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:

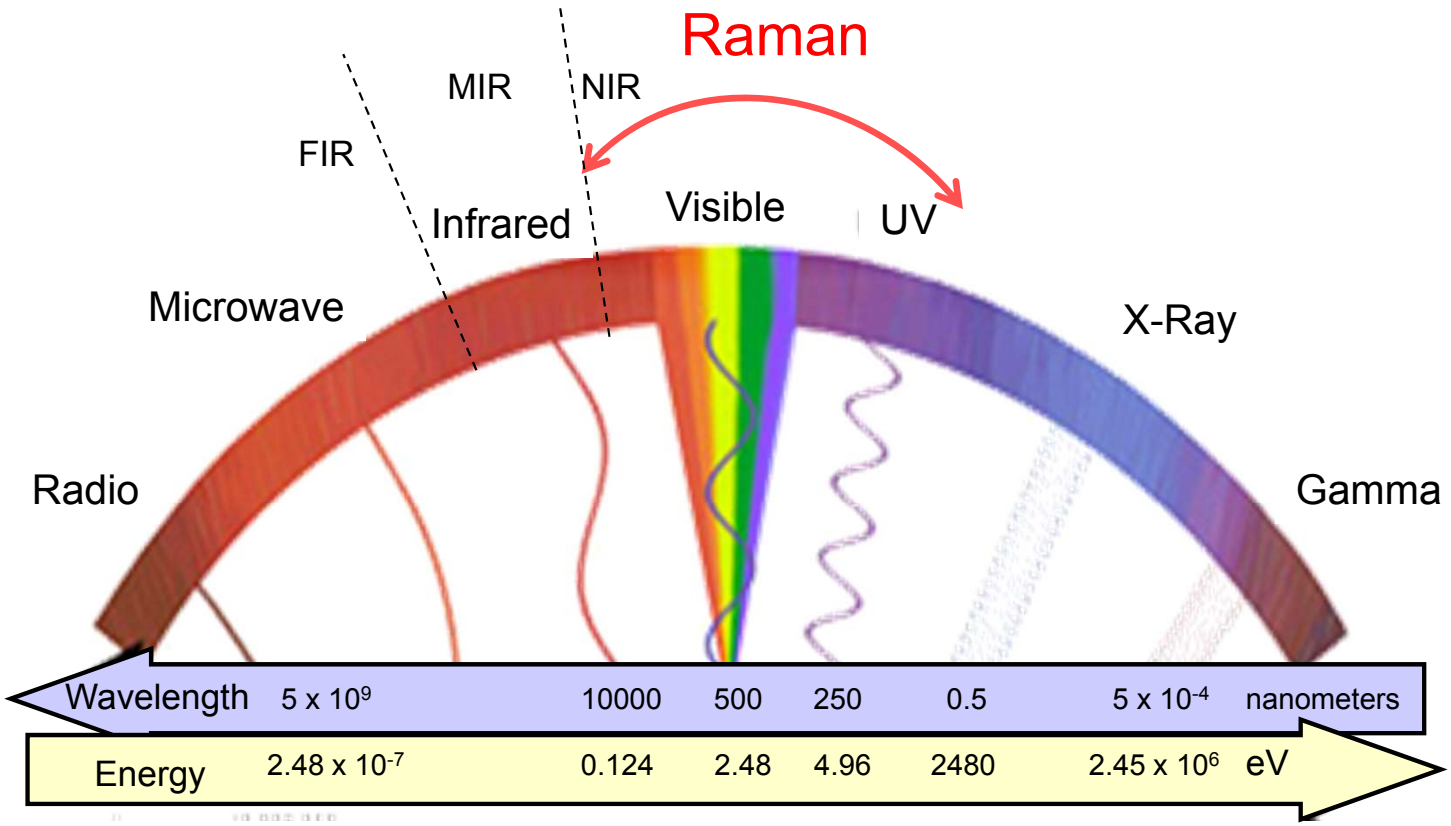
M.A. Banares, Raman Spectroscopy, in In situ spectroscopy of catalysts (Ed. B.M. Weckhuysen), ASP, Stevenson Ranch, CA, 2004, pp. 59-104

Ingle, Crouch, Spectrochemical Analysis, Prenctice Hall 1988

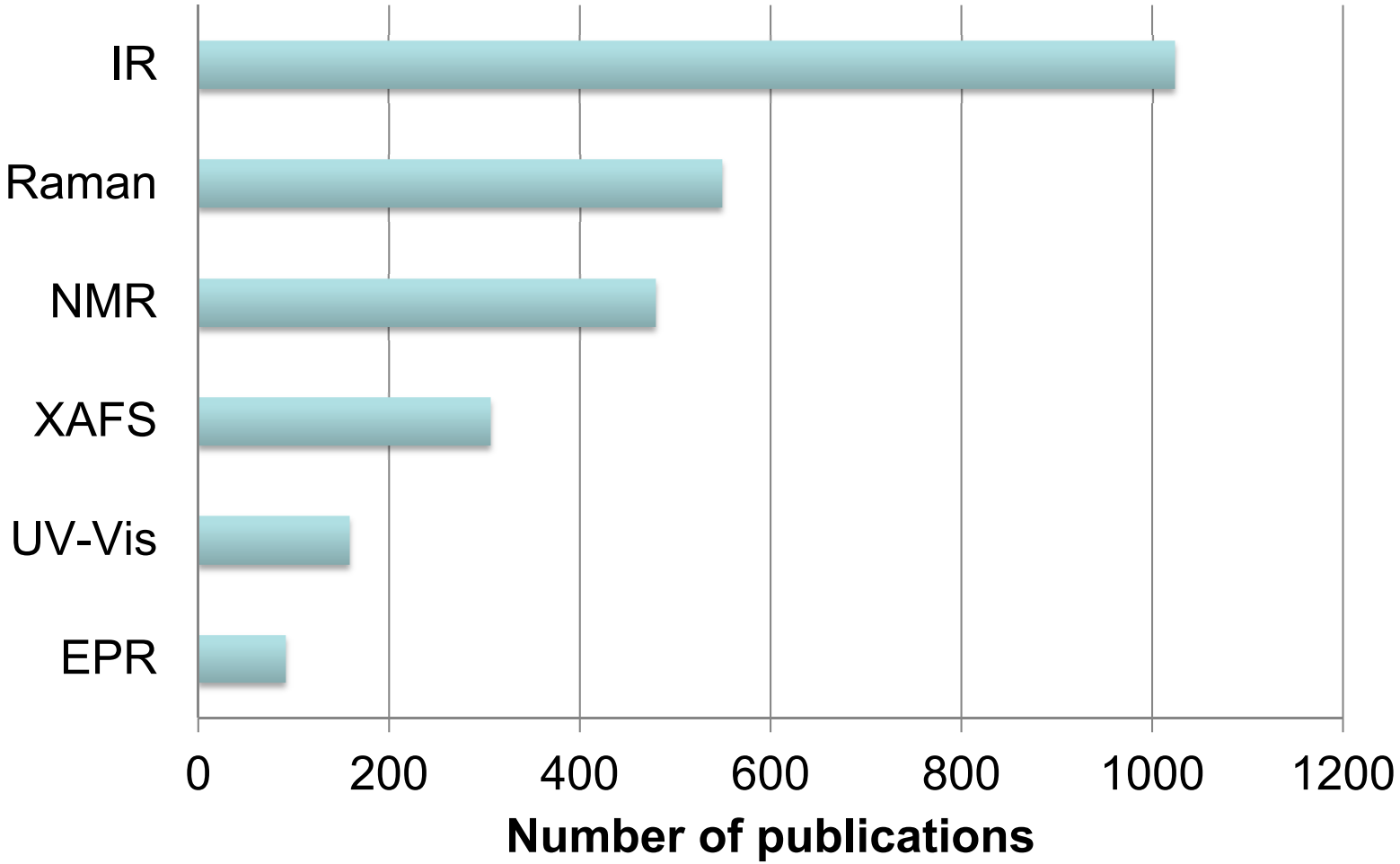
Handbook of Spectroscopy (Ed. Gauglitz, Vo-Dinh), Wiley, Vol. 1

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

Raman spectroscopy

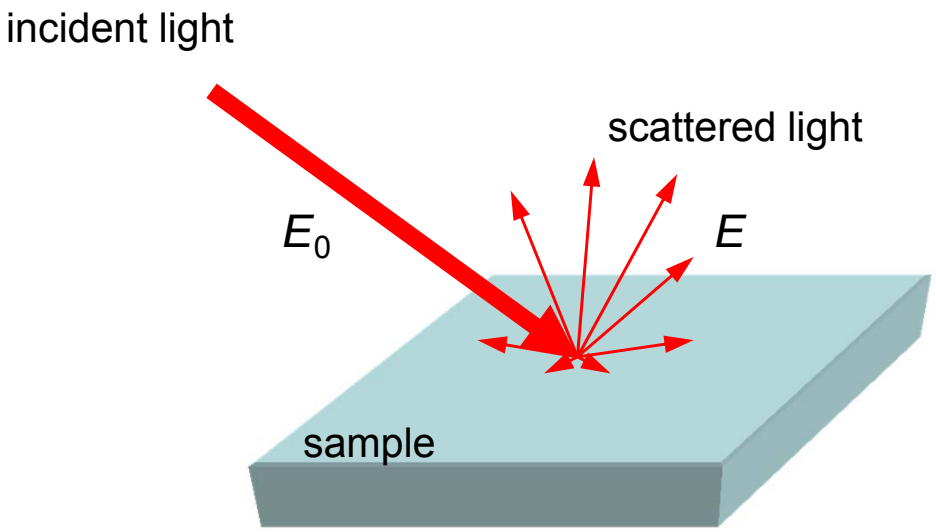


Importance of Raman spec. in catalysis



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)

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

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

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

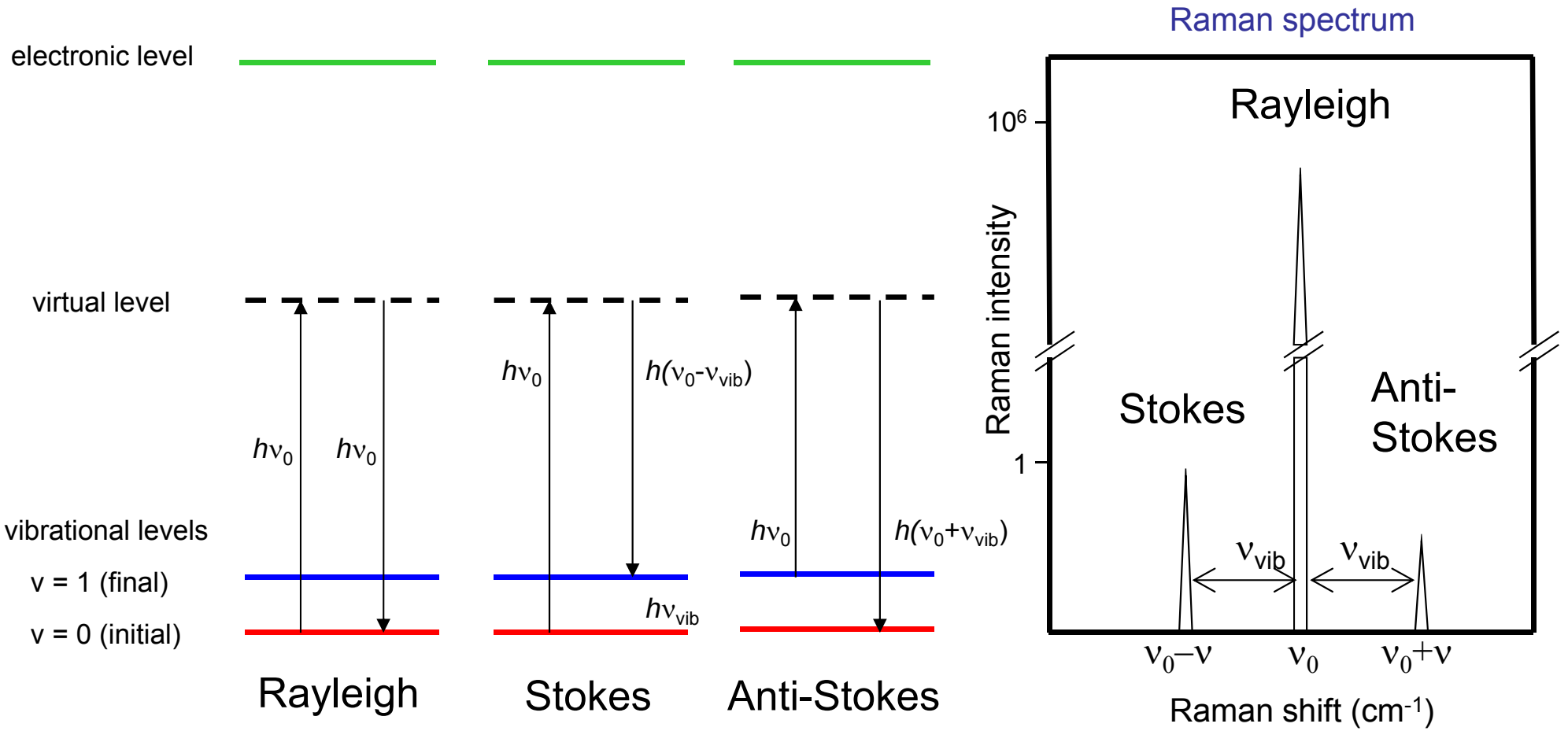
and

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

Rayleigh | Anti-Stokes | Stokes

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

Quantum mechanics approach



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

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 effect

- Change in **polarizability**, α
- Intensity of Raman signals depends on

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

  - 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** (at higher frequency)

