Optical Spectroscopy

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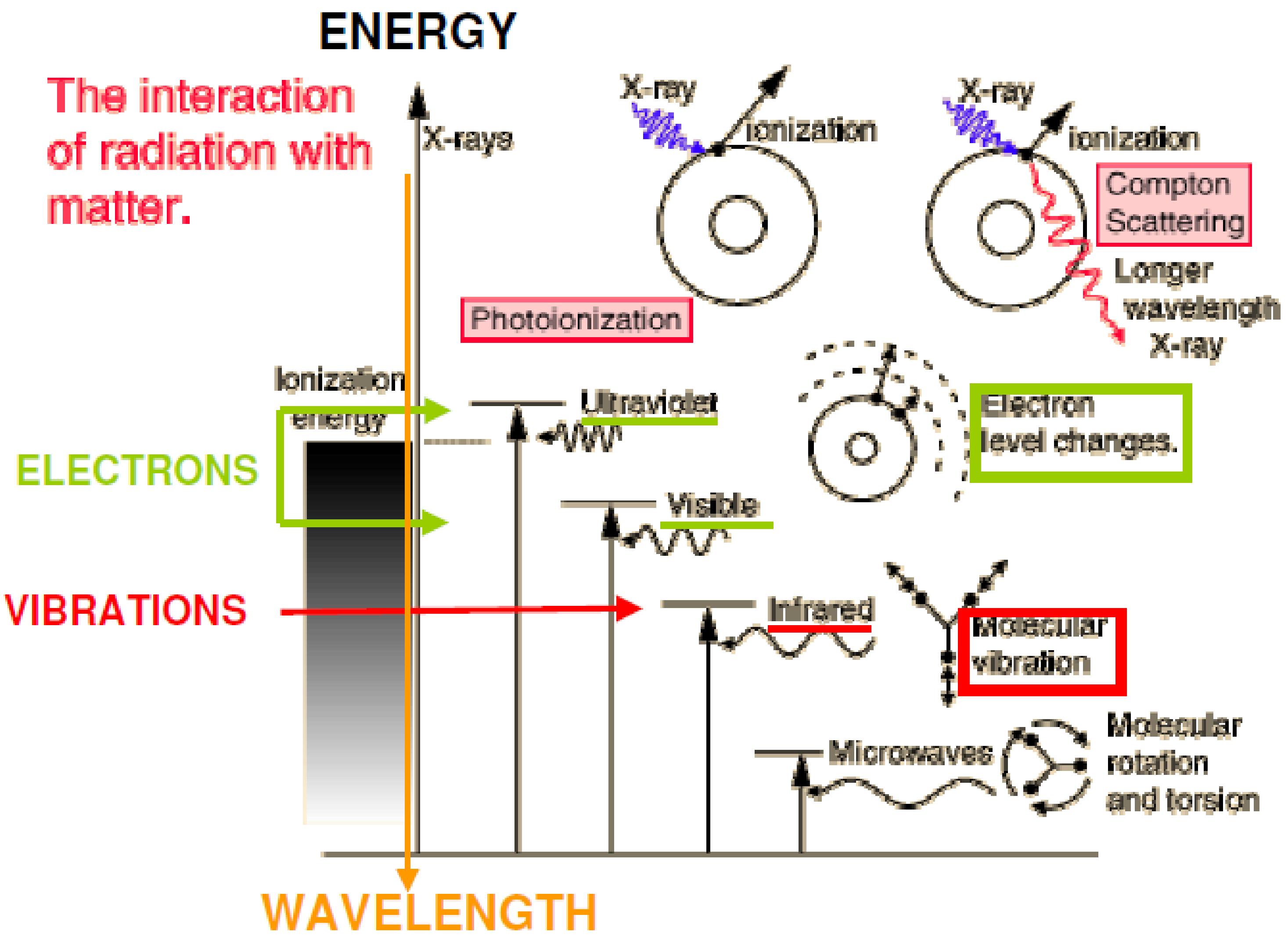
Interaction of EM Radiation with Matter



The interaction of radiation with matter.

Comparison of Catalyst Spectroscopic Methods

Spectroscopy	Temp./Pressure Limitations	Acquisition Time	Spatial Resolution	Molecular-level Information
LEIS	500°C/UHV	mins	150 nm	- - -
SIMS	500°C/UHV	mins	100 nm	YES
AES	500°C/UHV	mins	100 nm	- - -
XPS	500°C/mbar	mins	1 μm	- - -
HR-TEM	925 °C/mbar	0.5-mins	0.1 nm	- - -
EPR	500 °C/1 bar	mins	None	YES
NMR	325°C/several bar	min-hrs	Some	YES
STM	(conductor)/no press. limit	mins	0.1 nm	- - -
AFM	No temp/no press. limit	mins	30 nm	
IR	500 °C/no press. Limit	msec	10 μm	YES
UV/Vis	1500 °C/no press. limit	msec	10 μm	YES
Raman	1500 °C/no press. limit	~1 sec	1 μm	YES
EXAFS/XANES	925°C/no press. limit	min/msec	mm	- - -
XRD	1500°C/no press. limit	min	mm	- - -

IR Spectroscopy

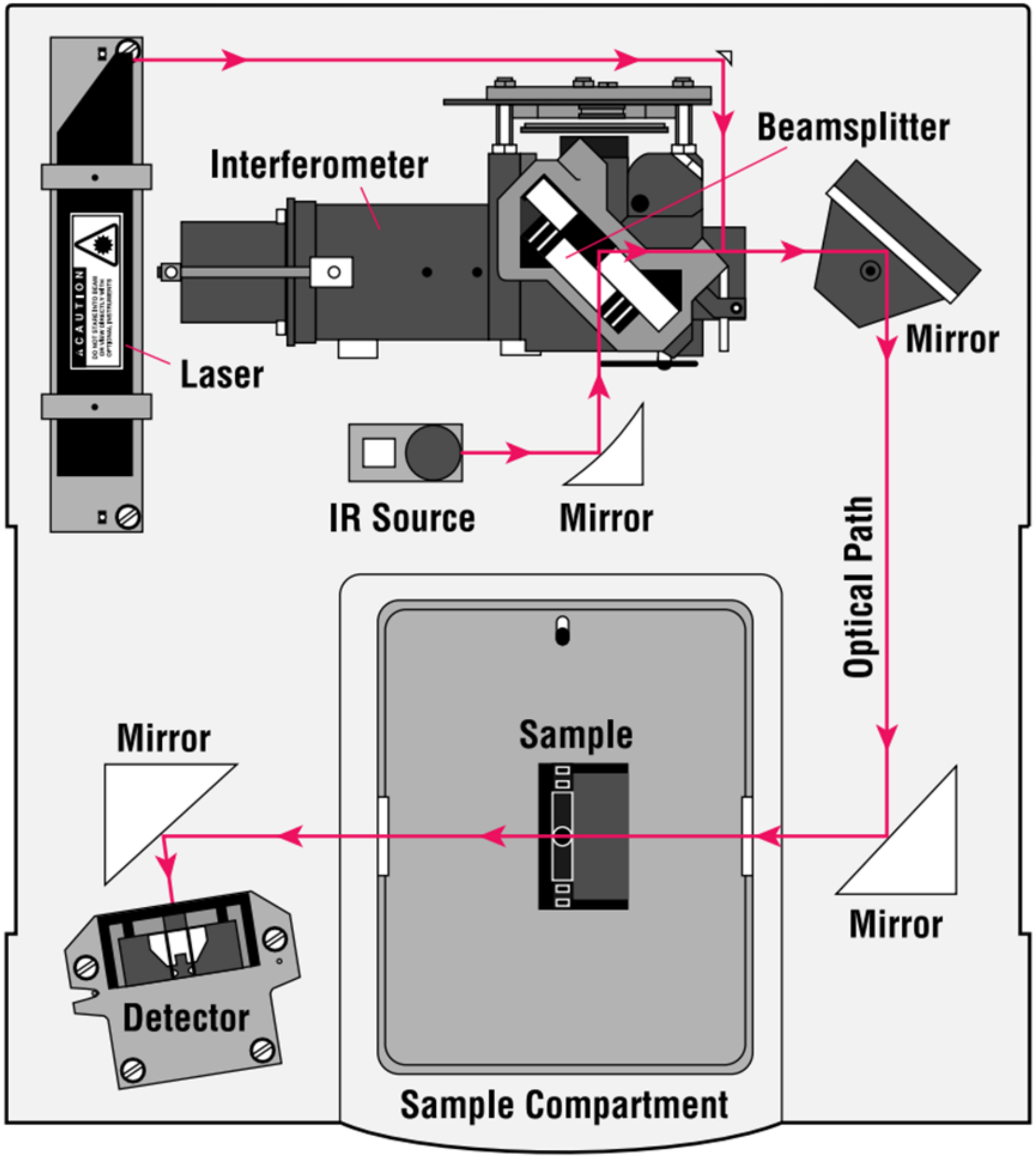
- Vibrations related to symmetry of molecule

- Only vibrations with a change in dipolar moment are IR-active (**asymmetric** vibrations; symmetric vibrations also present if regular symmetry is broken)

