5.12 Vibrational Surface Spectroscopy

One of the most powerful methods for surface chemical compositional analysis - produces vibrational spectrum of adsorbed species. Can:

- fingerprint adsorbed species
- use selection rules to deduce bonding orientation

Based on absorption of energy from incident particle (electron - EELS, IR photon - RAIRS) - (won't discuss Raman or SHG)

- measure intensity vs. energy distribution of particle following absorption

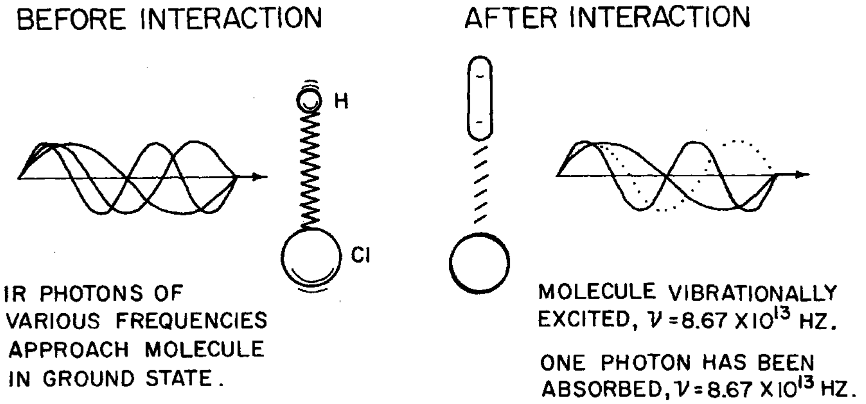


FIG. 1.5. Schematic illustration of infrared absorption. The HCl molecule whose vibrational frequency is 8.67×10^{13} Hz increases its vibrational energy by absorbing the energy of an infrared photon which has this same frequency.

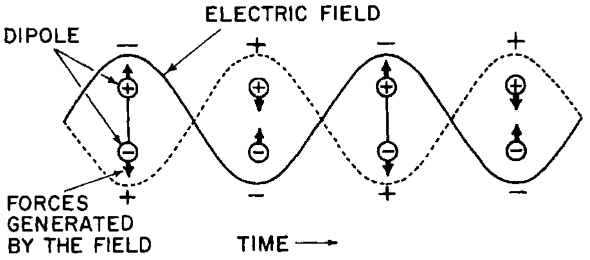


FIG. 1.6. Forces generated on a dipole by an oscillating electric field. These forces tend to alternately increase and decrease the dipole spacing.

5.12.1 Introduction to IR Methods

Can be performed using conventional (non-dispersive) FTIR instrument

- sample all channels simultaneously (Jaquinot advantage)
- high signal level at detector (Fellgett advantage)
- high accuracy (use of accurate internal standard HeNe laser)

in *transmission* or *reflectance* mode

In *transmission* mode

$$I = I_0 \exp(k \ c \ l) \qquad \frac{I}{I_0} = T = \exp(k \ c \ l) \qquad \text{Transmittance}$$

$$\ln\frac{I}{I_0} = k \ c \ l \qquad A = \varepsilon \ c \ l \qquad \text{Absorbance}$$

where k is the absorption coefficient, ε is absorptivity, c is surface concentration and l is pathlength

It can be shown that k is also the *imaginary* part of the *refractive index*

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

In a non-absorbing medium (*dielectric*), refractive index $\mathbf{n} = n$. In absorbing medium, refractive index contains a portion corresponding to absorption k.

Transmission experiments must be performed twice and difference calculated:

- reference spectrum with no absorbed material
- sample spectrum with adsorbed material

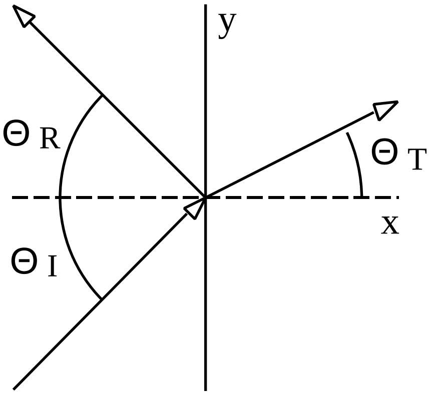
Surface transmission experiments less common

- large bulk contribution unless sample very thin
- many interesting samples not sufficiently transparent to IR

5.12.2 Reflection, Refraction and Absorption

Reflection, refraction and absorption all related through Maxwell's equations for electromagnetic radiation for interface of different **n**.

The *reflection* and *refraction angles* are given by Snell's Law:



$$\Theta_I = \Theta_R \text{ and } \frac{n_1}{n_2} = \frac{\sin\Theta_I}{\sin\Theta_T}$$

$$\text{for } \Theta_I < \Theta_{crit} = \sin^{-1}\left(\frac{n_2}{n_1}\right)$$

Where the plane containing the incident and reflected (and transmitted) waves is called the *plane of incidence*

The *intensities* of the reflected waves are given by Fresnel equations and are dependant on their *polarizations*:

When $\mathbf{n}_1 = 1.00$ (vacuum/air) and $\mathbf{n}_2 = n + ik$:

For *p*-polarized light (E-field || to plane of incidence)

$$R_p = \frac{\cos^2\Theta_T - 2n\cos\Theta_I\cos\Theta_T + \left(n^2 + k^2\right)\cos^2\Theta_I}{\cos^2\Theta_T + 2n\cos\Theta_I\cos\Theta_T + \left(n^2 + k^2\right)\cos^2\Theta_I}$$

and for *s*-polarized light (E-field to plane of incidence)

$$R_p = \frac{\cos^2\Theta_I - 2n\cos\Theta_I\cos\Theta_T + \left(n^2 + k^2\right)\cos^2\Theta_2}{\cos^2\Theta_I + 2n\cos\Theta_I\cos\Theta_T + \left(n^2 + k^2\right)\cos^2\Theta_2}$$

Such equations allow us to predict the reflectivity of materials ($\mathbf{n}_2$) with incidence angle

For very thick films on reflective surface (metal) Θ_I can be normal (0°) - double-pass transmission experiment

