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Adsorption Properties  
of CO on Metal Single-Crystal  
Surfaces

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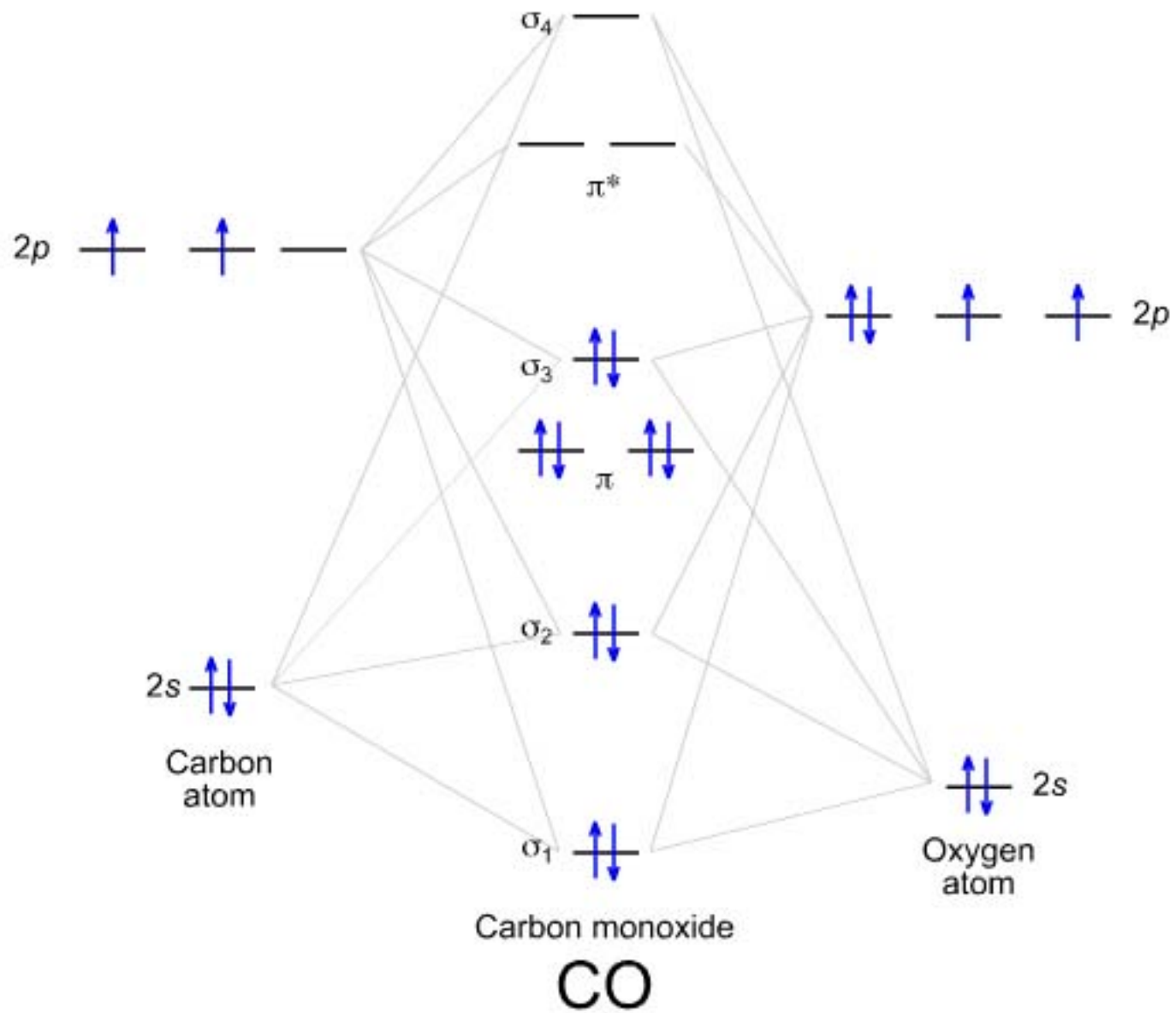
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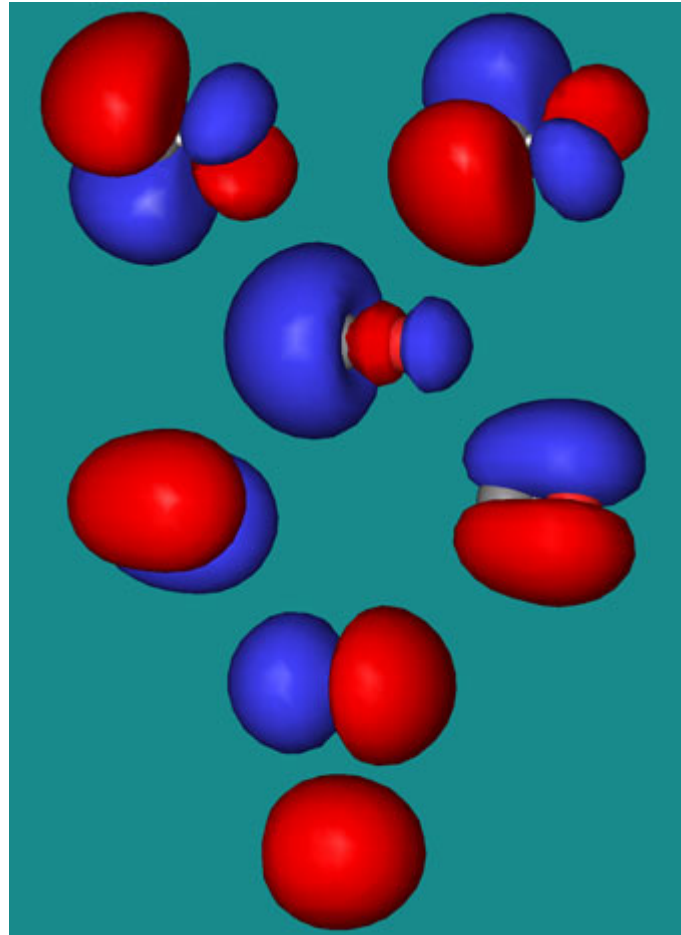
The adsorption of carbon monoxide on metal single-crystal surfaces has been studied extensively over the last thirty years with various surface techniques.

### PROBLEMS TO SOLVE:

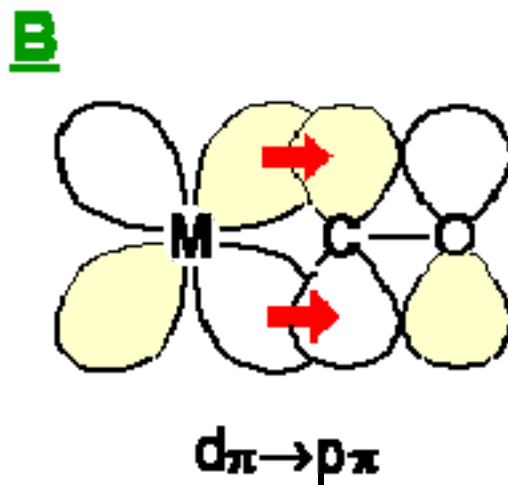
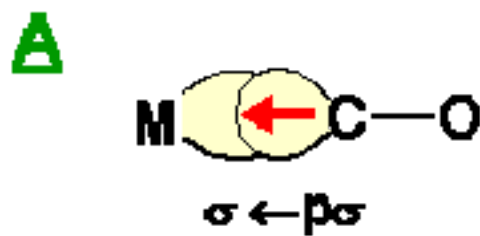
Molecular or dissociative adsorption  
Chemical bonding and orientation  
Adsorption site(s) as a function of coverage  
Overlayer long-range order

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Dewar-Chatt or *Blyholder model* for the bonding of CO to metals.



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This simple model considers the metal-CO bonding to consist of two main components :

**A** : this is a  $\sigma$  bonding interaction due to overlap of a filled  $\sigma$  - "lone pair" orbital on the carbon atom with empty metal orbitals of the correct symmetry - this leads to electron density transfer from the CO molecule to the metal centre.

**B** : this is a  $\pi$  bonding interaction due to overlap of filled metal  $d\pi$  (and  $p\pi$  ?) orbitals with the  $\pi^*$  antibonding molecular orbital of the CO molecule. Since this interaction leads to the introduction of electron density into the CO antibonding orbital there is a consequent reduction in the CO bond strength.

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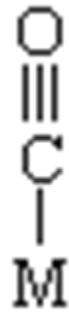
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When carbon monoxide is molecularly adsorbed onto metal surfaces, then it bonds to the surface through the carbon atom.

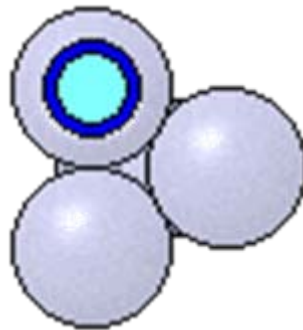
This would imply that the orientation of the molecule as it approaches the surface must be a factor in determining the probability of adsorption and the energy of interaction.

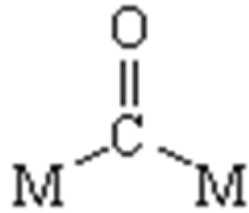
Spectroscopic studies show that CO adopts a range of bonding geometries in which it is preferentially coordinated to one, two or three metal atoms. This indicates that the lateral position of the molecule must, at the very least, affect the depth of the chemisorption well.

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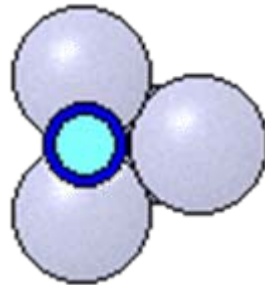


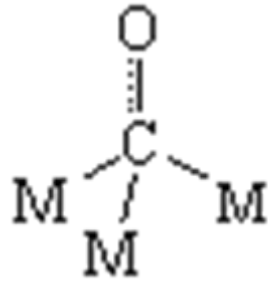
Terminal ("Linear")  
(all surfaces)



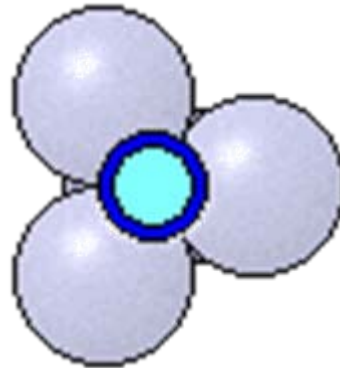


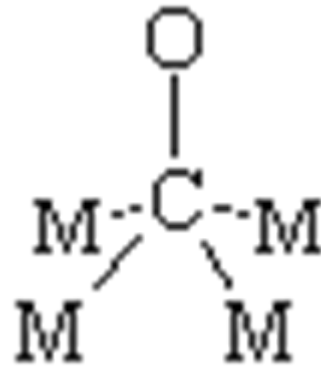
Bridging ( 2f site )  
(all surfaces)



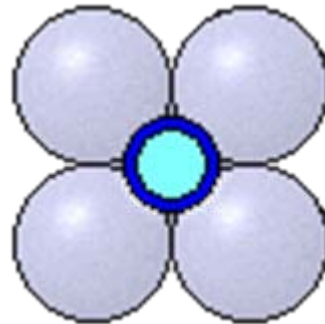


Bridging / 3f hollow  
( *fcc*(111) )





Bridging / 4f hollow  
(rare - *fcc*(100) )



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In many CO/metal systems there are strong coverage dependent effects - these may be associated with changes in the bonding geometry with coverage and/or intermolecular interactions between the adsorbed CO molecules at high coverages.