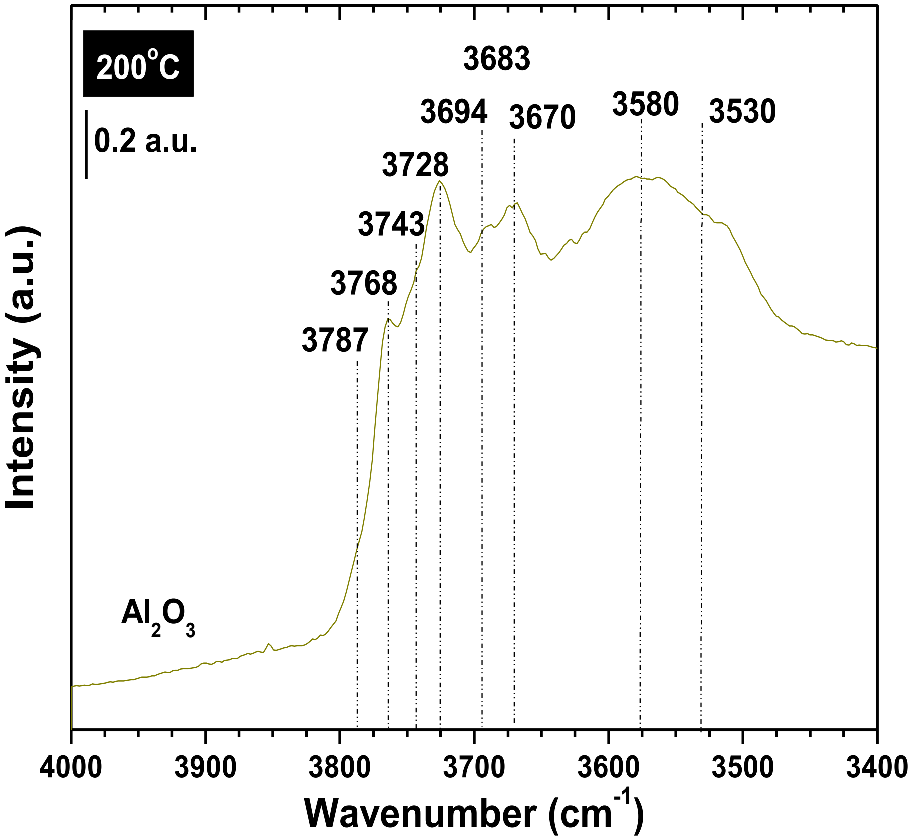
- IR is a *bulk* technique, but is also able to detect *surface* vibrations (**M-OH**, M=O, **adsorbed molecules** and **surface intermediates**)

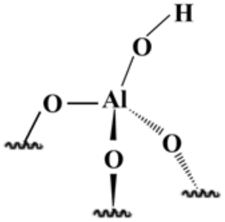
- Molecular nature of IR spectroscopy makes this a very powerful technique (esp. at high T and P)

Typical IR Spectrometer

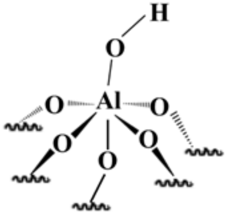


Surface Hydroxyls Present on Al_2O_3

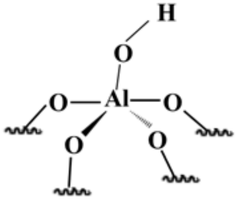




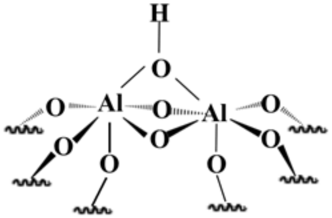
HO-μ_1-Al_{IV}
(3785-3800 cm^{-1})



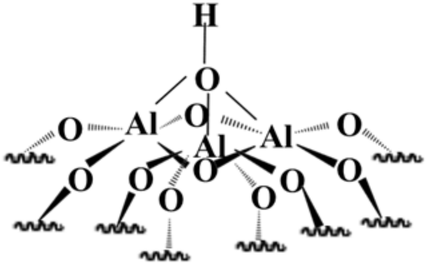
HO-μ_1-Al_{VI}
(3760-3780 cm^{-1})



HO-μ_1-Al_V
(3730-3735 cm^{-1})



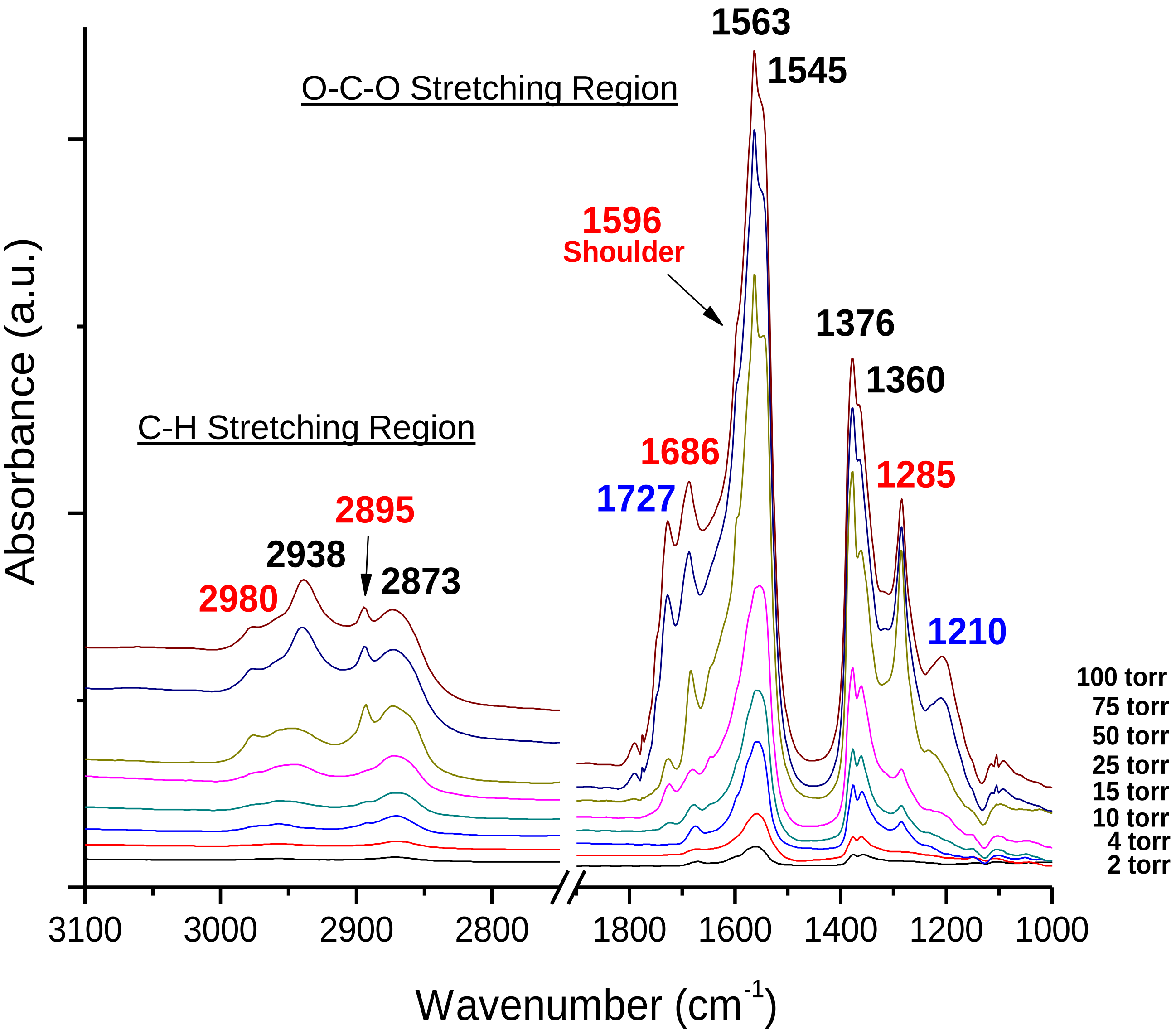
HO-μ_2-Al_{VI}
(3690-3710 cm^{-1})



HO-μ_3-Al_{VI} (3590-3650 cm^{-1})

Digne, M.; Sautet, P.; Raybaud, P.; Euzen, P.; Toulhoat, H. J. Catal. 2002, 211, 1-5.
Digne, M.; Sautet, P.; Raybaud, P.; Euzen, P.; Toulhoat, H. J. Catal. 2004, 226, 54-68.
Coperet, C. Pure Appl. Chem. 2009, 81, 585-896.

HCOOH Adsorption on Fe_2O_3 (@ T = 100ºC)



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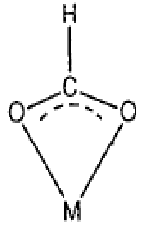
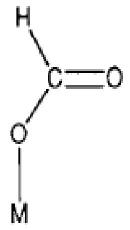


