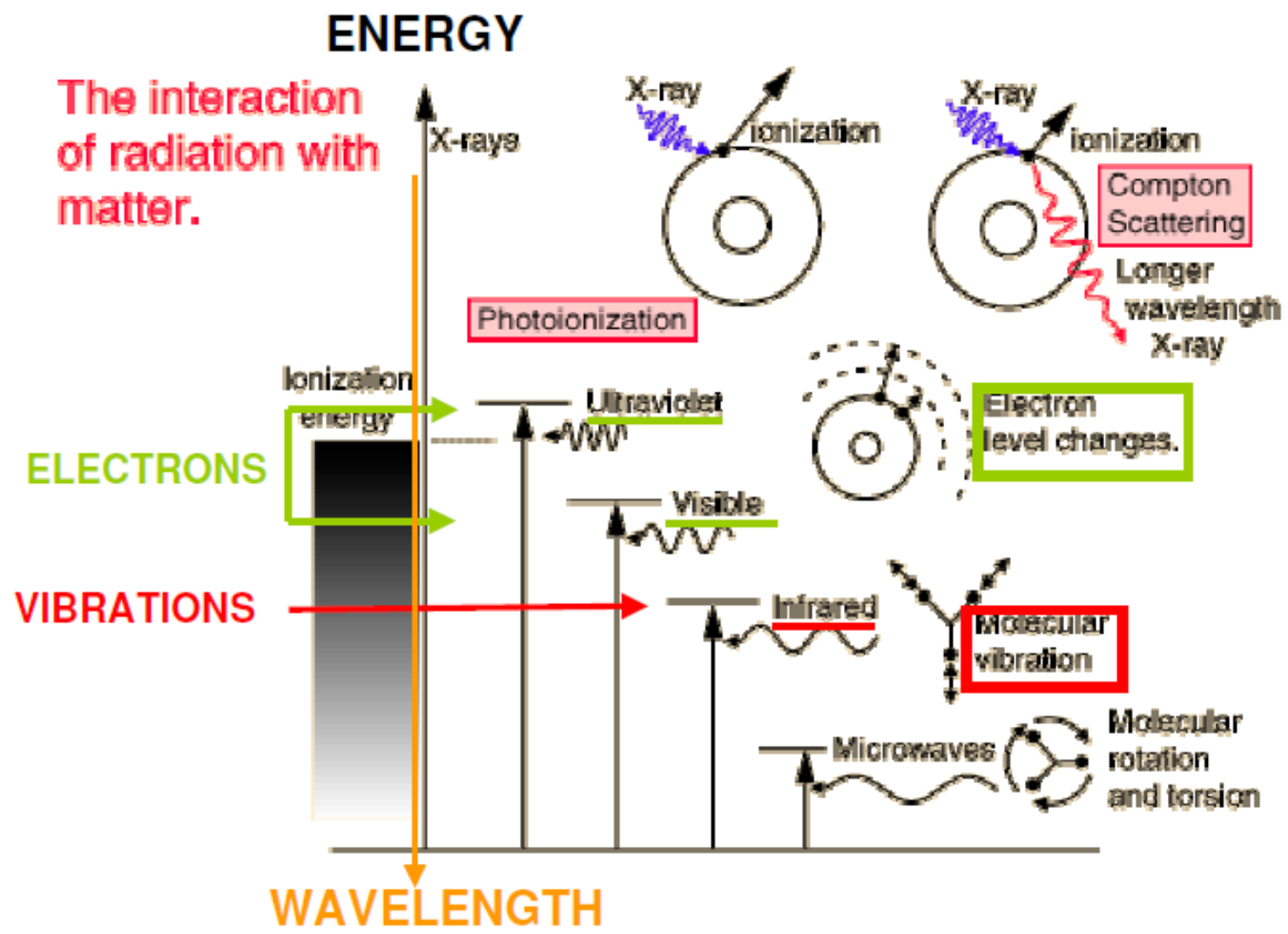


Optical Spectroscopy

Professor Israel E. Wachs

***Operando* Molecular Spectroscopy & Catalysis Lab**
Department of Chemical & Biomolecular Engineering
Lehigh University, Bethlehem PA

Interaction of EM Radiation with Matter



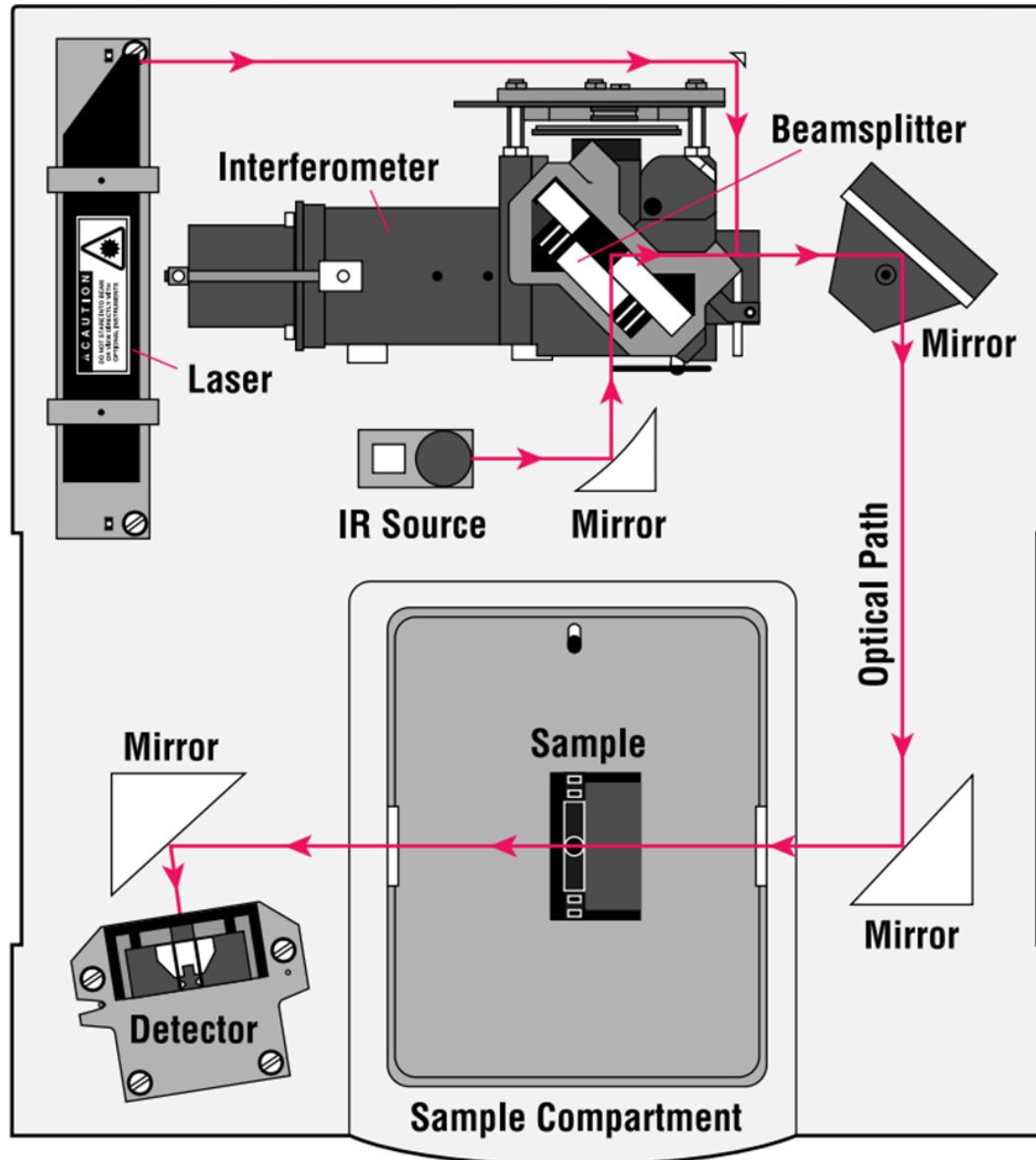
Comparison of Catalyst Spectroscopic Methods

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	---

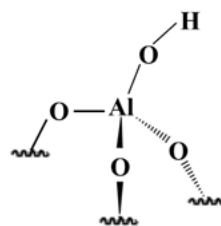
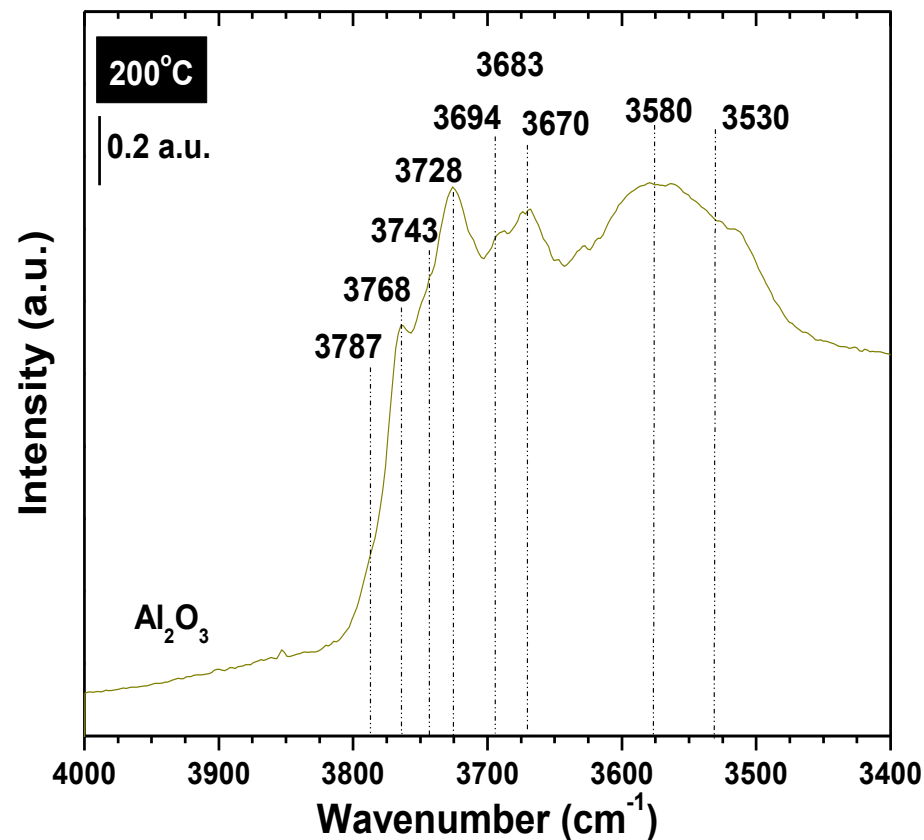
IR Spectroscopy