For very thin films on reflective surface Θ_I should be large (~75-85°) - grazing incidence experiment (RAIRS)

5.13 Reflection-Absorption Infrared Spectroscopy (RAIRS)

also known as Infrared Absorption-Reflection Spectroscopy (IRAS)

The intensity of light reflected from a surface (Fresnel equations) related to phase shift δ upon reflection

- *s*-polarized light almost cancelled by reflection at grazing incidence
- *p*-polarized light almost doubled by reflection at grazing incidence (until very grazing situations)

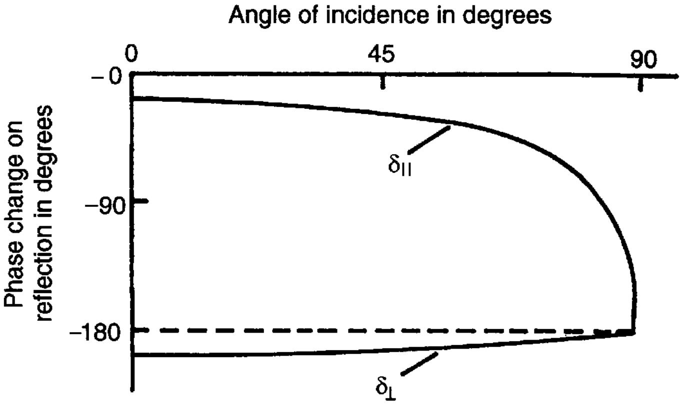
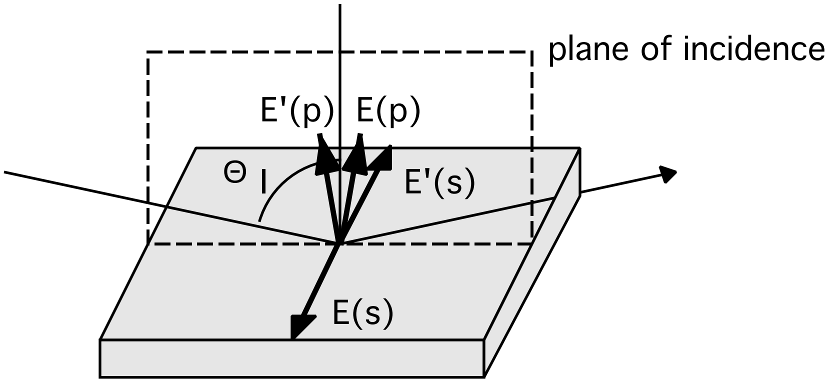


Figure 7.10. The phase shift for light reflected from a metal surface as calculated for light polarised both parallel to (p) and perpendicular to (s) the plane of incidence, after Greenler [9]



Only *p*-polarized component light can be reflected from surface at high incidence angles

Only vibrations with component dynamic dipole moment aligned to surface plane can interact with (*p*-polarized) incident light - *"surface selection rule"*

Group theory tells us which vibrations have components in x, y and z directions

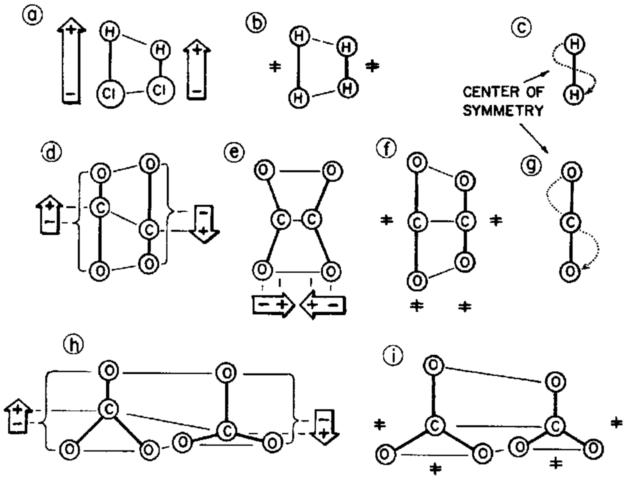


FIG. 1.7. **Dipole moment changes in certain molecular vibrations.**

Since absorbance A is proportional to E^2 and area of surface sampled increases as $1/\cos\Theta_I$, sensitivity of RAIRS increases as $E^2/\cos\Theta_I$

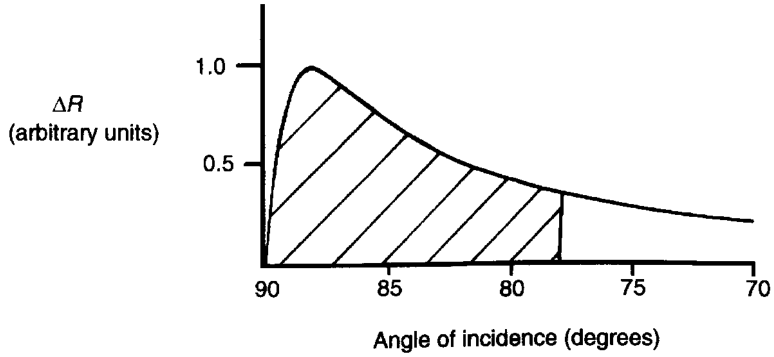


Figure 7.11. Schematic representation of the variation in band intensity with angle of incidence, after Chesters [10]

Best sensitivity for observing an absorption feature in RAIRS is

- *p*-polarized light
- grazing incidence
- molecule with transition dipole arranged along surface normal
- molecule with large transition moment

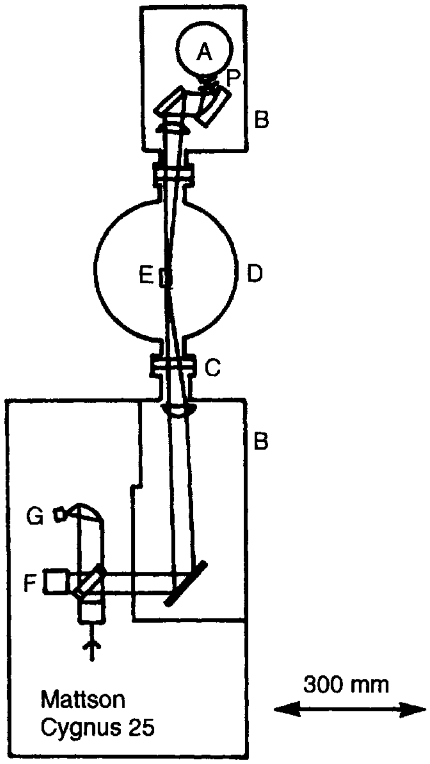


Figure 7.12. A schematic representation of the FT-RAIRS experiment as described by Chesters [10]

