

Vibrational Spectroscopy

Vibrational Spectroscopy of Adsorbates

R.F. Willis, Ed. (Springer-Verlag, New York, 1980)

Electron Energy Loss Spectroscopy and Surface Vibrations

H. Ibach and D. L. Mills (Academic Press, New York, 1982)

Vibrational Spectroscopy of Molecules on Surfaces

J. Yates and T. Madey (Plenum Press, New York, 1987)

Surface Infrared Reflection Spectroscopy

Y. Chabal, Surface Science Reports 8 (1988)

Elec. Spec. for Surface Analysis

H. Ibach, Ed. (Springer-Verlag, New York, 1977)

EELS chapter by Froitzheim

Low Energy Electrons and Surface Chemistry,

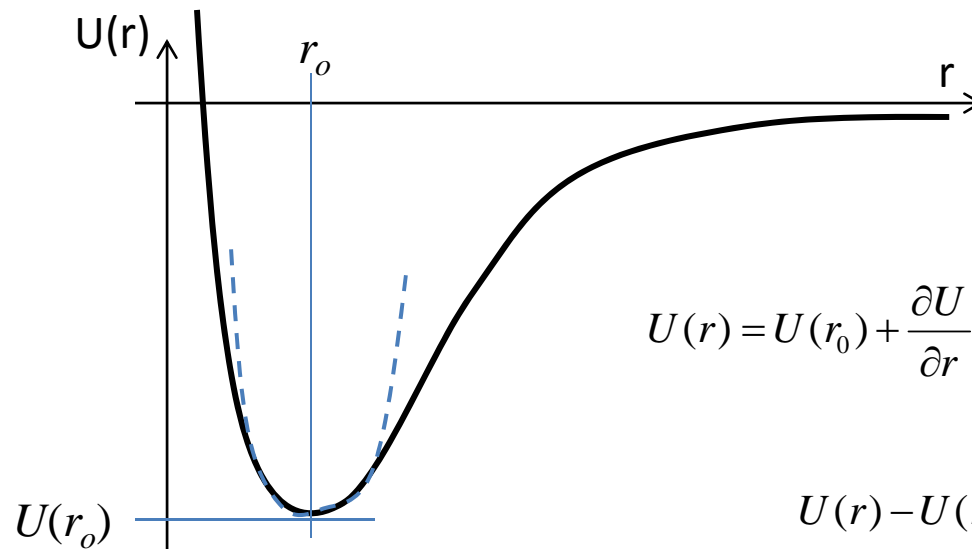
G. Ertl and J. Kuppers (Weinheim, Deerfield Beach, FL, 1985)

D. L. Mills and E. Evans, Physical Review B5, 4126 (1972); Z, 853 (1973).

D. L. Mills, Surface Science 48, p. 59 (1975)

Overview

- High Resolution Electron Energy Loss Spectroscopy
- Molecular Symmetry at Surfaces
- Adsorbate-adsorbate Interactions
- IR Spectroscopy



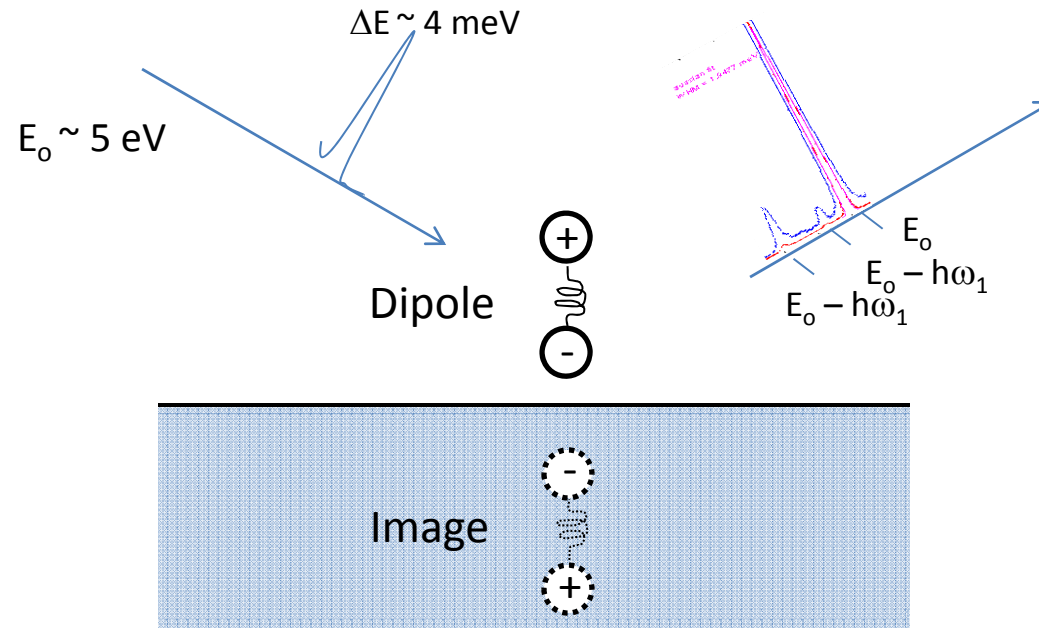
$$U(r) = U(r_0) + \left. \frac{\partial U}{\partial r} \right|_{r_0} (\Delta r) + \frac{1}{2!} \left. \frac{\partial^2 U}{\partial r^2} \right|_{r_0} (\Delta r)^2 + \dots$$

$$U(r) - U(r_0) = \frac{1}{2} k (\Delta r)^2 + \dots$$

Why Measure Vibrations at Surfaces?

- Molecular Identification
 - Gas phase spectra well known
 - Most retained at surfaces
- Adsorption site identification
 - symmetry
 - Molecular analogs and shifted wo
- Bonding identification
- Energy Transfer
- Adsorbate-Adsorbate Interaction
- Phonons, surface stress

High Resolution Electron Energy Loss Spectroscopy



Time varying dipole:

$$p = p_o + pe^{-i\omega t}$$

Potential seen by electron:

$$V(\vec{r}) = \left(\frac{2pz}{r^3} \right) e^{-i\omega t} + \text{c.c.}$$

Let: $\vec{r} = \vec{r}_{||} + z\hat{z}$ $\vec{Q}_{||} \equiv$ Wave vector || to surface

$$V(\vec{r}) = pe^{-i\omega_o t} \int \frac{dQ_{||}^2}{\pi} e^{-i\vec{Q}_{||} \cdot \vec{r}_{||}} e^{-iQ_{||}z} + \text{c.c.}$$

Component with wave vector $Q_{||}$ reaches into vacuum a distance $l \sim Q_{||}^{-1}$

Scattering Kinematics

Consider incident electron: \vec{k}_i, E_i scatters into state: \vec{k}_s, E_s where $E_s = E_i \pm \hbar\omega_o$

Born Approximation: Done by components of the potential with: $\vec{Q}_{\parallel} = \vec{k}_{\parallel}^s - \vec{k}_{\parallel}^i$

Suppose $\theta_i = 0$; θ_s small $\Rightarrow k_{\parallel}^s = \theta k^i = Q_{\parallel}$

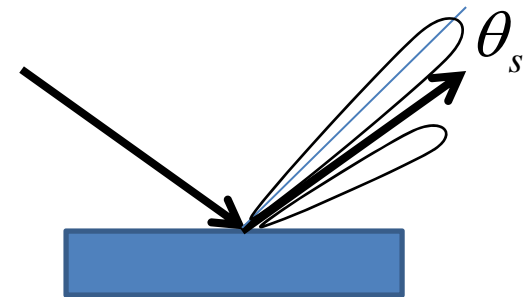
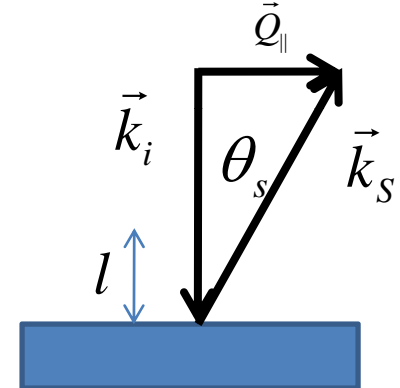
Interaction time:
$$\Delta t \approx \frac{2l}{v_o} = \frac{2}{v_o Q_{\parallel}} = \frac{2}{v_o k^i \theta_s} \sim \frac{\hbar}{E_i \theta_s}$$

