



Chemistry 4631

Instrumental Analysis

Lecture 17

Raman Spectroscopy

Overview

A vibrational spectroscopy technique like IR.

Routine energy range: 200 - 4000 cm^{-1}

Based on inelastic scattering of a monochromatic excitation source

Symmetry dictates which molecules are active in Raman or IR

Rule of thumb:

- Symmetric = Raman active Asymmetric = IR active**

Raman Spectroscopy

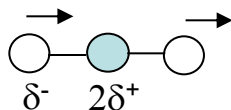
Overview

Comparing IR and Raman

IR

vibrational modes

change in dipole



excitation of vibrational states

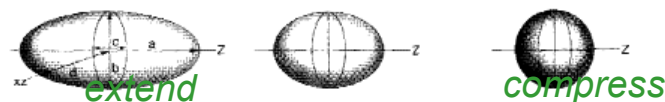
asymmetric vibrations

solvent – CCl_4 or CS_2

Raman

vibrational modes

change in polarizability



distortion of electrons around bonds

symmetric vibrations

solvent – H_2O

Intensity of Raman lines are 0.001% intensity of the source

Raman Spectroscopy

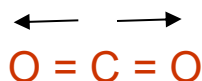
Overview

Active Raman Vibrations:

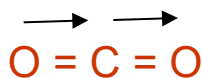
- need change in polarizability of molecule during vibration
- polarizability related to electron cloud distribution



example:



IR inactive
Raman active



IR active
Raman inactive

IR & Raman are complimentary. Can be cases where vibration is both IR & Raman active (eg. SO_2 – non-linear molecule)

In general:

IR tends to emphasize polar functional groups (R-OH, , etc.)

Raman emphasizes aromatic & carbon backbone (C=C, -CH₂-, etc.)

- Raman does not “see” many common polar solvents can use with aqueous samples-advantage over IR

Raman Spectroscopy

Determination of Polarizability Changes for Molecular Vibrations

There are three factors that contribute to polarizability changes during a vibration:

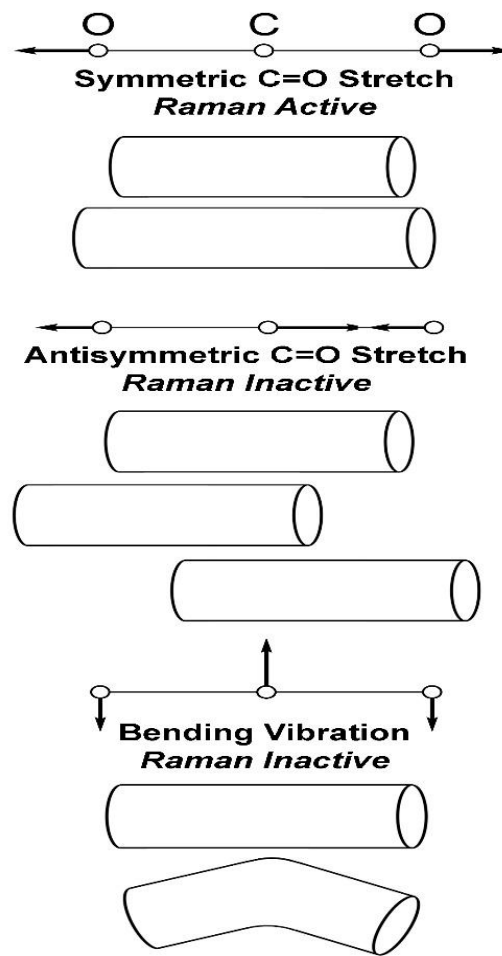
- A change in the volume of the molecular cloud.
- The strength with which the electrons are bound. Loosely bound electrons are more easily-polarized.
- The number of electrons in the constituent atoms.

Polarizability can be measured and it has units of VOLUME (cm^3). A vibration that produces a large volume change of the molecular cloud produces a large polarizability change.

Raman Spectroscopy

Molecular Volume Changes: Vibrations of CO₂

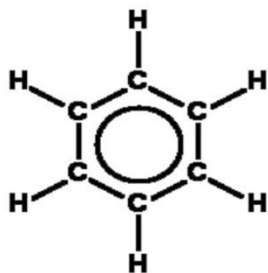
The symmetric stretch of CO₂ involves a volume change and is Raman active. The antisymmetric stretch and the bend do not involve volume changes and are Raman inactive.



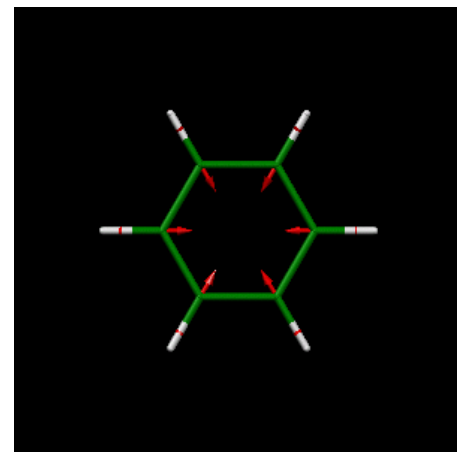
Raman Spectroscopy

Aromatic Ring “Breathing” Vibrations

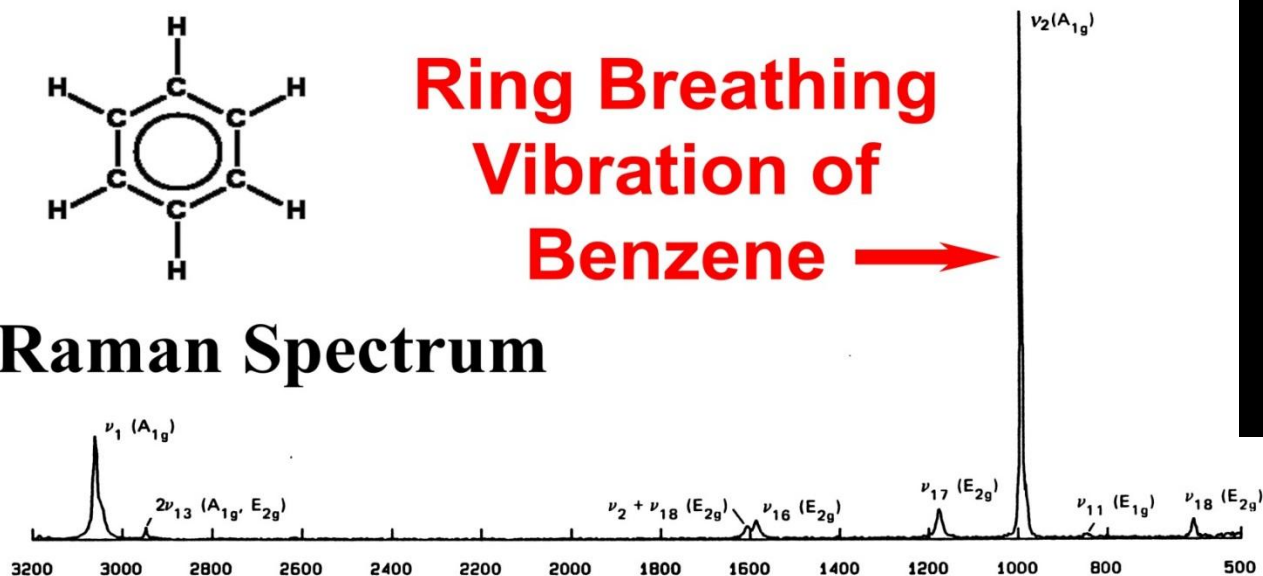
One of the vibrations of benzene involves a motion where all of the C=C bonds are stretching in phase. The entire ring is expanding or “breathing.” This involves loosely held pi electrons and results in a large volume change. A very strong Raman peak.



**Ring Breathing
Vibration of
Benzene** →



Raman Spectrum



Raman Spectroscopy

Typically a technique that is complementary to IR.

However some of the advantages include:

- Use water as a solvent
- Signals in vis or near IR – so can use glass and quartz

Raman Spectroscopy

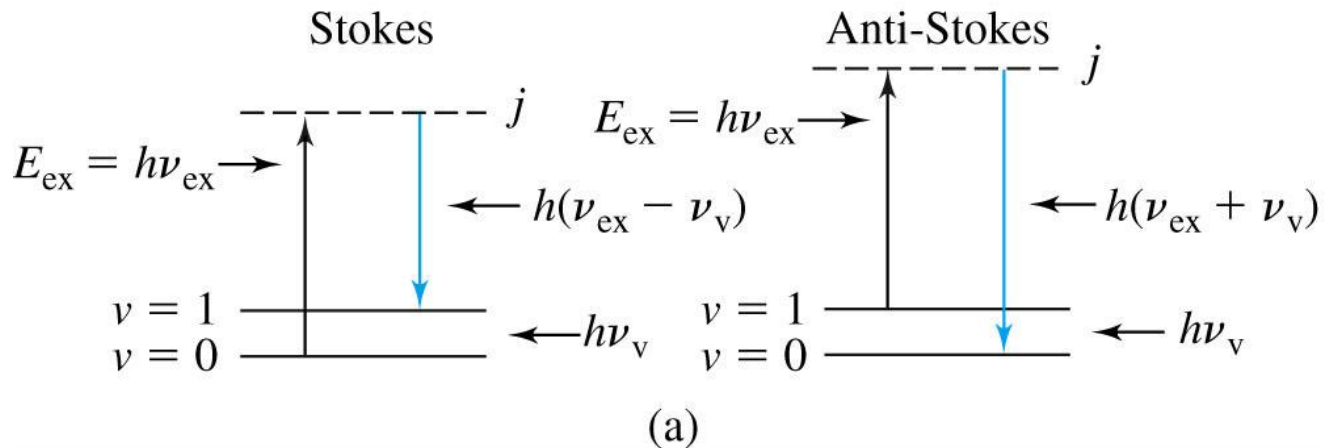
How does Raman work?

