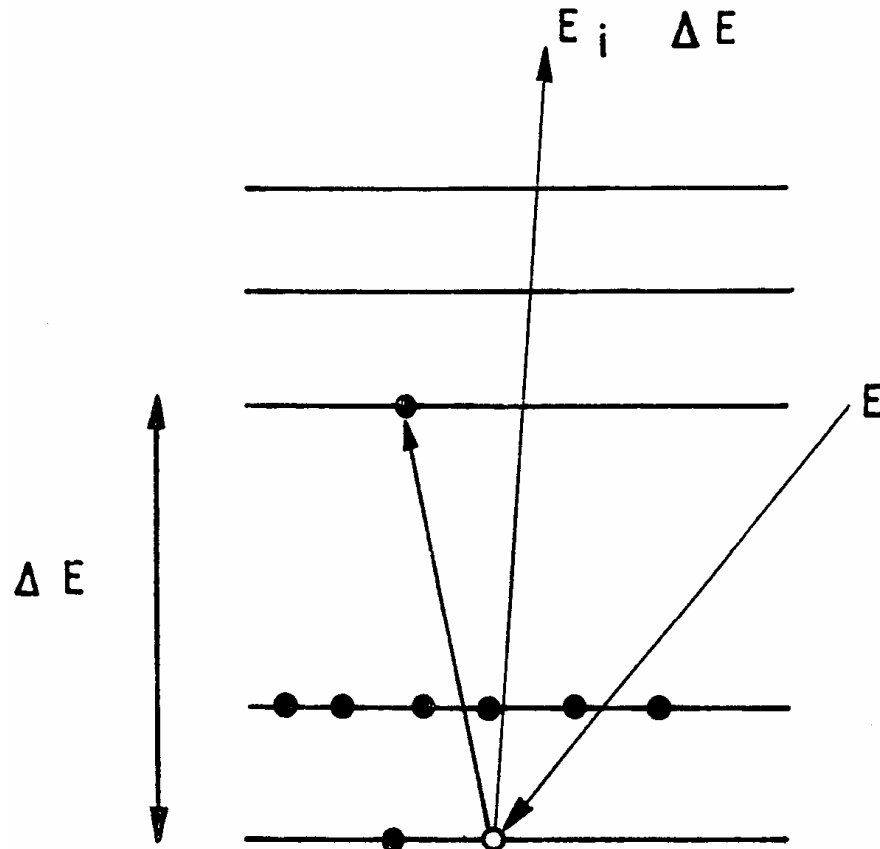


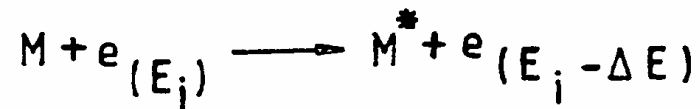
# Lecture 10

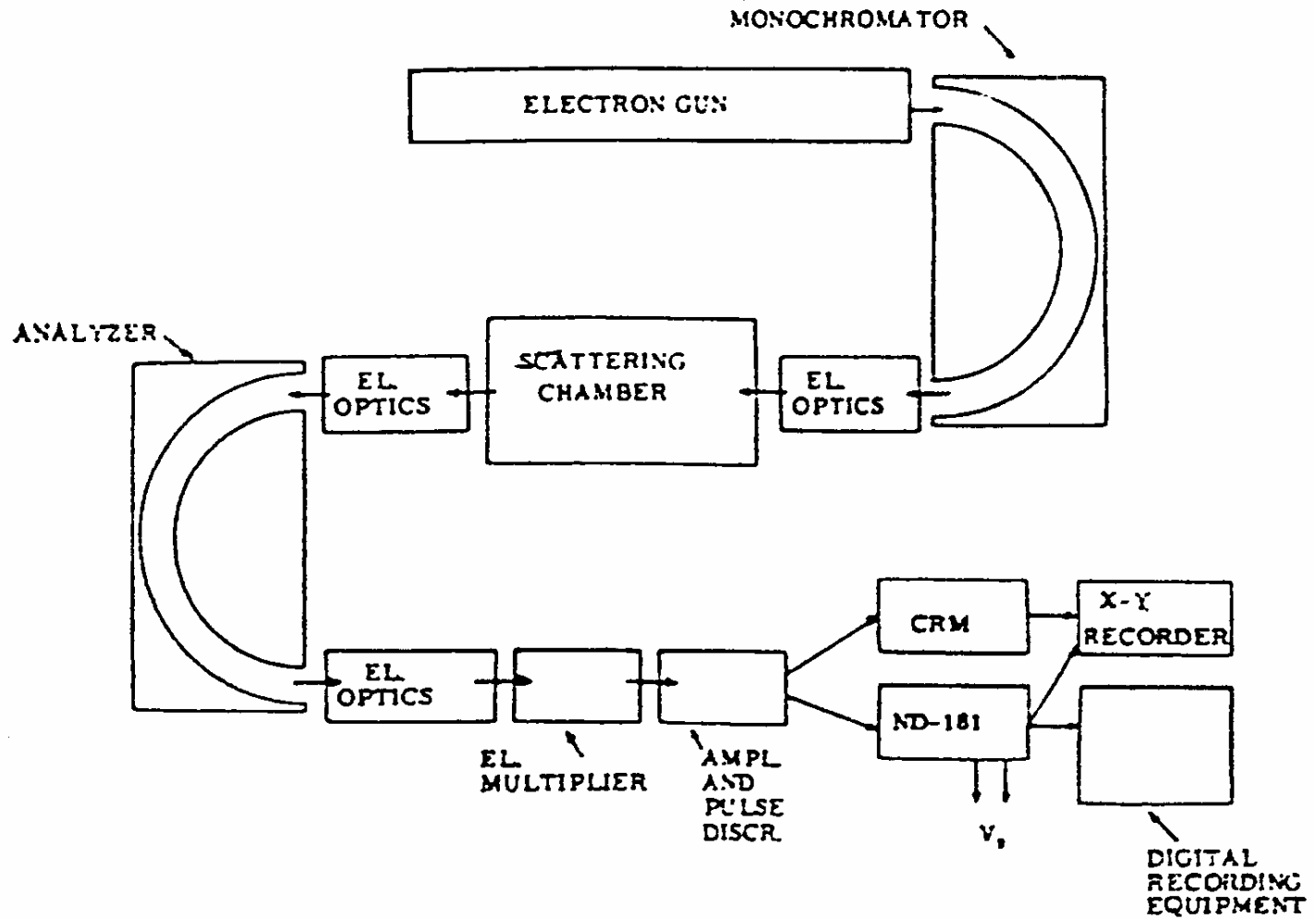
## A case study of surface reaction

# EELS



Electron Energy Loss Spectroscopy  
Electron Impact Spectroscopy  
Inelastic Electron Scattering





Schematic diagram of the electron-impact spectrometer.

