Vibrational Spectroscopies

C-874

University of Delaware

Vibrational Spectroscopies

"..everything that living things do can be understood in terms of the jigglings and wigglings of atoms.."

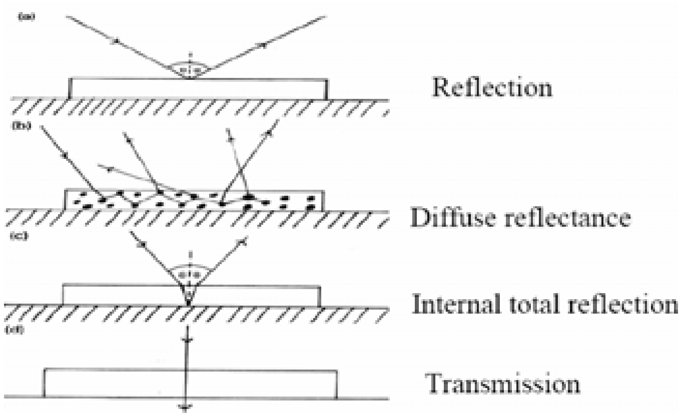
R. P. Feymann

Vibrational Spectroscopies

All vibrational spectroscopies are founded in interaction of functional groups in molecules with electro-magnetic radiation

What kinds of vibrational spectroscopies are outthere?

- **Infrared spectroscopy**
- **Raman scattering**
- **High-resolution electron energy loss spectroscopy**
- **Non-linear vibrational spectroscopies (sum frequency generation, second harmonic generation)**
- **Scanning tunneling vibrational spectroscopy (performed by analyzing inelastic tunneling spectra taken with scanning electron microscope on a single molecule)**



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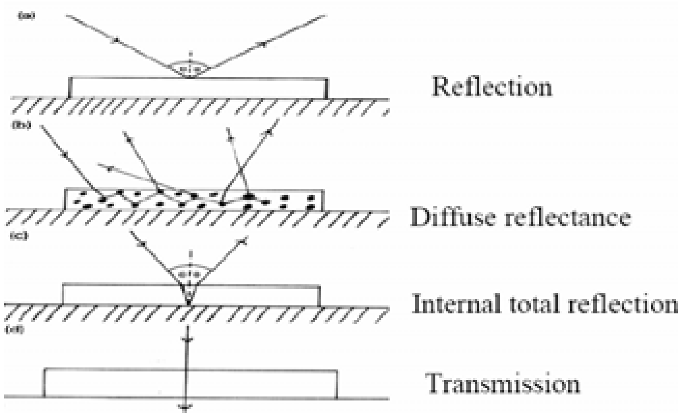


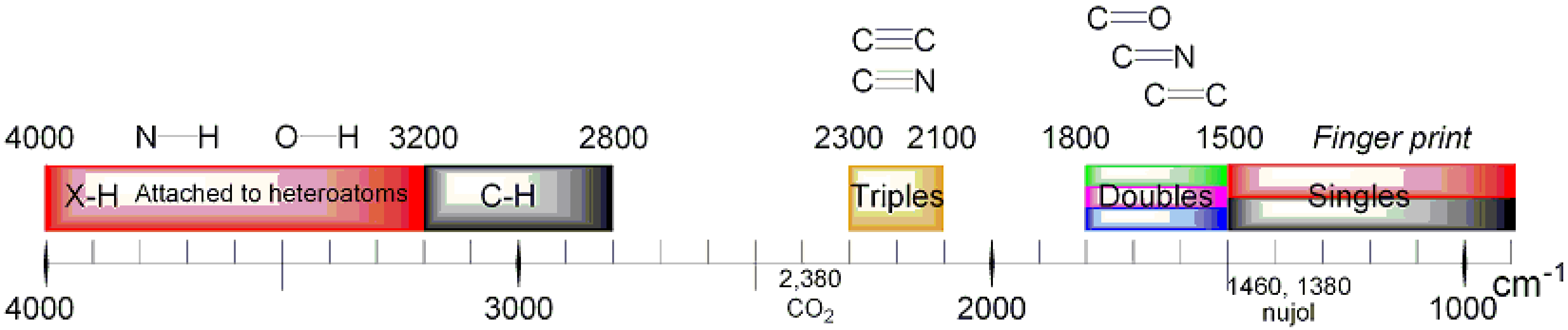
Infrared spectroscopy

Infrared spectroscopy exploits the fact that molecules have specific frequencies at which they rotate or vibrate corresponding to discrete energy levels (vibrational modes). These resonant frequencies are determined by the shape of the molecular potential energy surfaces, the masses of the atoms and, by the associated vibronic coupling. In order for a vibrational mode in a molecule to be IR active, it must be associated with changes in the **permanent dipole**.

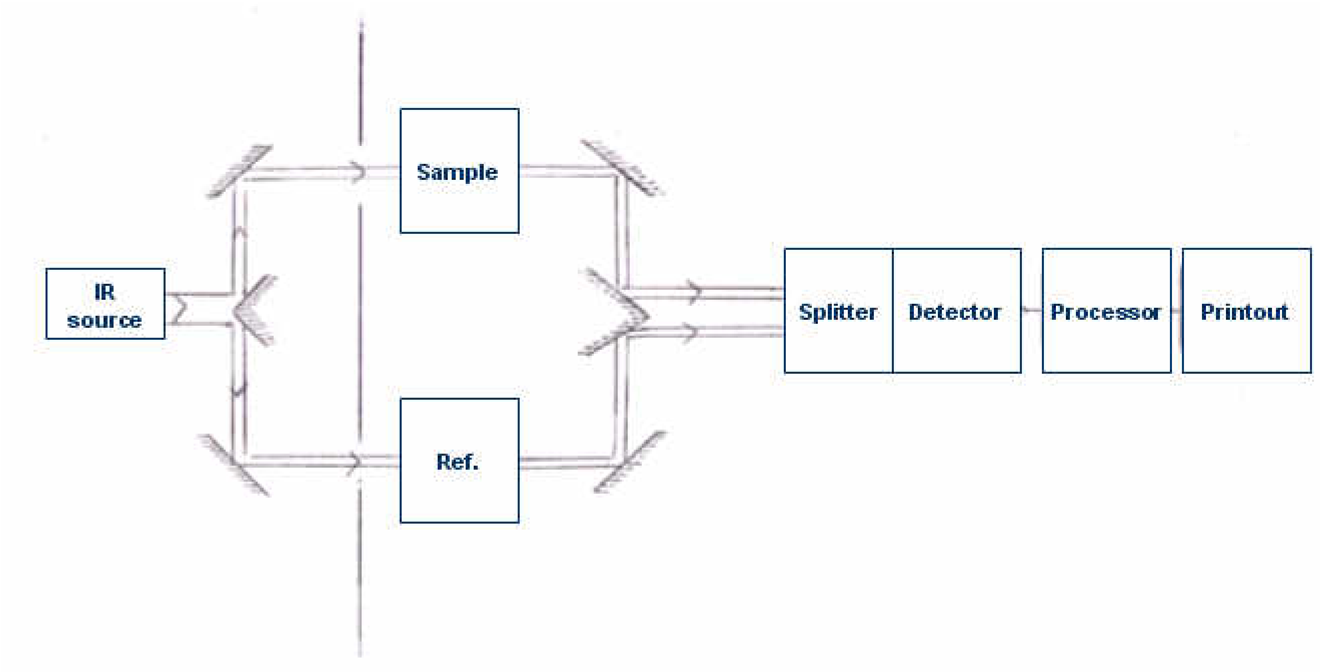
Infrared spectroscopy

The infrared portion of the electromagnetic spectrum is divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The far-infrared, approximately 400–10 cm^{-1} (1000–30 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The mid-infrared, approximately 4000–400 cm^{-1} (30–2.5 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The higher energy near-IR, approximately 14000–4000 cm^{-1} (2.5–0.8 μm) can excite overtone or harmonic vibrations. The names and classifications of these subregions are merely conventions. They are neither strict divisions nor based on exact molecular or electromagnetic properties.

Infrared Spectroscopy



Infrared Spectroscopy (Equipment)

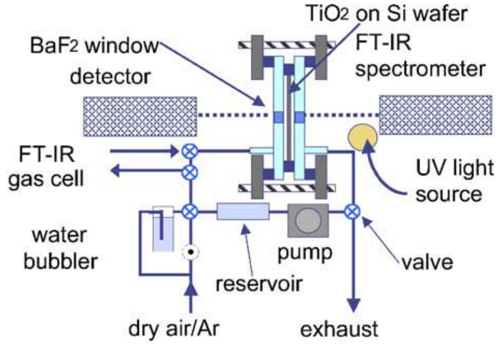


Infrared Spectroscopy Techniques

Fourier transform infrared (FTIR) spectroscopy is a measurement technique for collecting infrared spectra. Instead of recording the amount of energy absorbed when the frequency of the infra-red light is varied (monochromator), the IR light is guided through an interferometer. After passing through the sample, the measured signal is the interferogram. Performing a Fourier transform on this signal data results in a spectrum identical to that from conventional (dispersive) infrared spectroscopy.