If $\Delta t \omega_o \ll 1$ then too fast \rightarrow no excitation

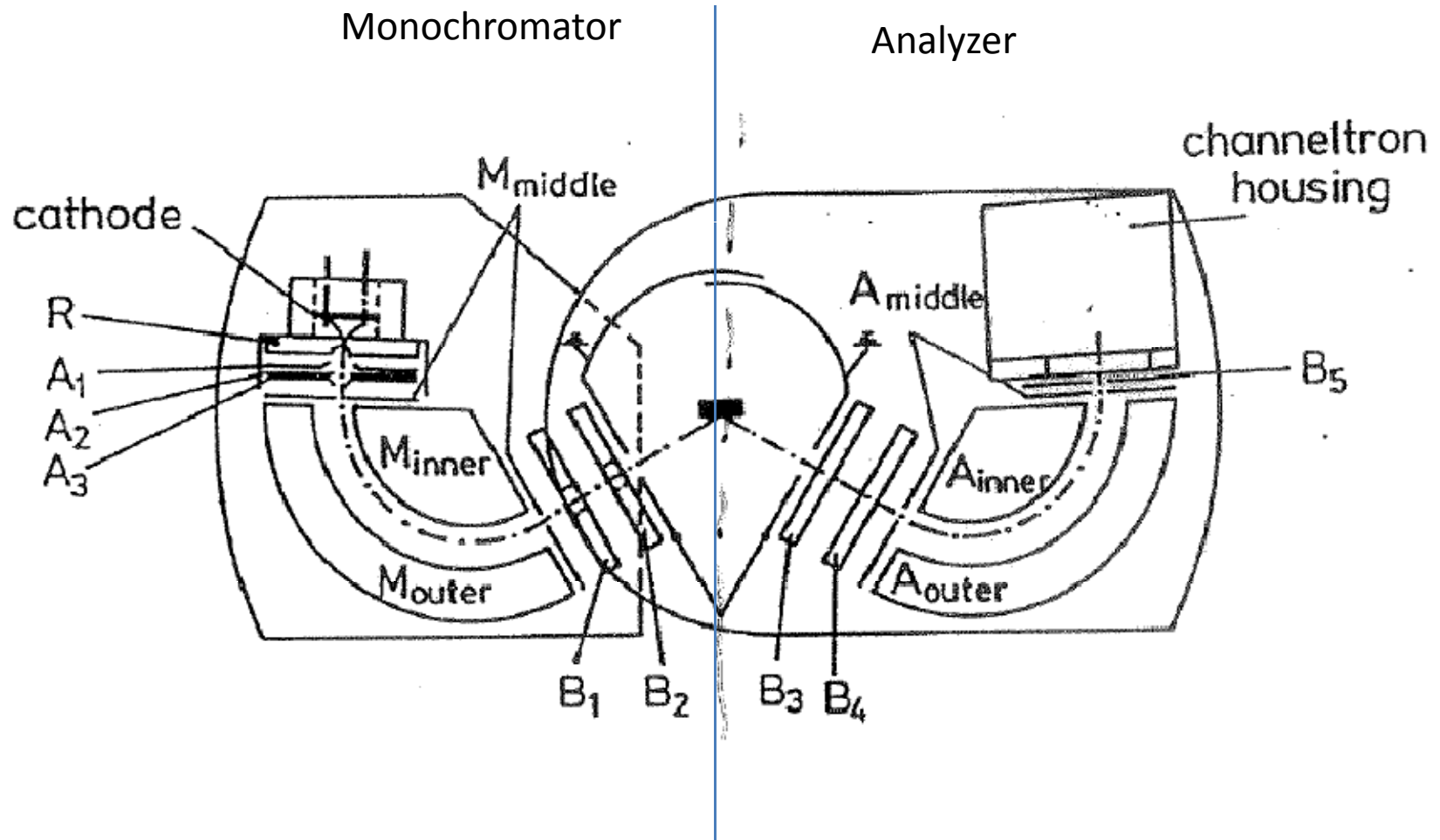
If $\Delta t \omega_o \gg 1$ then adiabatic \rightarrow no excitation

$$\Delta t \omega_o \approx 1 \Rightarrow \frac{\hbar \omega_o}{E_i \theta_s} \approx 1 \Rightarrow \theta_s \approx \frac{\hbar \omega_o}{E_i}$$

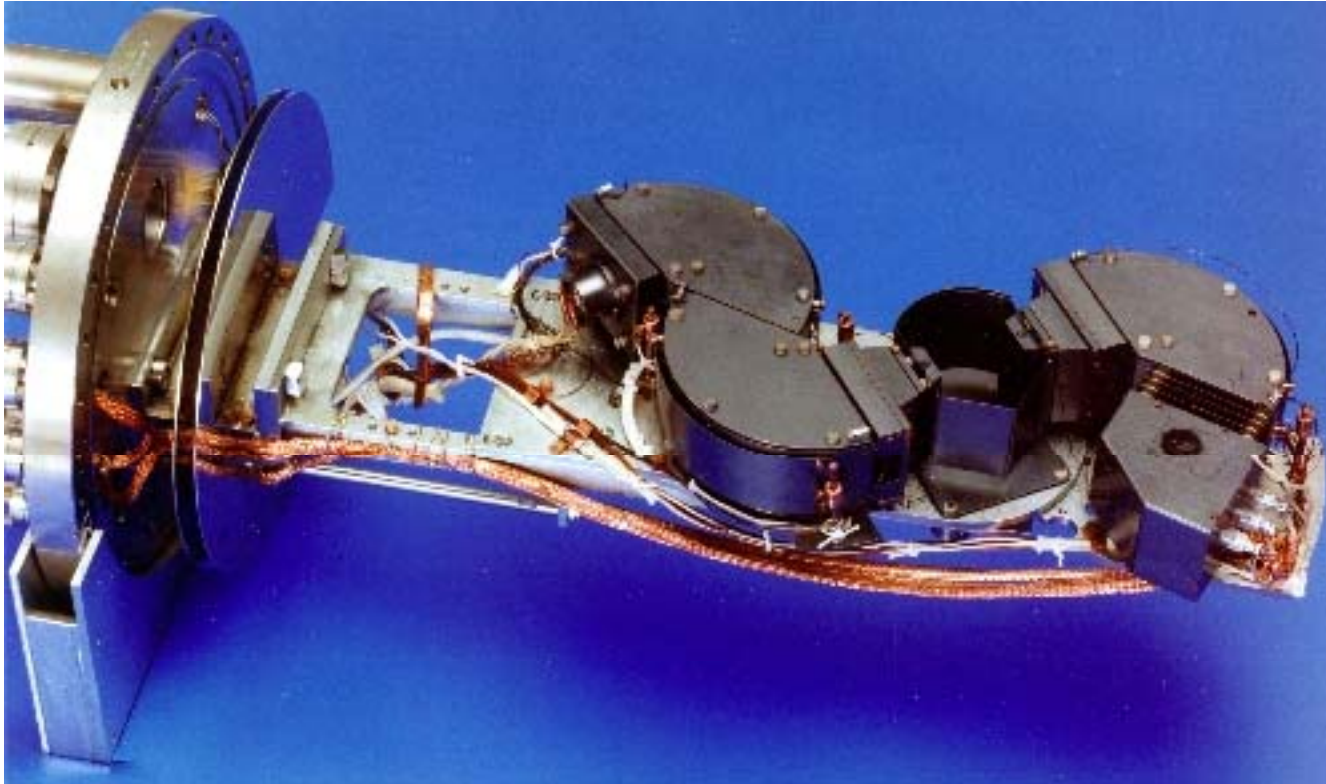
$$\frac{\hbar \omega_o \approx 100 \text{ meV}}{E_i = 5 \text{ eV}} \Rightarrow \theta_s \approx 0.02 \approx 0.6^\circ$$