Bidentate

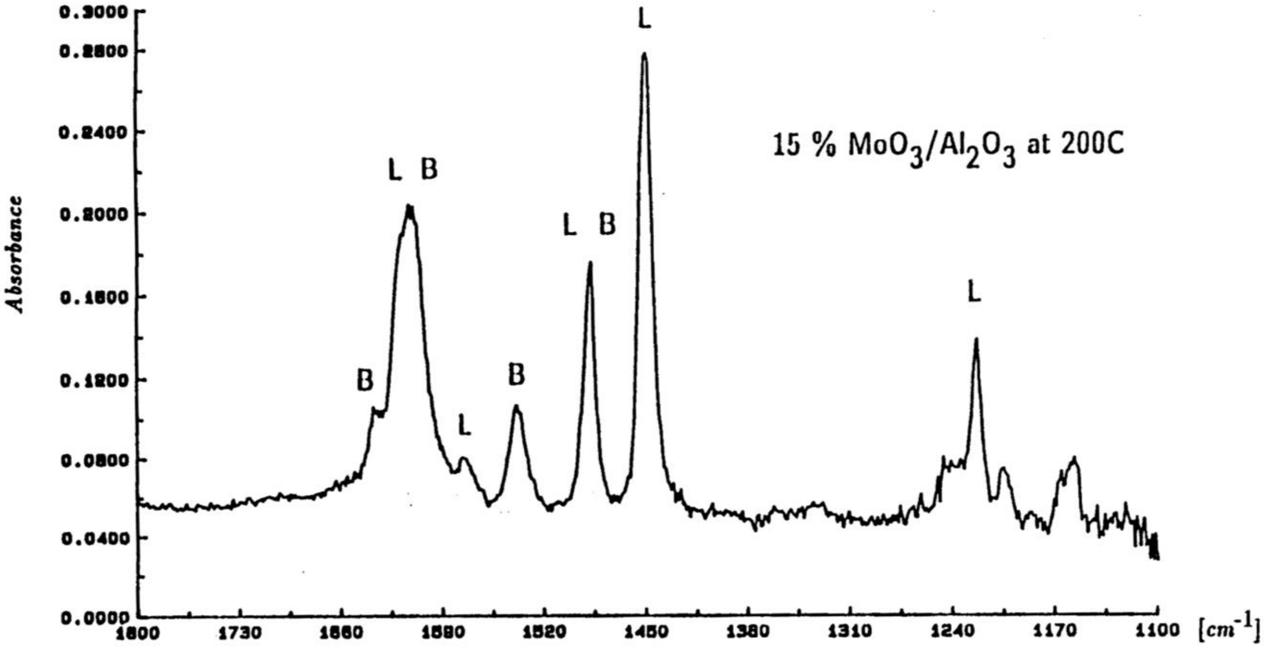
🟥 =



Monodentate

🟦 = **Molecularly Adsorbed HCOOH**

Bronsted and Lewis Surface Acid Sites

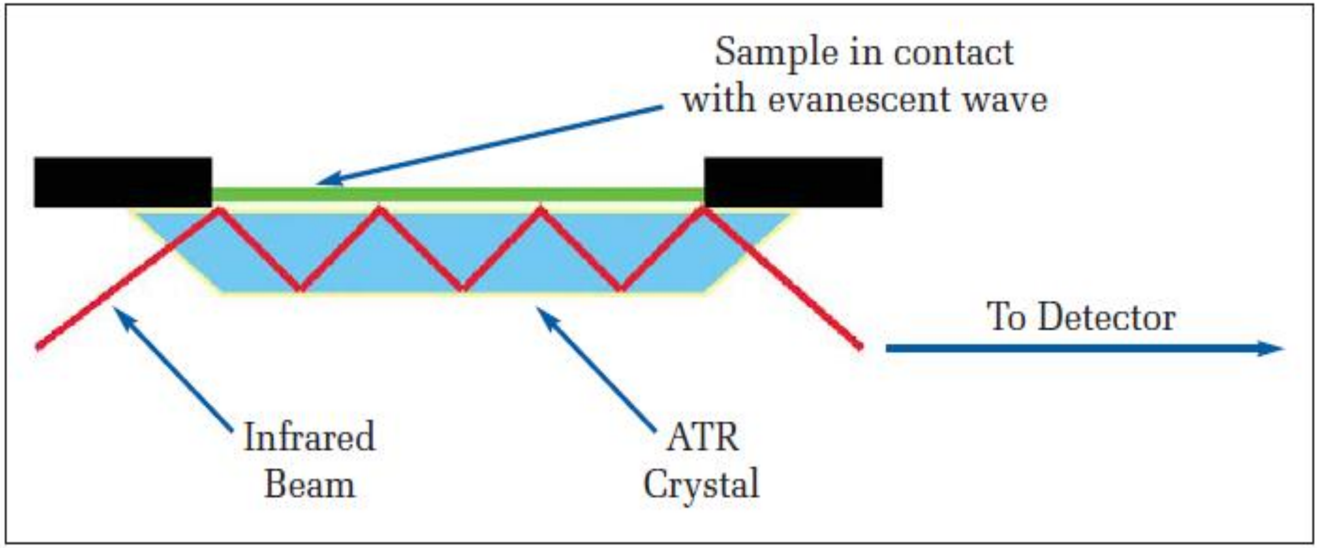


Typical FTIR absorption spectrum of pyridine adsorbed on an alumina supported metal oxide catalyst.

B - Characteristic absorption bands of the pyridinium ion PyH^+ chemisorbed to a Bronsted acid surface site appear at: 1490, 1540, 1620, 1640 cm^{-1}.

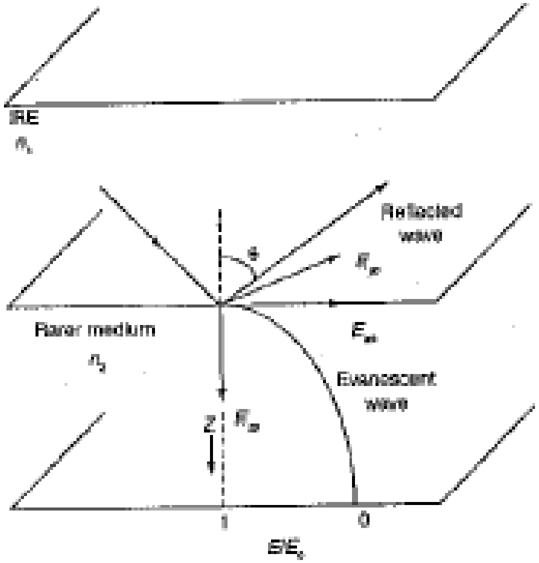
L - Characteristic absorption bands for coordinatively adsorbed pyridine (a Lewis acid surface site) appear at: 1220, 1450, 1490, 1580, 1600-1630 cm^{-1}.

ATR FT-IR Spectroscopy

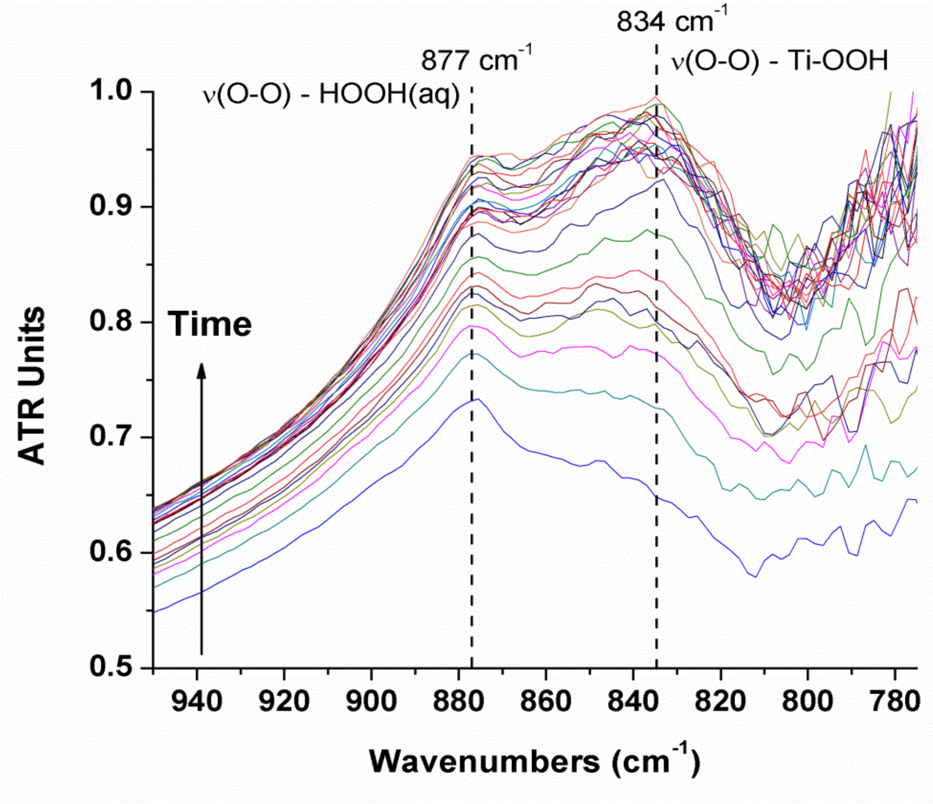


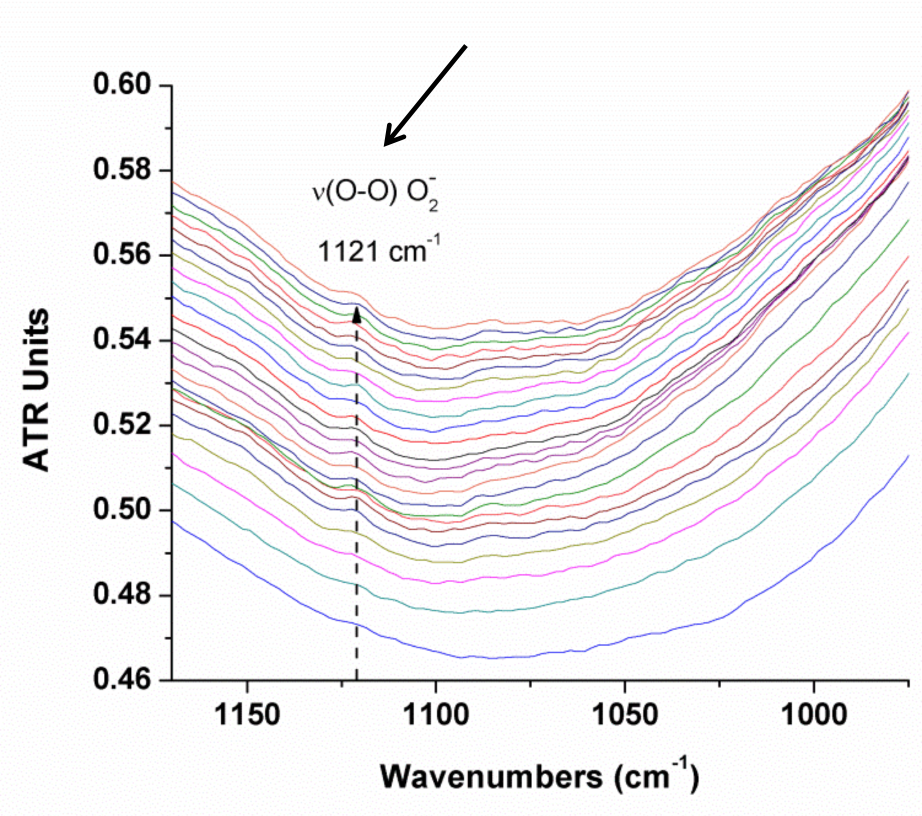
- Multiple reflections can be used depending on crystal type and shape
- The reflections are averaged into a single spectrum
- More reflections = greater sensitivity

- Uses phenomenon that occurs with light at the boundary between two media of different refractive indices.
- At an angle of incidence greater than the critical angle of the material, light is completely reflected.
- However, some energy penetrates the boundary: evanescent wave.
- The material at the boundary absorbs energy from the wave
- The absorbed energy is used to construct a spectrum.



Surface Ti-OOH Species Form on TiO_2 Upon Exposure to Aqueous HOOH





- Trace of surface superoxo $(O_2)^-$ species also present on TiO_2.