Raman effect

- **Polarizability**, α

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

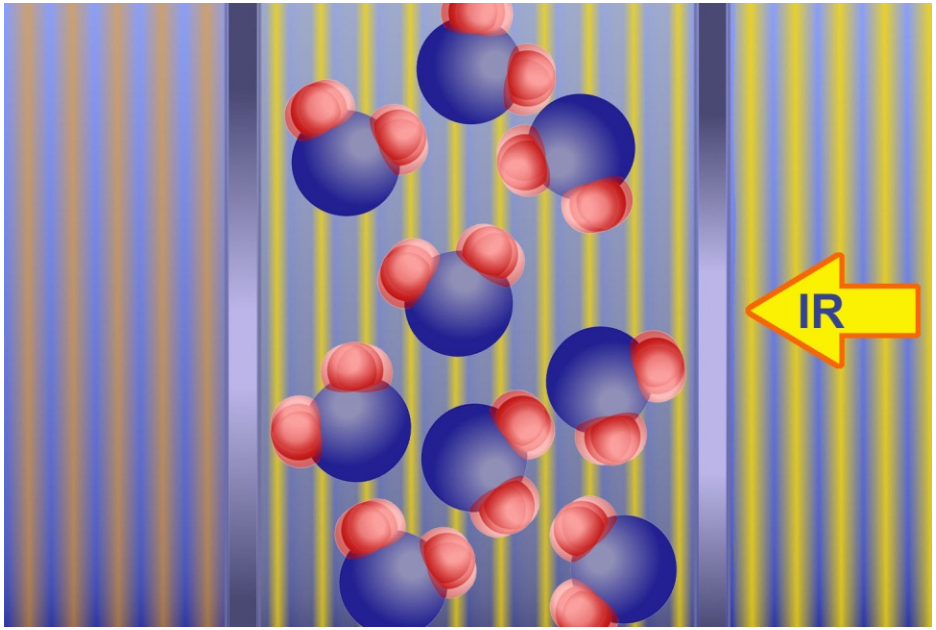
- properties of molecules
- strength/nature of bonds

covalent bond STRONG Raman signals

ionic bond WEAK Raman signals

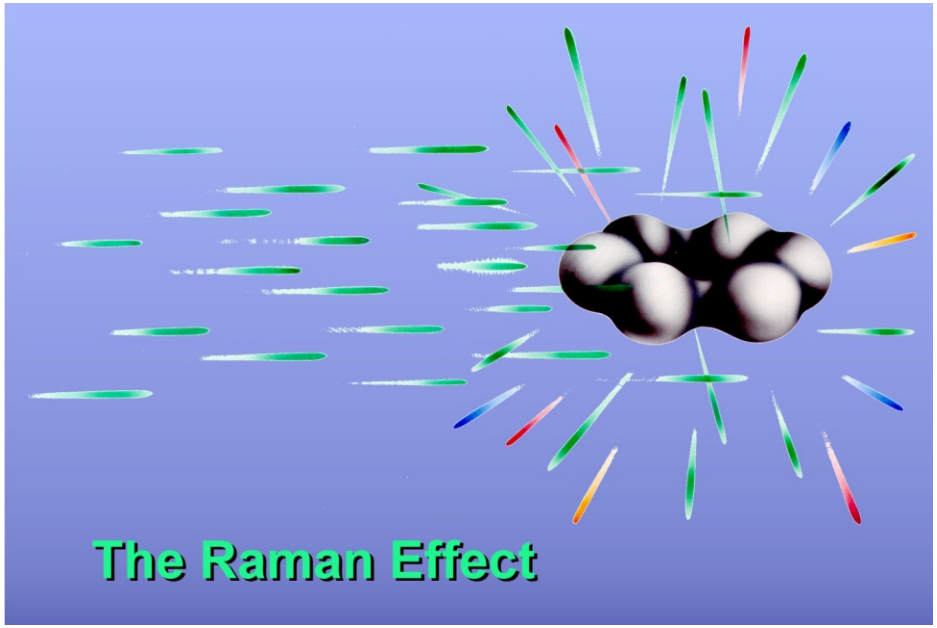
Raman *vs.* Infrared

Infrared



Absorption of IR light

Raman



Inelastic scattering of light

Raman *vs.* Infrared

Selection rules

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

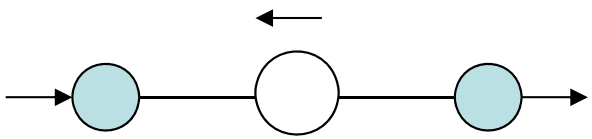
- high absorption for polar bonds (C=O, H_2O, NH, etc.)

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

- 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

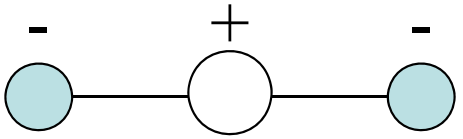
Raman *vs.* Infrared

CO_2



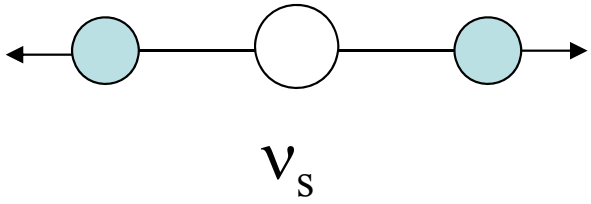
ν_{as}

2349 cm^{-1}



δ

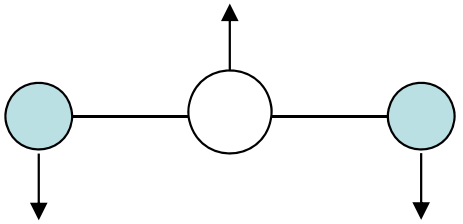
667 cm^{-1}



ν_s

1340 cm^{-1}

Raman active



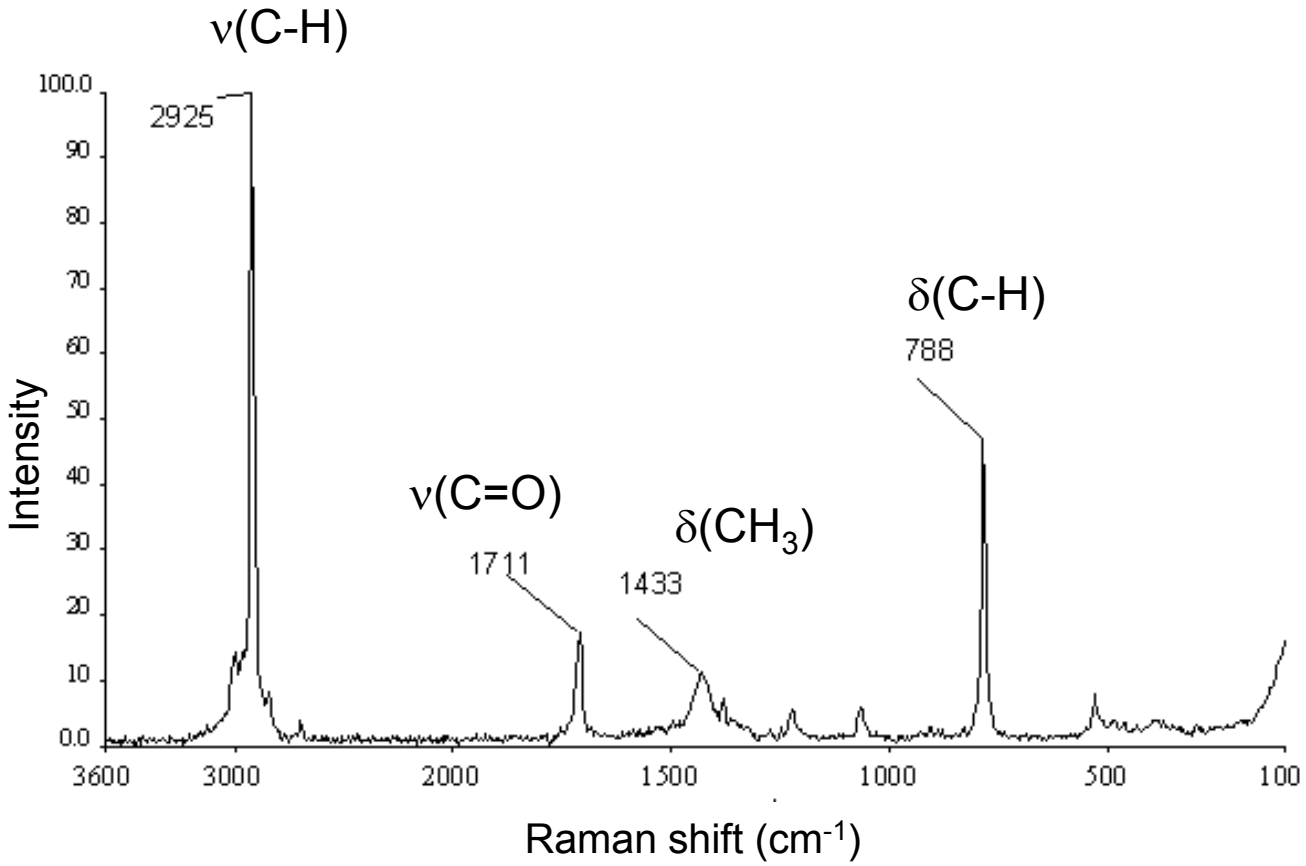
δ

667 cm^{-1}

degenerate modes

Raman *vs.* Infrared

Acetone



Raman *vs.* Infrared

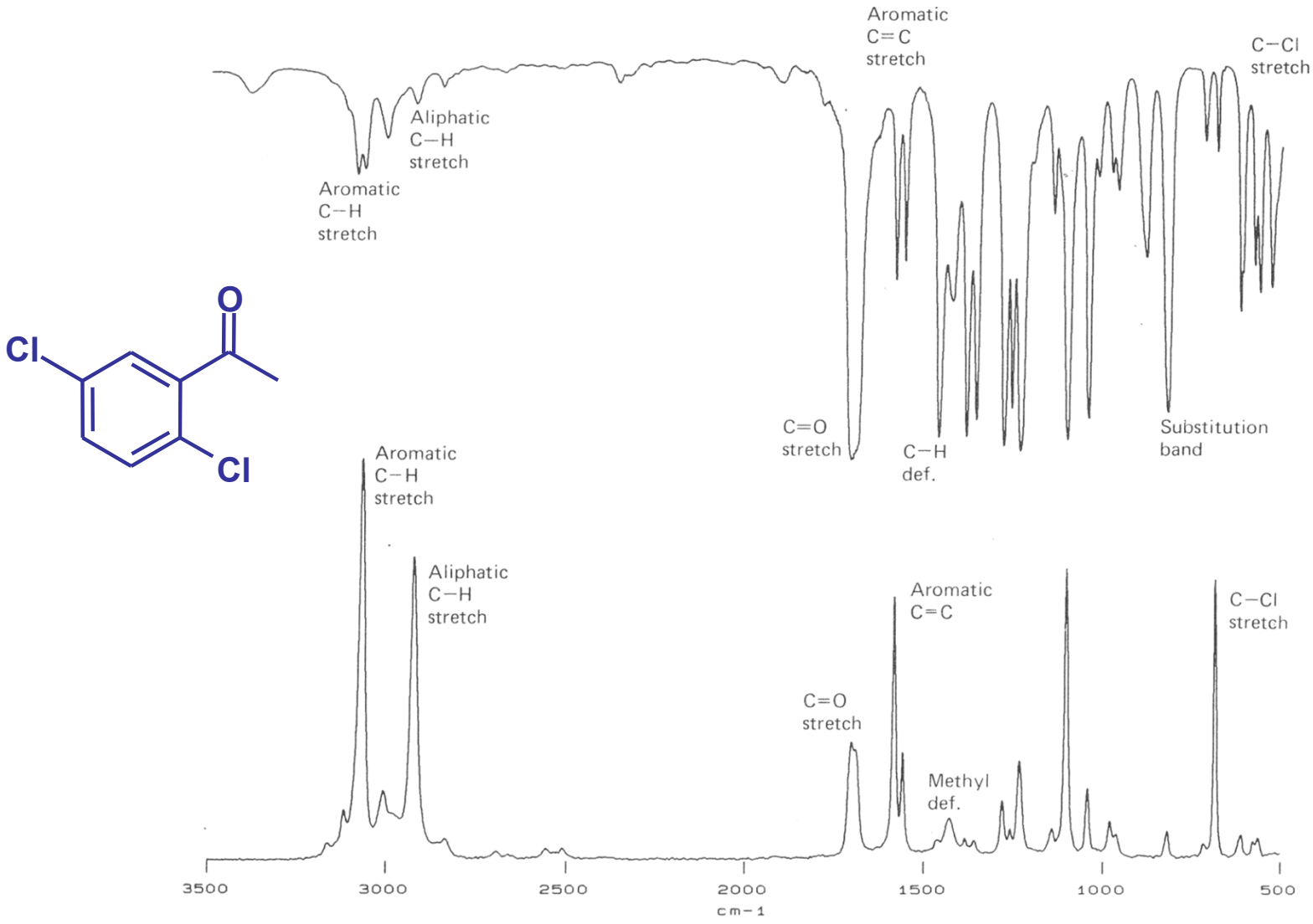
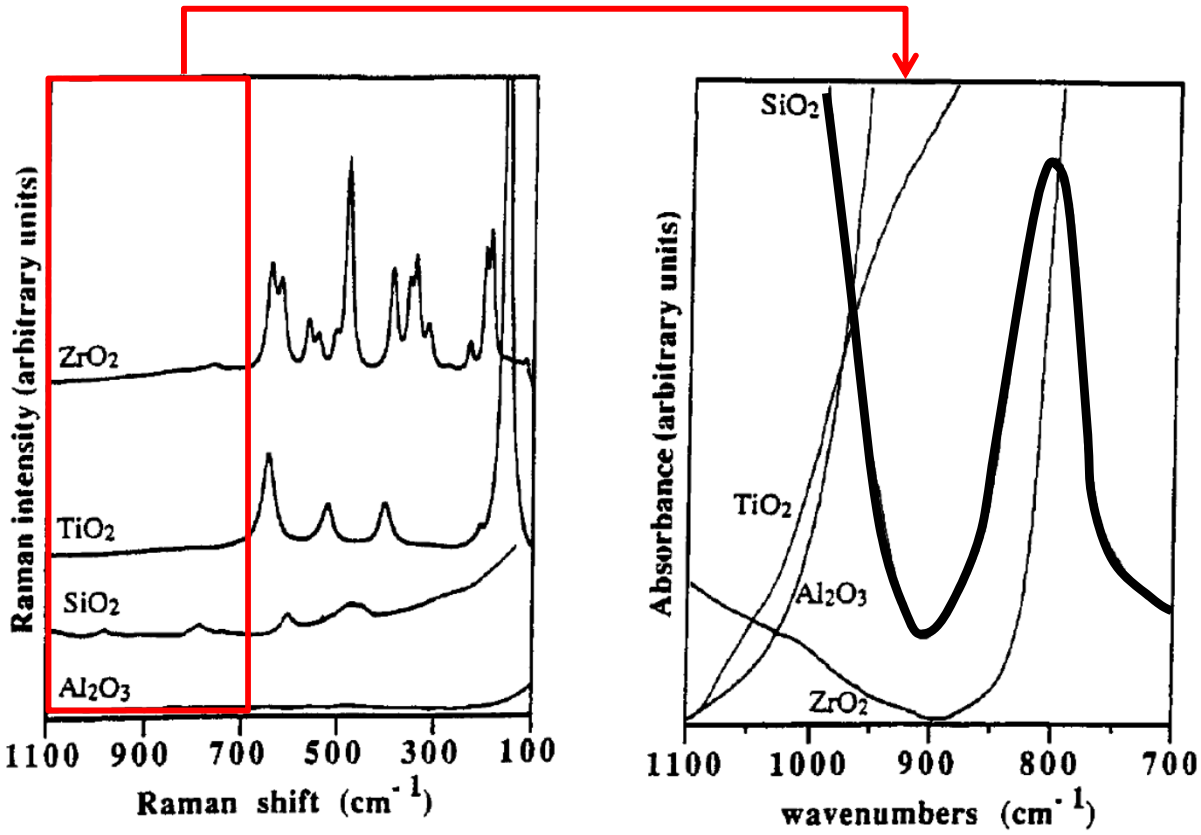