# Electron Energy Loss Spectroscopy EELS

## I. EELS of molecules

Valence transitions

core transitions

EELS

$E_{\text{ex}} < 100\text{eV}$

Resolution

$\sim 30\text{ meV}$

ISEELS Res  $\approx 100\text{ meV}$

$E_{\text{ex}} \approx \text{keV}$

## II. High resolution EELS or HREELS

For Surfaces

$E_{\text{ex}} \sim \text{eV}$

Res  $\sim 3\text{-}10\text{ meV}$

Best  $\sim 1.8\text{ meV} = 14.5\text{cm}^{-1}$

# EELS of molecules

Complementary to optical spectroscopy with several advantages over optical methods.

Light/molecule interaction is electromagnetic.

Electron/molecule is also electromagnetic.

Major component in this is coulombic

Electron/molecule collisions occur at large distances and electrons suffer only small deviations from their original path

Angular distribution will be forward peaked.

These transitions are similar to optical ones.

Differences occur when the impact energy is comparable to excitation energy.

## 1. Electron exchange

singlet  $\rightarrow$  triplet

great cross section enhancement

isotropic scattering

## 2. Polarization

symmetry forbidden

complex angular distribution

How to determine such transitions?

1. Angular dependence

2. Impact energy dependence

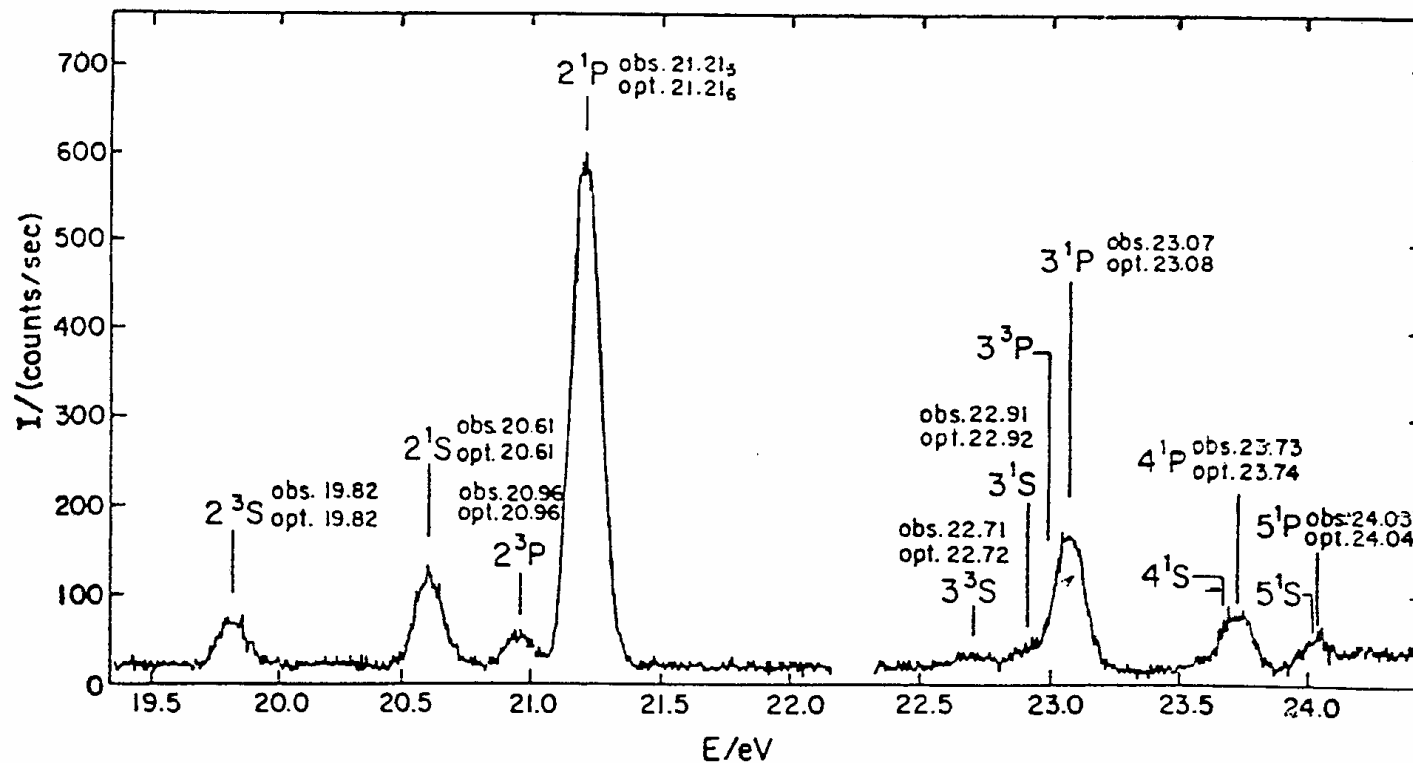
Other low energy electron impact spectroscopy

Threshold excitation spectroscopy

Neutral and negative ion states

Resonances in the integral cross sections

Due to  $-ve$  ion formation



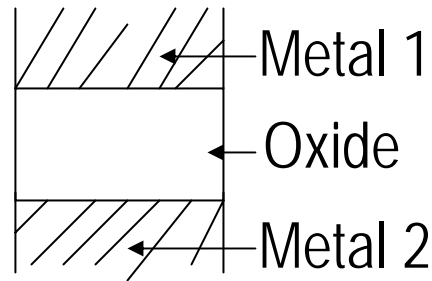
Electron energy-loss spectrum of helium; 35-eV incident electron energy;  $25^\circ$  scattering angle; torr pressure gauge reading;  $4 \times 10^{-9}$  A incident beam current; 0.15-eV resolution (FWHM of the elastic multichannel scaler mode-single sweep-with a voltage step of 5 mV/channel and a scan rate of 2 sec/channel).

High resolution electron energy  
loss spectroscopy, HREELS



# Other methods to study surface vibrations

## 1. Inelastic electron tunneling



For  $eV_0 > \hbar \omega_0$

When voltage is varied, a new tunneling channel opens up.

