

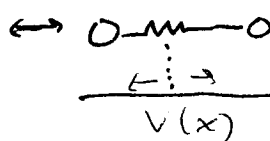
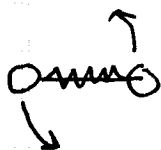
o (Infra-red) Vibrational Spectroscopy

- a standard technique in the chemist's arsenal, and of course for the study of adsorbed systems.  
Vibrational frequencies tell us about bonding + how it is affected by environment.

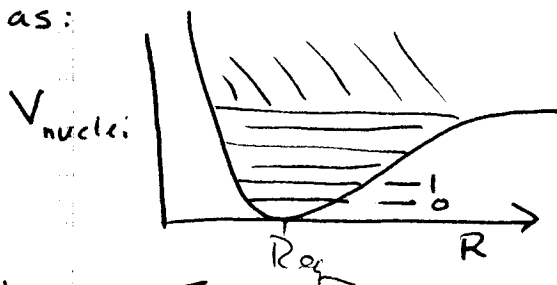
Methods: infrared absorption ← first electron energy loss  
Raman (inelastic light scattering)  
helium scattering  
inelastic electron scattering

Gas-phase: Vibration & rotation

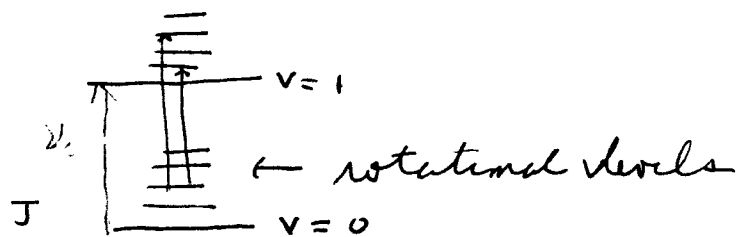
Surface: vibration, frustrated translation, frustrated rotation



Gas:



Fundamental Transition (1 ← 0)



Strongest Transitions

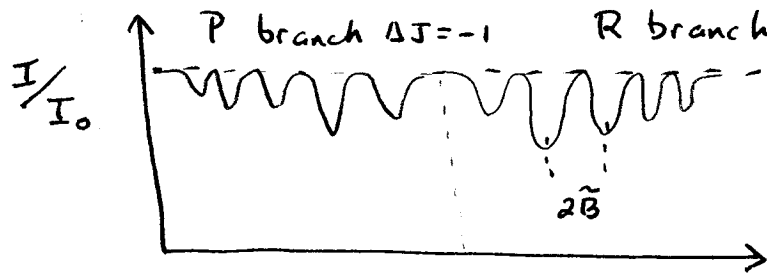
$\Delta v = \pm 1$  (overtones exist)  
 $\Delta J = \pm 1$

$E_{v,J} \approx hc \tilde{\nu}_0 (v + \frac{1}{2}) + hc \tilde{B} J(J+1)$

$\nu_0 = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$

$\tilde{\nu}_0 \sim 10^3 \text{ cm}^{-1}$

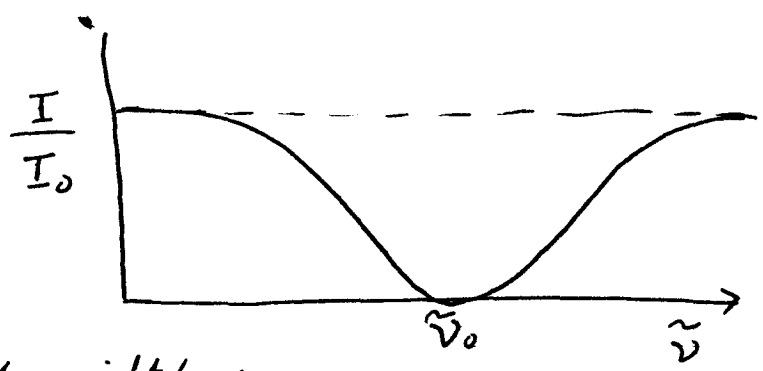
$\tilde{B} \sim 1 \text{ cm}^{-1}$



For vibrational transitions to be seen  $\frac{\partial \mu}{\partial Q_k} \neq 0$  (later)