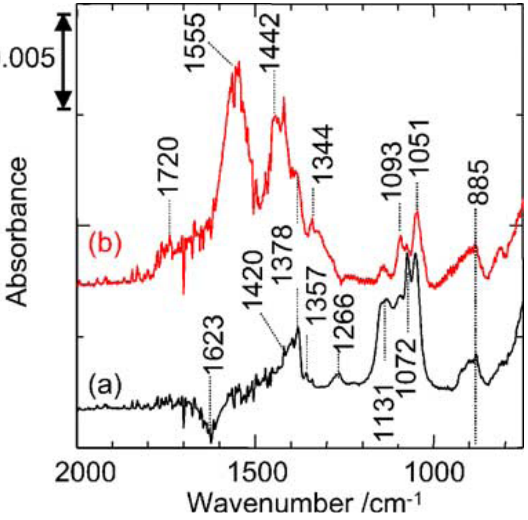
Infrared Spectroscopy Techniques

1) Transmission infrared spectroscopy



(a)

(b)

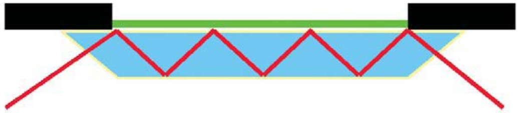


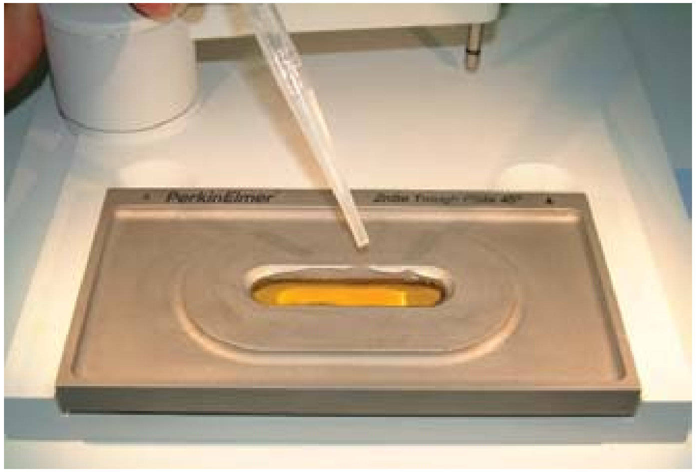
Thin-film transmission spectra of the photocatalytic decomposition of ethanol: (a) before UV illumination, (b) after 3 h of UV illumination

Sho Kataoka, M. Isabel Tejedor-Tejedor, Juan M. Coronado, Marc A. Anderson
Journal of Photochemistry and Photobiology A: Chemistry 163 (2004) 323–329

Infrared Spectroscopy Techniques

2) Attenuated total reflectance infrared spectroscopy (ATR-FTIR)





Using a pipette to add a liquid
sample to a ZnSe HATR trough plate.

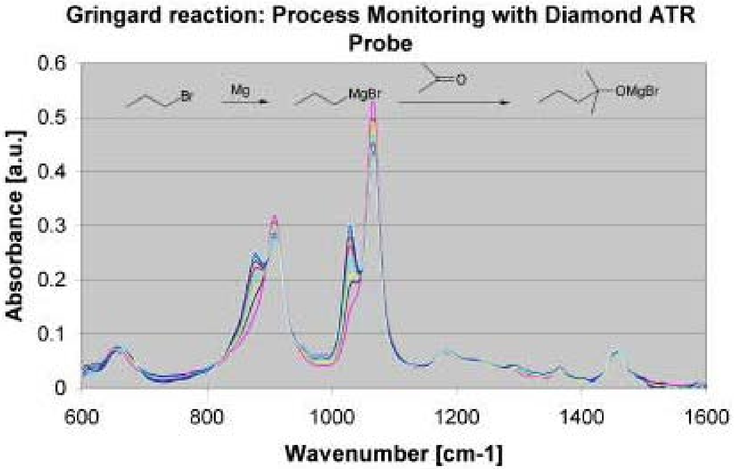
Applying pressure to a solid sample
on the Universal diamond ATR top-plate.

http://las.perkinelmer.com/content/TechnicalInfo/TCH_FTIRATR.pdf

Infrared Spectroscopy Techniques

2) Attenuated total reflectance infrared spectroscopy (ATR-FTIR)

Fiber-optic MolecularEye ATR diamond probe from

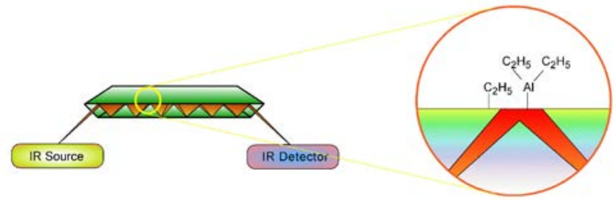


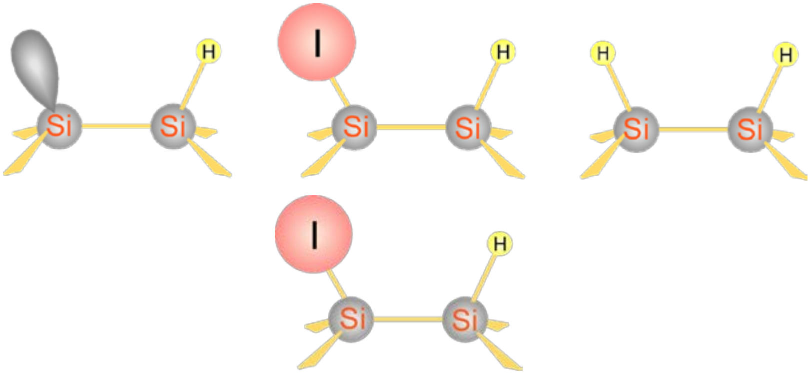
http://www.chemshow.cn/UploadFile/datum/1000/bosheng_2009114141928791780.pdf

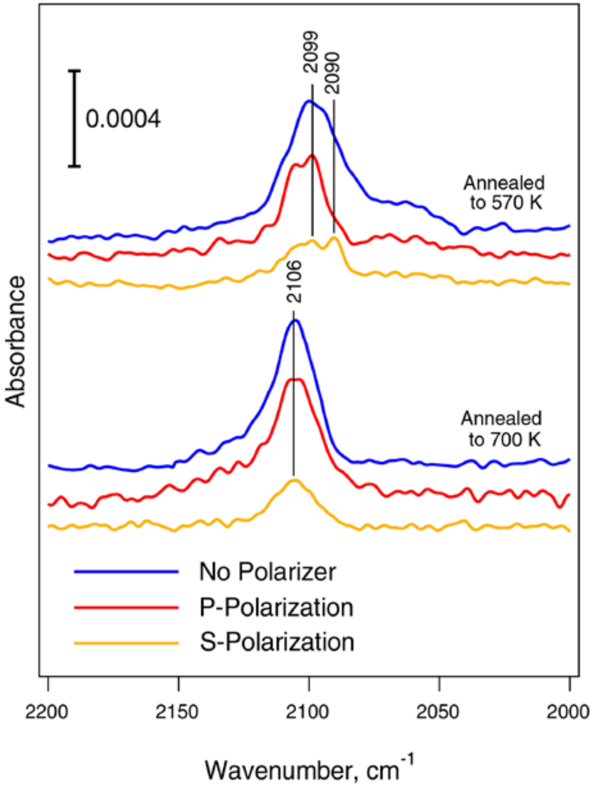
Infrared Spectroscopy Techniques

2) Attenuated total reflectance infrared spectroscopy (ATR-FTIR)

Multiple-internal reflectance Fourier-transform infrared spectroscopy (MIR-FTIR)



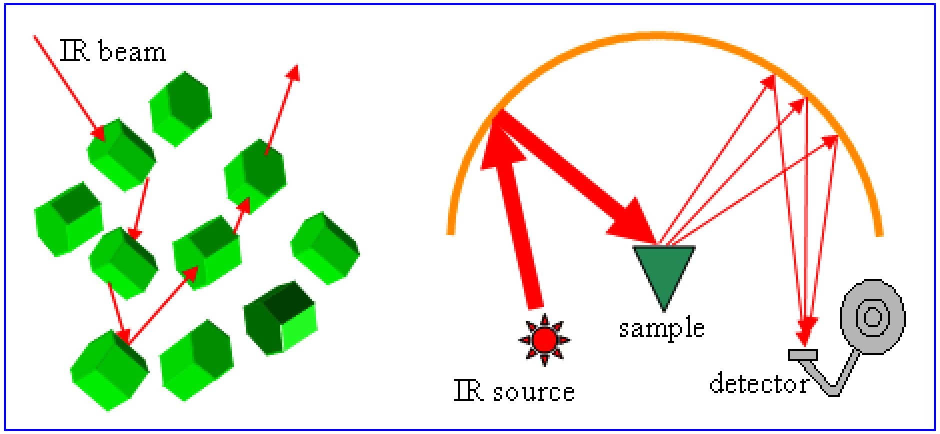




Bulanin, K.; Shah, A. and Teplyakov, A. V. Infrared spectroscopy studies of iodoethane on Si(100)-2x1: Adsorption and thermal decomposition leading to adsorbate ordering. *J. Chem. Phys*. **2001**, *115(15),* 7187-7195.

Infrared Spectroscopy Techniques

3) Diffuse reflectance



Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) is a technique that collects and analyzes scattered IR energy. It is used for measurement of fine particles and powders, as well as rough surface (e.g., the interaction of a surfactant with the inner particle, the adsorption of molecules on the particle surface). Sampling is fast and easy because little or no sample preparation is required.