- 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)

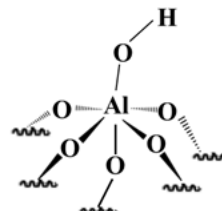
Typical IR Spectrometer



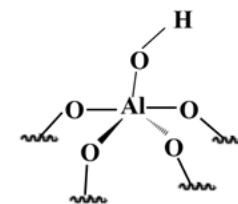
Surface Hydroxyls Present on Al₂O₃



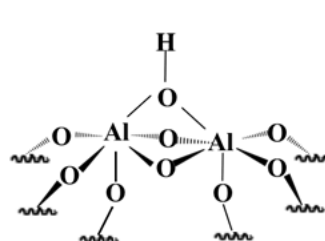
(3785-3800 cm⁻¹)



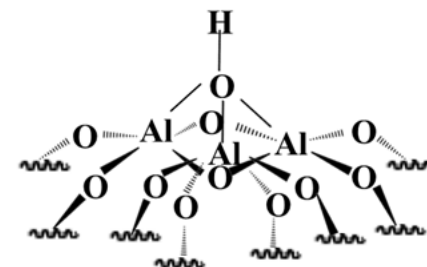
(3760-3780 cm⁻¹)



(3730-3735 cm⁻¹)



(3690-3710 cm⁻¹)



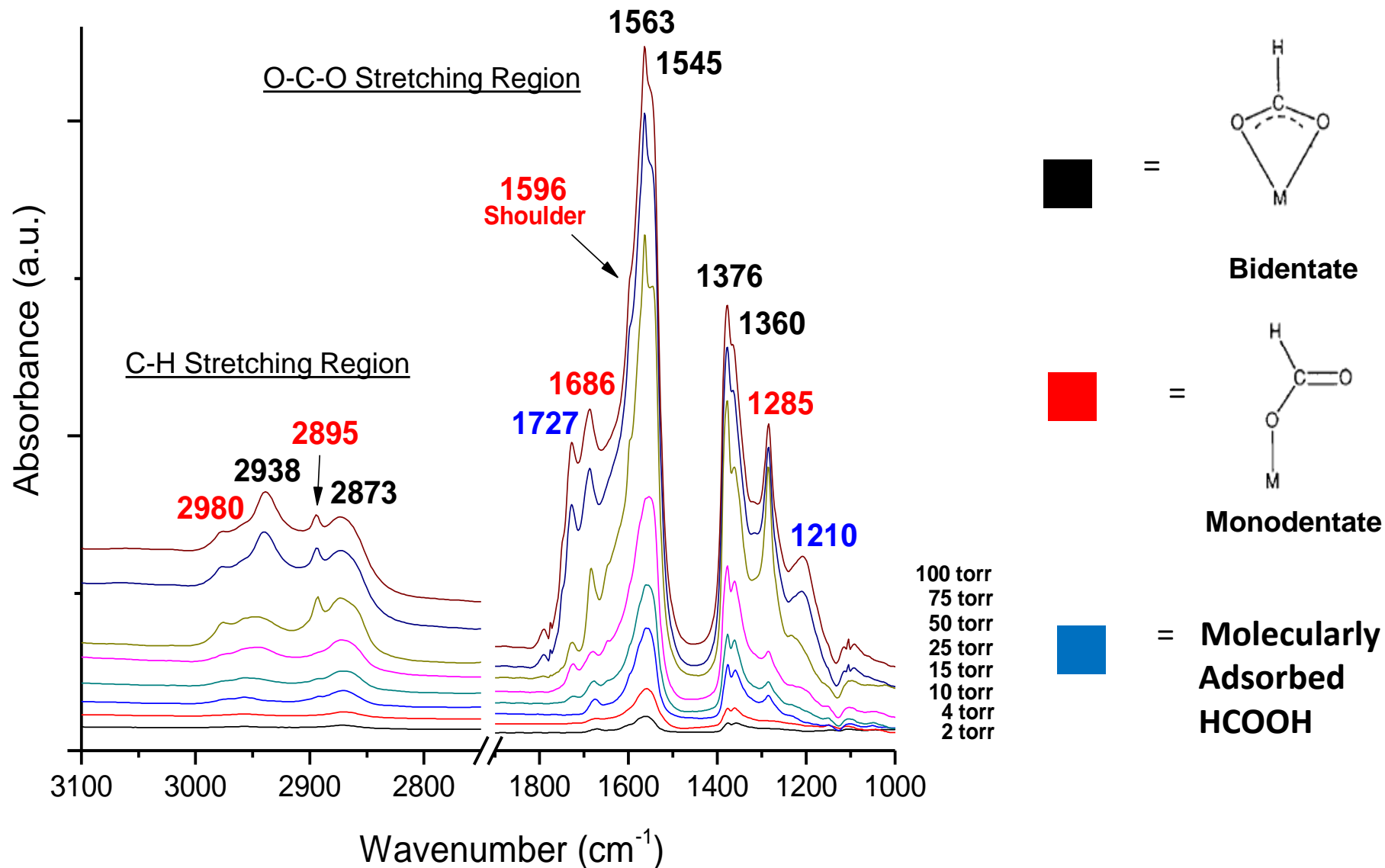
(3590-3650 cm⁻¹)

Digne, M.; Sautet, P.; Raybaud, P.; Euzen, P.; Toulhoat, H. J. Catal. 2002, 211, 1-5.

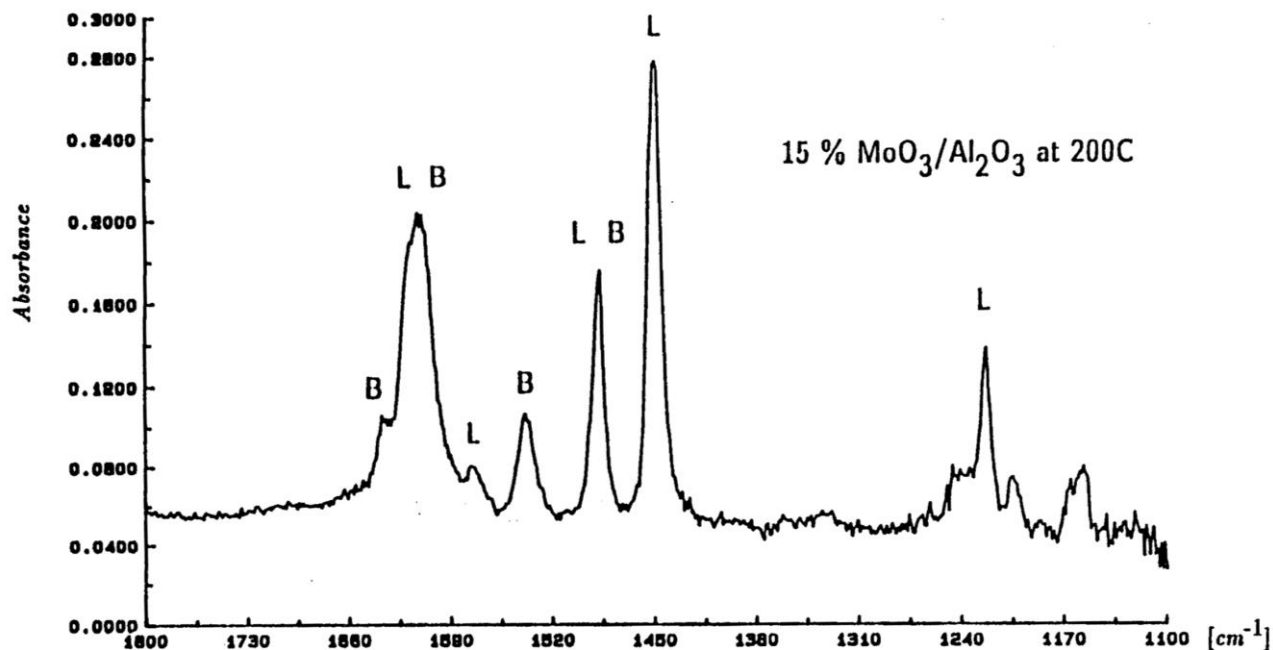
Digne, M.; Sautet, P.; Raybaud, P.; Euzen, P.; Toulhoat, H. J. Catal. 2004, 226, 54-68.

Coperet, C. Pure Appl. Chem. 2009, 81, 585-896.

