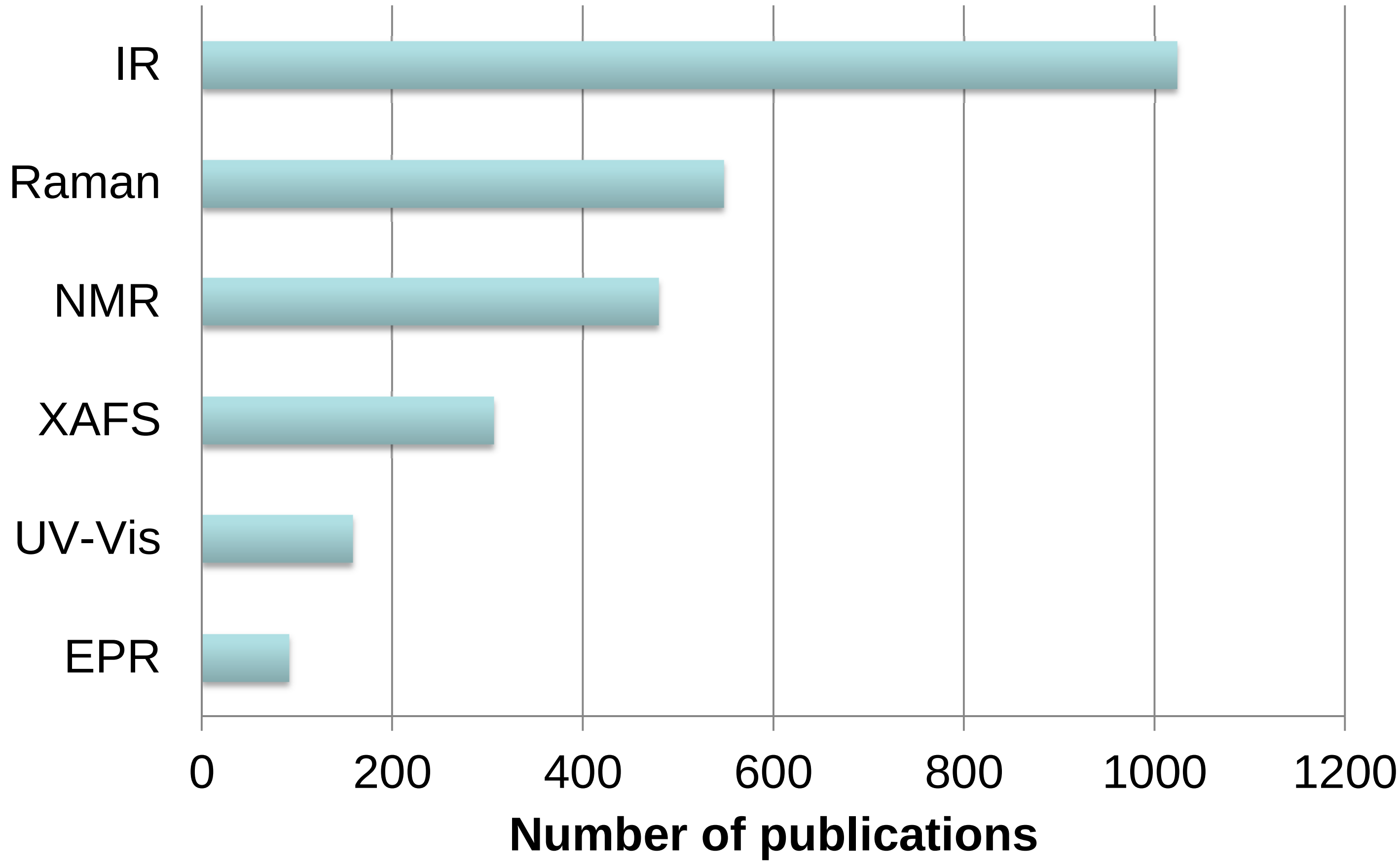
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

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

Raman spectroscopy

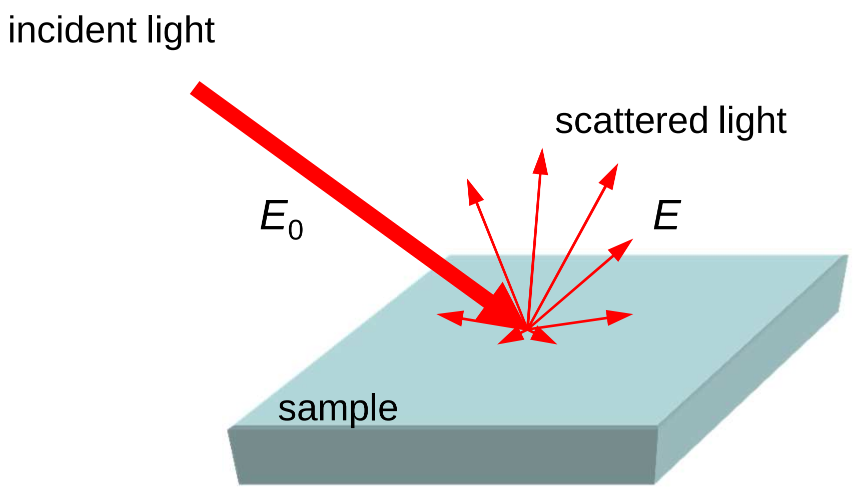


Importance of Raman spec. in catalysis



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

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

  - 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: $\alpha = \alpha_0 + \alpha\cos(2\pi\nu_{vib} t)$

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

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

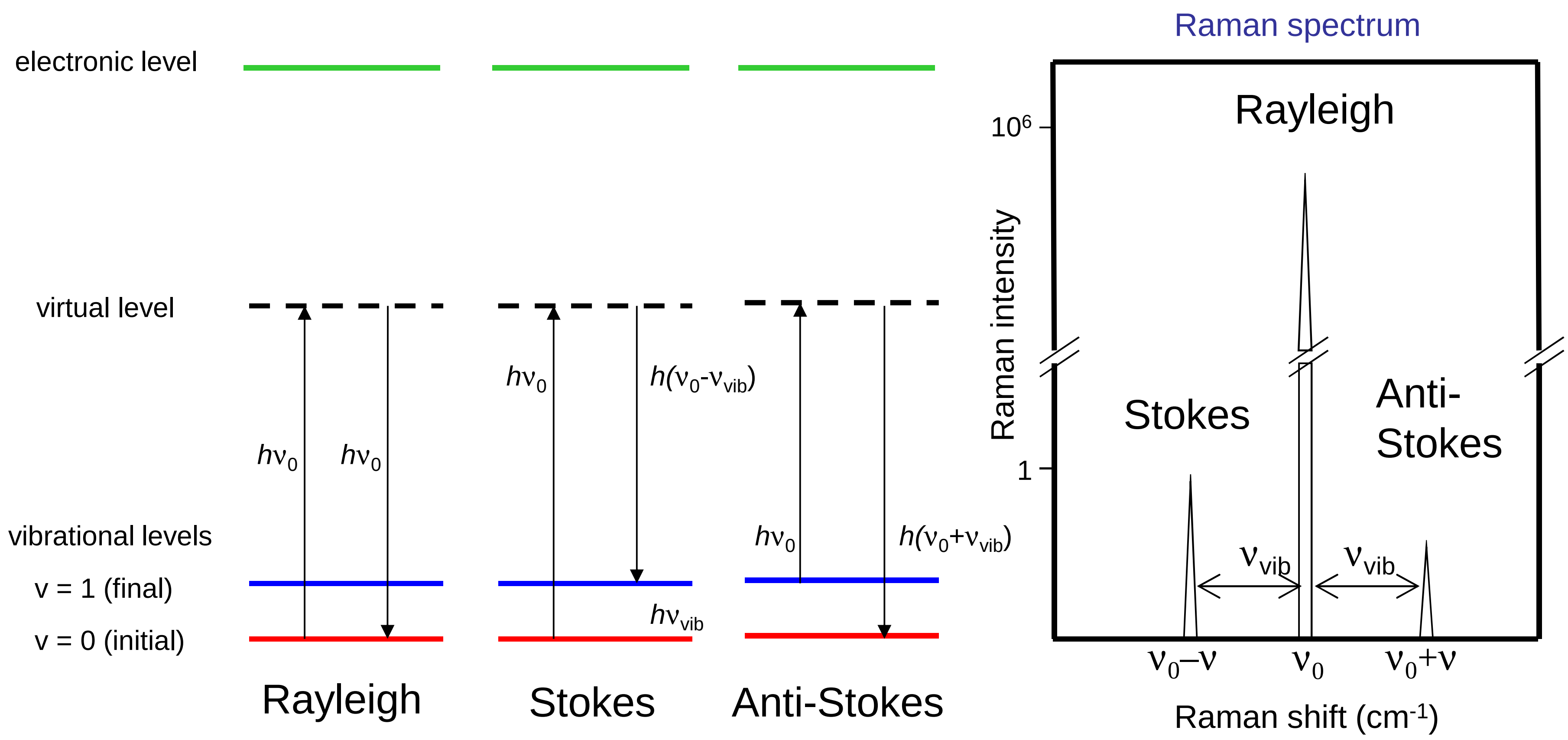
and

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

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:

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

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

↓

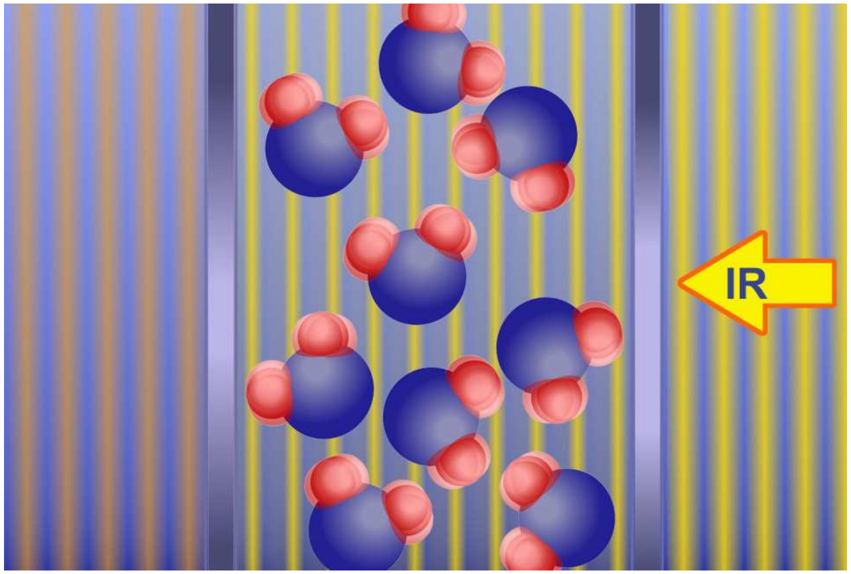
covalent bond — STRONG bands (catalysis!)

ionic bond — WEAK bands

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

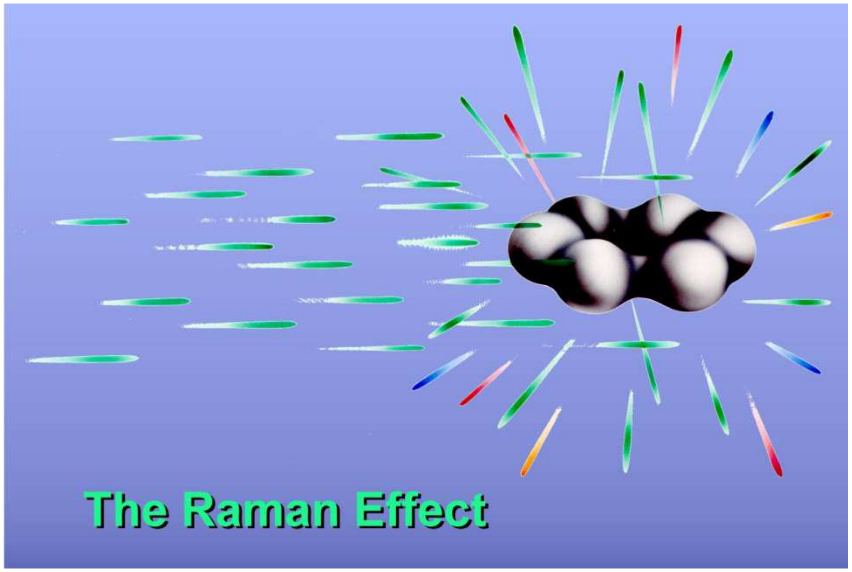
Raman *vs.* Infrared

Infrared



Absorption of IR light

Raman



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

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

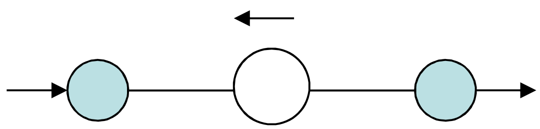
- high absorption for polar bonds ($C=O$, H_2O, NH, etc.)

