

SURFACE SCIENCE STUDIES OF MOLECULAR ADSORBATES ON SOLID SURFACES: A SERIES OF CASE STUDIES

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ABSTRACT. One goal of surface science studies is to unravel the changes in electronic and geometric structure a molecule experiences when bound to a substrate surface. In spite of the vast knowledge on molecular adsorbates on solid surfaces there are only very few examples where detailed and rather complete experimental information on the geometric and electronic structure has been collected. One example is the CO(2x1)p2mg/Ni(110) system and we shall discuss this case to exemplify the power of electron spectroscopic studies in this respect.

In light of the question "*How do surface science studies contribute relevant information to mechanistic problems in catalysis?*" we discuss the interaction of molecules with single crystal surfaces of metal and oxide surfaces as monitored with HREELS, TDS, ARUPS, XPS, and NEXAFS.

- We shall discuss the bonding of N₂ to a Fe(111) surface as the prototype system for a small molecule on a metal surface. This system is of some importance with respect to ammonia synthesis.

In connection with methanol synthesis from CO and H₂ the question of the role of CO₂ in the leading step of the mechanism has turned up. We consider systems where CO₂ is known to chemisorb and discuss possible consequences for the above catalytic reaction.

As an example for a rather complex reaction we shall discuss results for benzene on Os(0001) where we find interesting intermediate species on the way from molecular adsorption to complete dissociation.

The overwhelming majority of catalytic reactions takes place on oxide surfaces. Molecular adsorbates on various oxides and their bonding towards the oxide surfaces are discussed and compared with metal surfaces. We consider NiO(100) and Cr₂O₃(111) surfaces interacting with small molecules such as CO, NO, NO₂ and CO₂.

1. Introduction

Among the goals of surface science is the study of the changes in electronic and geometrical structure a molecule experiences when bound to a substrate surface. Quantum mechanically speaking the electronic part of the wavefunction with the wavefunction of the nuclei have to be studied. Of course, a large step towards an understanding of the system is the determination of its symmetry because both the electronic and the nuclear part of the wavefunction transform with respect to the same point or space group. Most of our knowledge of adsorbates stems from electron scattering and/or electron spectroscopy in their variations. Due to the very strong interaction of the electrons used as information carriers with the electrons of the systems, in most cases the geometric (nuclear) structure is indirectly deduced from electronic structure determinations [1,2,3].

This implies that, while we know quite a bit about symmetry properties of adsorbates, i.e. quantities such as orientation of molecular axes or planes, position of mirror and glide planes in two dimensionally ordered systems, our actual knowledge of bond lengths and bond angles is very limited. In the following we use the system CO(2x1)p2mg/Ni(110) as an example [4-11] to demonstrate how electron spectroscopy [6,8,10,11] and electron scattering [9] may be used in this context.

It should be familiar at this point to the reader that CO almost always binds to metal surfaces with its carbon atom oriented towards the surface and the oxygen atom sticking out into the vacuum such that the molecular axis is more or less ($\pm 10^\circ$) oriented perpendicularly with respect to the surface plane [1,2,3]. The so called "light-house" effect in connection with the molecular shape resonance of the oxygen 4 σ -lone-pair of CO has been employed to come to this conclusion experimentally [1-3]. We shall come back to this when we discuss the N₂/Fe(111) system [12,13]. The bonding of CO towards metal surfaces may be basically described by the Blyholder model [14], i.e. by the synergetic action of a 5 σ -donative and a 2 π -backdonative interaction. This leads to a relative shift of the 5 σ ionization towards, and often beyond (which means to higher binding energy) the 1 π ionization while the relative 4 σ ionization energy remains basically unperturbed [1-3]. Our description so far is valid for a single CO molecule interacting with a metal surface. It has to be modified if the adsorbed CO forms an ordered two dimensional array [1-3].

2. How electron spectroscopy is applied to the study of adsorbates

Exposure of a clean Ni(110) surface to CO at T ~ 120 K leads to the formation of a dense CO overlayer with coverage $\theta = 1.0$ which gives rise to a (2x1) LEED pattern [4] (Fig. 1a). This LEED pattern is characterized by spot extinctions along the (110) direction, indicating the existence of a glide plane. Without a detailed I/V analysis it is not possible to tell whether the space group is p1g1 or p2mg. In the former case there is only one glide plane in the (110) direction, in the latter case there is additionally a mirror plane in the (001) direction of the substrate.

Photoemission may be used to decide this problem [10]. Firstly, the symmetry of the wave functions is reflected in the transition matrix elements which determines the differential photoemission current [1-3]:

$$d\sigma/d\Omega \propto |\langle \Psi_f | p | \Psi_i \rangle|^2$$

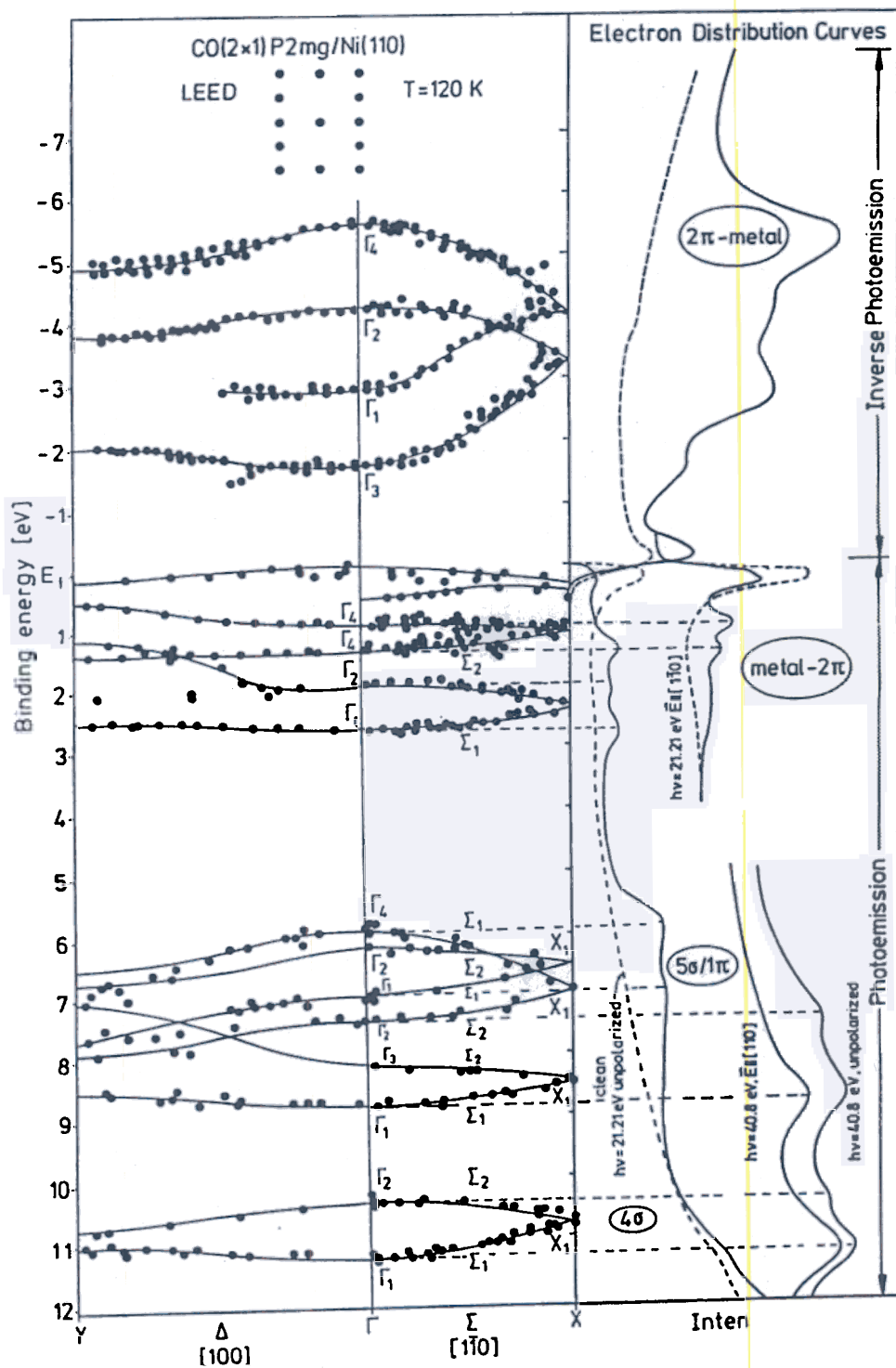


Figure 1. Band structure of the occupied and the unoccupied valence bands of CO(2x1)p2mg/Ni(110). On the right hand side IPE spectra (upper right panel) and photoelectron spectra (lower right panel) of the adsorbate system are shown. The band structure of the unoccupied states and the inverse photoemission spectra have been reproduced from ref. [11].

where Ψ_f and Ψ_i are the final and initial state wave functions involved in the ionization process and p is the momentum operator the direction of which may be varied by changing the polarization of the light. Secondly, the ordering in the adsorbate layer causes a band structure to develop, which reflects the symmetry of the system.

Fig. 1 shows the band structure of the system as determined by measuring the binding energies of the CO induced features as a function of the electron emission angle along two azimuths with respect to the Ni(110) substrate, i.e. the (110) and the (001) directions. Together with the experimental data we reproduce the result of a band structure calculation [6]. On the right hand side of the collected dispersion data [6,10,11] we show a set of photoelectron spectra at the Γ -point (normal emission), measured using unpolarized light of a He discharge source. Clearly, the number of outer valence features is larger than four, which would be the maximum number of features for a single molecule within the unit cell, i.e. 5σ , 4σ and two 1π components. This indicates that the unit cell contains more than one molecule. The region of the energetically well separated 4σ emissions points to a splitting into two features consistent with two molecules in the unit cell.

The different dipole selection rules for the $p2mg$ and the $p1g1$ symmetry groups can be used to decide whether the system possesses $p2mg$ or $p1g1$ symmetry. According to the $p2mg$ selection rules Γ_4 bands can only be observed with light polarized along the (110) azimuth whereas in $p1g1$ these states can also be ionized with light polarized perpendicular to the surface. The result of such a test is shown in Fig. 2. For the upper spectrum light polarized predominately along (110) was used whereas in the lower spectrum the component of the electric field vector along (110) was zero. If the adsorbate symmetry were $p1g1$ the $1\pi_x^+$ state, which transforms according to Γ_4 , should also be visible in the lower spectrum. Since this is not the case we conclude that the adsorbate symmetry is most likely $p2mg$ and not $p1g1$.

Considering the coverage $\theta=1$ and the symmetry of the overlayer, the structure model in Fig. 3 [6] is a reasonable first guess. The CO molecules are canonically bound carbon end down (see above) and tilted along the (001) azimuth in order to avoid the close intermolecular contact along (110) with a separation below $3\text{\AA}$ which could occur if the molecules were oriented perpendicularly.

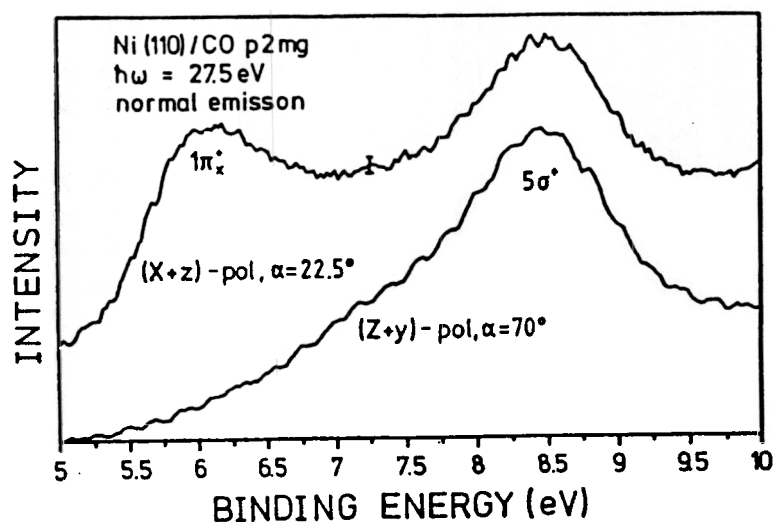


Figure 2. Photoelectron spectra of CO(2x1)p2mg taken with different polarizations of the incident light.