Using high quality FTIR spectrometers spectral acquisition (reference and sample) with high S/N can be acquired in few minutes with 2-4 cm^{-1} resolution

Width of absorption peak usually related to inhomogeneity of surface

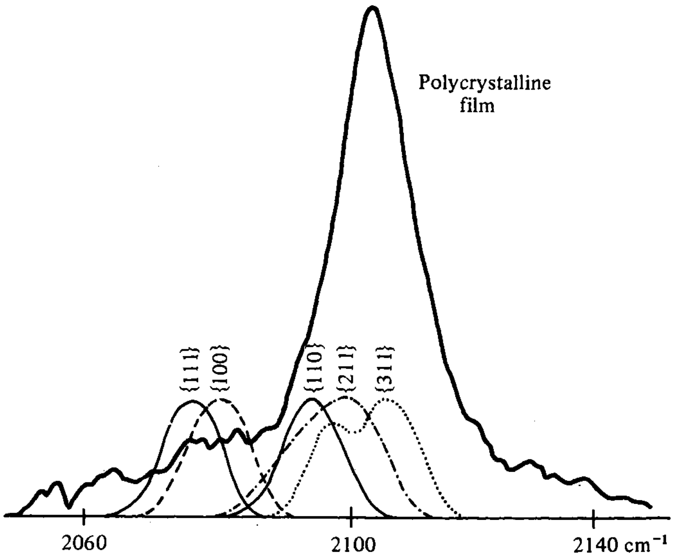


Fig. 9.7 Comparison of spectrum of CO on a polycrystalline Cu film with band shapes and positions found on individual single crystal planes (Pritchard, 1979b).

Frequency of *internal* vibrational mode often close to gas phase (red-shifted 200-800 cm^{-1})

Frequency used to infer nature of bonding with surface

- ν(X-Y) decreases as coordination to surface atoms increases
- occupation of sites often varies with coverage - high symmetry/coordination at low coverages → low symmetry/coordination at high coverages
- compared with organometallic compounds

"Softened" modes (by 100-200 cm^{-1}) sometimes appear due to substantial interactions with surface

$\Delta R/R$ often very small - absorbance 0.1 to 10^{-3}!

- sufficient for submonolayer sensitivity for molecule with strong dynamic dipole moment

$\Delta R/R$ approximately linear with coverage (unless molecular orientation change)

BUT relative intensity of band not good indicator of population

- dynamic dipoles of molecules in ordered array couple - modulates dynamic dipole moment and hence modulates absorption
- orientation affects absorbance

Cannot observe vibrations with $\nu < 800$ cm^{-1} - detector cut-off

5.13.1 Example Application of RAIRS: CO/NO on Metals

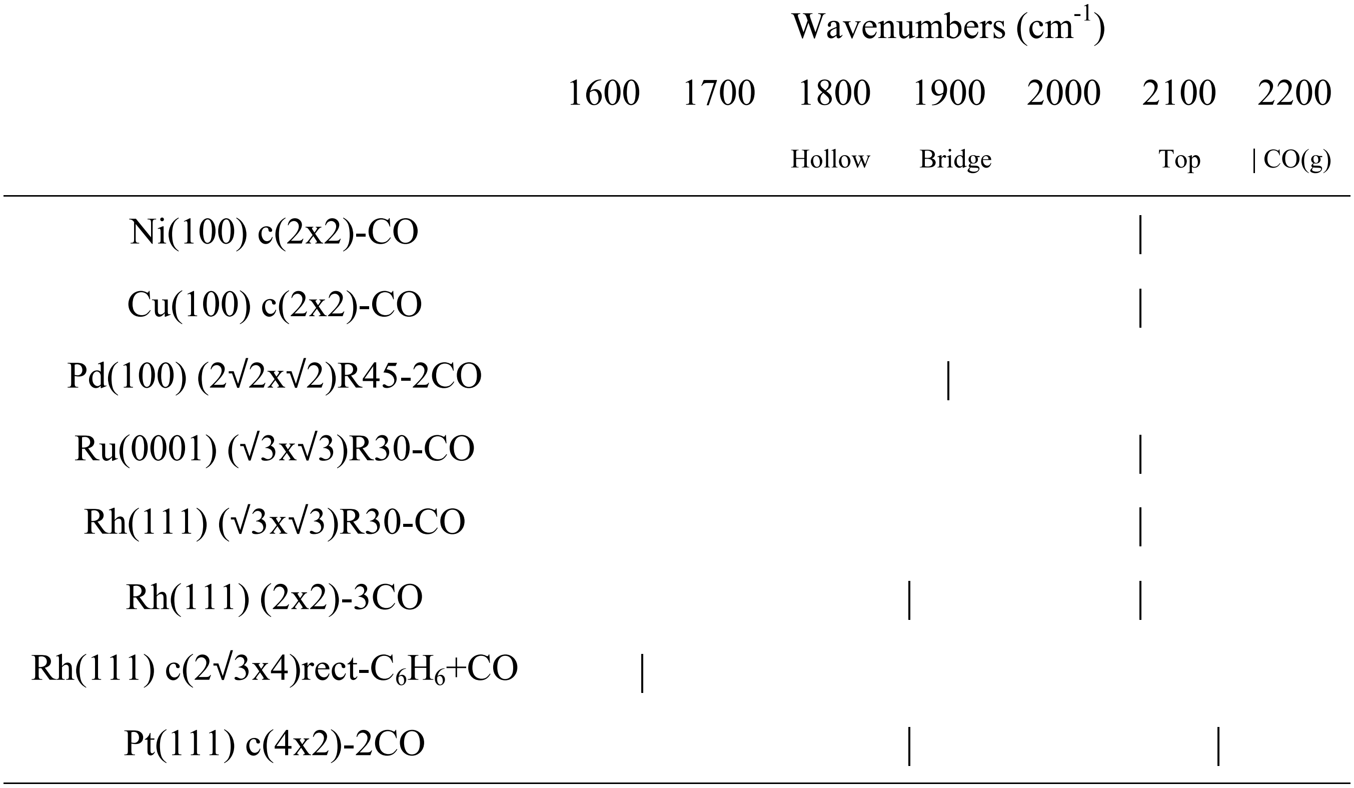
CO and NO have similar electronic structure