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

- 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

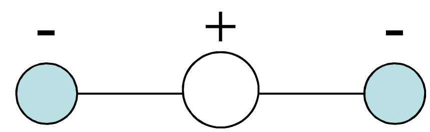
Raman *vs.* Infrared

CO_2



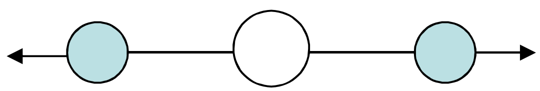
ν_{as}

2349 cm^{-1}



δ

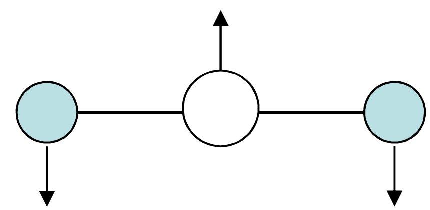
667 cm^{-1}



ν_s

1340 cm^{-1}

Raman active



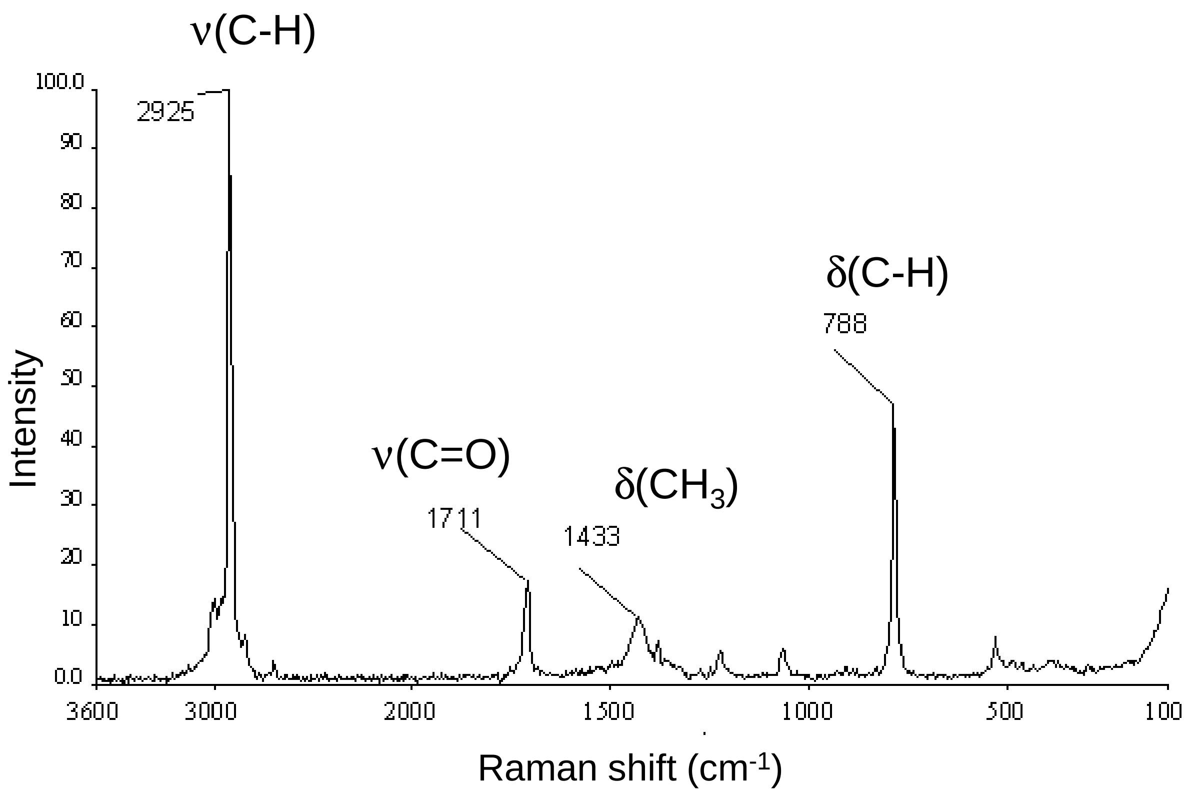
δ

667 cm^{-1}

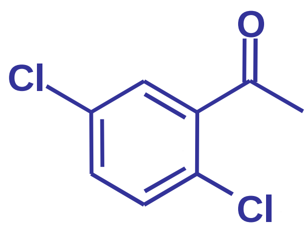
degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared



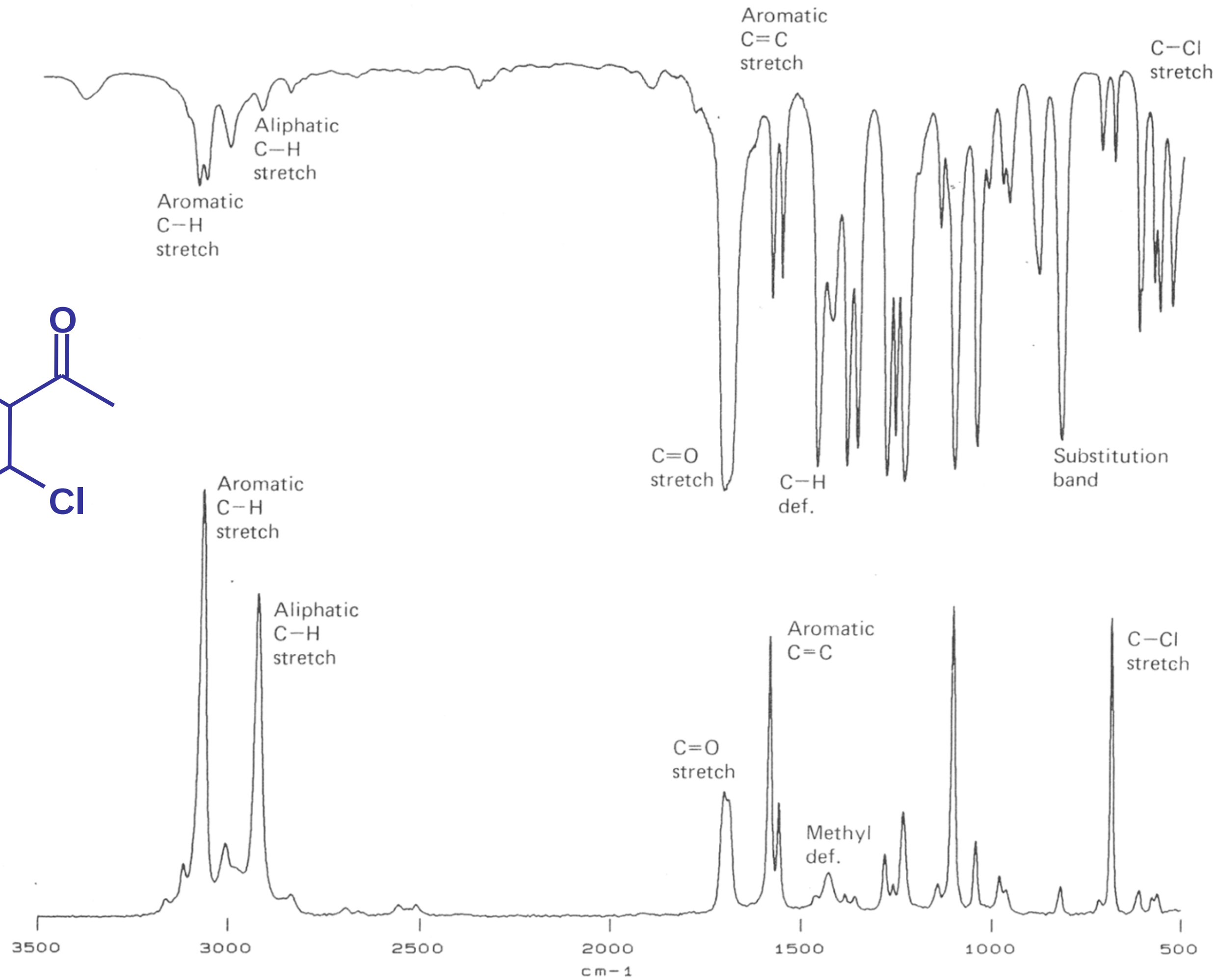


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

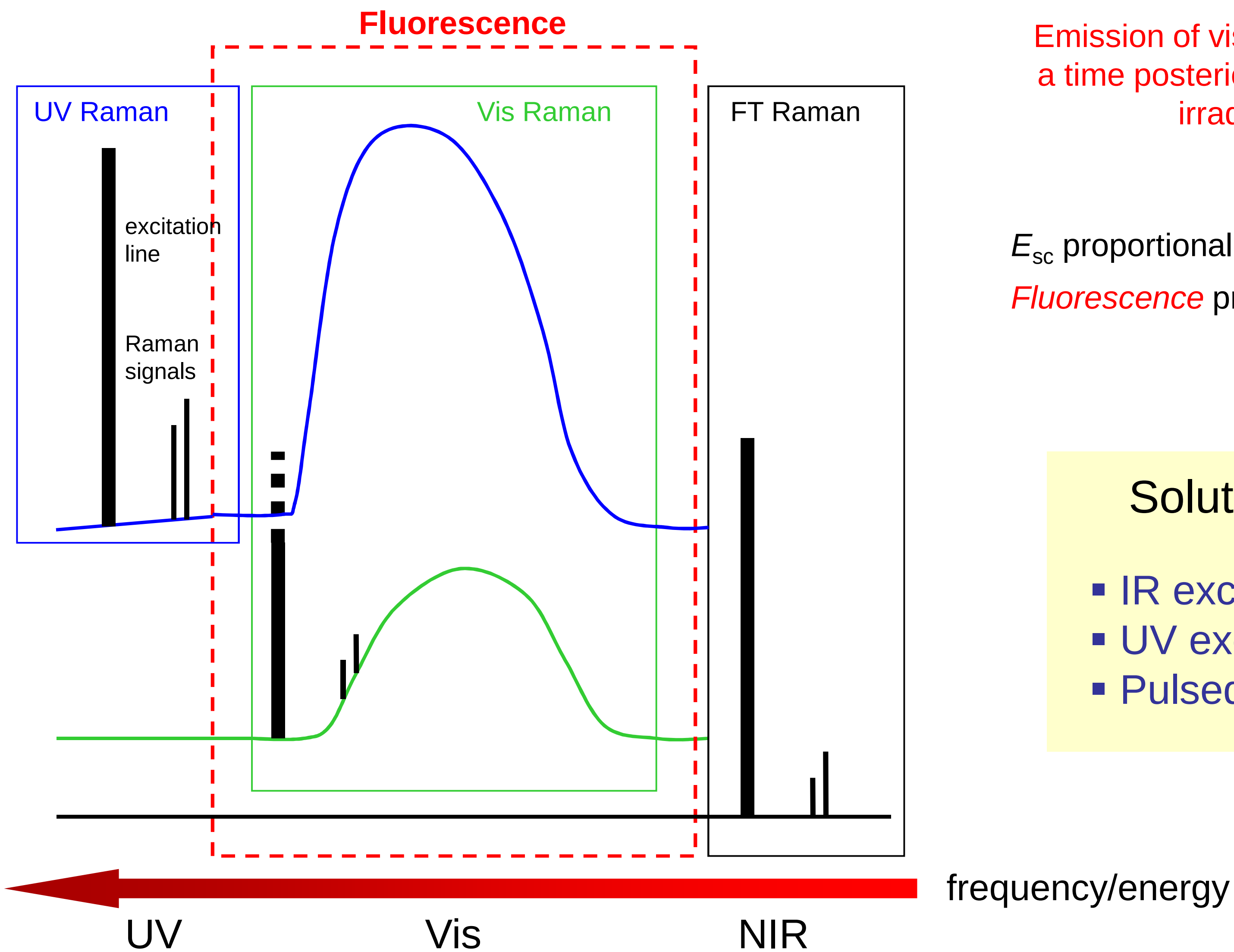
Advantages

- 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

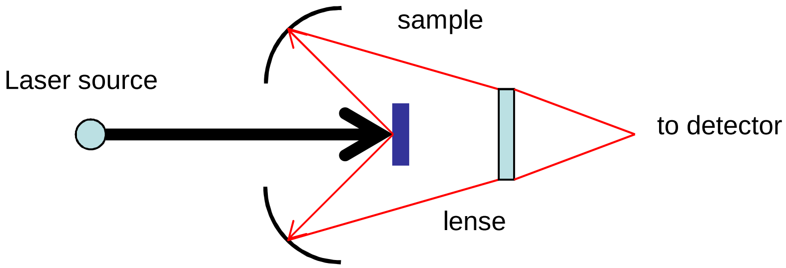
Fluorescence proportional to ν

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.

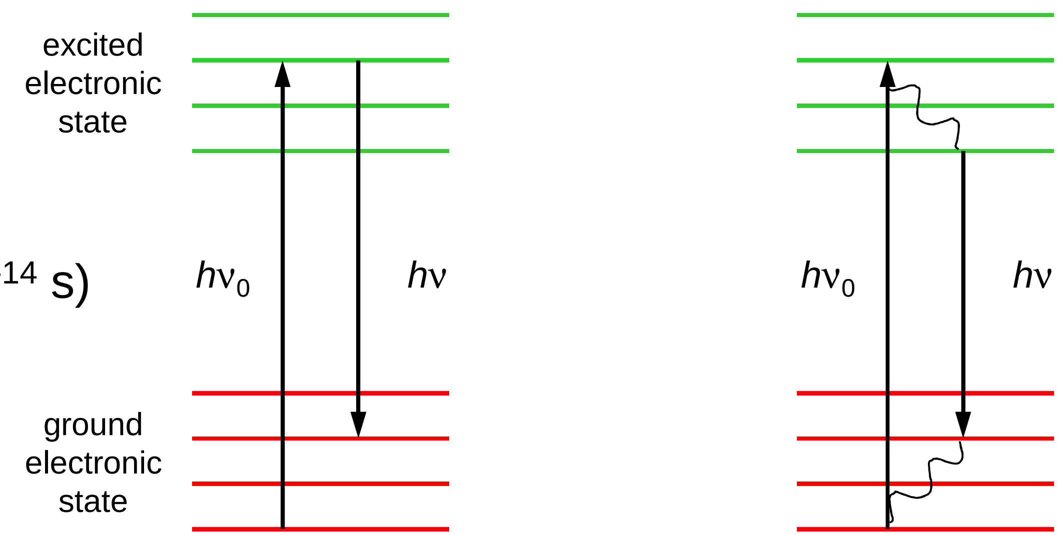
Laser	*Type*	*Type of radiation*	*Wave-length/nm*	*Max. power/W*	*Beam dia-meter/mm*	*Price; Comments*
Ar^+	Gas	CW	488.0 514.5	4 4	1.5	Medium; Standard source
Kr^+	Gas	CW	647.1 725.5	4	1.8	Medium; Standard source
He–Ne	Gas	CW	632.8	0.05	1.1	Low; Not intense
Liquid dye	Liquid	CW, Pulsed, tunable	Depends 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

fast (10^{-14} s)



slow (10^{-9}–10^{-6} s)

Resonance Raman scattering

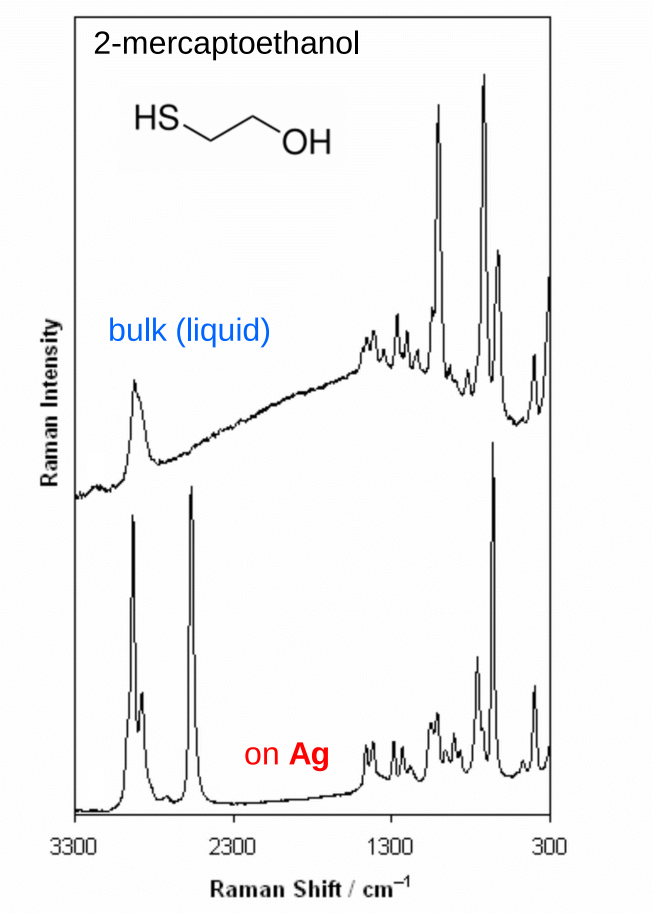
Fluorescence

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

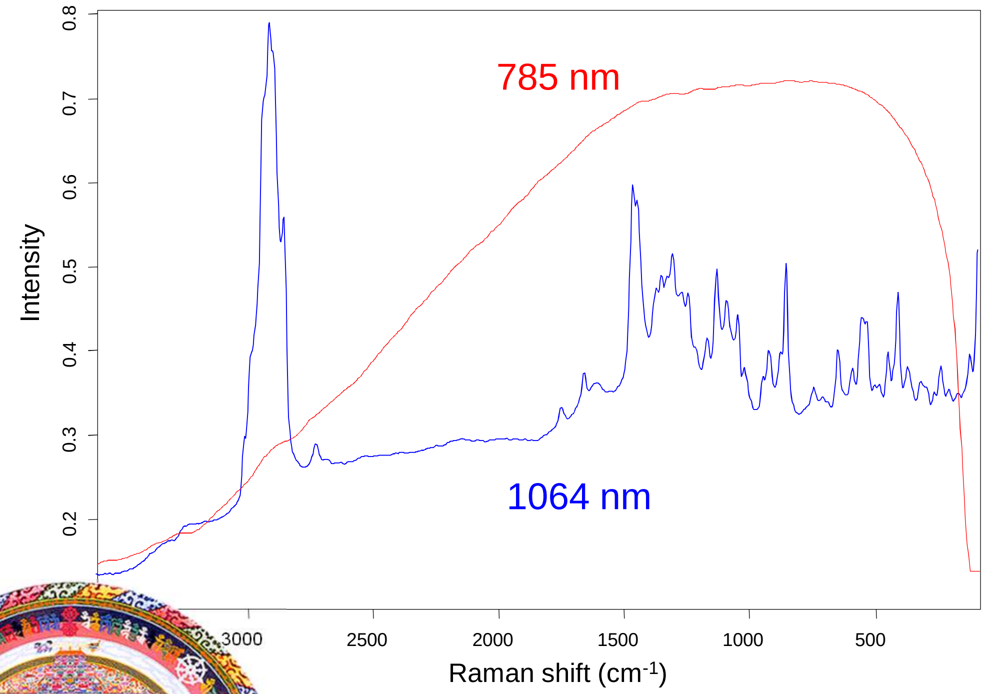
- Remarks:

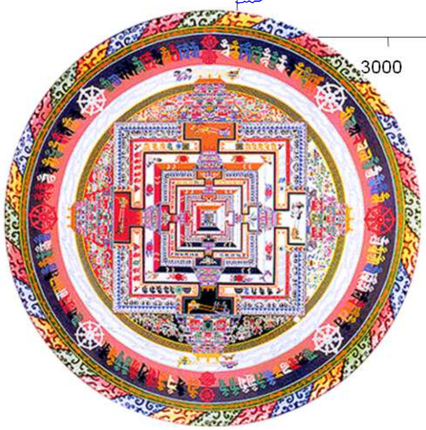
❑ rough surface; nanoparticles (10–100 nm) or kinks, steps etc.
(E always perpendicular to surface, locally)
❑ vibrations normal to surface are enhanced