Geometric structure of Ni(110)/CO(2×1)p2mg

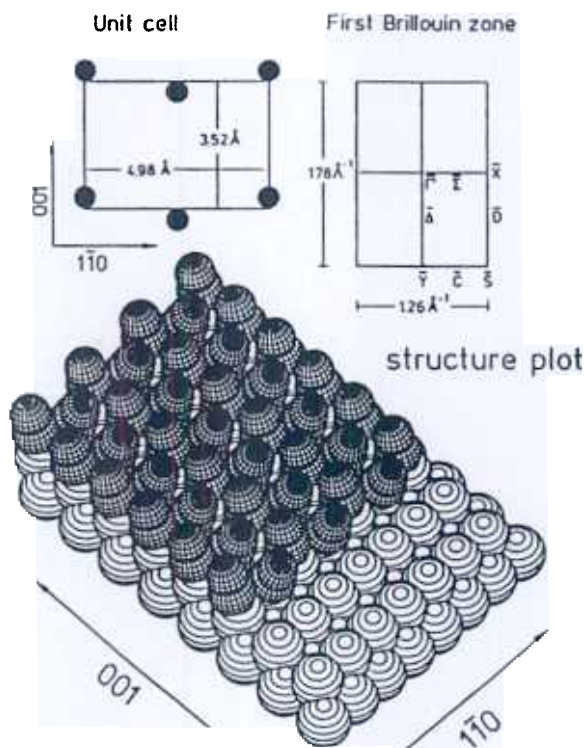


Figure 3. Upper left panel: Size, points, and lines of high symmetry within the Brillouin zone. Lower panel: Structure plot of the CO(2×1)p2mg adsorbate layer.

The determined band structure in the region of occupied (by angle resolved ultraviolet photoelectron spectroscopy, ARUPS) and unoccupied (by inverse photoelectron emission, IPE) states as shown in Fig. 1 reflects the structure of the adsorbate layer throughout the entire Brillouin zone. Two directions in k -space are plotted, i.e. the (110) direction of the glide plane, and the mirror plane direction (001). The solid lines are the result of a tight-binding calculation and the relatively good agreement between experiment and calculation reflects the fact that the observed band structure is mainly determined by the strong intermolecular repulsion of the CO molecules [6]. As stated above, the presence of two CO molecules per unit cell leads to a doubling of the number of bands at Γ and throughout the Brillouin zone, except for the line X-S, where the glide plane symmetry only allows degenerate bands. The individual band dispersions reflect the different strengths of intermolecular interaction, which the individual CO levels with their different extension of the radial wave functions experience.

Fig. 4 represents schematically two dimensional wave functions consisting of σ -type orbitals (left panel) and of π (π_x , π_y)-type orbitals (two right panels) at the Γ point [6]. The bonding and the antibonding combinations are shown. Consider Fig. 4 (left panel) to represent the 4σ orbital of CO. The splitting between the two components may be taken from experiment to be 0.85 eV. This value should be compared with 1.3 eV for the splitting between the 5σ levels, which hybridize with the $1\pi_x$ component. The increase

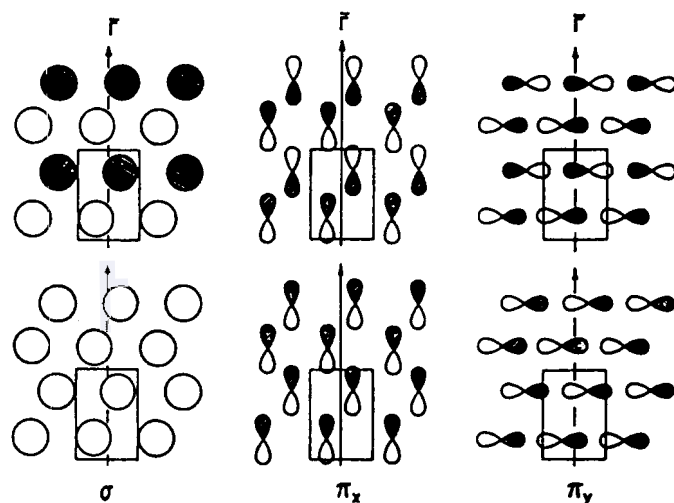


Figure 4. Symmetric and antisymmetric linear combinations of two dimensional wave functions of σ , π_x , and π_y symmetry at the Γ point of the (2×1) $p2mg$ Brillouin zone.

reflects the larger radial extent of the 5σ -carbon-lone-pair, as compared with the 4σ -oxygen-lone-pair. In addition, however, substrate mediated interaction is important for the 5σ levels, because they establish part of the bonding to the metal. The largest splitting in the occupied bands is observed for the $1\pi_x$ component reaching a value of almost 2.1 eV, while the $1\pi_y$ component splitting (0.8 eV) is relatively small. From Fig. 4 it is obvious that the direct overlap is the origin for this finding. On the other hand the 2π emission observed by IPE [11], and plotted in Fig. 1, exhibits even larger splitting for both, the $2\pi_x$ (3.8 eV) and the $2\pi_y$ (1.2 eV) components. This may be caused again by substrate mediated interaction due to 2π -backdonation, but an additional role may be played by the 2π wavefunctions themselves, which are expected to be considerably more diffuse as compared with the 1π levels.

A direct observation of the substrate mediated interaction is possible by following the CO induced features in the region of the metal band structure, i.e. between the Fermi energy and a binding energy of 3 eV [10]. In this energy range Fig. 1 shows bands which exhibit dispersions of up to 0.5 - 1.0 eV indicating a substantial contribution of this type of interaction. The magnitude of the dispersion may be correlated and explained by the interaction of the metal levels involved in the CO 2π -metal backbonding. We refer to the literature [10] for details.

Even though photoemission [6,10] and inverse photoemission data allow one to draw rather detailed conclusions on the intermolecular interactions and the electronic structure of the CO-metal bond, it is not possible in a straightforward manner to determine the site of adsorption, namely whether the molecule is terminally or bridge bonded to the surface. This may be done considering electron energy loss data recorded with very high resolution by H. Ibach and his group [9]. In the present case a simple decision on the basis of frequencies is not possible because the observed value, close to 1900 cm^{-1} , is on the border between on-top and bridge site frequencies. It is even more complicated in the present case. One spectrum showing all relevant features together with the phonon dispersions is shown in Fig. 5 [9]. The assignment of the modes is discussed in detail by Voigtländer et al [9]. Briefly, for a CO adsorbate system ($2000 - 1800\text{ cm}^{-1}$) we expect four or six normal modes depending on whether the CO molecule is bound on-top or via a bridge site.

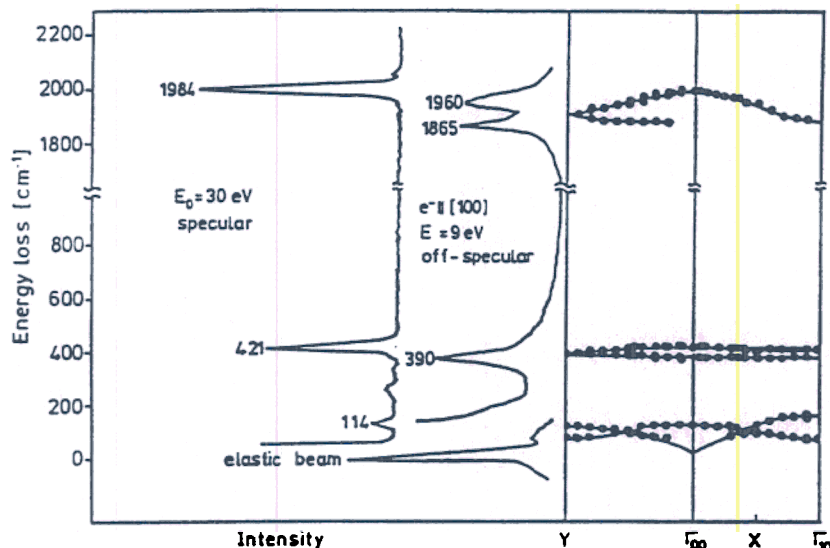


Figure 5. Electron energy loss spectra and phonon dispersion curves for the CO(2x1)p2mg/Ni(110) adsorbate. Data have been taken from ref. [9].

Schematic representations [9] are depicted in Fig. 6. In addition to the CO stretch (ν_2) which are located at different frequencies depending on the site, we expect one degenerate (for on-top site) and two non degenerate (for bridge site) "frustrated" rotations and in the same way "frustrated" translational modes. On the basis of cluster calculations for CO on Ni(100) the vibrational frequencies of the modes have been estimated [15]. Interestingly, the degenerate frustrated rotation for on-top sites should be situated slightly below the metal CO stretch, while for bridge sites the splitting of the degenerate mode is large so that the two components are located well above and below the metal-CO stretch. A measurement of the frustrated rotations of the system would thus allow us to differentiate between on-top and bridge site. However, to apply these considerations to our adsorbate of p2mg symmetry we have to take into account that there are two molecules in the unit cell, which introduces an additional, so called Davydov splitting of the vibrational modes. The splitting documents the fact that even and odd linear combinations of the normal modes of the individual molecules have to be formed and the linear combinations are not necessarily degenerate. The magnitude of the Davydov splitting and thus the observation of additional dispersions depends on the CO-CO intermolecular interaction, which may be classified according to direct through-space-interaction to indirect substrate mediated dipole-dipole interactions, and to interactions arising from the dynamic dipole moments of the CO molecules. Voigtländer et al. [9] have shown that it is mainly dipole-dipole interaction that determines the Davydov splitting although strong direct through-space-overlap causes the adsorbate to exhibit p2mg symmetry in the first place.

The most prominent effect of a Davydov splitting is observed for the CO stretch. The mode at 1984 cm^{-1} (at Γ) is the totally symmetric mode with both CO molecules in the unit cell vibrating in phase. This mode is observed in specular scattering and throughout the entire Brillouin zone. The mode with the CO molecules vibrating out of phase situated at lower frequencies is even with respect to the mirror plane and odd with respect to the glide plane. It is therefore not observed at Γ but along Γ -Y at off-specular scattering along the (001) azimuth. For electron scattering along (110) the even eigenmodes are observed only in the first Brillouin zone, the odd eigenmodes in the second. At the zone boundary

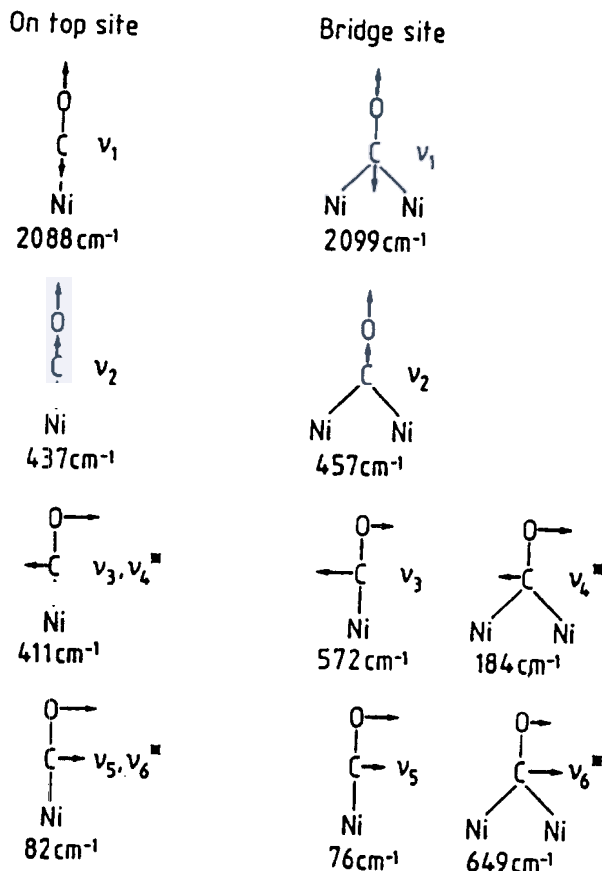


Figure 6. Schematic diagrams of the normal modes of CO adsorbed on-top sites and on bridge sites, and calculated loss energies for CO(2x1)p2mg/Ni(110). Data have been taken from ref. [9].

both modes are degenerate by symmetry. Therefore the modes appear as one mode without splitting in the dispersion curve from Γ_{00} to Γ_{10} . Also the other modes are expected to be split into even and odd combinations. However, the observed small dispersion, implying a small splitting of the losses at 422 and 385 cm^{-1} , prohibits the observation. The mode split off from the 113-60 cm^{-1} vibration which lies at 60 cm^{-1} at Γ has too low a frequency to be observed.

Summarizing the arguments at this point [9], the modes reproduced in Fig. 6 represent all modes of the system including the additional modes caused by the Davydov splittings. Clearly, the number of modes in the frustrated rotation-translation regime is not consistent with a bridge site. Therefore we must conclude that the molecule is bound on-top of the Ni atoms towards the surface. HREELS (high resolution electron energy loss spectroscopy) provides us thus with a further important structural detail of the adsorbate.