The junction conductance  $G(V_0) = dI/dV_0$  jumps discontinuously.

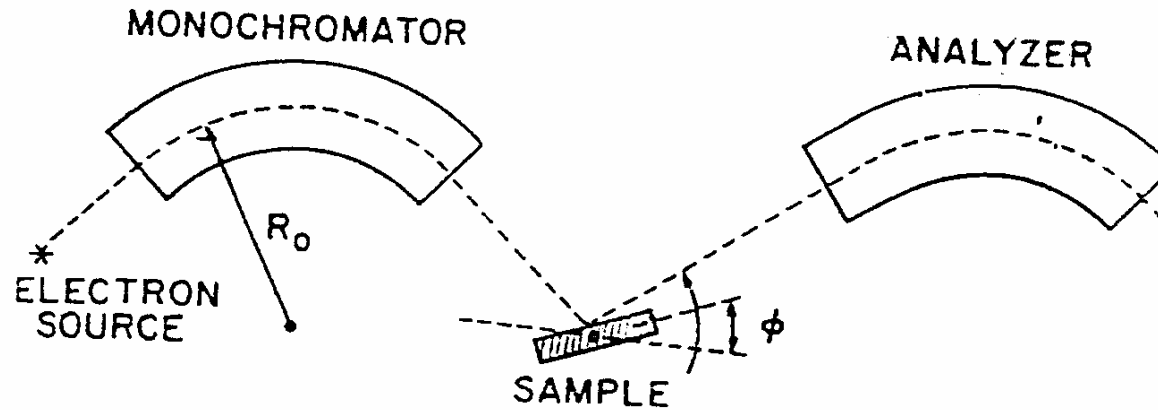
An important problem is thermal smearing of the Fermi Surface of the solid. This limits studies only at low temperatures.

## 2. Raman scattering

## 3. IR reflectivity of metal surfaces

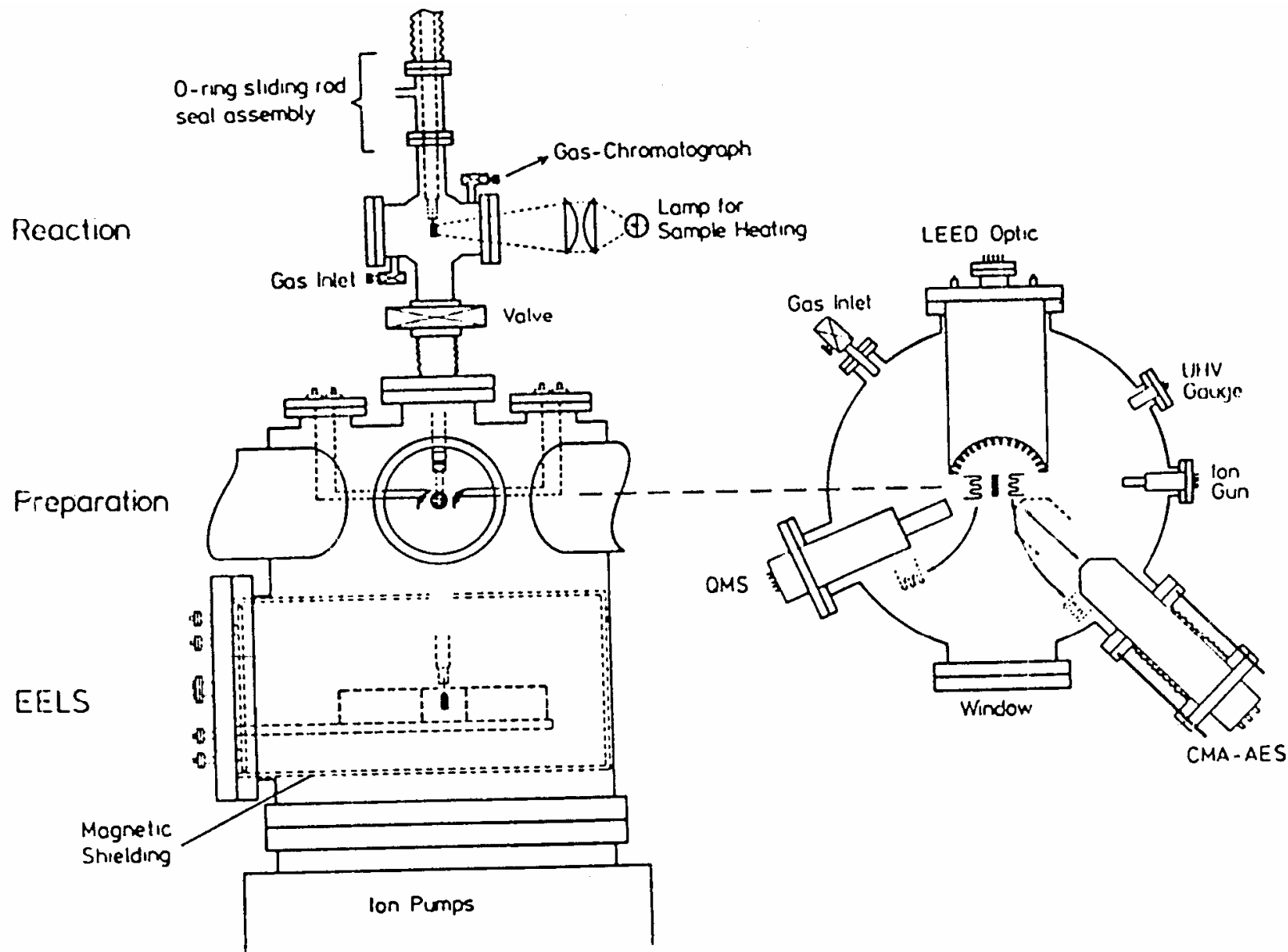
## 4. Low energy atom beam scattering

# Basic instrument



**Fig. 1.1** Schematic diagram of an electron energy loss experiment. Electrons from a cathode pass through a monochromator, strike the sample, and the energy spectrum of the scattered electrons is probed by a second monochromator.

The technique is only for solid surfaces.



The spectrometer has many other facilities, normally.

