

5. HIGH RESOLUTION ELECTRON ENERGY LOSS SPECTROSCOPY (HREELS)

5.1. BASIC PRINCIPLES

The solid materials are transparent under high electron energy (100 keV) exposure.

The electrons are **loosing energy** and changing **directions**.

$$\text{meV} = 8.066 \text{ cm}^{-1}$$

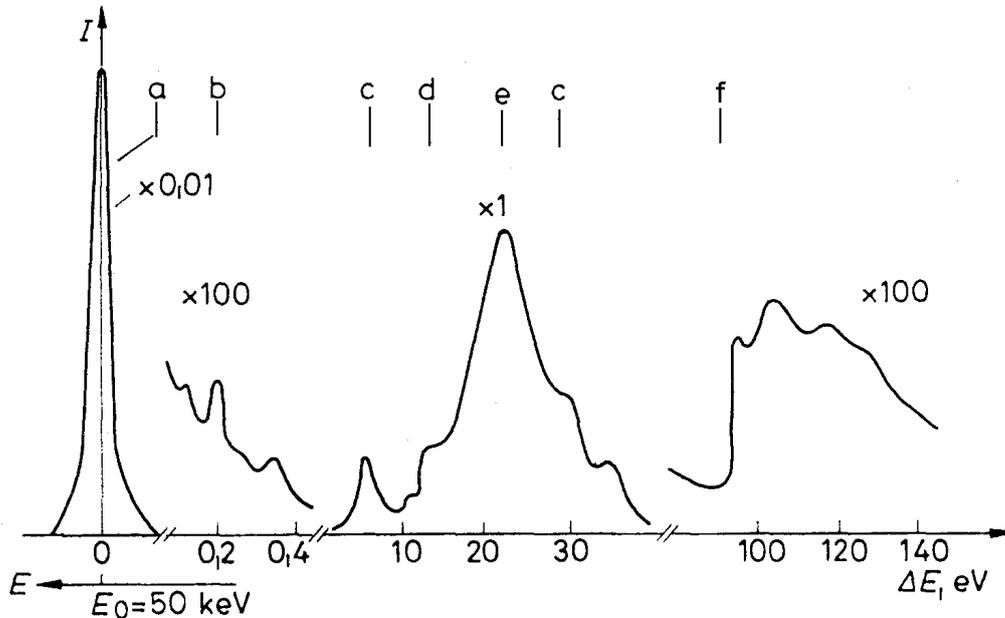
Ruthermann (1941)

Electron beam passing through Al-foil, the loss of energy 15 eV.

This loss is not dependent from original electron energy.

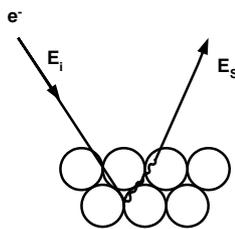
HIGH RESOLUTION ELECTRON ENERGY LOSS SPECTROSCOPY (HREELS)

PRINCIPLE:



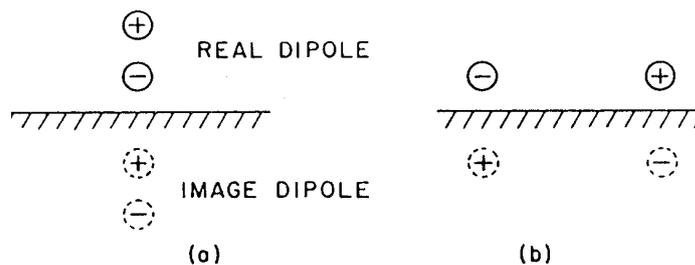
Electron energy loss spectral ranges

- a) Elastic scattering; b) Phonon excitations; c) Electron transitions; d) and e) Surface and bulk plasmons; f) Inner shell ionization