HCOOH Adsorption on Fe₂O₃ (@ T = 100°C)



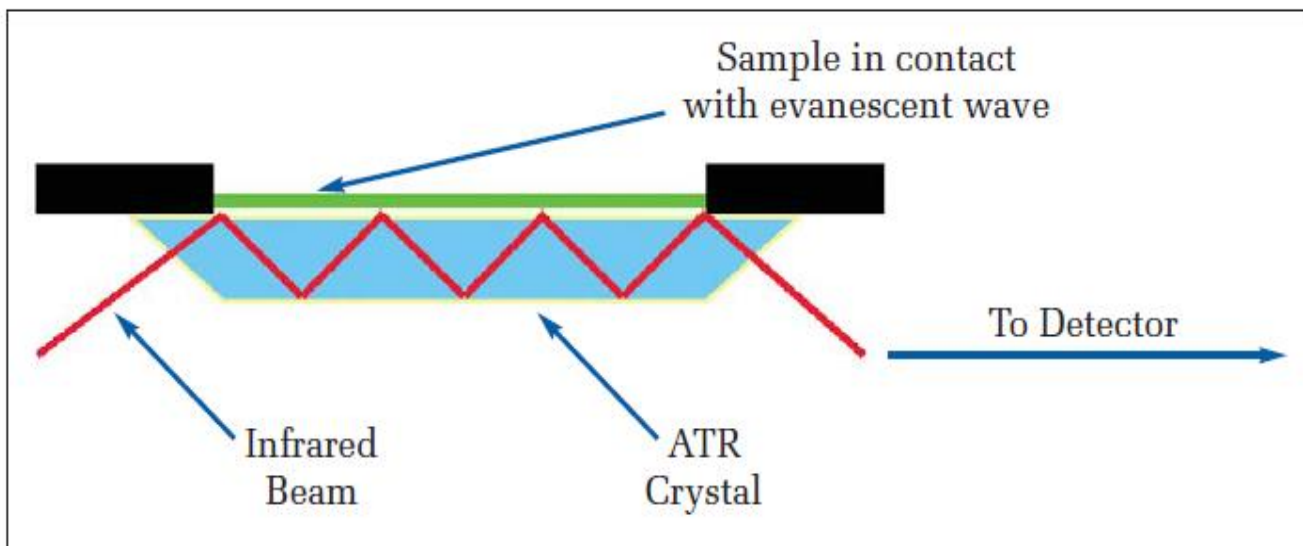
Bronsted and Lewis Surface Acid Sites



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

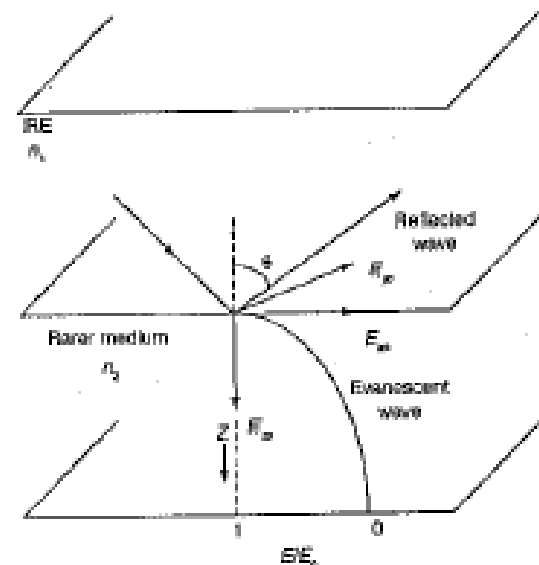
- B - Characteristic absorption bands of the pyridinium ion PyH⁺ chemisorbed to a Bronsted acid surface site appear at: 1490, 1540, 1620, 1640 cm⁻¹.
- L - Characteristic absorption bands for coordinatively adsorbed pyridine (a Lewis acid surface site) appear at: 1220, 1450, 1490, 1580, 1600-1630 cm⁻¹.

ATR FT-IR Spectroscopy

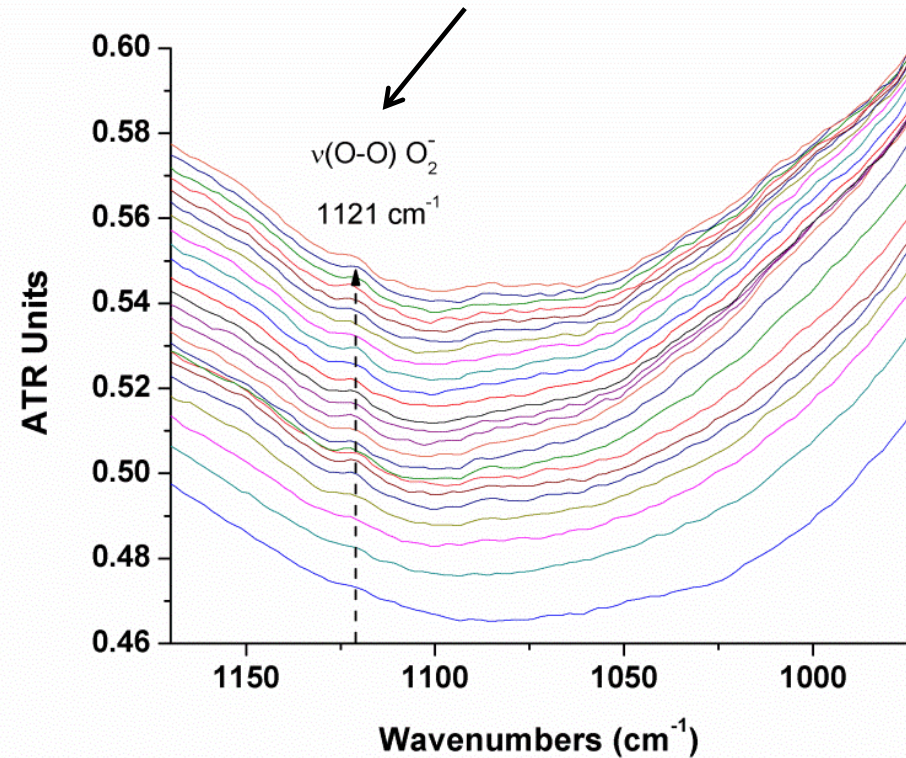
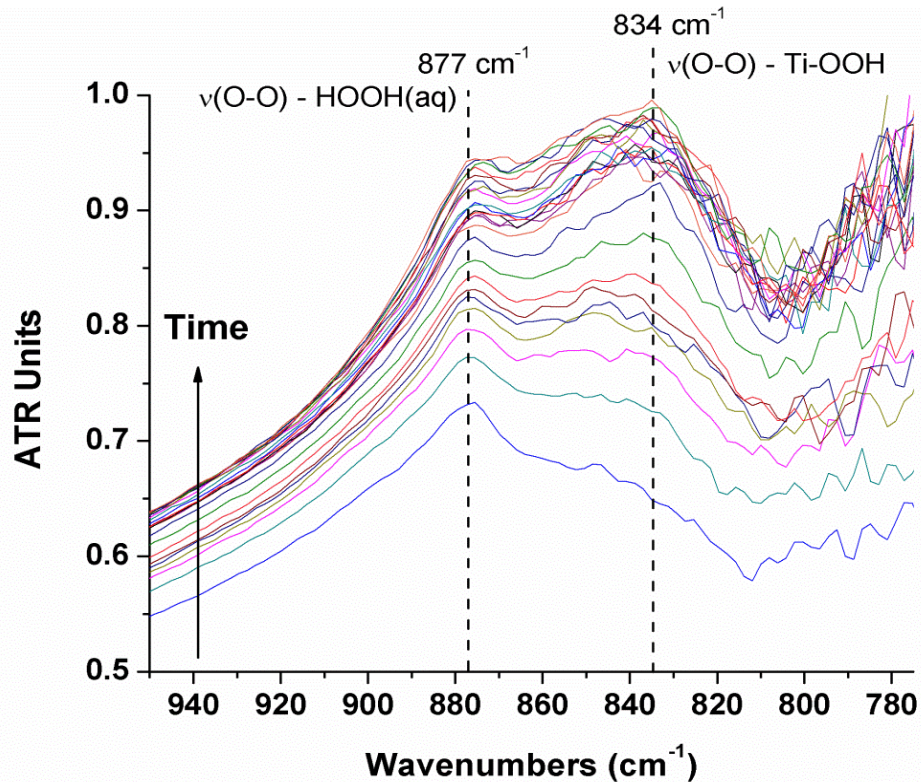


- Uses phenomenon that occurs with light at the boundary between two media of different refractive indices.
- At an angle of incidence greater than the critical angle of the material, light is completely reflected.
- However, some energy penetrates the boundary: evanescent wave.
- The material at the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

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



Surface Ti-OOH Species Form on TiO₂ Upon Exposure to Aqueous HOOH



- Trace of surface superoxo (O₂)⁻ species also present on TiO₂.

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

On a boat trip back from England in 1921, Indian physicist C.V. Raman, considering the question of why the sea is blue, got started on a line of research that would lead to the discovery in February 1928 of a new scattering effect, now known as the Raman effect, which is important in physics and chemistry.

C. V. Raman (his full name, Chandrasekhara Venkataraman, was shortened during his school years) was born in November 1898 in southern India. His father was a lecturer in physics and mathematics in 1902, at age 13, Raman entered Presidency College, Madras. He received his bachelor's degree in 1916 and master's degree in 1917. As a student he did research in optics and acoustics.

He loved science, but saw few career opportunities for a scientist in India, so after receiving his degrees he took the limited civil service exam and went to work for the government as an Assistant Accountant General. But he didn't give up science in his spare time; he carried out experiments at the Indian Association for the Cultivation of Science in Calcutta. His research included studies of the physics of the violet as well as unpaired Indian instruments and Indian drama. He also became known as a good lecturer, offering popular science lectures to the public.

In 1917 Raman was offered the Paley Chair of Physics at Calcutta University. In order to take the position he had to leave his prestigious and well paid civil service job, but he was finally able to devote himself full time to science.

In 1921 he made a trip to England, where he met with distinguished British physicists. He returned to Bombay aboard the S.S. Noronada, leaving England in September 1921. That was when he began contemplating the striking blue color of the Mediterranean Sea. Lord Rayleigh, who had previously explained the blue color of the sky as due to elastic scattering of light by molecules in the atmosphere, had suggested that the blue color of the sea was simply a reflection of the sky. Raman wasn't so sure this was the case.

Aboard the ship, Raman had carried with him some simple optical equipment, including a pocket-sized spectroscope and a prism. He used these to examine the water and became convinced that water molecules could scatter light just as air molecules could. He sent a letter to Nature as soon as he got to port in Bombay.

Inspired by his insight aboard the ship, when he

believed that something similar to the Compton Effect could be demonstrated with visible light scattering instead of off molecules.

Raman and his research group in Calcutta set up some simple experiments to look at the scattering of light in various liquids. As a light source they initially used sunlight, which was abundant in Calcutta. Using a colored filter they separated out blue-violet light, which then scattered off the sugar liquid. They used yellow-green and other colored filters to eventually detect a change in color of the scattered light. The

effect is weak and difficult to see, so they soon realized they needed a more intense light source. The research center acquired a seven inch telescope, which Raman used to concentrate sunlight for their experiments. Even with the fairly simple setup, they were able to observe a shift in the color of light scattered by many different liquids.

In February 1928 Raman observed that the scattered light was polarized, which distinguished the new scattering effect from fluorescence. He and colleague K.S. Krishnan sent off a short

paper to Nature titled "A New Type of Secondary Radiation," in which they reported having examined many different common liquids and observed the new scattering effect to some degree in all of them. Shortly afterwards Raman measured the exact wavelengths of the incident and scattered light using a spectroscope, and presented the quantitative results in a lecture to the South Indian Science Association in March and in the *Indian Journal of Physics*.