It helps to study  
adsorbate orientation

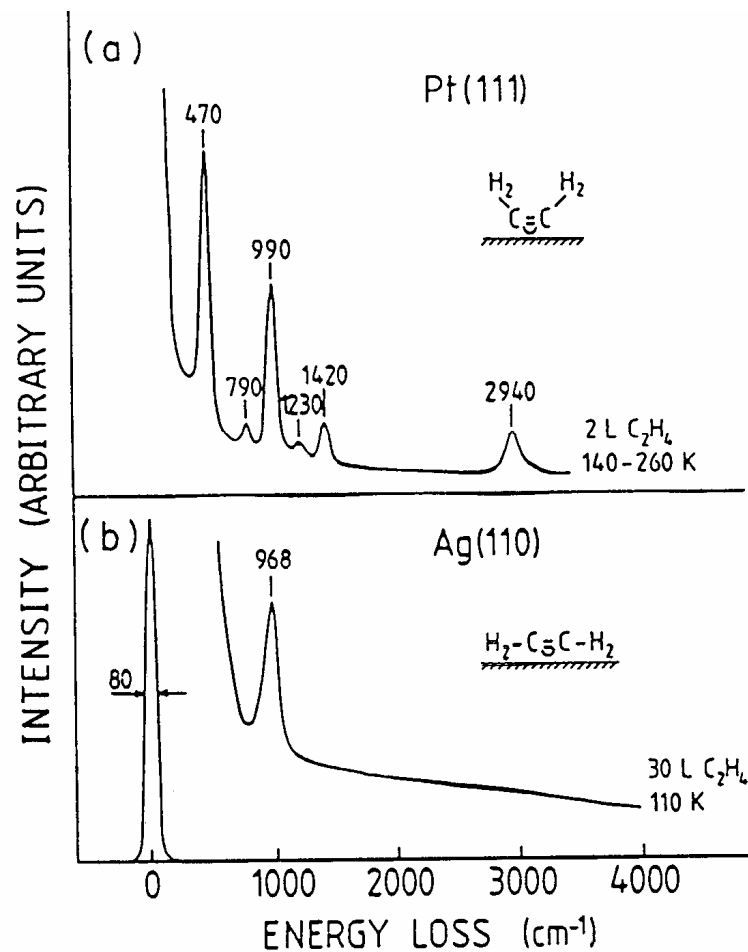


Fig. 4.9 Electron energy loss spectrum in specular reflection for ethylene on (a) Pt(111) and (b) Ag(110) (from Ibach and Lehwald [28], and Backx, de Groot, and Biloen [13], used with permission). For ethylene on silver, the surface hardly breaks the symmetry of the molecule. Therefore only the  $B_{1u}$  CH wagging mode with its dipole moment perpendicular to the plane of the molecule becomes observable as a dipole loss. The orientation of the molecule follows automatically from these considerations since the strongly IR-active  $B_{2u}$  and  $B_{3u}$  modes (see also frequency tables, Appendix B) which have their dipole moment oriented within the plane of the molecule, are not observed for the adsorbed molecule. On the platinum surface ethylene is strongly bonded. This is indicated by the CH stretching vibration which is typical for an  $sp^3$  complex. Strong bonding to the surface breaks the symmetry and new modes become dipole active.

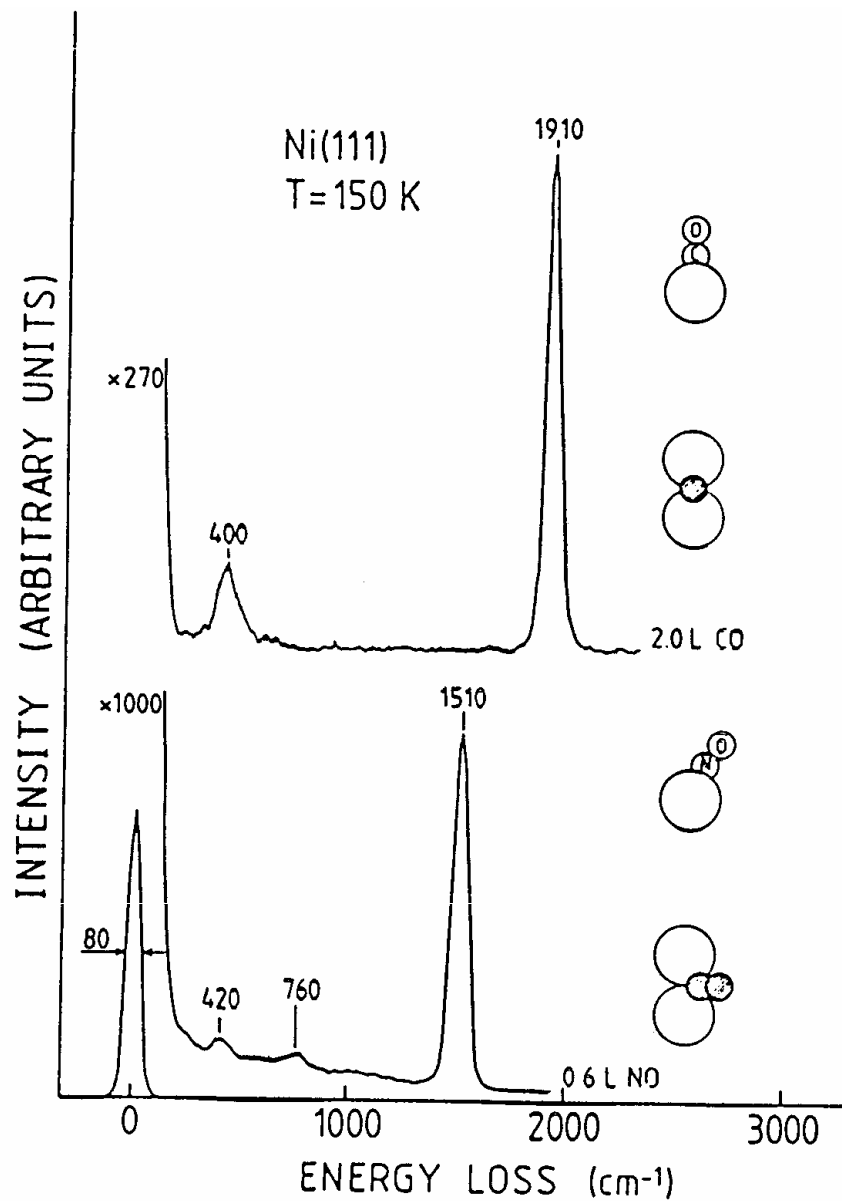


Fig. 4.11 Spectra of CO and NO on a Ni(111) surface at  $T = 150$  K (from Erley, Wagner, and Ibach [15], and Lehwald, Yates, and Ibach [16], used with permission). The two losses for CO correspond to the CO stretching and the Ni-C stretching vibration. The canted orientation of NO makes the Ni-N-O bending mode dipole active as well.