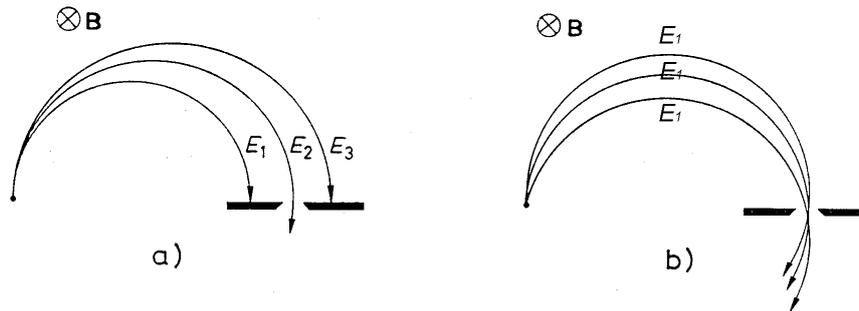


$$E_s = E_i - \underbrace{h \nu_i}_{\text{vibrational energy}}$$

Surface selection rule



Homogeneous magnetic fields perpendicular to picture

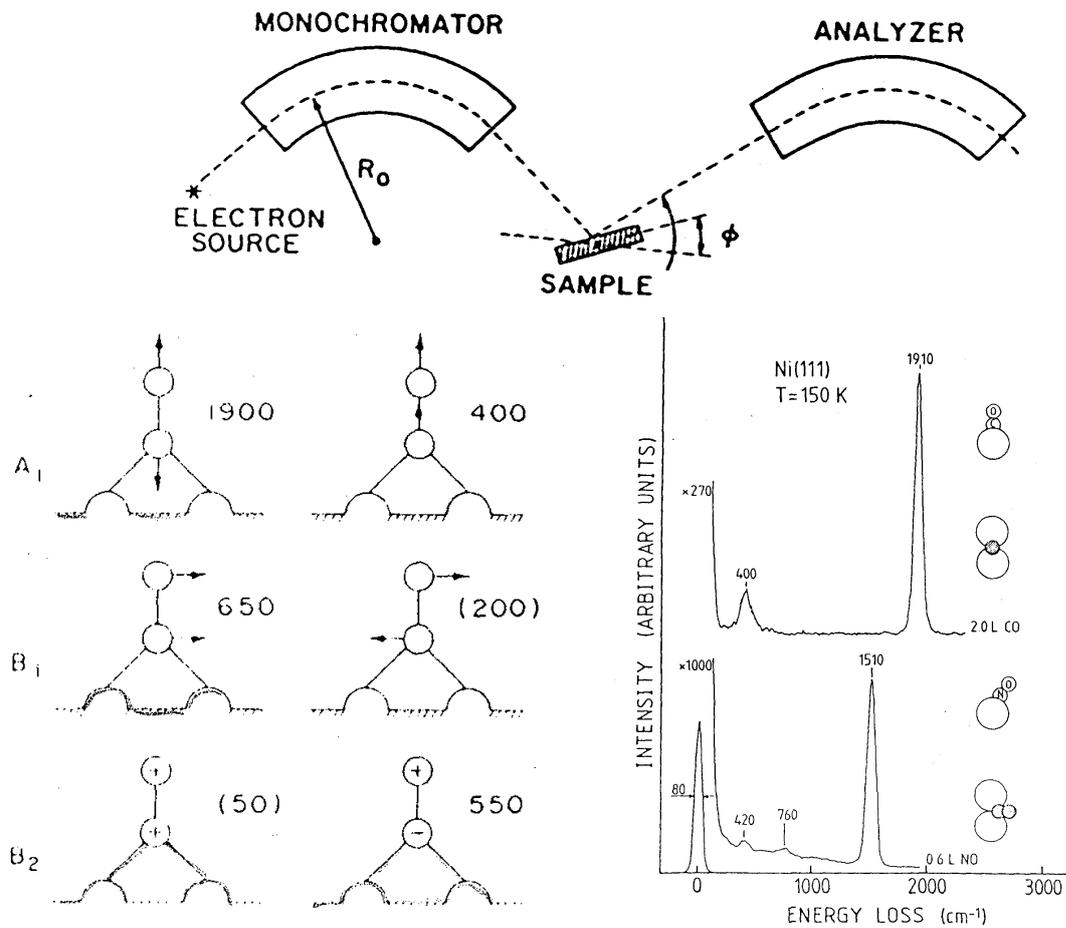


Monochromatization

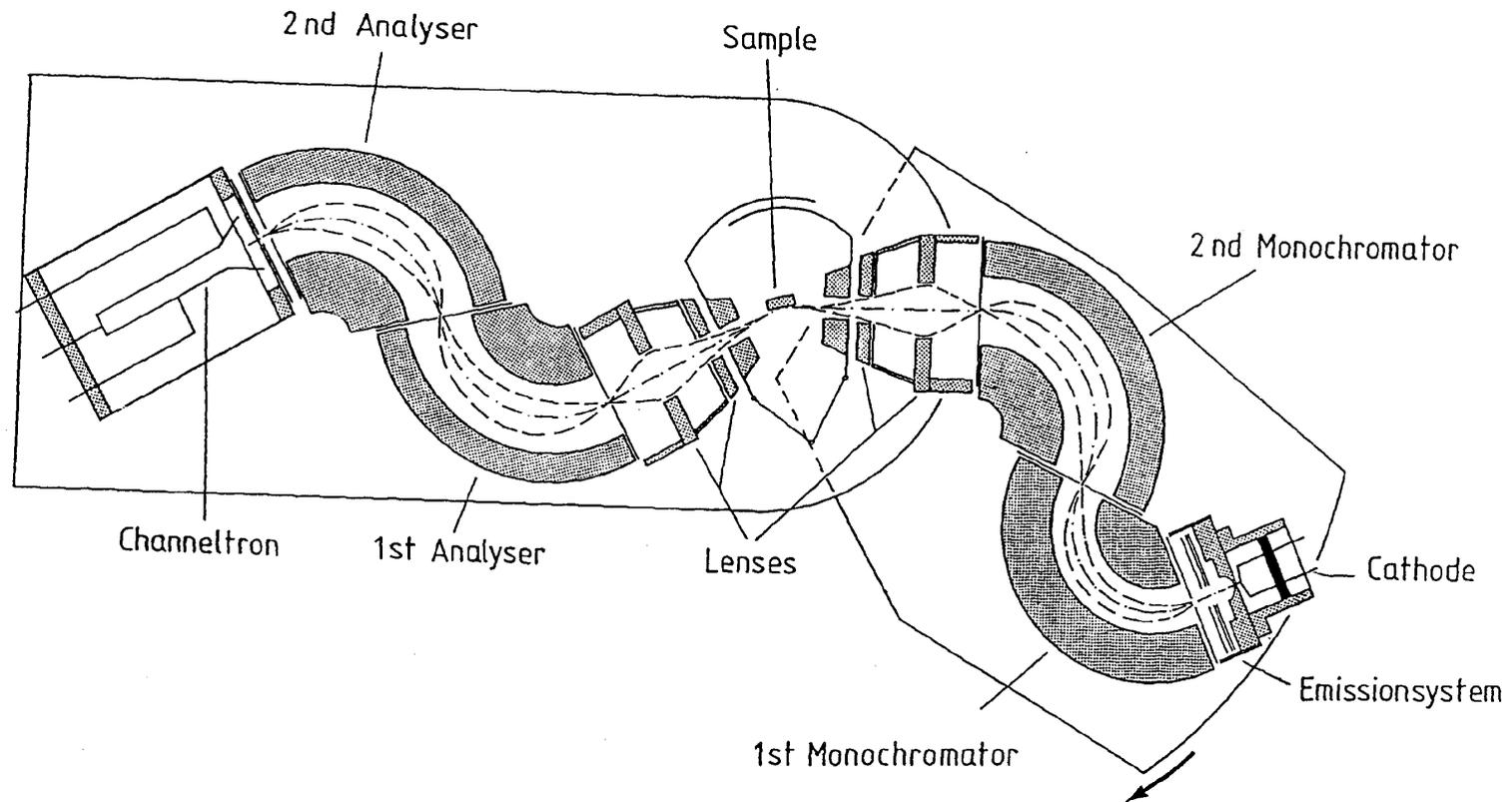
Focusing

Electron's trajectory in homogeneous magnetic field

- a) $E_1 < E_2 < E_3$ different electron energy;
- b) same energy but different directions



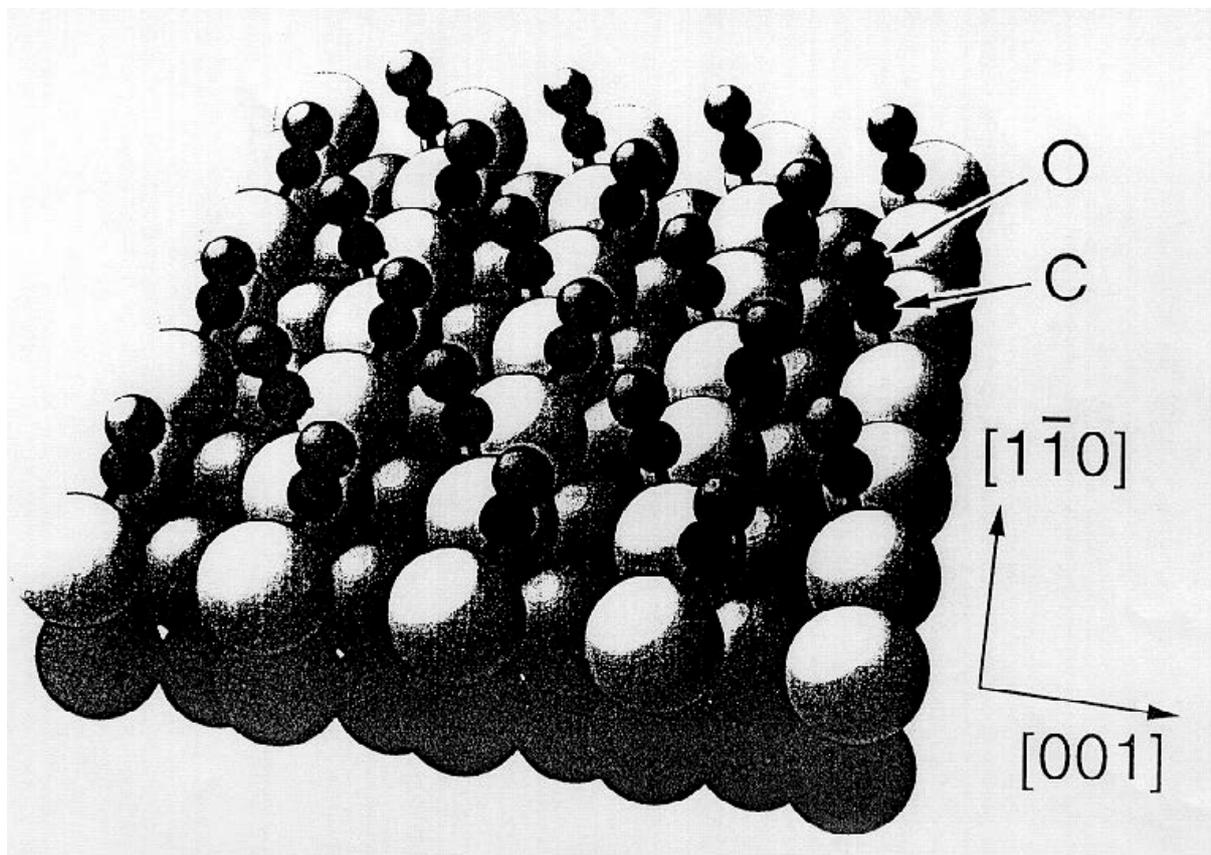
H. Ibach (Jülich)