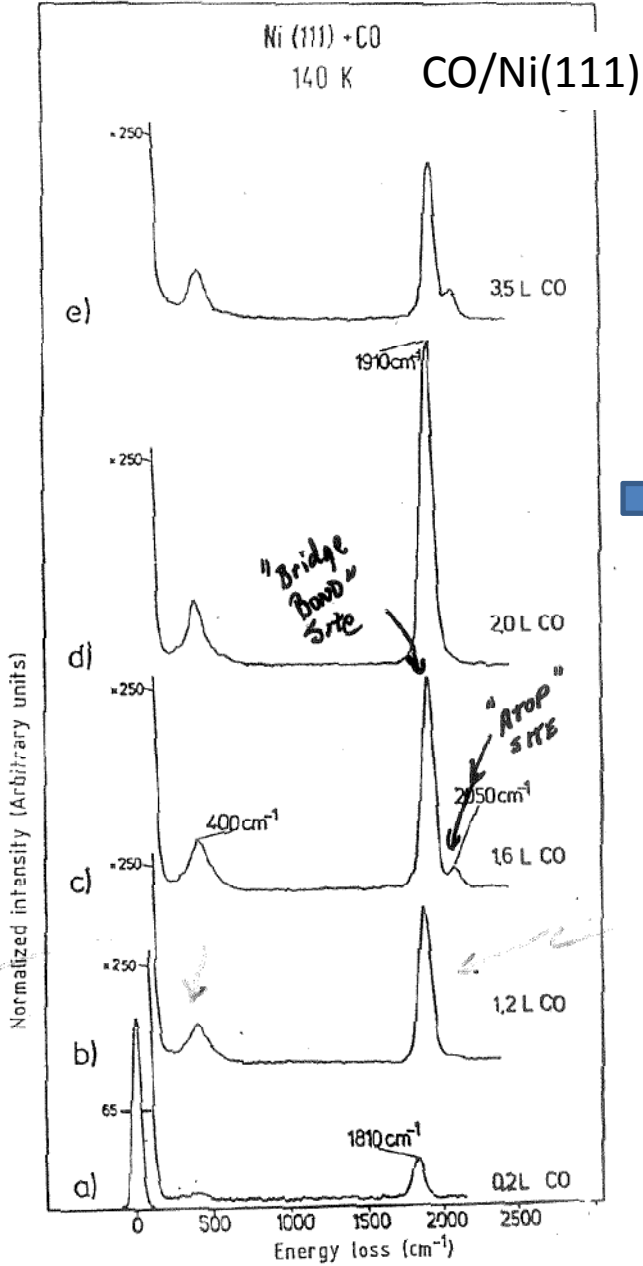
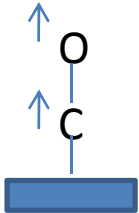
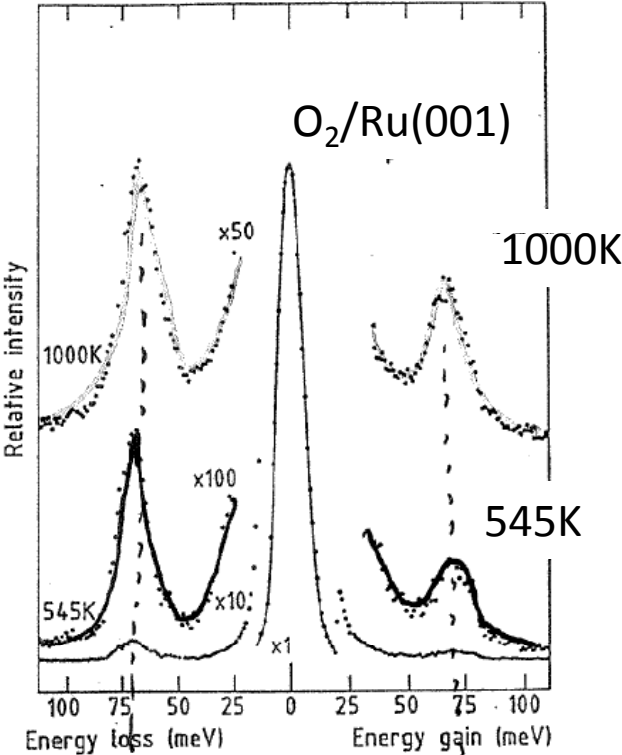
HEELS Spectrometer