Other researchers at the time had also been investigating light scattering effects. For instance, Russian physicists Gregory Landsberg and Lev Vladimirovich in 1925 began looking at light scattering in quartz. They were at first hindered by poor samples of quartz with many impurities, but by 1926 they managed to get a pure enough sample of quartz, and in February 1928 they independently observed the same scattering effect that Raman had found. They reported their results at a conference in Moscow in April.

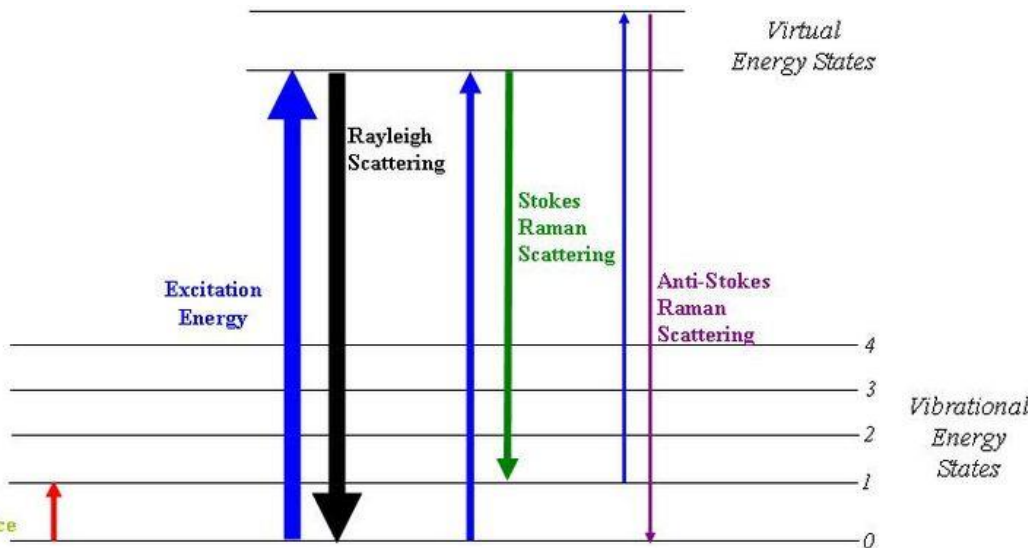
Physicists quickly recognized the importance of the Raman Effect. It provided another verification of quantum theory, and was useful in the study of vibration and rotation of molecules. Within a few years chemists were even using Raman spectroscopy for structural analysis.

Raman received the 1930 Nobel Prize for the discovery, as well as numerous other honors. He