Fig. 2.25 — The infrared and Raman spectra of 2,5-Dichloroacetophenone.

Raman *vs.* Infrared

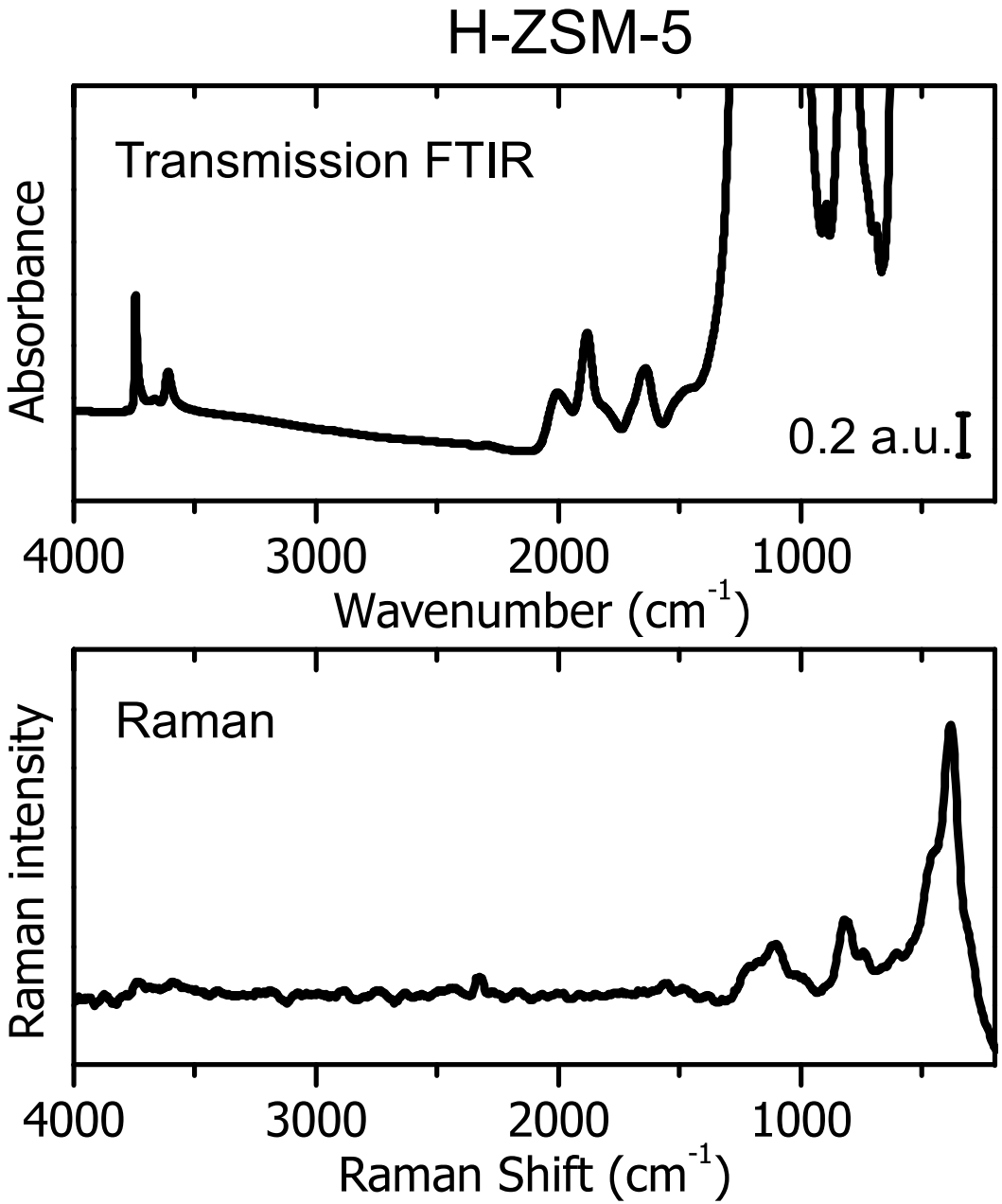
- Metal oxides



- <700 cm^{-1}: covalent bond character, strong signals in Raman
- >100 cm^{-1}: low polarizability of light elements (Si, Al, O) and ionic character: weak signals in Raman
- Raman more suitable than IR in low wavenumber range (M-O-M) but complementary in high wavenumber range (M=O)

Wachs, Catal. Today 27 (1996) 437

Raman *vs.* Infrared



- IR
  - suitable for M-OH vibrational modes
- Raman
  - characterization of bulk (i.e. framework modes)

  → structural information
  - possibility to exploit resonances

  → moiety selective
- Both applicable in a wide range of conditions

  → suitable for *in situ* studies

courtesy by M. Signorile, UniTO

Raman *vs.* Infrared

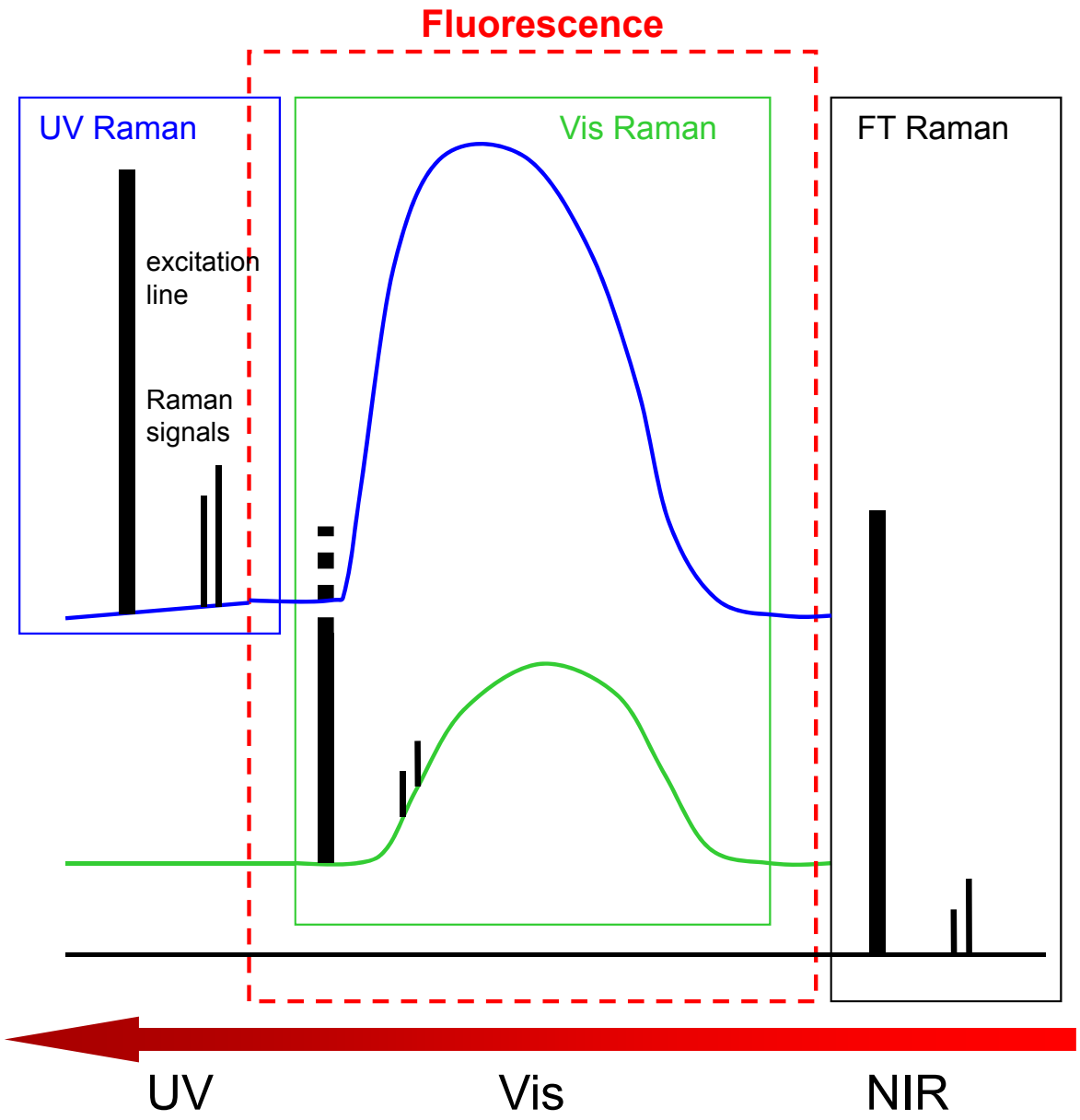
Advantages

- 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

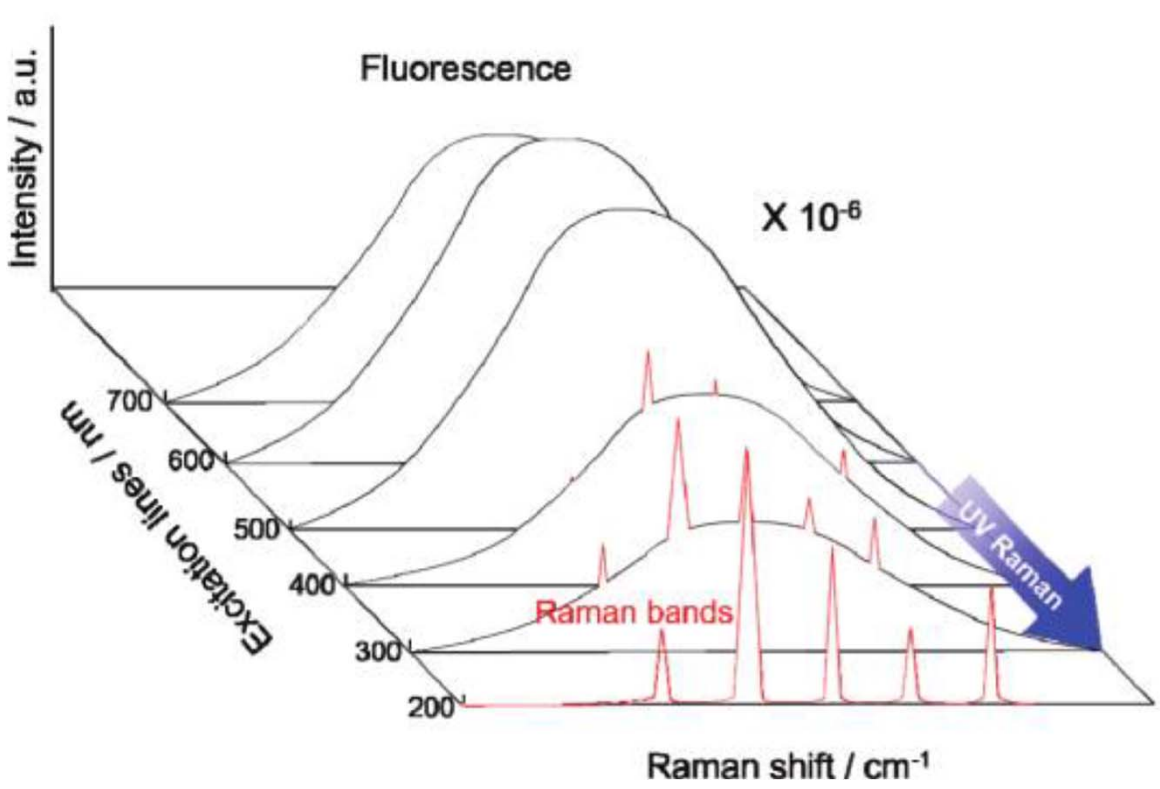
Fluorescence proportional to ν

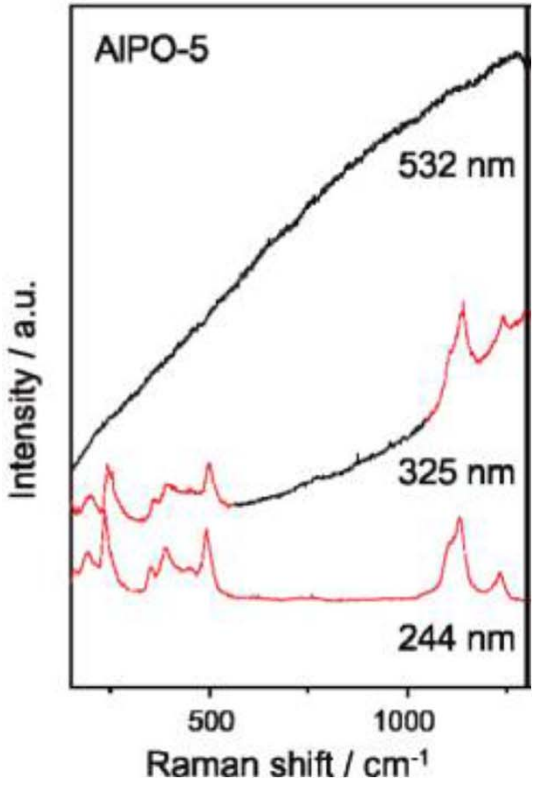
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