Depending upon the metal surface, carbon monoxide may adsorb either in a molecular form or in a dissociative fashion - in some cases both states coexist on particular surface planes and over specific ranges of temperature.

For the majority of the transition metals, however, the nature of the adsorption (dissociative v.'s molecular) is very sensitive to the surface temperature and surface structure (e.g. the Miller index plane, and the presence of any lower co-ordination sites such as step sites and defects).

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On the reactive surfaces of metals from the left-hand side of the periodic table (e.g. Na, Ca, Ti, rare earth metals) the adsorption is almost invariably dissociative, leading to the formation of adsorbed carbon and oxygen atoms (and thereafter to the formation of surface oxide and oxy-carbide compounds).

By contrast, on surfaces of the metals from the right hand side of the *d*-block (e.g. Cu, Ag) the interaction is predominantly molecular; the strength of interaction between the CO molecule and the metal is also much weaker, so the M-CO bond may be readily broken and the CO desorbed from the surface by raising the surface temperature without inducing any dissociation of the molecule.

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## How to distinguish between molecular and dissociative adsorption

We can rule out dissociation of adsorbed CO by the observation of the characteristic CO-group vibration frequency. It is well-known in organic chemistry, and with more relevance in the chemistry of transition metal carbonyls, that the CO group has a stretching frequency, which depends somewhat on its environment, but is generally of the order of 250 meV. The CO group stretching frequency has been observed with HREELS on Mo(100), W(100), Ni(100) and Pt(111), with a value around 250meV.

Furthermore, additional frequencies of a more variable magnitude, but much below the CO stretching mode, in the 50meV region, are also observed, which are related to the vibration of the whole molecule against the surface. Bending modes and internal vibrations of the surface should lie at a still lower frequency.

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For CO on W(100), the CO stretching mode is complemented by a mode at 45 meV, which is believed to be just such a CO-metal stretching mode. However, there are also modes indicating the presence of a layer of C and O formed by dissociation of CO on the surface. For Pt(111), Ni(100) and Rh, CO does not dissociate but a new phenomenon is the appearance of two different CO stretching frequencies of about 235 and 260 meV. When both peaks are present, two CO-metal stretching frequencies are also present. In the case of Ni(100) and Rh, the authors associate the higher CO stretching mode with a binding site on top of a substrate metal atom, and the lower mode with a bridge site. The carbon is invariably assumed to be between the surface and the O atom.

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# 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

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# Dipole scattering

Electron is scattered at long range (100's Å) by oscillating Coulombic field of surface

Electron momentum  $\perp$  to surface is conserved

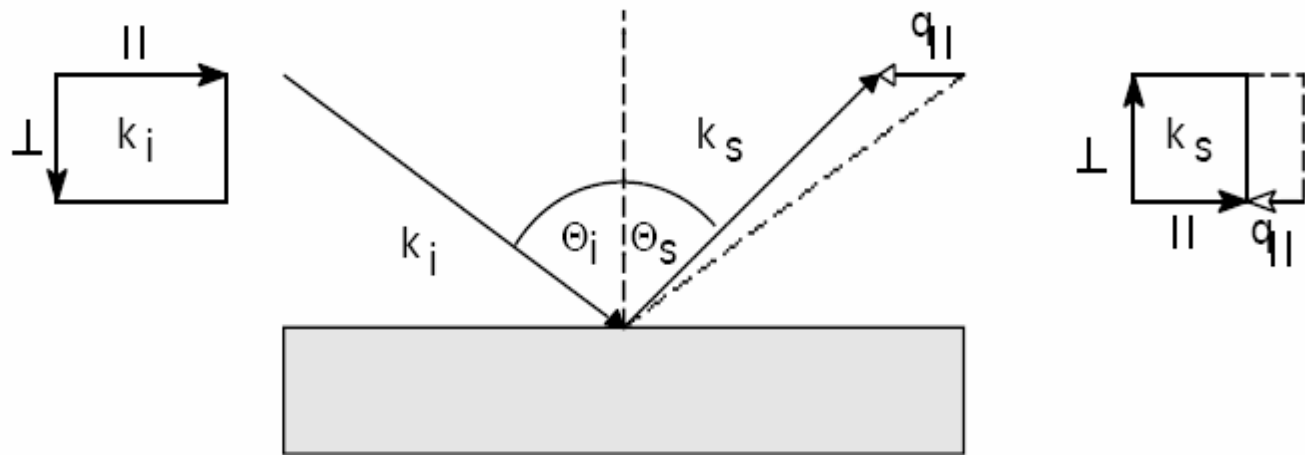
Energy loss results in small angle deflections around specular direction –dipole scattering lobe

Elastically-scattered electrons appear at  $\Theta_i = \Theta_s$  (specular)

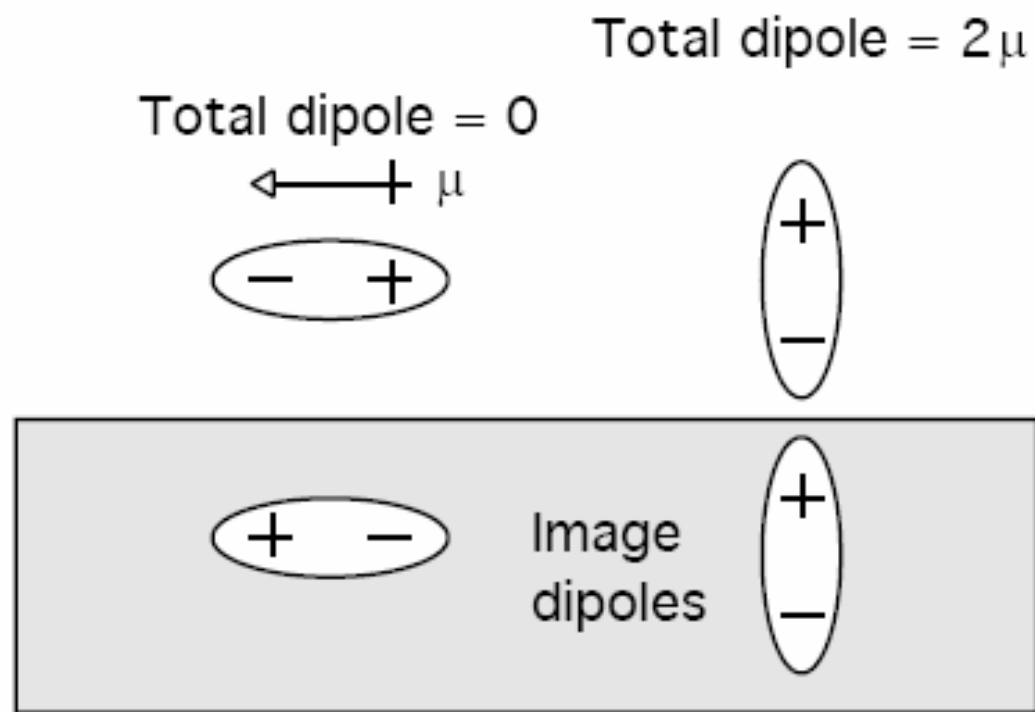
Inelastically-scattered electrons appear at  $\Theta_i \cong \Theta_s$  (sharply peaked near specular)

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Only modes with component of vibration perpendicular to surface can be excited (not parallel modes) - *surface selection rule*



small momentum loss  $q_{||} = h\nu$



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# 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)

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Neither electron momentum  $\parallel$  nor  $\perp$  conserved

one can see vibrational modes with dynamic dipoles  
both  $\parallel$  and  $\perp$  to  
surface plane (only off-specular)

Much lower cross-section than dipole scattering (weak  
loss features)

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- HREELS spectra are reported for a series of ordered CO overlayers on the (100) surfaces of Cu, Ni and Pd at half-monolayer coverage.
  - The spectra for the simple structures, i.e.  $c(2 \times 2)\text{CO}$  on Cu and Ni and  $p(2\sqrt{2} \times \sqrt{2})R45^\circ$  for CO on Pd, are fully compatible with on-top site adsorption (Cu, Ni) and bridge site adsorption (Pd) respectively.
  - The CO adsorption is molecular in all cases, with significant differences observed as a function of coverage
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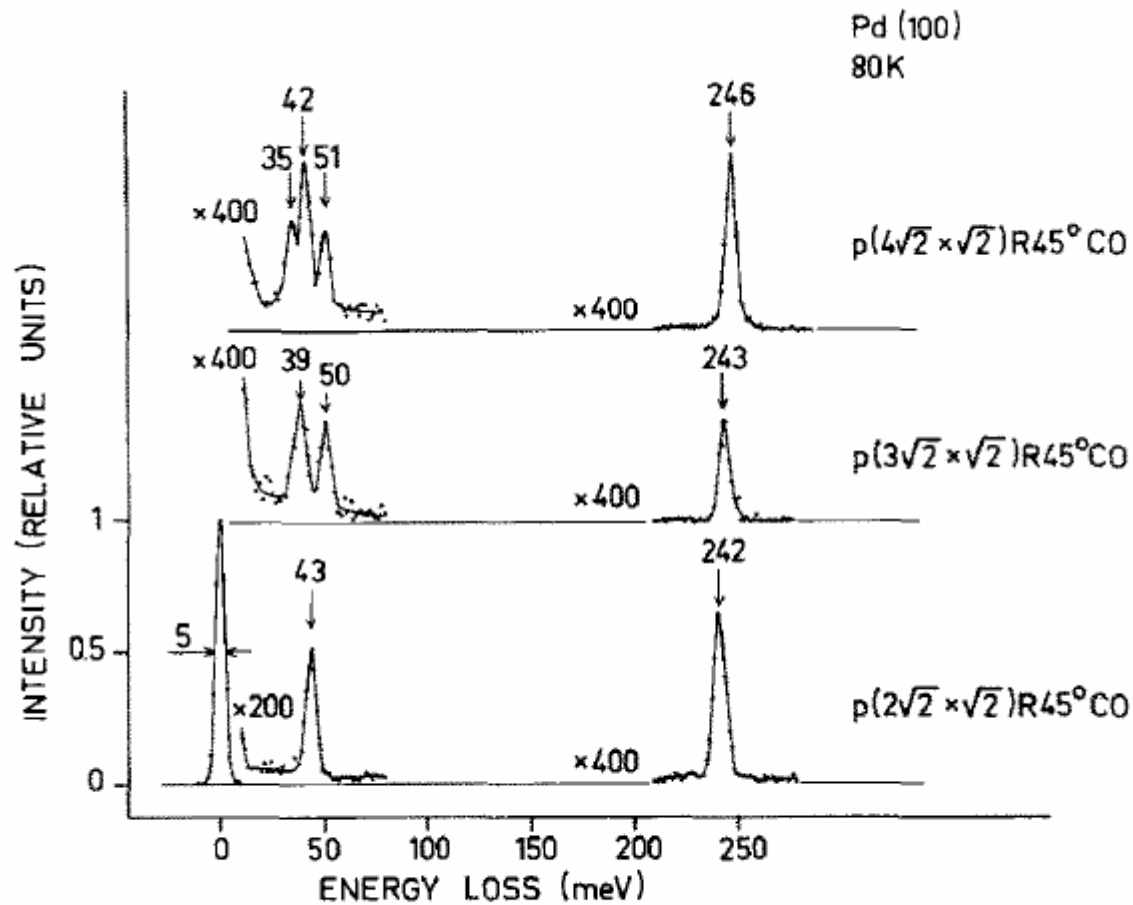


Fig. 5. EELS spectra of CO adsorbed on Pd(100) in different structures. The primary electron energy is 1.5 eV and the angle of incidence is  $51^\circ$ .