- HOMO is filled 5 σ and LUMO is 2 π^* MO

- Both considered σ donors and π* acceptors

Coadsorption of CO and NO on Rh/Pt/Ni extremely important in catalysis (vehicle emissions)

- CO most intensively studied adsorbate by vibrational spectroscopy



ν(CO(g)) = 2140 cm^{-1}

CO on Ni(111):

- 2-fold bridge at ~1840 cm^{-1} at low coverage
- additional on-top sites at ~2040 cm^{-1} at coverages >0.5 ML

NO on Ni(111):

- tilted 2-fold bridge at ~1480 cm^{-1} at very low coverages
- shifts to more perpendicular 2-fold bridge up to ~1580 cm^{-1} at low coverages

- on-top sites at >0.5 ML

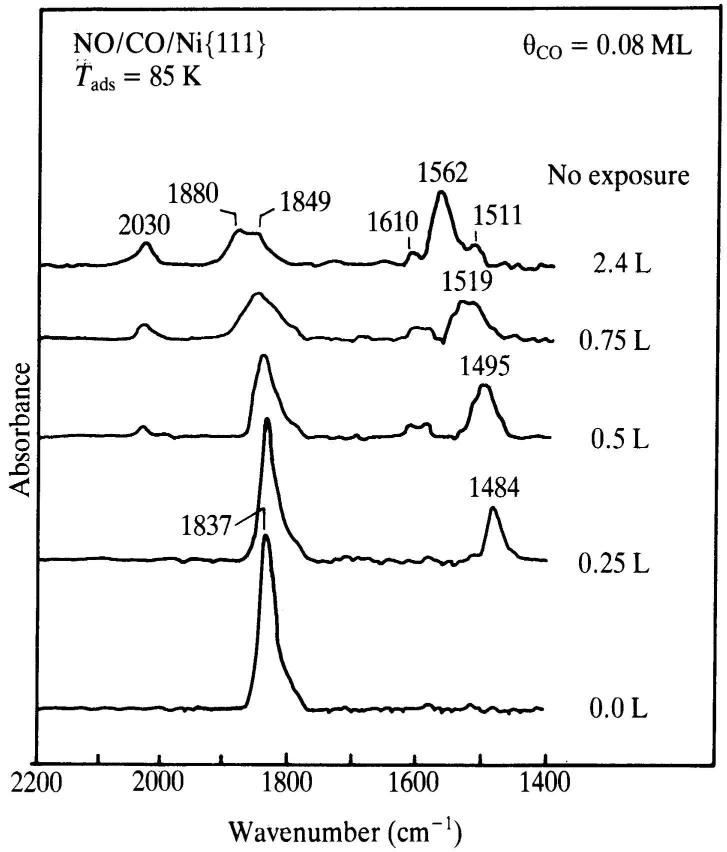


Fig. 9.9 Vibrational spectra recorded by Fourier transform RAIS spectroscopy for a Ni{111} surface following the adsorption of NO molecules on a CO-covered surface ($\theta_{CO} = 0.08$) at 85 K, and showing the marked broadening of the pre-adsorbed CO peak (after Chen, Erley & Ibach, 1990).

When NO is added to CO covered surface:

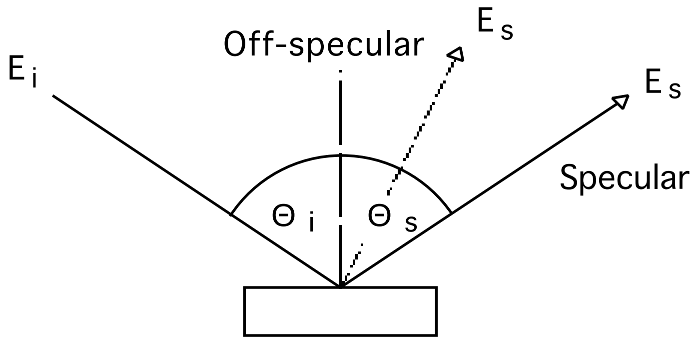
- on-top sites appear - CO displaced by NO
- bridge CO shifts to higher ν - strengthened CO internal bond
- bridge CO broadens into doublet - multiple adsorption sites?

(Recent results have suggested that this interpretation is not correct - CO and NO on Ni(111) occupy fcc and hcp sites at all coverages!)

5.14 Electron Energy Loss Spectroscopy (EELS)

also known as *high resolution* EELS (HREELS)

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 $h\nu \approx 4560$ cm^{-1} but for H on TM expect $h\nu \approx 800$-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)

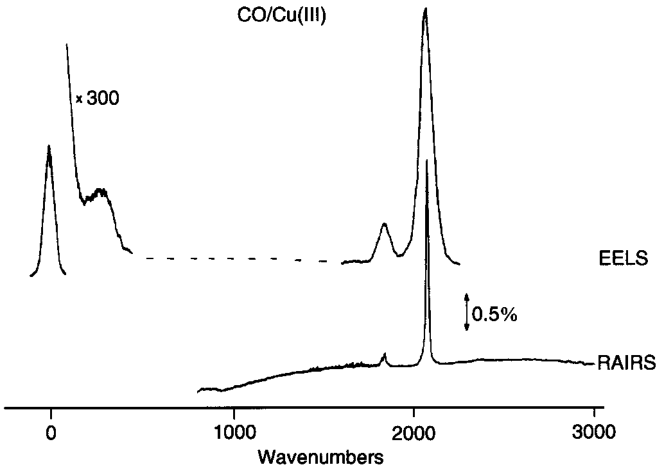


Figure 7.13. RAIRS spectrum of a monlayer of CO adsorbed on a Cu (111) surface at 95 K in comparison with analogous data obtained using electron energy loss spectroscopy, after Chesters *et al.* [10]