TABLE 5.1

Vibrational Frequencies of Atoms Perpendicular to the Surface for Different Ligancies and (Fundamental) Frequencies of Equivalent Diatomic Molecules<sup>a</sup>

System	Ligancy			Diatomic molecule	Ref.	Comment
	4	3	2			
O-W	610		740	1047	5	
O-Ni	430/310	580/450		~615	6-8	Two binding states
O-Pt		490		841	9	
O-Fe		400	500	~870	10	Fe atoms not in contact
O-Ru		515		865	11	
O-Cu	340				12	
H-Ni	600 (590)	(1210)	(1370)	~1926	13, 19	Values in parentheses are calculated [19]
H-Pt		550		~2200	14	Only $\omega_e$ known for PtH
C-Ni	390	520			15	
S-Ni	360				16	

<sup>a</sup> Cf. Appendix B. For oxygen on nickel, two different binding states are observed.

## Decomposition of NO

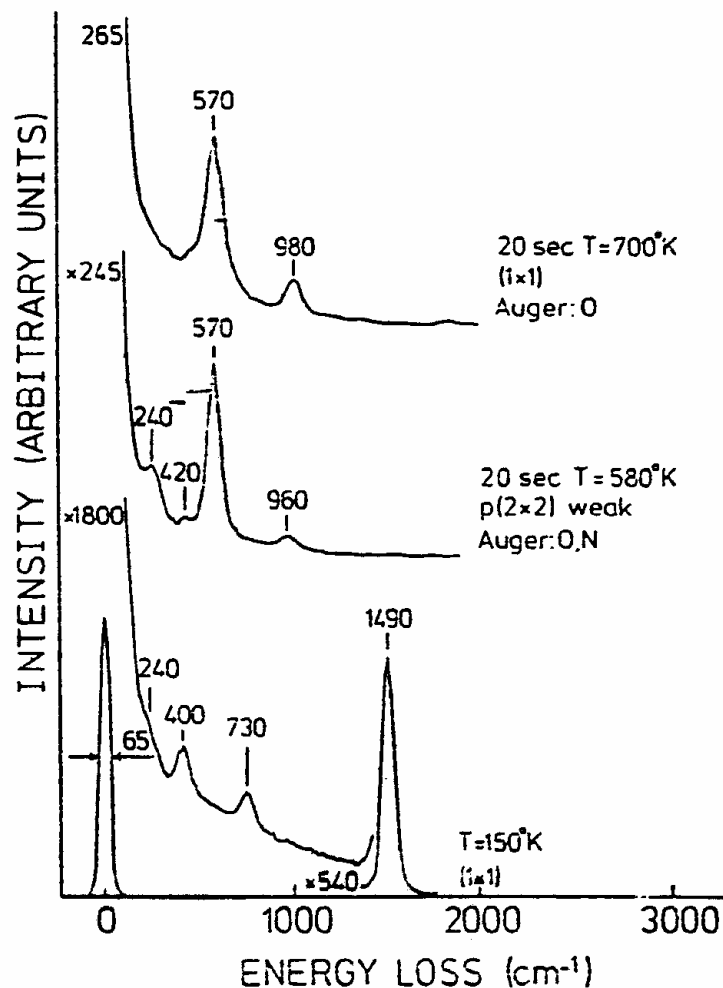
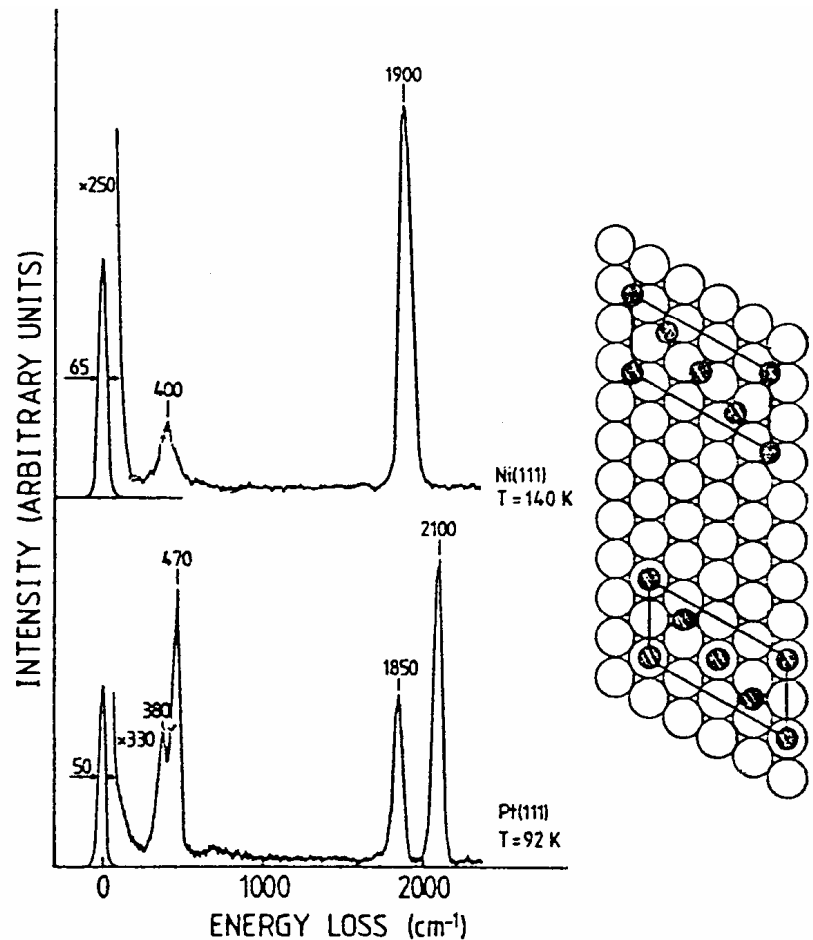


Fig. 6.5 Decomposition of NO by annealing the surface to 580 and 700°K at 0.5 langmuir. After annealing to 700°K the surface is nitrogen free since nitrogen desorbs. Again the remaining oxygen spectrum exhibits a peak at about 980 cm<sup>-1</sup>, this time with an even greater intensity than in Fig. 6.4.