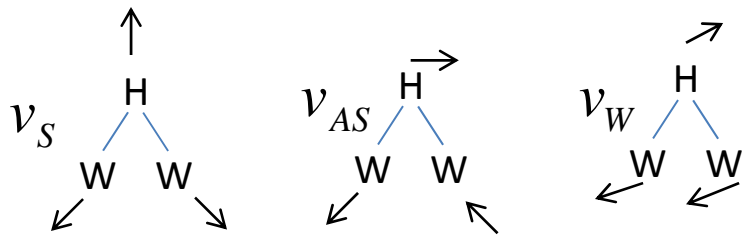


HEELS Spectrometer

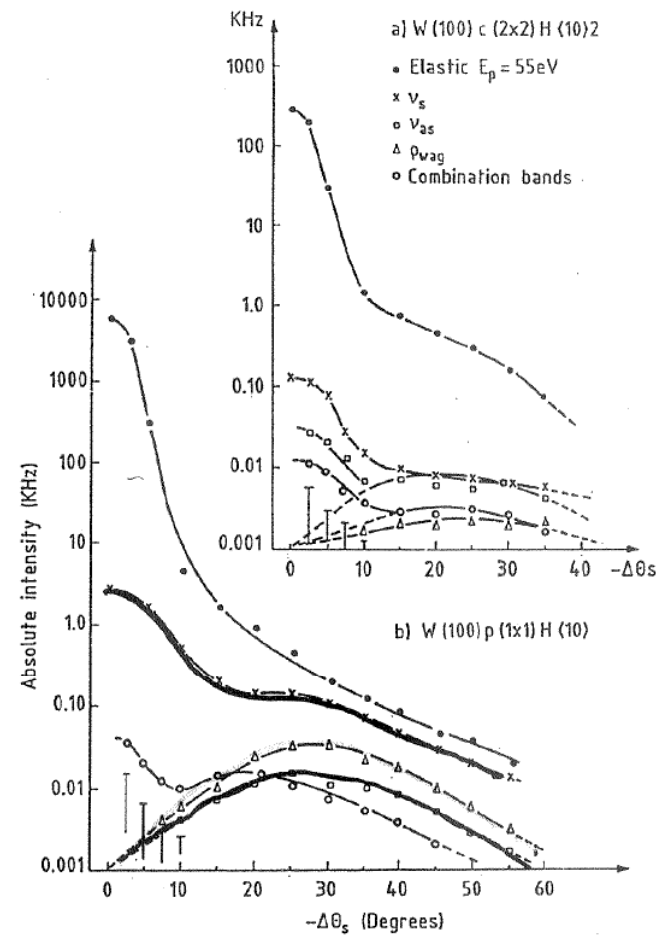
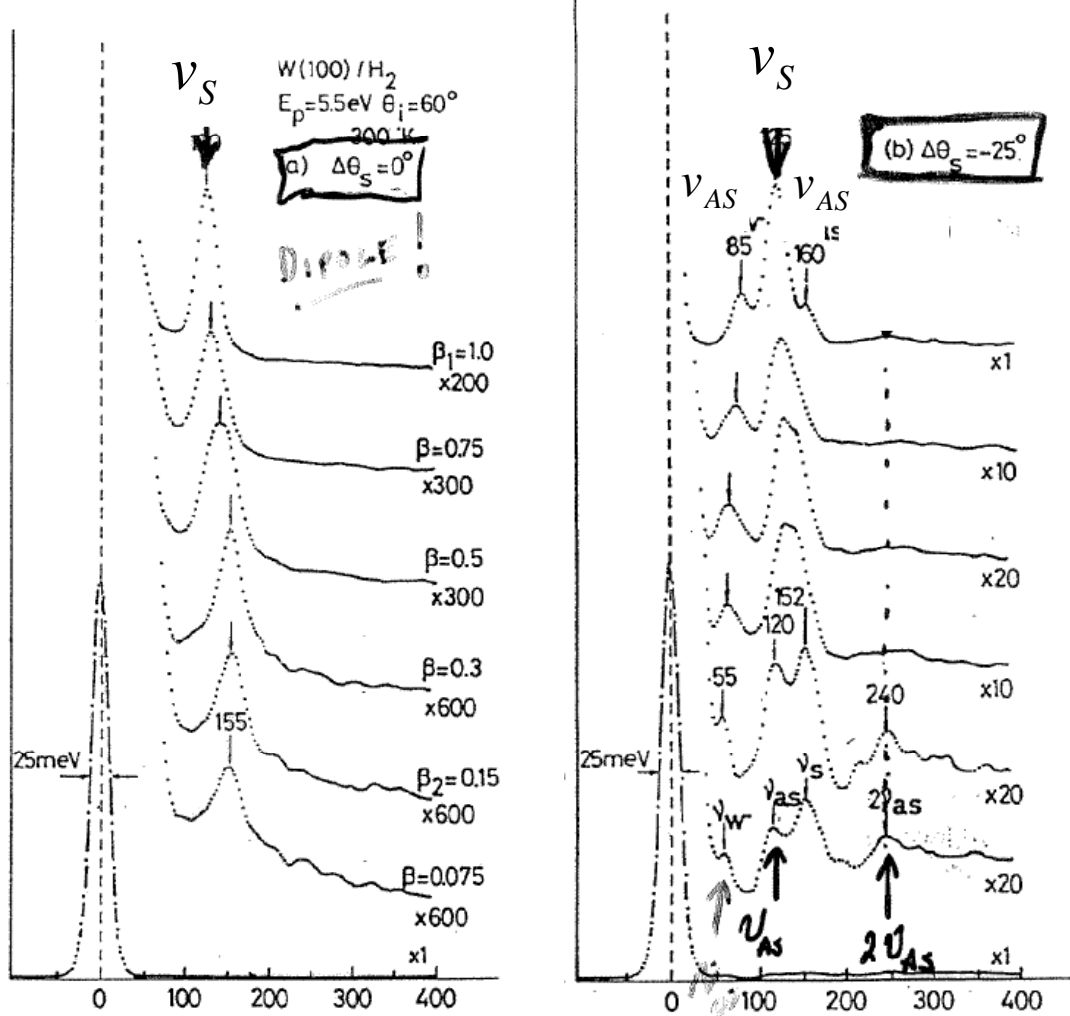


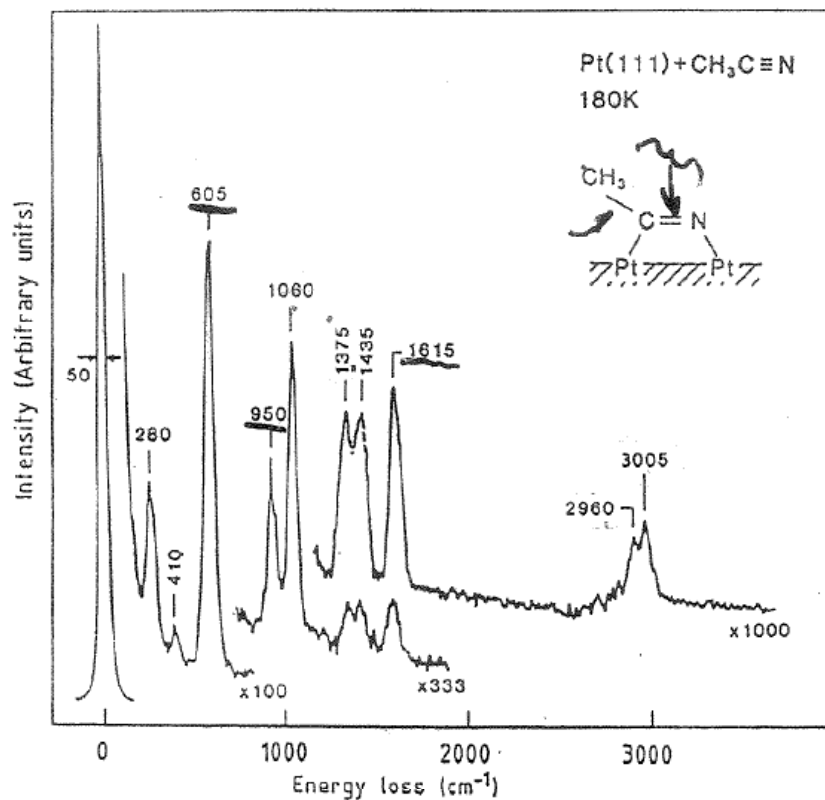
Examples: Molecular Adsorbates





Impact Scattering Non-dipole

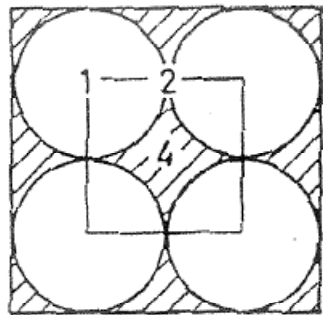
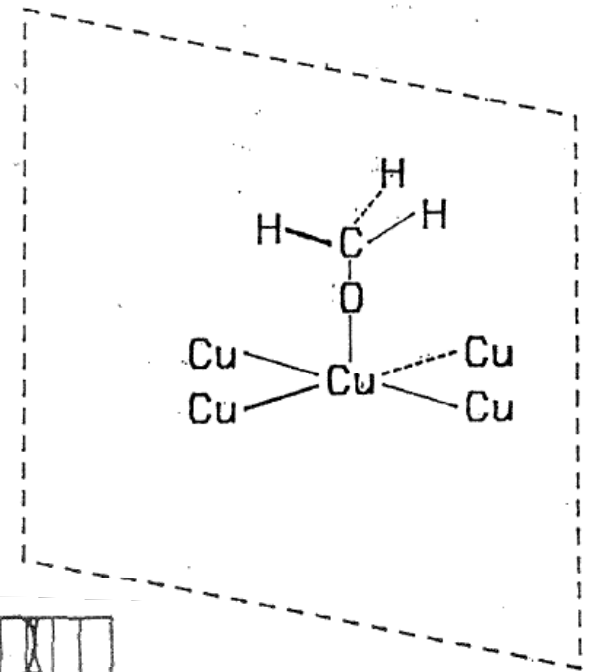




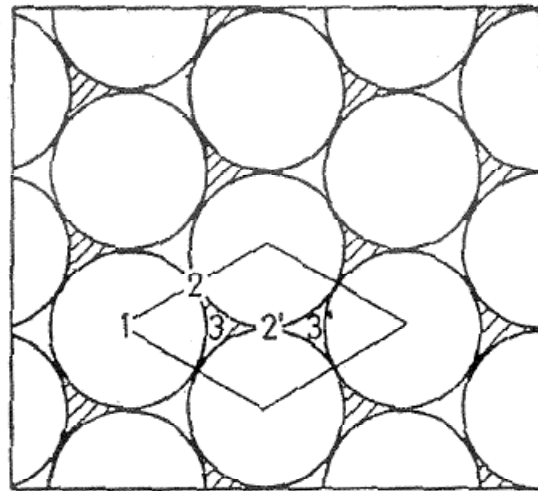
Molecular Bonding Geometry

Mode	Type	CH ₃ CN (gas)	CH ₃ CN at Pt(111)
ρ_t (MeCN)	torsion		280
ν_s (Pt-MeCN)	Pt-MeCN		410
ν_a (Pt-MeCN)		stretch	605
δ (C-C-N)	CCN bond	<u>361</u>	<u>605</u>
ν (C-C)	CC stretch	<u>920</u>	<u>950</u>
ρ_r (CH ₃)	Me rock	<u>1041</u>	<u>1060</u>
δ_s (CH ₃)	Me sym. bend	1389	1375
δ_d (CH ₃)	Me deg. bend	1454	1435
ν (CN)	CN stretch	<u>2268</u>	<u>1615</u>
ν_s (CH)	CH ₃ sym. stretch	2954	2960
ν_d (CH)	CH ₃ deg. stretch	3009	3005