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





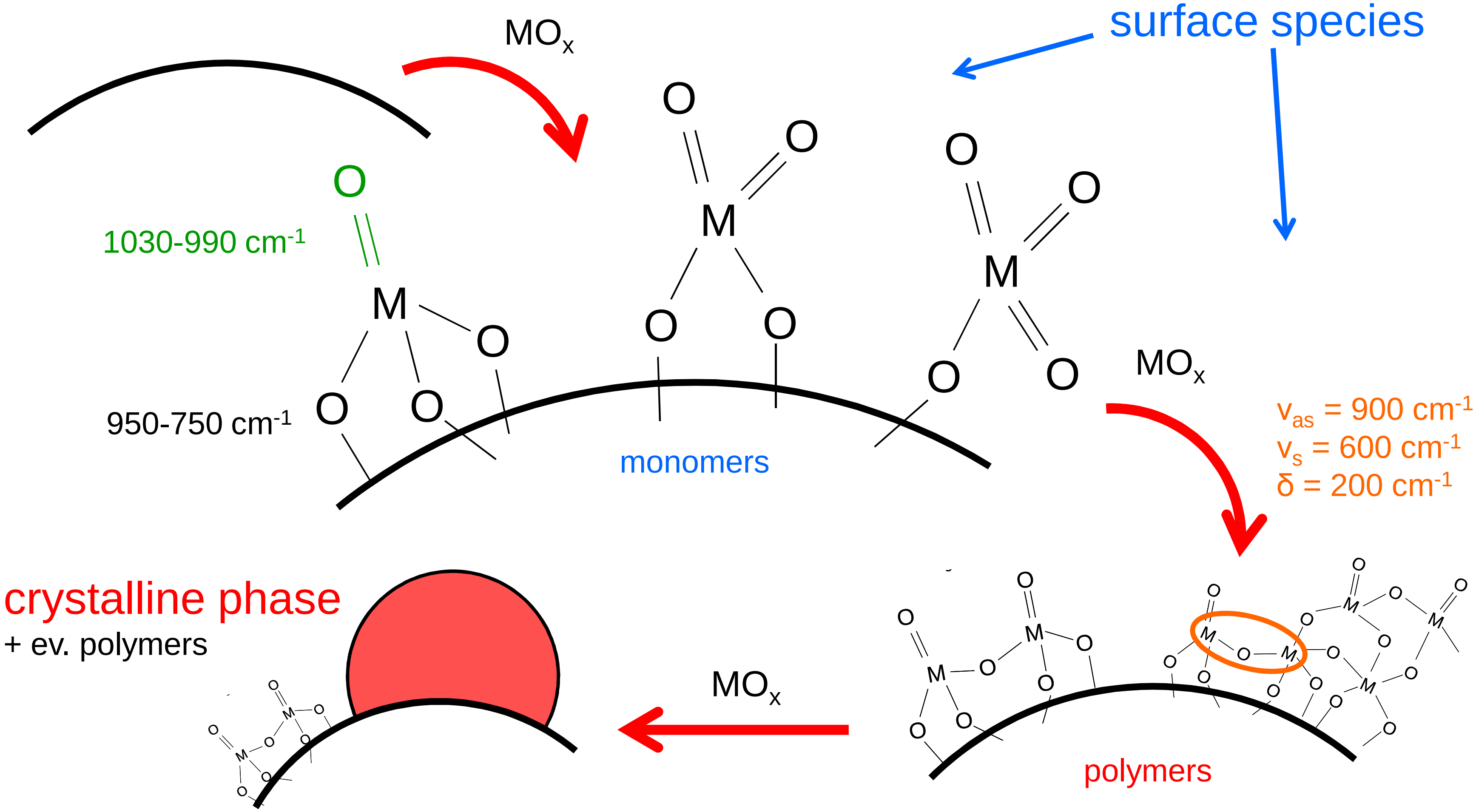
Applications

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

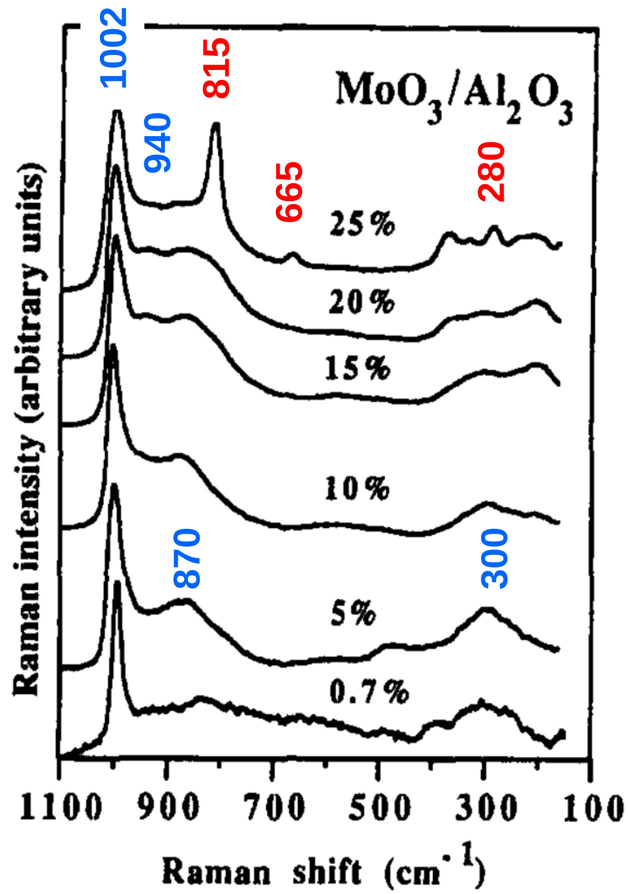


Applications

- Monomeric & polymeric species

Advantage over IR

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



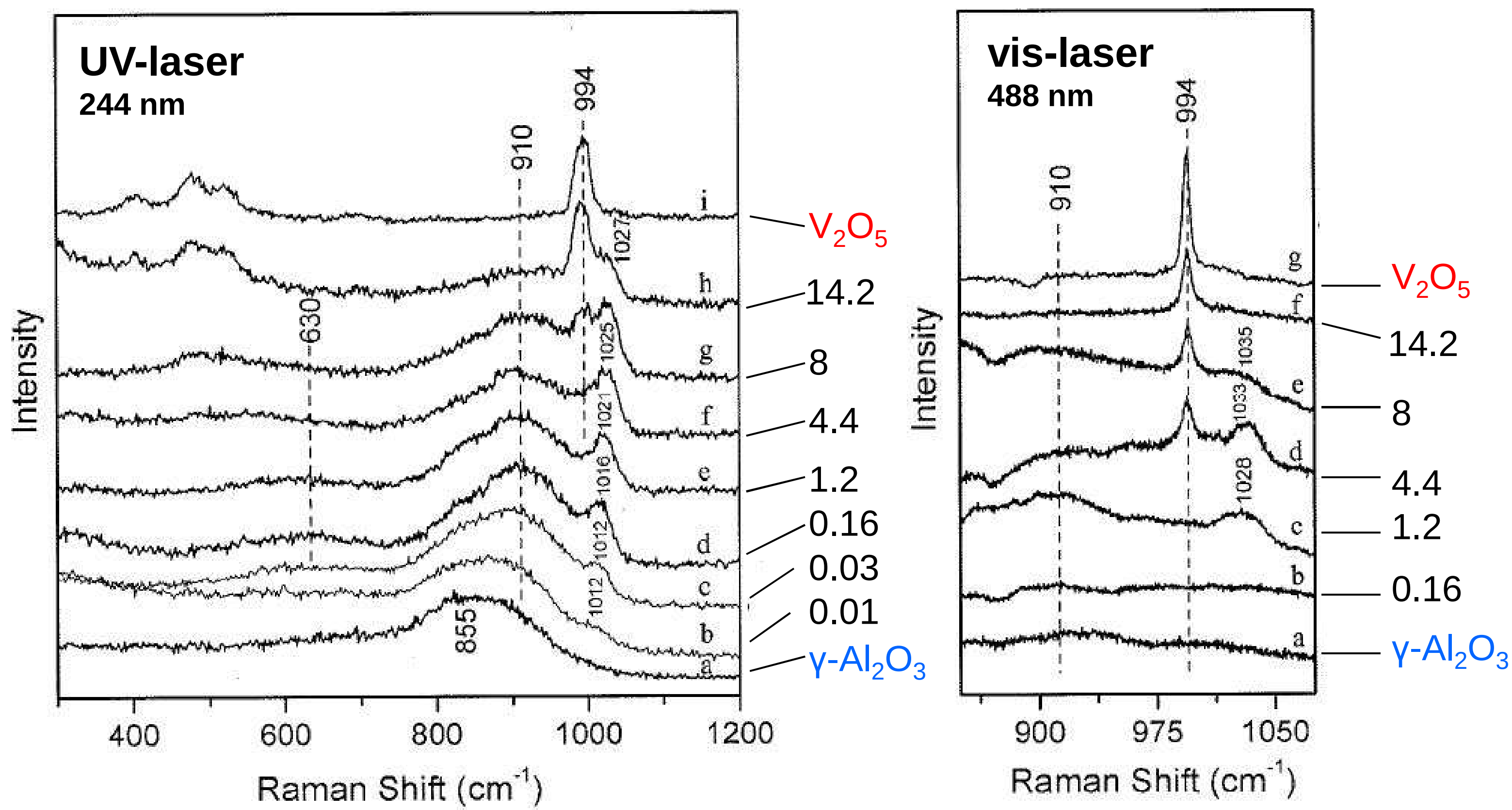
surface MoO_3
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500°C

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

Applications

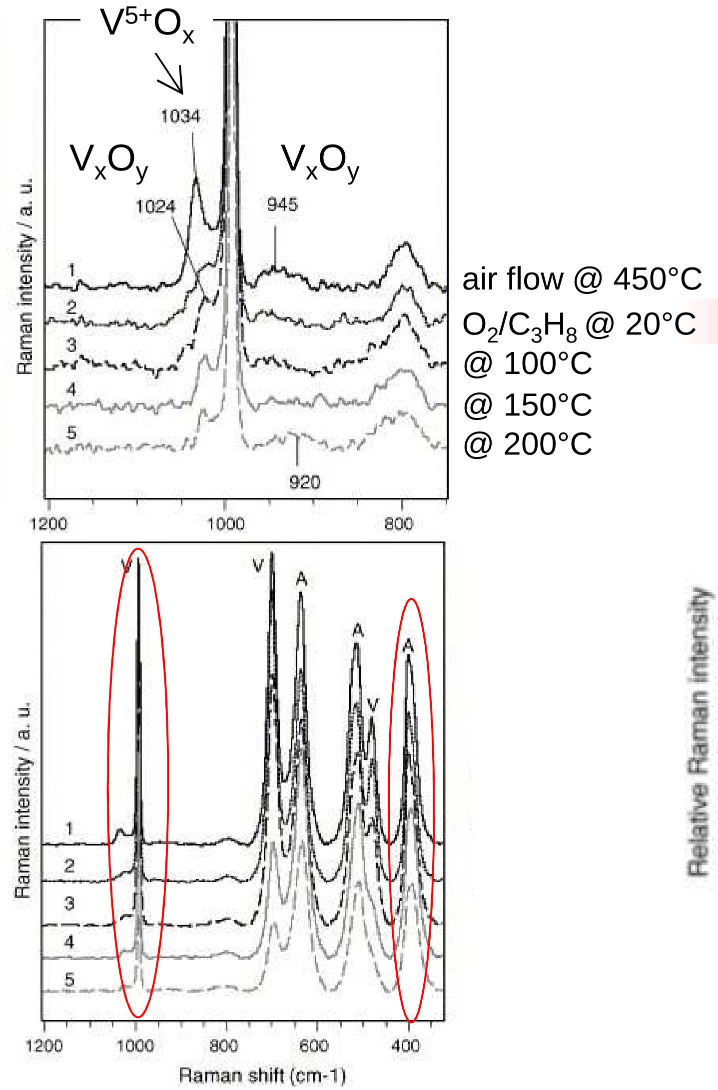
- Monomeric & polymeric species



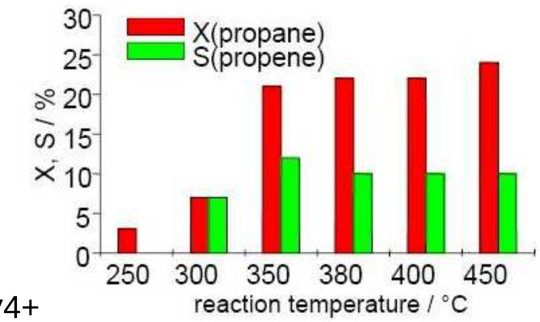
Wu et al., *J. Phys. Chem. B* **109** (2005) 2793