**Fig. 6.7** Electron energy loss spectra of the Ni(111) and Pt(111) surfaces each covered with half a monolayer of CO which orders into a  $c(4 \times 2)$  overlayer. On the nickel surface the vibration spectrum indicates only a single CO species in a site of high symmetry. The only possibility for positioning the two-dimensional CO lattice on the surface consistent with the single type of adsorption site is to place all CO molecules into twofold bridges. By similar reasoning, half the CO molecules must occupy on-top sites on the Pt(111) surface. This example shows how powerful the *in situ* comparison of vibrational spectra and diffraction pattern can be, since a qualitative structure analysis is achieved without analyzing diffraction intensities.



## Origin of frequency shifts

1. Mechanical renormalisation  $\sim 40\text{cm}^{-1}$
2. Lateral interactions  $\sim 30\text{cm}^{-1}$
3. Bond order

This is the most important effect. Eg.  $\text{C} \equiv \text{C}$  vibration of acetylene (at about  $2000\text{ cm}^{-1}$ ) get reduced to  $1200\text{ cm}^{-1}$  on Ni.

4. Hydrogen bonding

# Empirical fits

## Force constant and bond parameters

$$f \sim 5 \cdot 10^{-4} D_e^2$$

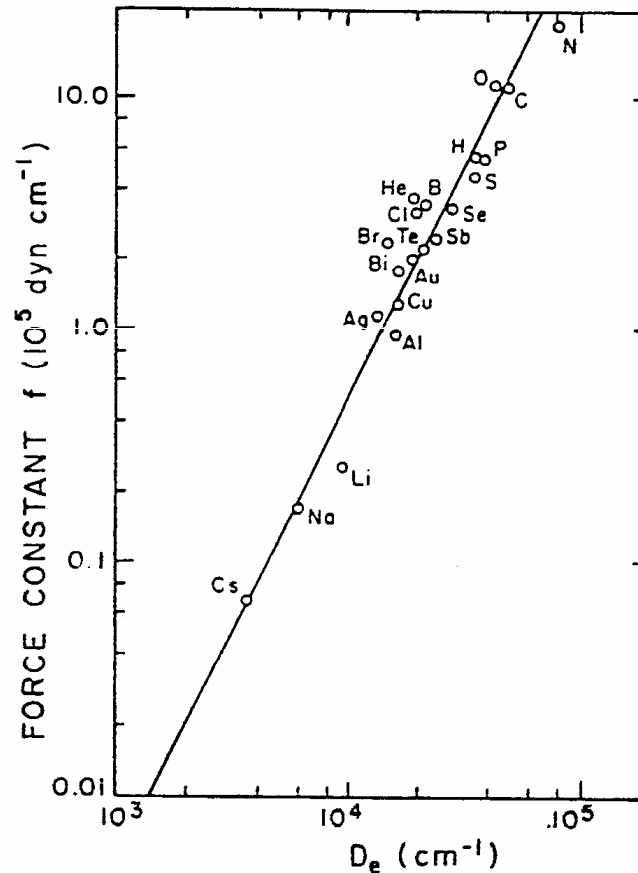


Fig. 6.15 Harmonic force constants versus depth of the potential well  $D_e$  for diatomic molecules (data from Ref. [B3] used with permission). Values for the C–C bond in hydrocarbons are also included.