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In fig. 5, we shown a sequence of spectra for the three different CO overlayers  $p(2\sqrt{2}\times\sqrt{2})R45^\circ$ ,  $p(3\sqrt{2}\times\sqrt{2})R45^\circ$  and  $p(4\sqrt{2}\times\sqrt{2})R45^\circ$ . The presence of only one C-O stretching frequency at  $\sim 244$  meV, in the high-frequency region for all structures, is characteristic of bridge site adsorption for all the structures. In the low-frequency region, however, we observed changes in the spectra with the transition to the different structures.

The spectrum corresponding to the  $p(2\sqrt{2}\times\sqrt{2})R45^\circ$  structure exhibits a single line at 43 meV. This loss is assigned to the symmetric Pd-C stretching vibration of bridge-bonded CO.

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The next spectrum in fig. 5, corresponding to a  $p(3\sqrt{2}\times\sqrt{2})R45^\circ$  structure, exhibits two EELS lines at 39 and 50 meV. Both losses are found to be dipole excited. Since all the CO molecules are adsorbed in bridge sites the appearance of a doublet indicates that a bending mode is now active. The loss at 39 meV, we assign to the symmetric Pd-C stretch i.e. the motion of the CO molecule against the metal surface. The loss at 50 meV is assigned (see below) to the bending mode perpendicular to the plane of the bridge. The CO molecules experience a non-uniform adsorbate-adsorbate interaction. The CO molecules must respond to this. The response is likely to involve *tilting* to reduce the nearest neighbour repulsion. In turn, this will give added intensity to the dipole active bending vibration.

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In the last spectrum of fig. 5, corresponding to a  $p(4\sqrt{2}\times\sqrt{2})R45^\circ$  structure, we observe three EELS lines at 35, 42 and 51 meV. In this model, the CO molecules are adsorbed in triplet rows. The CO molecules of the middle row experience a uniform adsorbate-adsorbate interaction. In the outer rows, however, the molecules experience a non-uniform interaction. Presumably, as a consequence of this, the molecules of the middle row are oriented perpendicular to the surface while those in the outer rows are tilted away from their nearest neighbours. The 35 meV line is assigned to the symmetric Pd-C stretching vibration of the tilted molecules.

The 51 meV line is again assigned to the bending mode perpendicular to the bridge plane, as for the  $p(3\sqrt{2}\times\sqrt{2})R45^\circ$  structure. Finally, the line at 42 meV is assigned to the symmetric Pd-C stretch of CO molecules in the middle rows oriented perpendicular to the surface.

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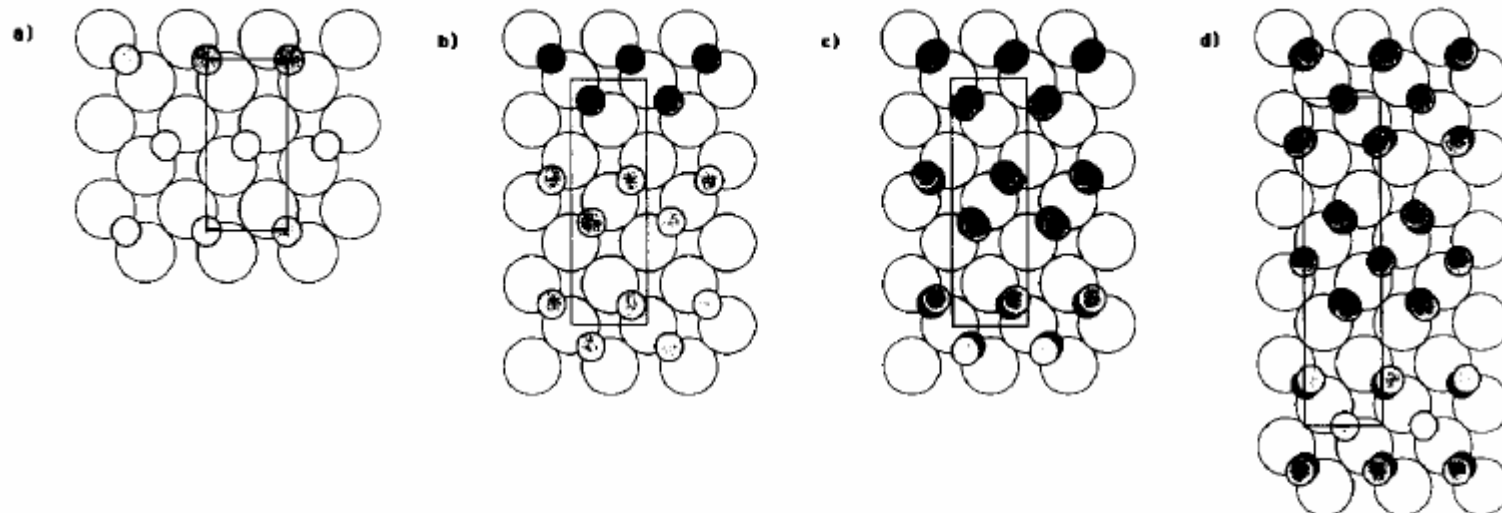


Fig. 7. Models proposed for the interpretations of different CO structures on Pd(100). All CO molecules are adsorbed in bridge sites. (a) The  $p(2\sqrt{2} \times \sqrt{2})R45^\circ$  structure: the CO molecular axis is parallel to the surface normal. (b) The  $p(3\sqrt{2} \times \sqrt{2})R45^\circ$  structure: the model proposed by Biberian and Van Hove [5]. (c) The  $p(3\sqrt{2} \times \sqrt{2})R45^\circ$ : All CO molecules are tilted away from the surface normal. (d) The  $p(4\sqrt{2} \times \sqrt{2})R45^\circ$  structure; 1/3 of the molecules are untilted and 2/3 are tilted with respect to the normal.

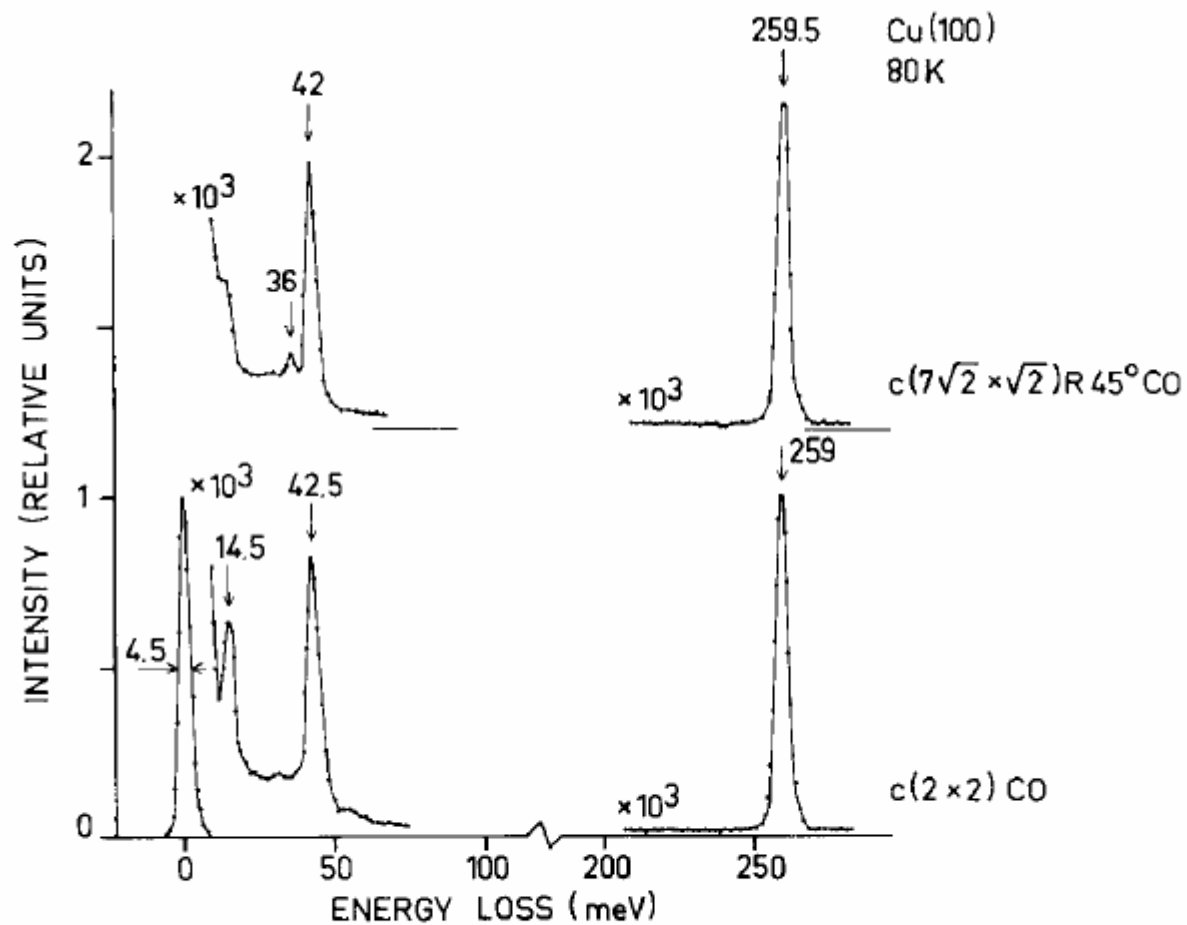


Fig. 8. EELS spectra of CO adsorbed on Cu(100) in different structures. Primary electron energy is 2 eV and angle of incidence is  $50^\circ$ .

In fig. 8, we show EELS spectra for the two CO overlayers;  $c(2 \times 2)$  and  $c(\sqrt{2} \times \sqrt{2})R45^\circ$  on Cu(100). As for the case of CO on Pd(100), we notice that there is no dramatic change in the C-O stretching region as a consequence of the structural transition. The fundamental C-O stretch shifts only slightly from 259 to 259.5 meV; the intensity changes marginally. The low-energy region shows more dramatic changes just as the Pd(100) case. The  $c(2 \times 2)$  structure has a spectrum consisting of two low-energy EELS peaks at 14.5 and 42.5 meV. These are due to a surface mode and Cu-C stretching vibration respectively.

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In the  $c(7\sqrt{2}\times\sqrt{2})R45^\circ$  structure a new peak develops around 36 meV which signals a distinct change in the CO environment compared to the  $c(2\times 2)$  case. The simplest explanation of this observation is that the 36 meV loss is related to a bending mode of CO molecules still adsorbed in single coordination with Cu atoms i.e. on-top sites. Such a mode, for terminally bonded CO molecules, is expected to be observed at a vibrational energy somewhat lower than the corresponding metal-carbon stretching vibration. The structural model indicates a tilting of terminal CO molecules in the densely packed rows, in order to provide for a reasonable O-O spacing.