Further information on the CO-Ni bonding may be deduced from the HREELS data: The quantitative theoretical description of the dispersion data is more sensitive to the displacement of the center of gravity of the CO molecules from the ideal on-top position and not so strongly sensitive to the tilt angle of the molecular axis. On the other hand XPD (X-ray photoelectron diffraction) data [8] of the system which are reproduced in Fig. 7 are dominated by the angular information. The XPD data, i.e. the variation of the

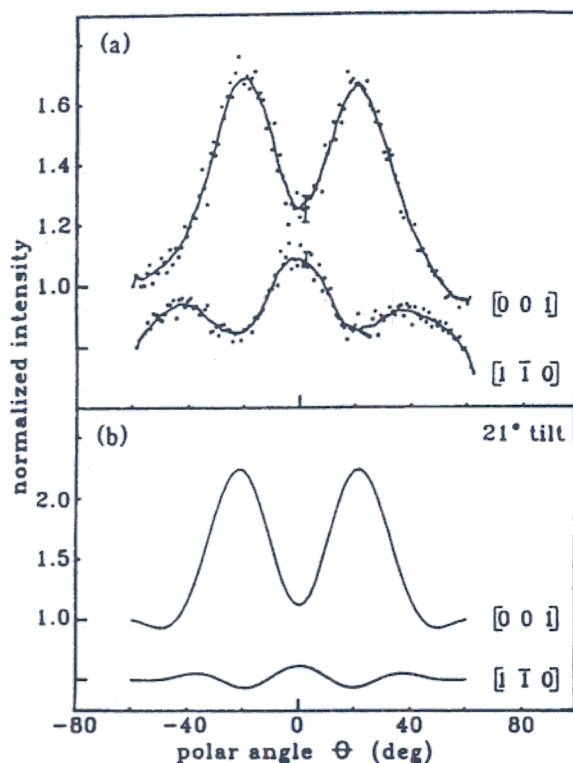


Figure 7. C1s intensity normalized to the O1s intensity as a function of the electron detection angle along two high symmetry azimuths of the CO(2x1)p2mg adsorbate on Ni(110). In the lower panel calculated curves for a CO tilt angle of 21° are shown. Data have been taken from ref. [8].

C1s emission intensity as a function of polar angle, indicates a tilt angle of 20° , very similar to the value deduced from ESDIAD (electron stimulated desorption of ions' angular distribution) [5,7] and ARUPS [6] data. Since the lateral displacement deduced from the vibrational data may be converted to a tilt angle of 20° in agreement with XPD we may conclude that the axis of the displaced CO molecule still points towards the center of the Ni atom of the first layer.

In light of the question: "How do surface science studies contribute relevant information to mechanistic problems in catalysis?" we discuss the interaction of molecules with single crystal surfaces of metal and oxide surfaces as monitored with HREELS, TDS, ARUPS, XPS and NEXAFS.

3. Case studies

3.1. CASE 1: N₂/Fe(111)

We shall discuss the bonding of N₂ to a Fe(111) surface [13] as the prototype system for a small molecule on a metal surface. This system is of some importance with respect to ammonia synthesis, where it has been shown by Ertl and his group [12] that N₂ dissociation on Fe is the rate limiting step in the formation of NH₃ from N₂ and H₂.

Adsorption of molecular nitrogen and its subsequent dissociation into atomic nitrogen on Fe(111) has been studied in some detail in recent years [12,16-19]. Two weakly chemisorbed molecular N_2 states have been identified mainly via high resolution electron energy loss spectroscopy (HREELS) [20-22], X-ray photoelectron spectroscopy (XPS) [20], and thermal desorption spectroscopy (TDS) [21,22]. In the so called γ -state, with an adsorption enthalpy of ~ 24 kJ/mol [19], the N_2 molecules are terminally bonded to first layer Fe atoms [22]. The slightly more strongly bound α -state, with an adsorption enthalpy of ~ 31 kJ/mol [20], which is the precursor to N_2 dissociation on the surface, has been attributed to N_2 π -bonded to the surface [20]. While the γ -state has recently been found to have a vibrational N-N stretching frequency of 2100 cm^{-1} [20], the α -state exhibits an unusually low stretching frequency of 1490 cm^{-1} [20], which in turn was used to infer together with XPS results the π -bonded nature of the state [20].

The separation of α - and γ -states by an activation barrier allows one to selectively depopulate the γ -states at higher temperature (110 K), while at lower temperature (below 77 K) α - and γ -states are both populated as has recently been clearly demonstrated through HREELS studies [22].

Fig. 8 shows the HREEL spectra at $T = 74$ K (a) dominated by the γ -state and at $T = 110$ K (b) dominated by the α -state. After heating the surface to $T = 160$ K both molecular states are no longer present on the surface [20-22].

Even though the cited HREELS and XPS results suggest that the α -state interacts "side-on" with the metal, the presented HREELS experimental results do not allow conclusions about the geometric structure. Unfortunately, a LEED structure analysis cannot be undertaken due to the lack of any sharp adsorbate induced pattern for molecular N_2 adsorption on Fe(111). Results of theoretical calculations [23] indicate that the γ -state is bonded normal, the α -state parallel to the surface. ARUPS is the method of choice to actually determine the orientation of the molecular axis. The directional properties of the so called shape resonance [24,25] may be used to approach the problem. Fig. 9 shows a schematic representation of the molecular states involved in the excitation processes. The

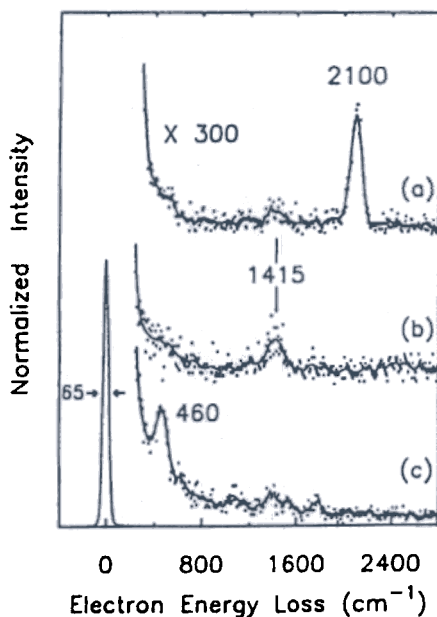


Figure 8. HREELS data for $^{15}N_2$ on Fe(111) taken at different temperatures. a) $T = 74$ K, b) annealed to $T = 110$ K, c) annealed to $T = 160$ K. Data have been taken from Ref. [22].

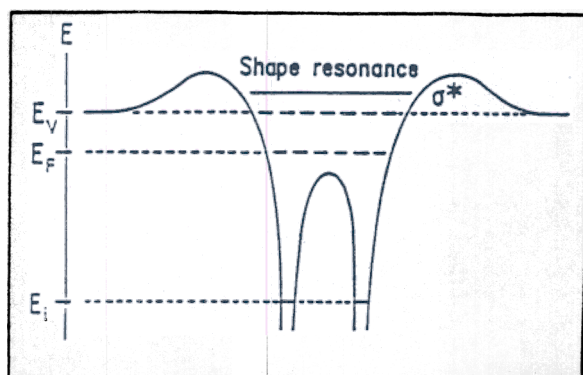


Figure 9. Schematic potential energy diagram for a diatomic molecule like N_2 .

molecular potential may be thought of as created by the superposition of the atomic potentials. Due to the centrifugal barrier the molecular potential exhibits potential energy barriers which lead to resonances within the continuum. These resonances may be connected with highly excited unoccupied orbitals. In the case of the diatomics this orbital is the antibonding σ -bond orbital. Since these resonances can be assigned to an irreducible representation of the molecular point group, selection rules are operative in the population of these states. In the present case the σ shape resonance may be only excited with the light polarization vector pointing along the molecular axis if the initial state of the excitation is a σ -state. Consequently, the electron emitted from the resonance by tunneling through the potential high barrier, propagates along the direction of the molecular axis [1-3]. With ARUPS it should be easy to detect this resonance and determine the direction of the axis. Fig. 10 shows a set of angle resolved spectra as a function of photon energy at low temperature ($T = 77$ K, γ - N_2) and higher temperature ($T = 110$ K, α - N_2) [13]. Fig. 10a reveals the σ -shape resonance in normal emission for z -polarized light at $T \sim 77$ K (see inset for the emission geometry of the experiment). Fig. 10b shows a σ -resonance, but only in off-normal emission for σ -polarized light (compare upper and lower panel of the figure). If we choose the same experimental conditions as for Fig. 10a we only see the 1π emission along the surface normal. The comparison clearly reveals the geometrical change between the γ - and the α -state of adsorbed N_2 . A detailed comparison of the shifts of the photoemission features with respect to the gas phase indicates that although the orientation of the molecular axis in the α -state is strongly inclined with respect to the surface normal the site appears to be non-symmetric [13]. A possible coordination site is shown schematically in Fig. 11. The tilted N_2 molecule binds five iron atoms, so that the surface can only accommodate a small number of N_2 molecules which explains the observed low coverage (10 - 20% of a monolayer) for the α -state [19].

To understand the bonding of N_2 to the surface it has to be noted that for several chemisorption systems the adsorbate molecule can be considered to be an ion state or an excited state molecule stabilized by the substrate [13].

We invoke this hypothesis in the present study for the α - N_2 species and consider which excited states of molecular N_2 might be reasonable candidates to form a surface complex. The lowest excited state of N_2 is the $A^3\Sigma_u$ state [26], which has a vibrational frequency of 1460 cm^{-1} (N_2 ground state $1\Sigma_g$: 2360 cm^{-1}) and a bond length of $1.29\text{ \AA}$ (N_2 ground state: $1.10\text{ \AA}$) and lies 6.22 eV above the ground state. This state has two attractive features as a candidate for the α - N_2 surface complex: (1) the vibrational frequency is very close to that observed for α - N_2 , and (2) the bond length is increased by

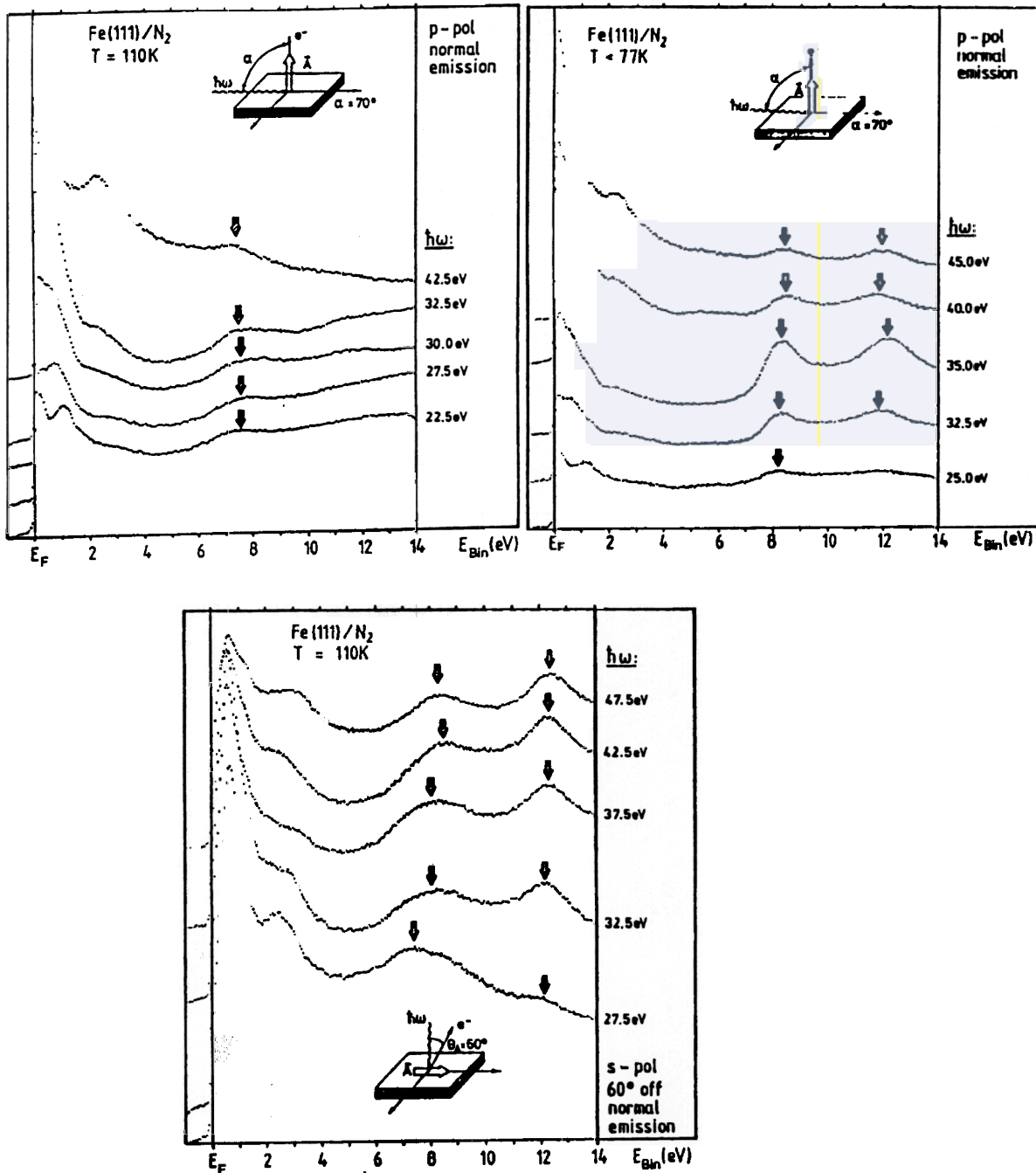


Figure 10a. (upper right panel): Photoelectron spectra in normal emission using p-polarized light as a function of photon energy for the low temperature phase of N₂ on Fe(111). Fig. 10b. (upper left panel): Normal emission photoelectron spectra of the high temperature phase of N₂ on Fe(111) using p-polarized light as a function of photon energy. Fig. 10c. (lower left panel): Normal emission photoelectron spectra of the high temperature phase of N₂ on Fe(111) excited with s-polarized light as a function of photon energy. The electrons have been collected 60° off normal.