Raman Spectroscopy

- Vibrations related to symmetry of molecule

- Only vibrations with a change in electron polarizability are Raman-active (**symmetric** and anti-symmetric vibrations)

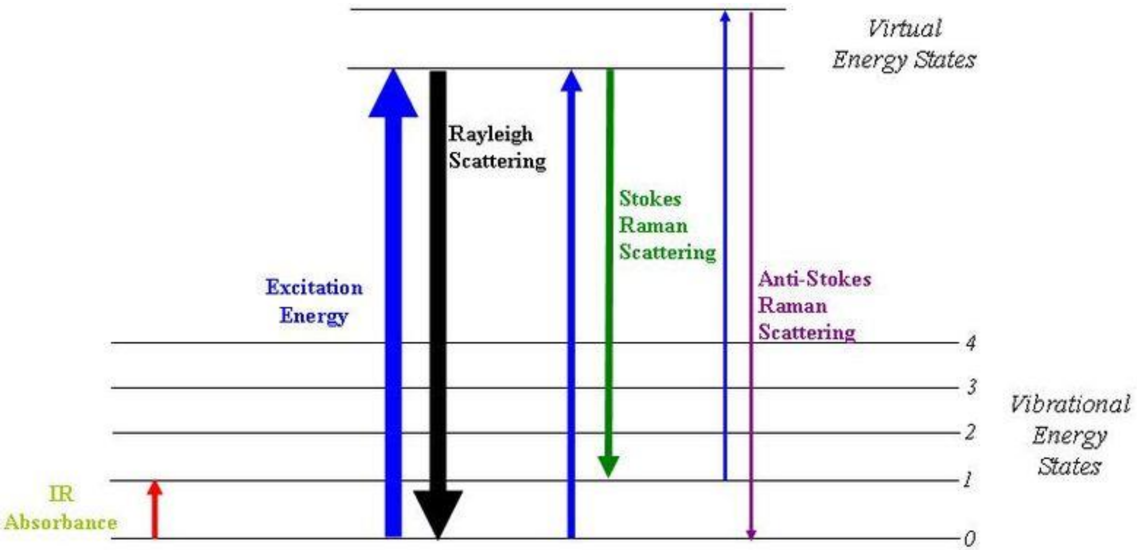
- Raman is a *bulk* technique, but is also able to detect *surface* vibrations (**M=O**, M-OH, adsorbed molecules and surface intermediates)

- Crystalline metal oxide phases give rise to much stronger Raman bands than surface metal oxide species

- Molecular nature of Raman spectroscopy makes this a very powerful technique (esp. at high T & P)