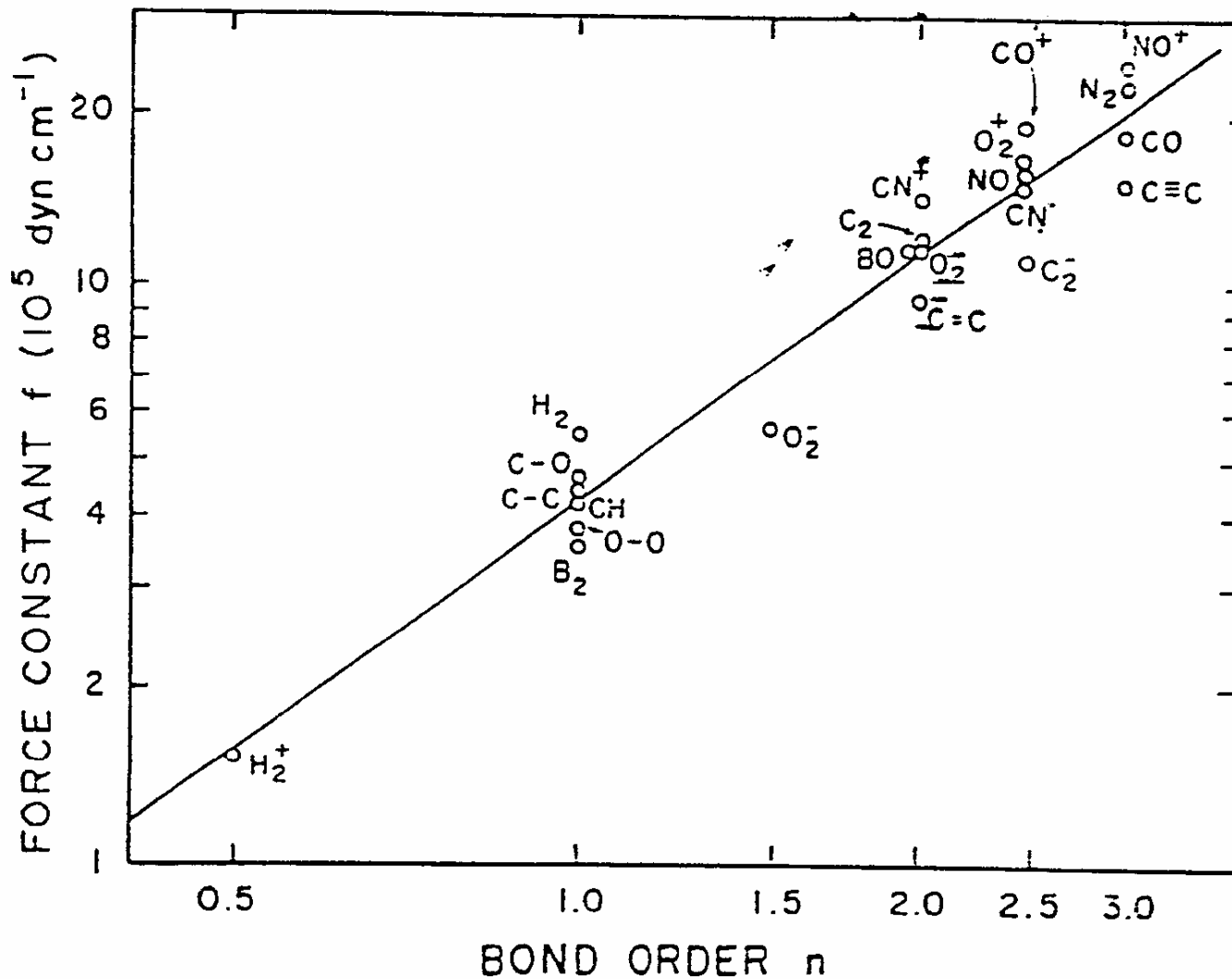
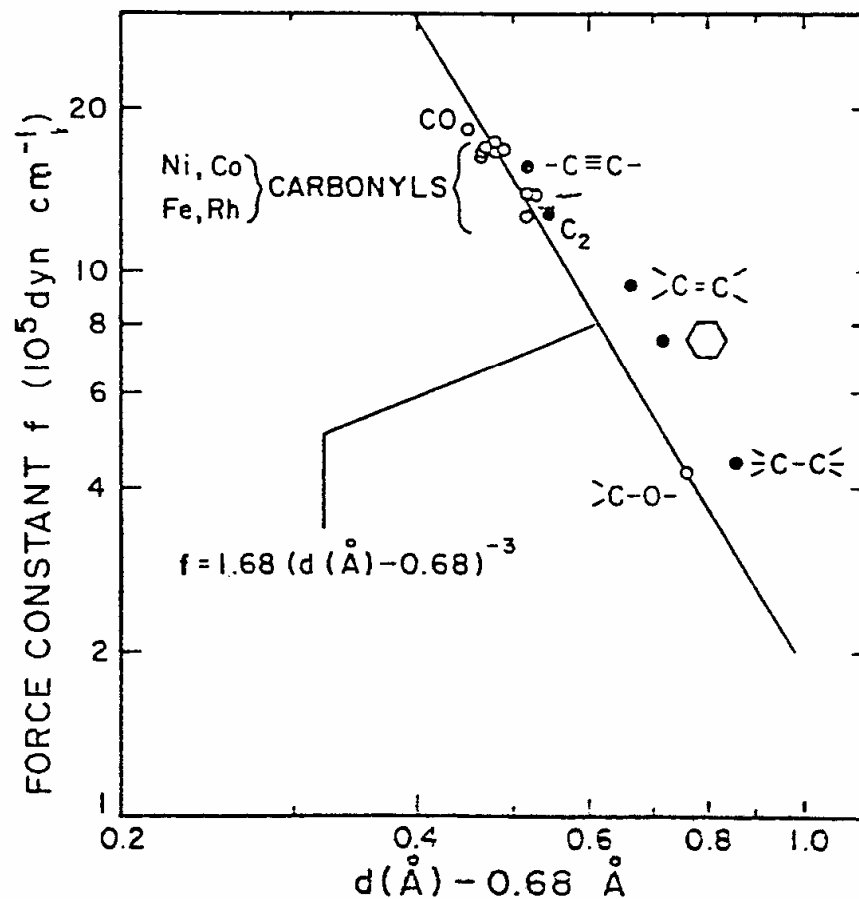


Fig. 6.17 Correlation between bond order as defined in the text and the force constant; again CC— bonds of hydrocarbons and the single bonds of  $\equiv\text{C}-\text{O}-$  and  $\text{HO}-\text{OH}$  are included.

$$f = 4.2 \times 10^5 n^{1.45} \text{ (dyne/cm)}$$



**Fig. 6.18** Force constants of CO— and CC— groups versus bond distance. For the CC— groups data are from Ref. [57] with permission. The carbonyl data are from Ref. [62] with permission. There the force constants have been calculated disregarding the coupling to the metal ligand.

$$f = 1.86 (r_e - d_{ij})^{-3} \quad d_{ij} = 0.68 \text{ \AA}$$

# Dissociation reactions

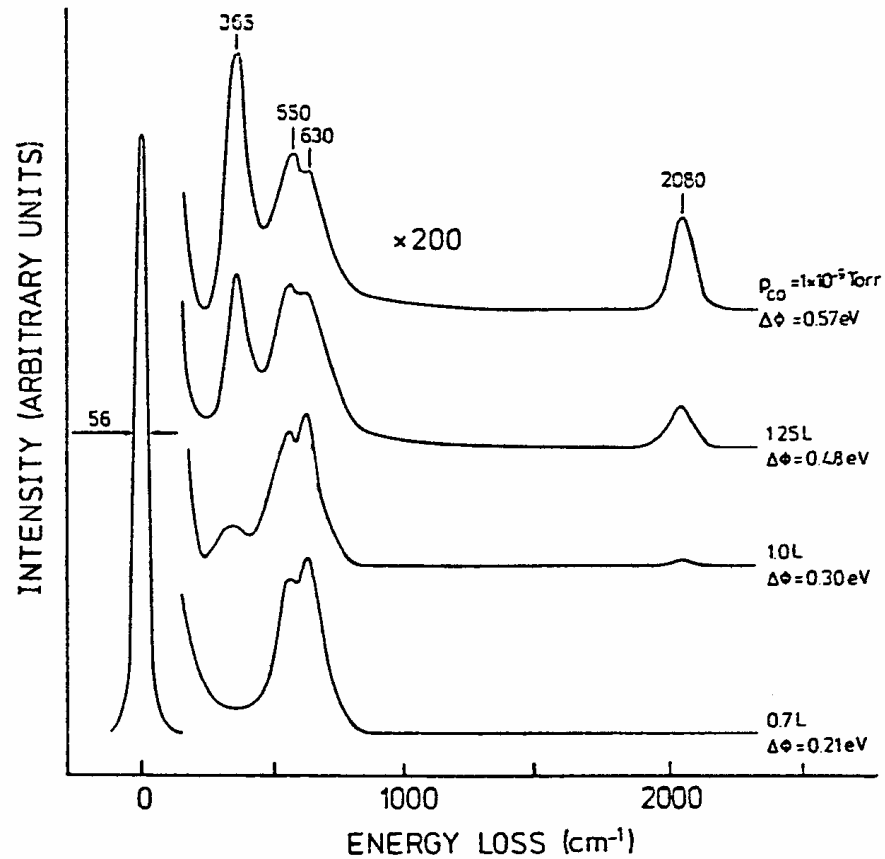


Fig. 6.23 Spectra of W(100) after CO exposure at  $\sim 300^\circ\text{K}$ . At low coverage no molecular CO is observed. The two energy losses at 550 and 630  $\text{cm}^{-1}$  are identified as due to vibrations of carbon and oxygen by decomposing  $\text{C}_2\text{H}_2$  on the surface and exposure to oxygen, respectively [38] (used with permission). With higher exposure molecular CO is also adsorbed. Saturation coverage is not reached at room temperature without an ambient pressure of CO.