- sufficient for submonolayer sensitivity, even for weak dynamic dipoles (best 10^{-3} ML)

5.14.1 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)

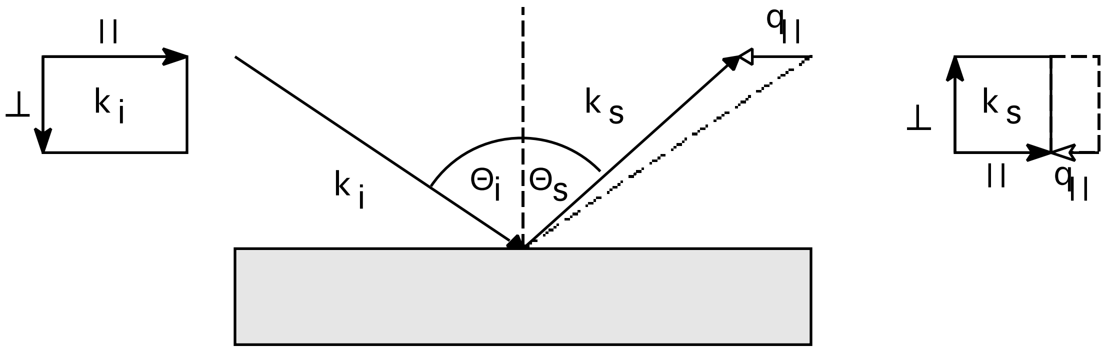
(1) Dipole scattering

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

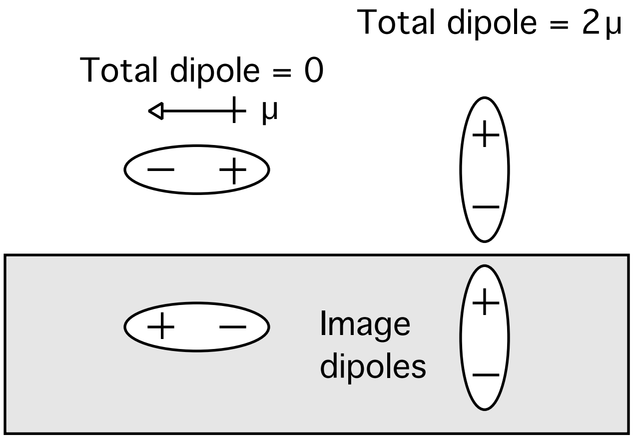
- Elastically-scattered electrons appear at $\Theta_i = \Theta_s$ (specular)
- Inelastically-scattered electrons appear at $\Theta_i \approx \Theta_s$ (sharply peaked near specular)



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

(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

(3) Negative Ion Resonance

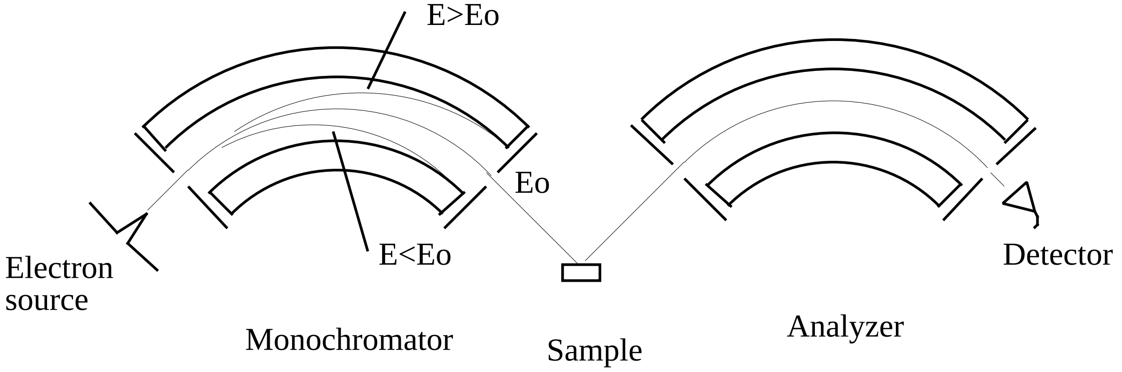
Incident electron becomes transiently trapped in empty, high lying MO of adsorbate - Rydberg state

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

5.14.2 Instrumentation for HREELS



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

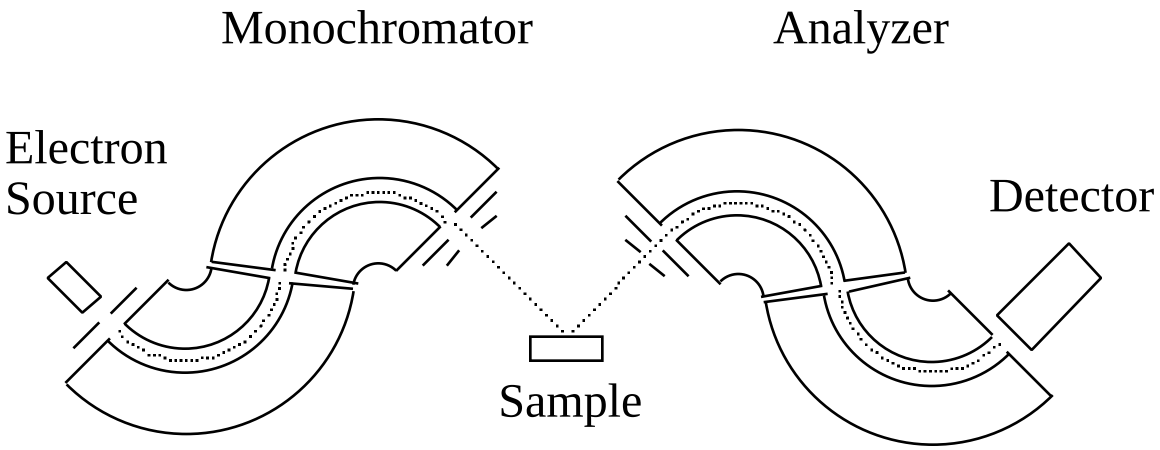
- typical radius 5 cm, typical pass energy <500 meV (in XPS, radius ~20-30 cm, pass energy 50-100 eV)