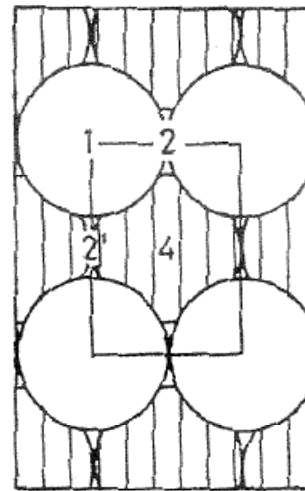
Group Symmetry Selection Rules



fcc (100)



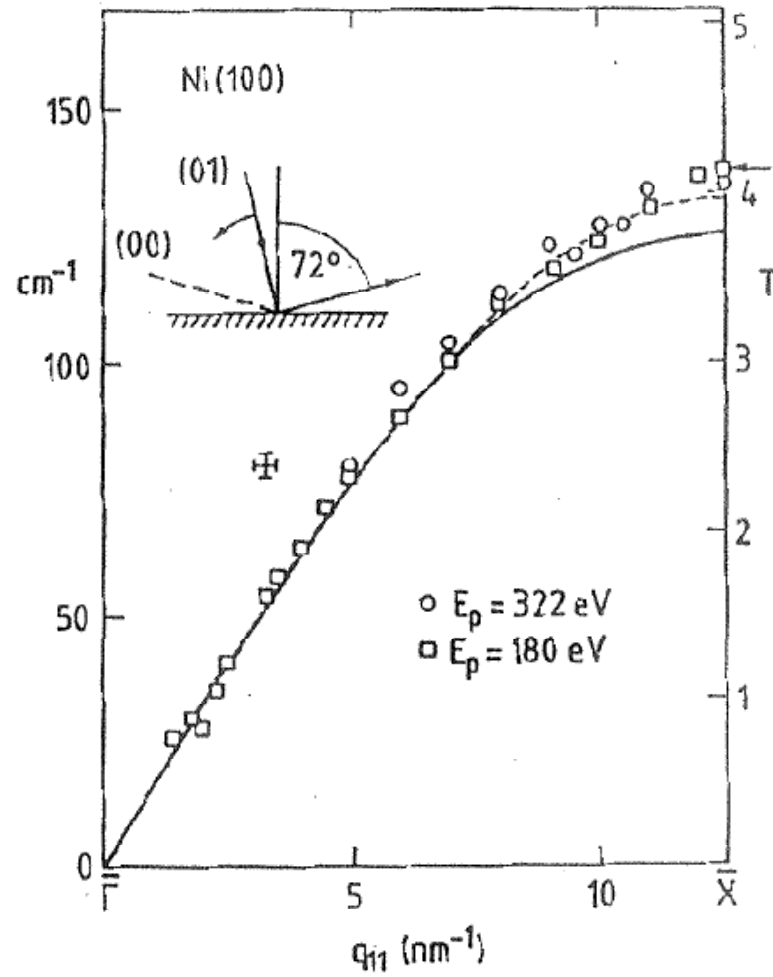
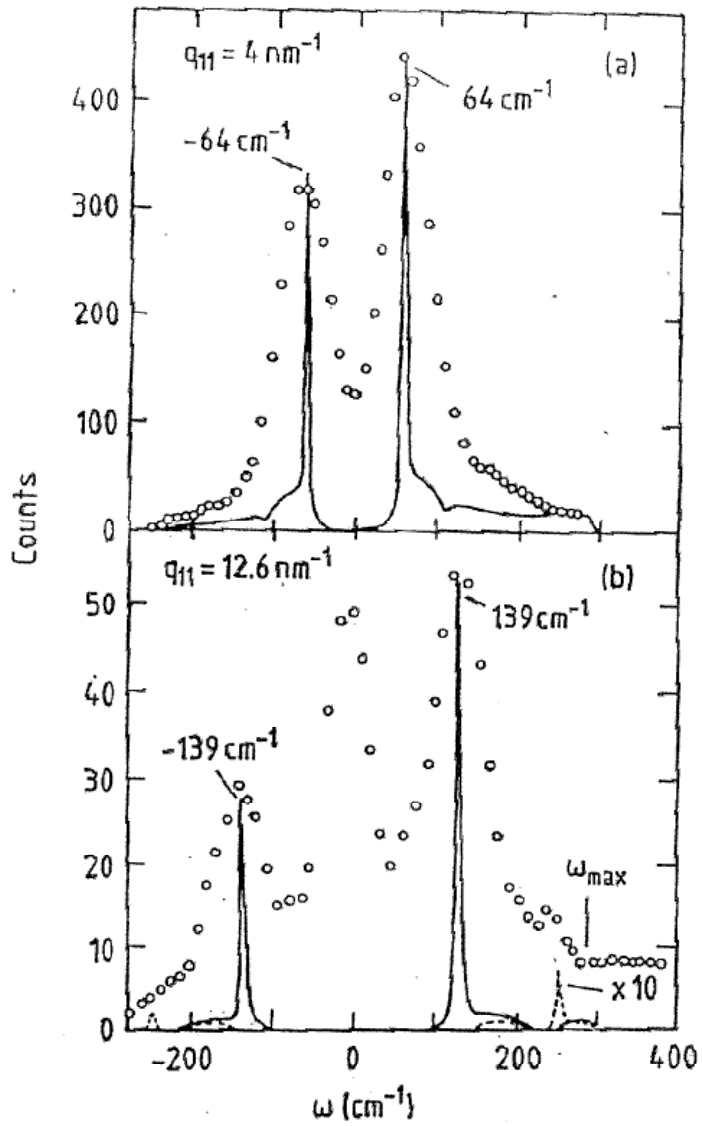
fcc (111)