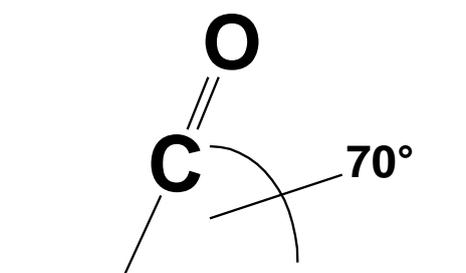
Electron Energy Loss (EELS) Spectrometer

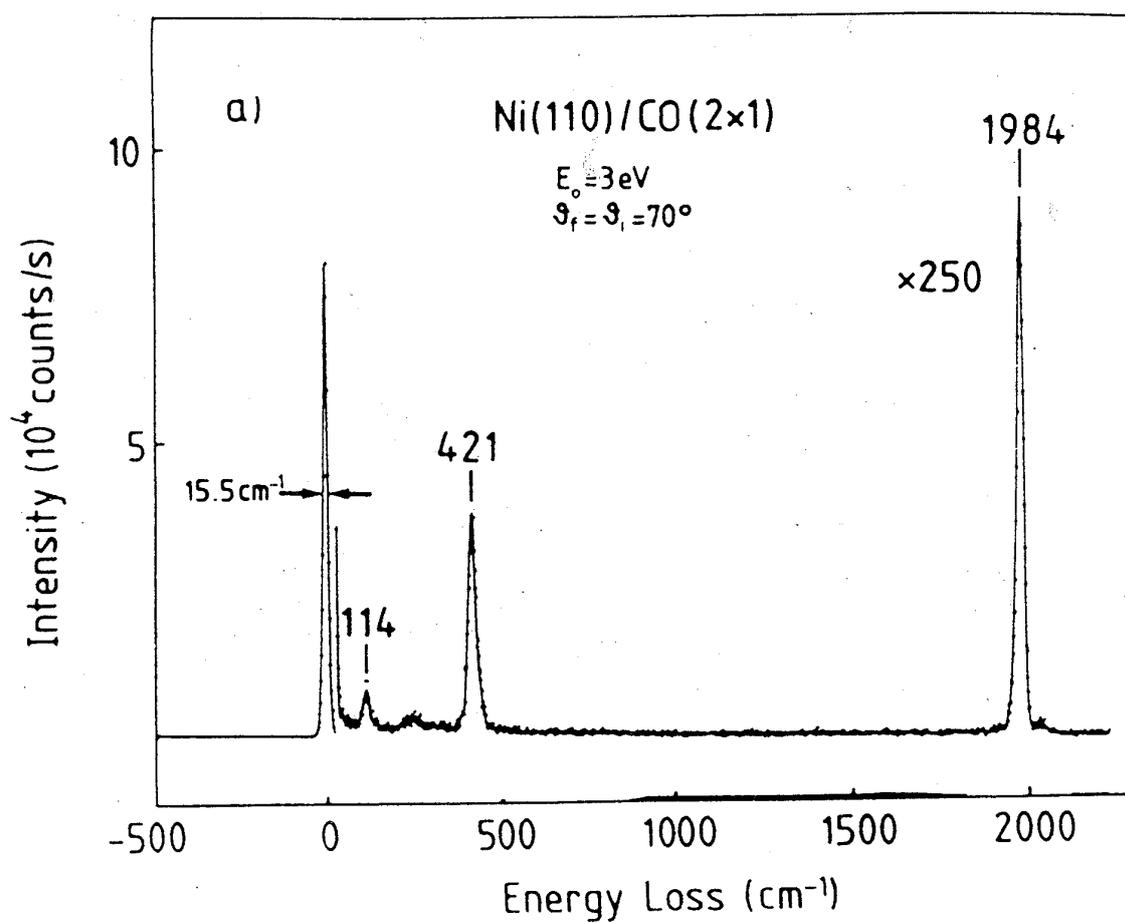
5.2. Examples and spectral interpretations