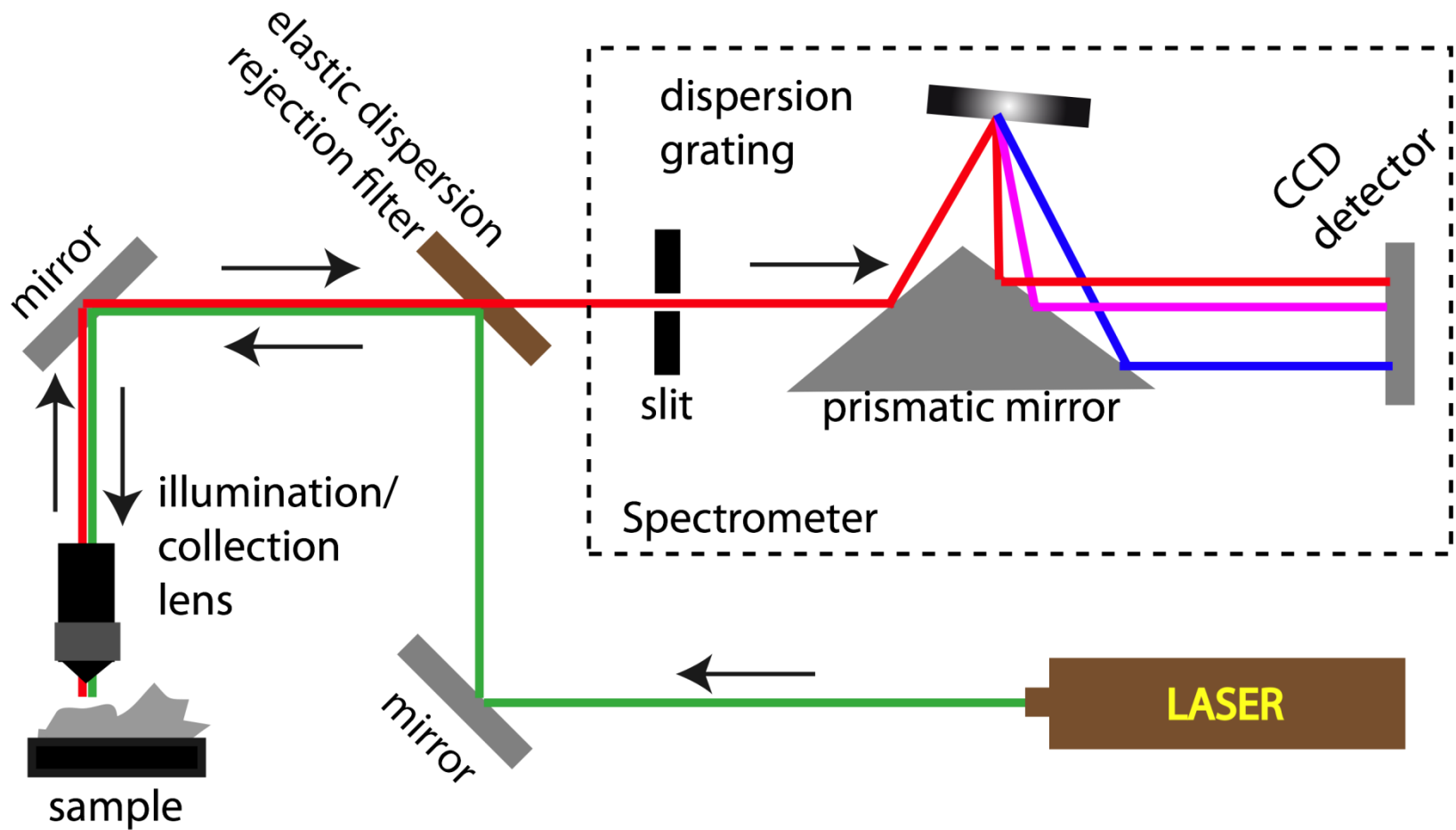


Portrait of the Indian physicist Chandrasekhara Venkataraman

C.V. Raman



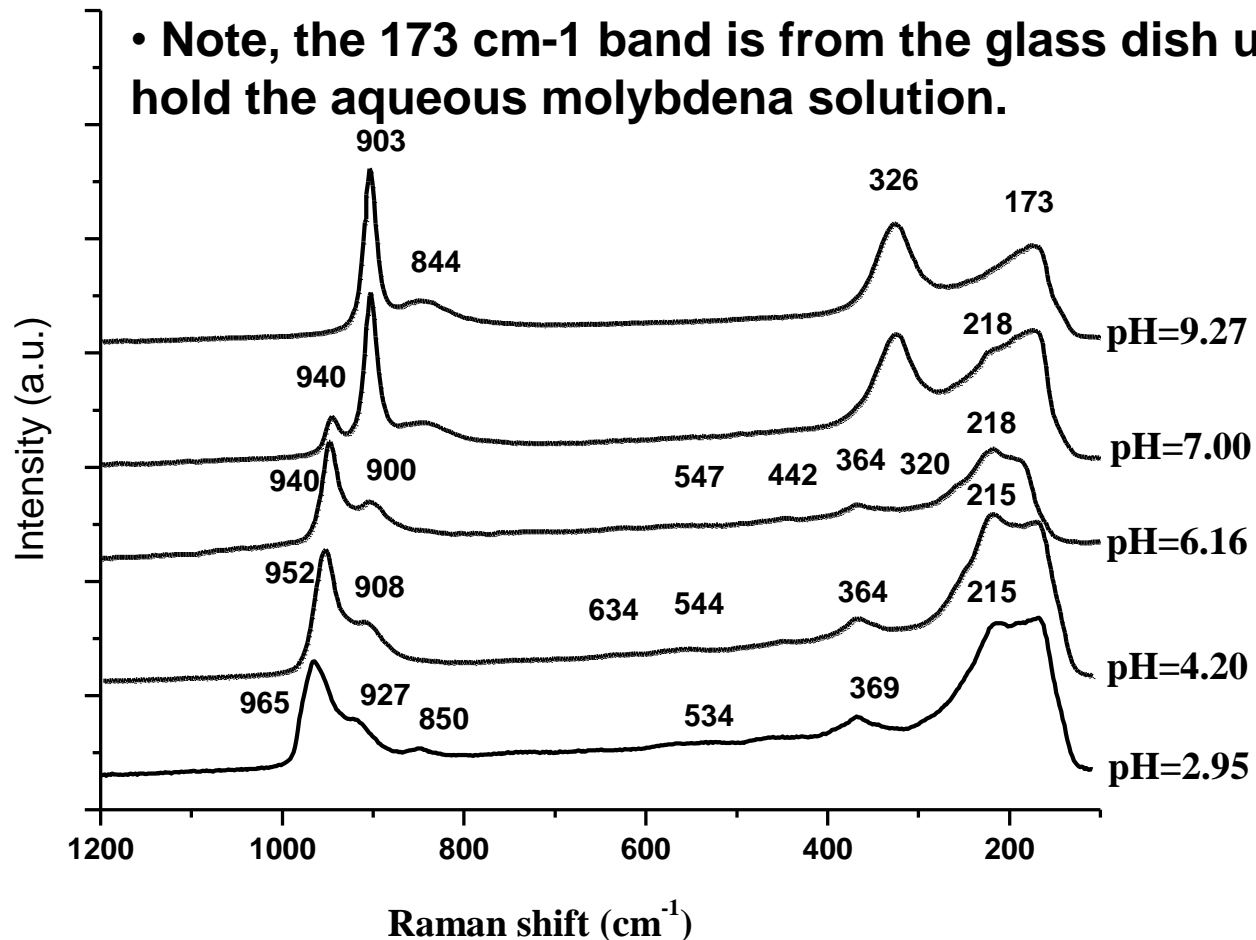
Typical Raman Spectrometer



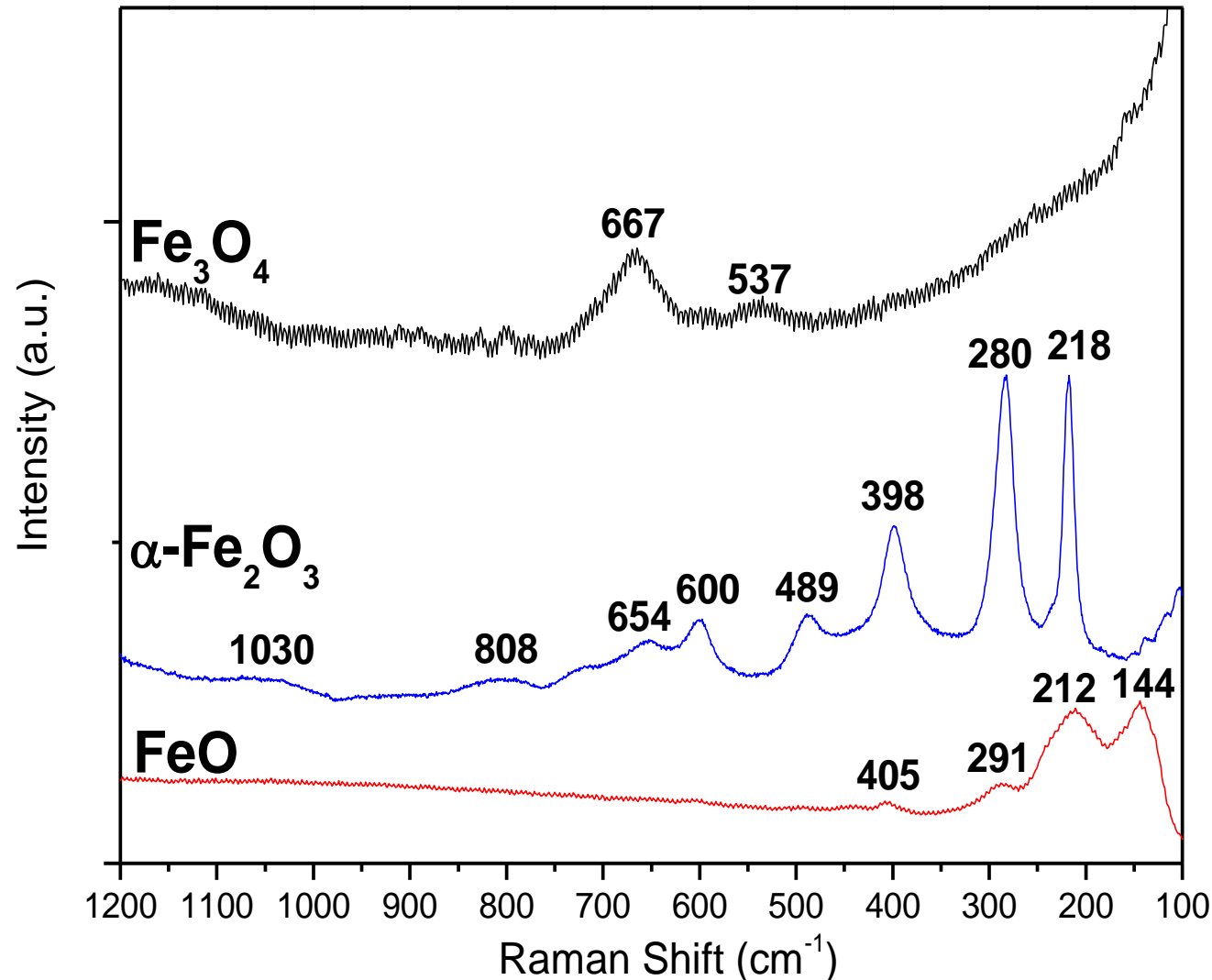
Raman Spectra of Aqueous Molybdenum Oxide Solution

- Raman spectra of aqueous 0.2M $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ solutions as a function of solution pH.

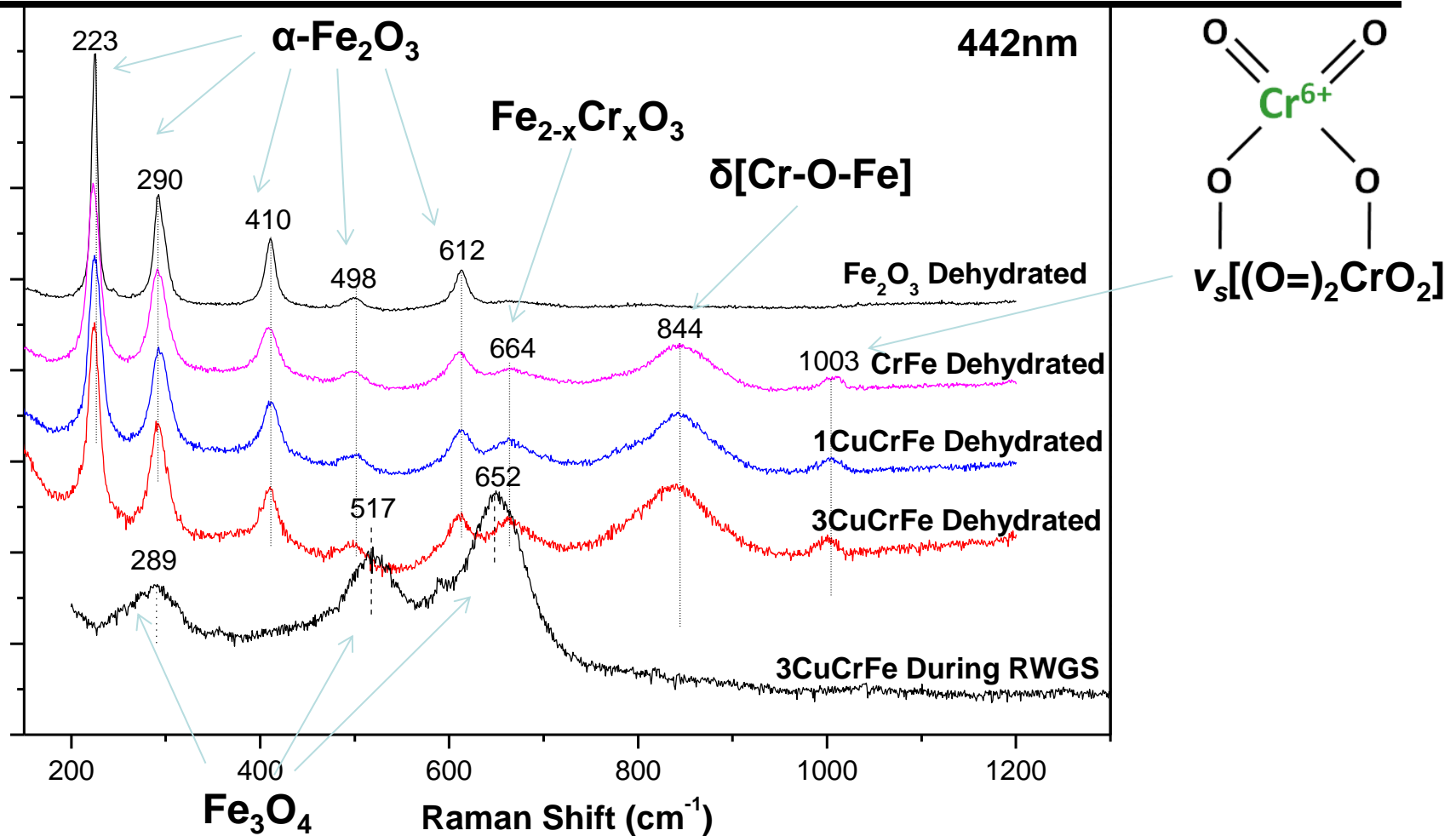
- Note, the 173 cm^{-1} band is from the glass dish used to hold the aqueous molybdena solution.



Raman Spectroscopy Discriminates Between Different FeOx Phases



Bulk FeOx Phase Transforms during HT-RWGS



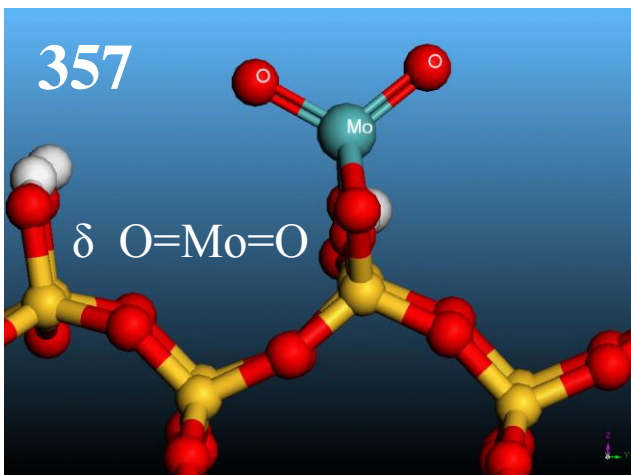
- Surface dioxo $(\text{O}=\text{O})_2\text{CrO}_2$ species reduce during HT-WGS