- The majority of light scattered is emitted at the identical frequency of the incident light, a process referred to as elastic scattering.

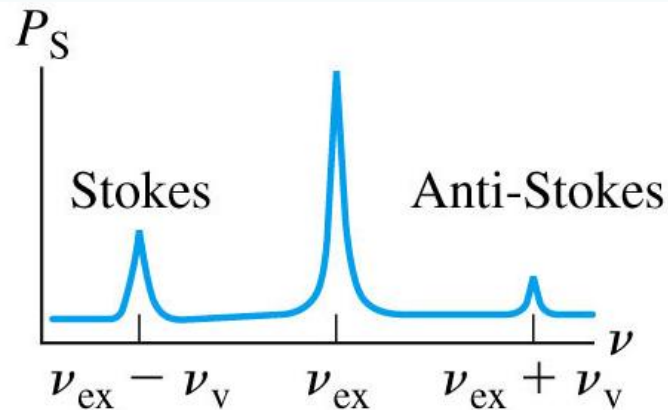
However Raman is inelastic scattering

- The sample is irradiated at a certain excitation λ of $h\nu_{\text{ex}}$
- A molecule in the ground state can absorb the photon ($h\nu_{\text{ex}}$) and reemit a photon of energy $h(\nu_{\text{ex}} - \nu_{\text{v}})$
- When scattered radiation is of lower frequency (longer λ) it is Stokes scattering
- When scattered radiation is of higher frequency (shorter λ) it is anti-Stokes scattering

Raman Spectroscopy



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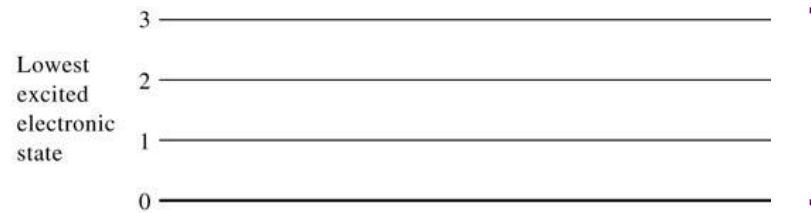


Probability of Emission Observed Intensity

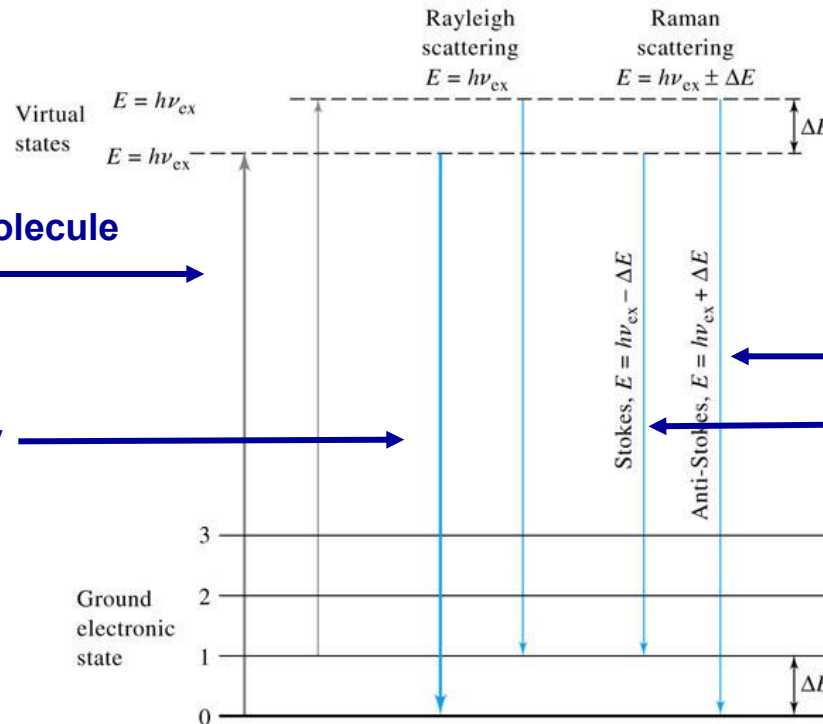
Raleigh scattering \gg Stokes \gg anti-Stokes

difference in population of energy levels of vibrational transitions

Raman Spectroscopy



No change in electronic states



Infinite number of virtual states

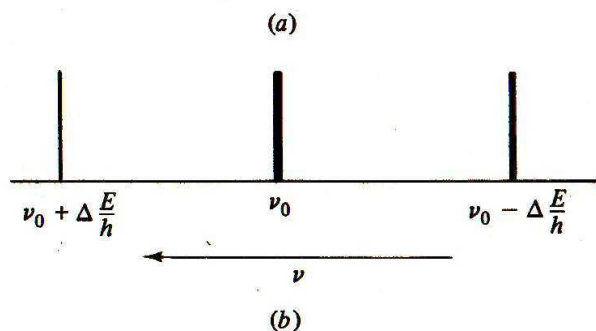
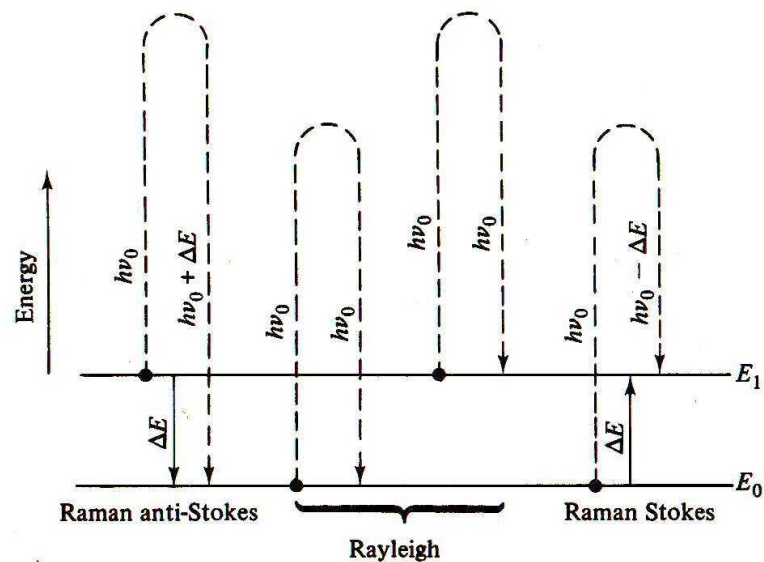
energy absorbed by molecule from photon of light not quantized

Rayleigh Scattering
no change in energy
 $h\nu_{in} = h\nu_{out}$

Raman Scattering
net change in energy
 $h\nu_{in} \neq h\nu_{out}$

Raman Spectroscopy

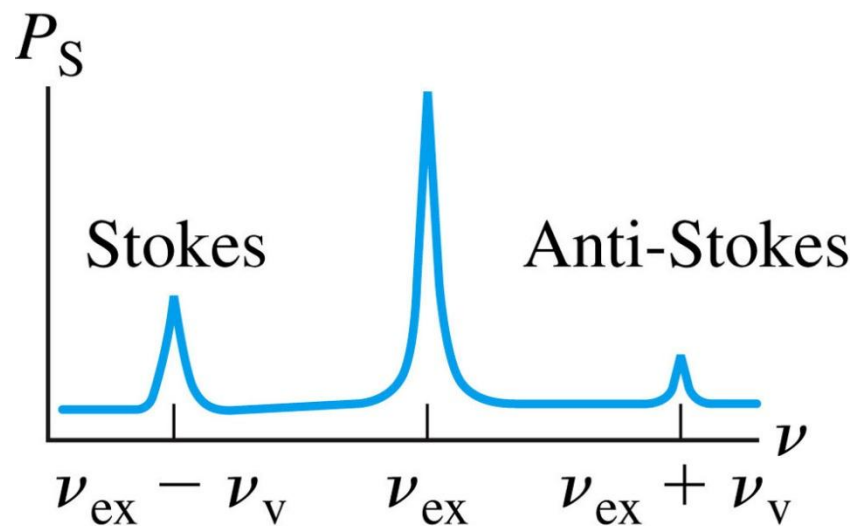
Virtual levels are not real levels –
concept formation only.



Raman Spectroscopy

How does Raman work?

- Scattered radiation at the same frequency is referred to as Rayleigh scattering.