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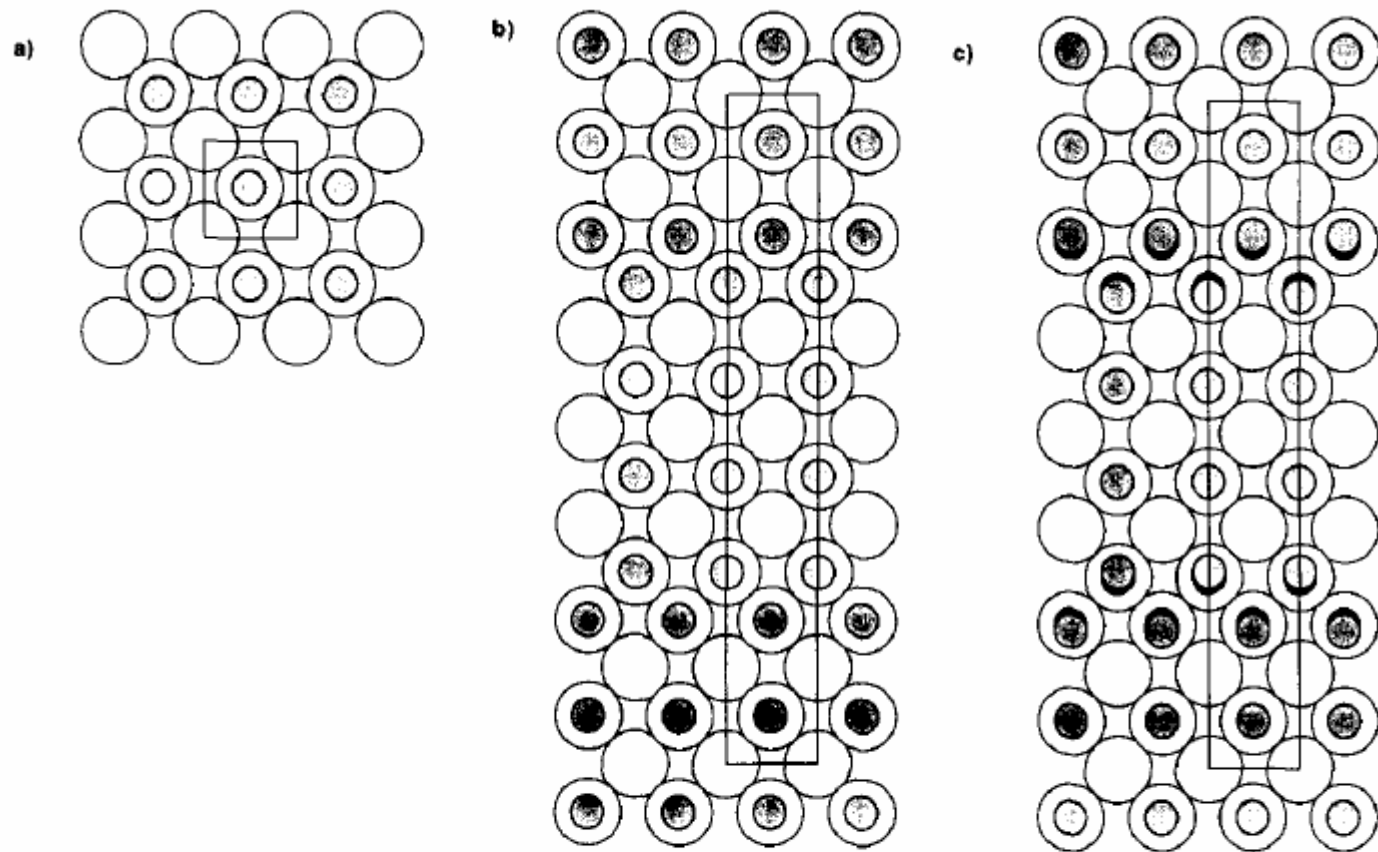


Fig. 9. Models proposed for the interpretation of CO structures on Cu(100). All CO molecules are adsorbed in on-top sites. (a) The  $c(2 \times 2)$  structure: the CO molecular axis is parallel to the surface normal. (b) The  $c(7\sqrt{2} \times \sqrt{2})R45^\circ$  structure:  $1/2$  of the molecules are untilted and  $1/2$  are tilted with respect to the normal.

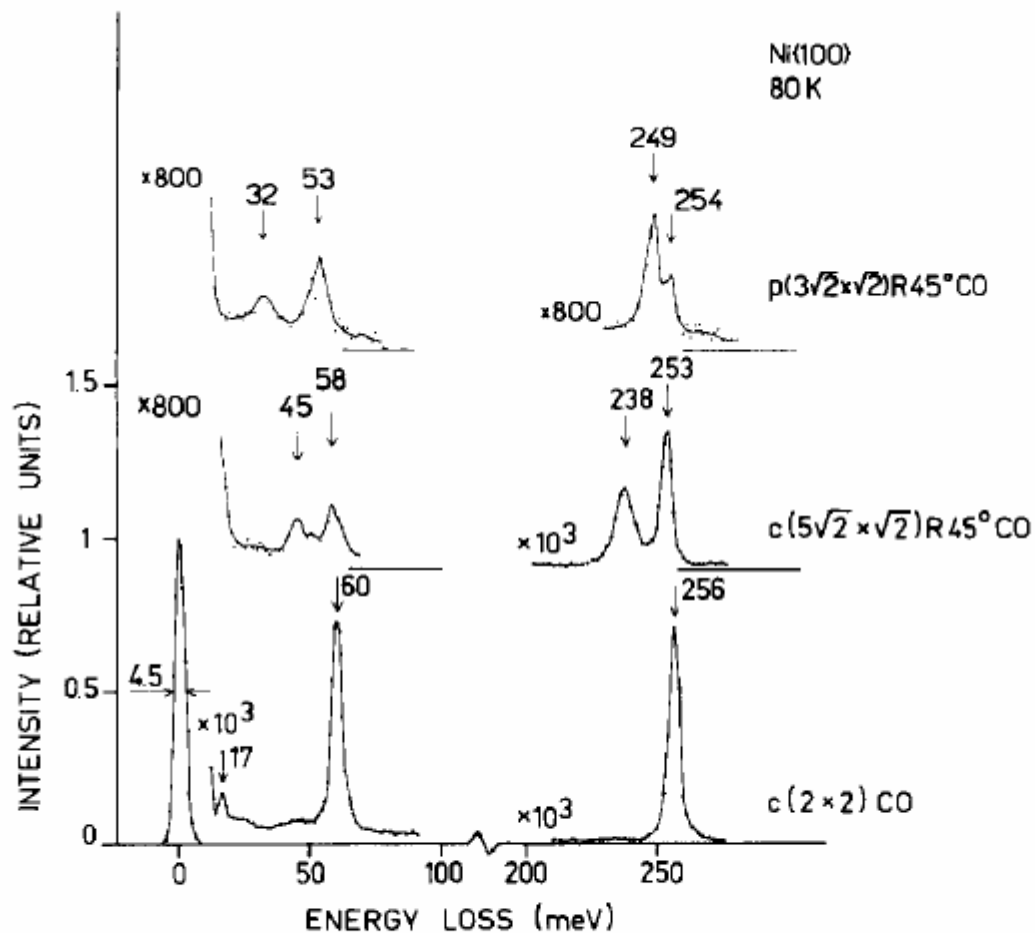


Fig. 10. EELS spectra of CO adsorbed on Ni(100) in different structures. Primary electron energy is 3 eV and the angle of incidence is  $50^\circ$ .

In fig. 10, we show EELS spectra for the three CO overlayers:  $c(2 \times 2)$ ,  $c(5\sqrt{2} \times \sqrt{2})R45^\circ$  and  $p(3\sqrt{2} \times \sqrt{2})R45^\circ$  on Ni(100). In this case, we notice that the C-O stretching region, as well as the low region, changes as a consequence of structural changes.

The  $c(2 \times 2)$  spectrum closely resembles the Cu(100)  $c(2 \times 2)$  spectrum i.e. the EELS lines 17, 60 and 256 meV corresponding to the excitation of the Ni(100) surface phonon, the Ni-C stretching vibration and the C-O stretching vibration, respectively, for the on top site CO. The transition to the  $c(5\sqrt{2} \times \sqrt{2})R45^\circ$  structure causes the C-O stretch and the Ni-C stretch for terminally bonded CO molecules to shift slightly to 253 and 58 meV, respectively.

New EELS lines appear at 45 and 238 meV. This signals a definite change in the coordination. From comparison with carbonyl compounds, vibrational energies around 40 and 240 meV imply CO adsorbed in a bridge bonded configuration. We, therefore, picture the  $c(5\sqrt{2} \times \sqrt{2})R45^\circ$  structure as a mixture of terminal and bridge bonded CO molecules.

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By analogy with the Cu(100) situation, we propose that the most realistic model is the one sketched in fig. 11c where we allow the terminally bonded CO molecules to relax via a small tilt of about  $4^\circ$ - $11^\circ$  to produce a O-O distance of 3.0 Å. We would expect the tilt to occur in the (012) direction, away from the nearest neighbour, bridge-bonded molecules. For this structure, we would expect the two bending modes of the terminally bonded CO species to be dipole active. These modes will not be distinguishable by their frequency. We assign the weak feature, between the lines at 45 and 58 meV, at 49 meV to these modes by analogy with the Cu(100) situation.

The transition to the  $p(3\sqrt{2} \times \sqrt{2})R45^\circ$  structure results in new EELS lines at 32,53 and 249 meV. The spectrum resembles the Pd(100)  $p(3\sqrt{2} \times \sqrt{2})R45^\circ$  spectrum.

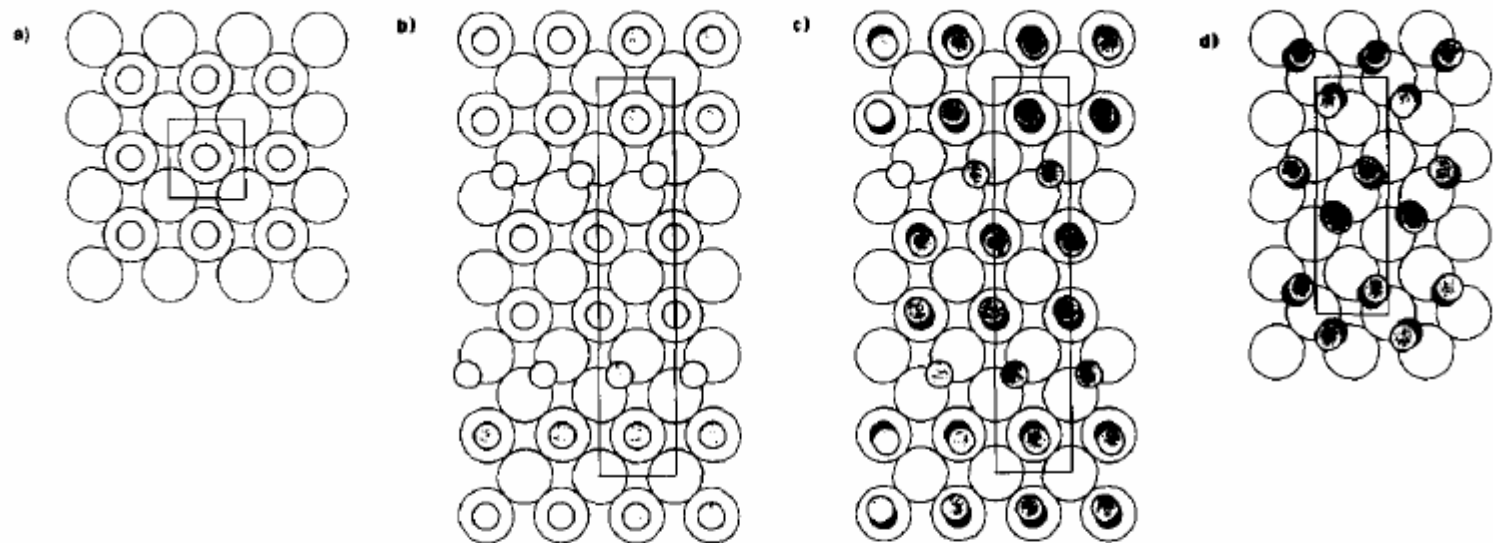
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All CO molecules must be adsorbed in bridge sites. For coverages between the  $c(5\sqrt{2} \times \sqrt{2})R45^\circ$  and the  $p(3\sqrt{2} \times \sqrt{2})R45^\circ$  structures we have observed that the C-O stretch, at 238 meV, associated with the bridge-bonded CO in the former structure is continuously shifted to higher energies when the coverage is increased. The line at 253 meV decreases in intensity and shifts marginally.