# A complex reaction at the surface

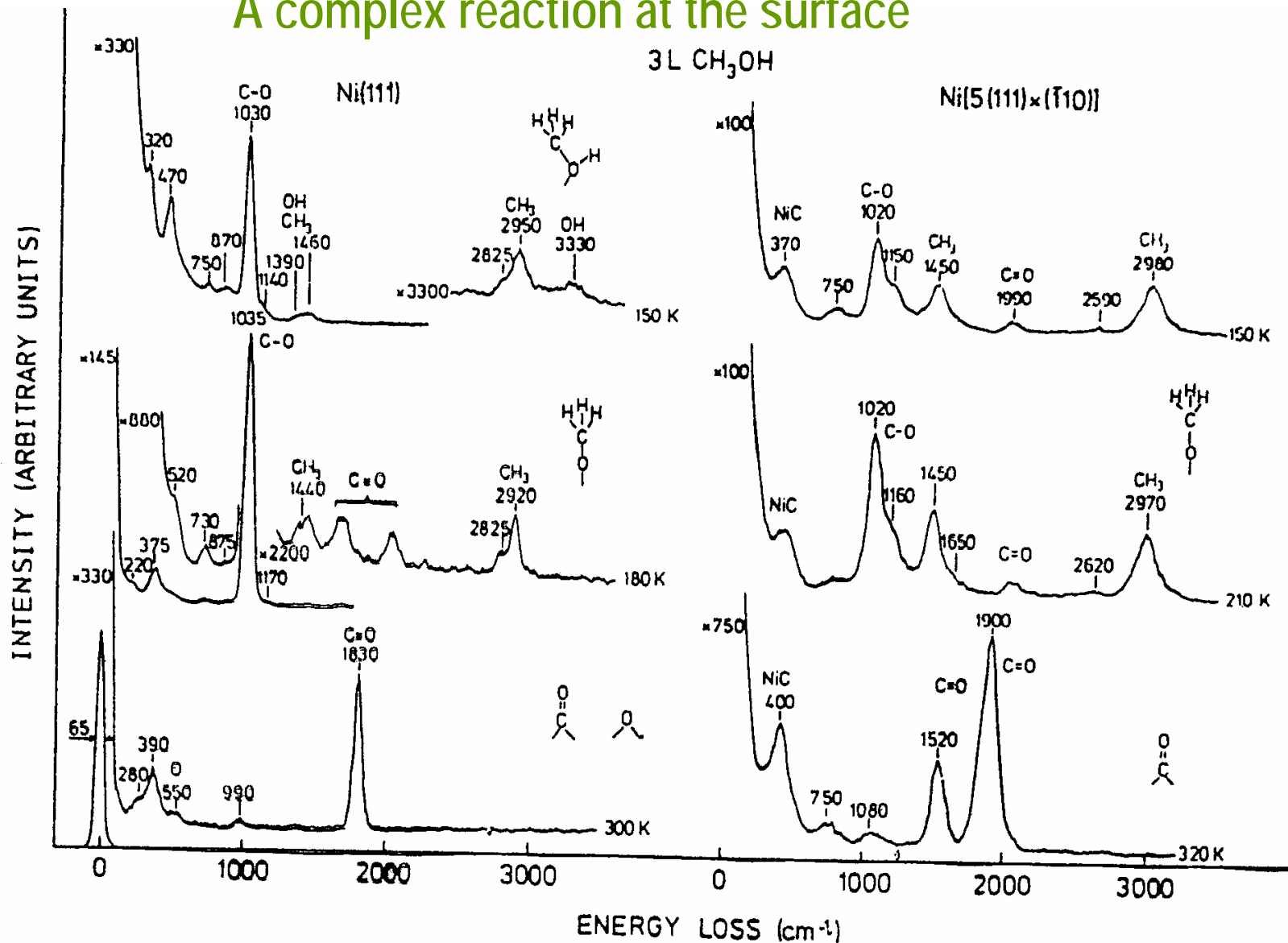
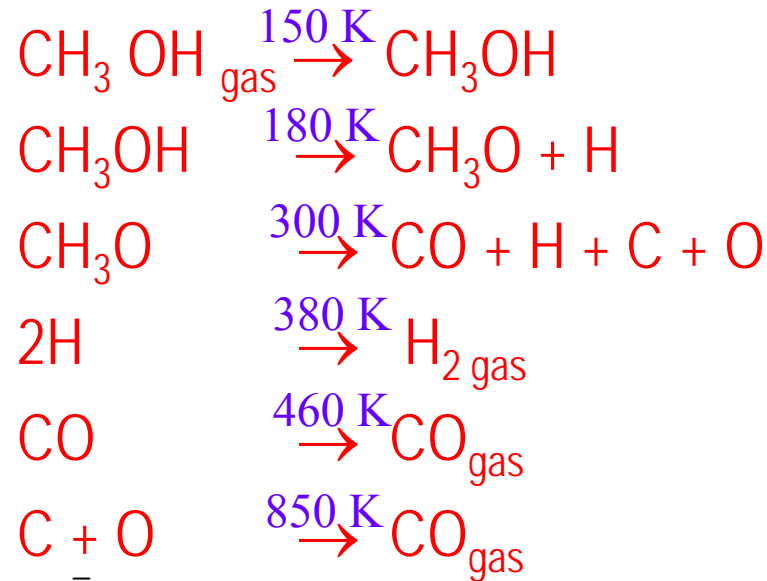


Fig. 6.27 The decomposition of methanol on Ni(111) and a stepped nickel surface with (111) terraces via an intermediate methoxy group. Earlier spectra of methanol on Ni(111) ([87], used with permission) were not completely free of water which is quite noticeable even when the fractional coverage is only 1%.

## Surface species

### Ni(111)



### Ni(5(111) x 110)