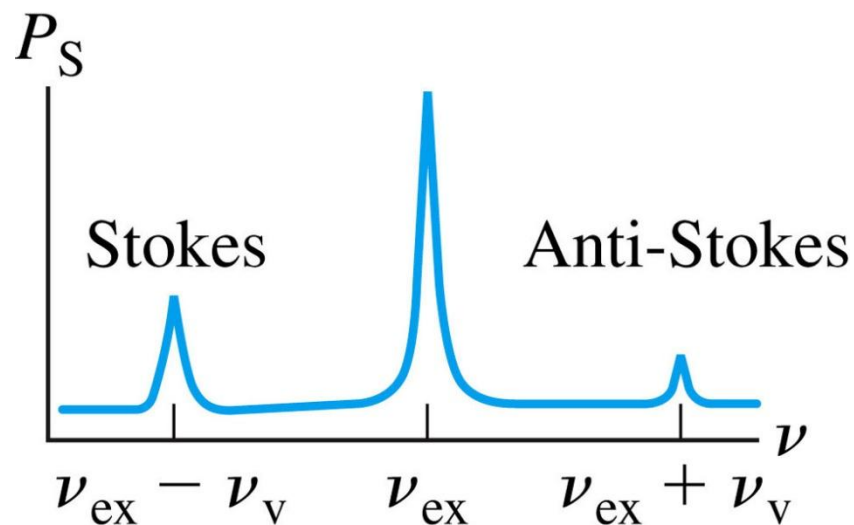


(b)

Raman Spectroscopy

How does Raman work?

- **Anti-Stokes lines are less intense than Stokes lines. However fluorescence sometimes interferes with the Stokes lines.**



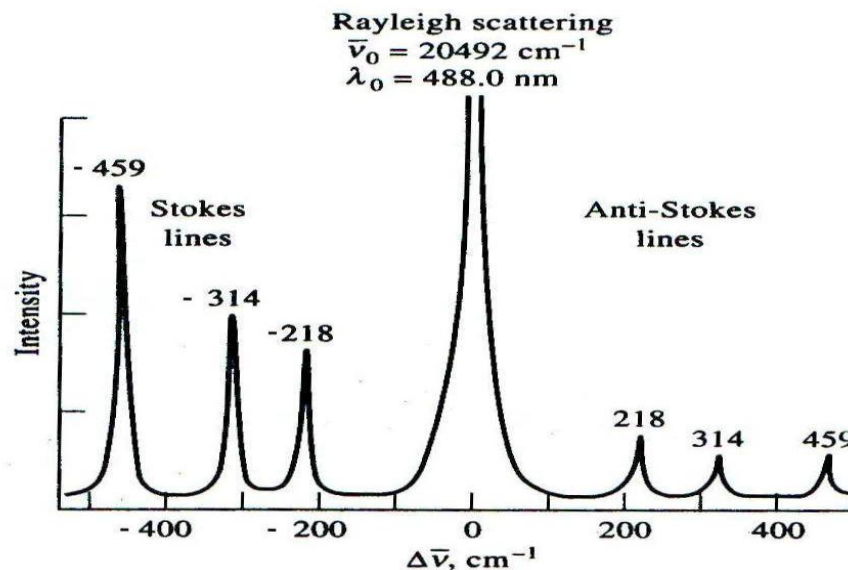
(b)

Raman Spectroscopy

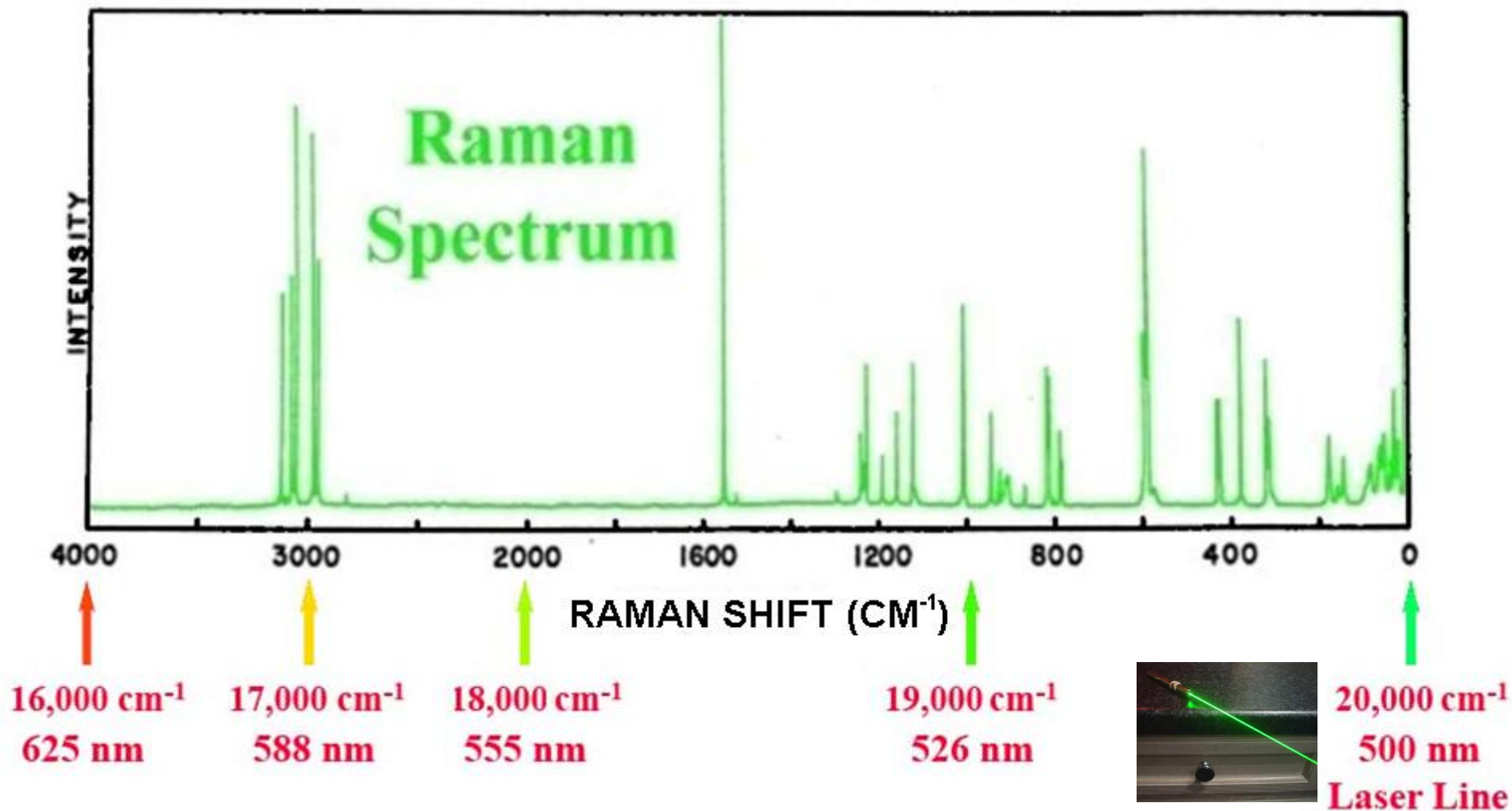
How does Raman work?

- The magnitude of Raman shifts is *independent* of the excitation wavelength. So a molecule will give the same spectrum for an argon-ion laser (488.0) as for a helium-neon laser (632.8 nm)

CCl4



Raman Data Are Plotted as *Shifts* from the Laser Frequency



Actual Frequency of Scattered Light Analyzed

Assume we are using a green visible laser (500.0 nm or 20,000 cm⁻¹) for excitation. The Raman peak at 3,000 cm⁻¹ is actually a scattered line at 17,000 cm⁻¹.

Raman Spectroscopy

Intensity of Scattering

$$I_s = \frac{8\pi^4 \alpha^2}{\lambda^4 r^2} (1 + \cos^2 \theta) I_o$$

α = polarizability of particle

λ = wavelength of incident radiation

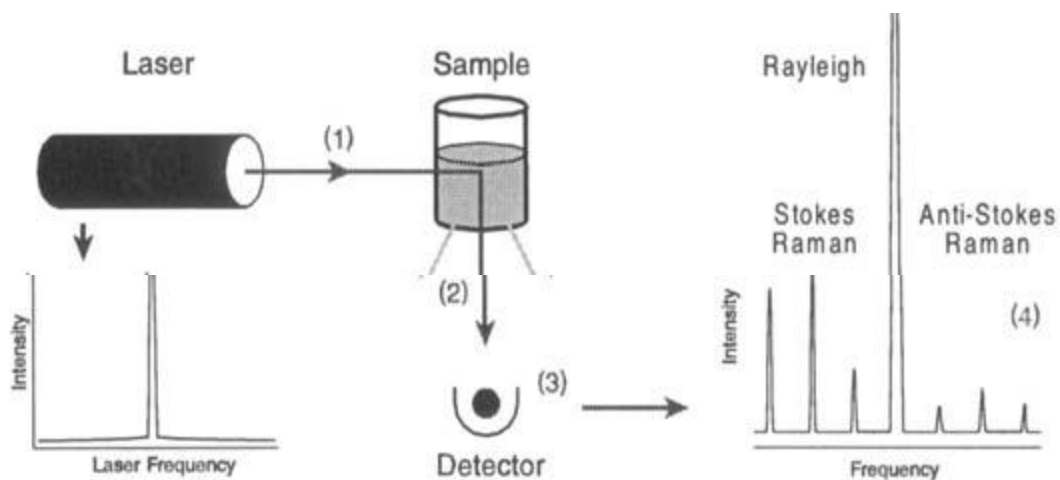
I_o = incident intensity

θ = angle incident /scattered ray

r = distance, center of scattering to detector

Raman Spectroscopy

Raman experiment



Raman Spectroscopy

Instrumentation

- Laser source
- Sample cell
- Wavelength selector
- Detector

Raman Spectroscopy

Sources

Always lasers – need high intensity to produce Raman scattering of enough intensity.