Consequently we assign the line at 249 meV to the internal CO stretch for CO molecules adsorbed in a bridge bonded configuration. The lines at 32 and 53 meV we assign, in accordance with the same CO structure on Pd(100), to the metal-C stretch and the bending mode perpendicular to the plane of the bridge, respectively.

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**Fig. 11. Models proposed for the interpretation of CO structures on Ni(100). (a) The  $c(2 \times 2)$  structure: all CO molecules are adsorbed in on top sites with the CO molecular axis parallel to the surface normal. (b) The  $c(5\sqrt{2} \times \sqrt{2})R45^\circ$  structure:  $1/3$  of the molecules are untilted and adsorbed in bridge sites while  $2/3$  are tilted with respect to the normal and adsorbed in on-top sites. (c) The  $p(3\sqrt{2} \times \sqrt{2})R45^\circ$  structure: all CO molecules are adsorbed in bridge sites with the CO molecular axis tilted with respect to the surface normal.**

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H. FROITZHEIM, H. IBACH and S. LEHWALD  
Surface Science 63 (1977) 56

High resolution electron energy-loss spectroscopy has been used to study the surface vibrations of CO on a W(100) surface at 300 K. For small exposures ( $\beta$ -CO) two losses at -68 meV and -78 meV are observed. This vibrational spectrum of  $\beta$ -CO is a clear indication of dissociative adsorption with the carbon and oxygen atoms in fourfold coordination sites each. With further exposure to CO two additional losses at 45 meV and 258 meV are observed, which represent the vibration of undissociated  $\alpha$ -CO in upright position on top of a W atom.

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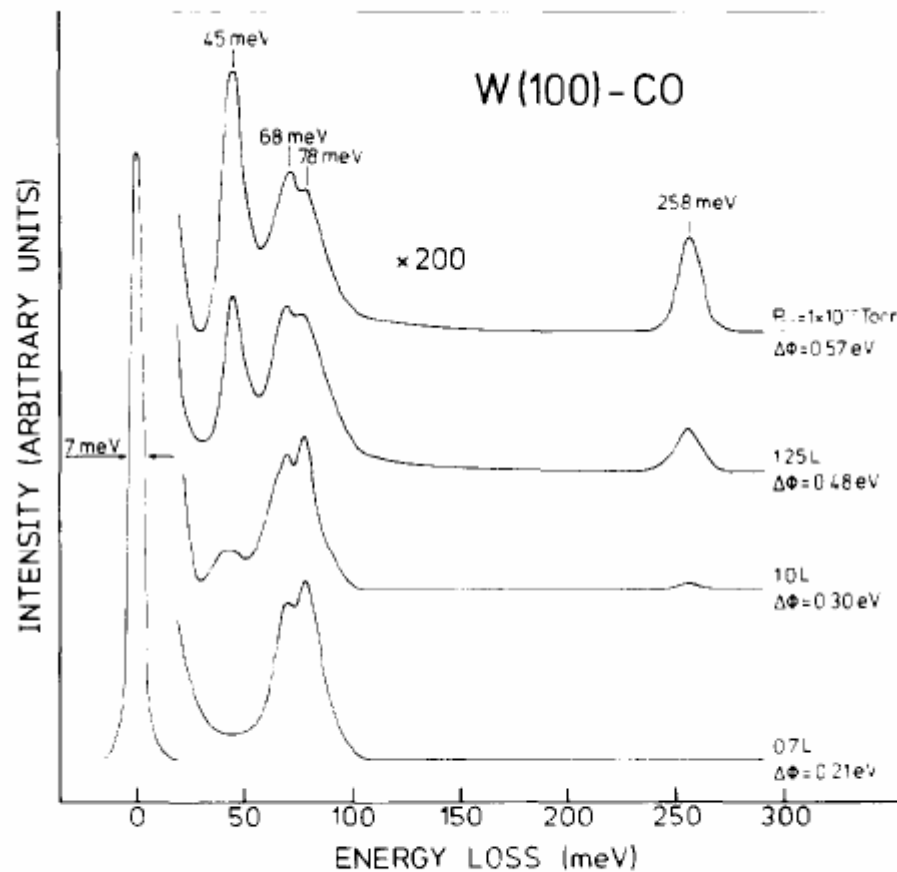


Fig. 1. Electron energy loss spectra of CO on W(100) at 300 K. The spectra are recorded at a primary electron energy of  $E_0 = 5$  eV and at an angle of incidence of  $\theta = 75^\circ$ . The exposures are calculated from the uncorrected ion gauge readings.  $\Delta\phi$  is the measured increase in work function.

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A series of spectra obtained for different coverages at 300 K is shown in fig. 1. The intensities in the spectra for different CO coverages have been normalized to the same area under the elastic peak. The spectra show: for small exposure to CO ( $<1$  L), that is when  $\beta$ -CO is adsorbed, only two losses at -68 and -78 meV are observed. With further exposure to CO two additional losses at 45 and 258 meV occur. The intensity of the two losses depends reversibly on the CO partial pressure.

As HREELS is sensitive only to localized vibrations with a dipole moment perpendicular to the surface, the polarization vector of the observed normal modes of the CO-surface complex must either be perpendicular to the surface or have at least a perpendicular component.

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The absence of a CO stretching frequency in the  $\beta$ -CO spectrum is therefore not necessarily an immediate proof of dissociative adsorption. For a CO molecule adsorbed flat and weakly bound to the surface also no stretching vibration would be observed. The observed vibration for  $\beta$ -CO however indicates a rather strong coupling to the surface.

Furthermore, oxygen atoms adsorbed in fourfold coordination sites on W(100) exhibit a loss spectrum with a single peak at 75 meV, while frequencies of 92 and 125 meV have been associated with bridge and on-top sites. The vibrational spectrum of  $\beta$ -CO therefore shows that the atoms of  $\beta$ -CO occupy fourfold sites. In addition we recorded a loss spectrum of a carbon contaminated W(100) surface with no oxygen present: Its spectrum showed a single peak at  $\sim$ 68 meV, giving evidence that the C atom is adsorbed in an on-top, fourfold or bridge site. Therefore the second peak in the  $\beta$ -CO spectrum is identified with the surface vibration of the C atom.

The two additional peaks at 45 and 258 meV occurring at higher coverages are identified as the vibrational spectrum of the undissociated  $\alpha$ -CO in the upright position. The 258 meV energy loss is close to the stretching vibration of the free CO molecule (269 meV) and that of the CO in the tungsten carbonyl  $W(CO)_6$  (263 meV). The 45 meV loss is the energy of vibration of the whole CO molecule against the W surface in good agreement with the infrared measured W-C stretching frequency in  $W(CO)_6$ , of 46 meV. The appearance of only one frequency (45 meV) for the vibration of the whole CO molecule against the W surface demands the CO molecule to be adsorbed in upright position, i.e. in an on-top or bridge position. The good agreement of the 45 meV loss with the W-C stretching frequency in  $W(CO)_6$  of 46 meV suggests that also in the case of the adsorbed CO the bond is concentrated on a single W atom. i.e. the  $\alpha$ -CO adsorbs in on-top position. A lower frequency would be expected for a bridge site.

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## Adsorption site assignment

There are several methods to establish which adsorption sites are occupied on a surface with more than one possible adsorption geometry.

One of these methods is core-level photoemission, since the O1s and the C1s binding energies are sensitive to the geometry of the adsorption site.

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G. Held , J. Schuler, W. Sklarek, H.-P. Steinrück  
Surface Science 398 (1998) 154

We have investigated the adsorption of CO on Ni(111) by high resolution XPS in order to determine the site occupation of CO under different conditions, such as temperature, coverage and chemical environment. The site assignment for the various layers is based on the characteristic C 1s and O 1s binding energies for CO at different adsorption sites that have also been observed for CO adsorption on other surfaces.

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In several earlier studies of CO adsorption on transition metal surfaces, a rule was established that the C 1s and O 1s core level binding energies of CO decrease with increasing coordination of the carbon atom to surface atoms.

By applying this rule, we assign the single peak found for coverages  $\leq 0.5$  ML to threefold-coordinated adsorption sites and the two peaks found for higher coverages to two lower coordinated sites. The two high coverage peaks with higher binding energies are then assigned to twofold bridge and single coordinated on-top sites, respectively.

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Table 1

Comparison of O 1s and C 1s binding energies for pure and coadsorbed CO on different surfaces

System	On-top		Bridge		Hollow	
	O 1s	C 1s	O 1s	C 1s	O 1s	C 1s
CO/Ni(111)	532.15	285.96	531.01	285.32	530.86	285.24
CO+O/Ni(111) (90 K)	532.50	286.03	531.11	285.40	—	—
CO+O/Ni(111) (260 K)	532.46	286.04	—	—	—	—
CO + benzene/Ni(111)	—	—	—	—	530.81	285.05
CO/Ni(100)	532.2	285.9	531.3	285.5	—	—
CO+H/Ni(100) (80 K)	532.9	286.3	—	—	—	—
CO+H/Ni(100) (170 K)	532.8	286.2	—	—	530.3	285.1
CO+H/Ni(100) (270 K)	—	—	531.2	285.4	—	—
CO/Cu(100)	533.0	286.3	—	—	—	—
CO/Cu/Ni(111)	533.3	286.15	—	—	—	—
CO/Pt(111)	532.6	286.8	531.1	285.8	—	—
CO/Pt(111)	532.7	286.7	531.0	286.0	—	—
CO/Rh(111)	532.0	286.1	530.8	285.3	—	—
CO/Rh(110)	531.9	—	530.8	—	—	—