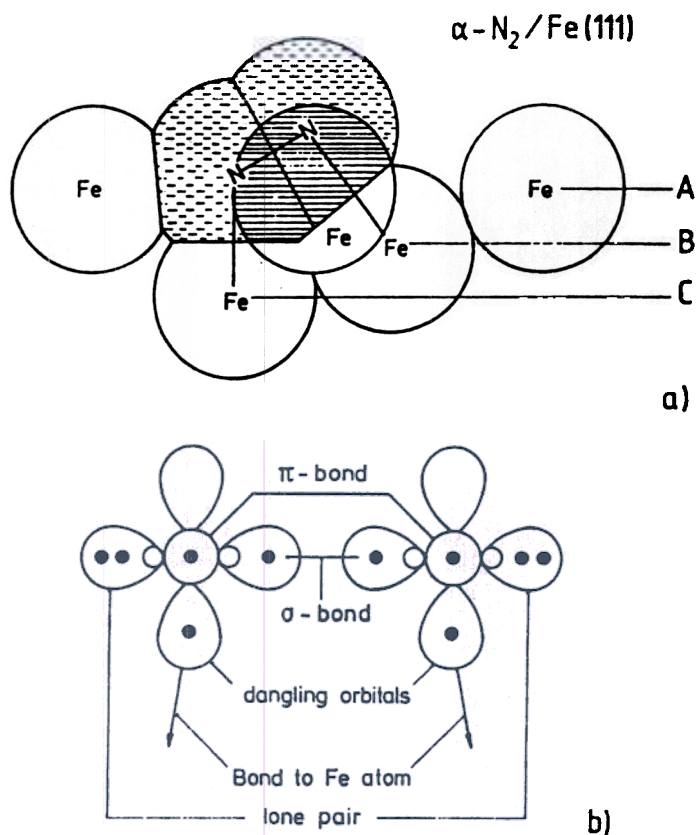


Figure 11. (a) Schematic representation of a possible non symmetric bonding site of $\alpha\text{-N}_2$ on $\text{Fe}(111)$. (b) Schematic representation of the $^3\Sigma_u^+$ excited state of N_2 which can form two covalent bonds towards the metal atoms in the geometry shown in (a).

about $0.2 \text{ \AA}$ from the ground state - an important ingredient for a potential precursor to dissociation. But, the excitation energy of 6.22 eV requires considerable bonding interactions to stabilize this state. However, two covalent nitrogen-iron single bonds can be formed by the $\text{N}_2 (^3\Sigma_u)$ state; each such bond should contribute a bond energy of about 2.5 eV . This is still not sufficient to counterbalance the 6.22 eV excitation energy and the remaining energy would have to be obtained via several dative bond interactions and electrostatic effects due to polarization. It is not unreasonable, therefore, that the combination of these contributions could yield a species consistent with the known properties of $\alpha\text{-N}_2$. By contrast, we expect the $\gamma\text{-N}_2$ state to be the ground state of N_2 ($^1\Sigma_g$) weakly bonded to the surface by a single dative interaction.

A schematic representation (in terms of correlated orbitals of σ - and π -symmetry) of this state as it might bond to the surface is given in Fig. 11 [13]. We note that the state corresponds to a broken " π -bond" with the two resulting dangling orbitals available for forming covalent bonds to the surface. In addition there is the potential for forming several dative bonds in this unique geometrical arrangement. Hence, it appears that the proposed site geometry does offer the considerable bonding interactions which are necessary to stabilize the $^3\Sigma_u$ state. It will require considerable further experimental and theoretical work to test the validity of our proposed bonding model for $\alpha\text{-N}_2$, however we feel it may be valuable as a starting point for discussion to have a definite microscopic model in mind.

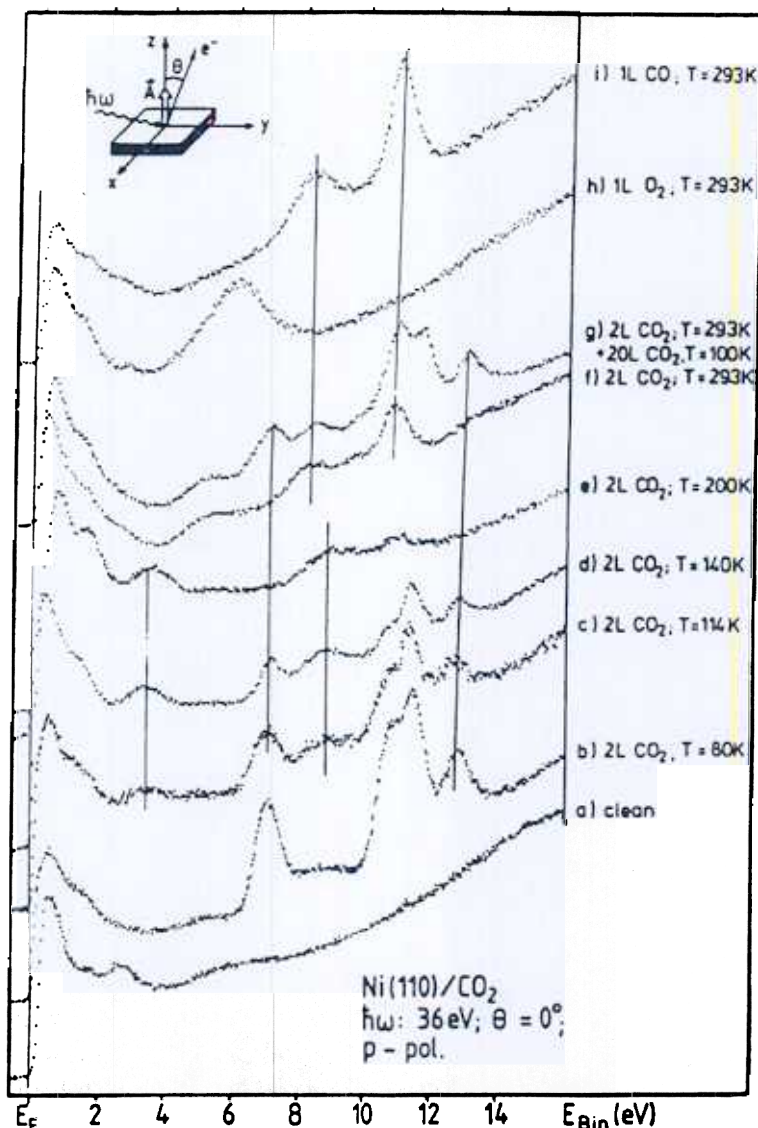
3.2. CASE 2: CO₂/Ni(110)

Figure 12. Photoelectron spectra of a CO₂/Ni(110) adsorbate taken at various temperatures in comparison with a clean (a), an oxygen covered (h) and a CO covered surface (i).

In connection with methanol synthesis from CO and H₂ the question of the role of CO₂ in the leading step of the mechanism has turned up [27]. Also, in connection with the elementary steps in the Fischer-Tropsch reaction, CO₂ adsorption may play an important role [28].

Several groups have studied the adsorption of CO₂ on metal surfaces [29-33], and for a long period of time it was assumed that CO₂ does not chemisorb on metal surfaces without dissociation [34,35]. We have investigated, as an example, interaction of CO₂ with a Ni(110) surface, applying a variety of methods [29,30,33,36]. A series of normal emission ARUP spectra of the system CO₂/Ni(110) [29] in Fig. 12 indicates the usefulness of ARUPS to identify reaction intermediates in favourable cases. At low temperature CO₂ adsorption leads to mixed chemisorbed/physisorbed layers (spectrum b),

and the physisorbed species desorbs selectively by elevating the temperature (spectra b)-e)). Around 200 K a spectrum of the pure chemisorbed species is found which shows three features. One additional feature around 5 eV is forbidden in normal emission, indicating C_{2v} symmetry of the adsorption site. Comparison with results of cluster calculations [37,38] shows that this is a bent anionic CO_2^- -species. Whether the CO_2^- -species is carbon or oxygen bound to the surface cannot be decided on the basis of the ARUPS results alone. However, we shall discuss HREELS results showing that the CO_2^- -species is bound through the oxygen atoms to the surface. Above 200 K (spectrum f)) this species dissociates into CO and O, both adsorbed on the surface, as is clear from a comparison with the spectra of pure CO and O adsorbates (spectra h)-i)). It was concluded from this study that CO_2^- is an intrinsic precursor for CO_2 dissociation [29].

Fig. 13 shows a set of HREELS spectra [29] after dosing a Ni(110) surface at low temperature ($T \sim 170$ K) with CO_2 and heating it up to above 200 K. At low temperature the strong band at 670 cm^{-1} indicates the presence of undistorted CO_2 and has been assigned to the CO_2 bending mode. The loss feature at 2350 cm^{-1} is due to the asymmetric stretch of linear CO_2 and exhibits small but appreciable intensity.

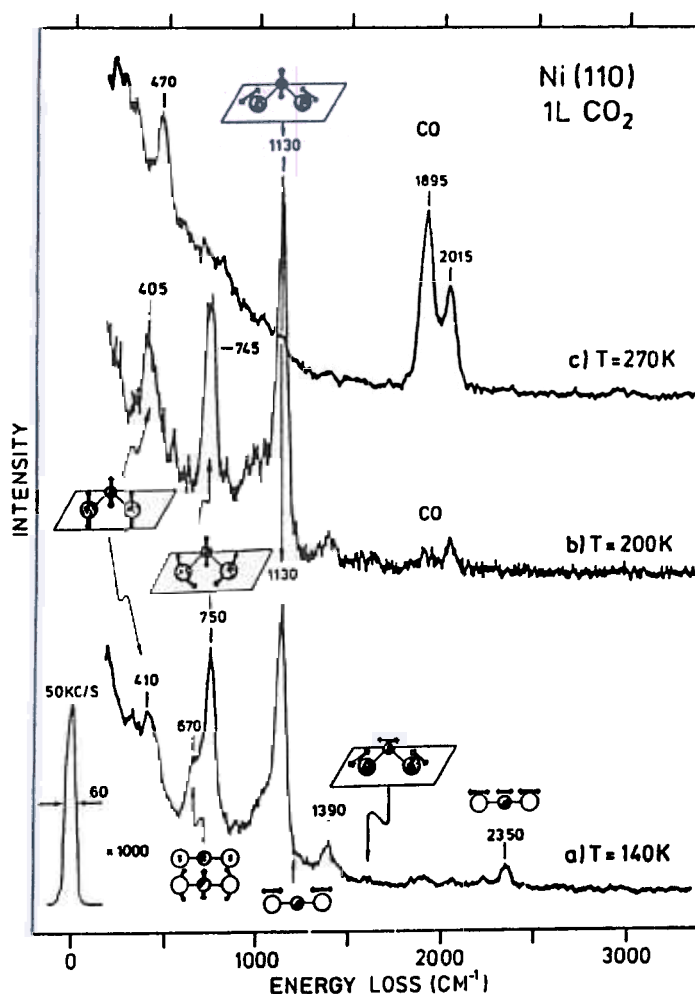


Figure 13. Vibrational electron energy loss spectra of a Ni(110) surface exposed to 1 L CO_2 at 140 K as a function of the annealing temperature.

The dynamic dipoles of the two mentioned CO_2 vibrations behave differently, i.e. the stretching mode is polarized along the molecular axis, the bending mode perpendicularly with respect to the molecular axis. Therefore, if the molecular axis were oriented parallel to the metal surface the stretching mode should be completely screened, if the molecular axis were oriented perpendicular to the metal surface the bending mode should be screened. Both modes are active, however, with the bending mode strongly dominating, which indicates that CO_2 is oriented not quite but almost parallel to the surface.

As has been discussed above in addition to linear CO_2 there is a bent CO_2^δ -species present on the surface which leads to losses at 272 cm^{-1} , at 1103 cm^{-1} , and at 403 cm^{-1} . These losses have been assigned to the bending mode, the symmetric stretch and the molecule-substrate stretching mode of CO_2^δ , respectively. The loss feature at 1352 cm^{-1} has been observed in earlier work [29] and has been attributed to the presence of carbonate. We shall provide conclusive evidence [36] that it is due to the formate symmetric stretch.