Raman Scattering

- **Discovered by Sir C.V. Raman**

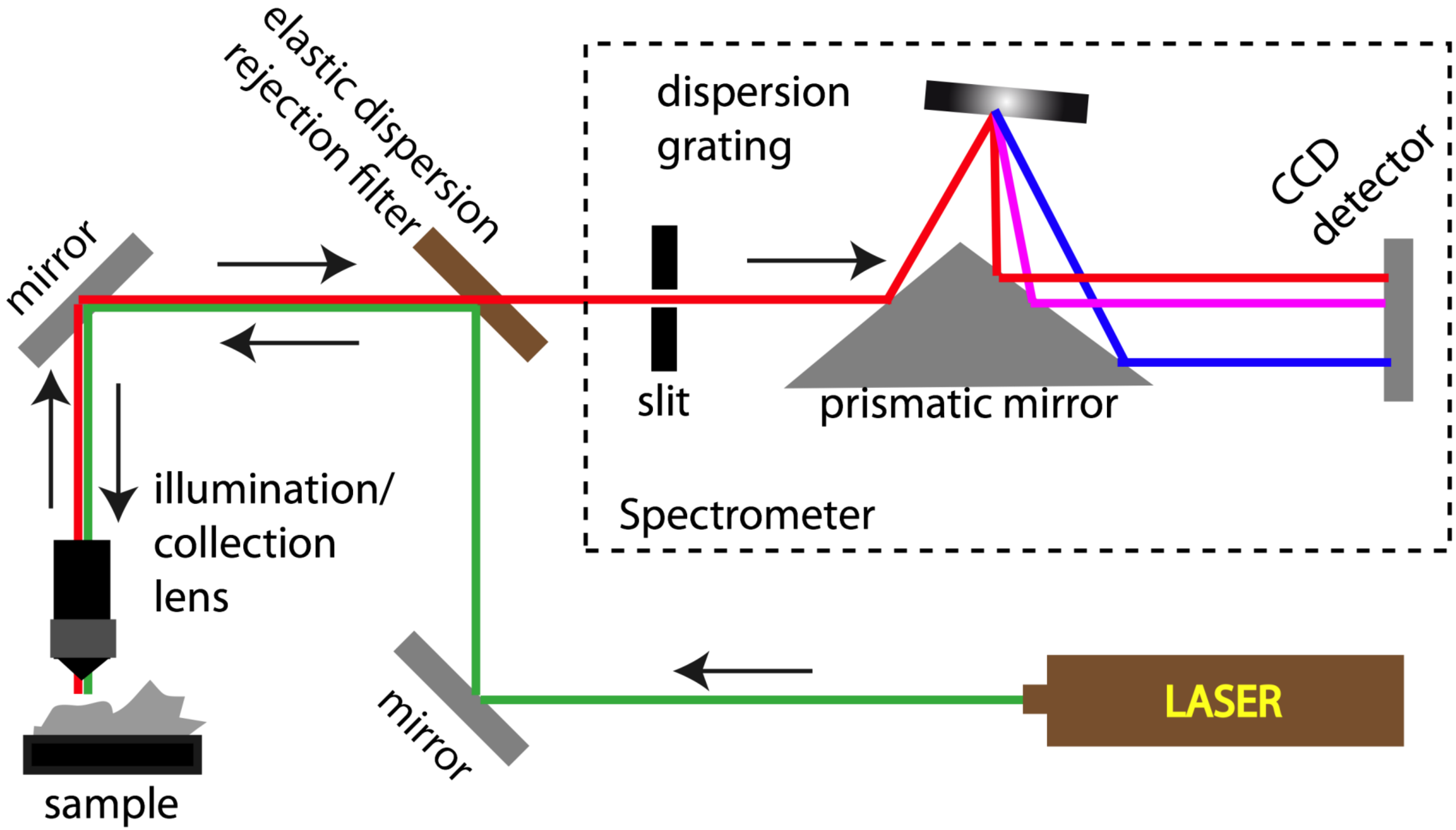


This Month in Physics History

February 1928: Raman scattering discovered

C.V. Raman

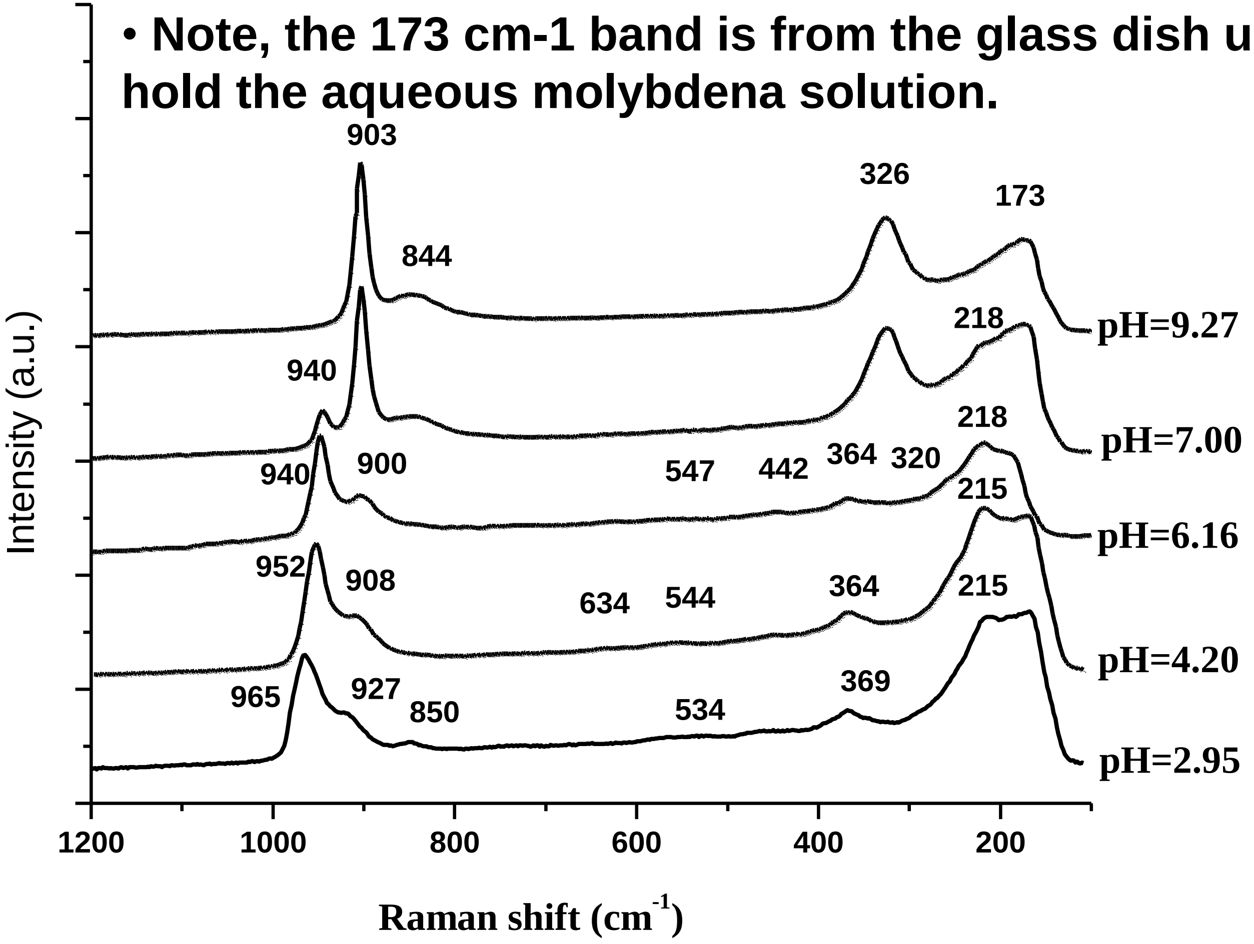
Typical Raman Spectrometer



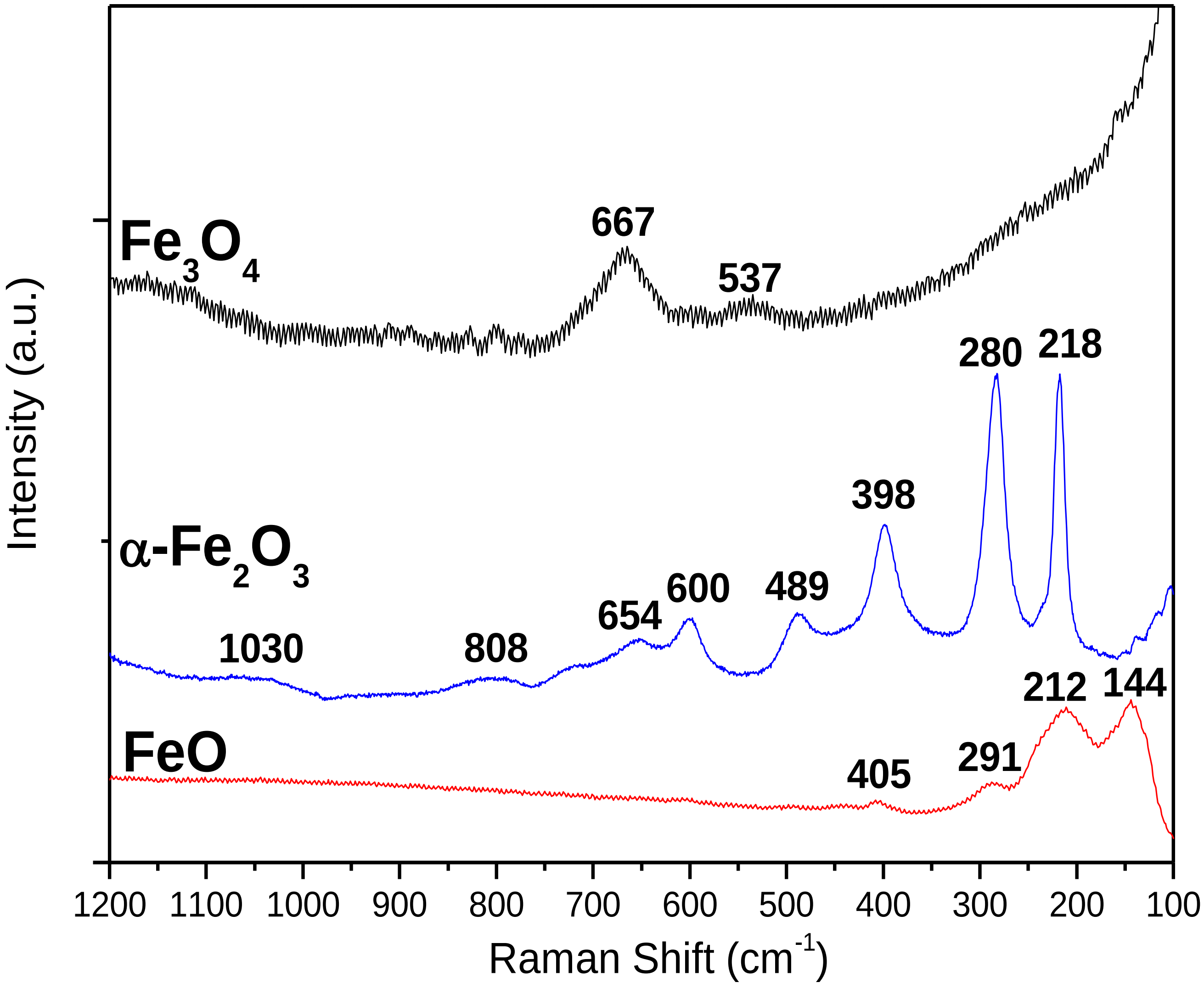
Raman Spectra of Aqueous Molybdenum Oxide Solution

- Raman spectra of aqueous 0.2M (NH4)6Mo7O24 solutions as a function of solution pH.

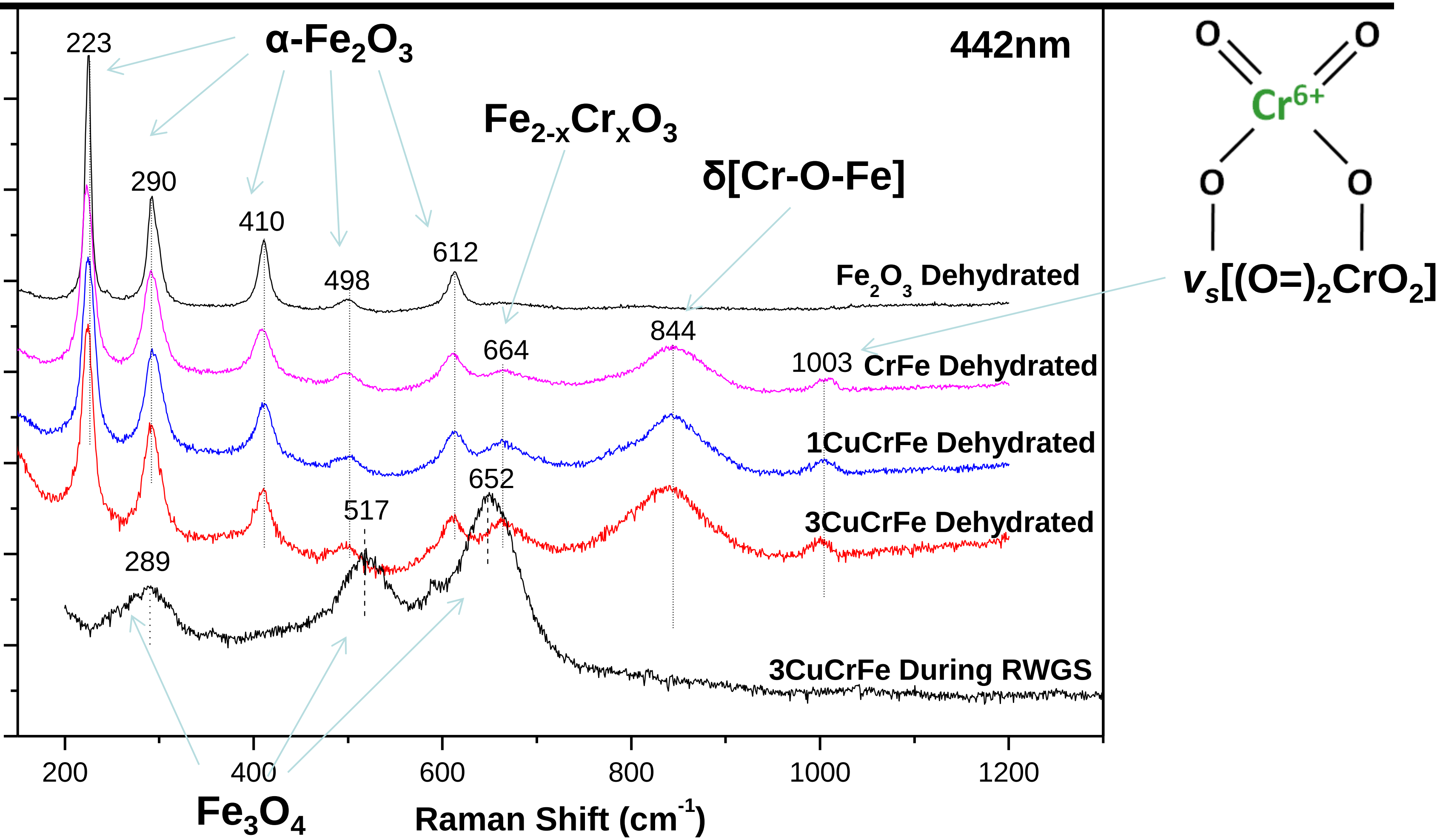
- Note, the 173 cm-1 band is from the glass dish used to hold the aqueous molybdena solution.



Raman Spectroscopy Discriminates Between Different FeOx Phases



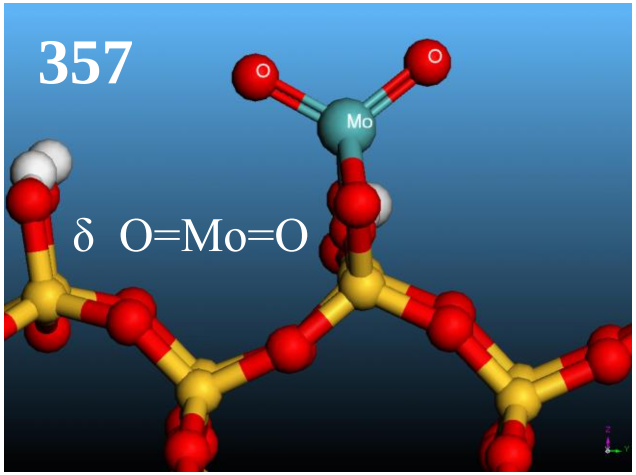
Bulk FeOx Phase Transforms during HT-RWGS



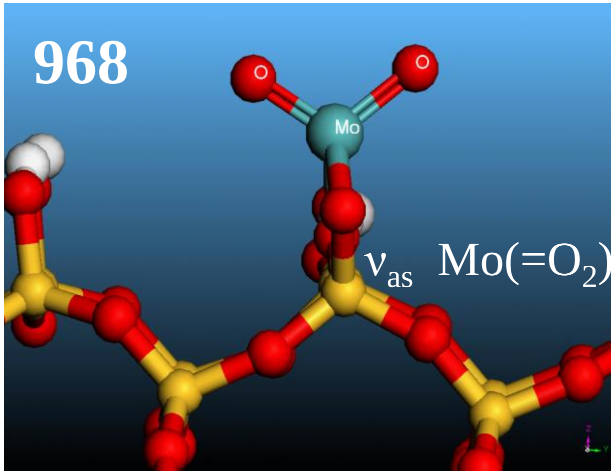
- **Surface dioxo $(O=)_2CrO_2$ species reduce during HT-WGS**