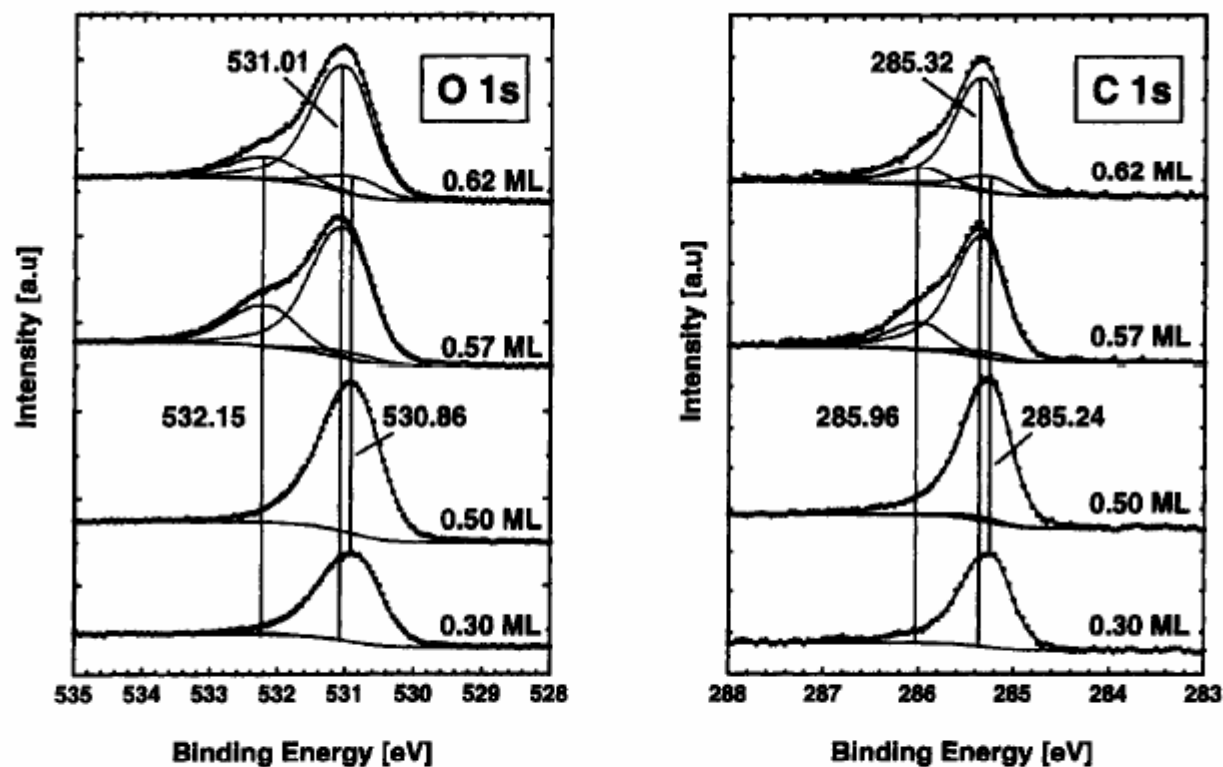


Fig. 3. High resolution O 1s and C 1s XP spectra ( $\hbar\omega = 1486.6$  eV, polar emission angle:  $70^\circ$  from the surface normal) for 0.30, 0.50, 0.57, and 0.62 ML CO on Ni(111), recorded at 80 K. The vertical lines indicate the positions of the peaks assigned to on-top (532.15/285.96 eV), bridge (531.01/285.32 eV), and hollow (530.86/285.24 eV) adsorption sites. The solid lines represent fits to the experimental spectra with peaks at these positions (see text).

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It is then possible to determine the specific occupation of each of the three adsorption sites over the whole coverage range.

The results of this analysis are depicted in Fig. 4 up to a coverage of 0.61 ML. The relative site occupations determined from both C 1s and O 1s are in very good agreement with each other. Both show a clear tendency from exclusively hollow sites at low coverages to on-top and bridge sites with a ratio of about 1:3 for high coverages with a narrow transition regime between 0.50 and 0.57 ML. For the highest coverages of about 0.62 ML the fits become less accurate, indicating a more complicated mixing of adsorption sites where probably also non-symmetric adsorption sites are involved.

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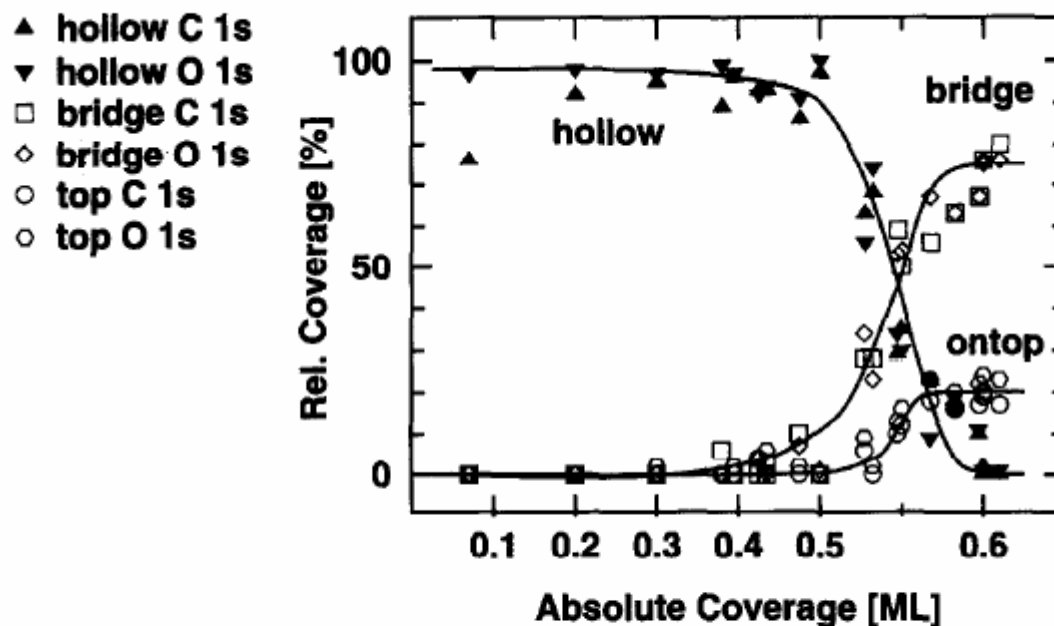


Fig. 4. Relative occupation of adsorption sites (i.e. ratio between fitted peak areas and total O 1s/C 1s intensity) versus absolute coverage in the coverage range up to 0.61 ML as retrieved from the analysis of the O 1s and C 1s peak shapes: ▲ hollow (C 1s), ▼ hollow (O 1s), □ bridge (C 1s), ◇ bridge (O 1s), ○ on-top (C 1s), (hexagons) on-top (O 1s). Note the expanded coverage axis for  $\theta > 0.5$  ML. The solid lines are guide lines for the eye.

In order to study temperature effects in the site occupation, the same measurements as above were carried out at room temperature (310 K). As for the low temperature measurements, coverages between 0.08 ML and 0.47 ML were prepared by saturating the surface at room temperature. ( $\theta_{\text{CO}} \sim 0.47$  ML) or annealing to temperatures between 350 and 410 K (for  $\theta_{\text{CO}} < 0.47$  ML).

Fig. 5 shows XP spectra in the O 1s regime for CO coverages of 0.08, 0.30, and 0.47 ML recorded at 310 K. At the top of Fig. 5 the corresponding low temperature spectrum for 0.30 ML is also included for comparison.

Already from the visual inspection it is evident that, in addition to hollow sites (EB= 530.86 eV) which are exclusively occupied at 80 K, a fraction of the molecules must also reside in lower coordinated adsorption sites at room temperature. The peak maxima at room temperature are shifted towards lower binding energies by 0.15 eV (O 1s) and 0.08 eV (C 1s).

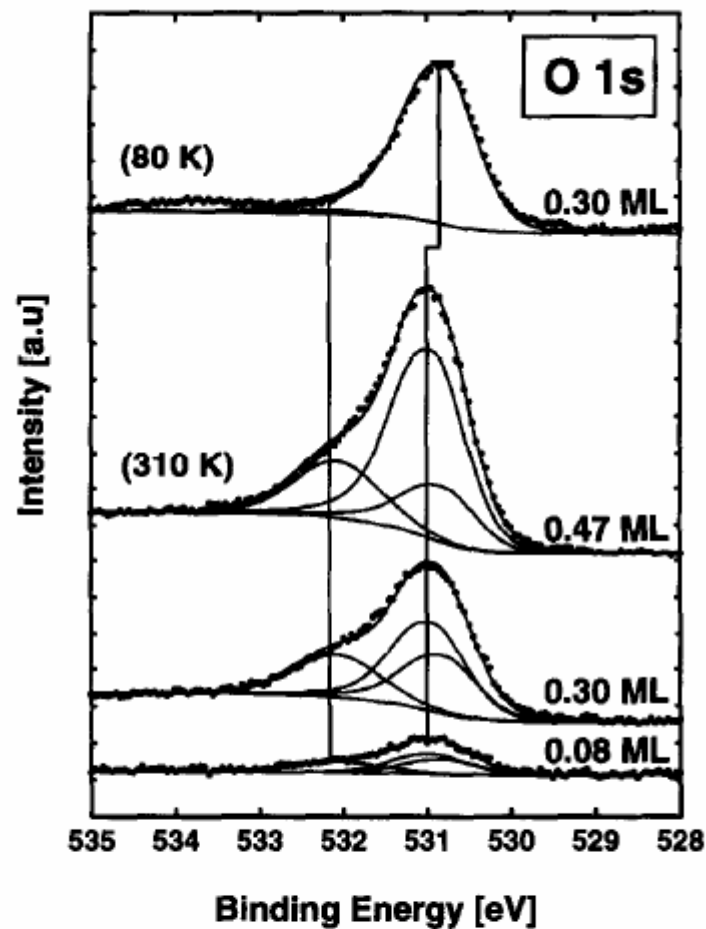


Fig. 5. High resolution O 1s XP spectra ( $\hbar\omega = 1486.6$  eV, polar emission angle:  $65^\circ$  from the surface normal) for 0.30 ML CO recorded at 80 K (top spectrum) and 0.08, 0.30, and 0.47 ML CO recorded at 300 K. The solid lines are fits using the peak positions found for the low temperature layers. The small feature around 534 eV in the topmost spectrum is due to adsorption of residual CO<sub>2</sub> gas at 80 K.