Ni{110}p(2x1)-2CO adsorbate system



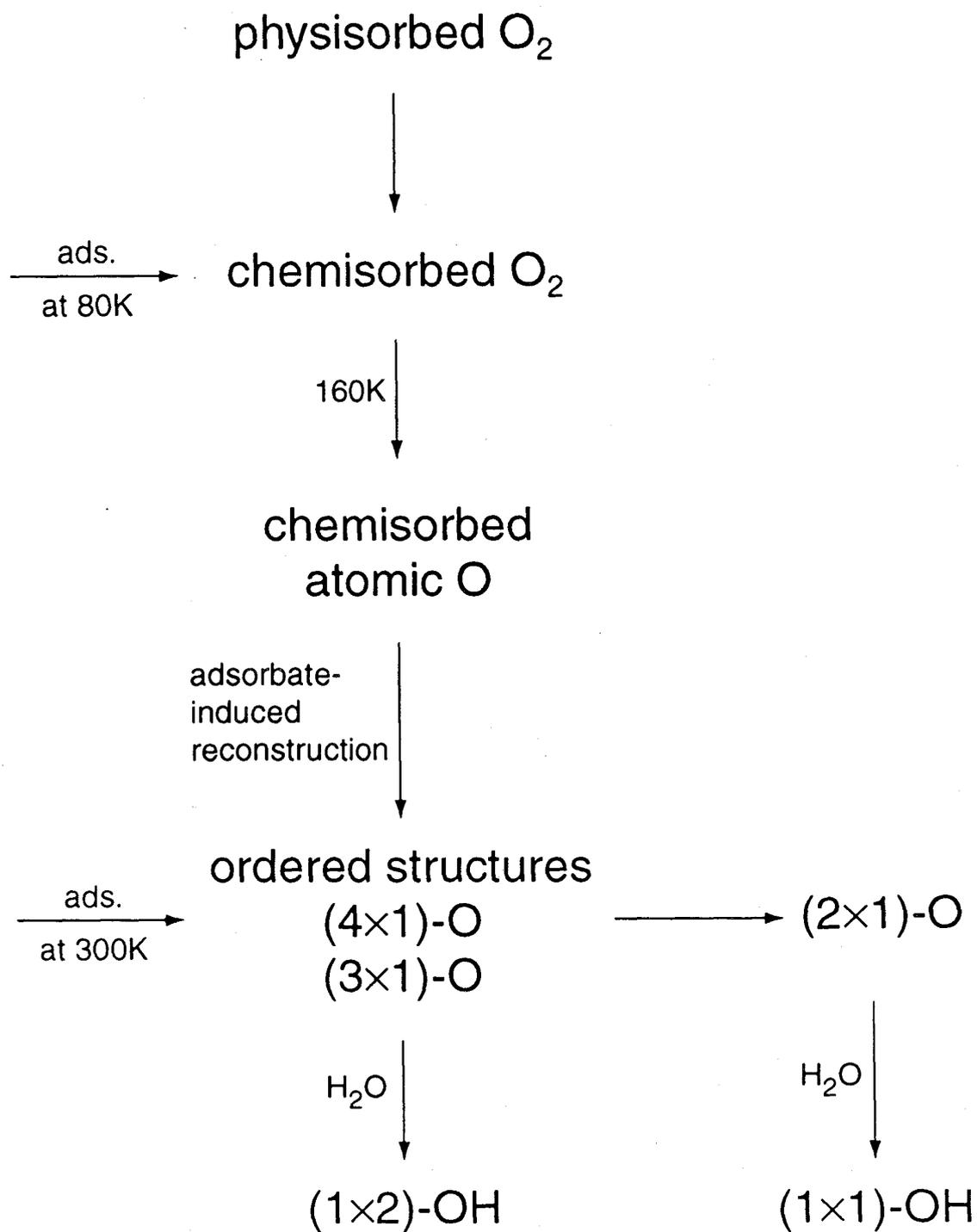
Bridged CO molecules in tilted directions
($\theta \approx 70^\circ$)