CO 2140  $\text{cm}^{-1}$   
(1-0)

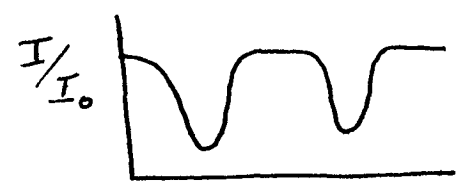
Adsorbate  
(or thin sample  
like dust)



Broad : both width +  
 $\tilde{\nu}$  dependent upon environment  
"inhomogeneous broadening"



Very different environments can lead to more than one line per mode.



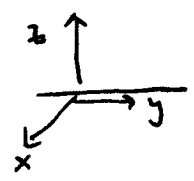
as in Figure 2.24  
(but wrong reason).

Also: some homogeneous broadening (interactions with bands)

Strength of Spectra : QM

$\mathcal{H} = -\vec{\mu} \cdot \vec{E}$  transition dipole +  $\vec{E}$  field  
must not be  $\perp$  to one another.

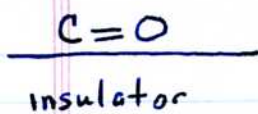
$\langle v=1 | \mu_x | v=0 \rangle \neq 0$      $\mu_i = \mu_i^e + \left( \frac{\partial \mu_i}{\partial Q_k} \right)_e Q_k + \dots$



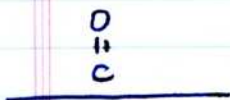
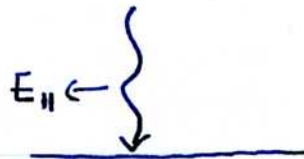
$\langle 1 | \mu_i | 0 \rangle = \left( \frac{\partial \mu_i}{\partial Q_k} \right)_e \langle 1 | Q_k | 0 \rangle$

must be  $\neq 0$

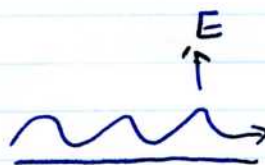
higher order terms in  $\mu_i$  expansion lead to overtones ( $\Delta v_k = \pm 2, \pm 3$ ) + combinations ( $\Delta v_i = \pm 1, \Delta v_j = \pm 1$ )



transition strongest for normal incidence



transition strongest for grazing incidence



But metals are more complex because of image charges.



adsorbate  
image charge  
(substrate)

$\therefore$  no net dipole  
 $\downarrow$  no transition

MSSR: metal-surface selection rule  
"Vibrations need a  $\perp$  component to be "allowed."

Types of Vibrational Modes

Phonons: bulk and surface  $0-600 \text{ cm}^{-1}$   
Low frequencies technologically difficult to study because sources are weak.  
(other techniques better)

Frustrated Modes:  $200-800 \text{ cm}^{-1}$  still hard to see

Intramolecular Modes: stretches, bends  
( $> 1500 \text{ cm}^{-1}$ ) ( $500-1500 \text{ cm}^{-1}$ )  
actual frequencies depend on masses.

How To Do It



appropriate only for transparent, porous, or thin substrates. Individual monolayers hard to detect.  
Dust particles detectable. ( $10 \text{ nm} - 100 \text{ nm}$ )

Chemistry      Experimental Parameters      Physics / Astronomy

Beer-Lambert Law

Law of Radiative Transfer

$$T = \frac{I}{I_0} = e^{-acl}$$

"transmittance"

length  
concentration

absorptivity  
( $cm^2$ )

$$\frac{I}{I_0} = e^{-\tau_\nu}$$

optical depth

$$\tau_\nu = \sigma_\nu n_\ell l$$

cross section  
( $cm^2$ )      density of  
lower state

$$A = -\ln T = acl = \alpha l$$

absorbance

$$\alpha = ac$$

absorption coefficient ( $cm^{-1}$ )

$$K_\nu = \sigma_\nu n_\ell$$

absorption coefficient ( $cm^{-1}$ )