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M. Kinne, T. Fuhrmann, C. M. Whelan, J. F. Zhu, J. Pantförder, M. Probst, G. Held, R. Denecke, and H.-P. Steinrück  
J:Chem. Phys117, (2002) 10852

- The kinetics of the adsorption system CO/Pt(111) has been studied by time-resolved high-resolution x-ray photoelectron spectroscopy using third generation synchrotron radiation at BESSY II.
  - The site-specific occupation of CO adsorbed on on-top and bridge sites is determined quantitatively from C 1s spectra, which can be taken with a minimum collection time of 1.5 s per spectrum.
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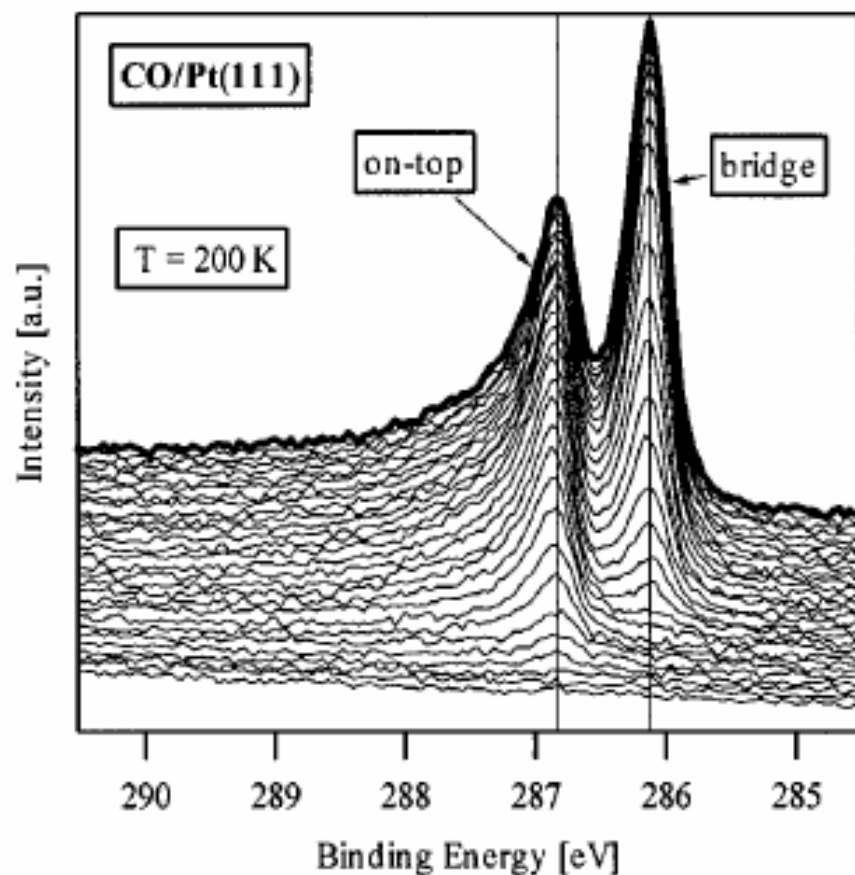


FIG. 2. Normal emission C 1s XP spectra taken during the uptake of CO,  $h\nu=380$  eV; bold line:  $c(4 \times 2)$  LEED structure observed after measurement. Time between spectra 60 s,  $p=1.7 \cdot 10^{-9}$  mbar, time per spectrum 4.8 s. For binding energy values, see text.

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Figure 2 shows C 1s spectra of a CO uptake measurement at a pressure of  $1.7 \times 10^{-9}$  mbar and a sample temperature of 200 K, which is well below the CO desorption temperature found in TPD experiments. Two well separated, asymmetric peaks evolve with CO exposure. The high binding energy peak, located at 286.8 eV, appears first, followed by a second peak at 286.1 eV for higher doses. In agreement with EELS results, the high binding energy peak is related to linearly bound (on-top) CO, and the low binding energy peak to twofold coordinated (bridge) CO.

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J.Stöhr and R.Jaeger

Phys.Rev.B 26, (1982) 4111

NEXAFS spectra are reported for CO on Ni(100) at both C and O K-edges and compared with gas-phase data.

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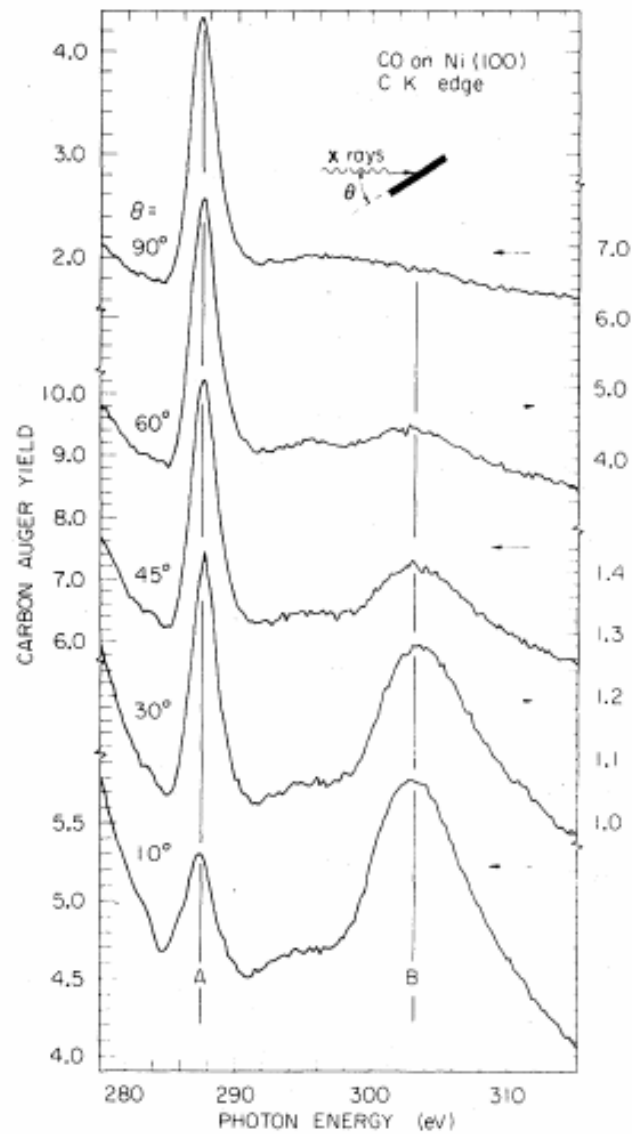


FIG. 10. NEXAFS spectra above the C K edge for CO on Ni(100) at  $T=180$  K as a function of incidence angle  $\theta$ .

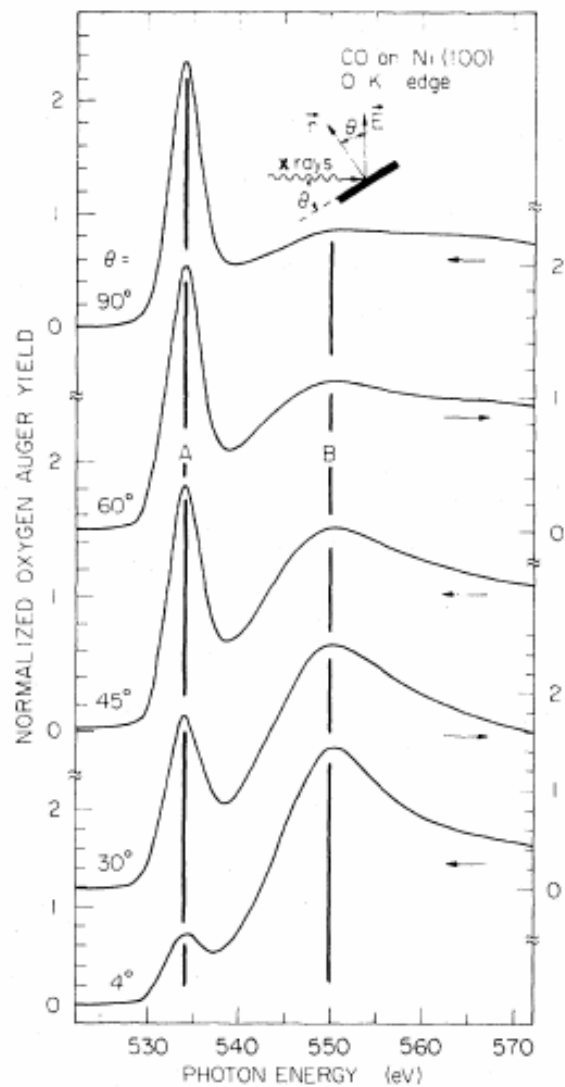


FIG. 12. Background subtracted NEXAFS spectra for CO on Ni(100) above the O K edge.

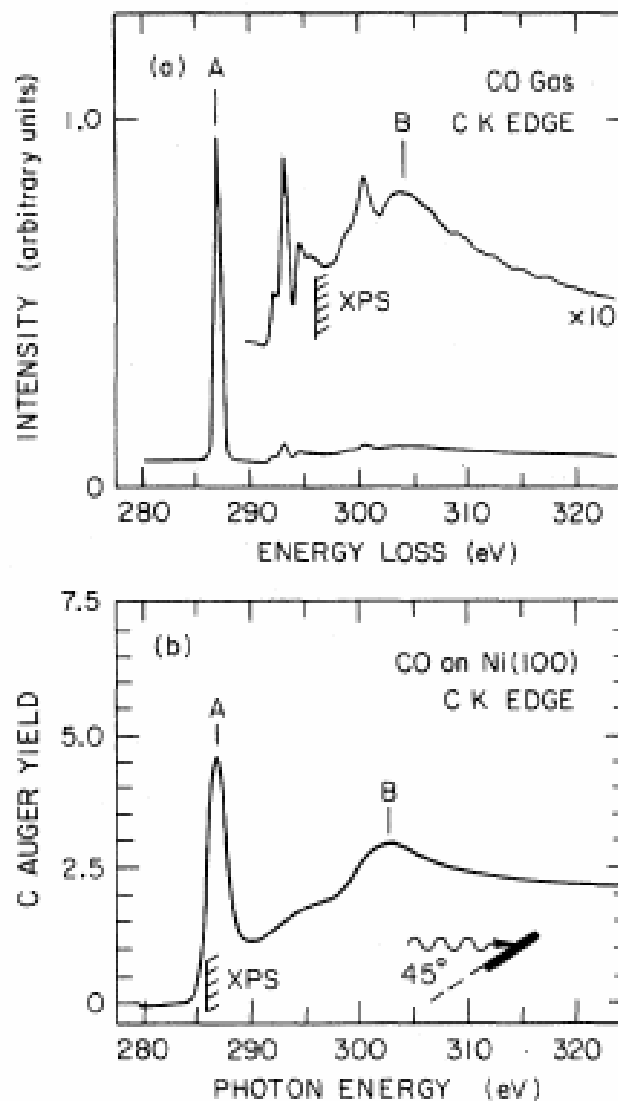


FIG. 17. Comparison of gas-phase (Ref.8) (a) and chemisorbed (b) absorption-edge fine structure near the C K edge for molecular CO. Photoemission binding energies (ionization potentials) are denoted by XPS.

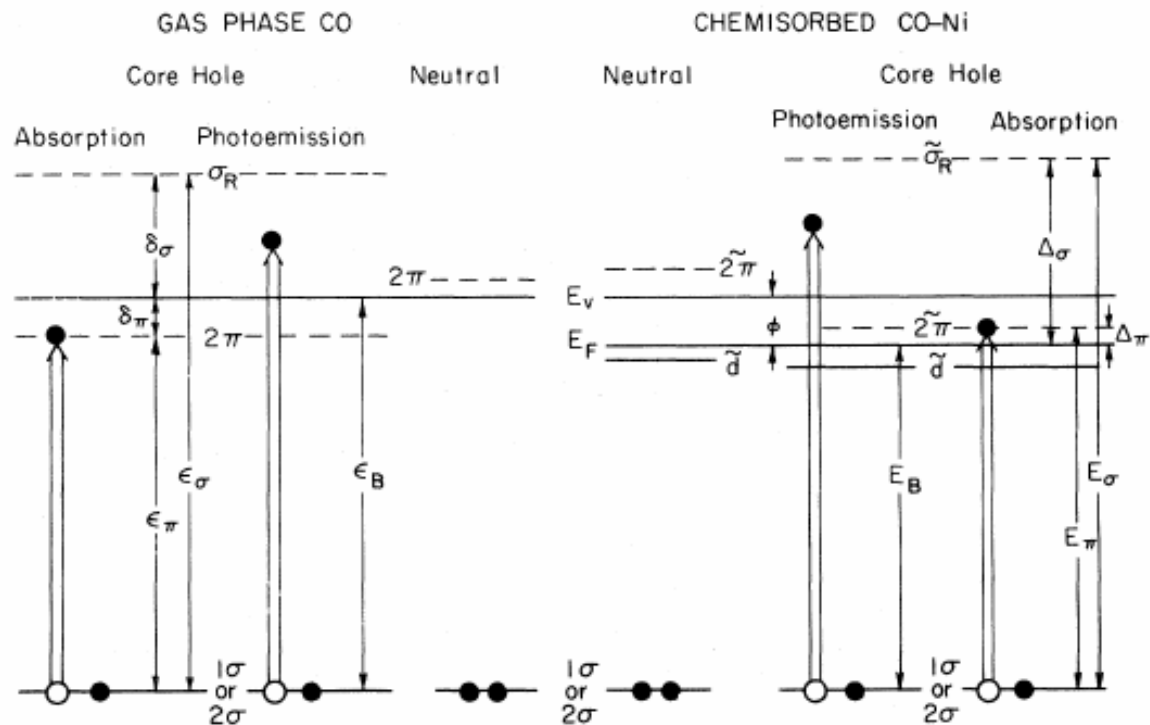


FIG. 18. Energy-level diagram for gas-phase and chemisorbed CO for the neutral (ground-state) and excited (core-molecule).  $E_B$  and  $\epsilon_B$  are the one-electron binding energies measured in photoemission and  $E_\pi$ ,  $\epsilon_\pi$ ,  $E_\sigma$ , and  $\epsilon_\sigma$  the resonance positions measured in an absorption experiment.