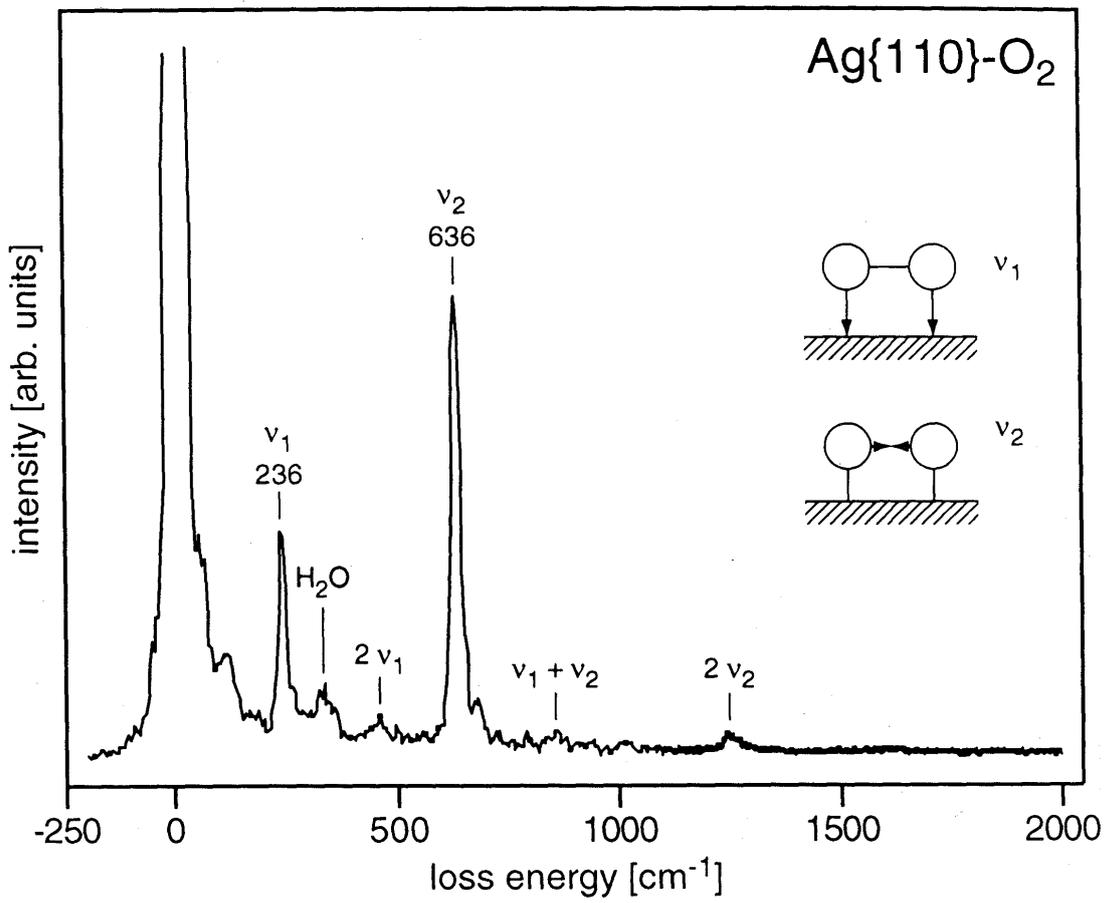




CO chemisorbed on Ni{110} surface

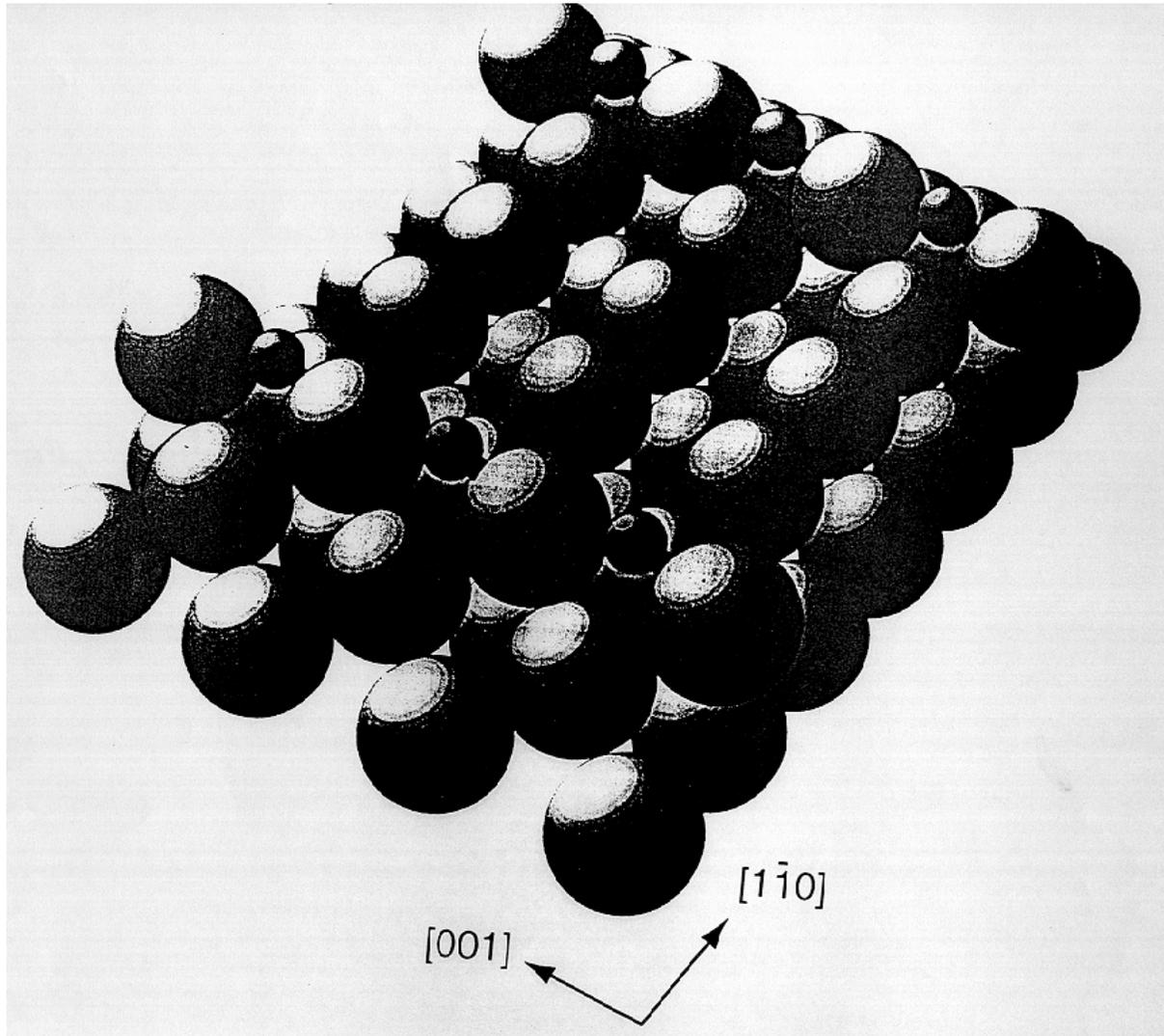
Oxygen adsorption and hydroxyl formation on Ag {110}