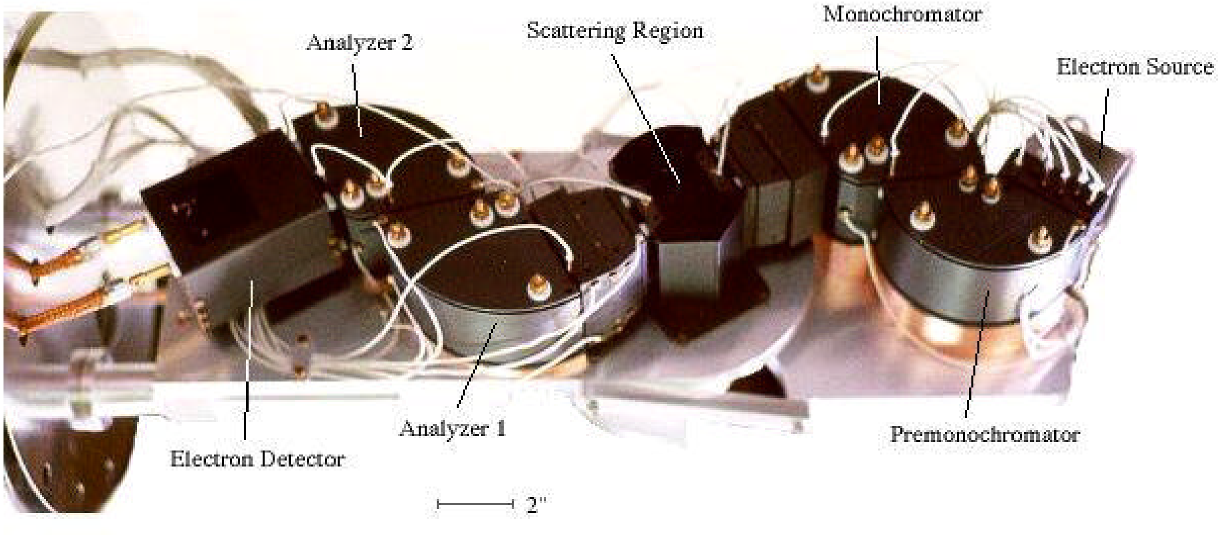
Electrons retarded before entry into sector, then accelerated to sample

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





Space-charge effects always tend to produce divergent beam

Optimization of lens and sector potentials very difficult - computer controlled

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}

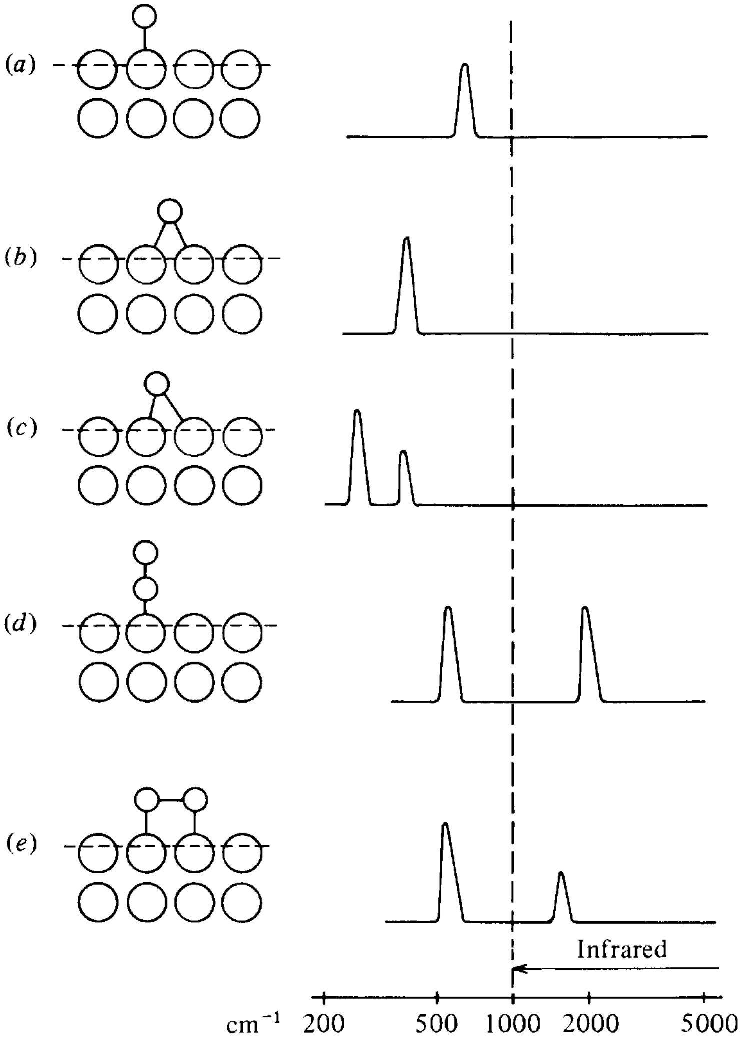


Fig. 9.11 Set of imaginary adsorption states showing the expected loss peaks associated with each structure.