Vibrational modes of Mo oxo species

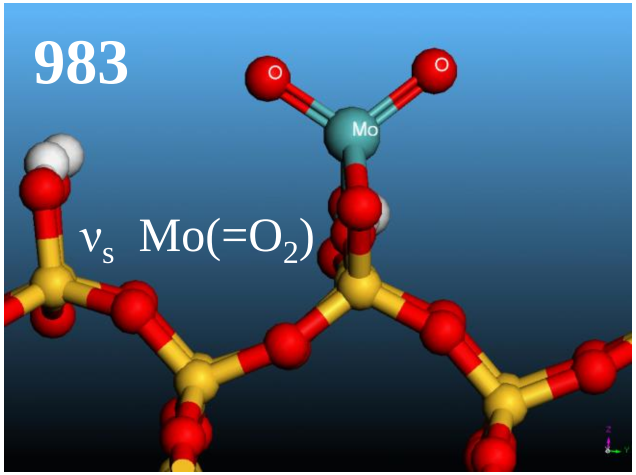
Dioxo $(O=)_2MoO_2$


357

δ O=Mo=O

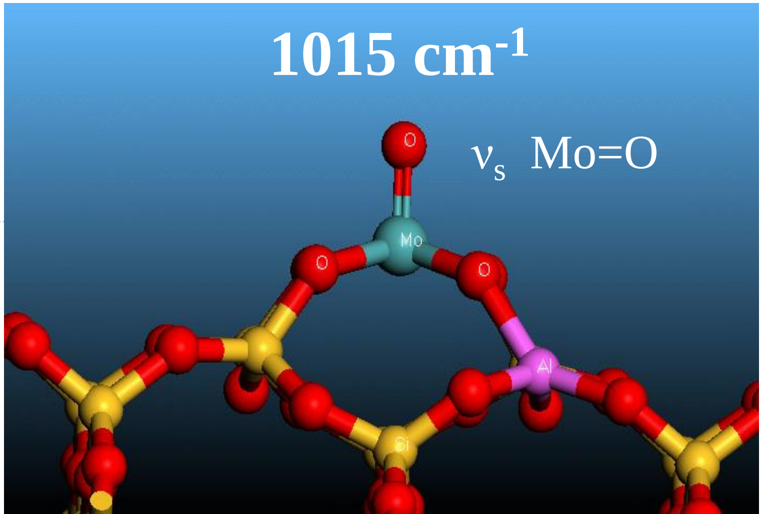

968

ν_{as} $Mo(=O_2)$


983

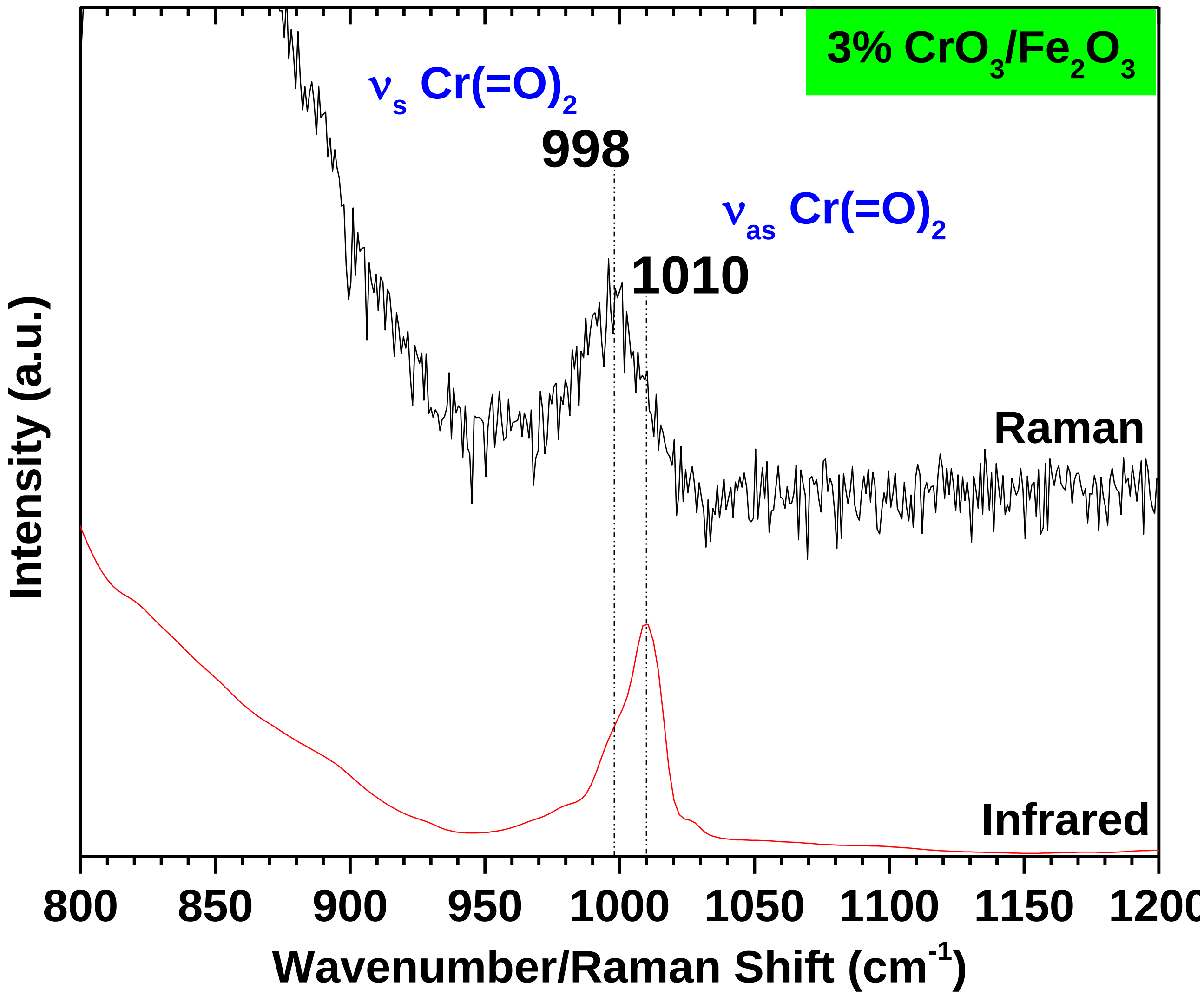
ν_s $Mo(=O_2)$

Mono-oxo $O=MoO_4$


1015 cm^{-1}

ν_s Mo=O

Surface **DIOXO** $(O=)_2Cr(-O)_2$ Species Present on Fe_2O_3



UV-vis DRS

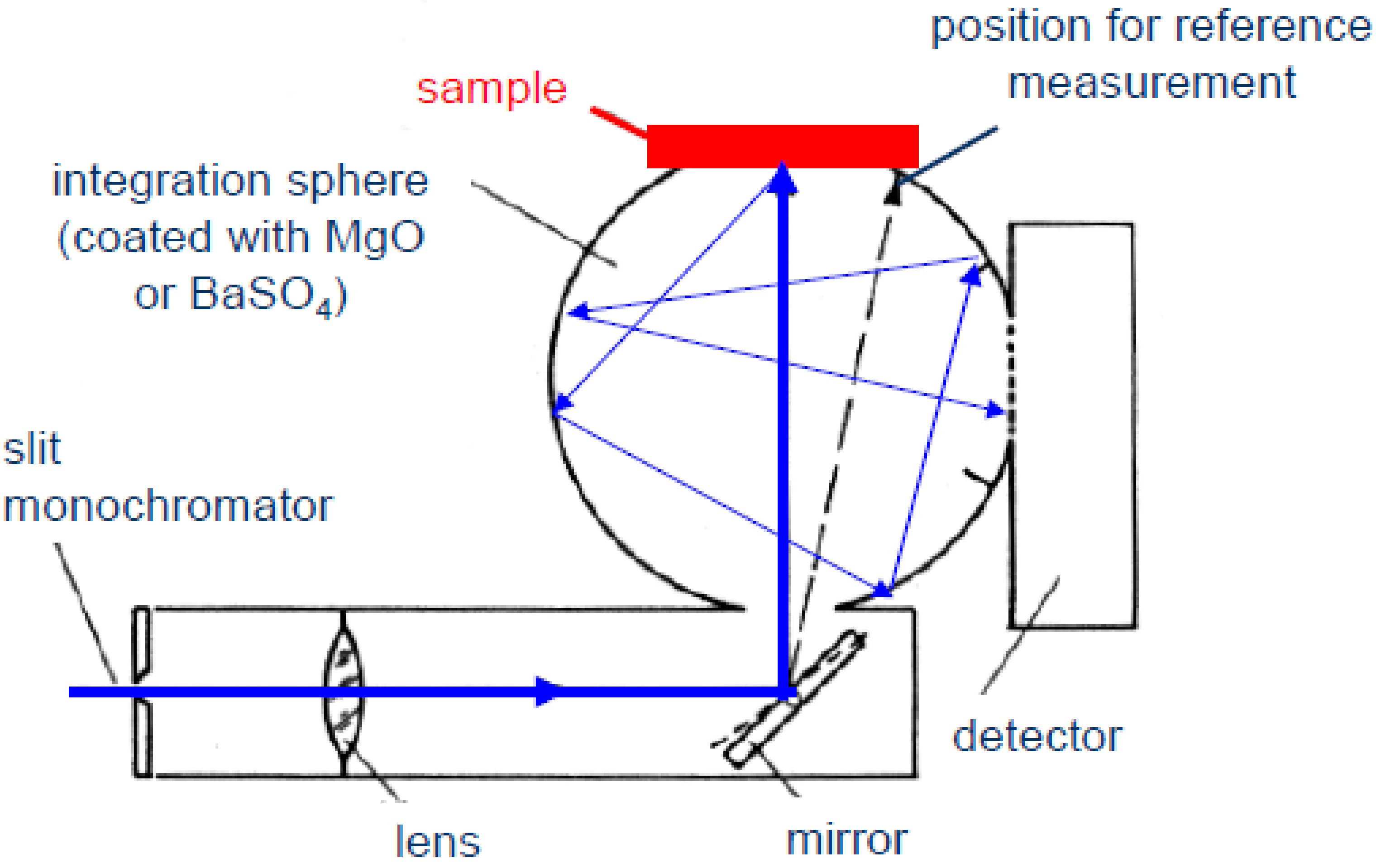
- UV-vis detects electronic transitions

- CT (M=O) transitions correspond to transition metal ions in highest oxidation state
  - → MOx **domain size** and coordination
  - → MOx dispersion