10^7 stronger than Raman scattering

Fluorescence and Raman signals

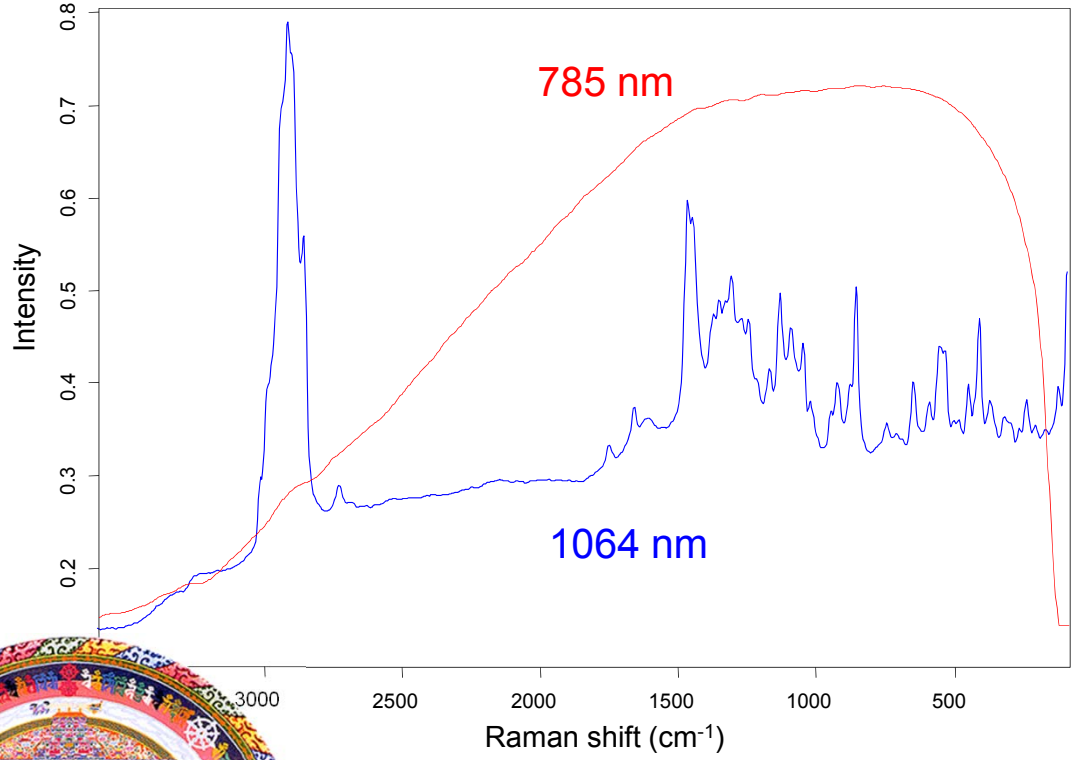


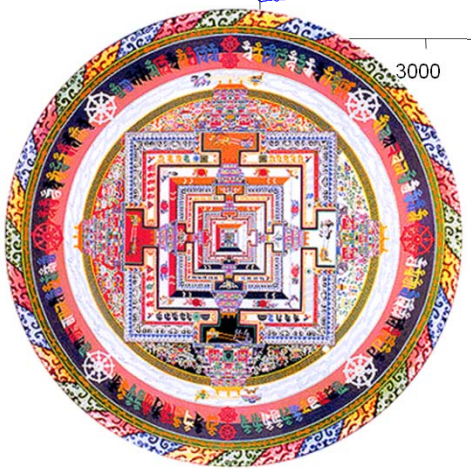


Fan et al., Acc. Chem. Res. 43 (2009) 378

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



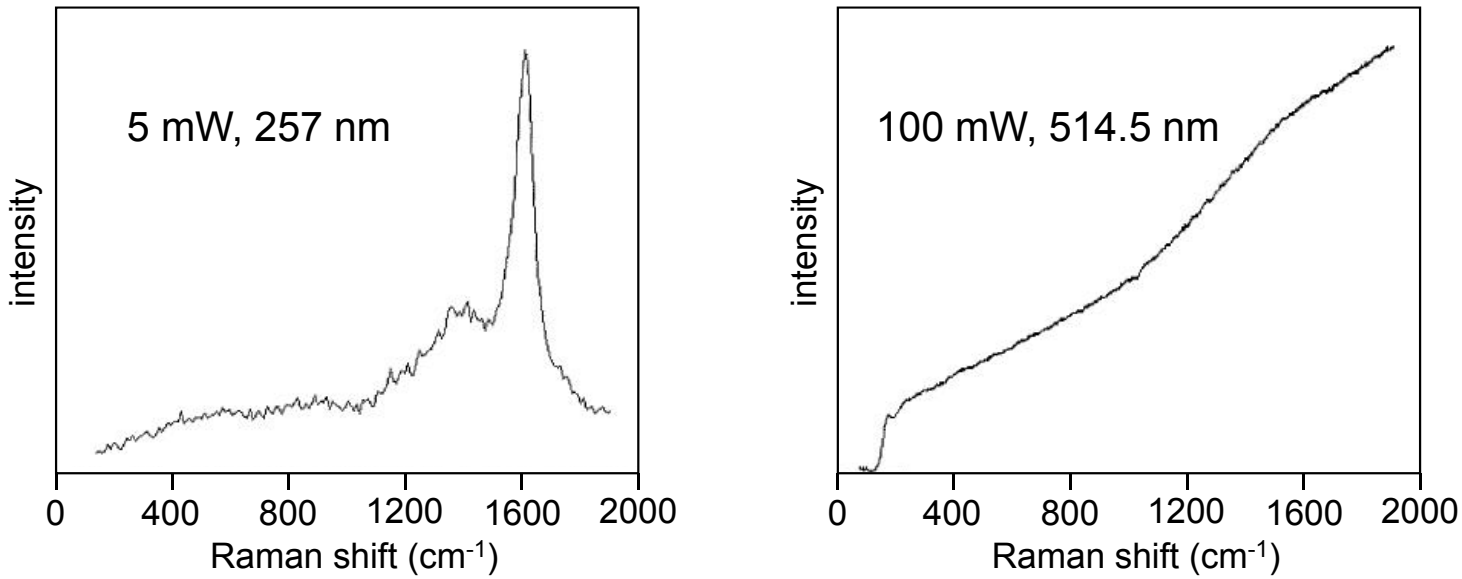


Applications

- 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

Resonance Raman spectroscopy

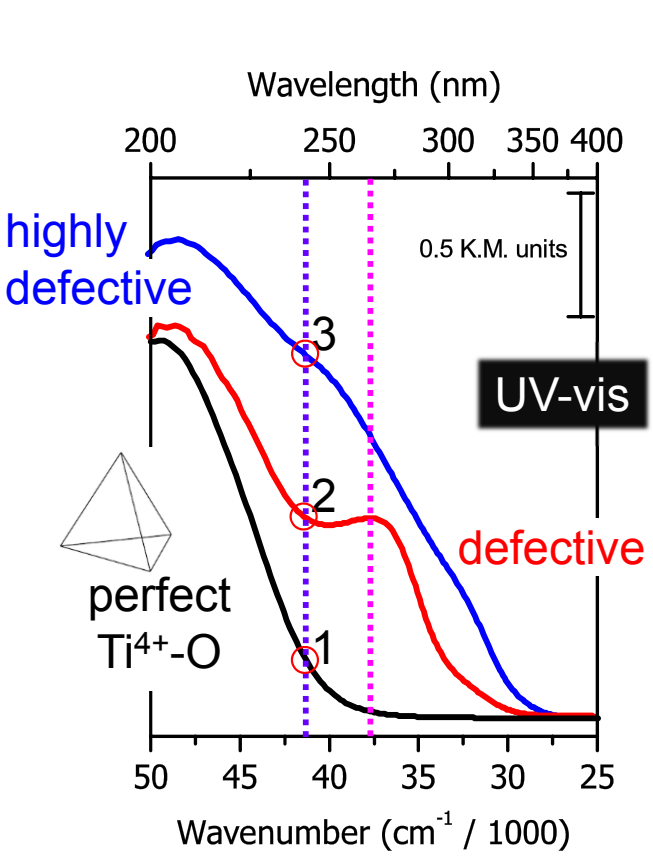
- Raman scattering is strongly enhanced (factor 10^6 !) if the excited state is not virtual, but an electronically excited state
- Vibrations related to an electronic transition are excited
- This can be tuned by changing the laser wavelength

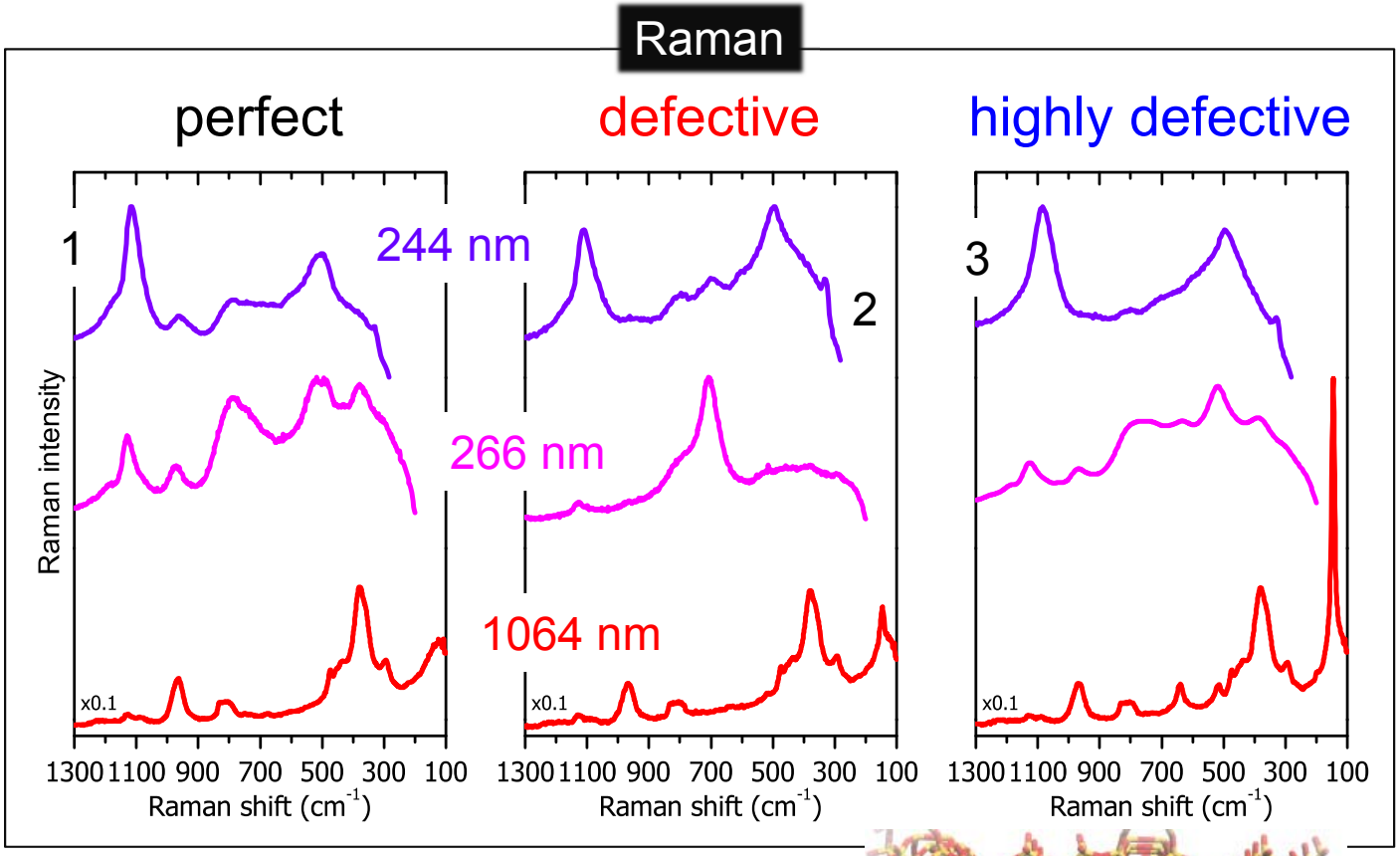
- Example organic molecules:

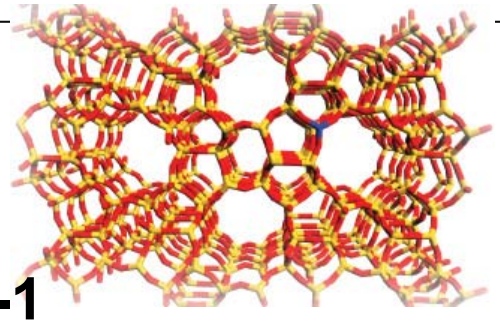
  resonance with a $\pi \rightarrow \pi^*$ transition enhances stretching modes of the π-bonds involved with the transition, while the other modes remain unaffected