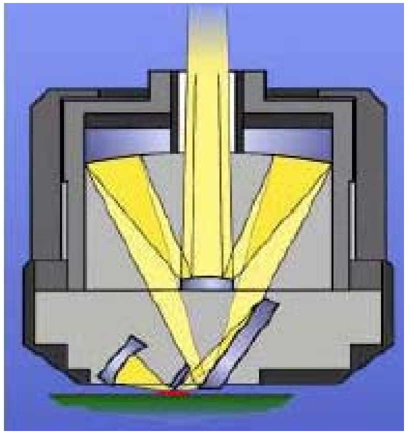
- **Specular reflection**: When an infrared beam is focused on the surface of a particulate sample, it can interact with the sample two ways. First it may simply reflect off the sample surface in the same way visible light reflect off a mirror. This phenomenon, called “ specular reflection”, is a function of the refractive index of the sample.
- **Specular reflection** is suitable for smooth surface that can strongly reflect IR beam.
- **Diffuse reflection** collects infrared radiation from the IR beam that passes through a particle can either reflect off the next particle or be transmitted through the next particle. This transmission-reflectance event can occur many times in the sample, which increases the pathlength.
- **Diffuse reflection** collects scattered IR energy,
- **Diffuse reflection** is used for rough sample and particle

Infrared Spectroscopy Techniques

4) FTIR Imaging

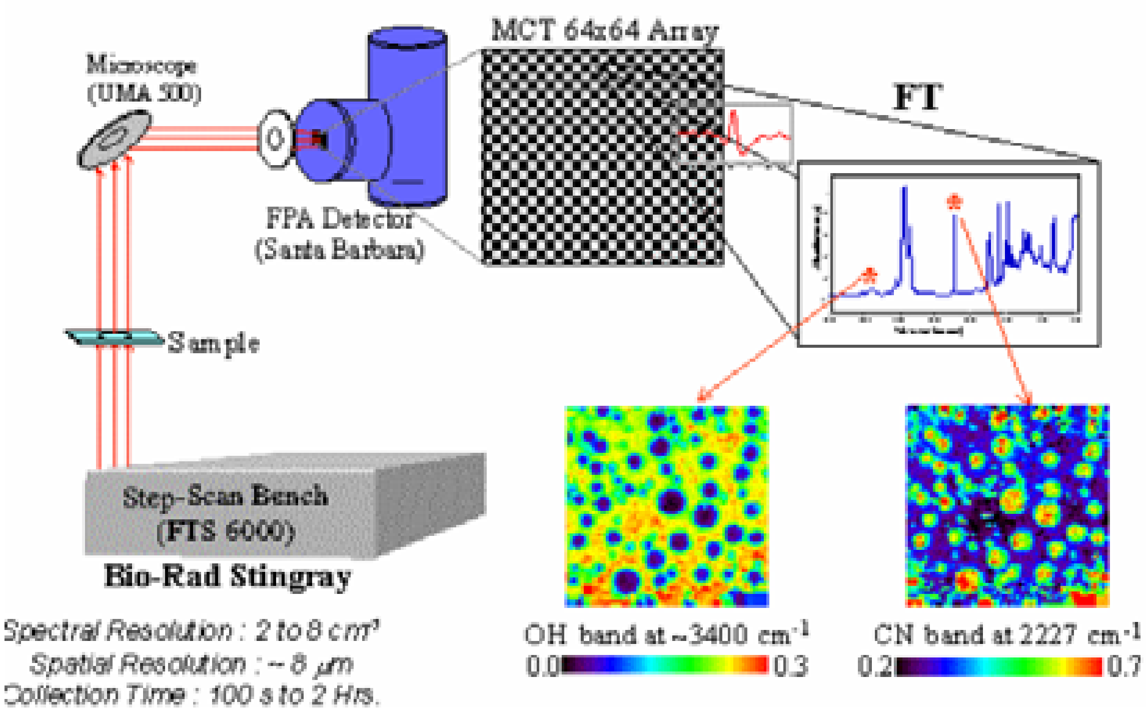
- **FTIR microscope**

- Provide FT-IR spectra for samples down to about 10 μm in size
- Two primary modes of FT-IR microscopy: reflectance and transmission
- More advanced mode: ATR



Infrared Spectroscopy Techniques

4) FTIR Imaging



Raman Spectroscopy

Raman spectroscopy (named after C. V. Raman, pronounced (rɑːmən) is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system. Infrared spectroscopy yields similar, but complementary, information.

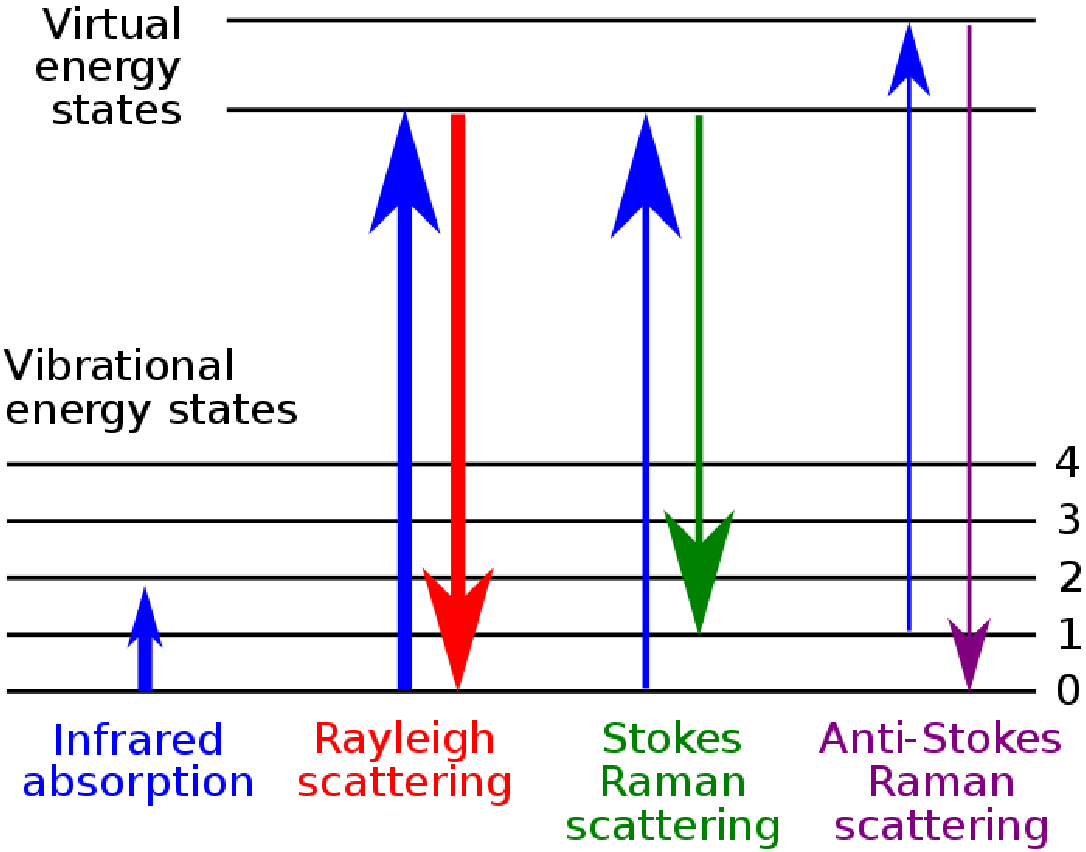
Raman Spectroscopy

The Raman effect occurs when light impinges upon a molecule and interacts with the electron cloud and the bonds of that molecule. For the spontaneous Raman effect, a photon excites the molecule from the ground state to a virtual energy state. When the molecule emits a photon and returns to the ground state, it returns to a different rotational or vibrational state. The difference in energy between the original state and this new state leads to a shift in the emitted photon's frequency away from the excitation frequency.

If the final state of the molecule is more energetic than the initial state, then the emitted photon will be shifted to a lower frequency in order for the total energy of the system to remain balanced. This shift in frequency is designated as a Stokes shift. If the final state is less energetic than the initial state, then the emitted photon will be shifted to a higher frequency, and this is designated as an anti-Stokes shift. Raman scattering is an example of inelastic scattering because of the energy transfer between the photons and the molecules during their interaction.

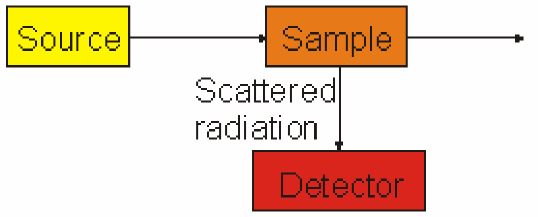
A change in the molecular polarization potential — or amount of deformation of the electron cloud — with respect to the vibrational coordinate is required for a molecule to exhibit a Raman effect. The amount of the polarizability change will determine the Raman scattering intensity. The pattern of shifted frequencies is determined by the rotational and vibrational states of the sample.

Raman Spectroscopy



Raman Spectroscopy

The basic set-up of a Raman spectrometer is shown on the right. Note that the detector is orthogonal to the direction of the incident radiation, so as to observe only the scattered light.
The source needs to provide intense monochromatic radiation, it is usually a laser.
1) Raman spectroscopy collects scattered radiation.
2) The criteria for a molecule to be Raman active are also different from other types of spectroscopy. It does NOT require a permanent dipole moment.



Raman Spectroscopy

Selection rule for Raman activity -- polarizability

For IR spectroscopy, it is necessary for the molecule to have a permanent electric dipole. This is not the case for Raman spectroscopy, rather it is the polarizability (α) of the molecule which is important.

The oscillating electric field of a photon causes charged particles (electrons and, to a lesser extent, nuclei) in the molecule to oscillate. This leads to an induced electric dipole moment, μ_{ind}, where

$$\boldsymbol{\mu_{ind} = \alpha E}$$

This induced dipole moment then emits a photon, leading to either Raman or Raleigh scattering.