$$N_\ell = n_\ell l$$

column density ( $cm^{-2}$ )

$$\alpha = \frac{4\pi K}{\lambda_0}$$

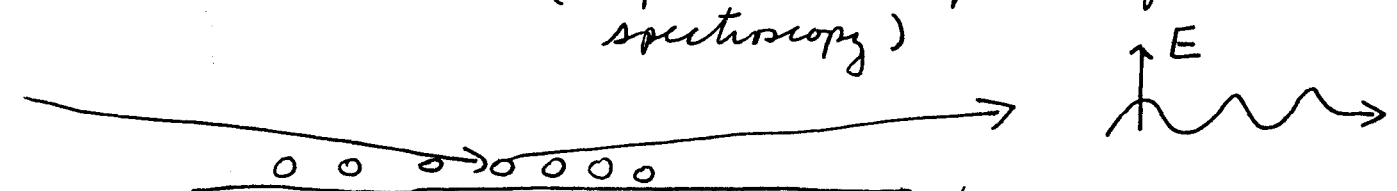
$$\int_{line} \tau_\nu d\nu = 8\pi^3 \tilde{\nu}_{ue} N_\ell |\mu_{ue}|^2$$

$$\tilde{n} = n + ik$$

complex refractive index

QM transition dipole

2. RAIRS (reflectance absorption infrared spectroscopy)



grazing incidence most appropriate for flat surface (e.g. metallic single crystal); enhanced column

First measure for clean substrate, then for adsorbate-substrate system.

R: reflectivity  $\frac{\Delta R(\nu)}{R_0(\nu)} = \frac{R_0(\nu) - R(\nu)}{R_0(\nu)} \quad (1)$

$\propto \sigma$  (molecules per unit area)

Proportionality only true if there are not strong interactions among adsorbates.

3. Diffuse Reflectance (DRIFTS: diffuse reflectance infrared Fourier transform spectroscopy)



used on rough surfaces or powders that scatter radiation diffusely rather than specularly

total  $I(\lambda)$  measured + converted to  $I(\nu)$

4. Internal Reflection (interface)

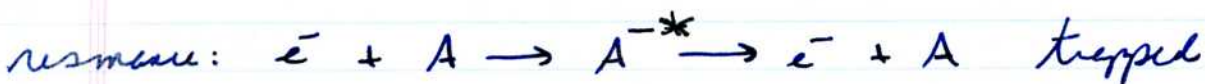
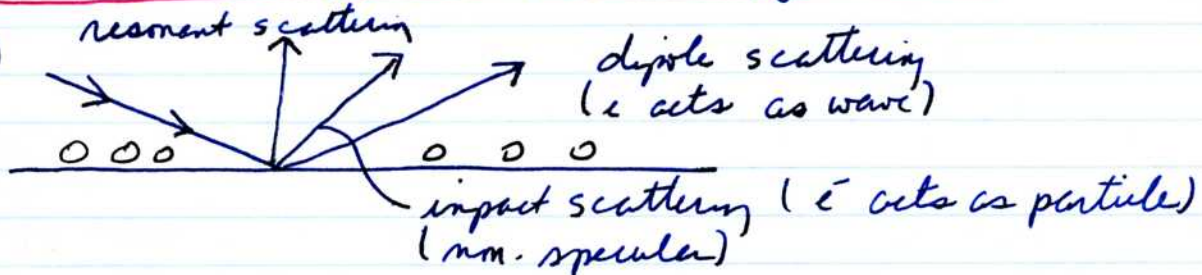
ATR: attenuated total reflection See eq. (1)

(MIR: multiple internal reflection: less used term)



(High Resolution) Electron Energy Loss Spectroscopy (EELS)

(UHV technique)