Vibrational modes of Mo oxo species

Dioxo $(\text{O}=\text{O})_2\text{MoO}_2$

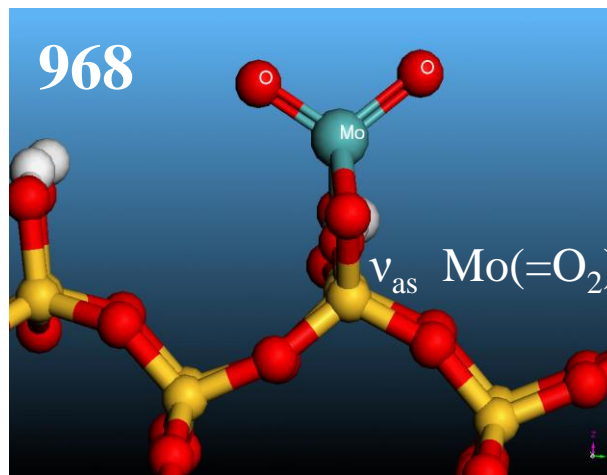
357

δ $\text{O}=\text{Mo}=\text{O}$



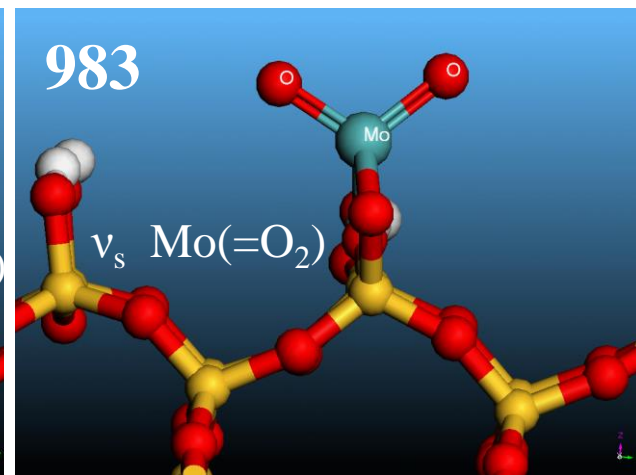
968

ν_{as} $\text{Mo}(=\text{O}_2)$



983

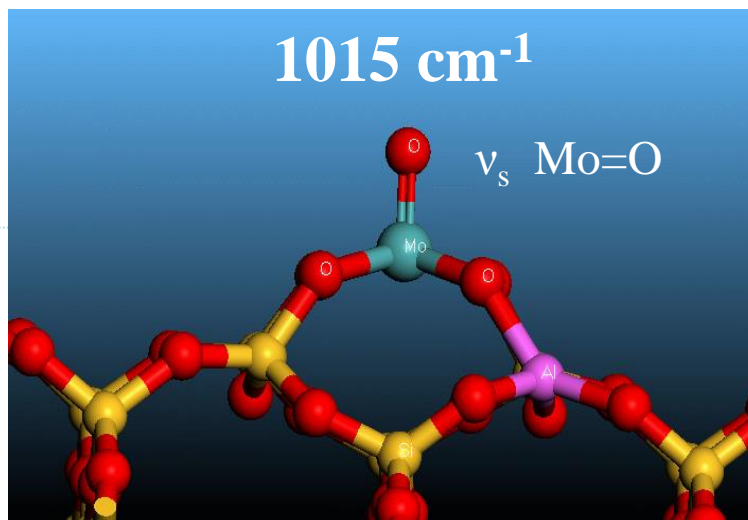
ν_{s} $\text{Mo}(=\text{O}_2)$



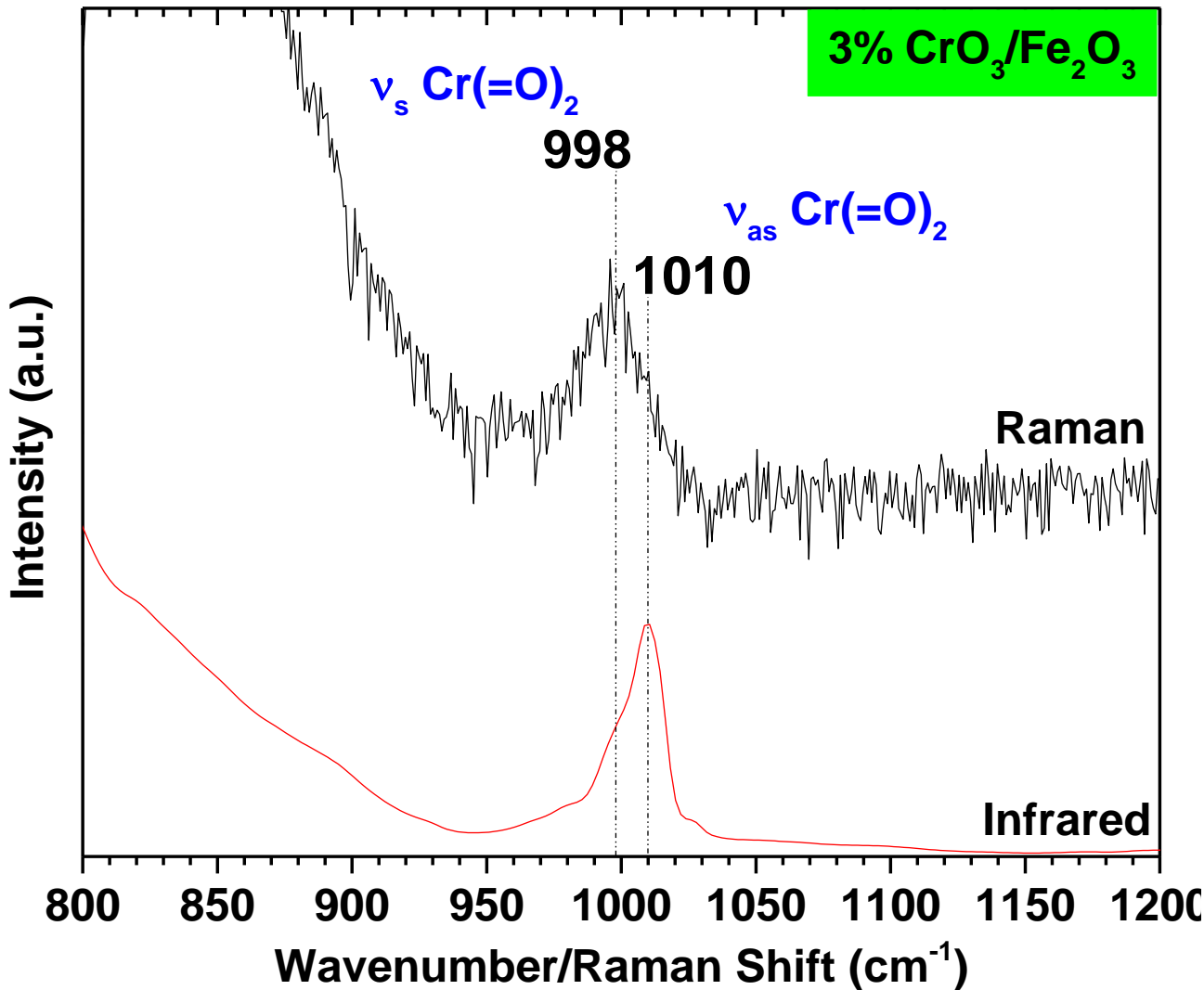
Mono-oxo $\text{O}=\text{MoO}_4$

1015 cm^{-1}

ν_{s} $\text{Mo}=\text{O}$



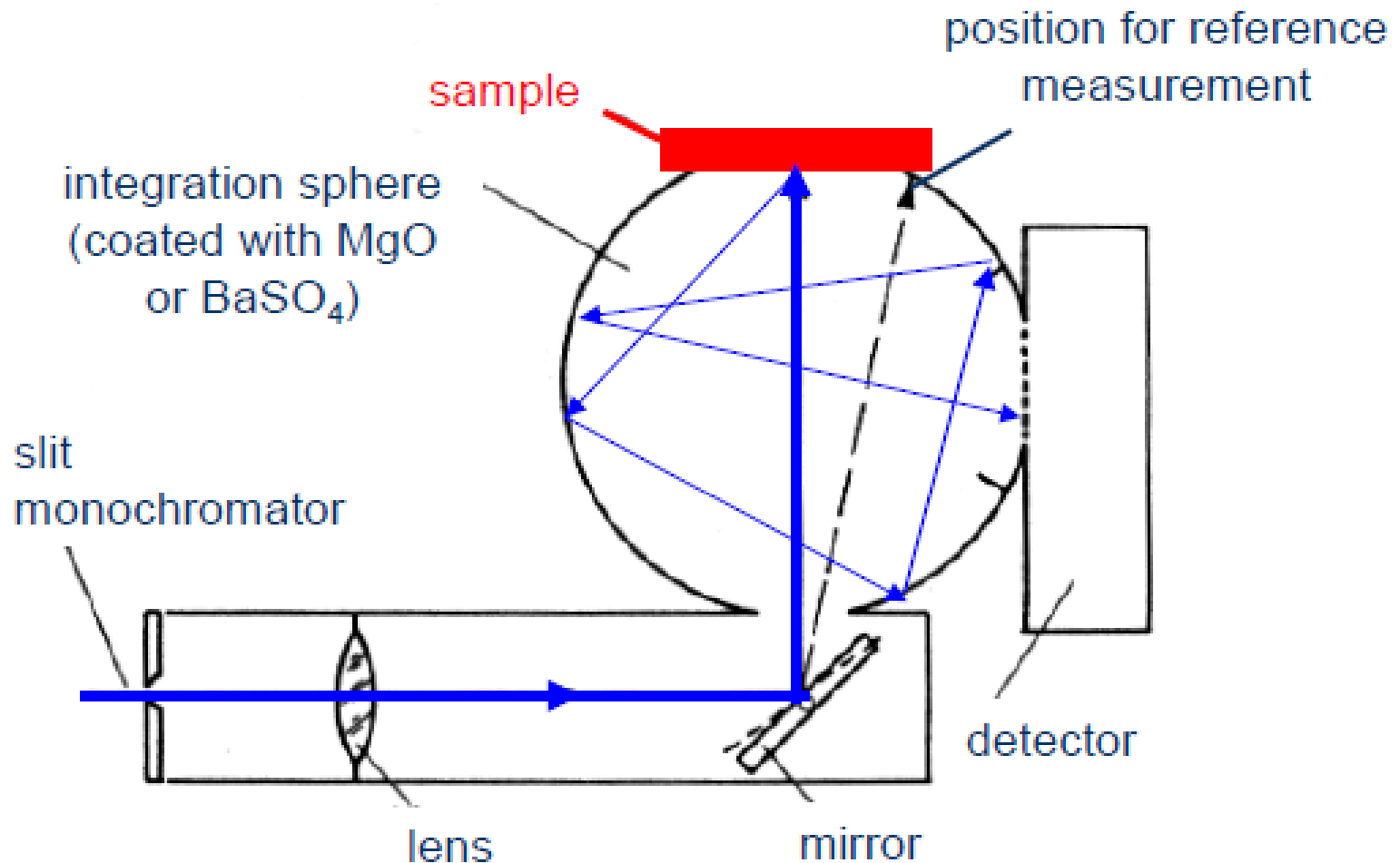
Surface DIOXO $(O=)_2Cr(-O)_2$ Species Present on Fe_2O_3