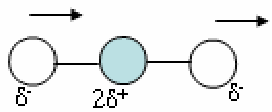
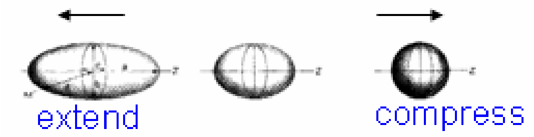
The energy of this interaction is also dependent on the polarizability:

Energy of interaction = $-1/2\alpha E^2$

The energies of Raman transitions are relatively weak. To counter this, a higher intensity of the exciting radiation is used.

For Raman scattering to occur, the polarizability of the molecule must vary with its orientation.

Raman Spectroscopy

IR	Raman
I. Vibrational Modes	Vibrational Modes
II. Change in dipole	II. Change in polarizability
	
III. Excitation of a molecule to the excited vibrational state	III. Momentary distortion of the electron distribution

Raman Spectroscopy

IR	Raman
IV. Absorption: (radiation at a certain frequency is absorbed due to the resonance of molecular vibration)	IV. (radiation at a certain frequency is scattered by the molecule with *shifts* in the wavelength of the incident beam)
V. Observed peak is due to molecular vibration	V. observed frequency shifts are related to vibrational changes in the molecule

Raman Spectroscopy

The molecule is originally at the E_2 energy state. The photon interacts with the molecule, exciting it with an energy hv_i. However, there is no stationary state of the molecule corresponding to this energy, and so the molecule relaxes down to the energy levels E_1 or E_3 . This process emits a photon in two ways:

Anti-Stokes transition:

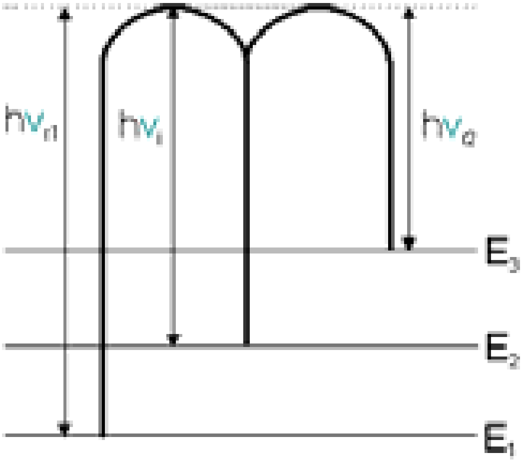
If the molecule relaxes to energy state E_1, it will have lost energy, and so the photon emitted will have energy hv_{r1}, where $hv_{r1} > hv_i$

Stokes transitions:

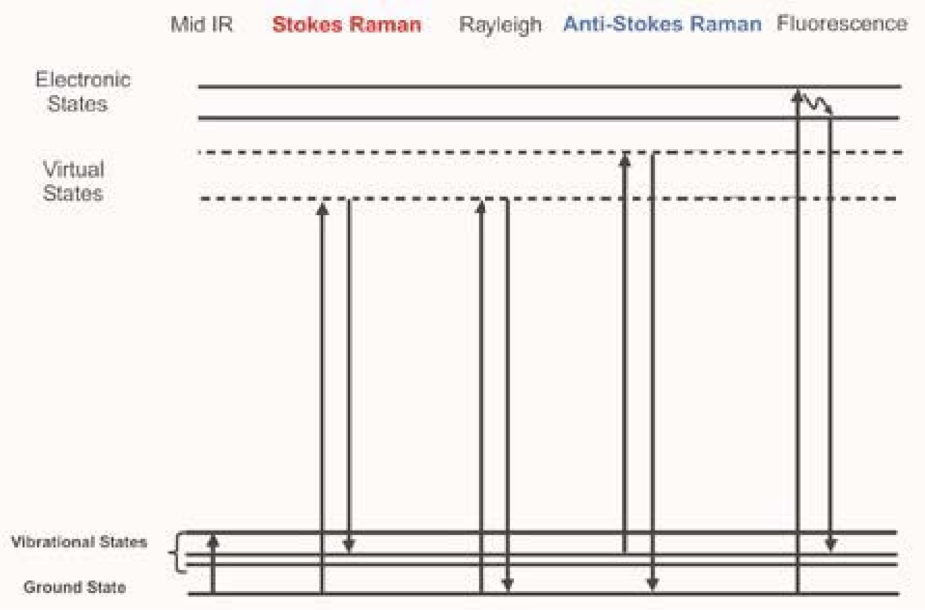
If the molecule relaxes to energy state E_3, it will have gained energy, and so the photon emitted will have energy hv_{r2}, where $hv_{r2} < hv_i$

For rotational spectroscopy, both Stokes and anti-Stokes transitions are observed.

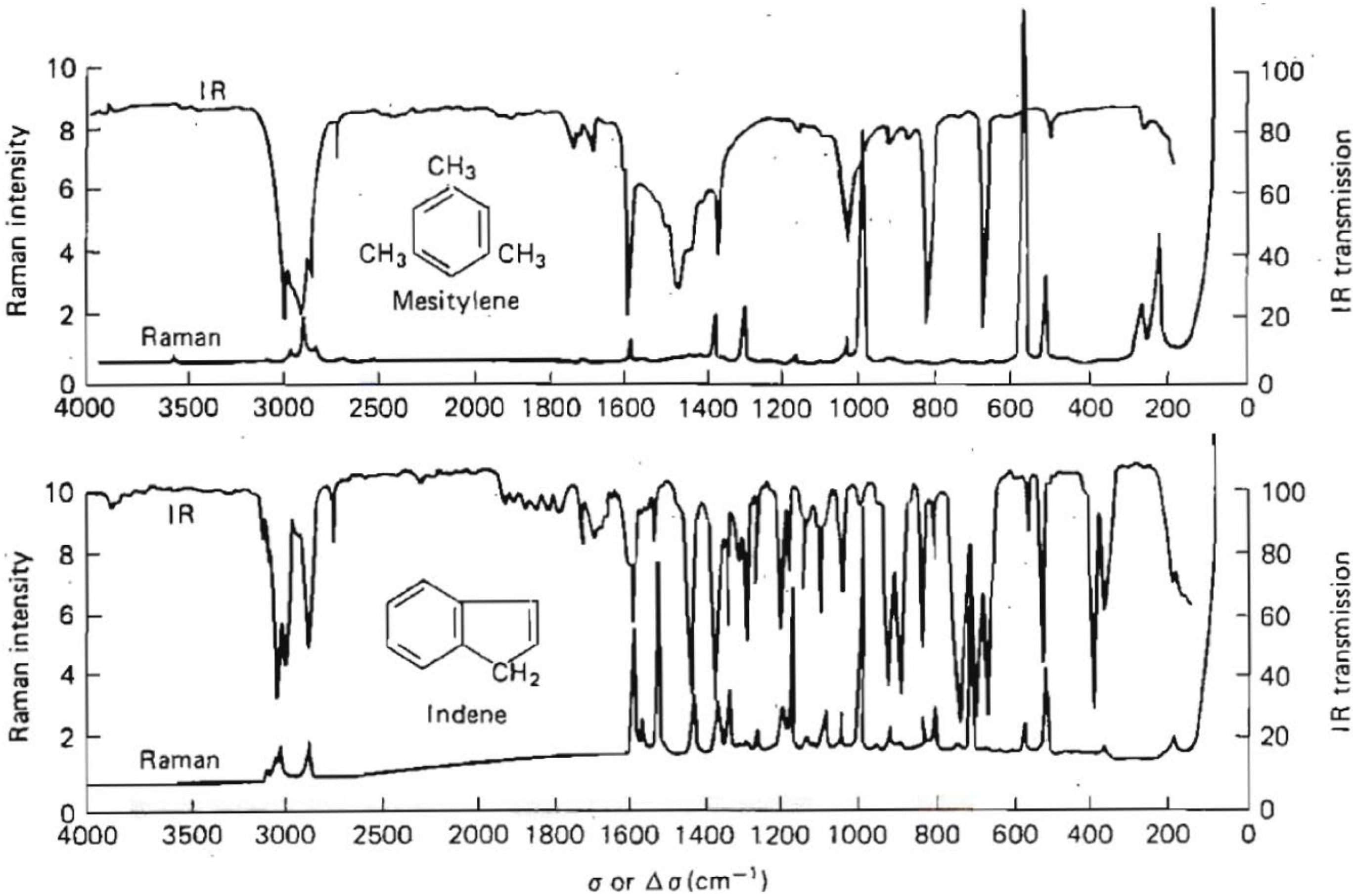
For vibrational spectroscopy, Stokes transitions are far more common, and so anti-Stokes transitions can effectively be ignored.