Raman Spectroscopy

TABLE 18-1 Some Common Laser Sources for Raman Spectroscopy

Laser Type	Wavelength, nm
Argon ion	488.0 or 514.5
Krypton ion	530.9 or 647.1
Helium-neon	632.8
Diode	785 or 830
Nd-YAG	1064

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Raman Spectroscopy

Lasers

Since the intensity of Raman varies as the fourth power of the frequency, argon and krypton sources are preferred.

However can produce significant fluorescence and cause photodecomposition of the sample.

Raman Spectroscopy

Samples

Can run gas, liquids, or solids.

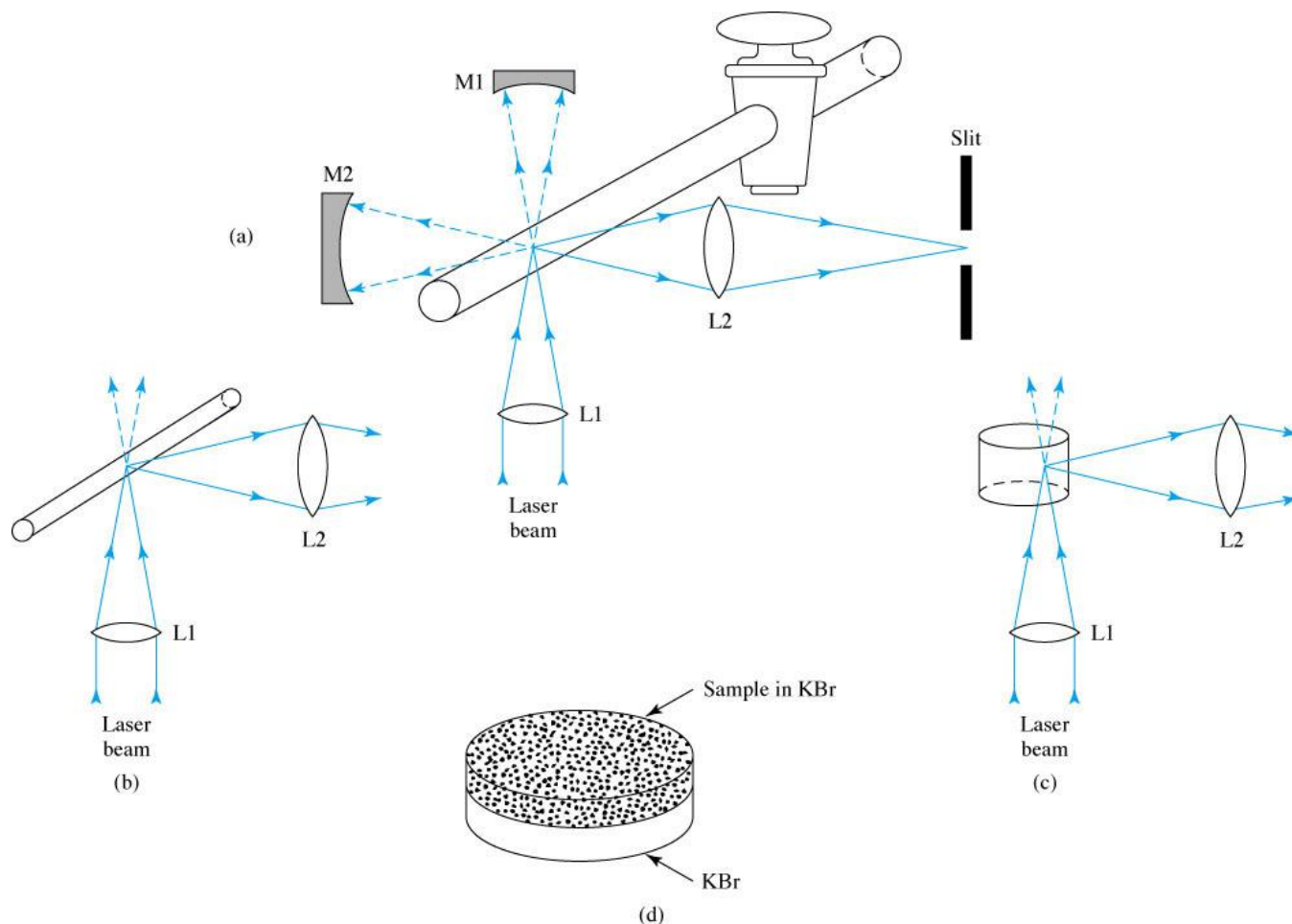
Liquids can be in glass and water as a solvent can be used.

Gases can be in sealed glass tubes.

Solids can be pellets or powders.

Raman Spectroscopy

Samples



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Raman Spectroscopy

Wavelength Selectors

Need a high quality selection device to separate the weak Raman lines from the intense Rayleigh scattered radiation.

Dispersive must use double or triple-grating monochromators.

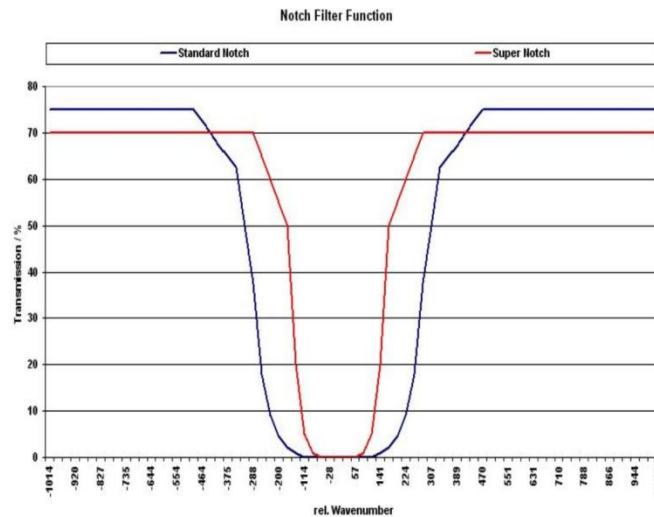
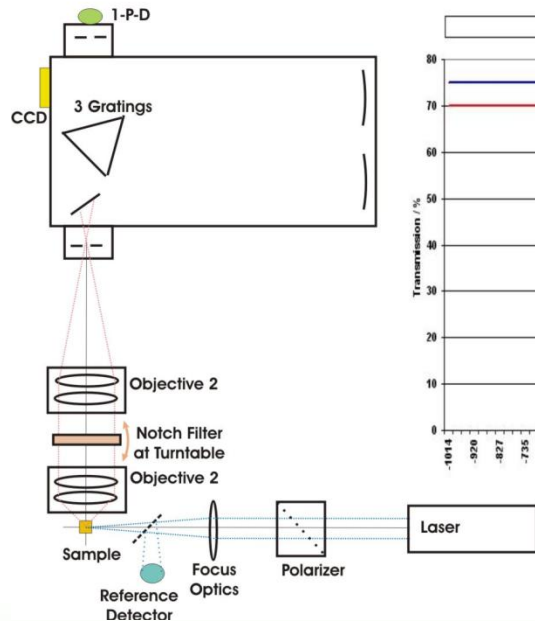
Also can use holographic interference filters (notch filters) and holographic gratings.

Most commercial instruments now combine both.

Raman Spectroscopy

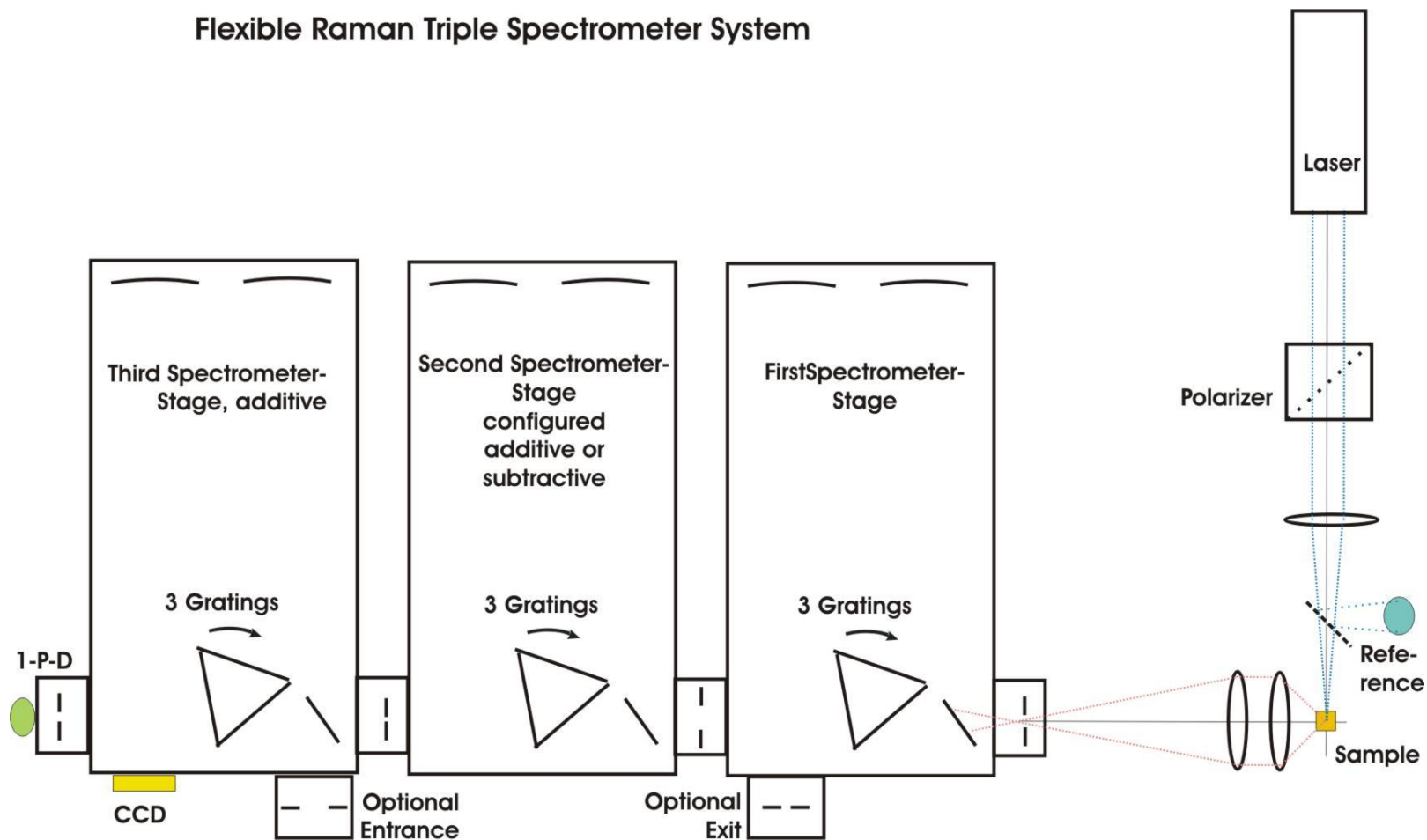
HNFs are made by recording interference pattern formed by laser beams in a layer of dichromated gelatin held between two plate glasses.