Resonance Raman spectroscopy

- Multiwavelength approach to achieve different resonances







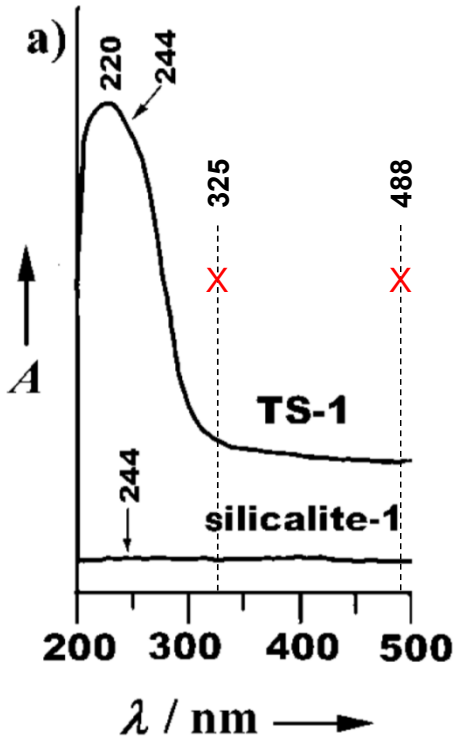
TS-1

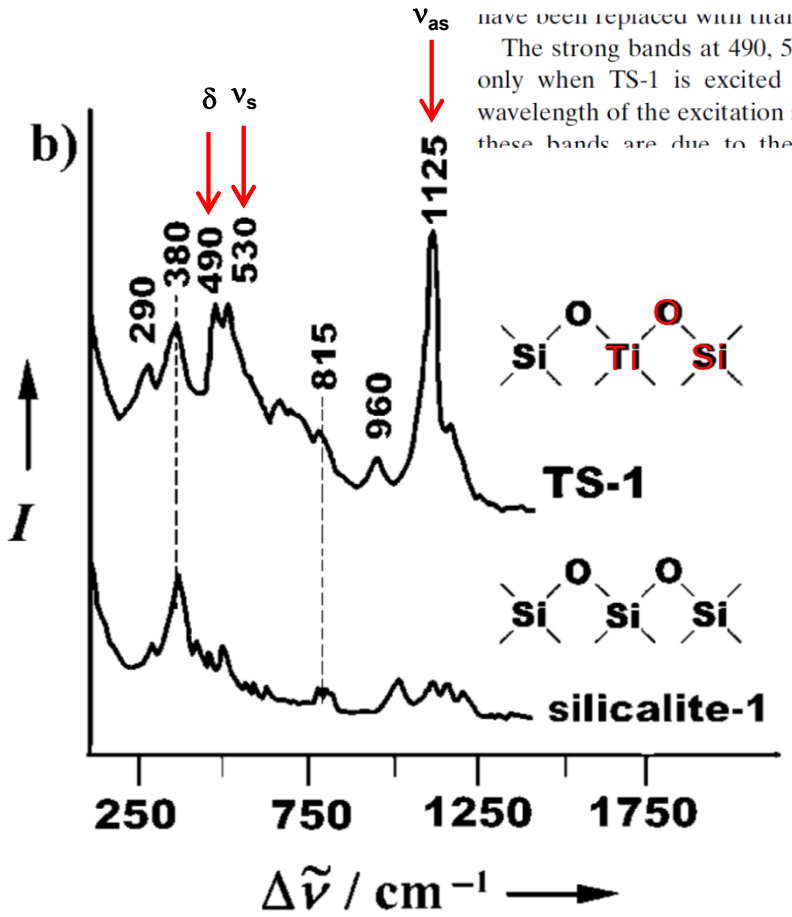
- 244 nm ⟶ perfect sites
- 266 nm ⟶ defect sites, perfect sites + ligands
- 1064 nm (out of resonance) ⟶ SiO_2 framework, bulk TiO_2

courtesy of M. Signorile, UniTO

Applications

- UV resonance





have been replaced with titanium atoms.

The strong bands at 490, 530, and 1125 cm^{-1} are observed only when TS-1 is excited at 244 nm, and not when the wavelength of the excitation source is 325 or 488 nm. Clearly these bands are due to the UV resonance Raman bands