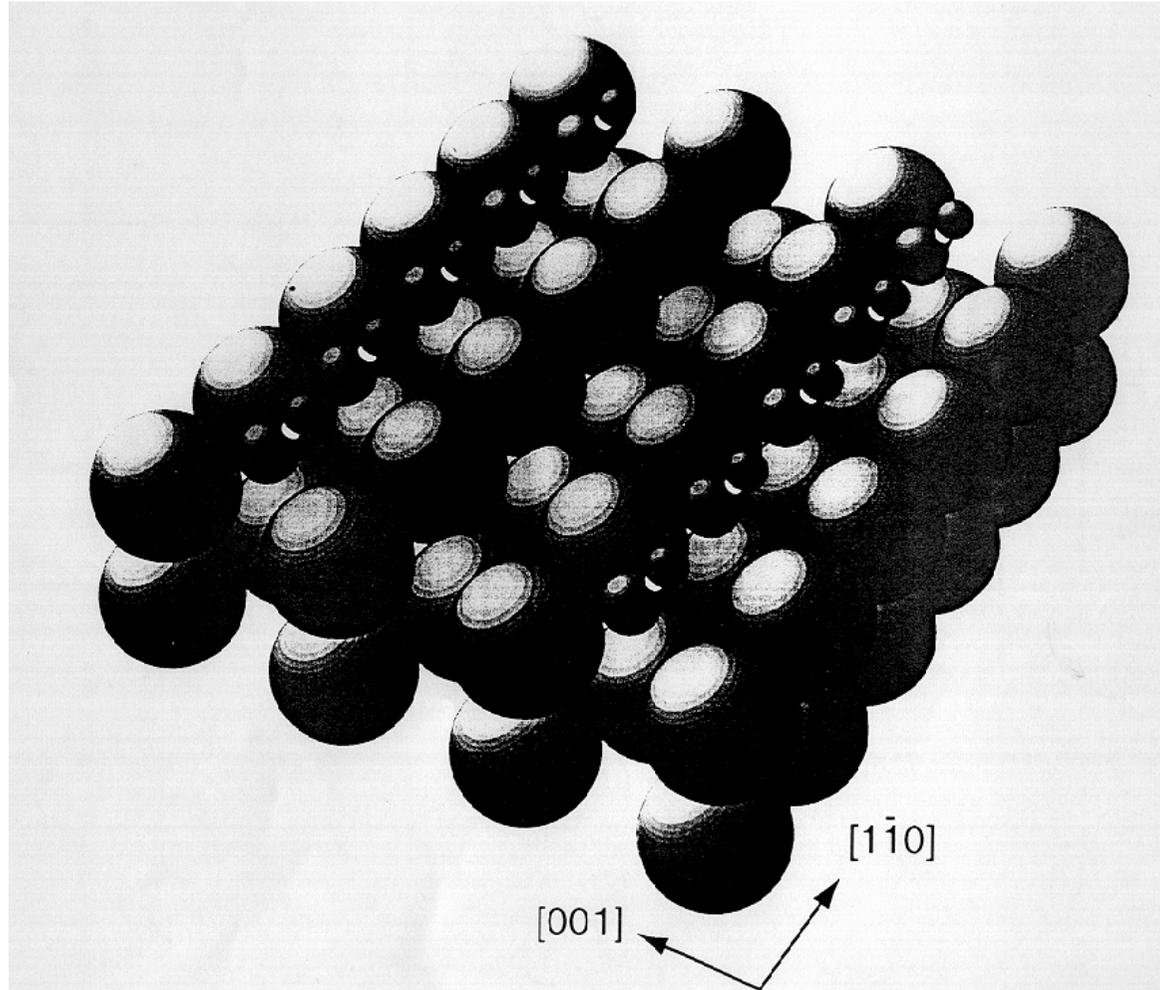


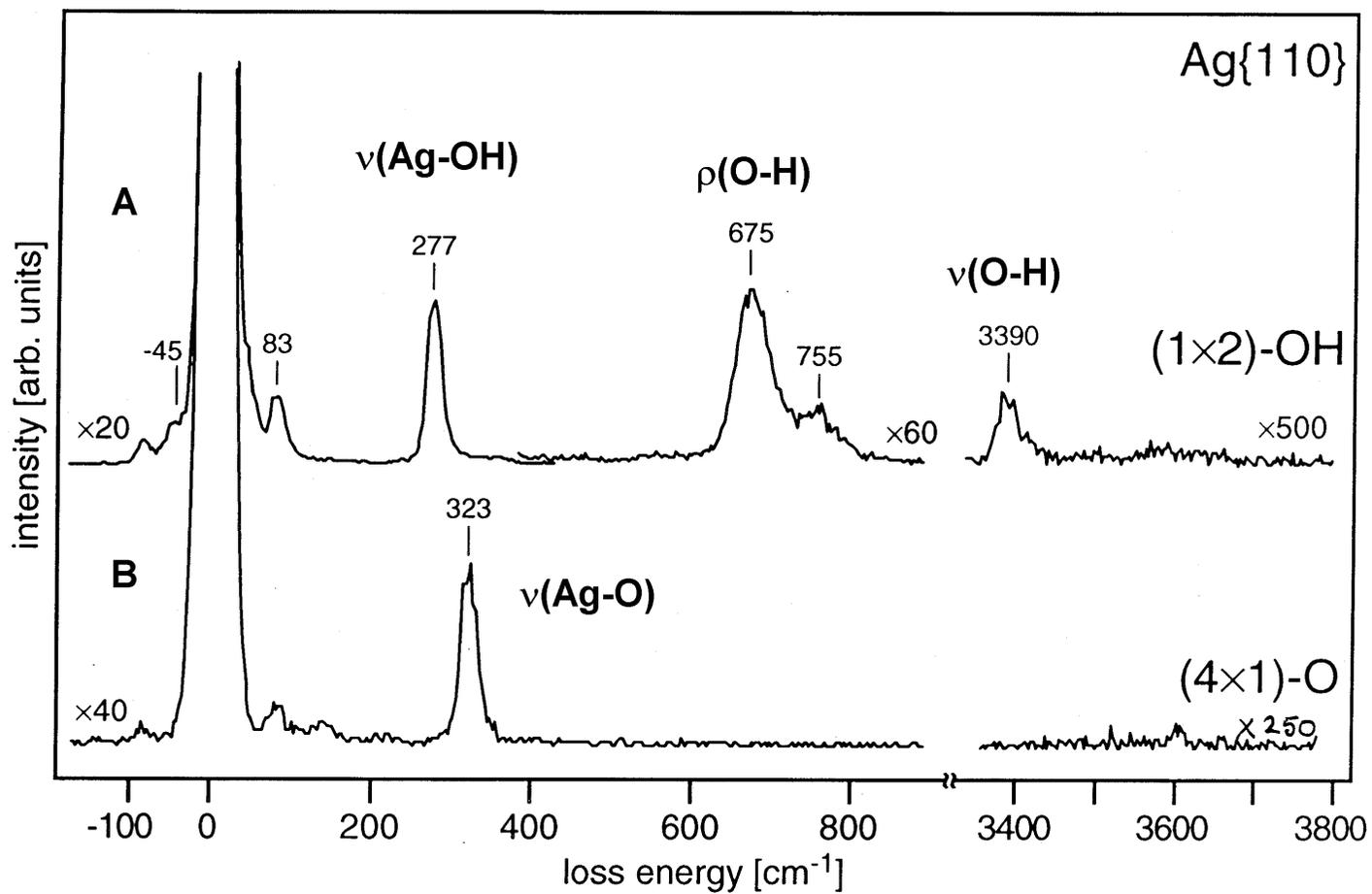
Dioxygen adsorption on Ag{111} surface

Ag{110} (4 x 1)-O

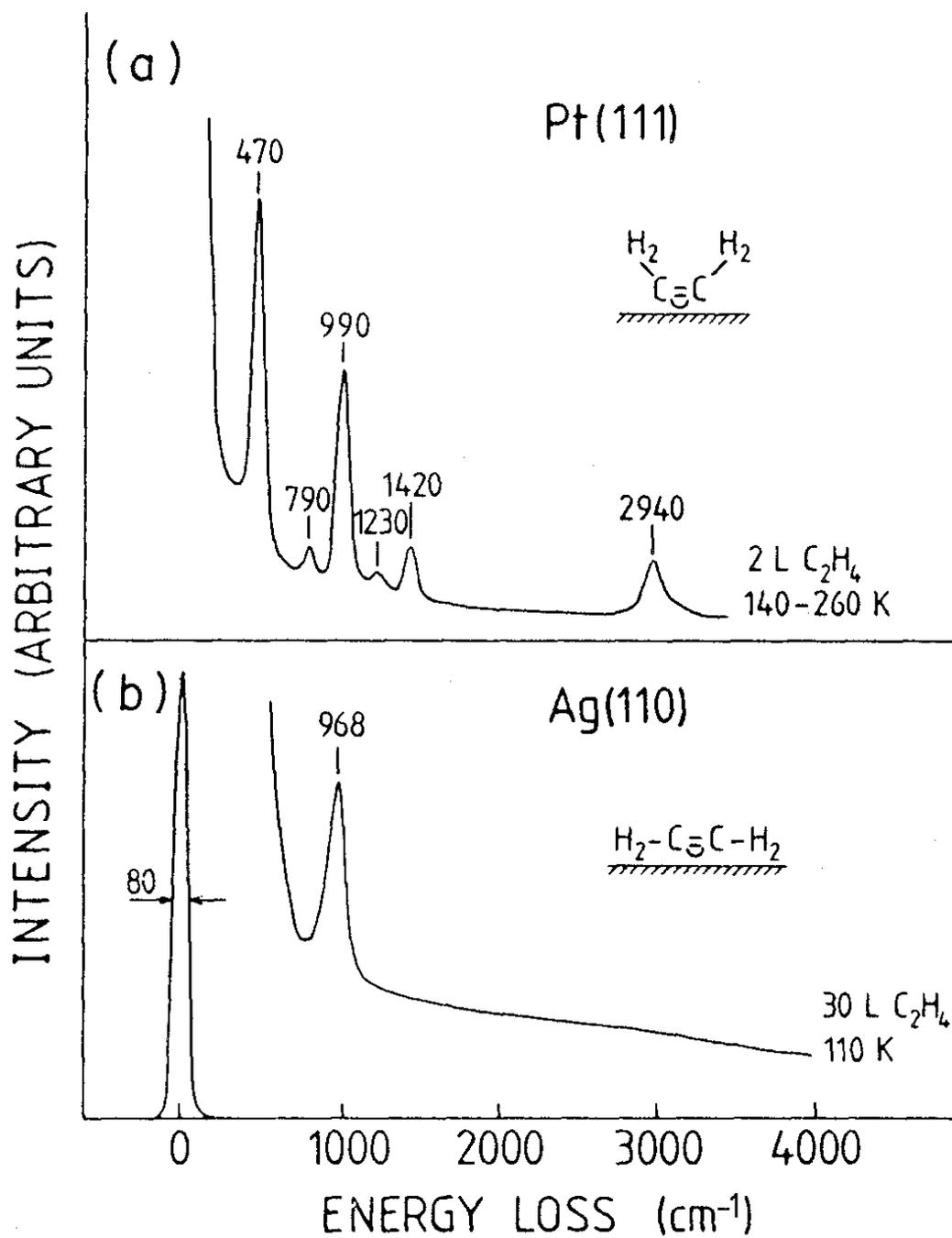


Ag{110} (1 x 2)-OH



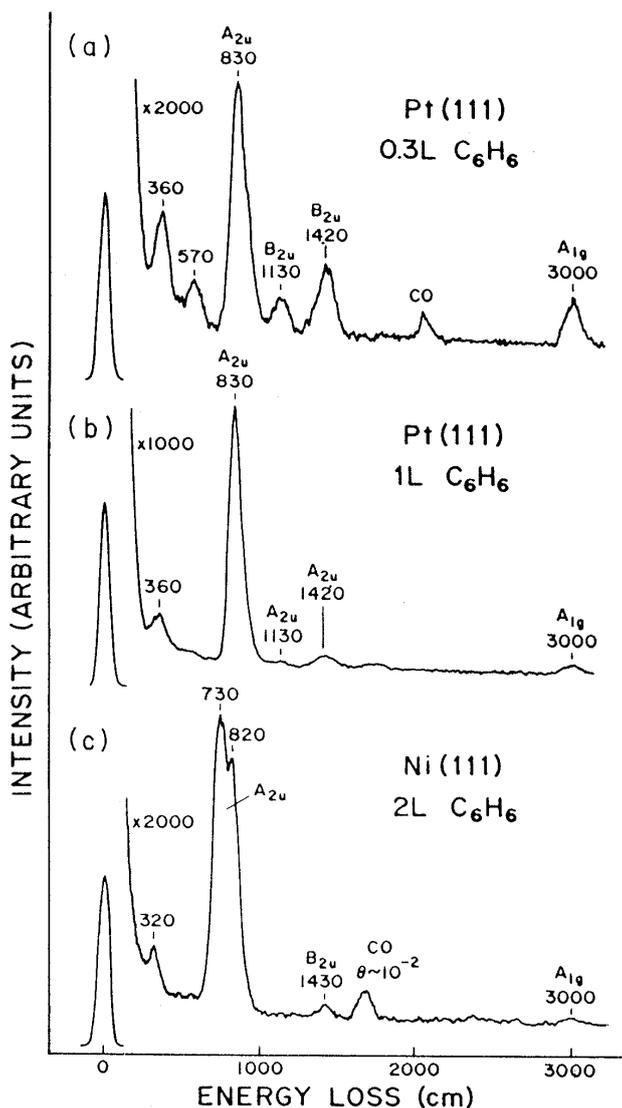


A - Surface OH-groups
 B - Surface oxide



Different bonding of C_2H_4 on different metal surfaces

Chemisorption of benzene on different metal surfaces



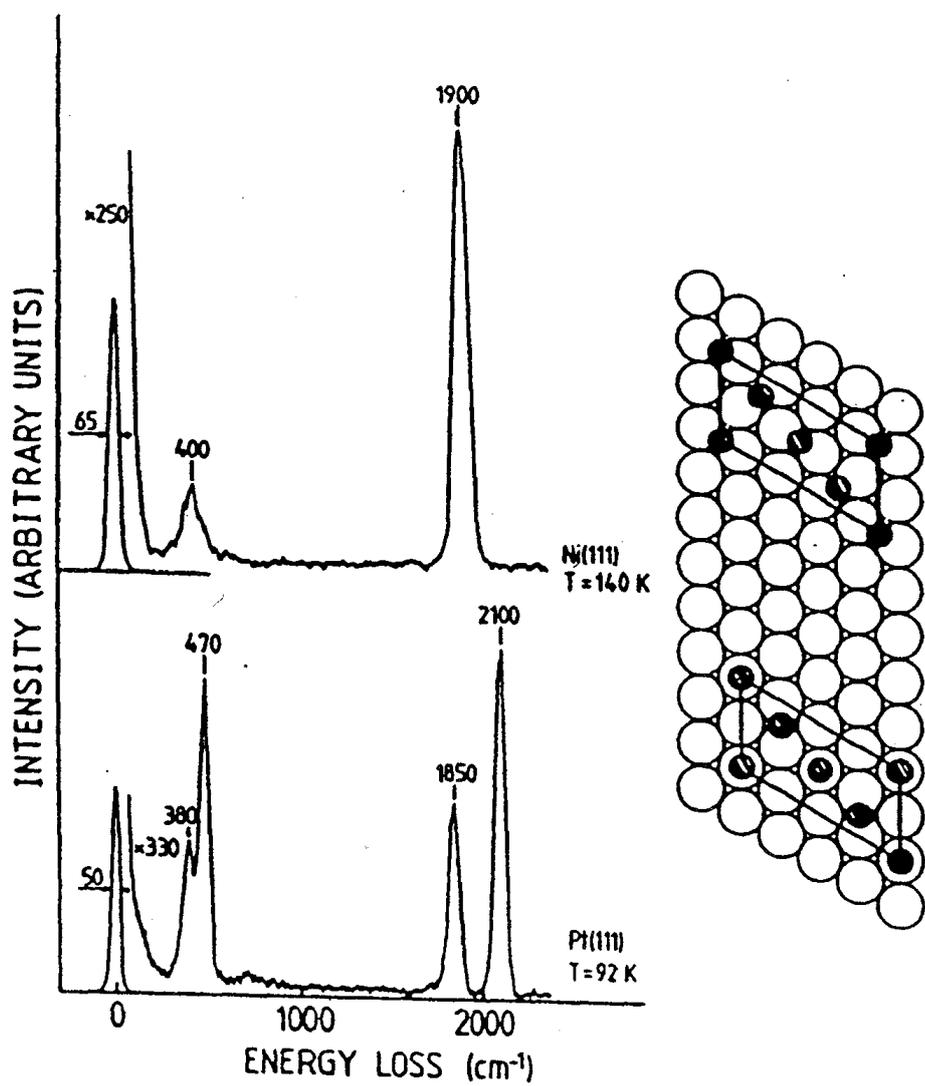
Predicted Set of Frequencies of adsorbed Benzene Assuming Various Symmetries

Oriented	D _{6h}	C _{6v}	C _{3v} (σ _v)	C _{3v} (σ _v)	Observed ^a
A _{2u}	673	673	673	673	830/910
A _{1g}		3062	3062	3062	3000
B _{2u}		992	992	992	
			1310		1420
			1150		1130
B _{1u}				3068	
				1010	
B _{2g}				995	
				703	

^a Observed frequencies for benzene (C₆H₆) on Pt(111).

CC Frequencies of Hydrocarbons

Molecule	$\nu(\text{C}-\text{C})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}\equiv\text{C})$
Ethane CH ₃ -CH ₃	995		
Ethylene CH ₂ =CH ₂		1623	
Acetylene CH≡CH			1974
Propane CH ₃ -CH ₂ -CH ₃	869 } 962		
Propylene CH ₂ -CH=CH ₂	1054 }	1647	
Allene CH ₂ =C=CH ₂	919 }	1071 } 1513	
		1956 }	
Methylacetylene CH ₂ -C≡CH	931		2142
	837 }		
Butane CH ₃ -CH ₂ -CH ₂ -CH ₃	1009 } 968		
(trans)	1059 }		
1,3-Butadiene CH ₃ =CH-CH=CH ₂	1196	1596 } 1613	
		1630 }	
2-Butyne CH ₃ -C≡C-CH ₃	725 } 1024		
	1152 }		
Butadiene CH≡C-C≡CH	874		2020 } 2102
			2184 }
Average frequency	~ 950	~ 1600	~ 2100



Electron energy loss spectra of the Ni{111} and Pt{111} surfaces, each covered with half a monolayer of CO. 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.