Single Stage Raman System with Notch Filter



Raman Spectroscopy

Flexible Raman Triple Spectrometer System



Raman Spectroscopy

Intensities of Raman are 0.001% of the intensity of the source but since the Raman scattered radiation is in the vis or near IR region can use very sensitive detectors.

Raman Spectroscopy

Detectors

- PMT, PDA, and CCD. (Dispersive)
- Ge (FT-Raman)

CCD's have become more popular as cost has gone down.

Raman Spectroscopy

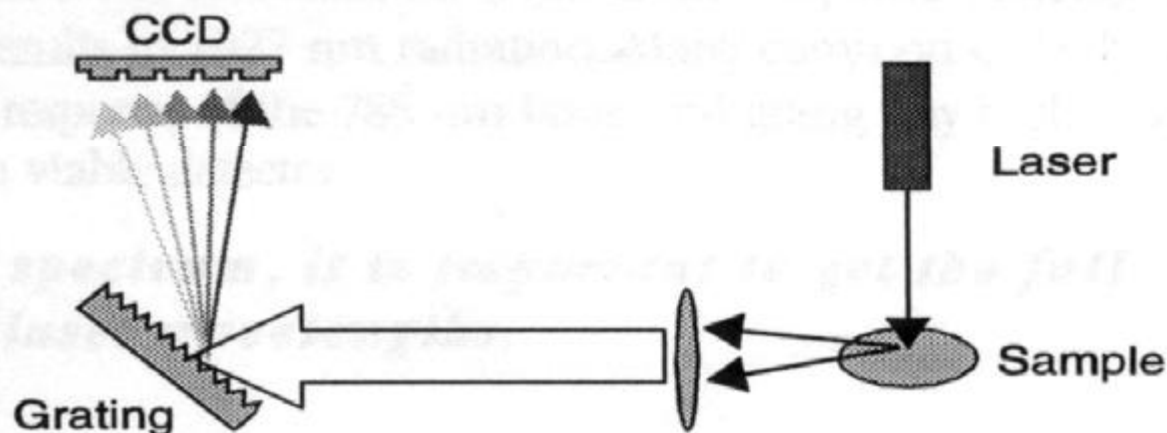
Raman spectrometers basically employ one of two technologies for the collection of spectra

- Dispersive Raman**
- Fourier Transform Raman (FT- Raman)**

Each technique has unique advantages and each is ideally suited to specific analyses but dispersive Raman dominates.

Raman Spectroscopy

Dispersive Raman Spectroscopy

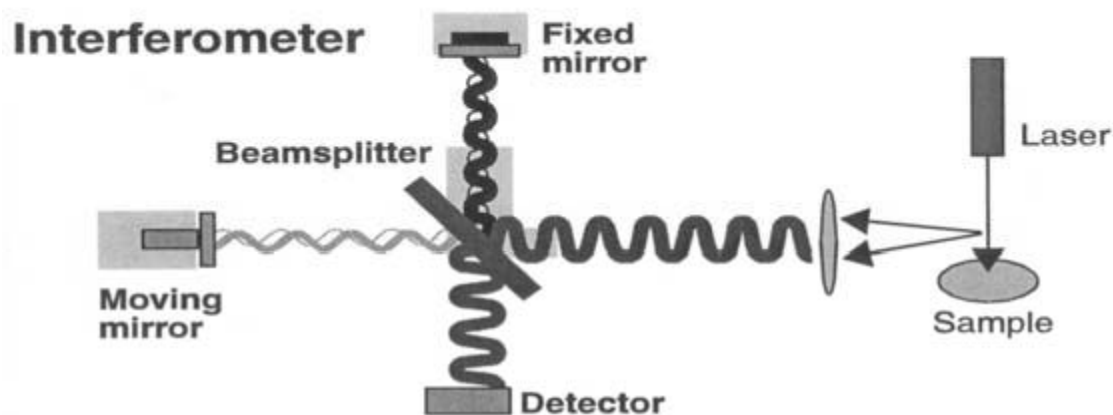


To separate the collected Raman scattered light into individual wavelengths, the Raman signal is focused onto a grating that separates the light into the different frequencies. Then, the **dispersed beam** is directed to the CCD (charged-coupled devices) detector to be collected

Raman Spectroscopy

FT-Raman (Nondispersive Raman)

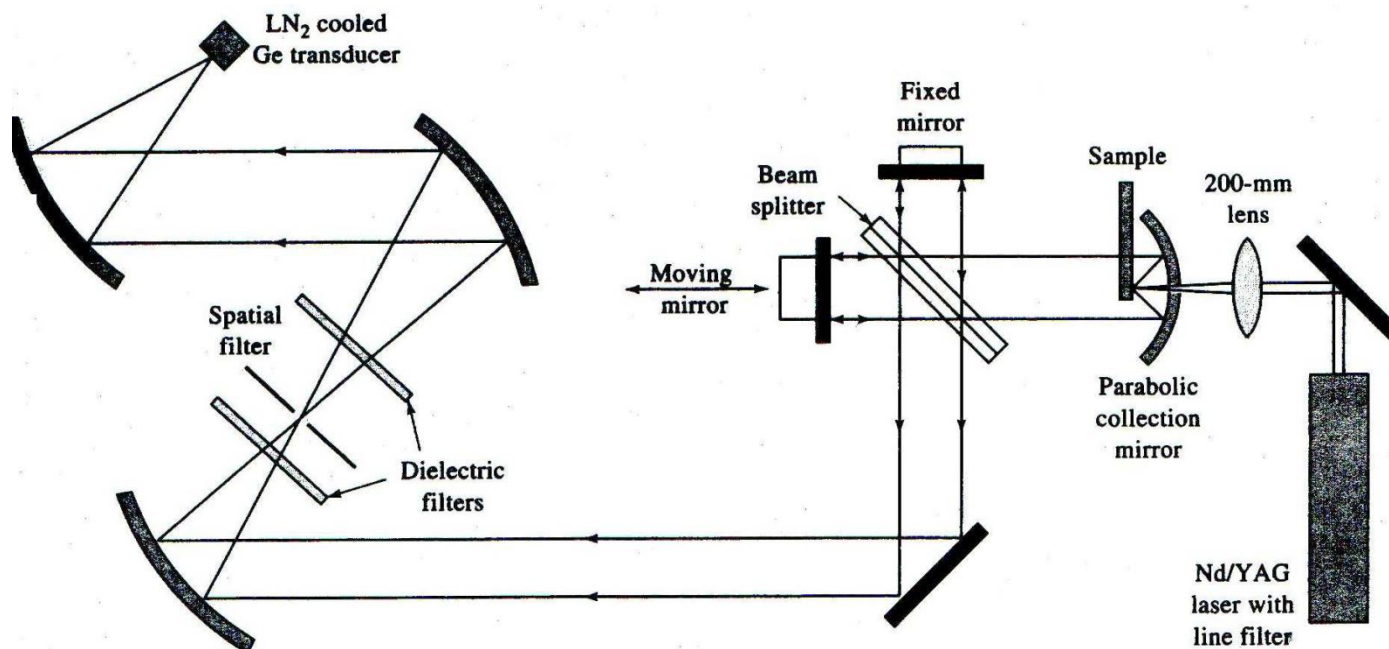
Consists of an excitation laser (longer wavelength), an interferometer and high sensitivity near IR detector.



Interferometer produces interferogram which encodes the unique frequencies of the Raman scattering into a single signal.