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Both spectra at C- and O K-edges show a pronounced polarization dependence, hinting for the  $\pi$  orbital being parallel to the surface and therefore at CO molecules standing up. The comparison with gas phase confirms the amolecular nature of the adsorption and the fact that the adsorbed molecules are not too strongly perturbed with respect to the free molecules.

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W. Braun, H.-P. Steinrück, G. Held

Surface Science 575 (2005) 343–35

The surface geometries of the  $p(\sqrt{7}\times\sqrt{7}) R19^\circ$ -(4CO) and  $c(2\times 4)$ -(2CO) layers on Ni{111} and the clean Ni{111} surface were determined by low energy electron diffraction structure analysis. For the clean surface small but significant contractions of  $d_{12}$  and  $d_{23}$  (both 2.02 Å) were found with respect to the bulk interlayer distance (2.03 Å). In the  $c(2\times 4)$ -(2CO) structure these distances are expanded, with values of  $d_{12} = 2.08$  Å and  $d_{23} = 2.06$  Å and buckling of 0.08 and 0.02 Å, respectively, in the first and second layer. CO resides near hcp and fcc hollow sites with relatively large lateral shifts away from the ideal positions leading to unequal C–Ni bond lengths between 1.76 and 1.99 Å.

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For the  $p(\sqrt{7}\times\sqrt{7}) R19^\circ$ -(4CO) layer two best fit geometries were found, which agree in most of their atomic positions, except for one out of four CO molecules, which is either near atop or between bridge and atop. The remaining three molecules reside near hcp and fcc sites, again with large lateral deviations from their ideal positions. The average C–Ni bond length for these molecules is, however, the same as for CO on hollow sites at low coverage. The average C–Ni bond length at hollow sites, the interlayer distances, and buckling in the first Ni layer are similar to the  $c(2\times 4)$ –(2CO) geometry, only the buckling in the second layer (0.08 Å) is significantly larger. Lateral and vertical shifts of the Ni atoms in the first layer lead to unsymmetric environments for the CO molecules.

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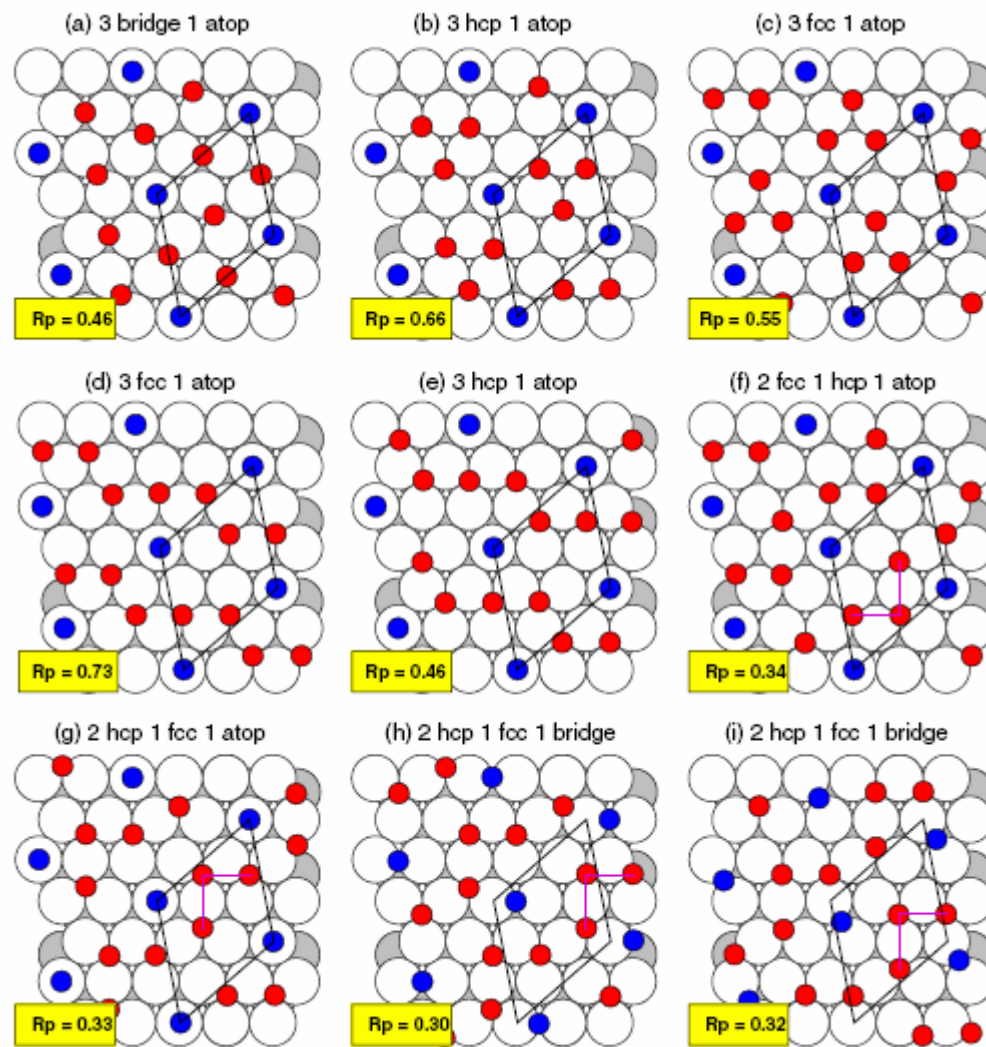


Fig. 3. Structure models tested in the search for the best fit geometry for  $p(\sqrt{7} \times \sqrt{7})R19^\circ-(4CO)$  on  $Ni\{111\}$ .

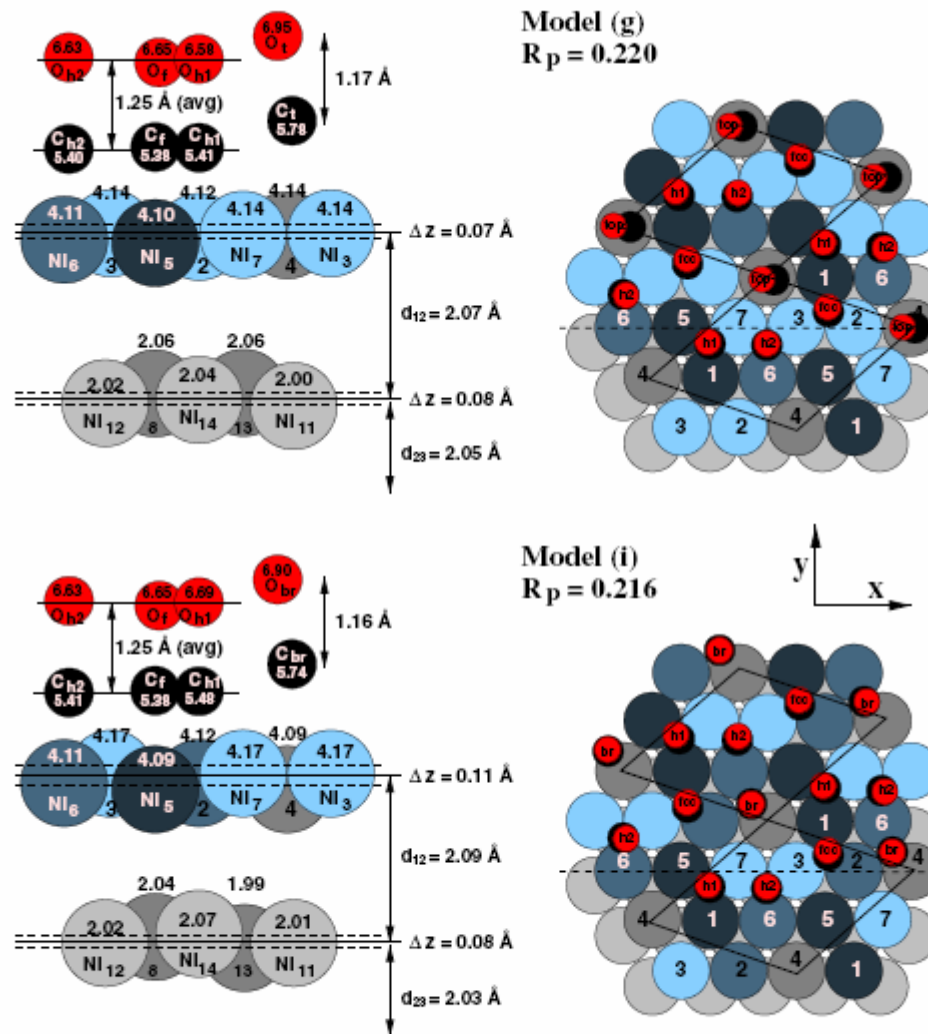


Fig. 4. Best fit geometries of models (g) and (i) for  $p(\sqrt{7} \times \sqrt{7})R19^\circ-(4CO)$  on  $Ni\{111\}$ . Left: side views, cut along the  $[1\bar{1}0]$  direction; for clarity one 'h2' molecule is omitted. Right: top views, the dashed line indicates the  $[1\bar{1}0]$  direction; some CO molecules are omitted at the bottom of the drawings for clarity. The labels of the atoms are the same as in Table 2.

- Two out of four CO molecules in the surface unit cell adsorb near hcp hollow sites and one near a fcc site with an average Ni–C bond length around 1.92 Å and an average C–O bond length of 1.25 Å.
- The fourth CO molecule adsorbs near the atop site above Ni<sub>4</sub> with a C–Ni bond length between 1.67 and 1.86 Å.
- The Ni interlayer distances are around  $d_{12} = 2.08$  Å and  $d_{23} = 2.04$  Å. This corresponds to an expansion of 3% and 1%, respectively, with respect to the clean surface.
- Buckling in the first Ni layer is around 0.09 Å (between 0.07 and 0.11 Å), with unequal heights of the Ni atoms surrounding the hcp and fcc adsorption sites.
- Buckling in the second Ni layer is around 0.08 Å.