If the adsorbate is heated from 90 K to a temperature close to 200 K we observe characteristic changes of the loss intensities.

Firstly, between 120 K and 170 K the features due to linear CO_2 disappear indicating the reaction of this surface species. Note, that upon elevating the temperature the relative intensities of CO_2 bending- and stretching modes change, i.e. the stretching vibration gains intensity. This may indicate a slightly different average adsorbate geometry of linear CO_2 with its axis assuming a smaller inclination with respect to the surface normal at higher surface temperature.

Secondly, while the CO_2 features disappear the CO_2^δ -losses gain intensity suggestive of the earlier finding CO_2 is partly transformed into bent CO_2^δ . As discussed in detail by Bartos et al. [29] before, the asymmetric stretch of the CO_2^δ is missing on Ni(110) due to the C_{2v} symmetry of the adsorbed species.

Above 200 K the CO_2^δ -signal has disappeared and the typical $\text{CO} + \text{O}$ spectrum is observed indicating similar to ARUPS the dissociation of CO_2 to $\text{CO} + \text{O}$. Such processes have been found on several clean and modified (by alkali metal) surfaces [39-46]. In particular alkali appears to promote the process. We have indications that the geometry of the chemisorbed CO_2^δ in the latter case is different from the one on pure Ni(110). One indication is the frequency of the molecule-metal vibration. While we observe a band at 405 cm^{-1} for Ni (110) typical for oxygen-metal vibration we find a band at 282 cm^{-1} compatible with a carbon coordination to the metal [39-41]. We may understand this behaviour on the basis of some simple consideration: the bonding on the unmodified surface is dominated by the greater stability of the oxygen-metal dative bond as compared with the covalent C-Ni bond involving a carbon 2p and a Ni-4s electron. However, if we modify the surface with alkali, a strong surface dipole is created which influences the metal- CO_2^δ -dipole in such a way that the molecule in its trying to maximize the compensation of the alkali-metal dipole has to reorient with respect to the surface.

Obviously, the existence of CO_2^δ on the surface opens up the possibility to try to react this intermediate with other species on the surface. In addition, the reactivity may depend on the CO_2^δ -metal-bond, e.g. it may be different for a clean and a modified surface. In fact, CO_2^δ on Ni(110) readily reacts with coadsorbed hydrogen as is shown in Fig. 14. At low temperature the situation is very similar to the one described above but starting at a surface temperature of $T = 125\text{ K}$. Above temperatures of $T = 200\text{ K}$ the spectrum is very simple. It is characterized by three losses (excluding the CO loss at 1880 cm^{-1}) at 403 cm^{-1} , 727 cm^{-1} and 1353 cm^{-1} , and a very weak loss at 2904 cm^{-1} . The latter one becomes clearly visible at off specular scattering angles (see Fig. 14). Clearly this is the

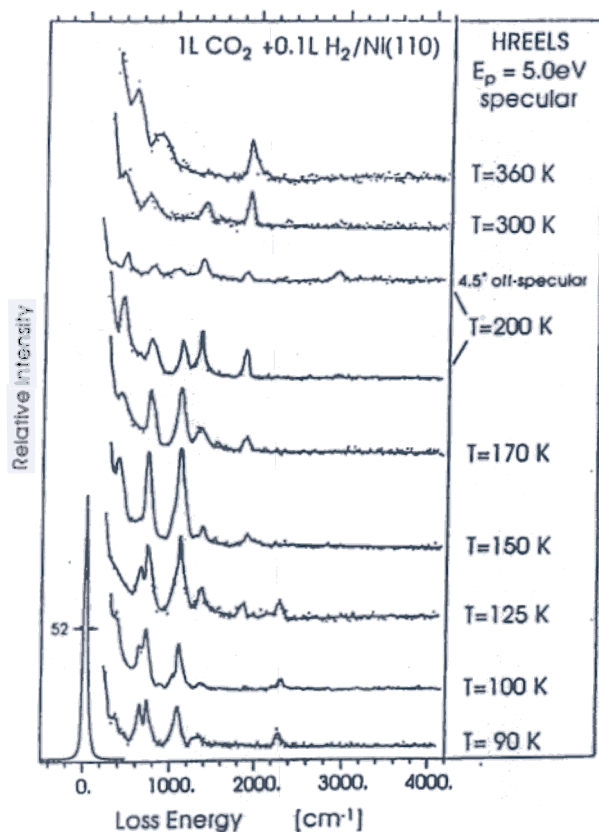


Figure 14. Series of HREEL spectra of 1 L CO₂ + 0.1 L H₂/Ni(110) as a function of temperature.

loss spectrum of adsorbed formate as reported by Richardson and coworkers [47], who also observed the unusual high intensity of the C-H stretch under off specular conditions. (Note that we are able to reproduce their results by adsorption of formic acid and subsequent heating to room temperatures). The formate species formed on the surface is stable up to temperatures between 300 K and 340 K. The only species stable on the surface close to 360 K appears to be adsorbed CO.

The above analysis of the reaction is also corroborated by the set of XP-spectra taken with synchrotron radiation shown in Fig. 15. The spectrum at the top reflects the relatively high concentration of physisorbed CO₂ (binding energy 291.2 eV) with respect to CO₂^{δ-} (at 286.6 eV). The binding energies are very similar to those reported by Illing et al. [30]. At T = 120 K physisorbed CO₂ has been widely attenuated, but CO₂^{δ-} remains on the surface. At the same time a small CO induced feature grows in at 285.6 eV. At 170 K a new feature has developed at a binding energy of 287.0 eV and the CO induced peak has grown. A surface temperature of 320 K leaves CO as the only remaining surface species. The feature at 287.0 eV observed between 170 K and 300 K must be connected with the formate species. As is shown in the inset of Fig. 15 (top spectrum) a peak due to formate at 287.0 eV is observed if adsorbed formic acid is thermally treated. According to the work of Madix et al. [48] and of Illing [49] we know that the additional feature at 288.5 eV is due to formic acid solvating the formate formed in the monolayer. The lower trace in the inset of Fig. 15 is taken after CO₂/H₂ adsorption, heating to T = 180 K and

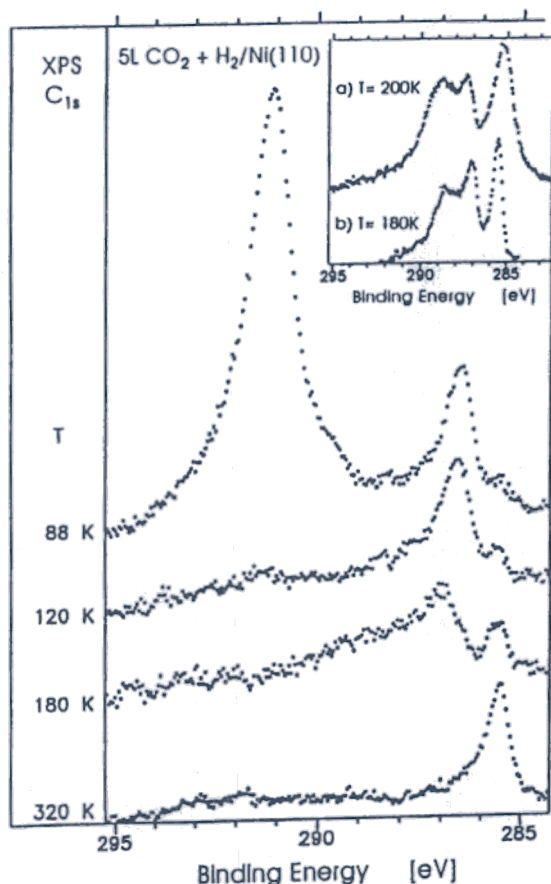


Figure 15. Series of high resolution C1s XP spectra of 5 L CO₂ + H₂/Ni(110) as a function of temperature. The inset compares formate species formed a) (in the top spectrum) out of formic acid by heating to 200 K with formic acid as solvent, and b) after reaction of CO₂ and H₂ at 180 K solvated with readsorbed CO₂.

allowing CO₂ to readsorb at low temperature. As for the formic acid, the CO₂ solvating the formate leads to an additional feature at higher binding energy, a trace of which is also seen in the spectrum shown in Fig. 15. We have shown before [29] that without presence of hydrogen only CO₂^{δ-} forms on the surface which above 200 K dissociates into adsorbed CO and oxygen. Only with the presence of hydrogen (or deuterium) do we observe formate formation [36].

However, the tendency for formate formation is a rather complex function of the hydrogen coverage. Clearly, if we preadsorb hydrogen (or deuterium) at room temperature to saturation coverage (1 L), CO₂ adsorption and even CO₂ physisorption at low temperature is suppressed. Note, that at saturation coverage, the Ni(110) surface undergoes a (2x1) reconstruction, which was monitored using LEED [50]. We have to go to low H₂ doses (0.2 L) before we see CO₂ physisorption. CO₂^{δ-} formation appears to be suppressed by higher coverages of hydrogen but favoured by low hydrogen precoverages. It is not clear at present what causes the effect but we have noted earlier [9] that CO₂^{δ-} formation appears to be correlated with the substrate workfunction for typical

δ -type substrates. Hydrogen is known to increase the workfunction by about 0.5 eV (from 4.5 eV to 5.0 eV) for saturation coverage [50-54]. It is not unreasonable to assume that it is the increase in workfunction that quenches $\text{CO}_2^{\delta-}$ formation and its further reaction.

3.3. CASE 3: $\text{C}_6\text{H}_6/\text{Os}(0001)$

As an example for a rather complex reaction we discuss the reaction of benzene on $\text{Os}(0001)$ [55]. Fig. 16 shows a set of complicated TD spectra obtained after dosing the $\text{Os}(0001)$ surface at low temperature ($T \sim 200$ K) and detecting the desorbing hydrogen. In the temperature range $200 \text{ K} < T < 290 \text{ K}$ a chemisorbed ordered $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ monolayer, the low temperature phase, exists as monitored by LEED and ARUPS experiments [18]. Very small amounts of molecular C_6H_6 desorption are observed up to a temperature of 320 K. Increasing the temperature to $T > 290 \text{ K}$ leads to dissociative chemisorption. Fig. 16 shows a series of H_2 TD spectra from $\text{C}_6\text{H}_6 + \text{Os}(0001)$ with variation of the initial coverage and a constant heating rate β ($\beta = dT/dt = 3.5 \text{ K/s}$). Five desorption states are detected in the range of $300 \text{ K} < T < 830 \text{ K}$ for high coverages. The first H_2 desorption peak α is observed at 326 K followed by a second more intense feature β at 372 K. The combined areas of the structures α and β take about 1/3 of the whole area covered by the spectrum at saturation coverage. This indicates the loss of two H atoms per benzene molecule at 400 K. Further heating leads subsequently to three desorption peaks, γ , δ and ϵ at 460, 675 and 750 K, respectively. H_2 desorption ends at 830 K and an ordered (9×9) graphitic structure is formed as indicated by LEED and AES.

The number of dehydrogenation steps is dependent on the coverage. Lower coverages lead to a broad dehydrogenation feature in the TD spectrum with only two peaks whereas high coverages cause five clearly distinguishable dehydrogenation steps.

No shift of the α -peak maxima at various exposures is observed. This indicates a first order desorption reaction, perhaps related to C-H bond breaking. In contrast to this finding the β -peak maximum shifts towards lower temperatures with increasing coverages. A superposition of a low coverage effect and a high coverage effect has to be considered which may be responsible for the observed shift. In the temperature range $290 \text{ K} < T < 340 \text{ K}$ the observed $(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$ benzene structure develops broad LEED spots with increasing background intensity and vanishes subsequently.

ARUPS data were recorded in the temperature range of $200 \text{ K} < T < 1000 \text{ K}$ [55]. Fig. 17 shows a series of normal emission spectra at different temperatures and saturation coverage with a photon energy of $h\nu = 21.21 \text{ eV}$ and the angle of incidence $\alpha = 72.5^\circ$, i.e. dominant z-polarization [56]. The experiments were performed by heating the sample up to the temperature T noted on the left hand side of the diagram and then cooling it down to $\sim 200 \text{ K}$. This procedure was applicable because the observed transition processes turned out to be irreversible.