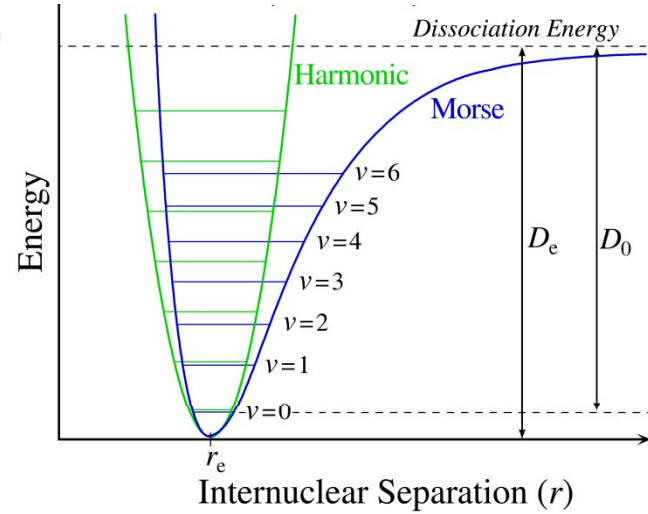
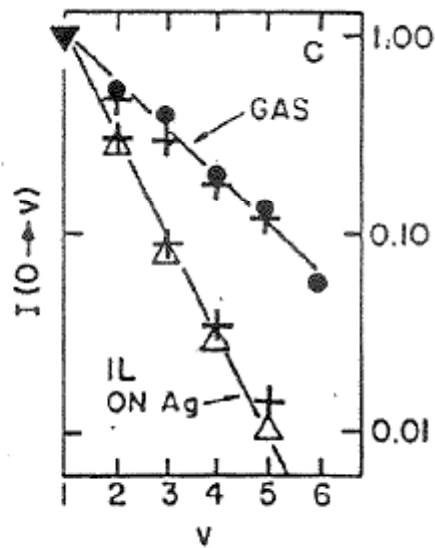
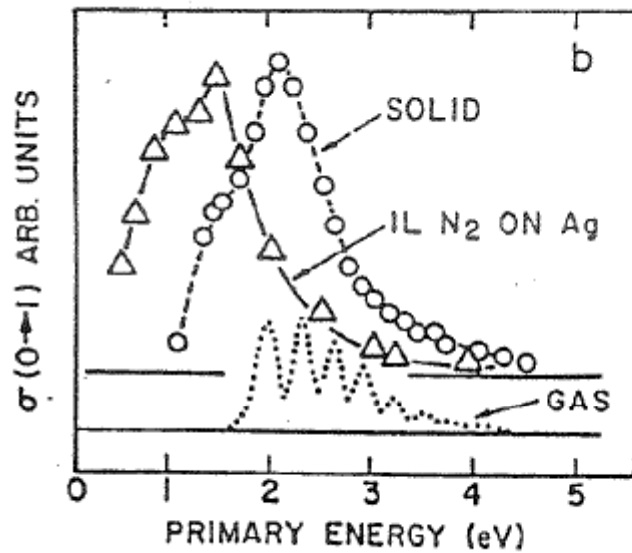
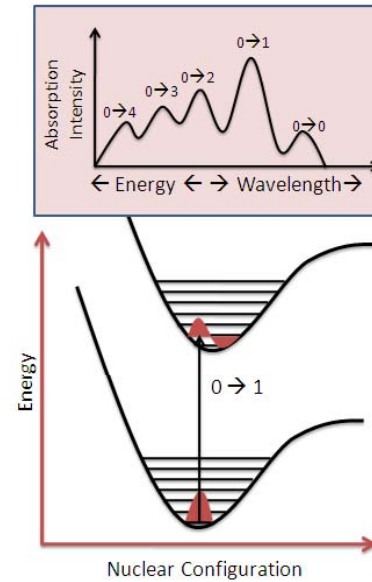
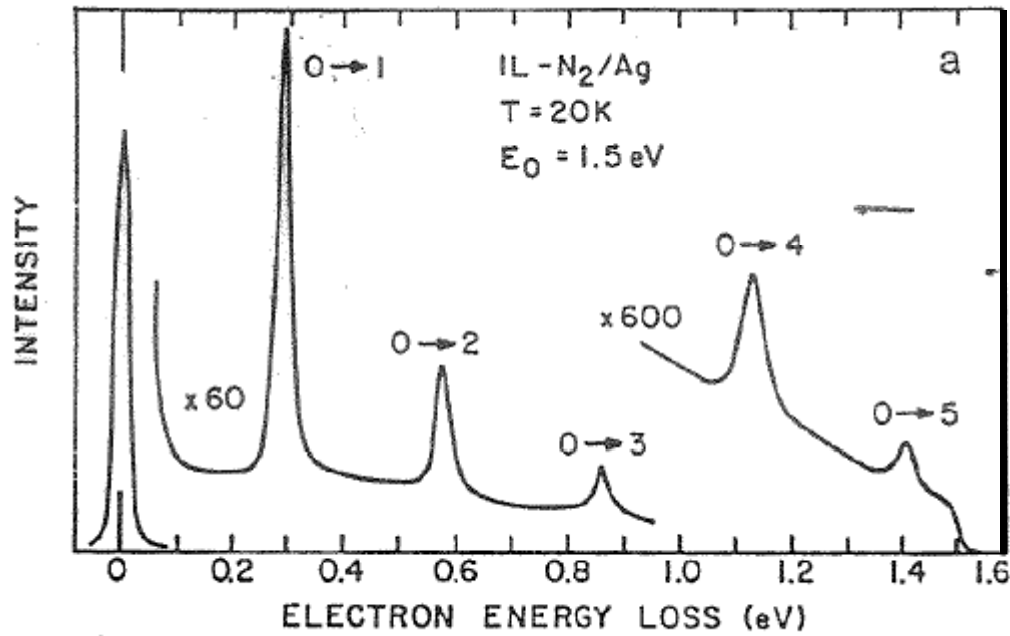
fcc (110)

Figure 2. The arrangements of metal atoms on the (100), (111), and (110) faces face-centered cubic (fcc) metal crystal. Second layer atoms are hatched. High-symmetry potential adsorbate sites are labelled 1, 2, 3, or 4 according to the nearest-neighbor atom coordination number in the site.

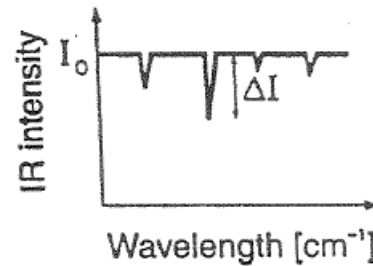
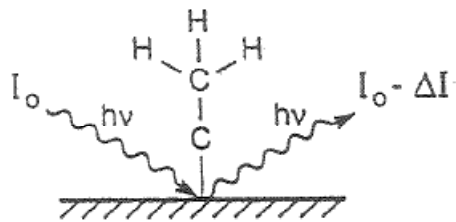
Surface Phonons



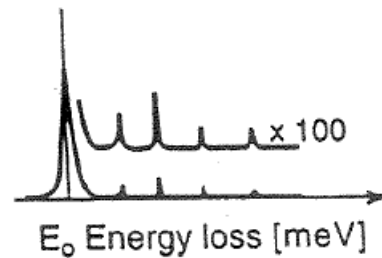
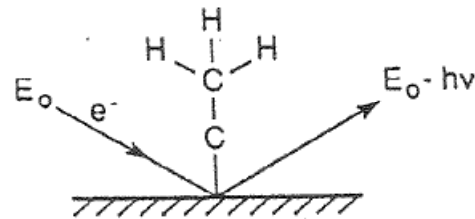
Negative Ion Resonance (vibrational overtones)



Infrared Reflection Absorption Spectroscopy

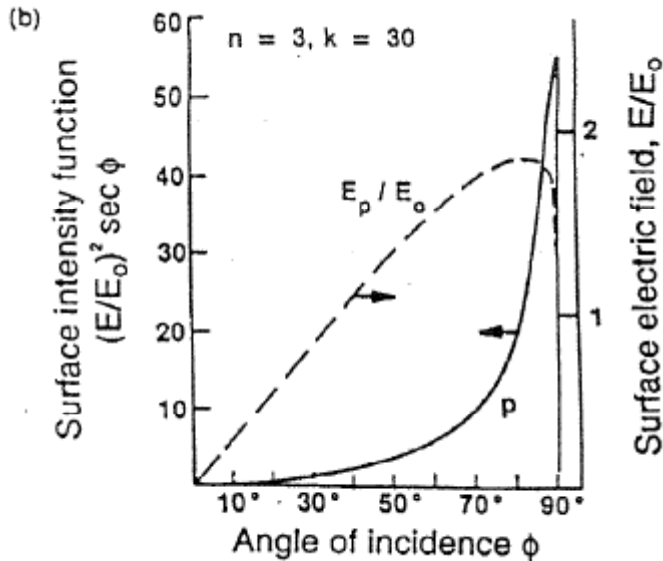
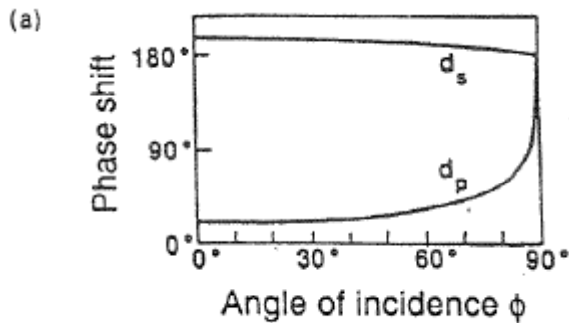
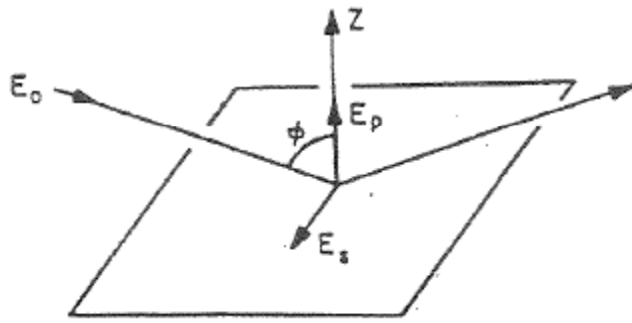