Raman Spectroscopy

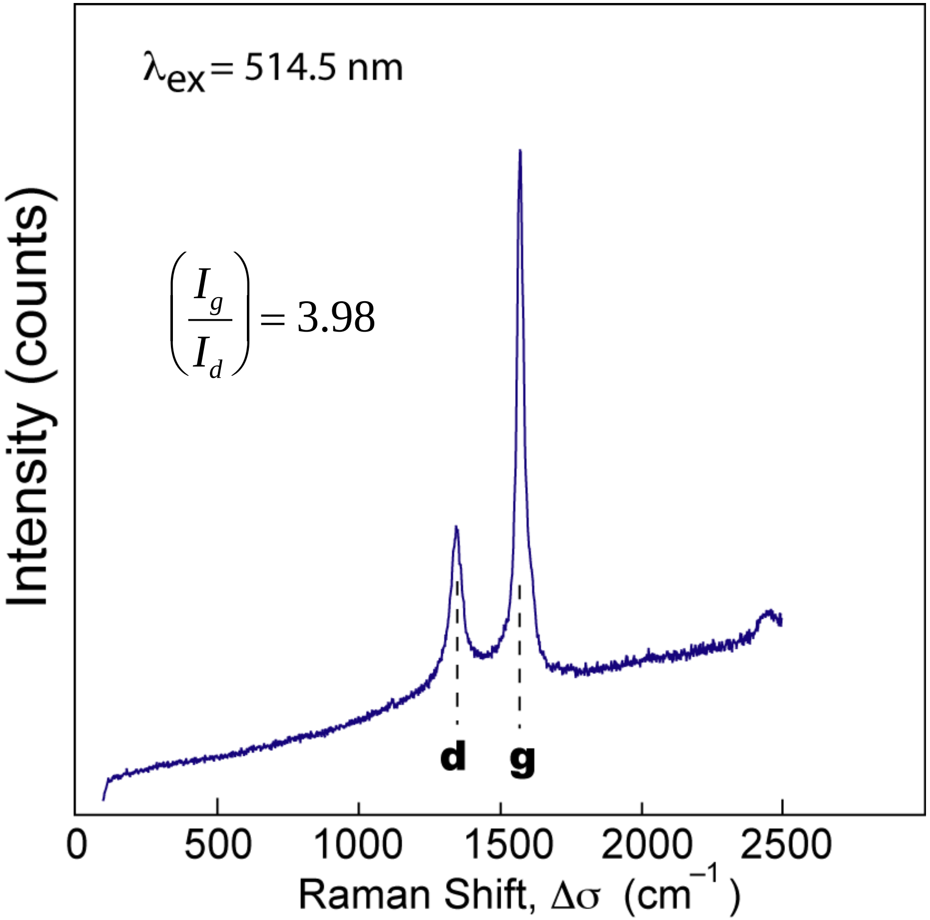


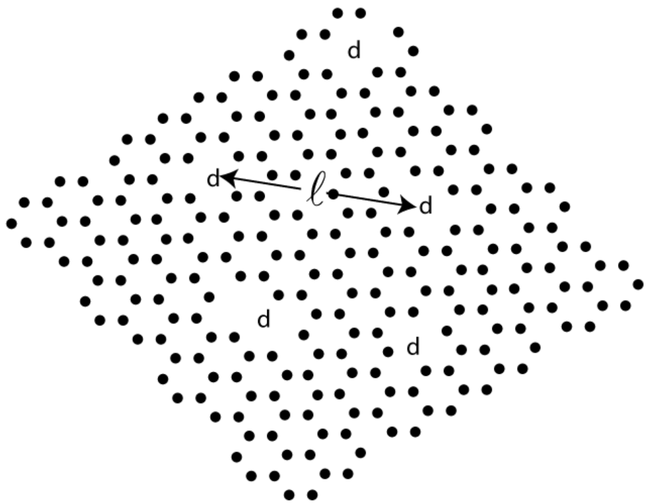
Raman Spectroscopy



Raman Spectroscopy

Flow Field Plate - Graphite





Nanocrystalline graphite has graphitic (**g**) and disorder (**d**) peaks. The characteristic dimension of graphitic domains is given by:

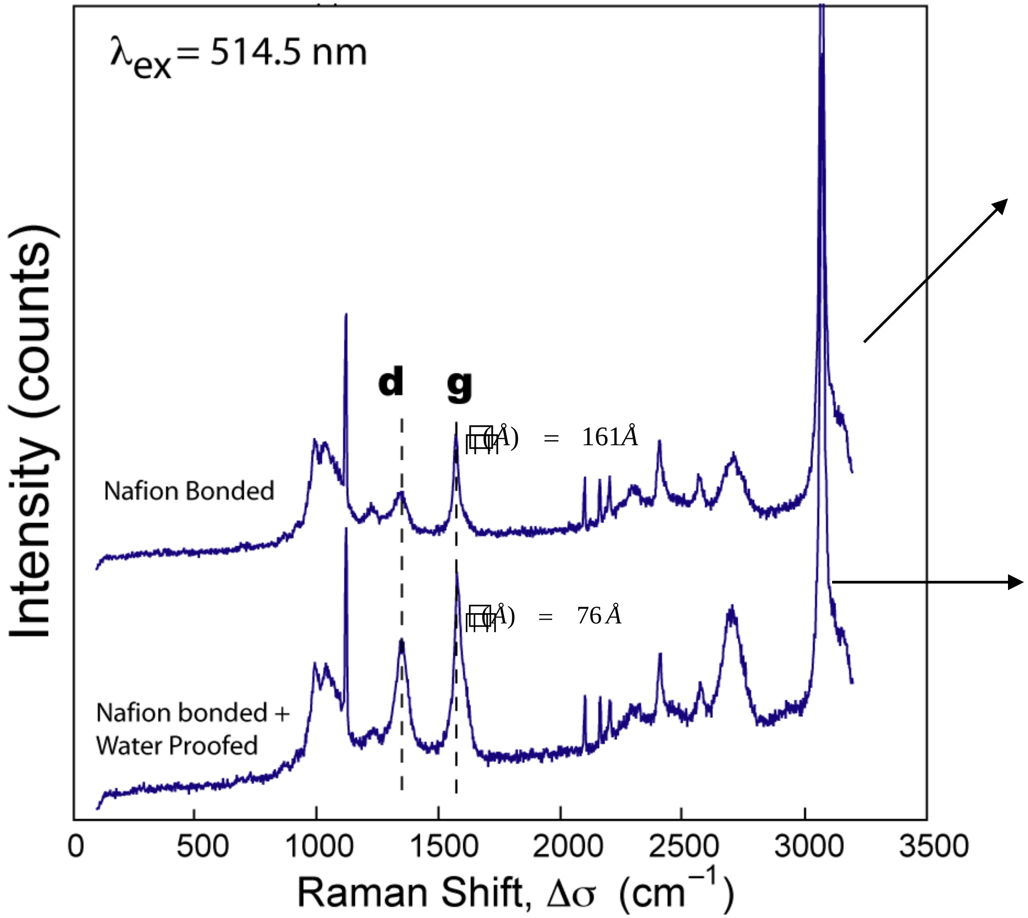
$$\ell(\AA) = 44\left(\frac{I_g}{I_d}\right)$$

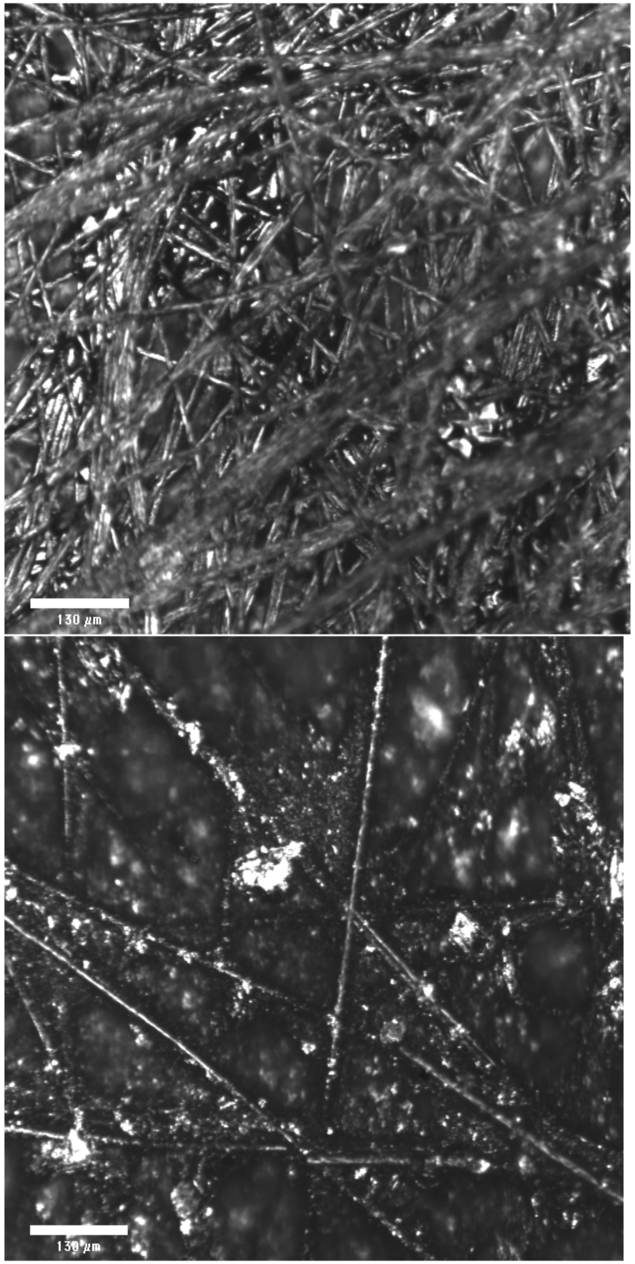
$$\ell = 175\AA$$

From early literature on graphitic materials
Tuinstra and Koenig, J. Chem Phys. 53, 1126 (1970).