Raman Spectroscopy

FT-Raman (Nondispersive Raman)

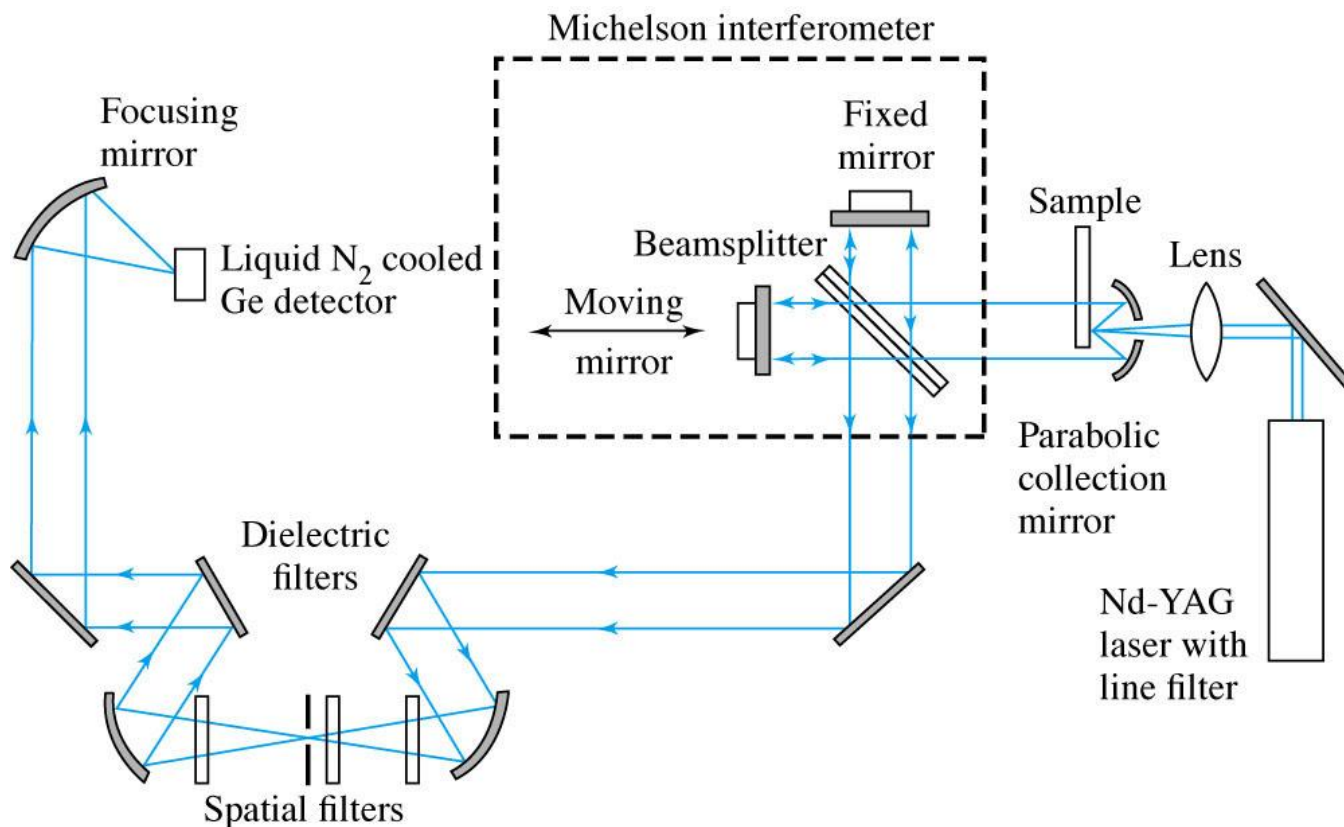


Dielectric filters remove the Rayleigh line

– either a notch filter, or a low (frequency) pass filter (high wavelength pass) - high pass limits to Stokes lines

Raman Spectroscopy

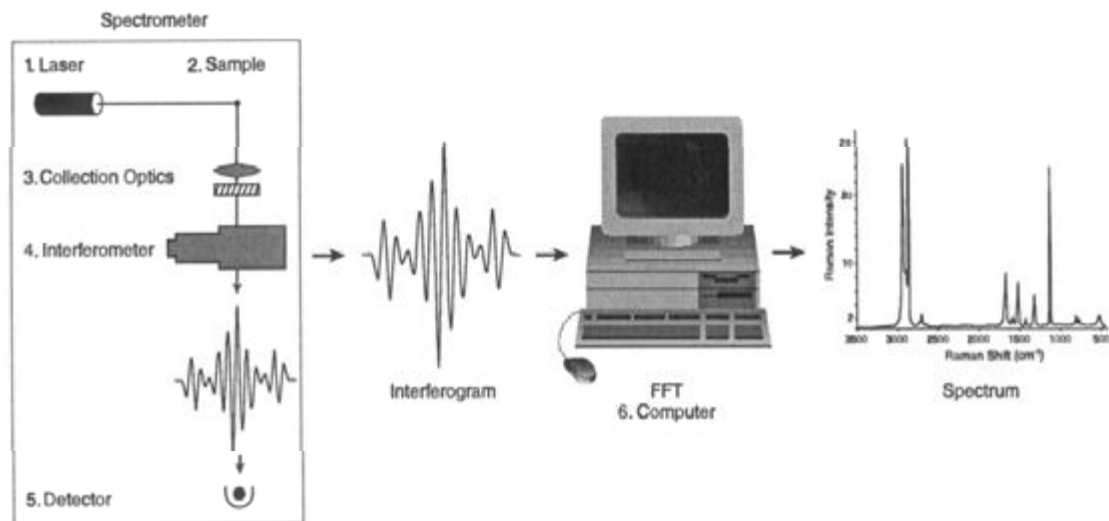
FT-Raman (Nondispersive Raman)



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Raman Spectroscopy

How does FT-Raman work



Vibrational spectra are presented as frequency spectra, which are then decoded using Fourier transformation mathematical techniques, and finally the desired spectral information is presented.

Raman Spectroscopy

Dispersive vs. FT-Raman Spectrometers

Feature	Dispersive (Raman)	FT (Raman)
Available Wavelength	<200 nm to 850 nm	1064 nm (IR region)
Fluorescence	More fluorescence (Except UV)	Better fluorescence avoidance
Detector	CCD	Ge or GaAs
Best Spectral Resolution	Typically 1-4 cm^{-1}	$\sim 0.5\text{cm}^{-1}$
Advantages	Extremely sensitive. Can run samples with water.	Less fluorescence and photodecomposition. Can run dyes. Do spectral subtraction.
Disadvantages	Much more expensive. Intensive alignments.	Water absorbs in 1000 nm region. Must cool detector.

Raman Spectroscopy

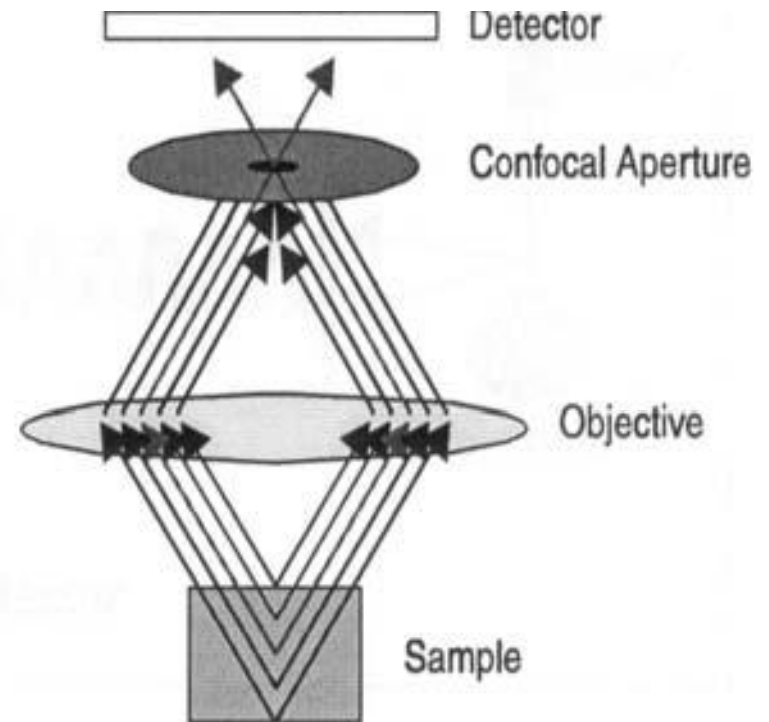
Couple Raman Spectroscopy with a Microscope

Why?

- Allows analysis of very small samples
- Distinguish the substance of interest from its surrounding.

How does it work?