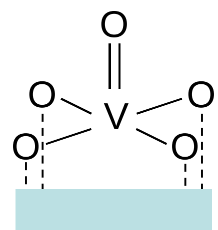
Applications

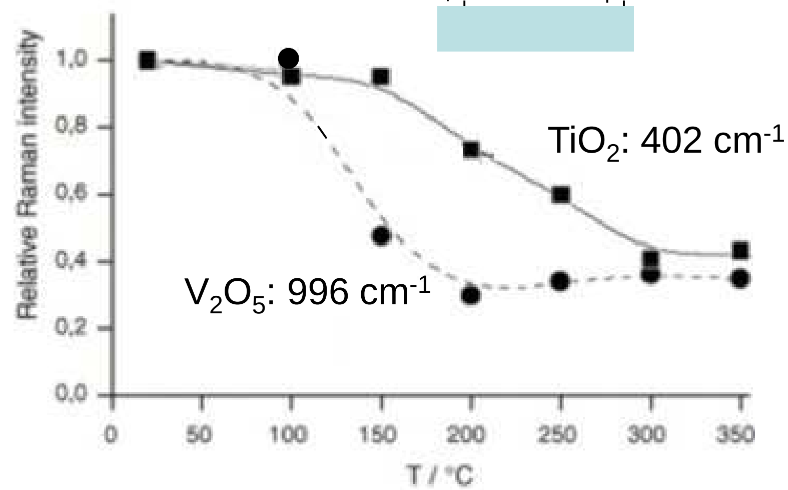
- Reactivity of V/TiO_2 after oxidative treatment



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







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

Examples for in situ studies

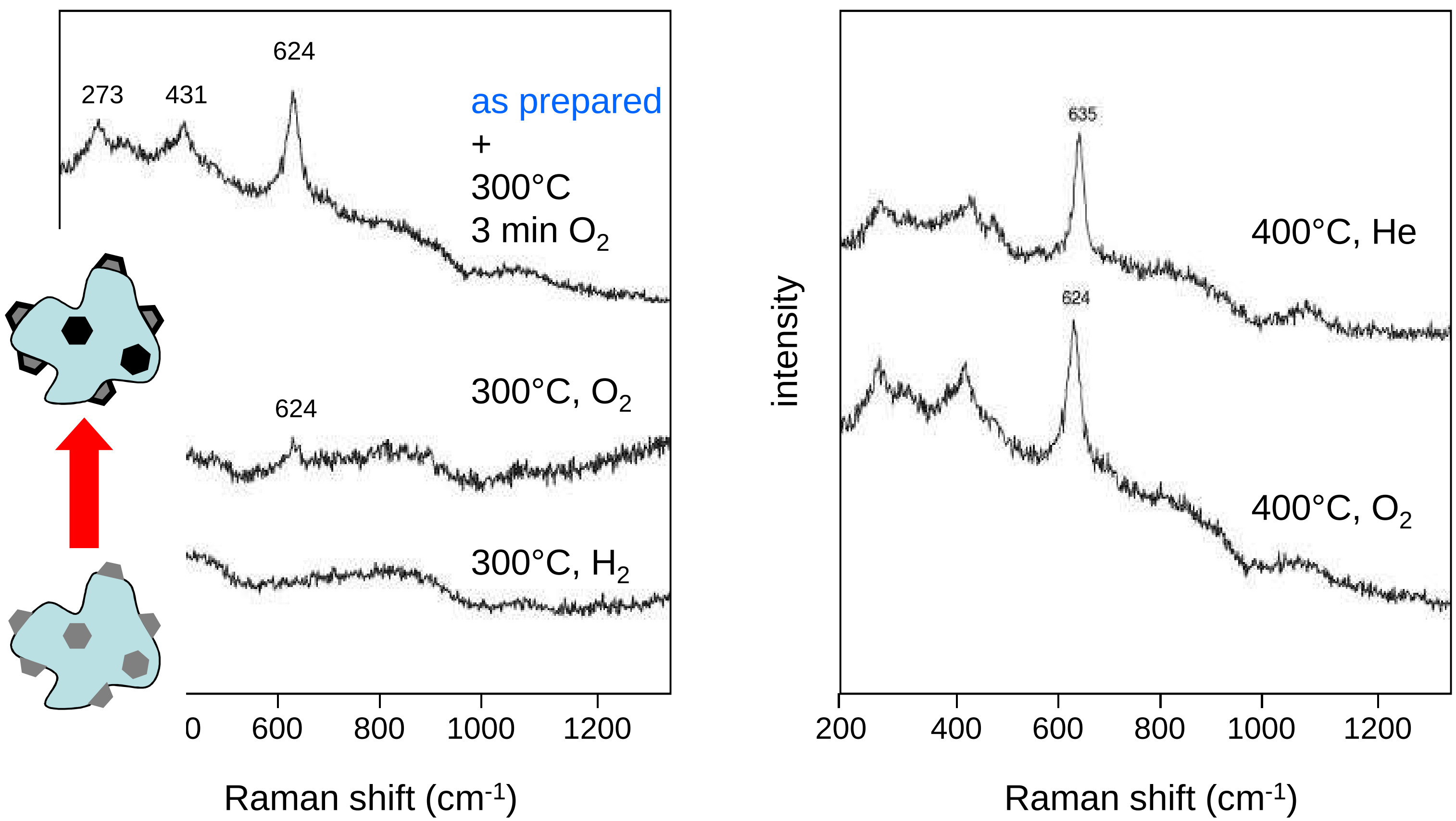
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…) used for total and partial oxidation reactions

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



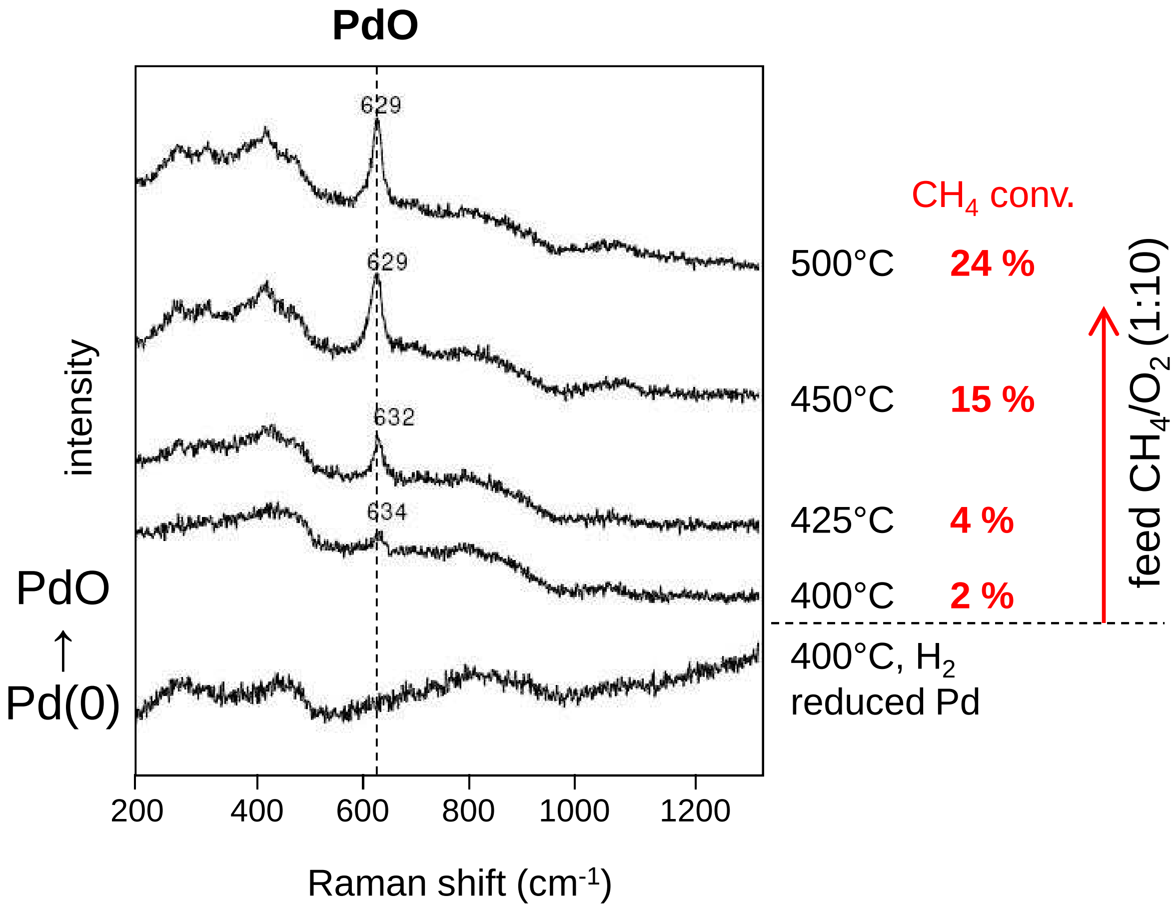
2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

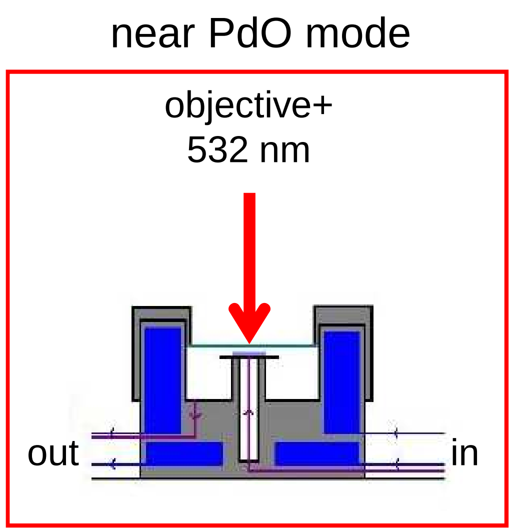
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3