- d-d transitions correspond to reduced transition metal ions → MOx coordination

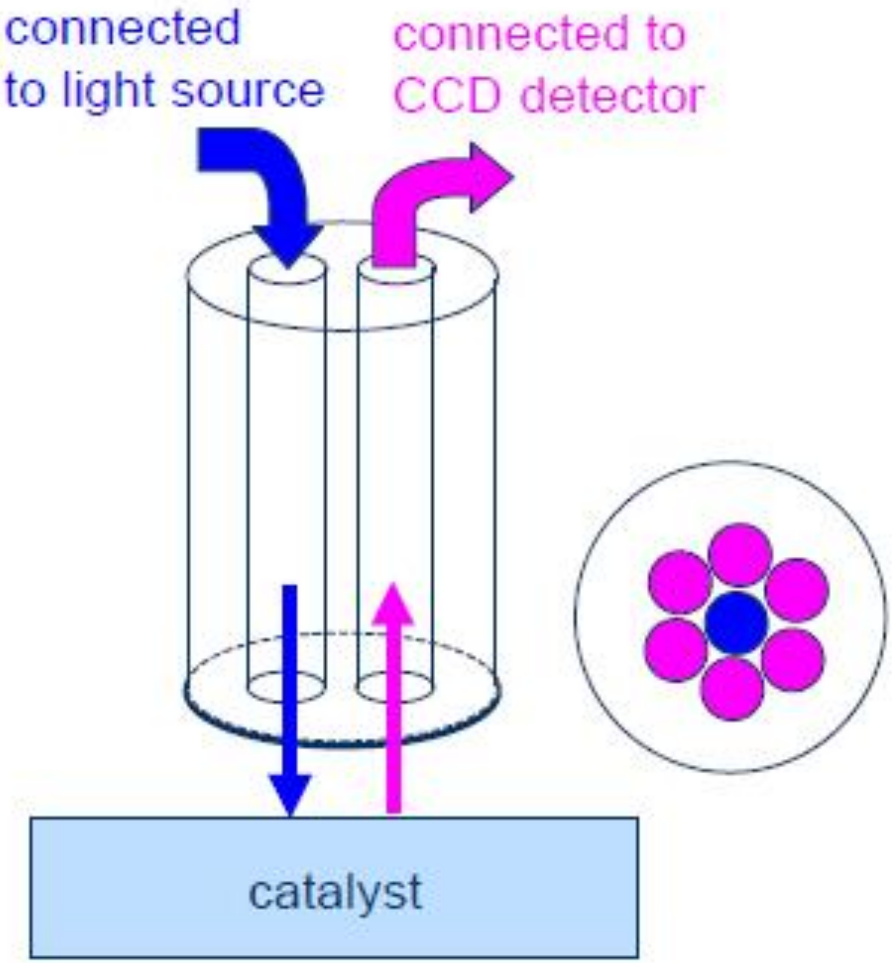
- UV-vis generally quantitative at low transition metal ion concentrations (sensitive to low concentrations)

UV-vis DRS Integration Sphere



Advantage ➡ higher fraction of reflected light reaches detector

UV-vis Fiber Optic Probe



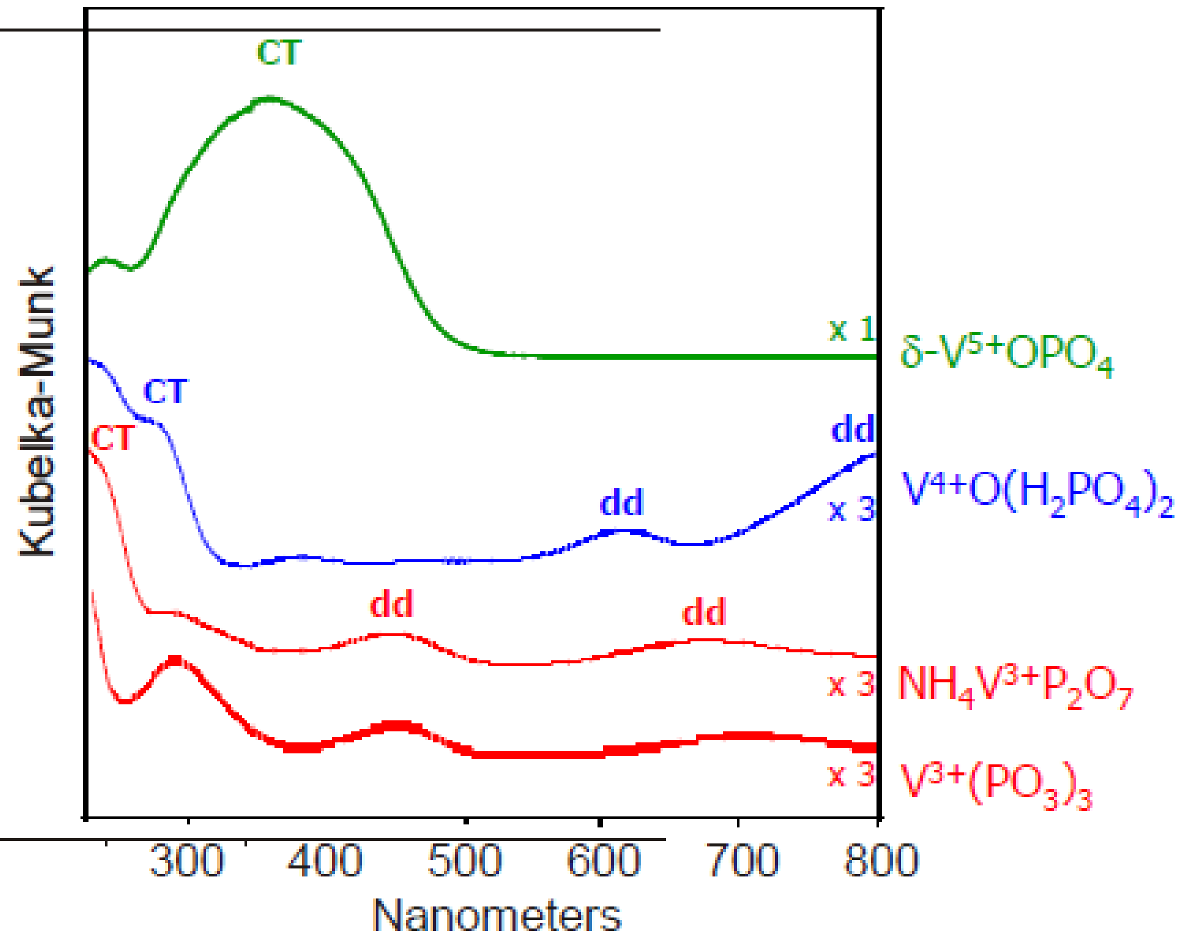
connected
to light source

connected to
CCD detector

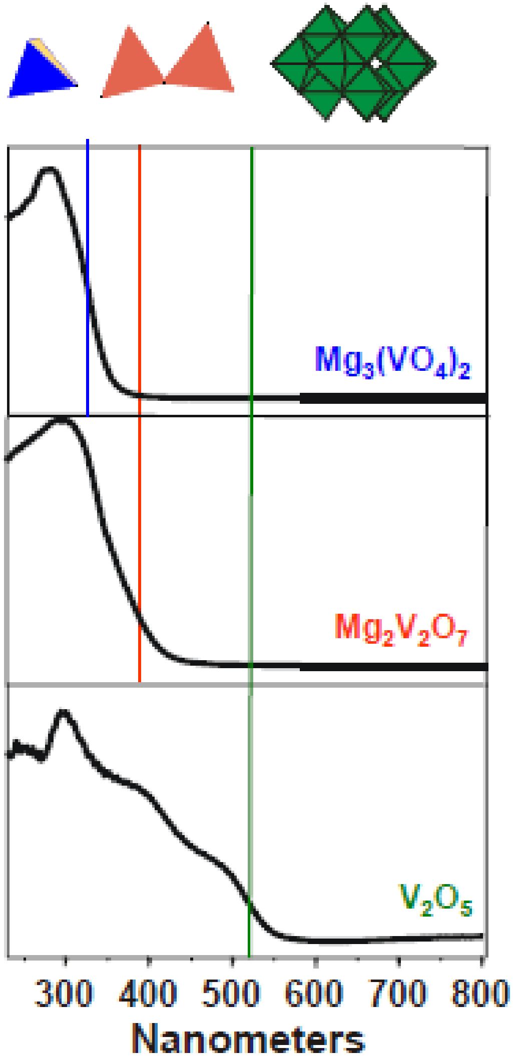
catalyst

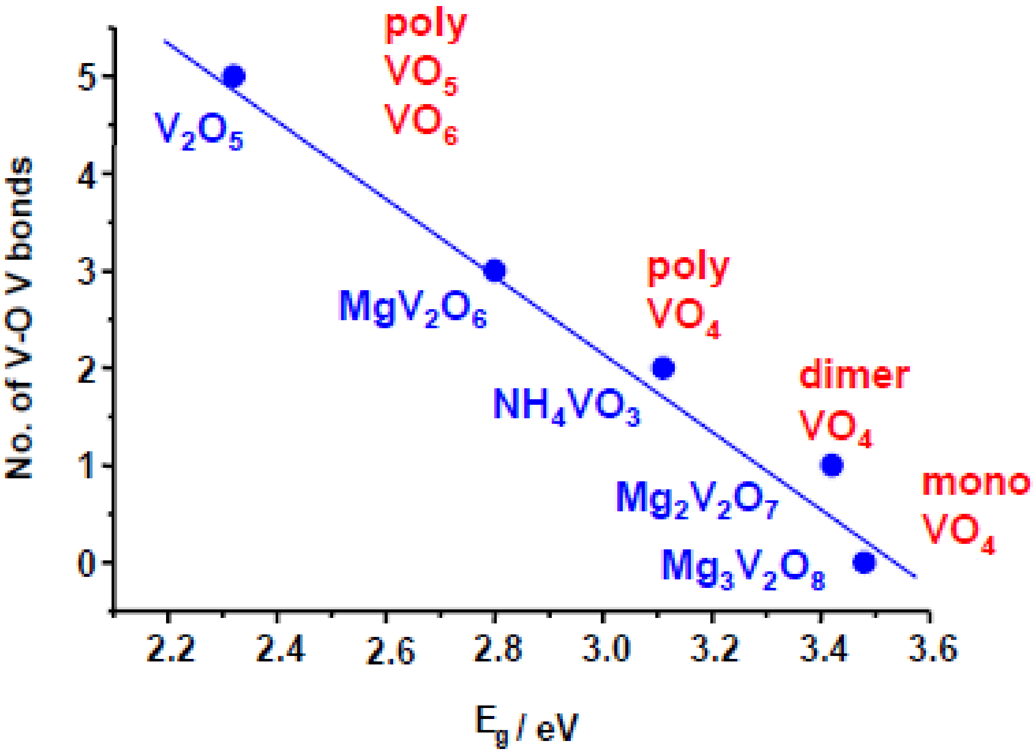
UV-vis Spectra of Vanadium Oxide Reference Compounds