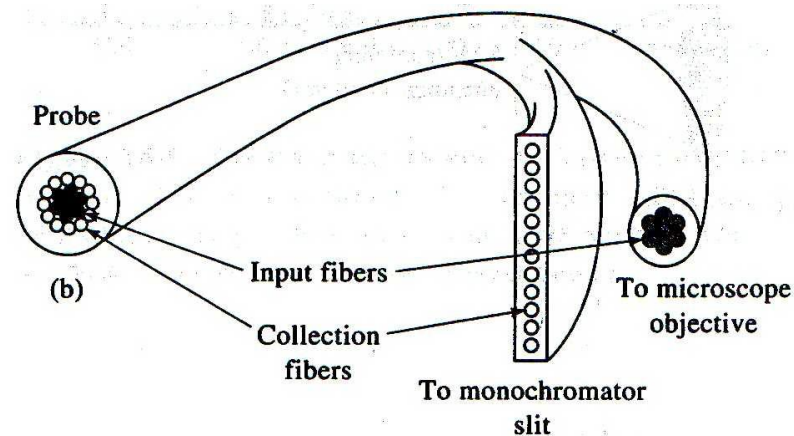
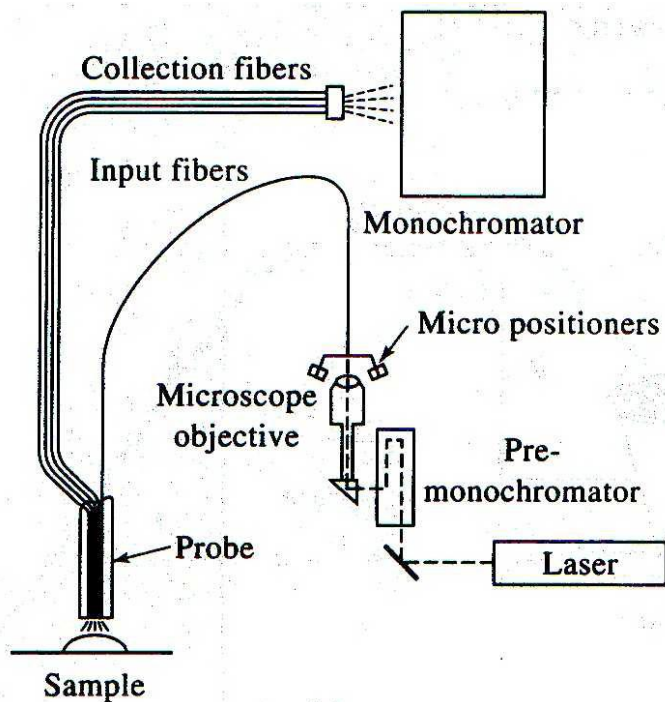
- By focusing the laser beam onto the sample, and passing the returning beam into the system for analysis and detection.



Raman Spectroscopy

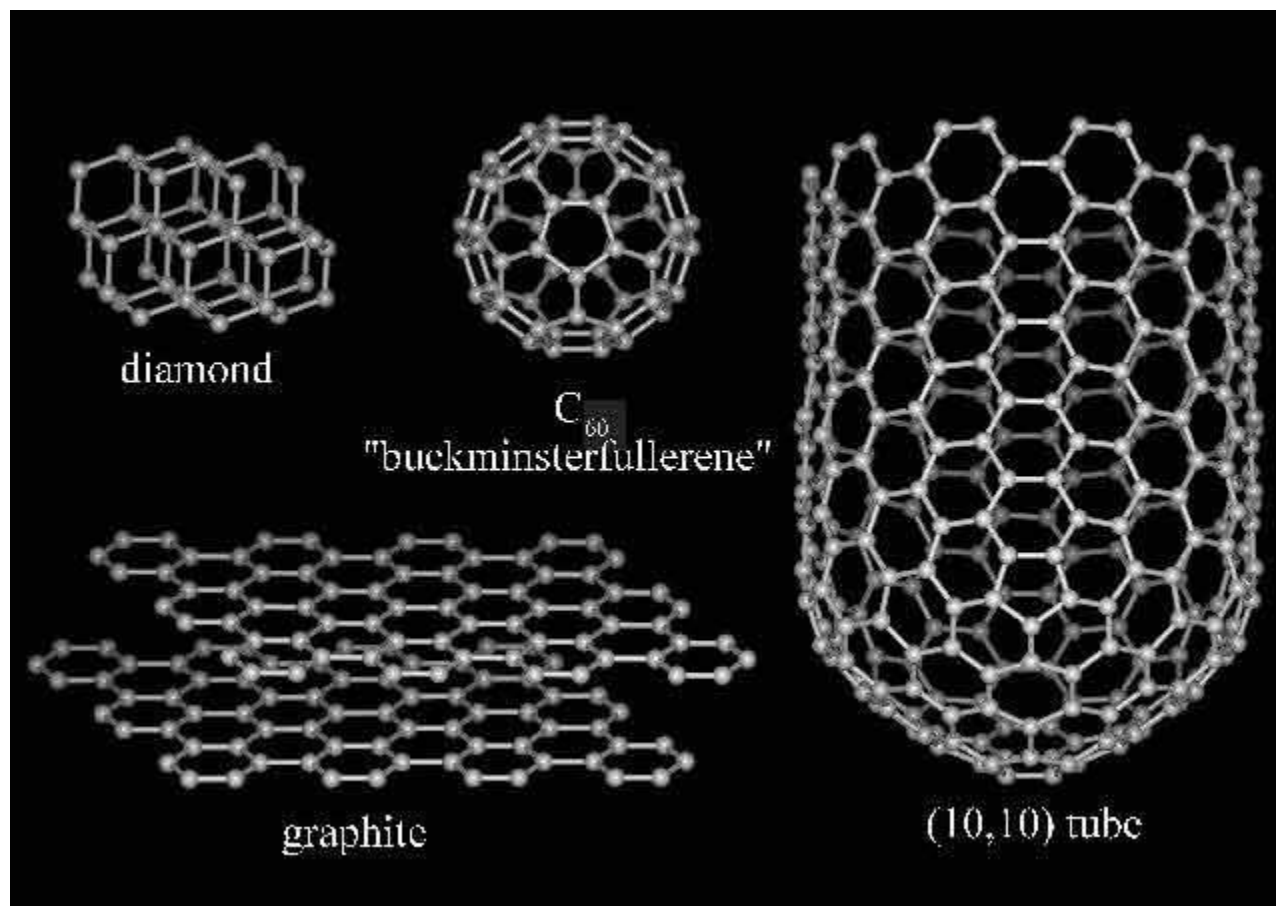
Raman Probe

Portable instrument



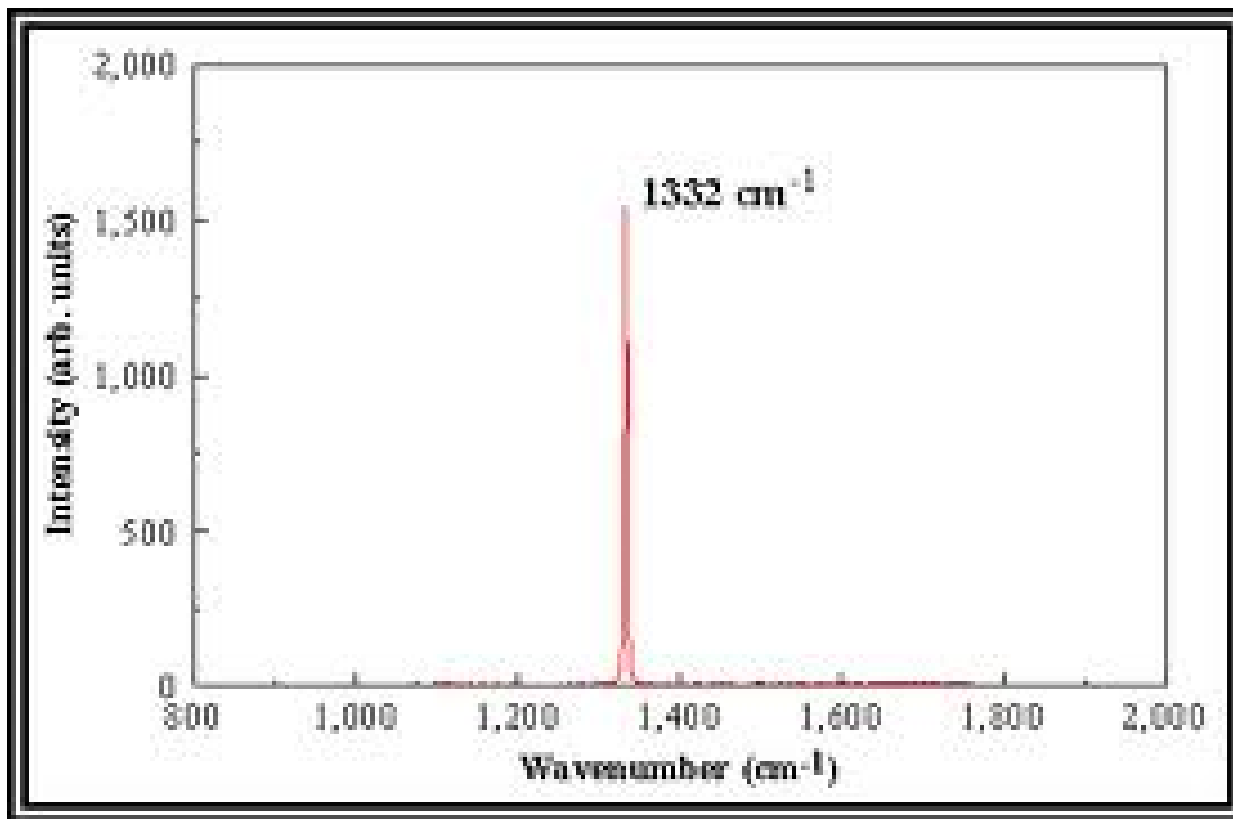
Raman Spectroscopy

Carbon Allotropes



Raman Spectroscopy

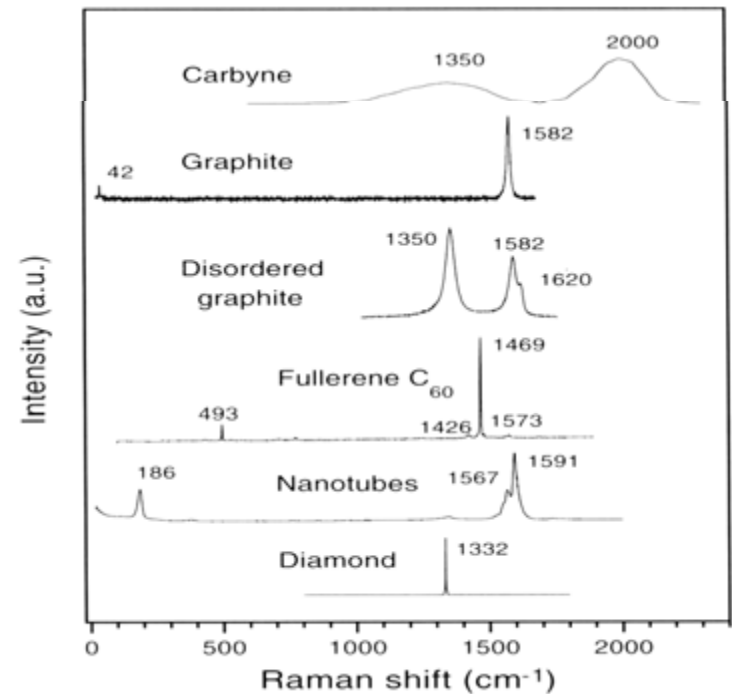
Diamond Raman Spectrum



Raman Spectroscopy

Raman Spectroscopy is Useful For Various Carbon Materials

- Carbyne (sp bonded carbon)
- Graphite (sp² bonded carbon)
- Disordered sp² bonded graphite
- Fullerene C₆₀
- Carbon Nanotubes
- Diamond (sp³ bonded carbon)