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

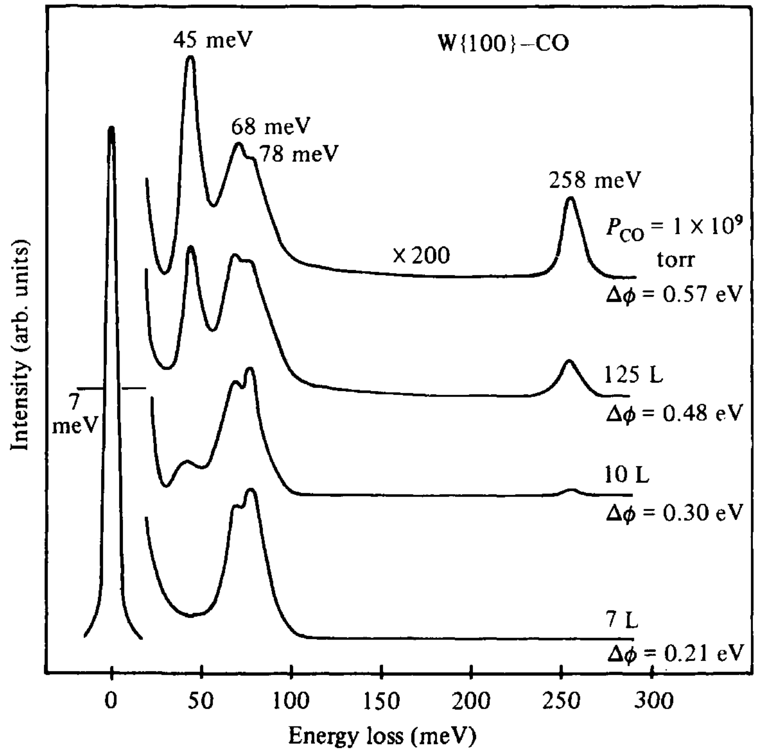


Fig. 9.13 Electron energy loss spectra of CO on W{100} at 300 K. The spectra are recorded with a primary electron beam energy of 5 eV incident at an angle of 75°; Δϕ is the measured increase in work function (Froitzheim *et al.*, 1976).

(gas exposure units 1 L = 1 Langmuir = 10^{-6} torr·s)

At low CO exposures

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

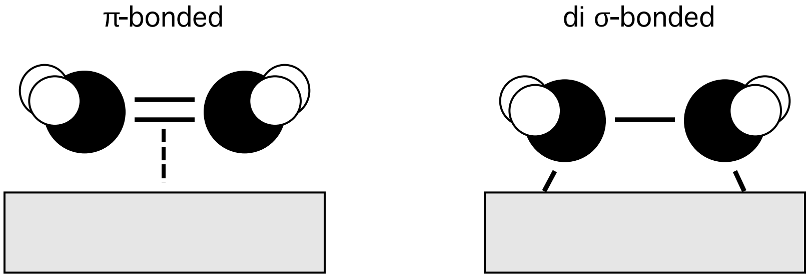
At high *p*CO

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

5.14.4 Example Application of HREELS: Ethylene adsorption on Rh(111)

Ethylene is an important starting material in many industrial catalytic processes

How does it bond to transition metal catalyst surface?



	Wavenumber (cm^{-1})	
	π-bonded	di σ-bonded
$\nu_s(CH_2)$	3075-2990	3000-2910
ν(C-C)/wag(CH_2)	1560-1500	1170-830
ν(C-M)	<400	480-400

Low temp (<150 K)-

π-bonded: Cu(100), Pd(111), Pd(100), Pd(110)

di σ-bonded: Fe(111), Fe(110), Ni(111), Ni(100), Ru(001), Pd(100), Pt(111), Pt(100)

(see N. Sheppard, Ann. Rev. Phys. Chem. 39 (1988) 589-644)

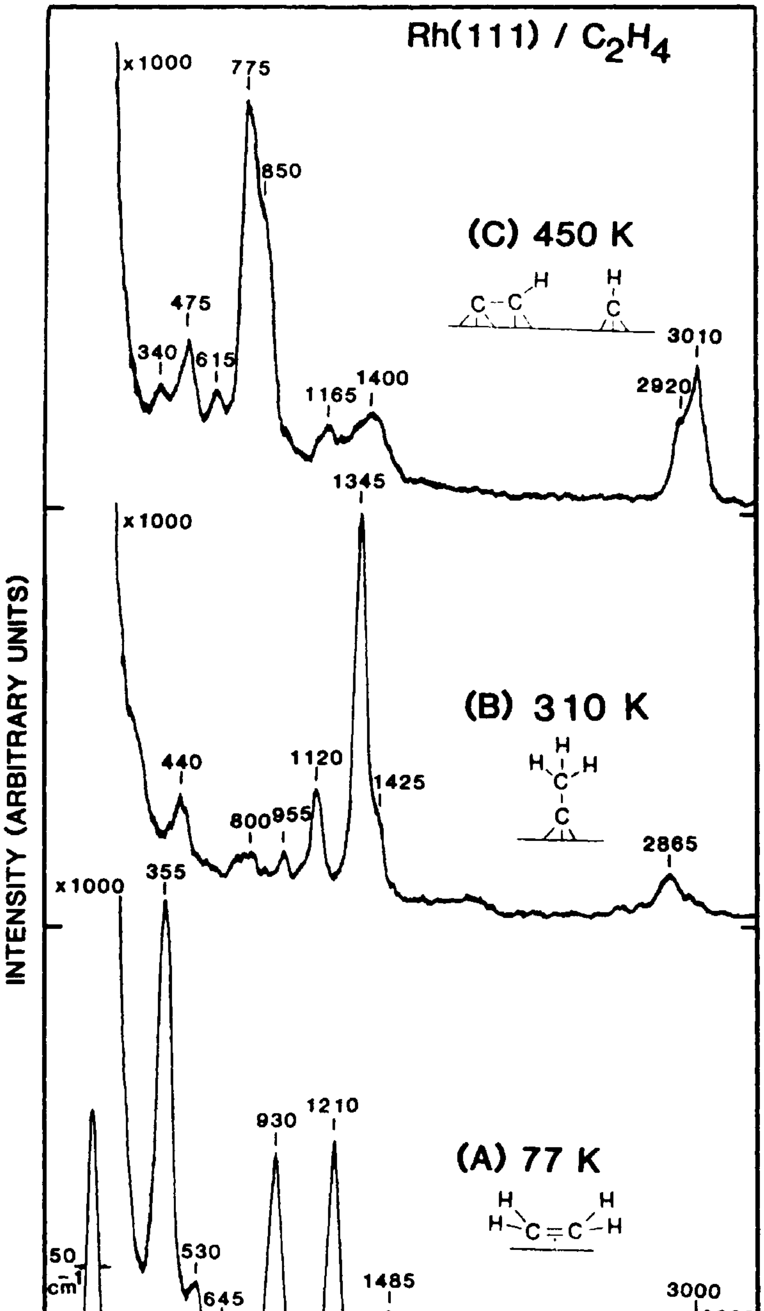


Figure 2.25. Vibrational spectra from chemisorbed ethylene on Rh(111) at different temperatures obtained by HREELS. Note the sequential dehydrogenation process.