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

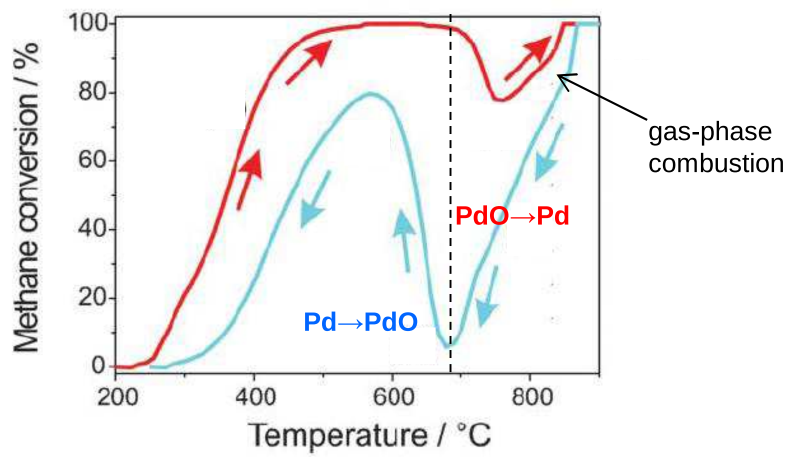


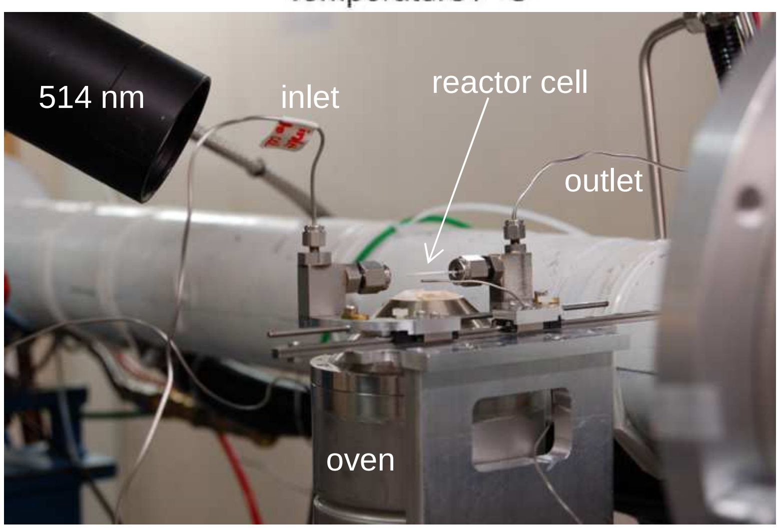


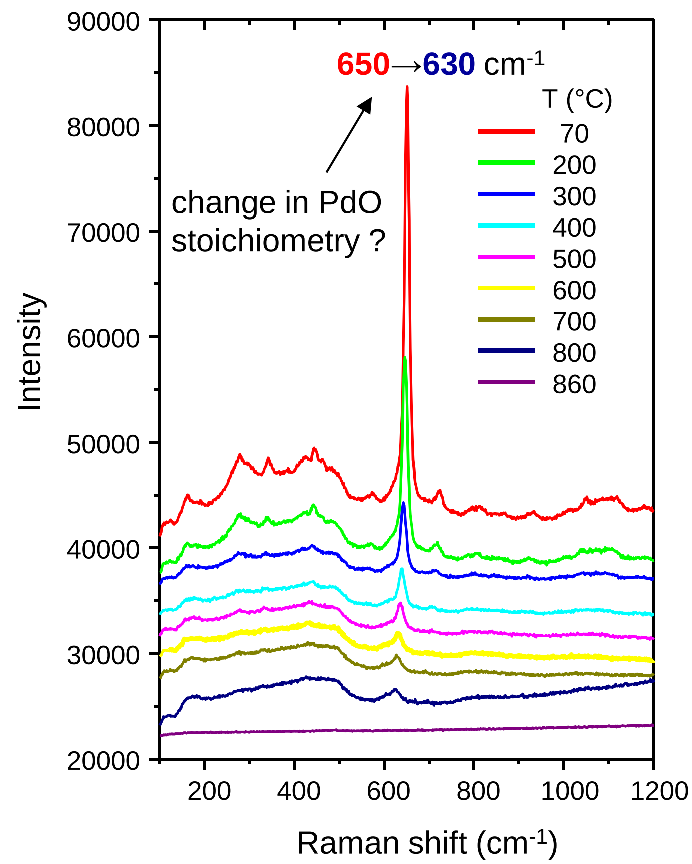
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2







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

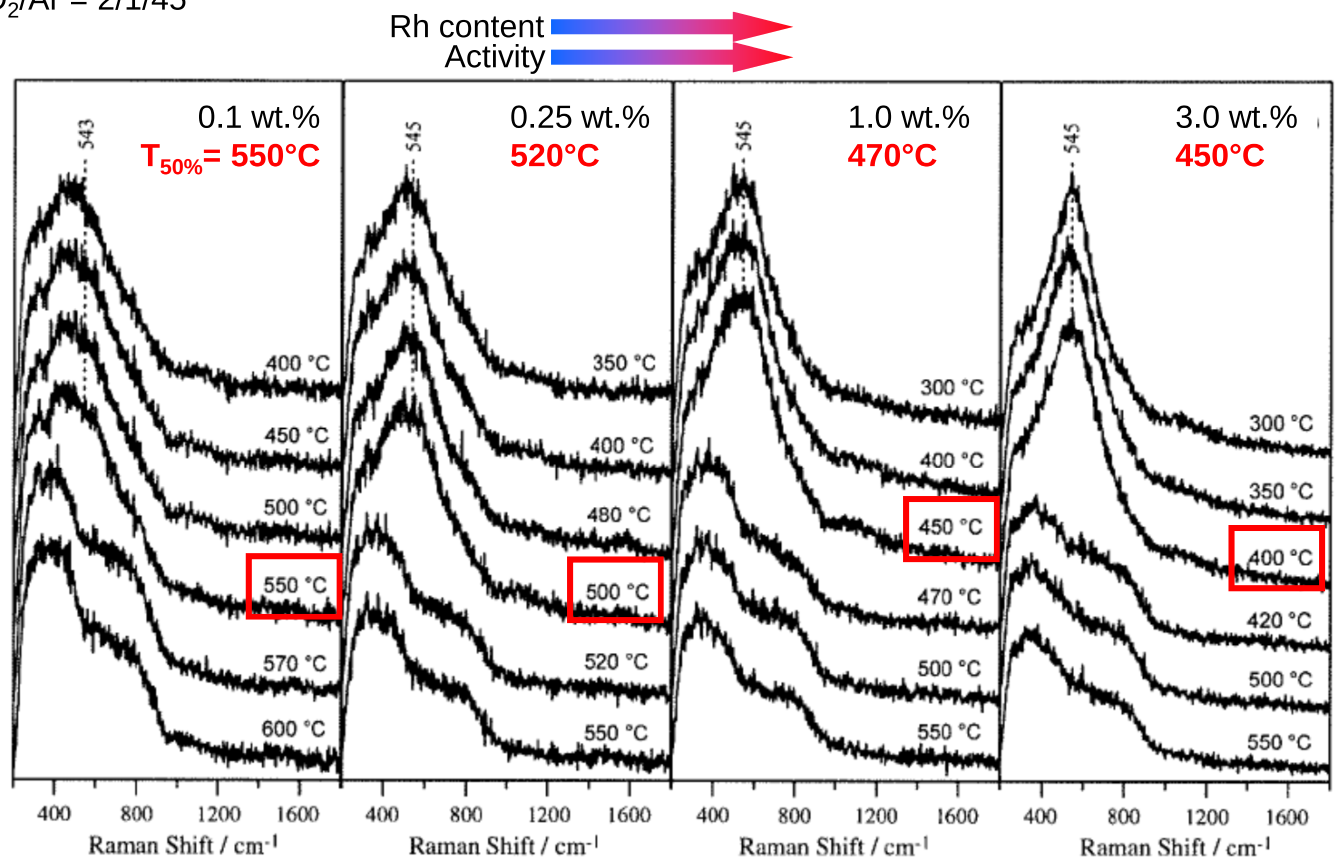
Applications

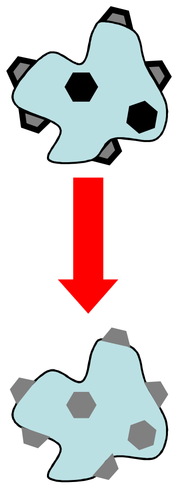
- Methane partial oxidation over Rh/Al_2O_3

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

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

RhO_x
↓
Rh(0)





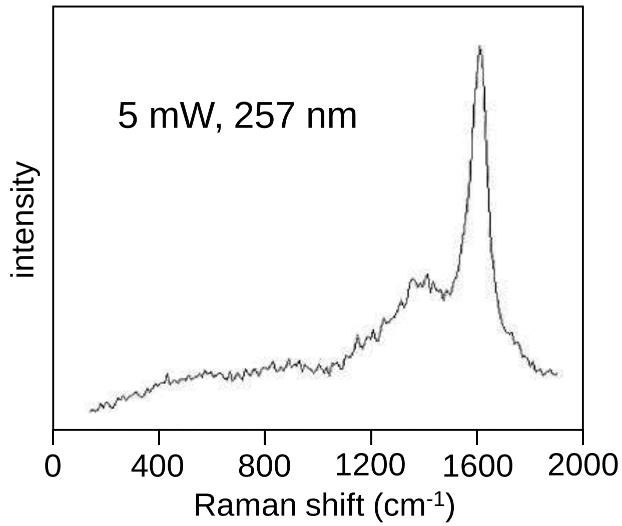
Li et al., *Catal. Today* **131** (2008) 179

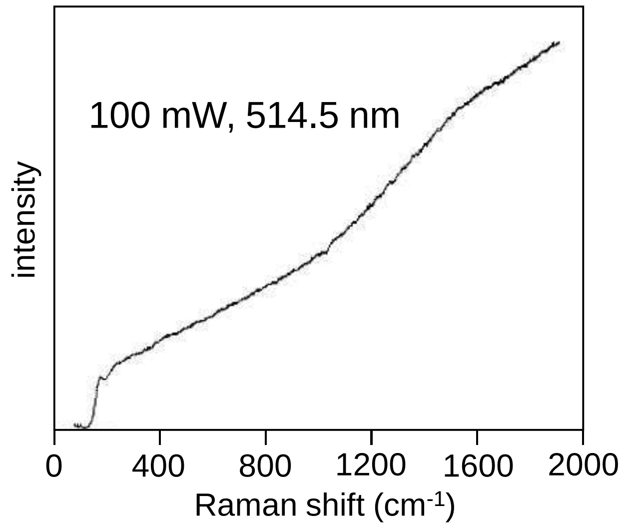
Applications

- UV-Raman
  - No fluorescence

  (only few molecules fluoresce below 260 nm)