Raman Spectroscopy

Raman Spectroscopy is Useful For Various Carbon Materials

Frequency (cm ⁻¹)	Assignment
1100~1600 (broad) ** 1140	Amorphous Carbon Microcrystalline or Nanocrystalline Diamond
1140 and 1470 ** 1270	Polymeric Chains like <i>trans</i> Polyacetylene or Polyenes Amorphous Diamond
1332	Crystalline Diamond
1350	Microcrystalline Graphite
** 1350 (D band) and 1550 (G band)	Disorder Graphite and Graphite in Typical DLC Film
1470	Tetrahedrally Bonded Diamond Precursor Phase
1582	Crystalline Graphite

Raman Spectrometry

Raman Spectroscopy in Materials Research

Corrosion

- Analysis of corrosion products and anticorrosion coatings, as well as the identification of micron-sized contaminants within the coatings can be measured.
- In-situ electrochemical studies concerned with corrosion product formation are now possible.
- Measure the composition of corrosion products over a large surface with a $1\mu\text{m}$ sample analysis area can be done.

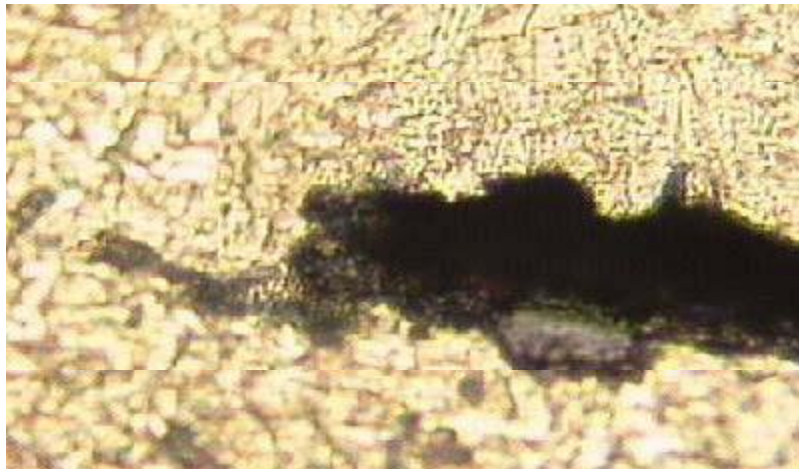
Raman Spectrometry

Raman Bands of the Main Corrosion Products of Steel

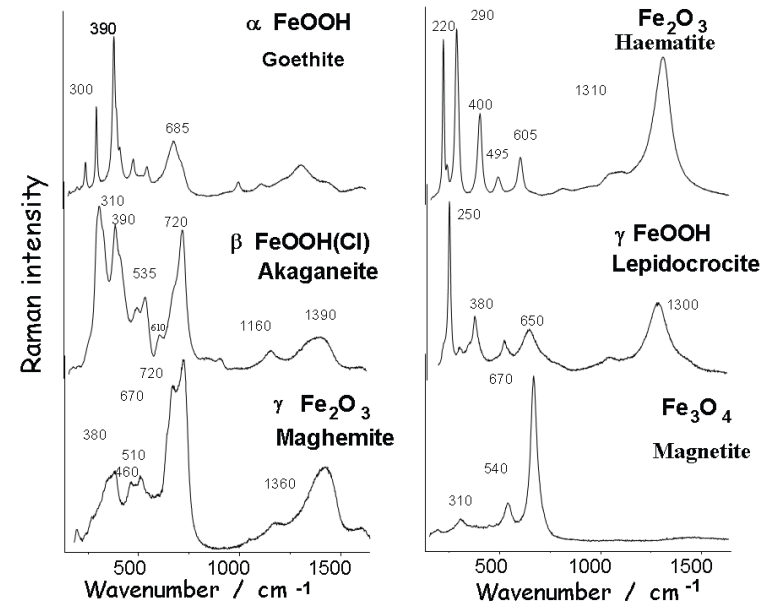
- α -FeOOH peaks at about 245, 300, 390, 420, 480, 550 and 685 cm^{-1})
- γ - FeOOH (peaks at about 250 and 380 cm^{-1})
- Fe₃O₄ (peaks at about 540 and 665 cm^{-1})
- γ -Fe₂O₃ (peaks at about 265, 300, 345, 395, 515, 645, 670, 715 and 1440 cm^{-1})
- α -Fe₂O₃ (peaks at about 225, 245, 295, 415, 500, 615, and 1320 cm^{-1})

Raman Spectrometry

Raman Analysis of Corrosion Products at SCC (Stress Corrosion Cracking)



Polished cross-section, tip of an SCC crack
Zhang, Gogotsi, Chudnovsky, Teitsma 1998



Assignment

- HW6 Chapter 16: 7, 8, 11, 12
- HW7 Chapter 17: 2, 4, 5
- HW6 - Due 2-27
- HW7 - Due 2-27
- Exam 2- Lectures 9 to 17 – Wednesday March 4th
- Read Chapter 18
- HW 8 Chapter 18: 1, 2, 3, 5, 6, 8
- HW 8 Chapter 18 Due 3-4

Raman Spectroscopy

Molecular Raman Spectroscopy

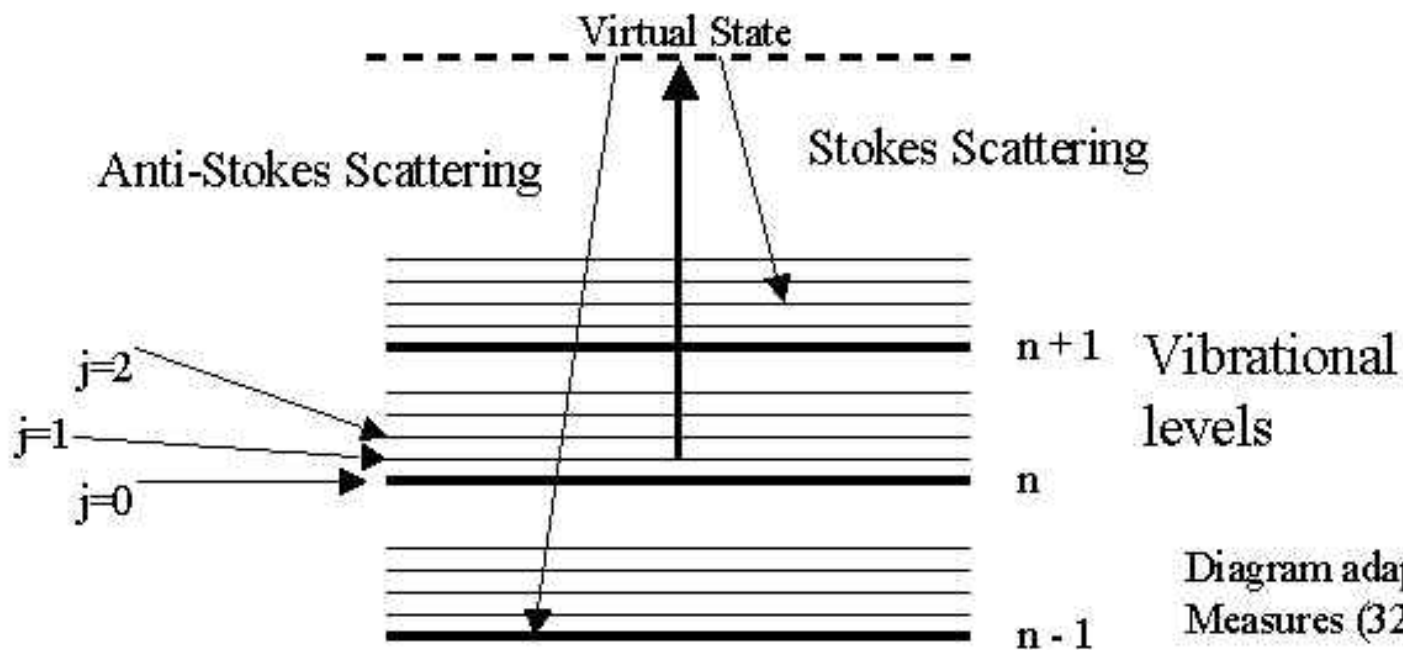


Diagram adapted from
Measures (321).