Raman Spectroscopy

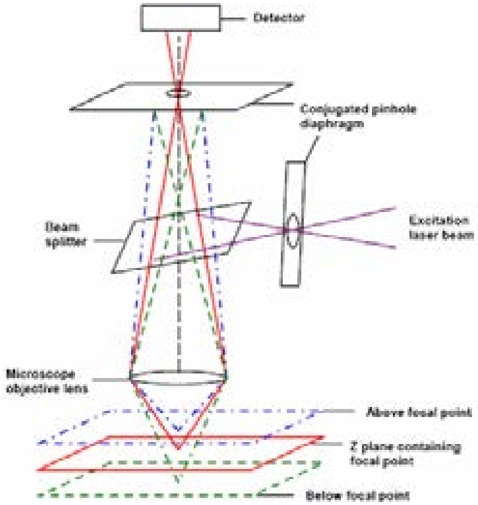
Gas Diffusion Layers (graphite paper)

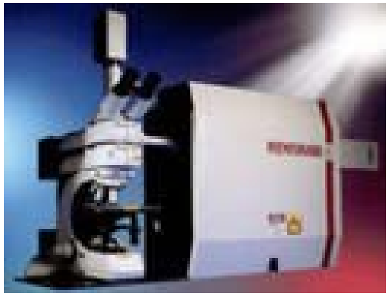


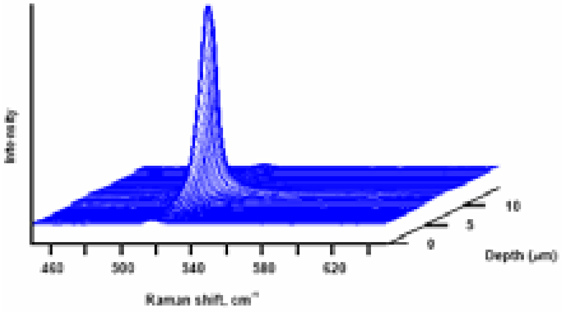


Raman Spectroscopy

Confocal Raman microscopy for three-dimensional imaging



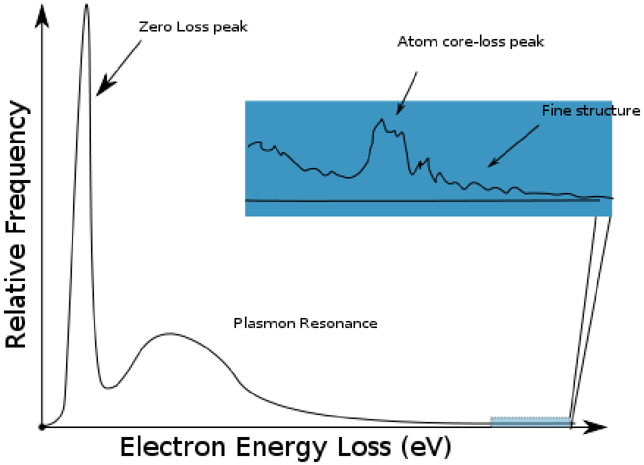




HREELS (or EELS)

Electron Energy Loss Spectroscopy (EELS)

In **electron energy loss spectroscopy** (EELS) a material is exposed to a beam of electrons with a known, narrow range of kinetic energies. Some of the electrons will undergo inelastic scattering, which means that they lose energy and have their paths slightly and randomly deflected. The amount of energy loss can be measured via an electron spectrometer and interpreted in terms of what caused the energy loss. Inelastic interactions include phonon excitations, inter and intra band transitions, plasmon excitations, inner shell ionisations, and Cherenkov radiation. The inner shell ionizations are particularly useful for detecting the elemental components of a material. For example, one might find that a larger-than expected number of electrons comes through the material with 285 eV (electron volts, a unit of energy) less energy than they had when they entered the material. It so happens that this is about the amount of energy needed to remove an inner-shell electron from a carbon atom. This can be taken as evidence that there's a significant amount of carbon in the part of the material that's being hit by the electron beam. With some care, and looking at a wide range of energy losses, one can determine the types of atoms, and the numbers of atoms of each type, being struck by the beam. The scattering angle (that is, the amount that the electron's path is deflected) can also be measured, giving information about the dispersion relation of whatever material excitation caused the inelastic scattering.



HREELS (or EELS)

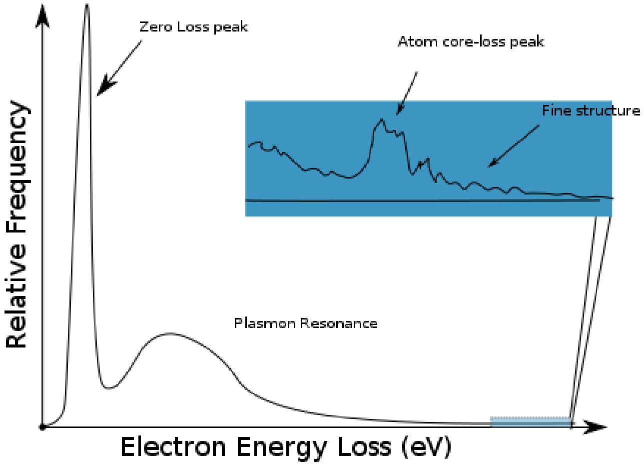
Based on inelastic scattering of monoenergetic beam of low energy electrons (E_i = 1-10 eV) from surface

- kinetic energy analysis of inelastically-scattered electrons gives information about energy transfer to surface vibrational modes

- $E_s = E_i - h\nu$ --- energy *loss*

H_2 adsorbed on TM expect $h\nu$ = 4560 cm^{-1} but for H on TM expect $h\nu$= 800-1000 cm^{-1}

- minimum resolution ΔE_i (FWHM of incident beam) of EELS > RAIRS - best <8 cm^{-1}, typically 20-30 cm^{-1} (8 cm^{-1} @ 1 meV)



HREELS (or EELS)

Electron Scattering Mechanisms in EELS
Three basic scattering modes for electron, each with own selection rules:
(1) *Dipole* scattering
(2) *Impact* scattering
(3) *Negative ion resonance* scattering
- gives EELS added versatility over RAIRS
- all three modes operative (one usually dominates under certain experimental conditions)

HREELS (or EELS)

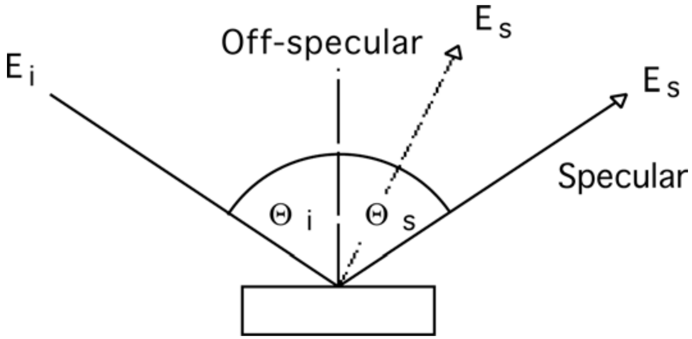
(1) Dipole scattering

Electron is scattered at long range (100's Å) by oscillating Coulombic field of surface

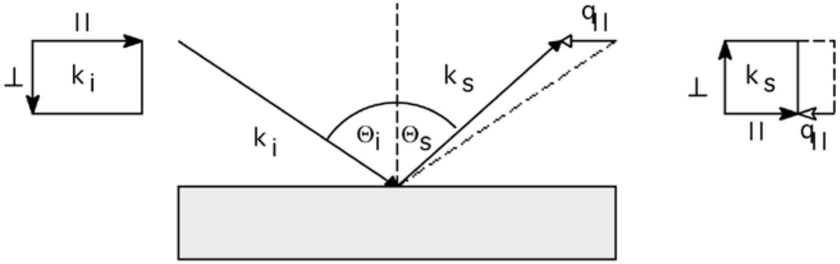
Electron momentum ⊥ to surface is conserved

Energy loss results in small angle deflections around specular direction - dipole scattering lobe

- Elastically-scattered electrons appear at $\Theta_i = \Theta_s$ (specular)
- Inelastically-scattered electrons appear at $\Theta_i \approx \Theta_s$ (sharply peaked near specular)



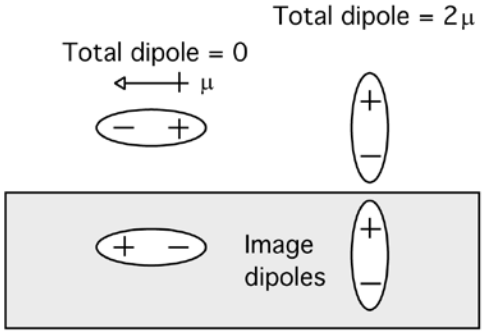
HREELS (or EELS)



small momentum loss $q_{||} = h\nu$

Only modes with component of vibration perpendicular to surface can be excited (not parallel modes) - *surface selection rule*

same selection rules as RAIRS



Large cross-section for small E_i's (<20 eV) - dominant mechanism near specular

Well-developed/straightforward theory

HREELS (or EELS)

(2) Impact scattering:

Electron is "kinematically" scattered at short range (few Å) by atomic core potentials of surface - modulated by nuclear motion (vibration)

Electron scattered over wide range of angles (in and out of plane of incidence)

Probability of scattering depends on surface dipole amplitude/direction (symmetry of mode) and electron energy (momentum)

Neither electron momentum || nor ⊥ conserved

- can see vibrational modes with dynamic dipoles both || and ⊥ to surface plane (only off-specular)

Much lower cross-section than dipole scattering (weak loss features)

Poorly-developed/complex theory

HREELS (or EELS)