Additional detailed structural information not available upon vis irradiation

Li et al., *Angew. Chemie* **38** (1999) 2220

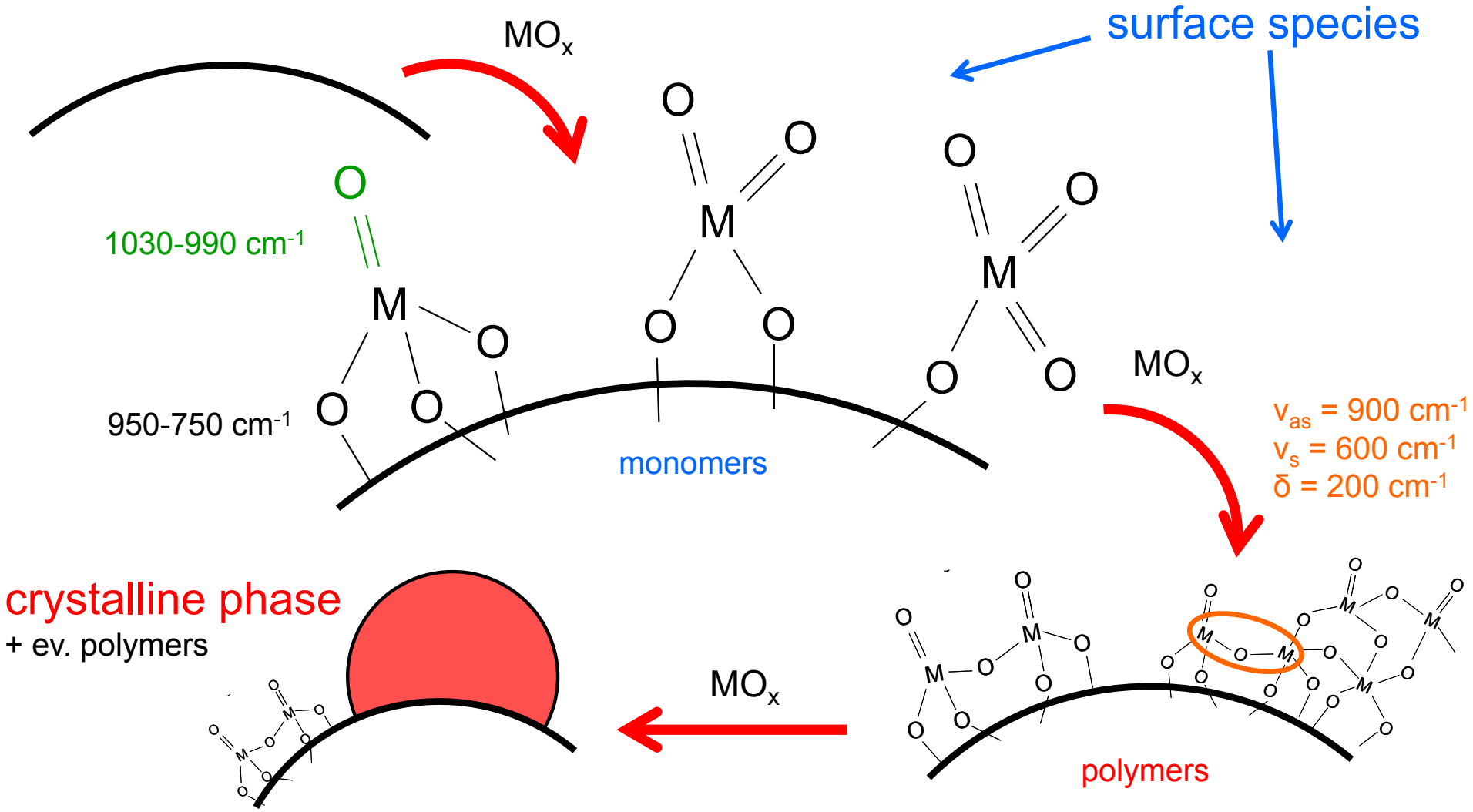
Applications

$MO_x/M'O_X$ 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

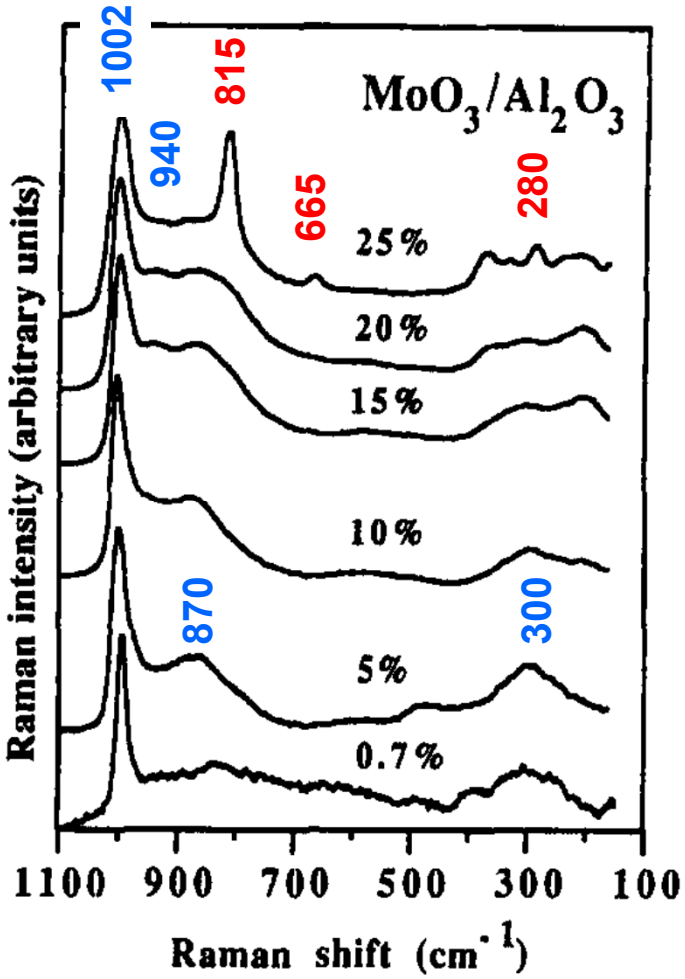


Applications

- Monomeric & polymeric species

Advantage over IR

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



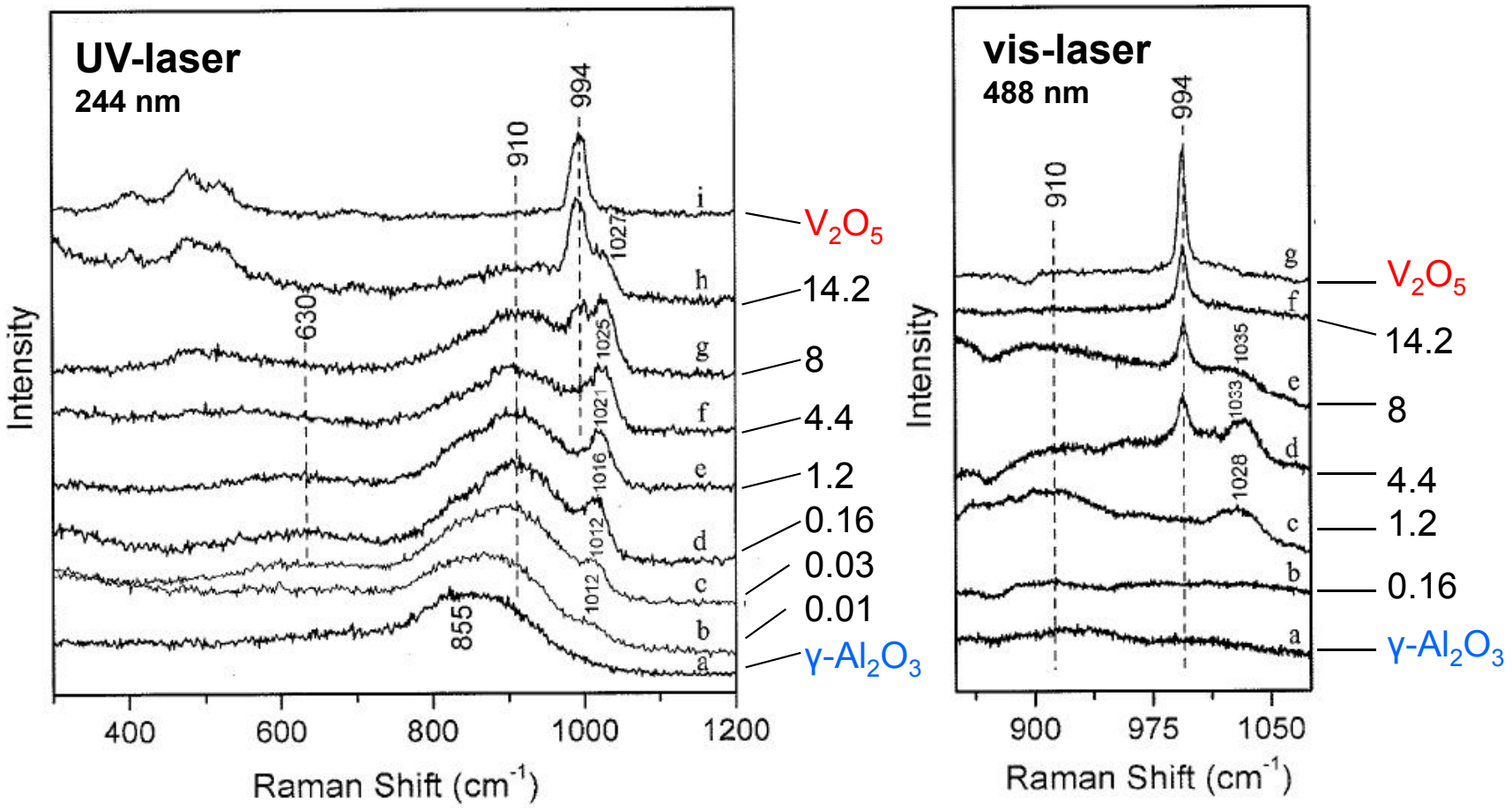
surface MoO_3
crystalline MoO_3

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

Examples for in situ studies

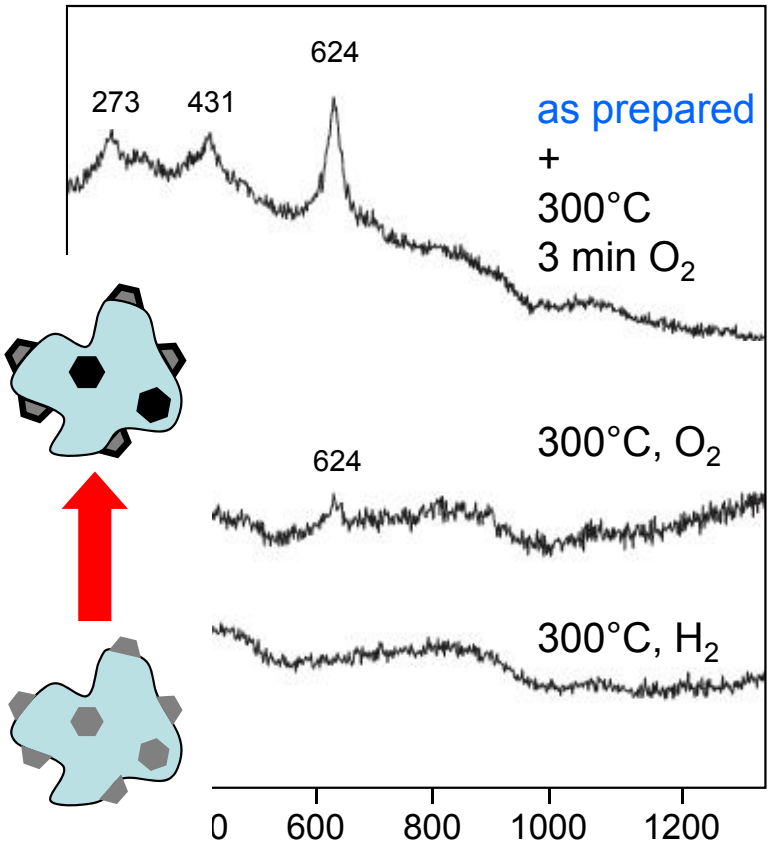
M/MO_X (M= Pd, Pt, Rh; MOx= Al_2O_3, ZrO_2, CeO_2…) used for total and partial oxidation reactions

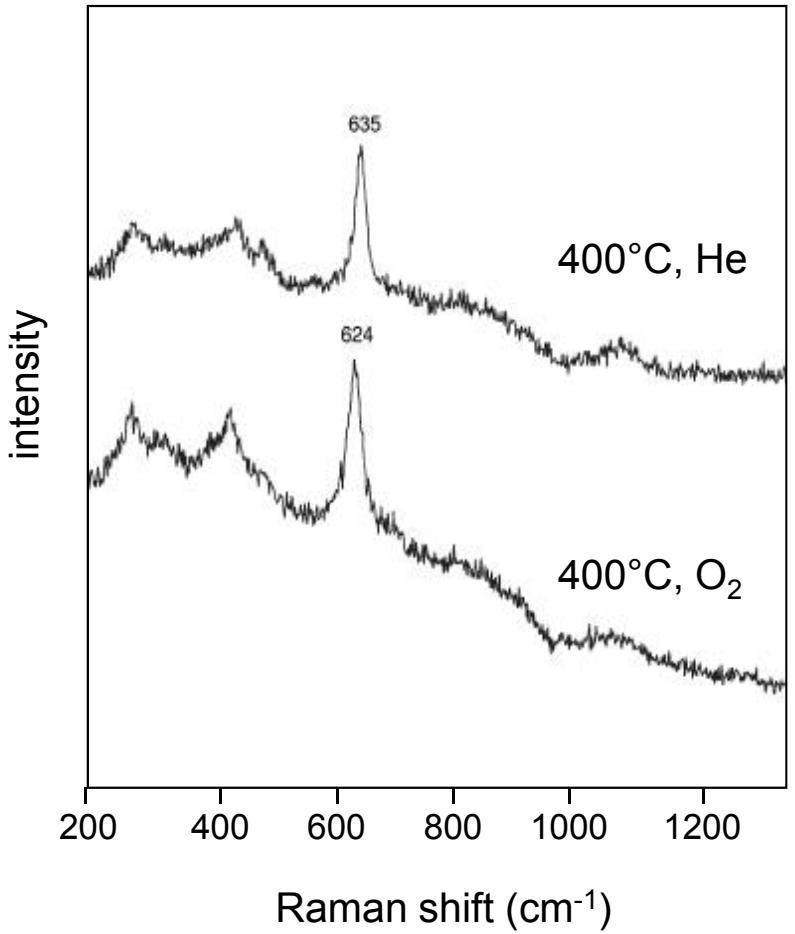
Question: what is the state of Pd during reaction?

Examples: Pd for CH_4 combustion
Rh for CH_4 partial oxidation

Applications

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



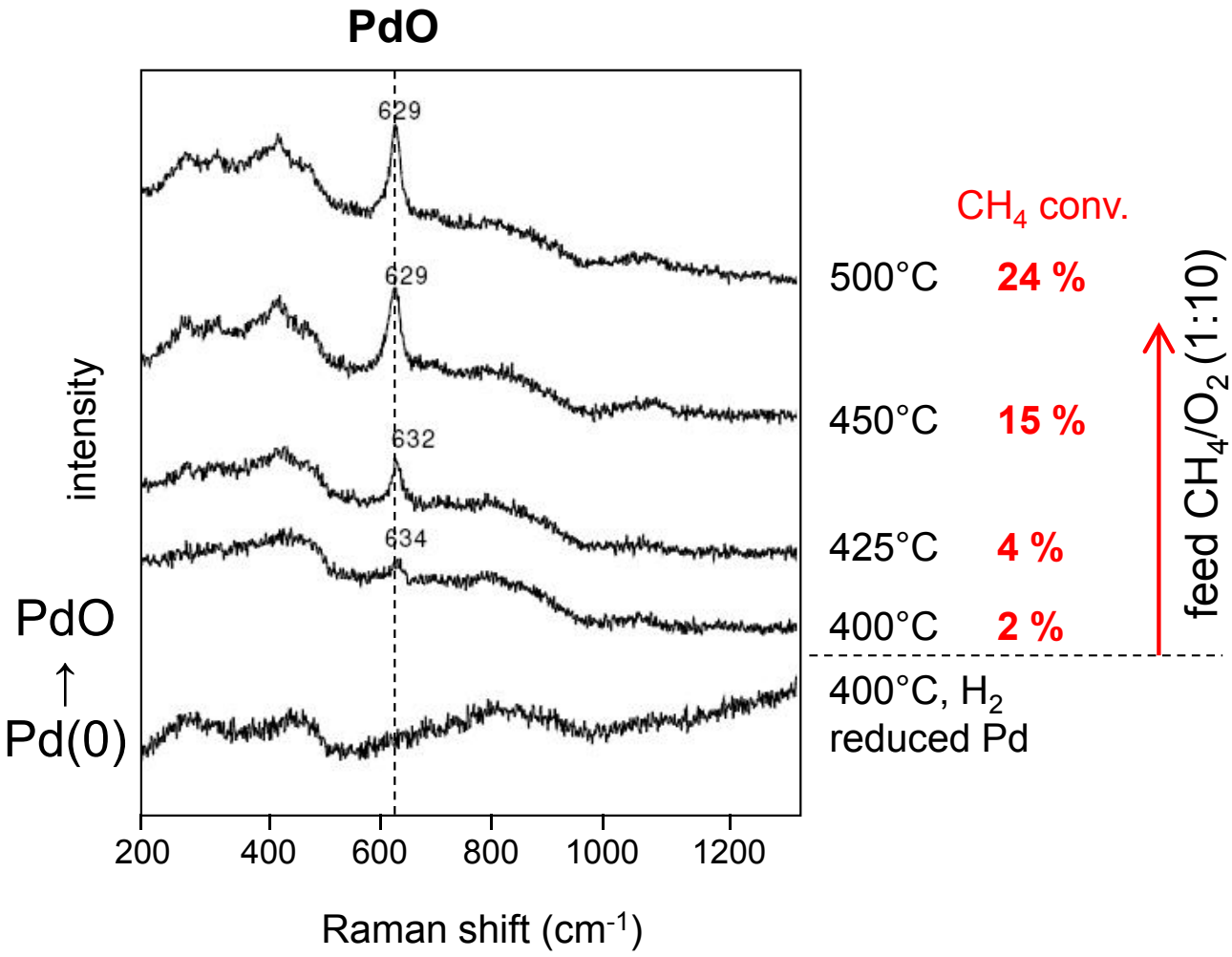


2 wt.% Pd/Al_2O_3, red. 400°C (3 h) + calcined 600°C (3 h)

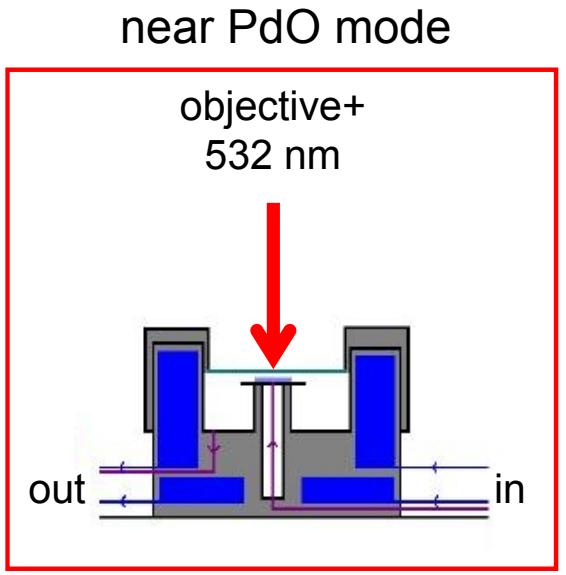
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/Al_2O_3



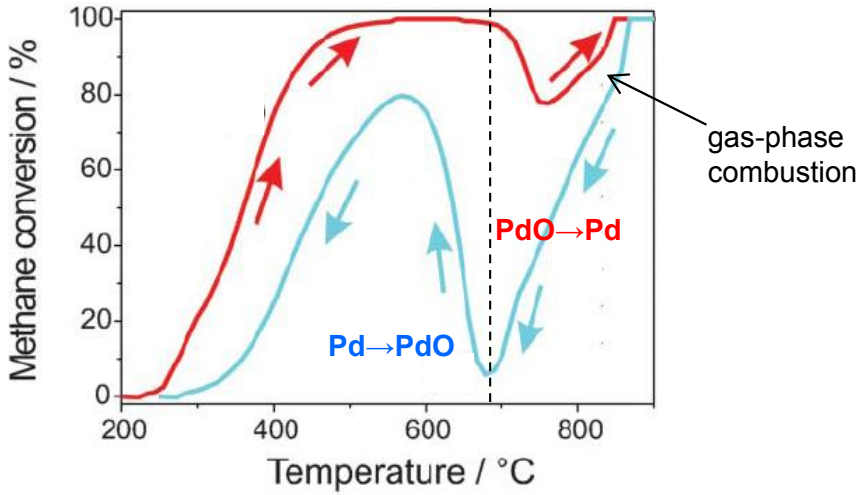
$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

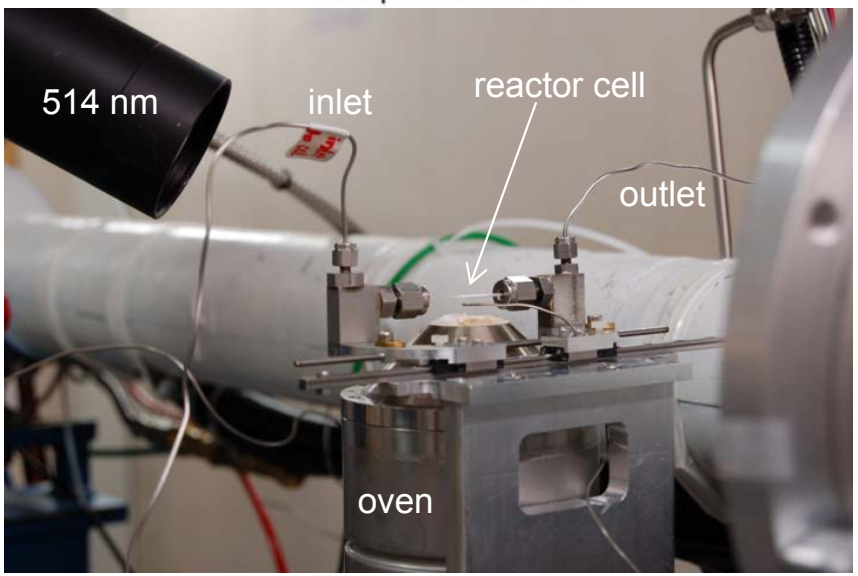


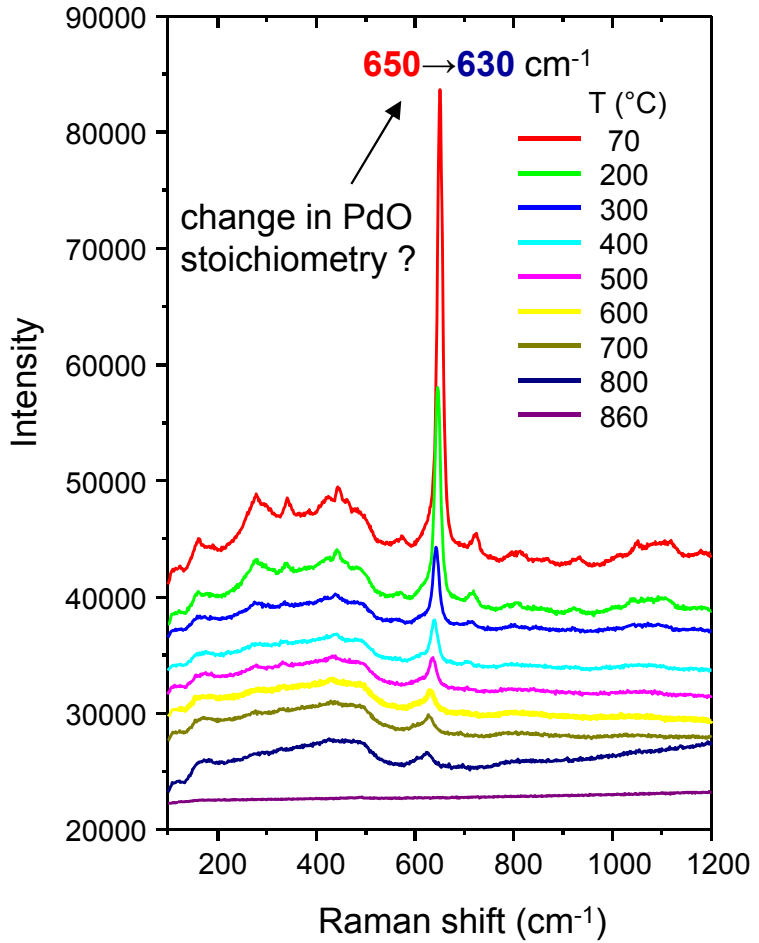
Demoulin et al., *PCCP* **5** (2003) 4394