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

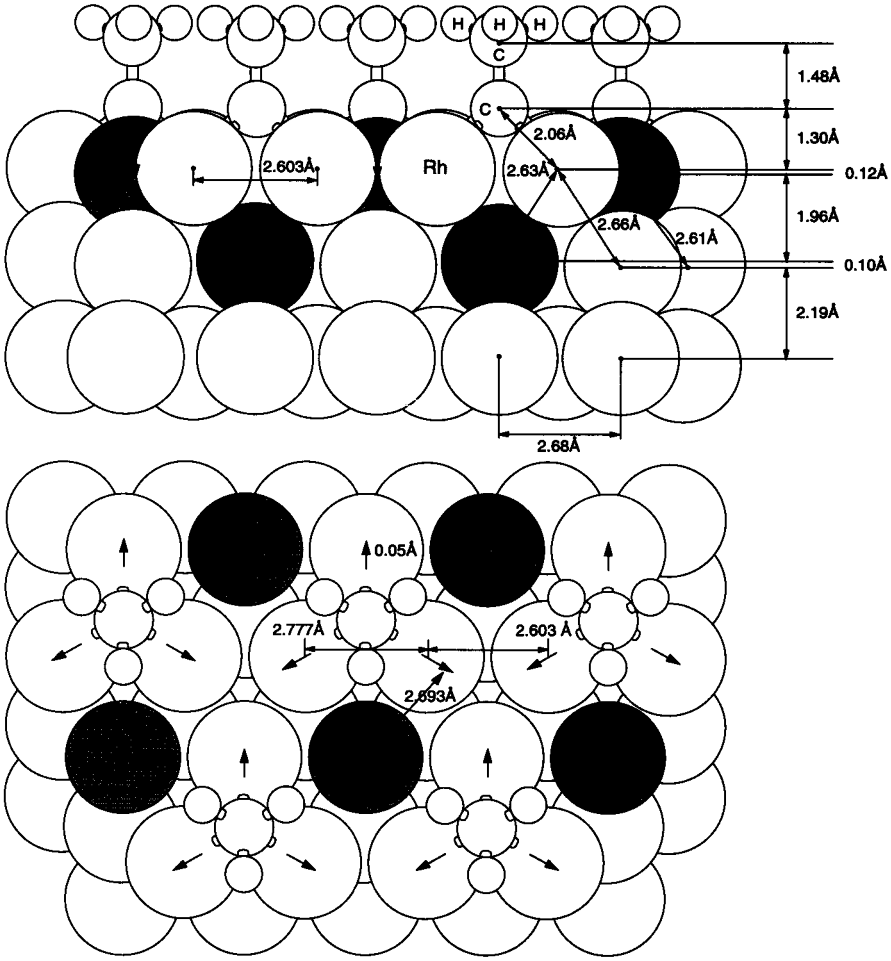
At 320 K-

- (i) v(C-C) (1120 cm^{-1}) more like C-C than C=C
- (ii) appearance of CH_3-type stretches
- (iii) 1/4 of total hydrogen desorbed between 100 and 300 K

Internal rearrangement to produce C_2H_3 - ethylidyne

At higher temperatures, sequential dehydrogenation → H-terminated C polymers → graphite

Also observe adsorbate-induced reconstruction:



Rh (111) - (2x2) - C_2H_3

Figure 2.27. Ethylidyne-chemisorption-induced restructuring of the Rh(111) crystal face. Note the expansion of metal atoms around the adsorption site.

Before HREELS (and LEED) analysis, ethylidyne structure never proposed

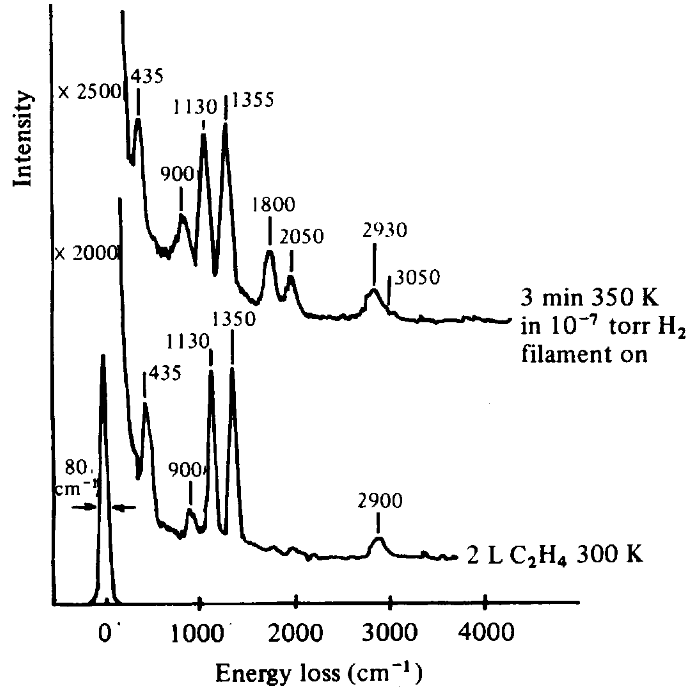


Fig. 9.14 Electron energy loss spectra of acetylene on Pt{111} at 140 K and 2 L exposure following temperature cycling in vacuum and in a H atmosphere. Acetylene plus H and ethylene produce essentially the same room temperature spectrum (Ibach & Lehwald, 1978).

Acetylene + H_2 or ethylene adsorption at room temperature produce ethylidyne on many transition metal surfaces

5.15 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