The lowest spectrum in Fig. 17 is typical for the low temperature phase observed after adsorption of benzene at temperatures below 290 K. Structures close to the Fermi edge up to 4 eV binding energy can be attributed to emission from the osmium 5d bands. Adsorbate induced features are observed in the binding energy range 4-14 eV, with a prominent peak at 11 eV, a double peak around 8 eV and weaker structures around 6 and 4 eV. After heating the sample, the shapes of the spectra vary significantly indicating several adsorption phases. The first variation is observed at $T \sim 330 \text{ K}$, when hydrogen desorption starts (cf. Figs. 16 and 17). At $T = 340 \text{ K}$ desorption of the α -peak is complete and the photoemission spectrum changes. The former intense peak at 11 eV

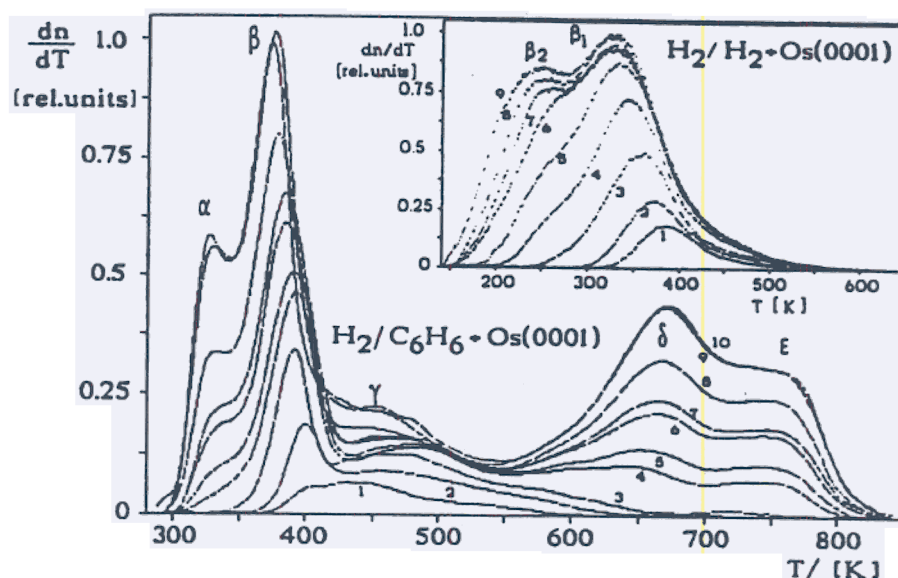


Figure 16. Hydrogen desorption spectra after adsorption of benzene on Os(0001) at $T = 180$ K for various exposures. The benzene dose is given as the pressure in the gas inlet system (Pa) multiplied by the dosing time (sec). (1) 0.065, (2) 0.13, (3) 0.26, (4) 0.52 (5) 0.63, (6) 0.78, (7) 0.94, (8) 1.25, (9) 3.12, (10) 12.6 Pa sec. The heating rate was 3.5 K/sec. In the inset hydrogen desorption spectra obtained after adsorption of H_2 at $T = 180$ K are shown. Hydrogen doses: (1) 1.58, (2) 3.15, (3) 6.3, (4) 12.6, (5) 25.2, (6) 50.4, (7) 196.0, (8) 211.0, (9) 660.0 Pa sec. The heating rate was 3.5 K/sec.

weakens and eventually disappears, and the spectrum is now dominated by a peak at 8.5 eV. The work function shows no significant variation during this phase transition. Further heating of the sample to 380 K leads to further desorption of hydrogen (β -peak in Fig. 16) and to the formation of another adsorbate phase. The absence of the peak at 11 eV and the appearance of a new feature at 10.5 eV (Fig. 17) are characteristic for this phase. The work function increases from 3.7 to 3.92 eV. Heating to temperatures above 380 K leads to less structured spectra. Finally the clean surface was obtained by flashing the sample up to very high temperatures above 2000 K for a longer time. The work function of the clean surface was determined to be 5.6 eV and could also be used as a monitor of the cleanliness of the Os(0001) surface. In order to characterize the different adsorption phases in more detail, angle resolved photoemission spectra are presented as a function of the electron emission angle θ .

We use the $2a_{1g}$ emission of the benzene (D-band), i.e. the totally symmetric C-H-bonding orbital as the level to apply the oriented free molecule approach (OFM) for a determination of the orientation of the molecular plane. Fig. 18 shows the polar angle variations of the intensity of the D-band for three different temperatures indicating a geometrical distortion as a function of temperature. The temperatures have been chosen to represent the α , β and γ states as marked in the TD spectra (Fig. 17). Together with the HREELS studies, discussed in the following, we are able to propose a sequence of reactions and interpret the changes as a function of temperature in the ARUP spectra.

Fig. 19a collects a series of HREEL spectra of benzene on Os(0001) as a function of temperature [57].

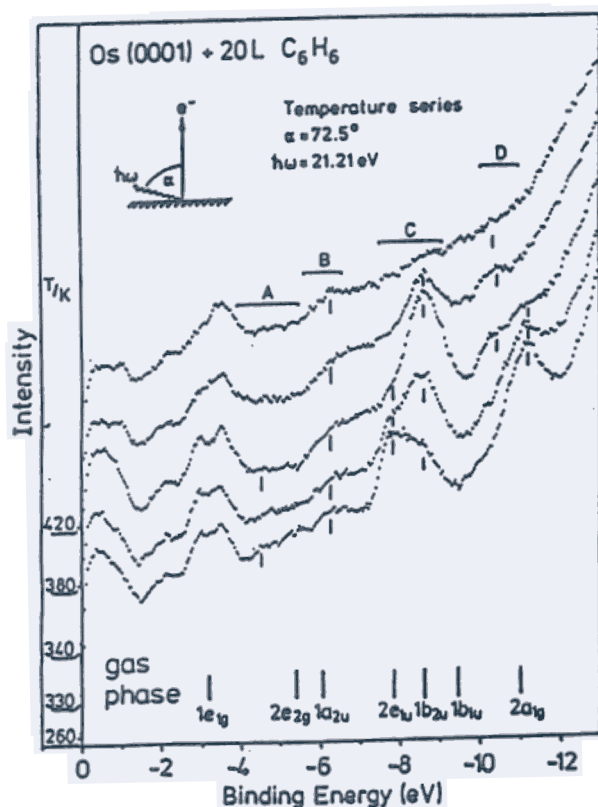


Figure 17. HeI photoelectron spectra of a saturated benzene adlayer on Os(0001) at selected temperatures. Adsorbate levels are labeled A-D.

Spectrum (a) shows the data of a benzene adsorbate phase at $T = 273$ K. This adsorbate gives rise to a $(\sqrt{7} \times \sqrt{7})R19.1^\circ$ LEED pattern [55]. The HREEL spectrum in specular scattering is dominated by one transition which can be assigned by comparison with similar spectra on other benzene adsorbate systems [58]. A comparison of specular and 5° off-specular spectra of adsorbed benzene is given in Fig. 19b. This comparison basically reveals the fact that dipole selection rules determine the dominant C_6H_6 vibration at 810 cm^{-1} . The strong band at 810 cm^{-1} in specular scattering geometry has to be assigned to a C-H wagging(γ) mode. These modes lead to strong dynamic dipoles perpendicular to the metal surface, if the molecular plane is oriented parallel to the Os surface. Other vibrational modes show negligible intensities in the specular scattering direction (Fig. 19a), but gain intensity off specular (Fig. 19b). All studies presented so far conclude from such behaviour that chemisorbed benzene lies flat on metal surfaces at room temperature. The small peak at 1885 cm^{-1} is probably due to residual CO. We only note that at even lower temperature ($T = 80\text{ K}$) we find the growth of benzene multilayers, as indicated in the EEL spectra (not shown) by additional lines similar to those reported by Jakob and Menzel for $C_6H_6/Ru(0001)$ [59].

Upon elevating the temperature to $T = 325\text{ K}$ (spectrum (b)), which is equivalent to the temperature where the system loses the first hydrogen atom [55], the wagging mode shifts to lower values, namely 760 cm^{-1} . Simultaneously, a sharp band at 400 cm^{-1} in the C-C wagging region gains intensity, while the region of C-H vibrations above 3000 cm^{-1} only shows a slight intensity, considerably more though than for the flat-lying benzene

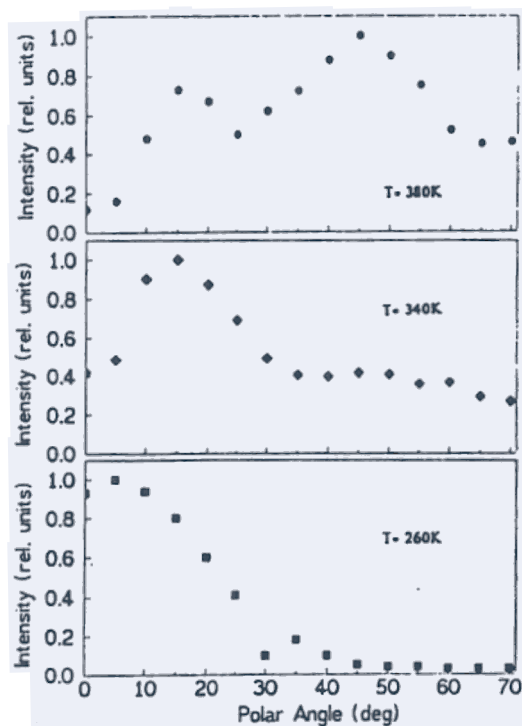


Figure 18. Polar plot of the integrated intensities of the D band ion states (see Fig. 17) of benzene on Os(0001) at different temperatures.

adsorbate. However, C-H bending modes at 1110 and 1390 cm^{-1} are detectable. Further increase of the temperature to a value ($T = 382\text{ K}$), where the second hydrogen atom is lost, leads to several further changes in the EEL spectrum (spectrum (c) in Fig. 19a): firstly, the intensity of the elastic peak decreases by orders of magnitude, indicating a pronounced disordering of the adsorbate layer; secondly, several modes in the region of C-C frame vibrations between 465 and 700 cm^{-1} , as well as in the region of C-H bending modes between 980 and 1400 cm^{-1} grow in. Most pronounced, however, is the considerable intensity in the region of the C-H stretching modes above 3000 cm^{-1} . Note that the observed vibrational frequencies are only slightly shifted with respect to those observed for the benzene moiety. For a definite assignment it would be desirable to compare the observed frequencies with those of the benzyne- Os_3 cluster compounds for which X-ray structure determinations are reported showing an inclined C_6H_4 ring with respect to the Os cluster plane [60,61]. Unfortunately, the vibrational spectra of these compounds in the hydrocarbon region have not been reported. However, the vibrational spectrum of matrix-isolated benzyne has been determined and assigned on the basis of a normal mode analysis [62-65].

A comparison with the benzene spectrum shows that except for one vibration, i.e. the $\nu_{\text{C-C}}$ mode at 2082 cm^{-1} , the benzyne vibrational energies are in the neighbourhood of those of C_6H_6 . For the adsorbed benzyne we find indications of losses at 2000 and 2565 cm^{-1} , which may be due to the ring vibration. The other observed vibrational losses are in the range of those for benzene. The band at 2000 cm^{-1} might also be due to co-adsorbed CO. On the other hand the changes of the loss intensities in going from benzene to adsorbed benzyne are most characteristic and consistent with a pronounced geometrical

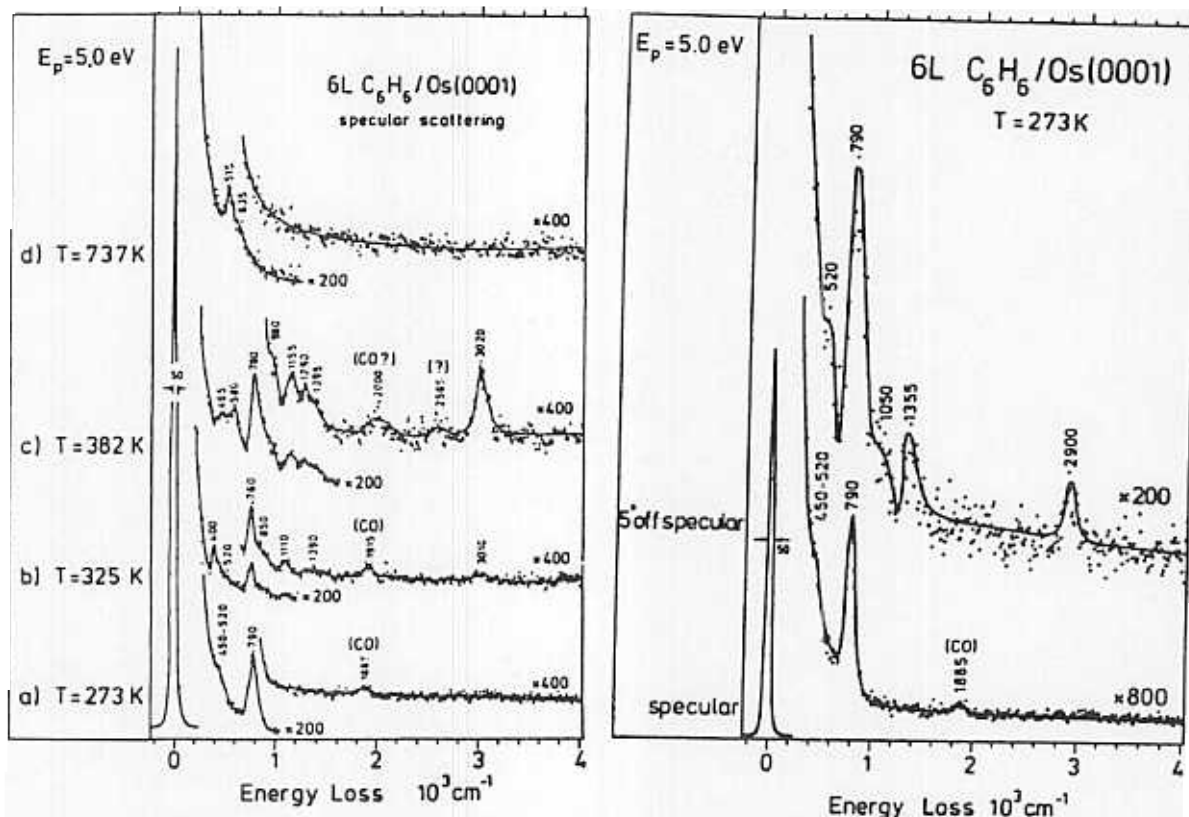


Figure 19. HREEL spectra of benzene on Os(0001). Left panel: HREEL spectra taken for various annealing temperatures. Right panel: HREEL spectra taken at room temperature. A spectrum taken in specular direction is compared with a spectrum taken at 5° off specular.