Applications

- Resonance Raman – Methane oxidation over Pd/ZrO_2



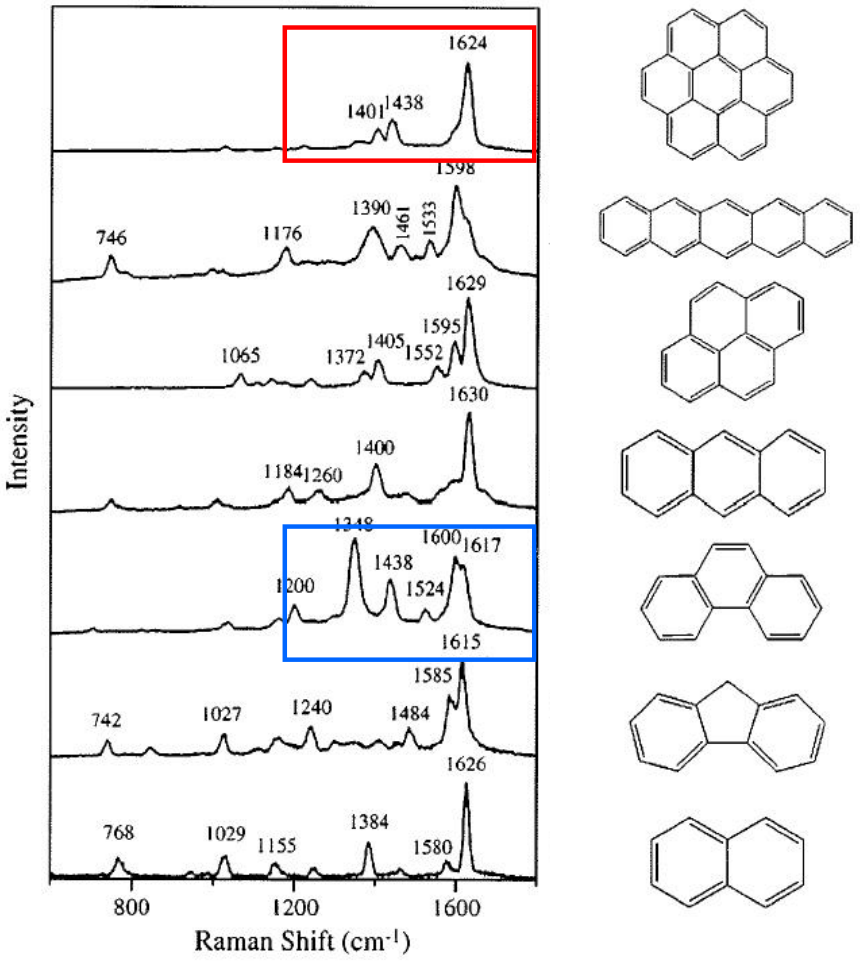


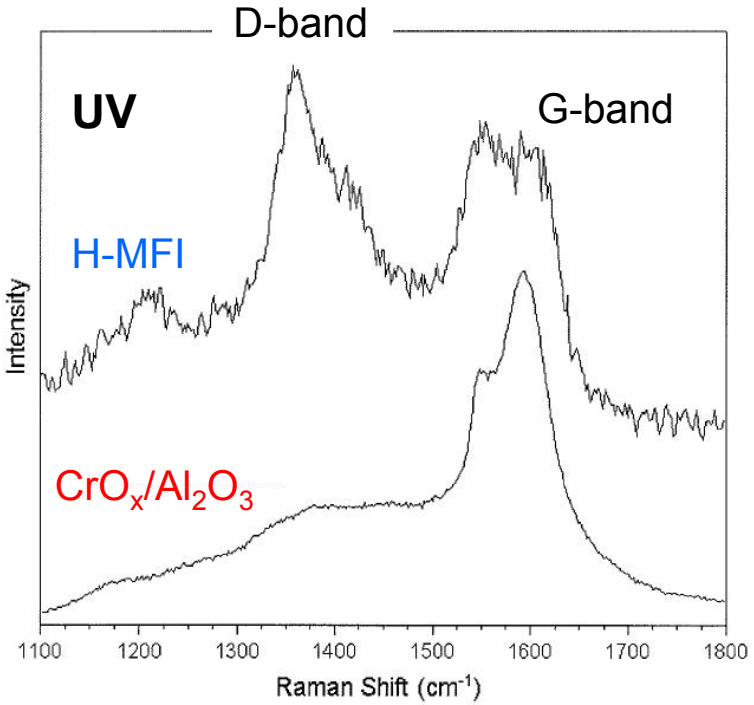


1 vol% CH_4/4 vol.% O_2/He
10 wt.% Pd/ZrO_2

Applications

- (Polyaromatic) Coke formation and characterization





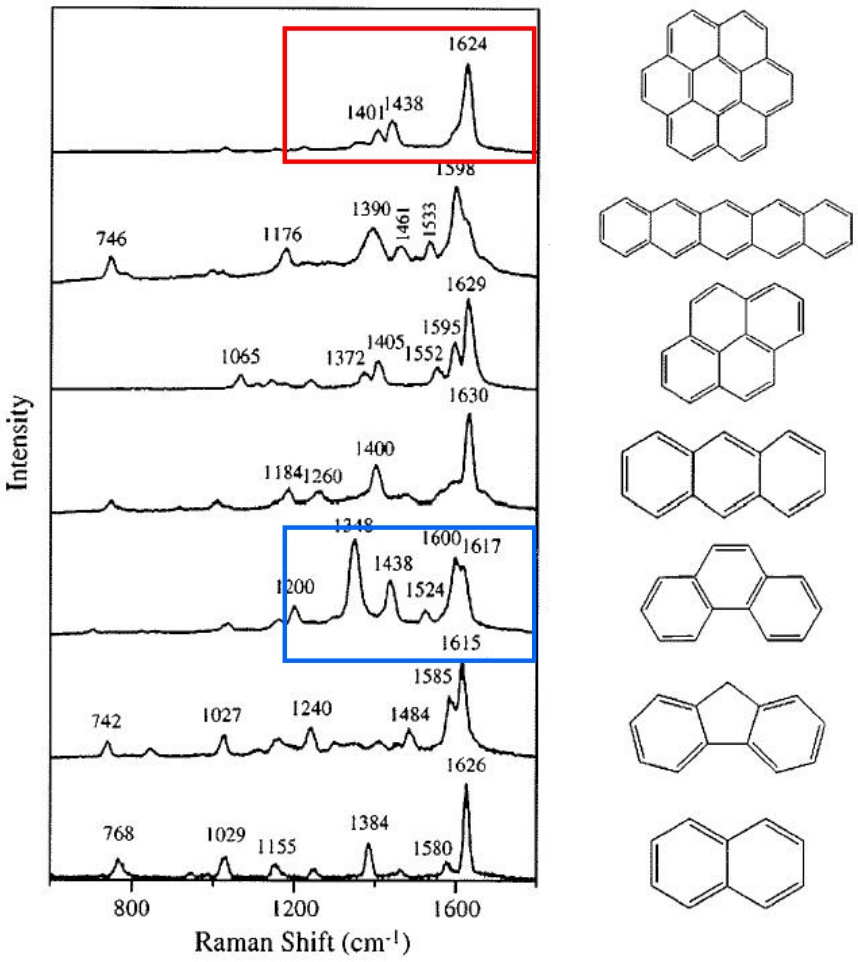
Coke classification
1D topology, chain-like
2D topology, sheet-like

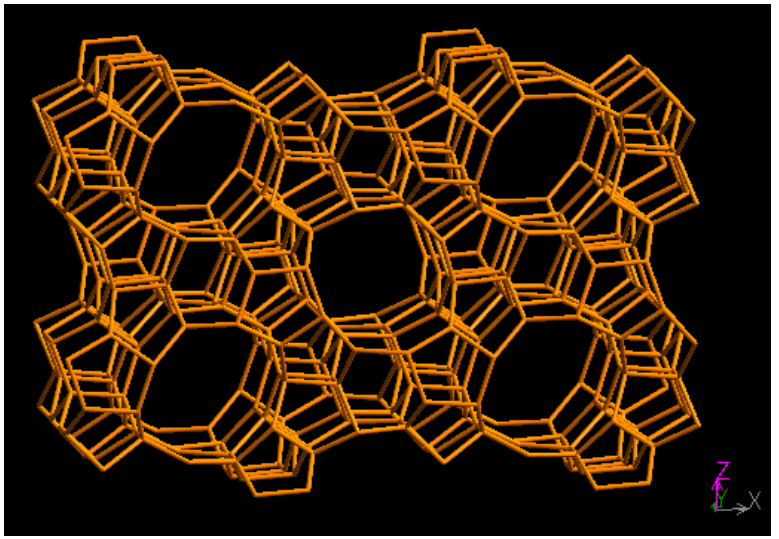
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

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

Applications

- (Polyaromatic) Coke formation and characterization





Coke classification
1D topology, chain-like
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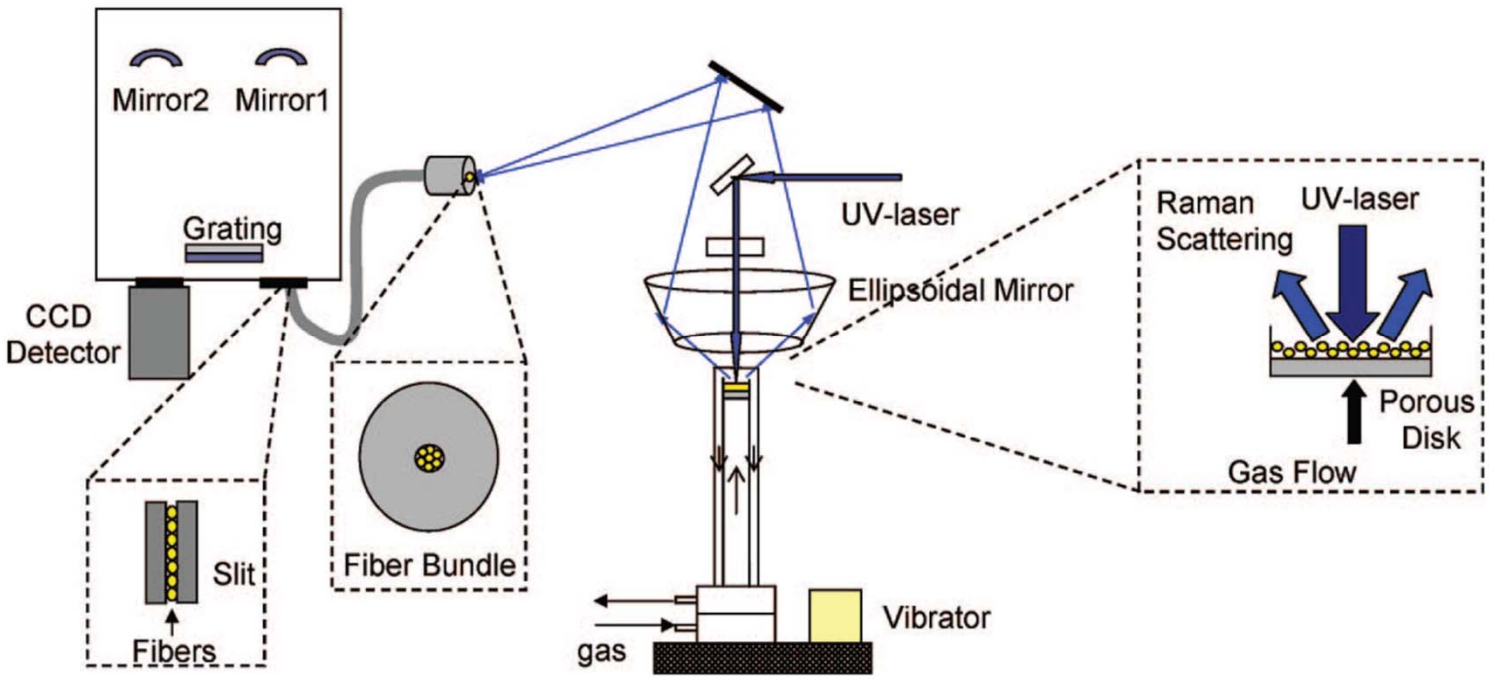
Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