(3) Negative Ion Resonance

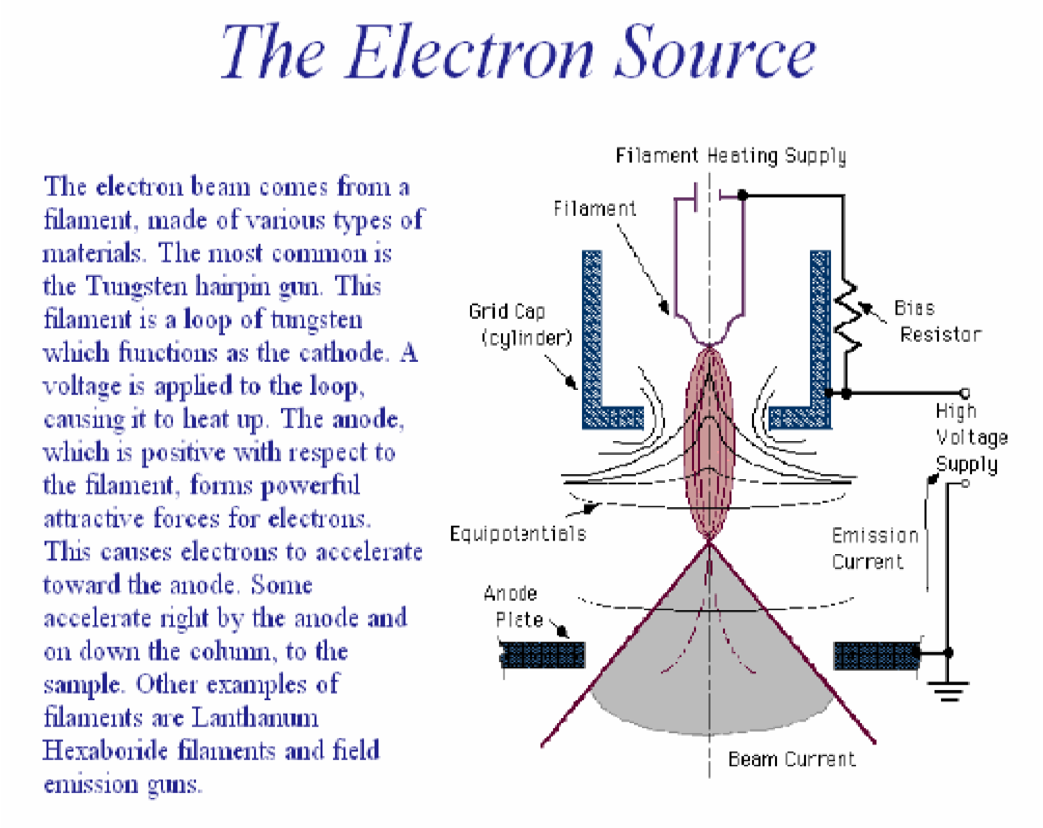
Incident electron becomes transiently trapped in empty, high lying MO of adsorbate - Rydberg state

Vibrational feature intensity strongly depends on incident energy - resonances

Very small cross-section off-resonance (rare)

Regardless of mechanism, most electrons scattered *elastically* - loss spectrum usually very weak

HREELS (or EELS)



The Electron Source

The electron beam comes from a filament, made of various types of materials. The most common is the Tungsten hairpin gun. This filament is a loop of tungsten which functions as the cathode. A voltage is applied to the loop, causing it to heat up. The anode, which is positive with respect to the filament, forms powerful attractive forces for electrons. This causes electrons to accelerate toward the anode. Some accelerate right by the anode and on down the column, to the sample. Other examples of filaments are Lanthanum Hexaboride filaments and field emission guns.

HREELS (or EELS)

Instrumentation for HREELS

Monochromation of electrons emitted by thermionic emission achieved by passing through spherical-sector electron energy analyzer

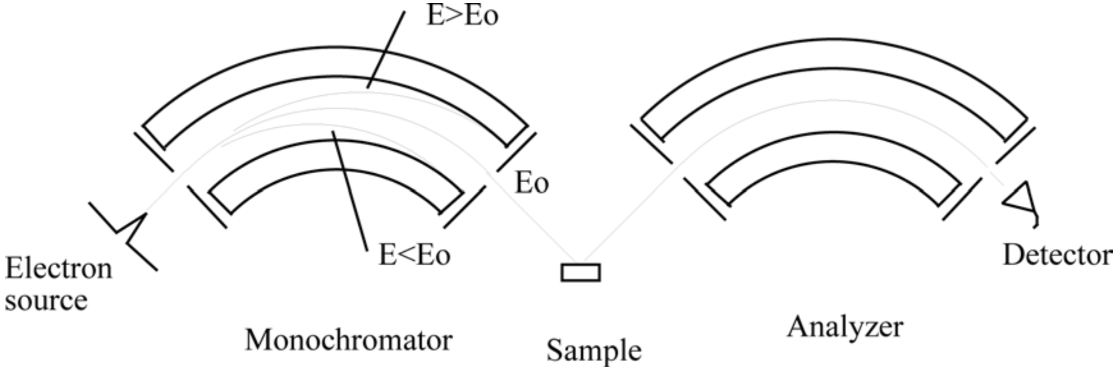
- typical radius 5 cm, typical pass energy <500 meV (in XPS, radius ~20-30 cm, pass energy 50-100 eV)

Electrons retarded before entry into sector, then accelerated to sample

Second spherical-sector used to analyze electron kinetic energy

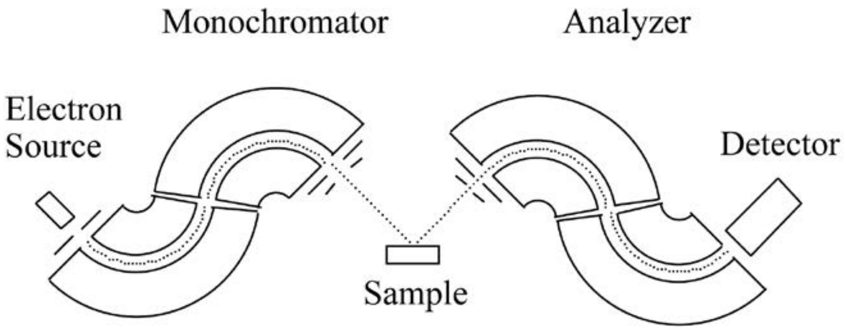
Entire instrument magnetically shielded - no magnetic materials for construction

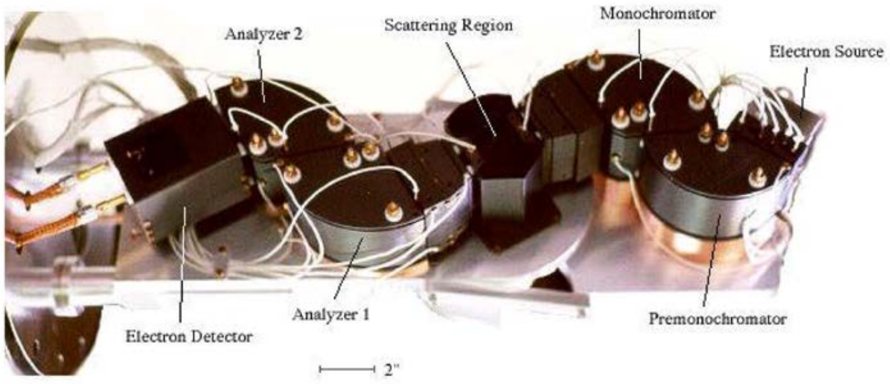
In very high resolution instruments, two sectors for monochromator and two for analyzer



HREELS (or EELS)

Instrumentation for HREELS





HREELS (or EELS)

Space-charge effects always tend to produce divergent beam

Optimization of lens and sector potentials very difficult - computer controllec

In best HREELS, analyzer rotatable for off-specular (impact scattering) analysis

E_i variable 1-50 eV or more - can study vibrational and electronic loss processes (plasmons)

- observe electronic excitation from 0->50 eV
- observe vibrational modes from 0->4000 cm^{-1}

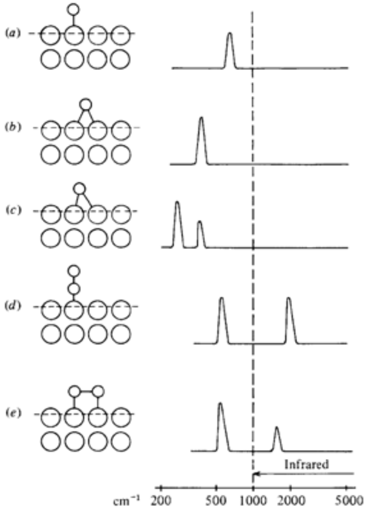


Fig. 9.11 Set of imaginary adsorption states showing the expected loss peaks associated with each structure.