Calculated and measured fundamental frequencies of Pd₃(CCH₃)

		Calculated (DFT) [1]	Pd{111} / (CCH ₃) [2]
a₁	CH str.	2914	2900
	CH₃ def.	1296	1334
	CC str.	1149	1080
	PdC str.	401	410
a₂	CC tors.	157	-
e	CH str.	2990	-
	CH₃ def.	1353	1400
	CH₃ rock	915	914
	PdC str.	553	-
	PdCC def.	154	-

[1] I. Pápai et. al., Surf. Sci. Lett. **240**, (1990) L604

[2] J.A. Gates et. al., Surf. Sci., **124**, (1982) 68

Characterization of C-M bond for $M_3(CCH_3)$ surface species

	Pd{111}	Rh{111}	Pt{111}	Units
$\nu_s(M_3C)$	410	420	410	cm^{-1} [1]
$F_s(M_3C)$	1.68	1.86	1.97	Ncm^{-1} [2]

- [1] J.A. Gates et al., *Surf. Sci.*, **124** (1982) 68
G. Somorjai et al. *Surf. Sci.*, **146** (1984) 211
H. Ibach et al. *Surf. Sci.*, **117** (1982) 685
- [2] J. Mink et al., *Surf. Sci.*, (under preparation)

5.3. ADSORBEATUM-SUBSTRATUM (METAL-CARBON) STRETCHING MODES

Platinum-hydrogen stretching frequencies observed on Pt/SiO₂ and calculated force constants

$\nu(\text{Pt-H})$ (cm ⁻¹)	$\nu(\text{Pt-D})^{\text{a}}$ (cm ⁻¹)	K(PtH) (cm ⁻¹)
2129 s	1537	2.73
2118 s	1528	2.70
2097 m, b	1513	2.64

^a Predicted (calculated) band components of the asymmetric shape experimental band at 1530 cm⁻¹ using harmonic approximation

. Metal-arene stretching vibrations

Surface/system	M-L stretch ^a (cm ⁻¹)	Temperature ^b K
Pt(111)/C ₆ H ₆	360	300
Pt(111)/C ₆ D ₆	350	300
Ni(100)/C ₆ H ₆	360	r.t.
Ni(100)/C ₆ D ₆	360	r.t.
Rh(111)/C ₆ H ₆	345	286
Ni(111)/C ₆ H ₆	290	r.t.
Ni(111)/C ₆ D ₆	290	r.t.
Ag(111)/C ₆ H ₆	n.o.	140
Pd(111)/C ₆ H ₆	n.o.	180
Pd(111)/C ₆ D ₆	n.o.	180
Ag(111)/C ₆ H ₅ N	200	140
Ag(111)/C ₆ D ₅ N	175	140
Pd(111)/C ₆ H ₅ N	n.o.	170
Pd(111)/C ₆ D ₅ N	n.o.	170
Pt(111)/C ₆ H ₅ CH ₃	355	300
Pt(111)/C ₆ D ₅ CD ₃	340	300
Pd(111)/C ₆ H ₅ CH ₃	220	180
Pd(111)/C ₆ D ₅ CH ₃	210	180
Pd(111)/C ₆ D ₅ CD ₃	210	180

^a n.o. = not observed

^b r.t. = room temperature

IR emission spectra (cm⁻¹) of CO on metal single crystals

Surface	Coverage			Assignment
	$\theta = 0.1$	$\theta = 0.4$	$\theta = 1.0$	
Ni(100) [35—38]	2010 vs 1889 w n.o.	2031 vs 1900 w n.o.	2035 vs 1930 w 479 vw	linearly bonded bridged $\nu(\text{Ni-C})$
Surface	Coverage			Assignment
	$\theta = 0.03$	$\theta = 0.55$		
Pt(111) [39]	2076 w n.o. n.o. 466 w 453 w	2089 vs 1850 vw 1810 vw 462 w 448 w	bridged	linearly bonded three-fold coor. $\nu(\text{Pt-}^{12}\text{C})$ $\nu(\text{Pt-}^{13}\text{C})$

Remarks: number of frequencies read from the published spectra;
n.o. = not observed

Stretching frequencies (cm⁻¹) and calculated force constants (N cm⁻¹) for adsorbed CO on supported Pt and [Pt(CO)Cl₃]- anion

Stretching vibrations and force constants	Pt/Al ₂ O ₃ emission (420 K)		Pt/SiO ₂ transmission (300 K)	Pt/NaY emission (383 K)	[Pt(CO)Cl ₃] ⁻ solution ref. [58]
	Pt ⁺	Pt ⁰	Pt ^{0c}	Pt ^{0d}	Pt(II)
CO str ^a	2125 w	2043 vs	2098 vs	2070 s	2083 vs
CO str ^b	—	1800 m, b	1850 w, b	1850 w, b	—
PtC str ^a	437 vw	457 w, b	(475)	465 m	504 sh
PtC str ^b	—	523 vw (?)	(569)	580 w (?)	—
K(CO) ^a	18.2	16.9	16.5	17.3	16.5
K(CO) ^b	—	13.1	12.6	13.8	—
K(PtC) ^a	2.92	3.53	3.72	3.34	3.9
K(PtC) ^b	—	5.25	5.34	4.85	—

Remarks: Calculated frequencies are shown in brackets

^a Linearly bonded CO

^b Bridged or multicentered CO group

^c Experimental data taken from ref. [59]

^d Experimental data taken from ref. [55]

Low frequency vibrations of adsorbed benzene on Ni/SiO₂

C ₆ H ₆ liquid IR ^a	C ₆ H ₆ Ni/SiO ₂ IR ^a	C ₆ H ₆ Ni/SiO ₂ Raman ^b	Assignments ^c		
1249 vw	1260 m		ν_{14}	b_2	(b_{2u})
1177 w		1184 m	ν_9	e_2	(e_{2g})
1150 w		1161 m	ν_{15}	b_2	(b_{2u})
1039 m	1125 w, m	1120 vw	ν_{18}	e_1	(e_{1u})
		1056 w			
992 vvw		995 vw	ν_1	a_1	(a_{2g})
969 vvw		969 w	ν_{17}	e_2	(e_{2u})
851 w	875 vw	864 m	ν_{10}	e_1	(e_{1g})
813 vw, sh	816 w				
775 w		776 w			
670 vvs	680 vs	684 m	ν_{11}	a_1	(a_{2u})
		603 w	ν_6	e_2	(e_{2g})
		407 w	ν_{16}	e_2	(e_{2u})
		304 w	$\nu(\text{Ni-Ar}) a_1$		
(400)	(600)	(100)	cm ⁻¹ limit of observation		

^a Ref. [43], support Cabosil, 5% Ni

^b Ref. [44]

^c Assignments refer to C_{6v} symmetry, in brackets are the species for D_{6h} symmetry