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

Applications

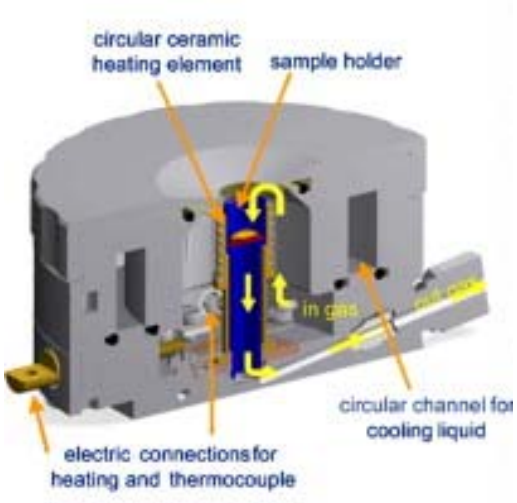
- Fluidized bed reactor cell

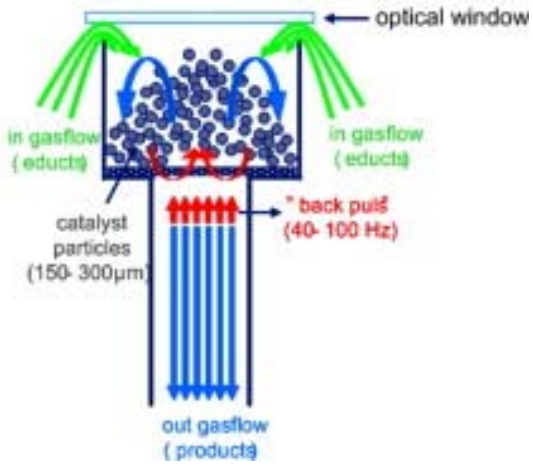


Chua et al., *J. Catal.* 196 (2000) 66

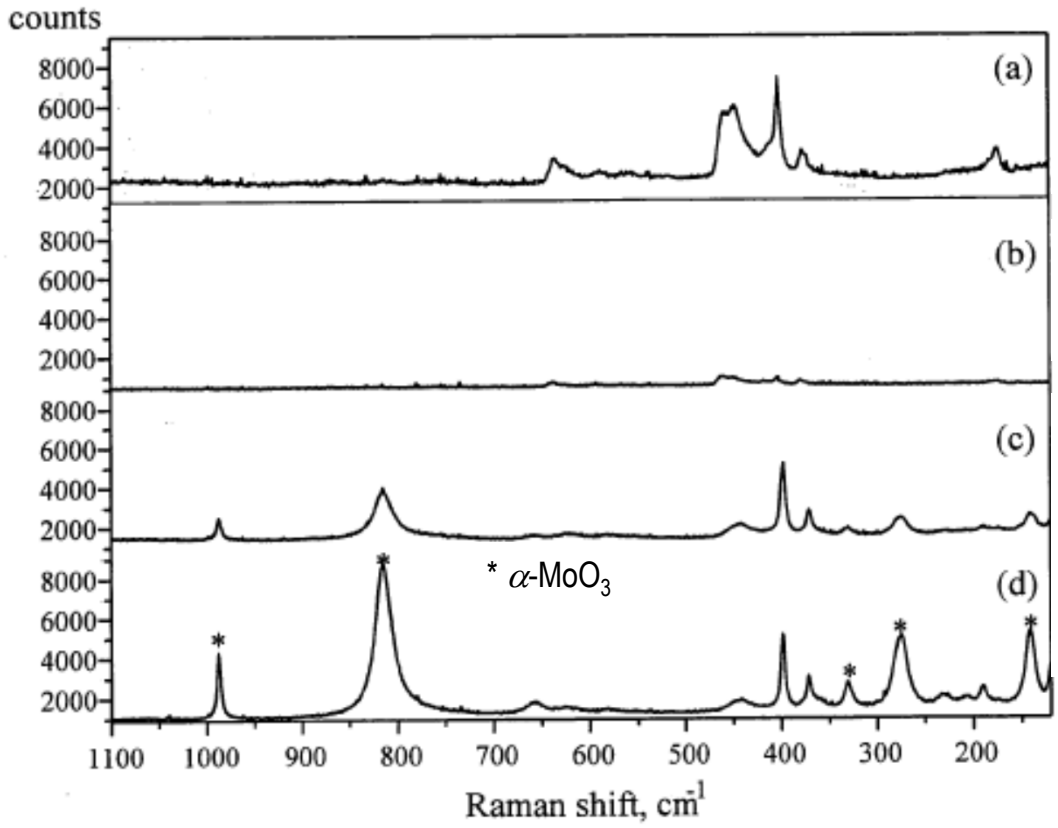
Applications

- 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

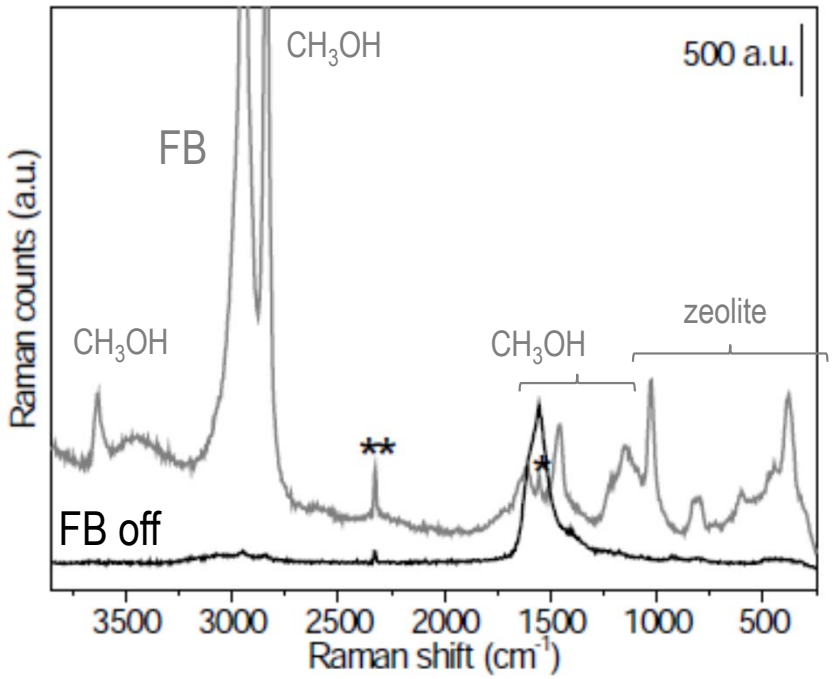
MoS_2, 6 min full power

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

Applications

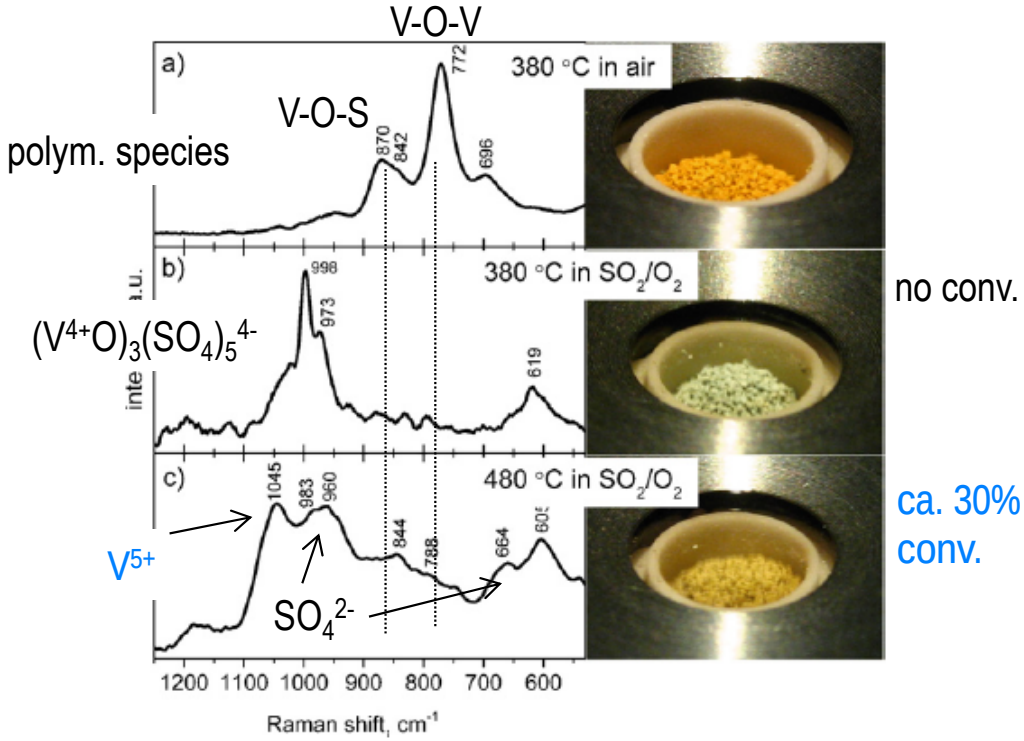
- Fluidized bed reactor cell

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

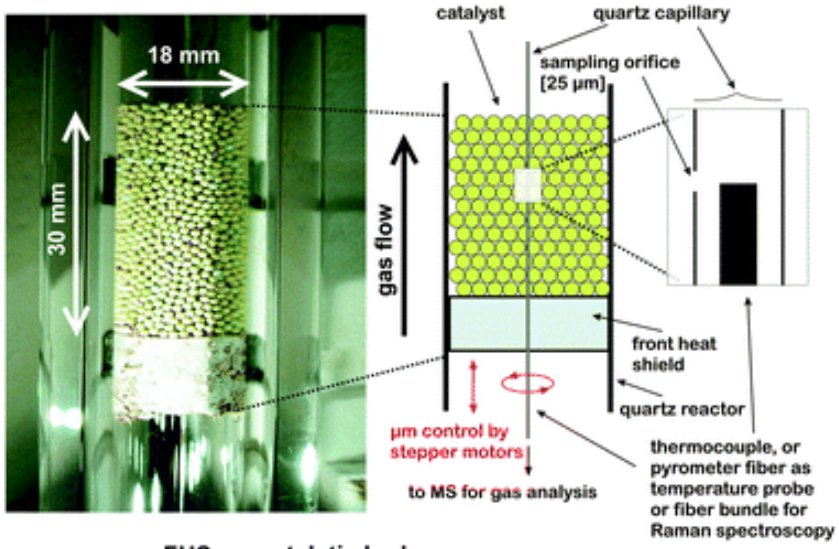


active species: mono- & dimeric V^{5+} oxosulfate species

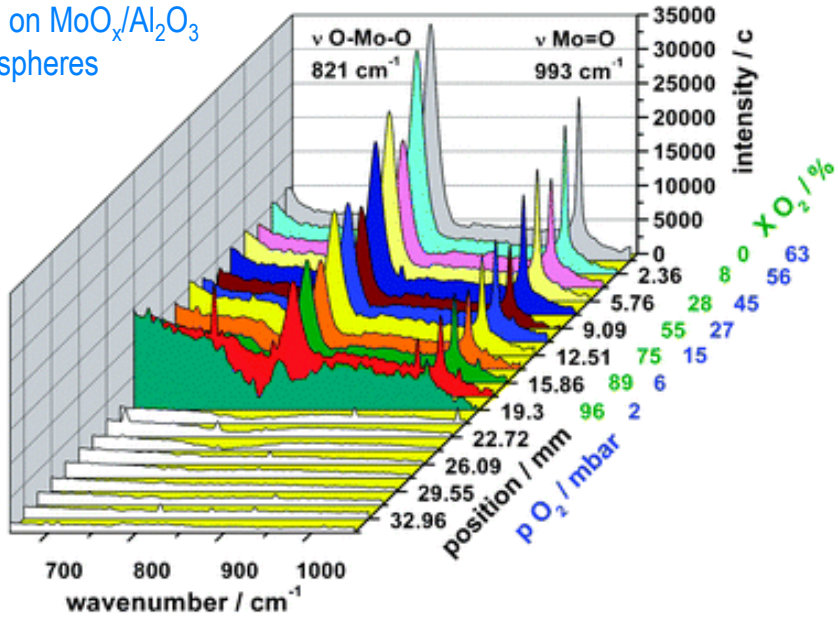
Beato et al., *Catal. Today* 205 (2013) 128

Applications

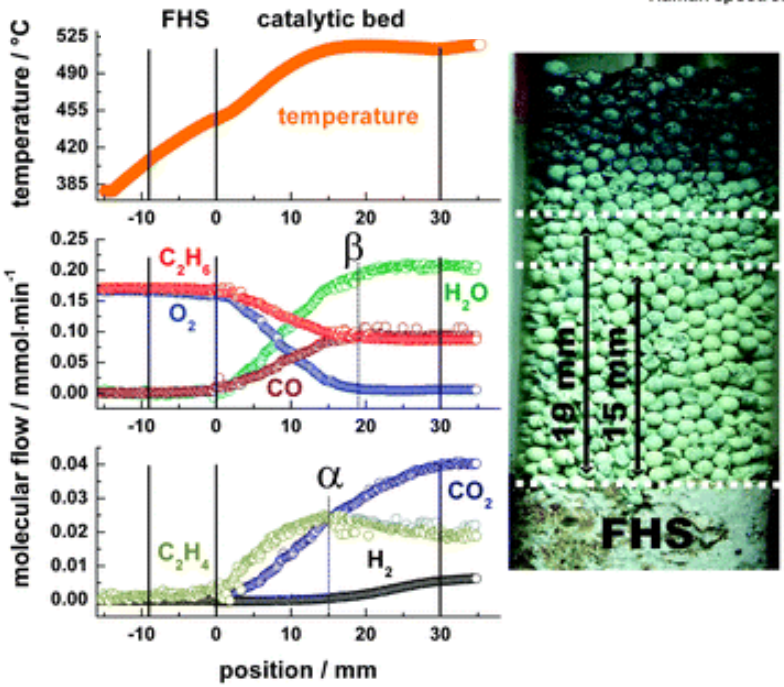
- Fixed bed reactor



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