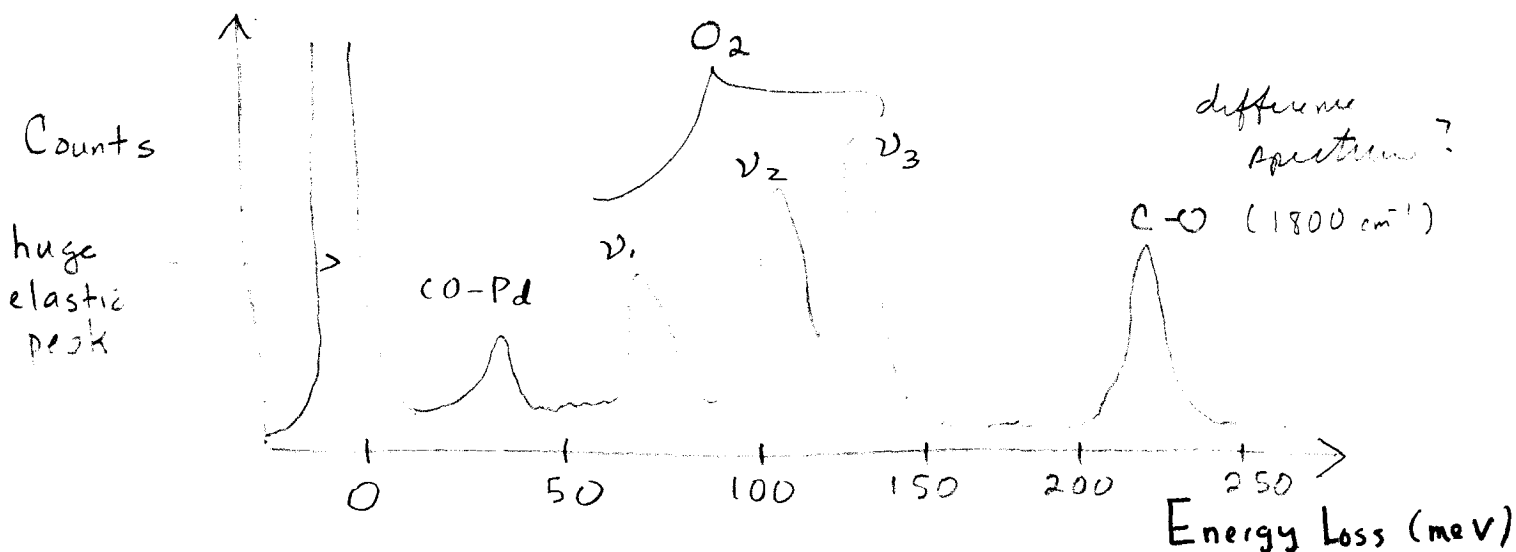


Energy loss measured from beam. Loss in kinetic energy: excitation of vibrational modes near or at surface.  
 Analysis of dipole scattering same as RAIRS.  
 Impact scattering follow different selection rules. (non-MSSR)

$$E = E_0 - h\nu = E_0 - hc\tilde{\nu}$$

energy of inelastic peak      elastic peak (often set to zero)      frequency of excited transition  
 $E_0 - E = h\nu = hc\tilde{\nu}$

• Example :  $O_2 + CO$  adsorbed on Pd (111) 100 K

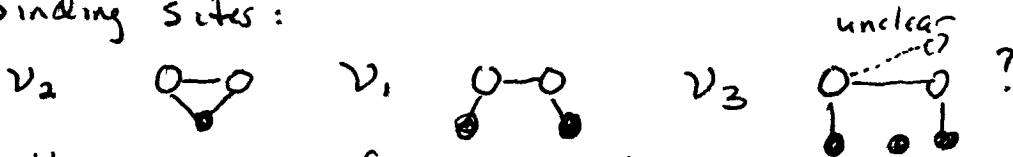


1 meV = 8.065  $cm^{-1}$

Some basic points : a) can study low frequency adsorbate-substrate modes (CO-Pd  $\sim 300 cm^{-1}$ )  
 b) can study non-polar adsorbates ( $O_2$ ).

Here 3 peaks correspond to 3 different binding sites:

can study || dipoles on metal!



Note that the gas phase fundamental for  $O_2$  would occur at 196 meV ( $1580 cm^{-1}$ ) if allowed.

Strongest binding to Pd  $\Rightarrow$  lowest  $\nu$