HREELS (or EELS)

Example Application of HREELS: CO adsorption on W(100)

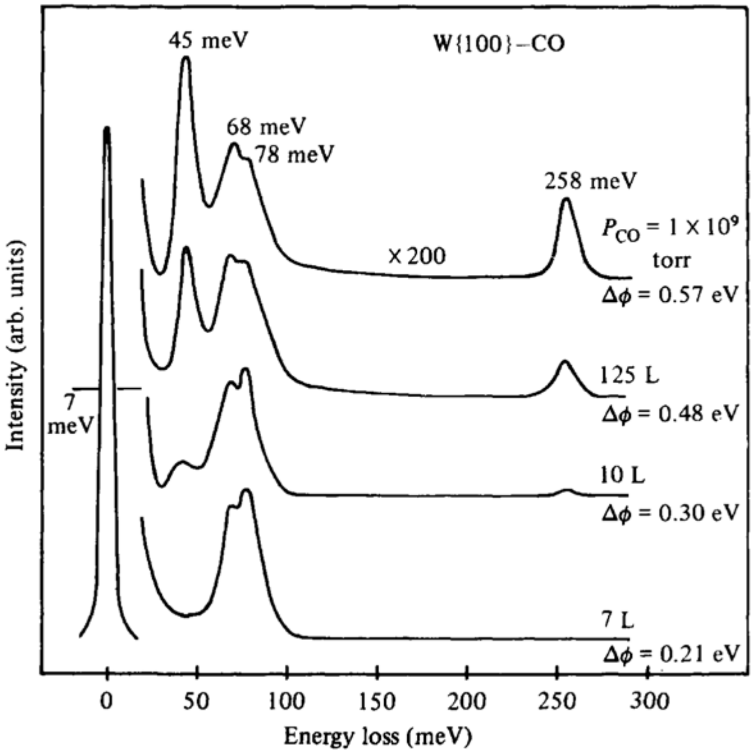


Fig. 9.13 Electron energy loss spectra of CO on W{100} at 300 K. The spectra are recorded with a primary electron beam energy of 5 eV incident at an angle of 75°; $\Delta\phi$ is the measured increase in work function (Froitzheim *et al.*, 1976).

At low CO exposures

- 70 meV (565 cm^{-1}) W-C (hollow site)
- 78 meV (630 cm^{-1}) W-O (hollow site)

At high *p*CO

- 45 meV (363 cm^{-1}) W-CO (on-top)
- 258 meV (2081 cm^{-1}) -C≡O   (CO(g) = 2140 cm^{-1})

HREELS (or EELS)

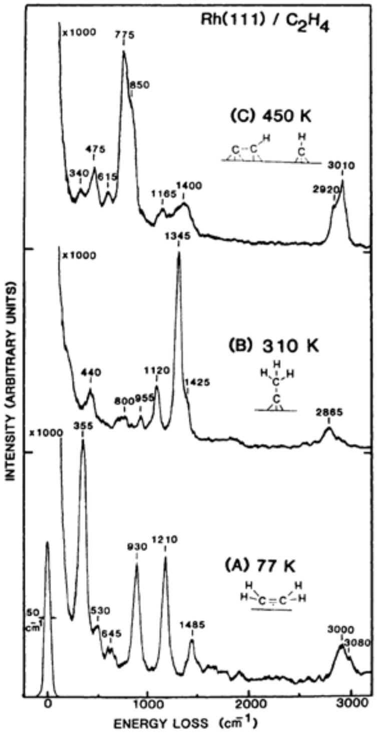


Figure 2.25. Vibrational spectra from chemisorbed ethylene on Rh(111) at different temperatures obtained by HREELS. Note the sequential dehydrogenation process.

At 77 K, ethylene non-dissociatively chemisorbs on Rh(111) with C=C approximately parallel to surface in π-bonded configuration

HREELS (or EELS)

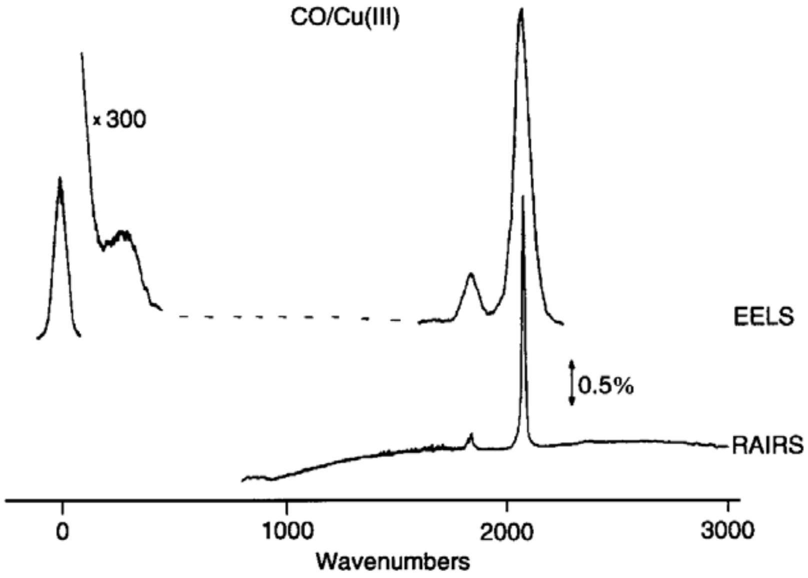
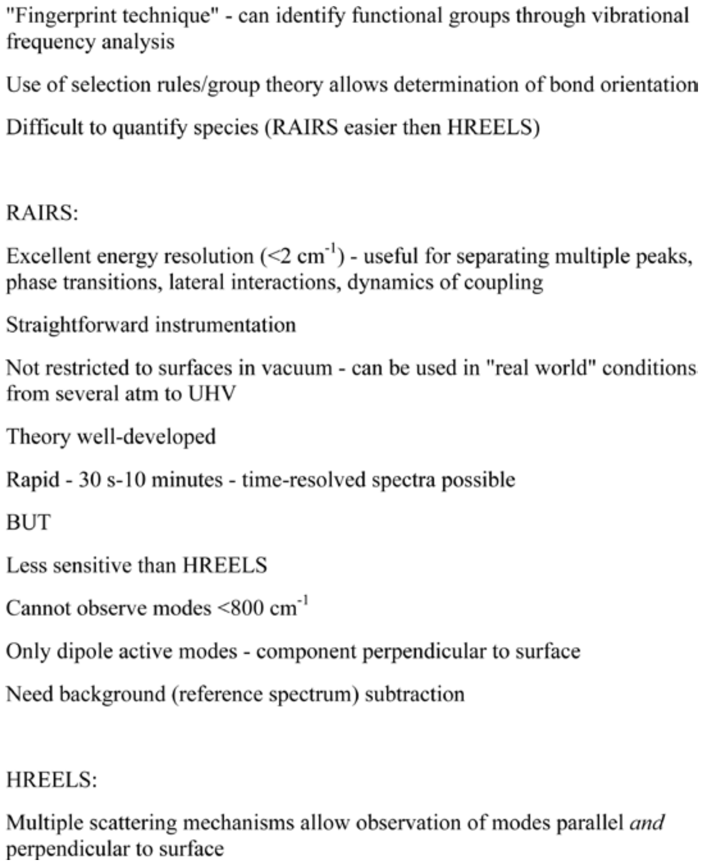


Figure 7.13. RAIRS spectrum of a monlayer of CO adsorbed on a Cu (111) surface at 95 K in comparison with analogous data obtained using electron energy loss spectroscopy, after Chesters *et al.* [10]

Summary:



"Fingerprint technique" - can identify functional groups through vibrational frequency analysis

Use of selection rules/group theory allows determination of bond orientation

Difficult to quantify species (RAIRS easier then HREELS)

RAIRS:

Excellent energy resolution (<2 cm^{-1}) - useful for separating multiple peaks, phase transitions, lateral interactions, dynamics of coupling

Straightforward instrumentation

Not restricted to surfaces in vacuum - can be used in "real world" conditions from several atm to UHV

Theory well-developed

Rapid - 30 s-10 minutes - time-resolved spectra possible

BUT

Less sensitive than HREELS

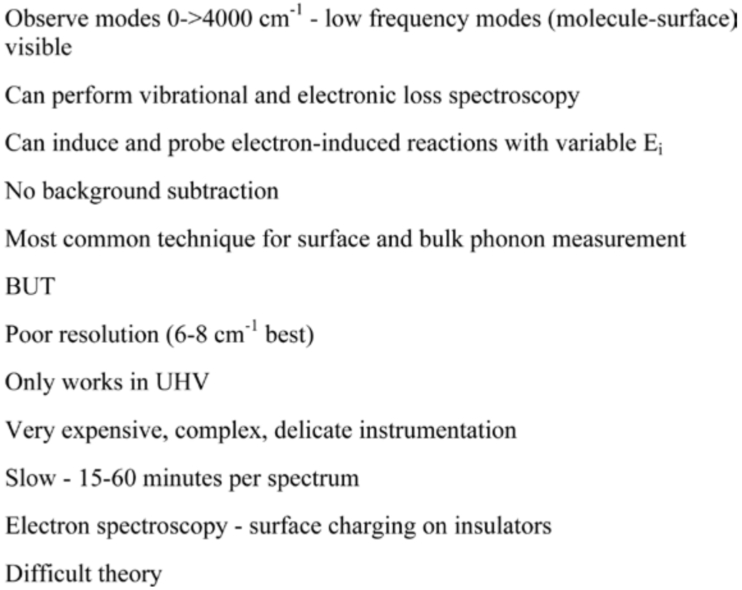
Cannot observe modes <800 cm^{-1}

Only dipole active modes - component perpendicular to surface

Need background (reference spectrum) subtraction

HREELS:

Multiple scattering mechanisms allow observation of modes parallel *and* perpendicular to surface



Observe modes 0->4000 cm^{-1} - low frequency modes (molecule-surface) visible

Can perform vibrational and electronic loss spectroscopy

Can induce and probe electron-induced reactions with variable E_i

No background subtraction

Most common technique for surface and bulk phonon measurement

BUT

Poor resolution (6-8 cm^{-1} best)

Only works in UHV

Very expensive, complex, delicate instrumentation

Slow - 15-60 minutes per spectrum

Electron spectroscopy - surface charging on insulators

Difficult theory