change of the adsorbed species as shall be alluded to in the following. The simplest way to explain the observed changes of intensities is to consider a molecular plane which is no longer parallel to the surface plane but rather tilted to a certain angle. It is very hard to estimate the tilt angle quantitatively. Jakob and Menzel [59] qualitatively estimate the tilt of the molecular plane by forming the ratio (R_i) of the vibrational loss intensities of the C-H stretch modes above 3000 cm^{-1} with respect to the C-H wagging mode ($\gamma_{\text{C-H}}$) below 1000 cm^{-1} under specular scattering conditions. These authors find R_i values of 2×10^{-2} for flat lying C_6H_6 and 12×10^{-2} for C_6H_6 , where the molecular plane is inclined in a physisorbed C_6H_6 layer. We find values of 1×10^{-2} for adsorbed C_6H_6 , 4×10^{-2} for the phenyl phase, and 30×10^{-2} for adsorbed C_6H_4 . Since we know that the C-H-framework in phenyl and benzyne stays coplanar within a few degrees in the cluster compound - as it is in gaseous benzene - we may draw the conclusion from the change of R_i as a function of temperature that the tilt angle with respect to the surface normal decreases from 90° in the C_6H_6 adsorbate to a value comparable to or even larger than C_6H_6 physisorbed on Ru(0001). A reasonable value for the physisorbed phase is 45° , so that we can expect a tilt angle in the neighbourhood of this value for the benzyne species on Os(0001). Our photoemission study (see above) is compatible with these findings. Also, as a result of the photoemission study we concluded that in the phenyl adsorbate the tilt angle of the molecular plane increases only slightly with respect to the benzene adsorbate. The

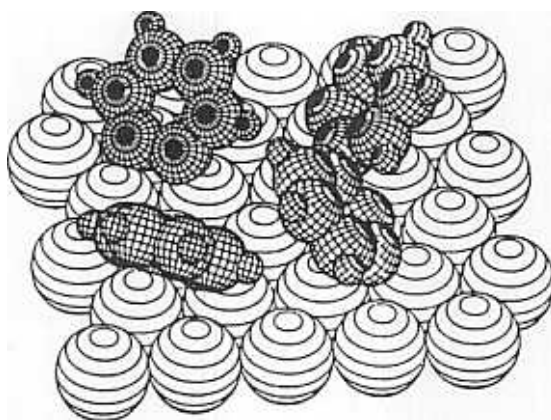
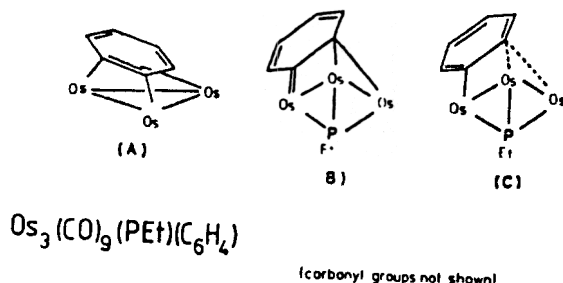


Figure 20. Top: structure formula for possible adsorbate-substrate bondings of C_6H_4 on an Os_3 cluster reported in ref. [60]. Bottom: schematic (not site specific) 3D plot of the proposed ortho C_6H_4 type intermediates at the $\text{Os}(0001)$ surface at $T \sim 380$ K for different domains. The molecules are inclined by 45° .

HREELS data corroborate these findings as well. Upon heating the surface above 400 K the spectra continuously change and, at temperatures above $T = 500$ K, the vibrational wagging modes, characteristic of the existence of a six-membered ring, have disappeared. This is compatible with the conclusions based on the TDS data [55] that above this temperature the ring structure breaks up. We have not studied this latter temperature region in detail with HREELS and leave this for future studies.

The HREELS data provide further experimental evidence to support a reaction channel of adsorbed benzene proposed above, namely a successive loss of hydrogen accompanied by the formation of at least two intermediate species which we believe to be a phenyl and a benzyne species, before the six-membered ring structure starts to break up, and finally leads to the formation of a carbon overlayer on the $\text{Os}(0001)$ surface. To our knowledge there is only one other study reported in the literature where the authors find experimental indications of an adsorbed benzene moiety on a solid surface. Liu and Friend [66] have published XPS and NEXAFS (near edge X-ray absorption fine structure spectroscopy) data for the system $\text{C}_6\text{H}_6/\text{Mo}(110)$. By comparison with reference data (gained via decomposition of $\text{C}_6\text{H}_5\text{SH}$ on $\text{Mo}(110)$) [66] they deduce the presence of a benzyne species on the surface. Evidence from vibrational spectroscopy has so far not been reported. The present study represents the first experimental indication via HREELS for the existence of a benzyne precursor for benzene dissociation.

3.4. CASE 4: ADSORPTION ON OXIDES

Metal oxides, and transition-metal oxides in particular, are in use as catalysts in industrial processes. This is certainly one of the reasons why the study of adsorption and reaction on oxide surfaces has been pioneered rather early in the fifties and sixties. With the advent of surface science the interest has shifted towards clean metal surfaces and the study of metal oxides has been abandoned to some extent. During the last decade or so, however, the interest in oxide surfaces has been revitalized and some clean single-crystal surfaces have been studied by applying surface-science methodology. Henrich [67] has recently published an excellent review of this field. For certain oxides, i.e., semiconducting oxides such as ZnO, a great deal of information already exists even for molecular adsorbates on these surfaces. Much of this literature has been collected in a review by Heiland and Lüth [68]. It appears, though, that ZnO is a singular case. One issue has been that many oxides exhibit only limited conductivity which in turn limits the applicability of electron-spectroscopic techniques which play a central role in the characterization of clean surfaces and of molecular adsorbates on these surfaces. Some of the latter difficulties may be circumvented by looking at thin oxide films grown on metallic substrates.

As an example we briefly discuss the situation of NO on NiO(100) [69].

We have investigated the adsorption of NO on a thin NiO(100) film of several layers thickness grown on top of a Ni(100) surface in comparison with data of an *in vacuo* cleaved NiO(100) single crystal. The layer exhibits a high defect density. We demonstrate via application of several surface-sensitive electron-spectroscopic techniques (XPS, ARUPS, NEXAFS, HREELS) that the occupied (ARUPS) and unoccupied (NEXAFS) electronic states are similar to those of a bulk NiO(100) sample. In spite of its limited thickness, the band structure of the thin film exhibits band dispersion perpendicular to the surface that are compatible with those of bulk NiO(100). It is shown that the electronic structure of the oxygen sublattice can be described in a band-structure picture while for the Ni sublattice electron localization effects lead to a breakdown of the band-structure picture.

NO on NiO desorbs at 220 K. Fig. 21 shows the thermal desorption spectra of NO from a bulk Ni(100) surface in comparison with desorption from the oxide layer [69]. The desorption temperatures for both systems are only marginally different. If we consider the different heating rates and identical, commonly used frequency factors we calculate on the basis of the Readhead formula [P.A. Readhead, Vacuum 12, 203 (1962)] almost identical desorption energies for both cases, i.e., 0.52 eV. This means that NO is weakly chemisorbed on a NiO surface. It is quite surprising that the desorption energies on both surfaces are the same because the defect densities are different by orders of magnitude as judged from the LEED spots [70], and one is tempted to expect a strong influence of the defects on the desorption temperature. However, even though we do not know the exact nature of the defects the similarity of the desorption temperatures indicates that the defects are not the sites of NO adsorption on the oxide film. The NO coverage is close to 0.2 relative to the number of Ni surface atoms as determined by XPS. HREELS reveals that there is only one species on the surface documented by the observation of only one bond-stretching frequency.

Fig. 22 shows some HREEL spectra of NO on a NiO(100) film at different temperatures. Upon exposure to NO at low temperature, we observe in addition to the very strong NiO surface phonons one peak at the high-frequency side of the third multiple-phonon-loss. This peak vanishes at about 200 K surface temperature in agreement with the thermal desorption data which showed a peak temperature only a little

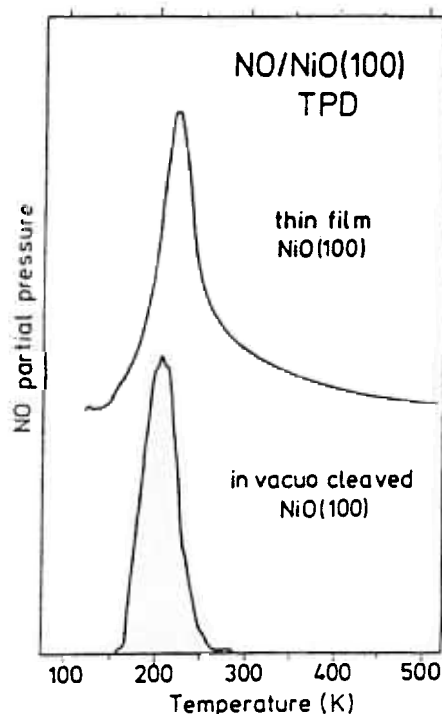


Figure 21. Comparison of TPD spectra for NO adsorbed on a NiO(100) single crystal surface cleaved in vacuo with a TPD spectrum for NO adsorbed on NiO(100) epitaxially grown on Ni(100).

above $T = 200$ K. We assign this peak to the N=O bond-stretching vibration of NO adsorbed on top of Ni sites in the NiO layer. This assignment is based on a detailed HREELS study of NO-O-coadsorption on Ni(100) [71]. We have plotted HREELS spectra of NO on Ni(100) and NO + O on Ni(100) for comparison in Fig. 22. Both spectra are rather complex, and a detailed discussion shows that the spectra are caused by the superposition of a set of different species [71]. The important aspect for the present purpose is the appearance of a single peak at 1800 cm^{-1} for adsorption near coadsorbed oxygen. This peak has been assigned to NO adsorbed on top of Ni atoms with a bent Ni-NO bond. The bending of the axis in the coadsorbate is also indicated by the appearance of a bending vibration at 640 cm^{-1} , typical for a strongly bound system [72].