UV-vis DRS

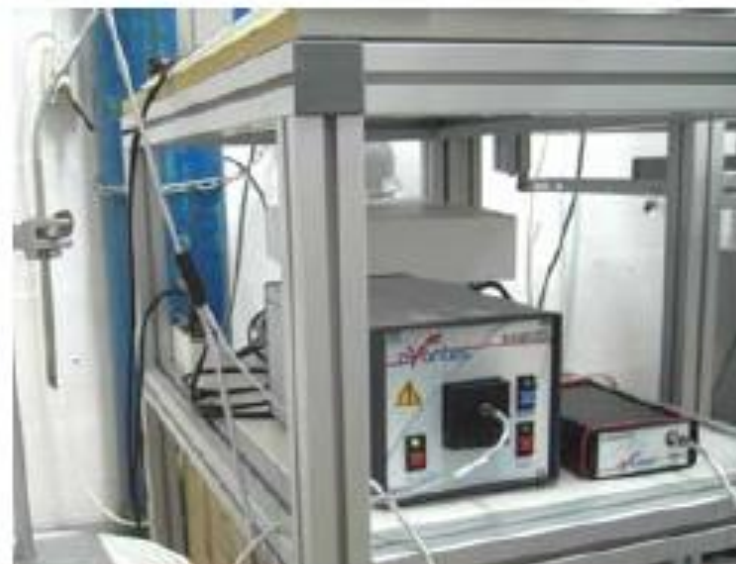
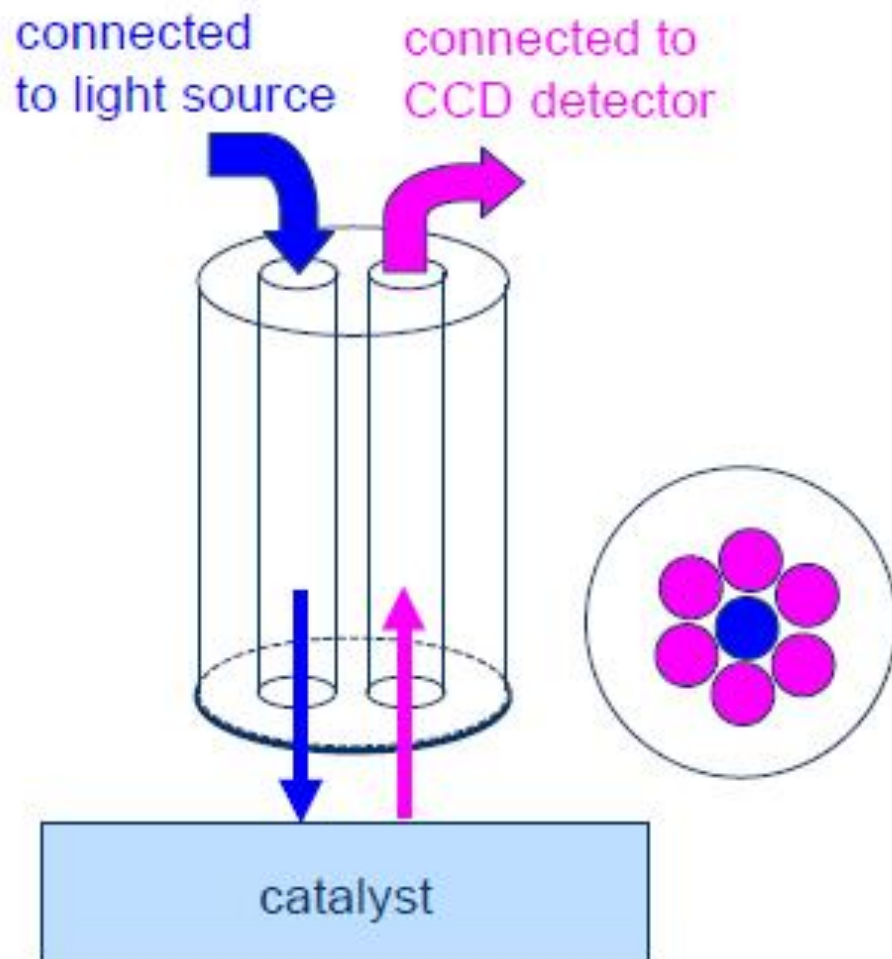
- UV-vis detects electronic transitions
- CT (M=O) transitions correspond to transition metal ions in highest oxidation state
 - MO_x **domain size** and coordination
 - MO_x dispersion
- d-d transitions correspond to reduced transition metal ions → MO_x coordination
- UV-vis generally quantitative at low transition metal ion concentrations (sensitive to low concentrations)

UV-vis DRS Integration Sphere



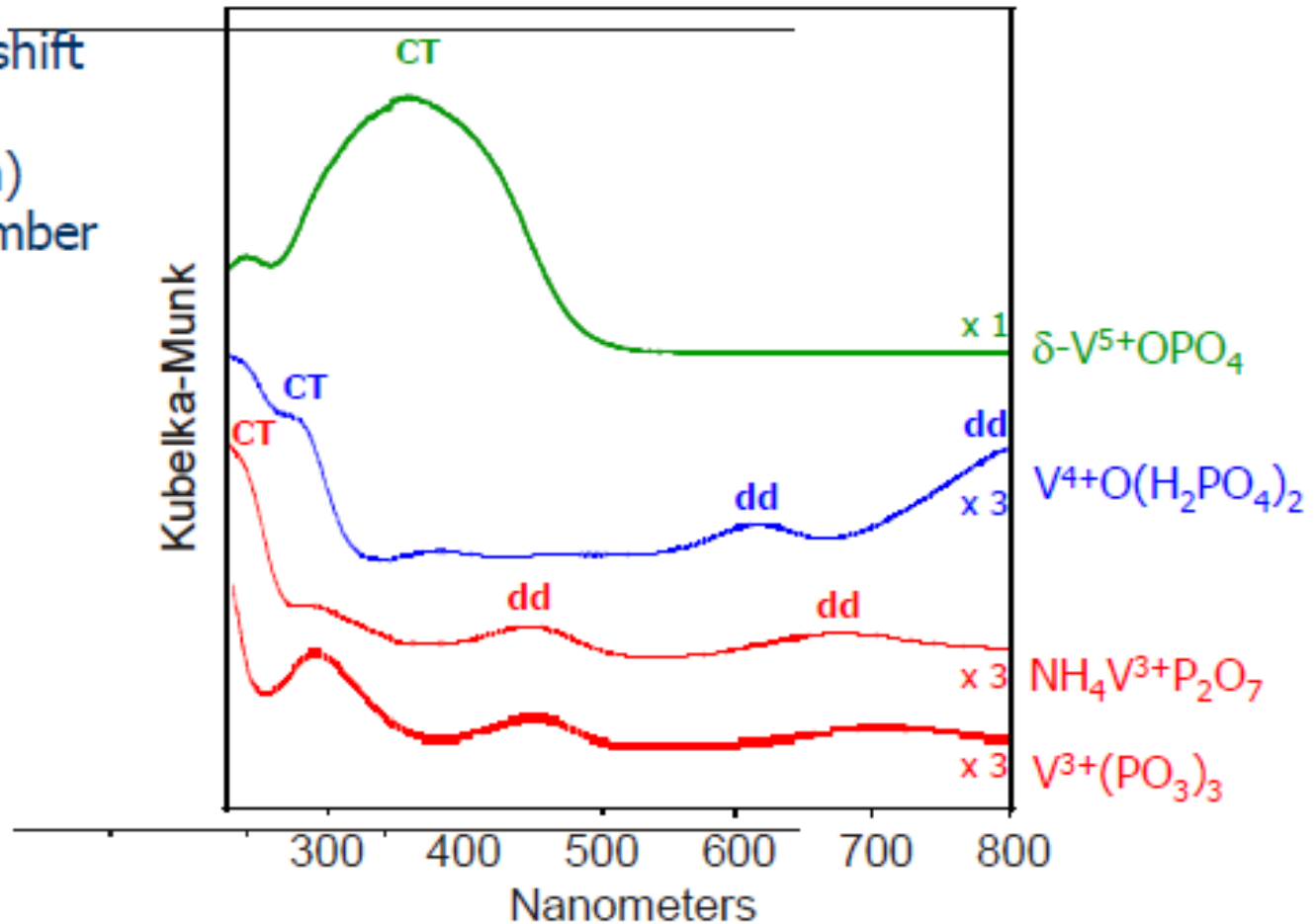
Advantage → higher fraction of reflected light reaches detector