CT and d-d bands shift to higher energies (lower wave length) with increasing number of d electrons



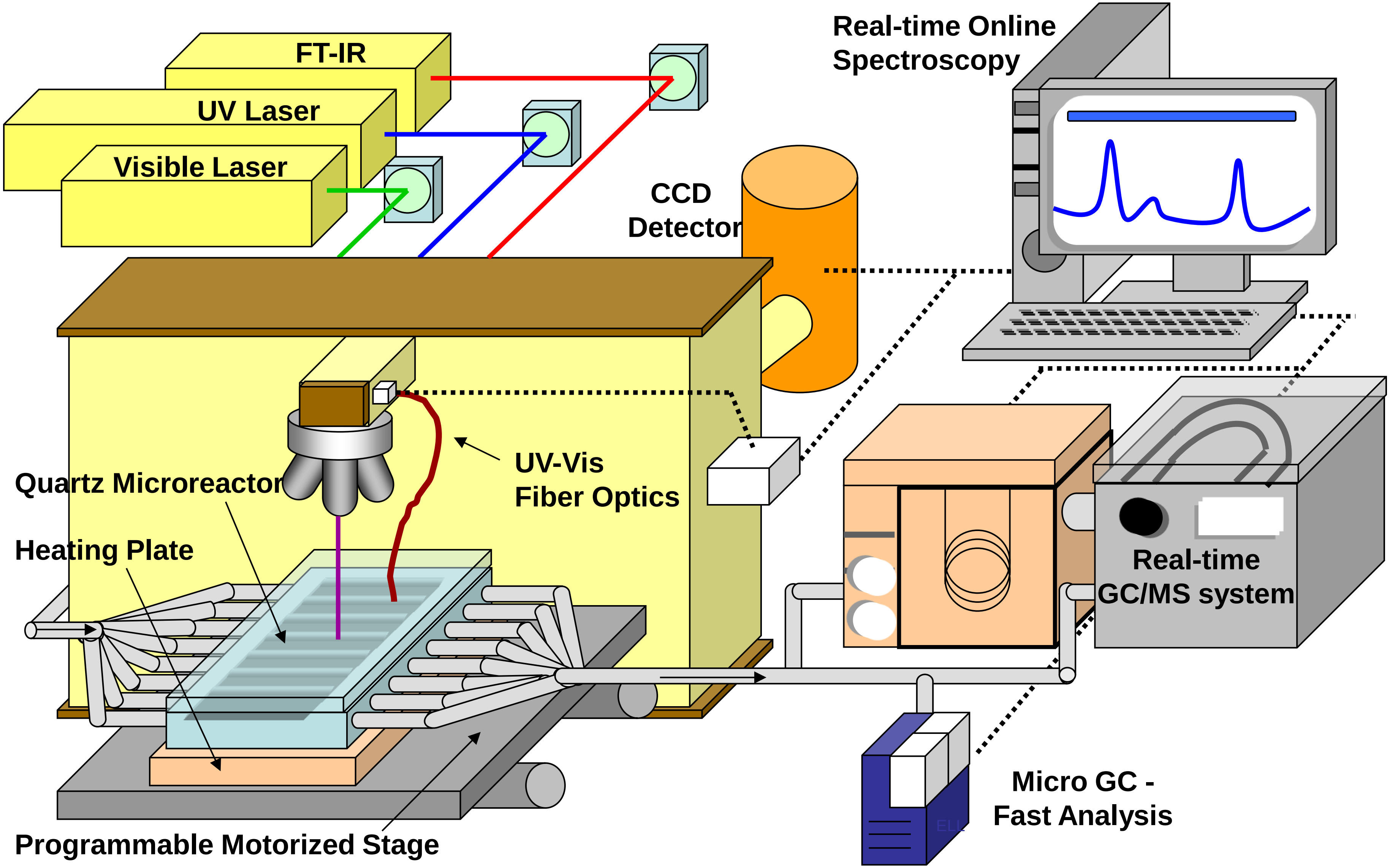
Dependence of CT Absorption Edge Energy on Structure of V^{5+}





X. Gao and I. E. Wachs, *J. Phys. Chem. B* **104** (2000) 103.

Horiba LabRam-IR High Resolution System for
Operando Raman/IR/UV-vis/TPSR Molecular Spectroscopy & Microscopy



FT-IR

UV Laser

Visible Laser

CCD Detector

Real-time Online Spectroscopy

UV-Vis Fiber Optics

Quartz Microreactor

Heating Plate

Programmable Motorized Stage

Real-time GC/MS system

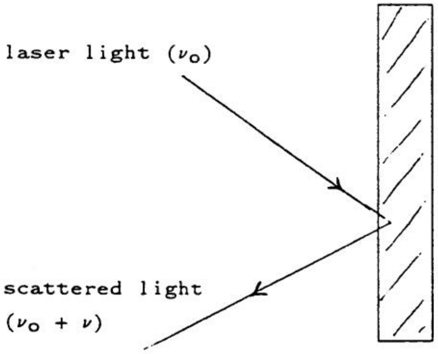
Micro GC - Fast Analysis

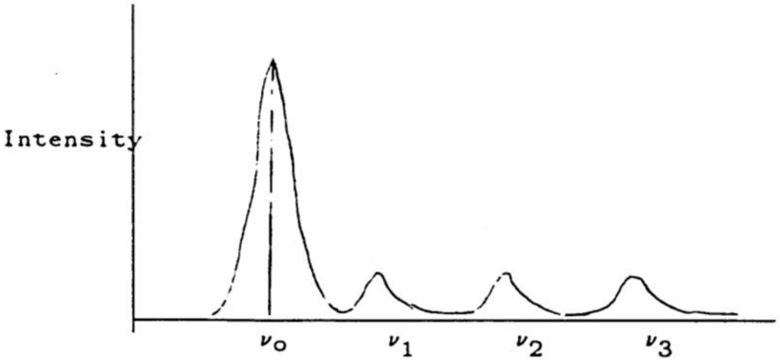
Summary

- Optical spectroscopy provides molecular and electronic structural information.
- Can be performed at HT and HP with solids and condensed phases.
- Raman & IR → molecular structure.
- UV-vis → Domain size and oxidation state.

Raman Spectroscopy

- Single line of a continuous gas laser is focused on sample surface; measurement of inelastic light scattering yields information about vibrational frequencies of chemical bonds.
  - Penetrates bulk of solid
  - Nature of surface chemical species (especially metal oxides)
  - Sub-monolayer sensitivities
  - Types, concentrations, and strengths of chemical bonds
  - *In situ* (high temperature, high pressure)
  - Can penetrate through water





- Limitations
  - Fluorescence (signal noise)
  - Gives signals in the 10-4000 cm^{-1} range
  - Weak oxide support signals below 1000 cm^{-1}

UV-Vis (Ultraviolet-Visible) Diffuse Reflectance Spectroscopy

- **UV-vis light shined on a material and inelastically scattered light contains information about electronic transitions (position and intensity)**

- bulk technique (solids & liquids) **- can be performed at high T and P**
- sensitive at low concentrations & quantitative **- can penetrate through water**

+ charge transfer (CT) bands
***coordination and dispersion of transition metal ions highest oxidation state**
(V^{+5}, Cr^{+6}, Re^{+7}, Ni^{+2}, etc.)

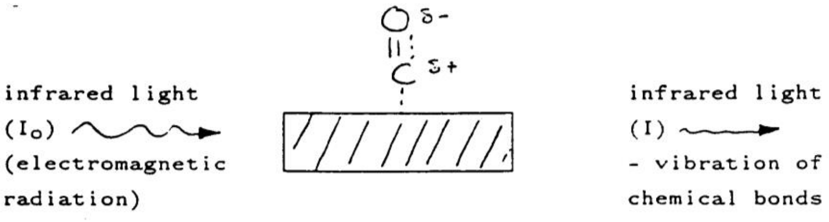
***optical band gap or edge energy (Eg) related to domain size**
(monomer, dimer, polymer, cluster, bulk particle)

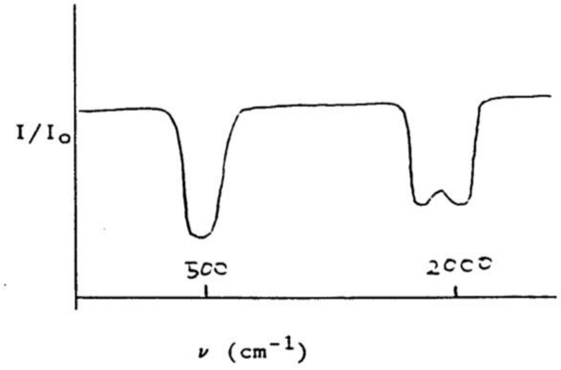
+ d-d transition bands
***coordination and oxidation state of reduced transition metal ions**
(V^{+4}, V^{+3}, Cr^{+5}, Cr^{+3}, etc.)

- **Limitations**
- d-d transitions are weak and may overlap CT and nearby d-d bands

Infrared Spectroscopy

- The intensity of a beam of infrared radiation is measured before (I_0) and after (I) it interacts with the sample as a function of light frequency. It probes vibrational motions of chemically bonded constituents.
  - Penetrates bulk of solid
  - Nature of surface chemical species
  - Sub-monolayer sensitivity
  - Types, concentrations, and strengths of chemical bonds
  - *In situ* (high temperature, low pressure)





- Limitations
  - Primarily gives signals in the 1000-4000 cm^{-1} range for practical catalysts
  - Oxide supports absorb signals below 1000 cm^{-1} which obscures surface signals
- Cannot penetrate through water (*absorbed* by water)

UV-vis Selection Rules

photon energy must match energetic difference between states	$h\nu = \Delta E$
light absorption does not couple or decouple electron spins	$\Delta s = 0$
orbital angular momentum must change	$\Delta l \neq 0$
transitions between states of equal parity are symmetry forbidden	$\xcancel{\begin{array}{c} u \leftrightarrow u \\ g \leftrightarrow g \end{array}}$ $u \leftrightarrow g$