IRAS: Absorption of monochromatic light - excitation of molecular vibrations



EELS: Energy loss of electrons - excitation of molecular vibrations

- Spectral Range:
 - $\sim 65 - 500 \text{ meV}$
 - $\sim 500 - 4000 \text{ cm}^{-1}$
- Resolution
 - $0.125 - 0.625 \text{ meV}$
 - $1 - 5 \text{ cm}^{-1}$
- Sensitivity: $\sim 10^{-3} \text{ ML}$
 - Selection Rules:
 - Strict dipole
- Versatility:
 - photon in-photon out:



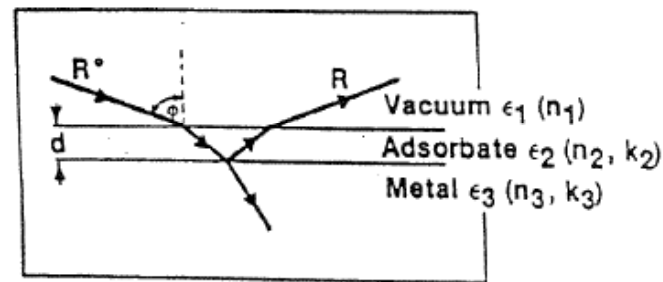
$$R_s = \frac{(n - \sec \phi)^2 + k^2}{(n + \sec \phi)^2 + k^2}$$

$$R_p = \frac{(n - \cos \phi)^2 + k^2}{(n + \cos \phi)^2 + k^2}$$

- Only p-component of light survives at the surface

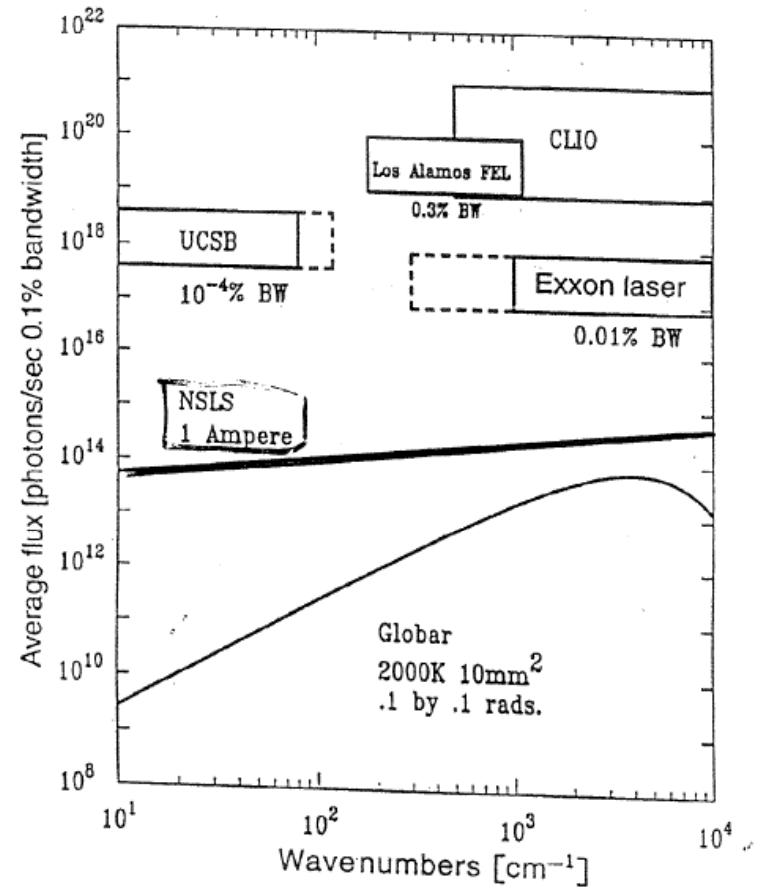
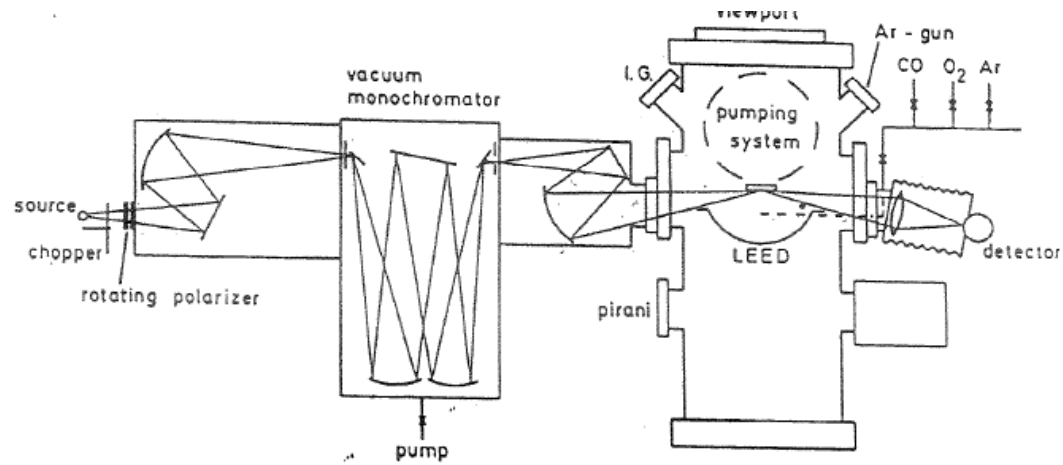
$$\tan \Delta = \tan(d_p - d_s) = \frac{2k \tan \phi \sin \phi}{\tan^2 \phi - (n^2 + k^2)}$$

- Only μ_{\perp} is observed
- High substrate reflectivity (at grazing angle)
- Versatility: photon in-photon out:

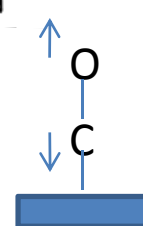
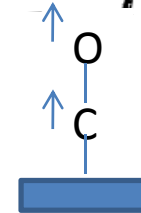
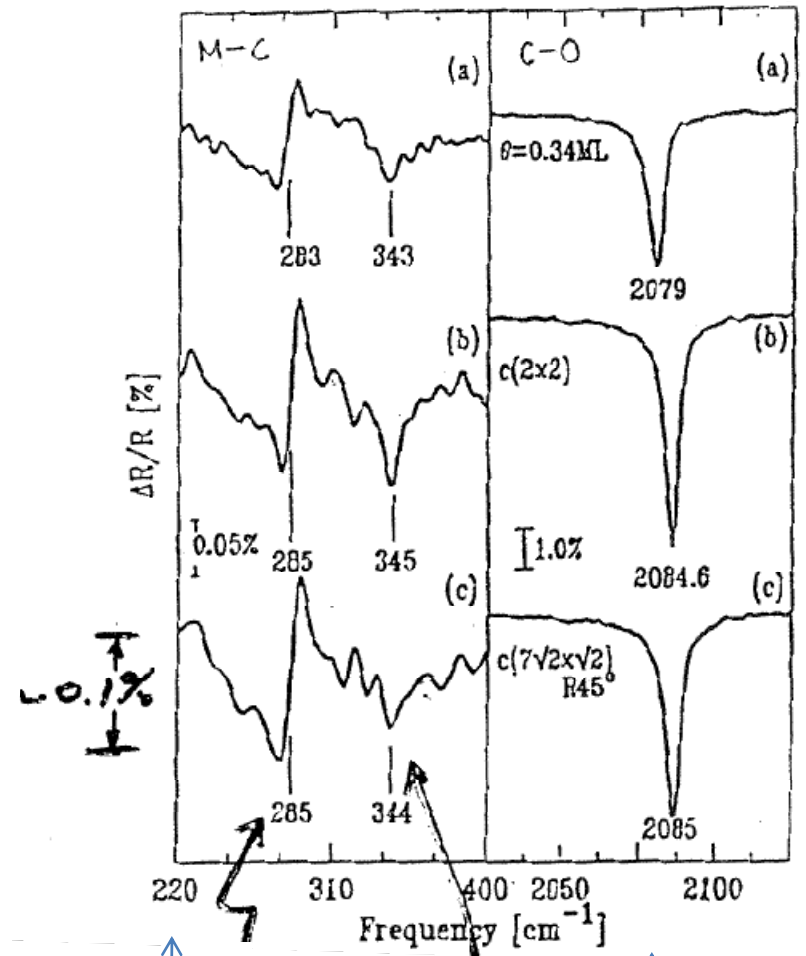
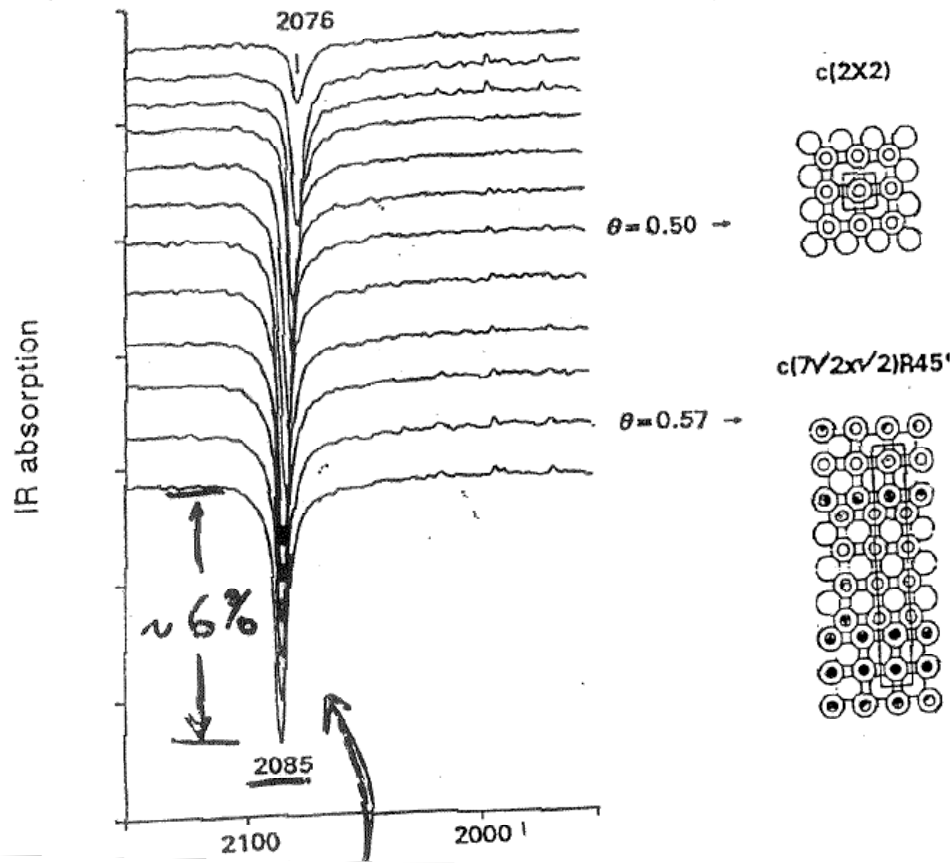


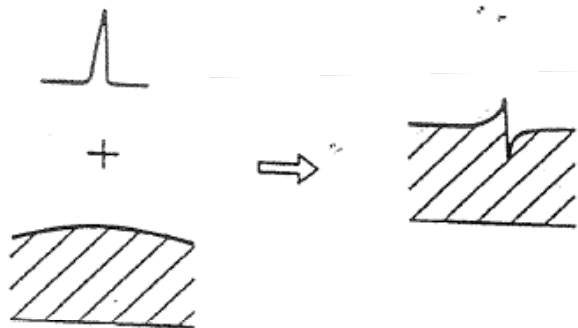
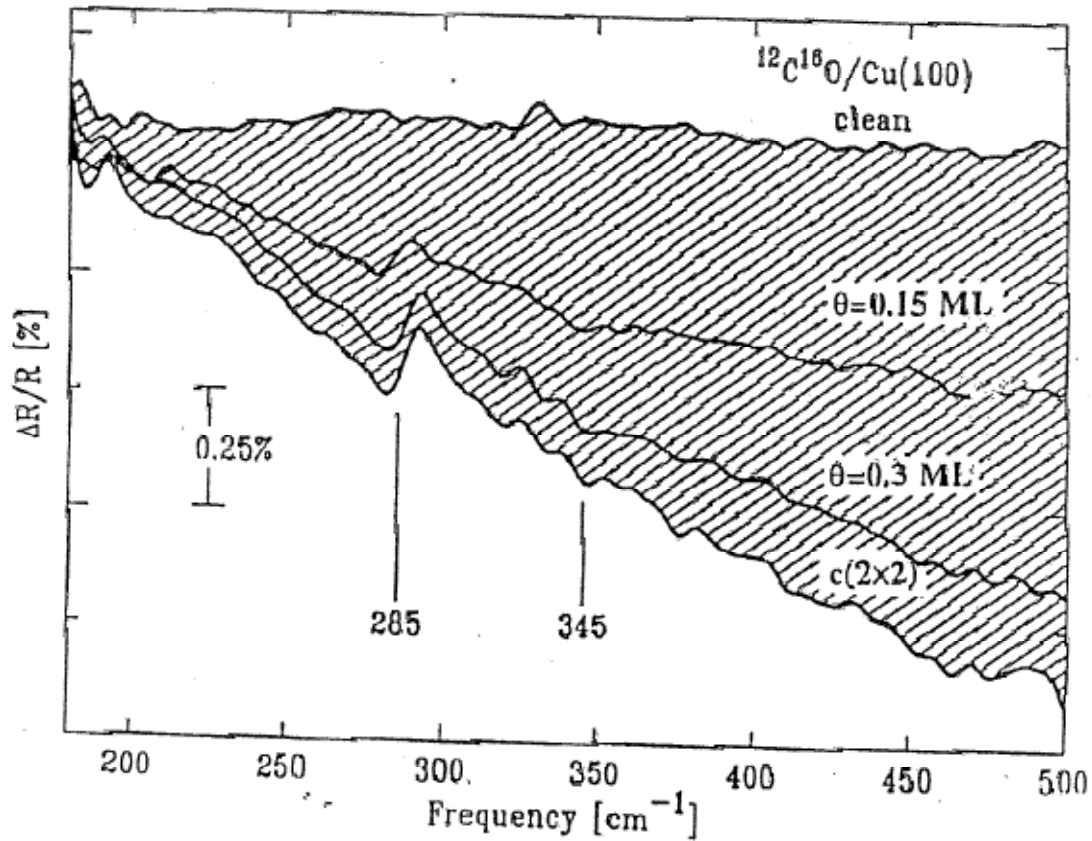
$$\frac{\Delta R_p}{R_p} = \left(\frac{8\pi d \sin^2 \phi}{\lambda \cos \phi} \right) \text{Im} \left\{ \frac{1}{1 - \epsilon_2} \right\}$$

IRAS Instrumentation



IRAS Examples





- Observation of dipole forbidden mode at 285 cm^{-1}
- Coupling of discrete vibrational mode of molecule with continuum excitation of substrate
- Broadband absorption as function of coverage \rightarrow electron resistivity