UV-vis Fiber Optic Probe

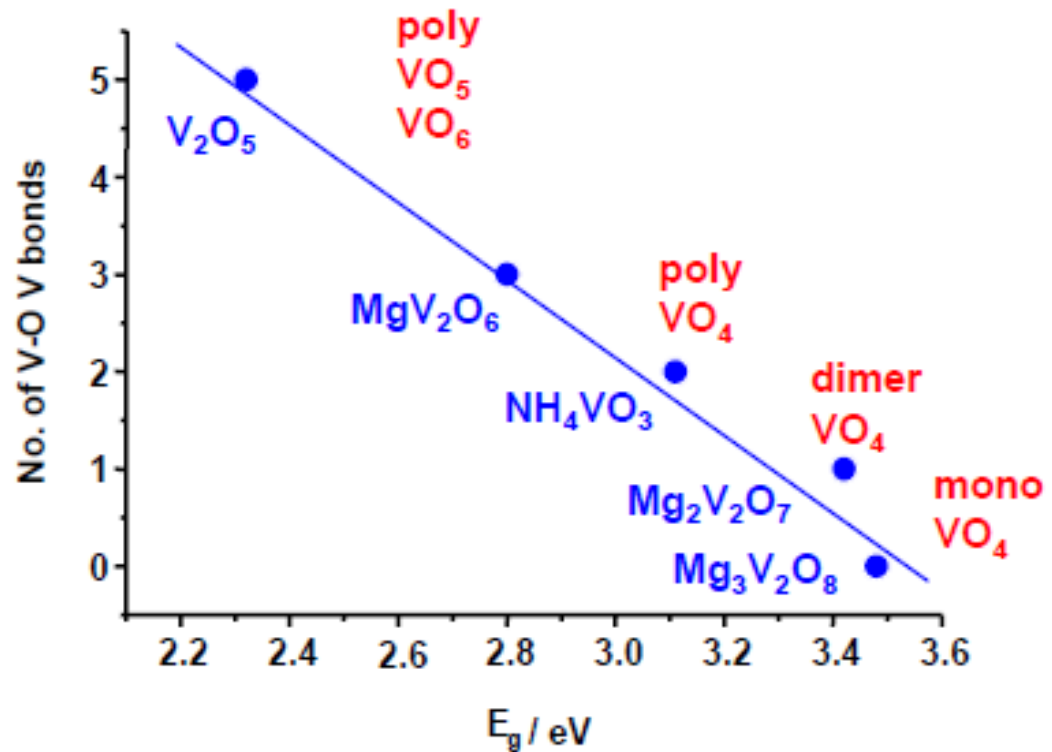
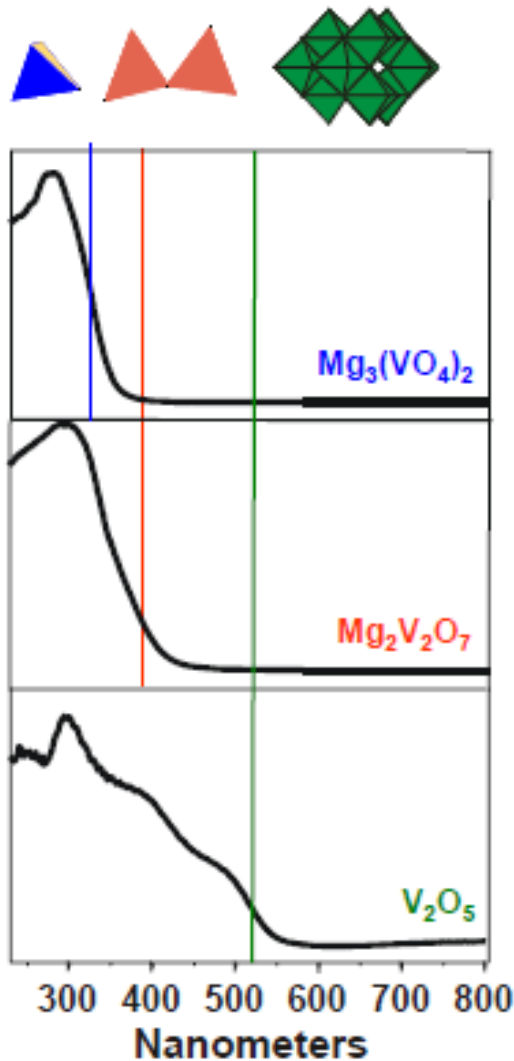


UV-vis Spectra of Vanadium Oxide Reference Compounds

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

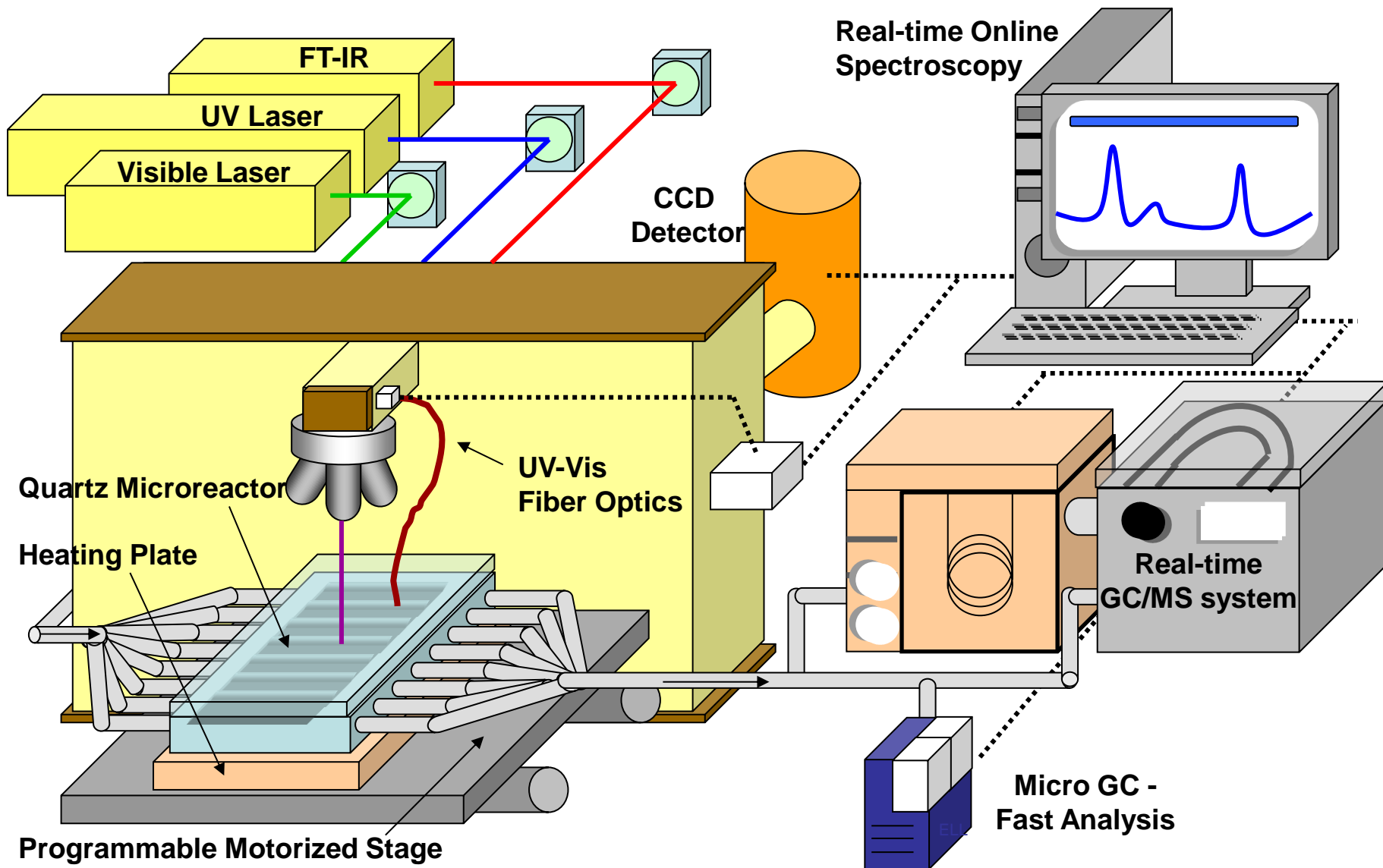


Dependence of CT Absorption Edge Energy on Structure of V^{5+}



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

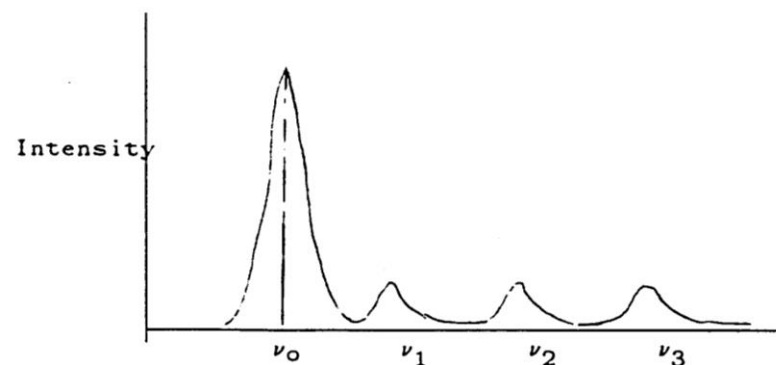
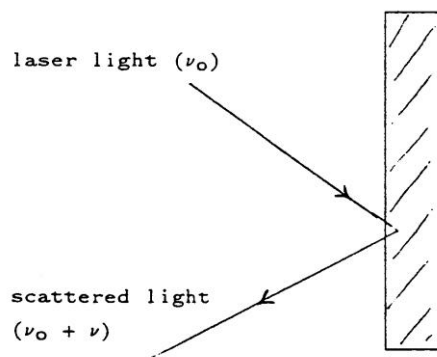


Summary

- 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 $10\text{-}4000\text{ cm}^{-1}$ 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)

- sensitive at low concentrations & quantitative

- can be performed at high T and P

- 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 (E_g) related to domain size (monomer, dimer, polymer, cluster, bulk particle)

- + d-d transition bands

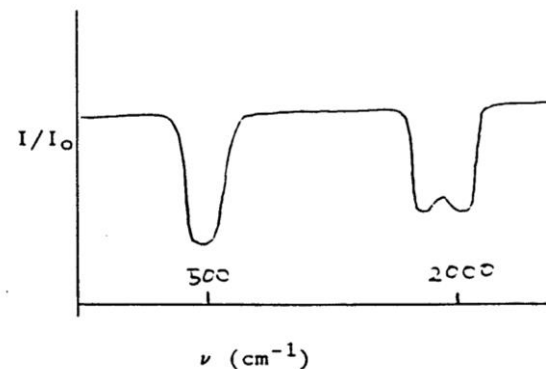
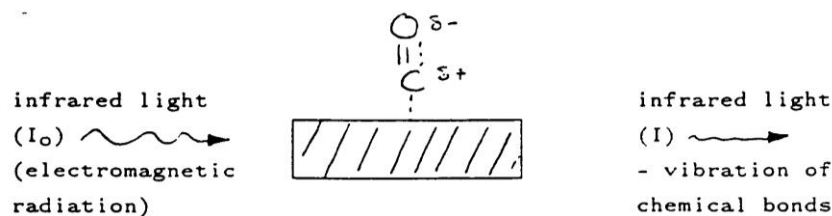
- *coordination and oxidation state of reduced transition metal ions (V⁺⁴, V⁺³, Cr⁺⁵, Cr⁺³, etc.)

- 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 $1000\text{-}4000$ 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