Rh/Al_2O_3, coked 500°C in naphtha

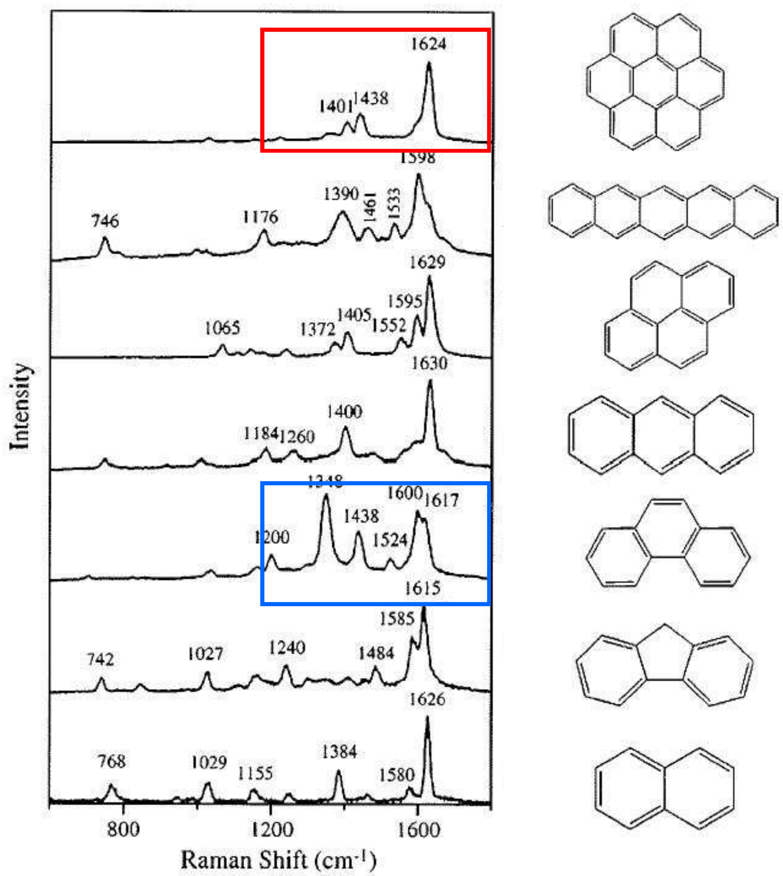


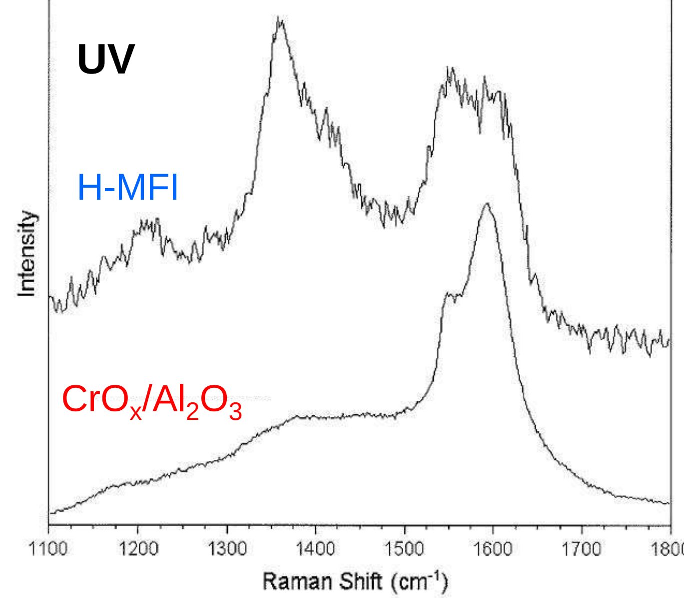


Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Applications

- (Polyaromatic) Coke formation and characterization





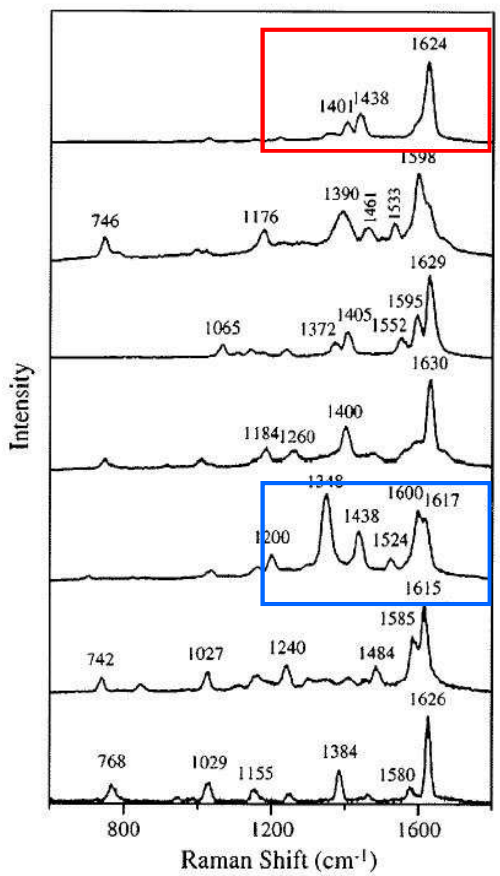
Coke classification
1D topology, chain-like
2D topology, sheet-like

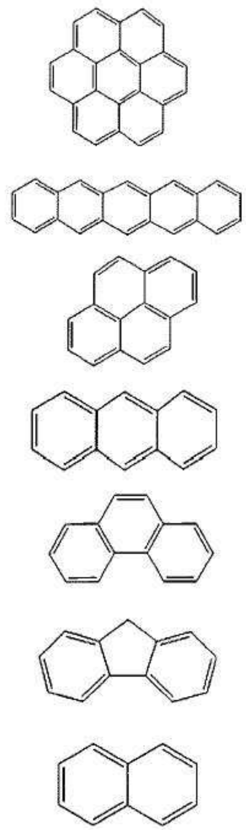
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

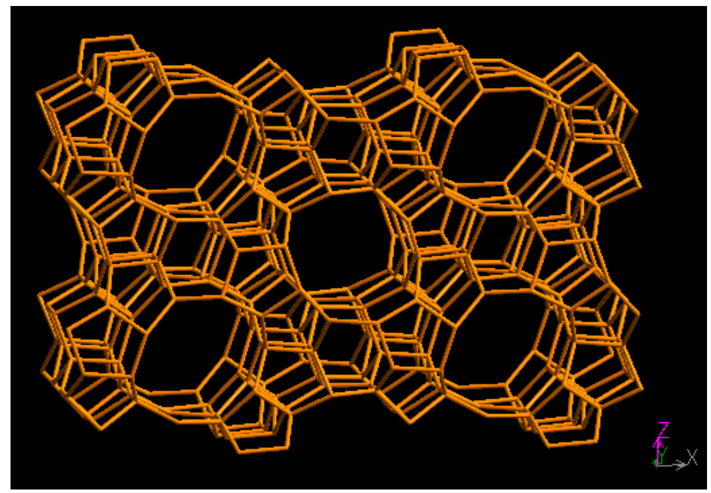
Stair, *Adv. Catal.* **51** (2007) 75

Applications

- (Polyaromatic) Coke formation and characterization







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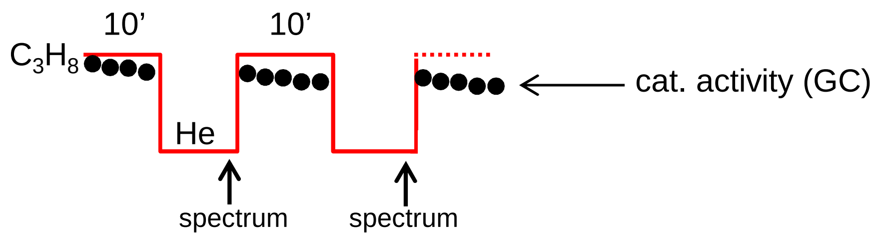
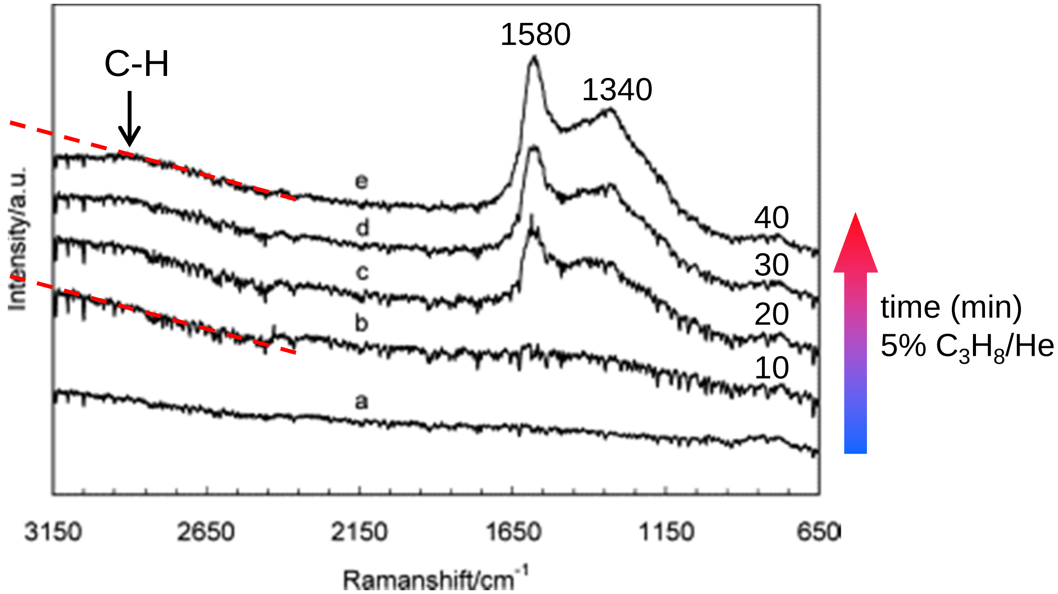
Stair, *Adv. Catal.* **51** (2007) 75

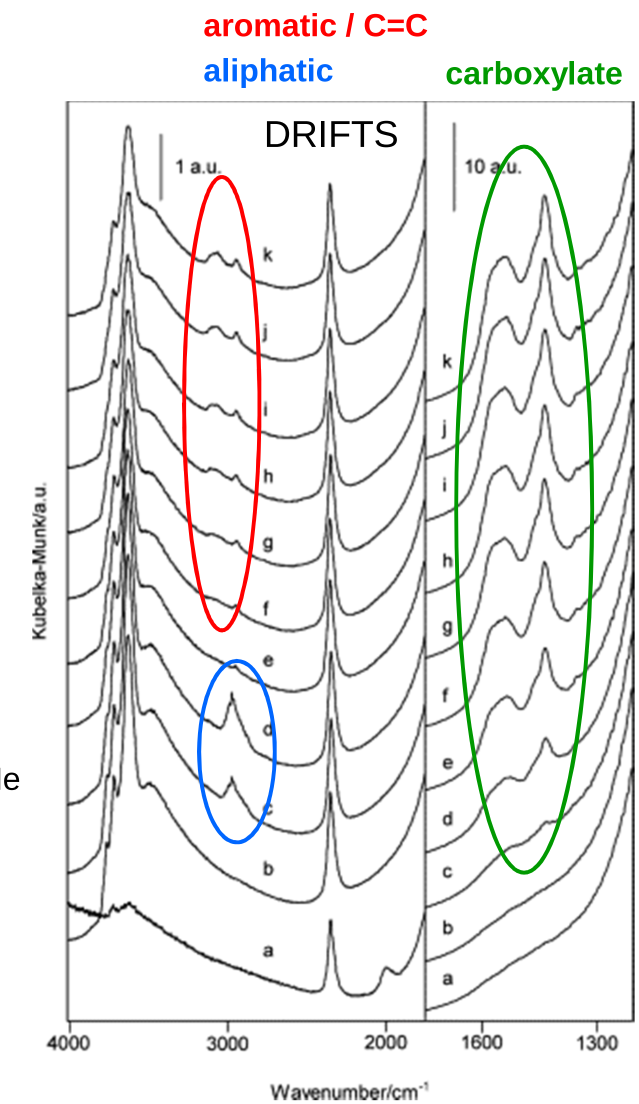
Applications

- Propane dehydrogenation



Cr_2O_3/Al_2O_3, 580°C, 514 nm

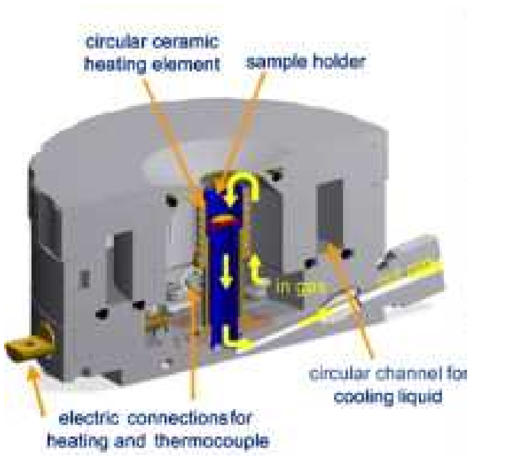


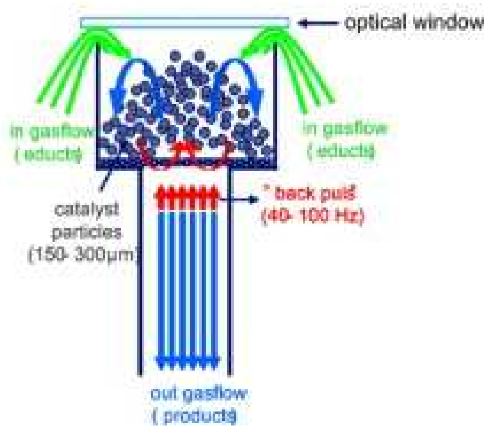


Airaksinen et al., *J. Catal.* **230** (2005) 507

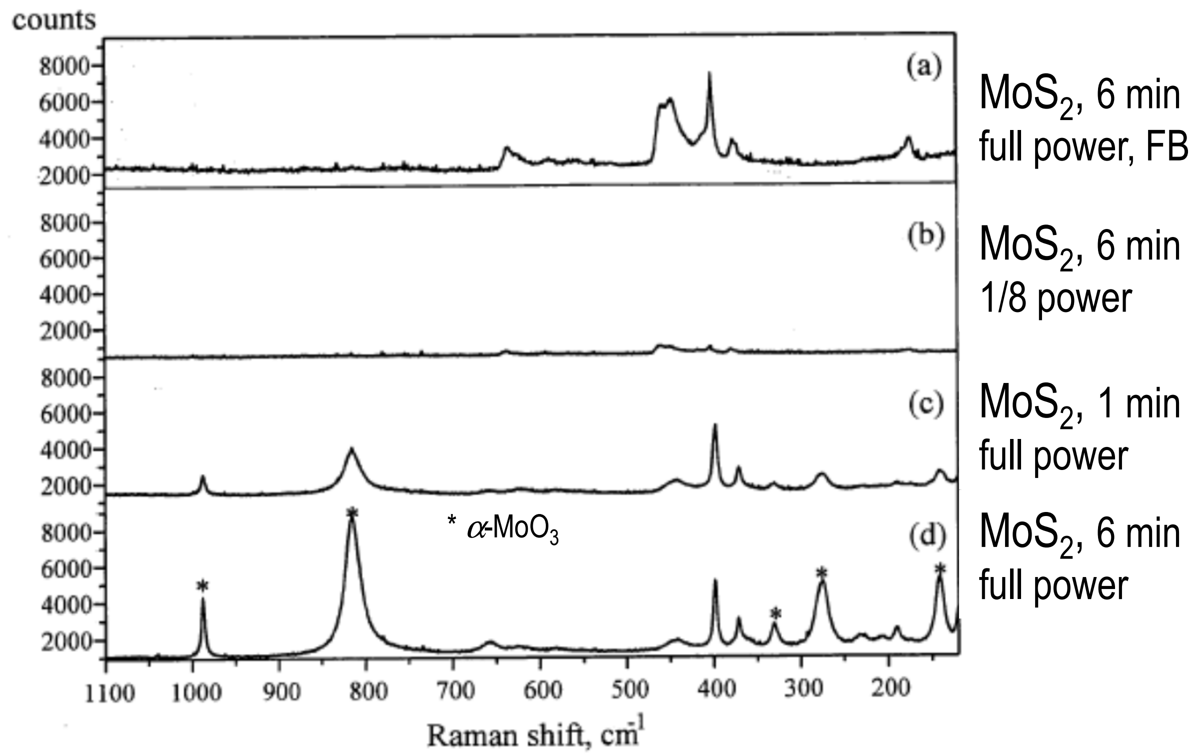
Applications

- Fluidized bed reactor cell





hydrodesulfurization

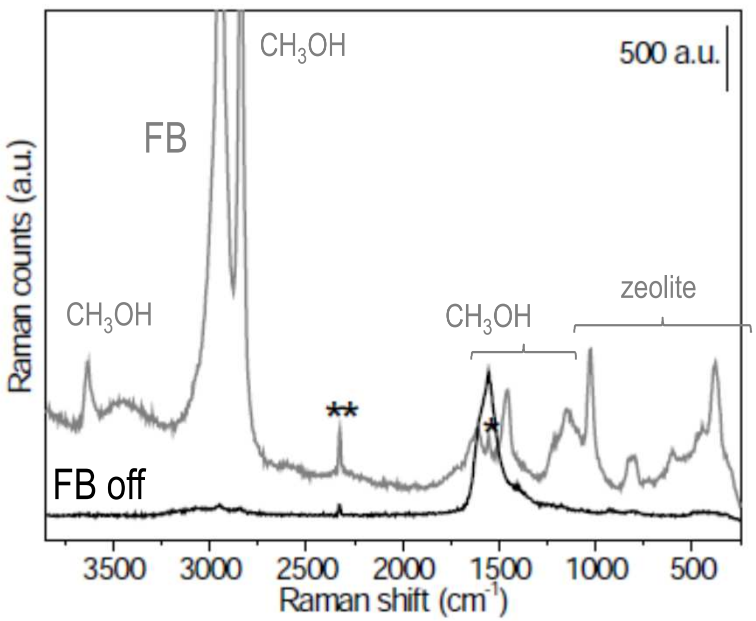


Beato et al., *Catal. Today* 205 (2013) 128

Applications

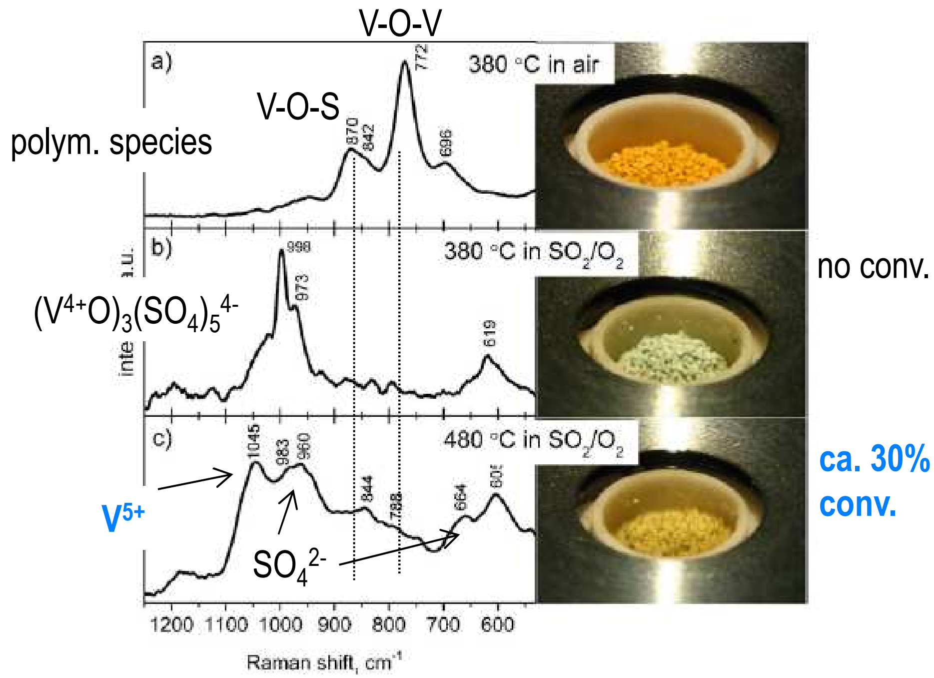
- Fluidized bed reactor cell

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

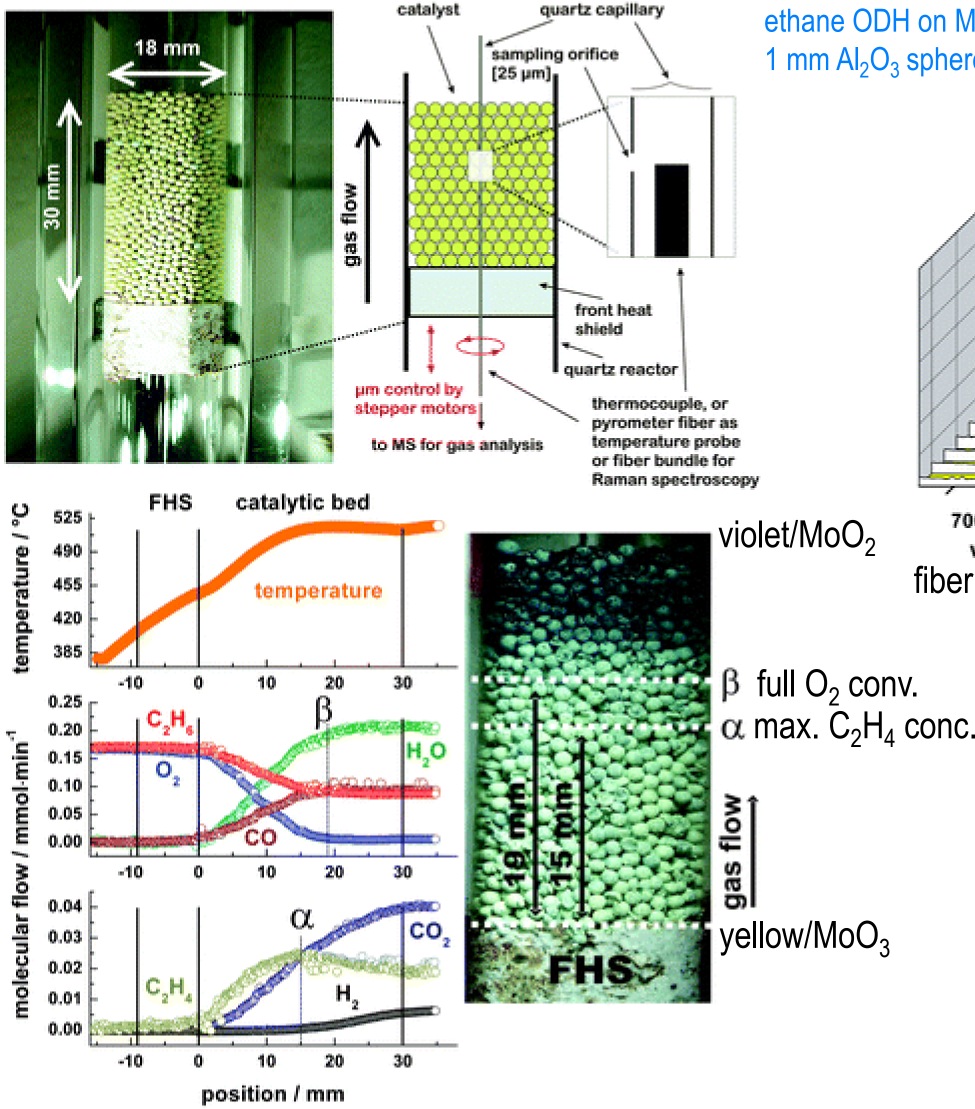


active species: mono- & dimeric V^{5+} oxosulfate species

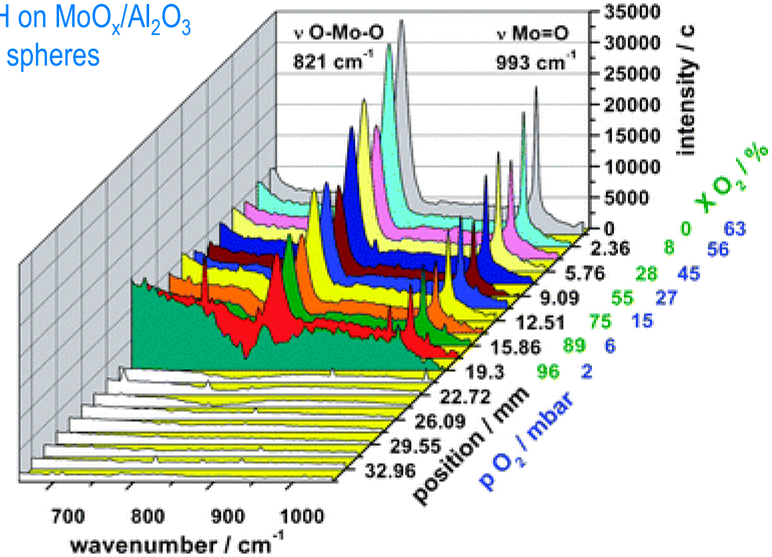
Beato et al., *Catal. Today* 205 (2013) 128

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