We have transferred this assignment to the oxide surface although we do not observe a bending mode. We cannot exclude at present that such a bending vibration is situated near the position of the NiO phonon loss but this would imply that the force constant of the bending mode on the oxide surface is similar to the adsorbate on the metal surface. However, we know that the molecule-substrate bonding is much weaker on the oxide surface as compared with the metal surface, so that we expect a reduced bending force constant. This would shift the bending mode to lower frequencies which might render the bending mode unobservable under the present conditions. Clearly, an independent experimental clue as to the geometry of the molecular axis is highly desirable. We have therefore performed NEXAFS investigations on the NO/NiO(100) adsorbate [69]. NEXAFS data on the system and a comparison with previous data on the system NO/Ni(100) indicate that the molecular axis of adsorbed NO is tilted by an angle of approximately 45° relative to the surface normal. The N1s XP spectra of the weakly

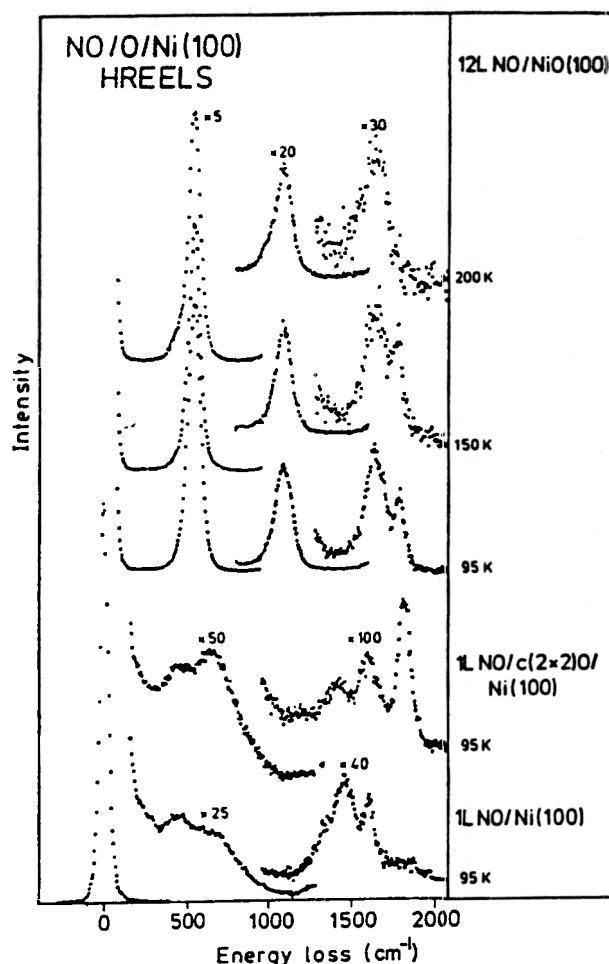


Figure 22. HREEL spectra for NO on NiO(100) in comparison with HREEL spectra of NO on a clean and on an oxygen covered Ni(100) surface.

chemisorbed species show giant satellites similar to the previously observed cases for weak chemisorption on metal surfaces. This is the first observation of an intense satellite structure for an adsorbate on an insulator surface, which shows that there must be sufficient screening channels even on an insulating surface. A theoretical assignment of the peaks is discussed. We compare the spectroscopic properties of the NO species on the thin-film oxide surface, which is likely to contain a certain number of defects, with NO adsorbed on a basically defect-free bulk oxide surface by TD and XP spectra. TD and XP spectra of the bulk system are basically identical as compared with the oxide film, indicating that the majority of species adsorbed on the films is not adsorbed on defects but rather on regular NiO sites. Results of *ab-initio*-oxide-cluster-calculations are used to explain the bonding geometry of NO on regular NiO sites [69].

As a second example we summarize some of the results we have collected for a more reactive oxide surface, namely the $\text{Cr}_2\text{O}_3(111)$ surface [73].

We have chosen Cr_2O_3 as a substrate for our investigations since it is well known that the catalytic activity of this oxide for various reactions, like for instance polymerization of

olefins [74], hydrogenation of alkenes and dehydrogenation of alkanes [75], reduction of NO and decomposition of N_2O_4 [76] is rather high.

For CO we observe a well ordered $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ superstructure in the LEED pattern. The ARUPS and NEXAFS data obtained for this adsorbate are compatible with an adsorption geometry where the CO molecules lie flat on the surface interacting with the oxide via the σ valence states and the π systems. Fig. 23 shows a schematic representation of the CO-adsorbate system as it is deduced from the experimentally available information. The CO molecules interact with two Cr-ions on the surface. The CO $1\pi_z$ electrons interact repulsively with the oxygen layer underneath. The combined interactions lead to interestingly different ionization potentials of CO on an oxide surface as compared with metal surfaces. This is summarized in Fig. 24. Worth noting is the comparison between Cr_2O_3 and Cr metal because in both cases the molecule is known to lie flat on the surface. Clearly, the interaction with the oxide is much different from the CO-metal interaction.

For CO_2 not only adsorption on the surface but also reaction with the surface is observed. At low temperatures CO_2 is partly adsorbed in a molecular physisorbed state and partly it reacts with the oxide surface to form a surface carbonate. After slight annealing only carbonate is found on the surface. It appears that adsorption, respectively reaction of CO and CO_2 only takes place on those parts of the surface that expose chromium atoms to the respective adsorbate since the surface reactivity is strongly suppressed by preadsorption of oxygen. The adsorption of oxygen leads to a surface which exposes far fewer chromium atoms. A clean, freshly flashed oxide surface exhibits chromium atoms that are in a different oxidation state than those in the bulk as judged from EELS. These atoms are most likely responsible for the high reactivity of the $\text{Cr}_2\text{O}_3(111)$ surface.

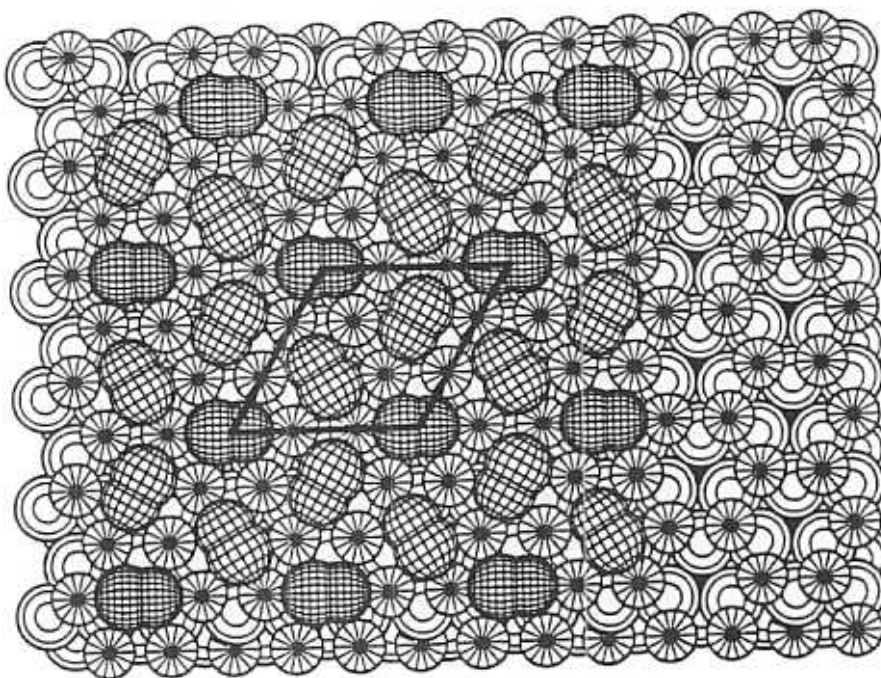


Figure 23. Structure model for $\text{CO}(\sqrt{3}\times\sqrt{3})\text{R}30^\circ/\text{Cr}_2\text{O}_3(111)$. The unit cell of the adlayer is indicated.

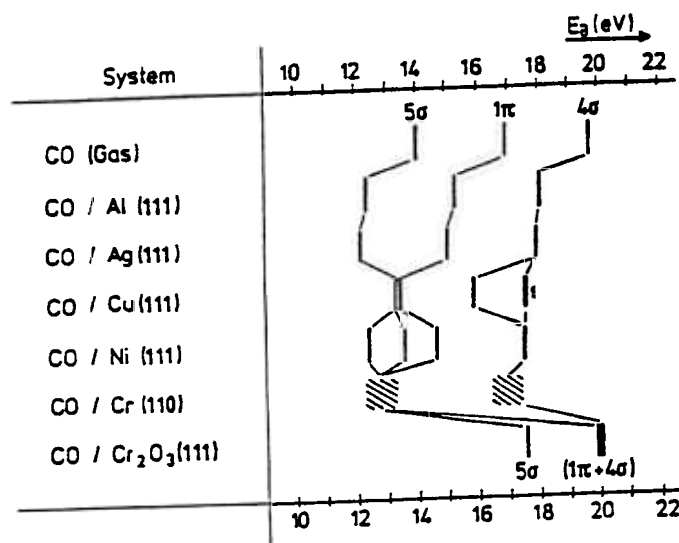


Figure 24. Binding energies of the valence levels of CO adsorbed on different hexagonal or quasihexagonal surfaces with respect to the vacuum level. Since we do not know the work function change for the adsorption of CO on Cr(110) we have hatched the binding energy region in which we expect the ionizations to occur. The data have been taken from refs. [77-82].

Fig. 25 shows a set of off-specular HREEL spectra for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ on $\text{Cr}_2\text{O}_3(111)$ taken at two different temperatures. The strongest losses in these spectra, i.e. those at 410 cm^{-1} , 700 cm^{-1} , 1420 cm^{-1} and 2100 cm^{-1} are due to the optical phonons of the oxide film. The adsorption of CO_2 and thus the formation of carbonate shifts these losses by some cm^{-1} , indicating the strong interaction of the carbonate with the oxide surface. At $T = 100\text{ K}$ the asymmetric stretching vibrations of linear, undistorted CO_2 at 2360 cm^{-1} and 2290 cm^{-1} , respectively, are clearly visible. Upon annealing to 220 K these losses strongly decrease in intensity. Some residual intensity is due to readorption of CO_2 from the residual gas since the sample was only shortly annealed to $T = 220\text{ K}$. The measurements were performed when the crystal was cooled down to 100 K .

In the spectra of the cold layer some weak structure is visible to the left and the right of the phonon loss at 1420 cm^{-1} . Upon annealing these get stronger so that they are most likely due to carbonate. We identify losses at $(1630 \pm 20)\text{ cm}^{-1}$ [$(1600 \pm 20)\text{ cm}^{-1}$], $(1285 \pm 20)\text{ cm}^{-1}$ [$(1260 \pm 20)\text{ cm}^{-1}$], $(1035 \pm 20)\text{ cm}^{-1}$ [$(1015 \pm 15)\text{ cm}^{-1}$] and $(920 \pm 20)\text{ cm}^{-1}$ [$(900 \pm 20)\text{ cm}^{-1}$]. The numbers in brackets are the loss energies for $^{13}\text{CO}_3^{2-}$. These loss energies are graphically represented in Fig. 26 in comparison with data from the literature for differently coordinated carbonate species. The different surface coordinations of carbonate are schematically shown in Fig. 26. From the data shown in Fig. 26 it is clear that the carbonate species on $\text{Cr}_2\text{O}_3(111)$ is most likely doubly coordinated to the oxide, i.e. it is bidentate.

4. Synopsis

The system $\text{CO}(2 \times 1) \text{ p}2\text{mg}/\text{Ni}(110)$ is used to demonstrate the possibilities of electron spectroscopies. Photoelectron and inverse photoelectron spectroscopy are used to probe

the electronic structure of the system. The strong intermolecular interactions lead to pronounced E vs. k dispersions which may be monitored through angle dependent measurements. Inelastic electron scattering may be used to deduce the site of adsorption, dispersion measurements infer the lateral displacements and from X-ray photoelectron diffraction results the tilt angle of the molecular axis.

We have used various examples to illustrate how surface science techniques may be applied to identify metal-molecule interactions and how these interactions change in the course of the increase of surface temperature.

Finally we show that these techniques may be applied for semi-conductive and even insulating oxide surfaces if the adsorption is studied on oxide films grown on metal substrates. With non electron spectroscopic techniques such as TDS and high energy electron spectroscopic techniques such as XPS comparison to adsorption on bulk single crystal is possible. Through this approach we learn about the influence of defects on oxide surfaces onto the adsorption behaviour.

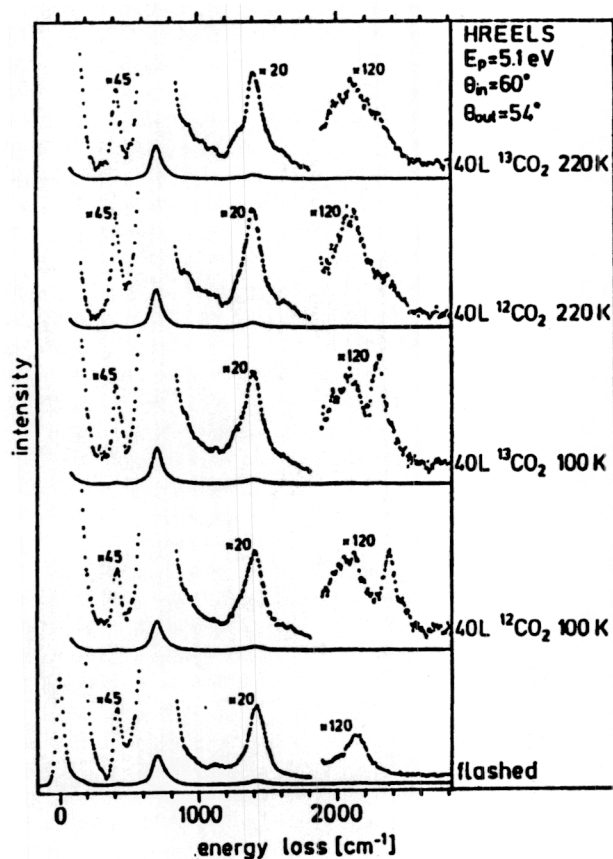


Figure 25. HREEL spectra for $^{12}\text{CO}_2$ and $^{13}\text{CO}_2$ on $\text{Cr}_2\text{O}_3(111)$ taken at two different temperatures.

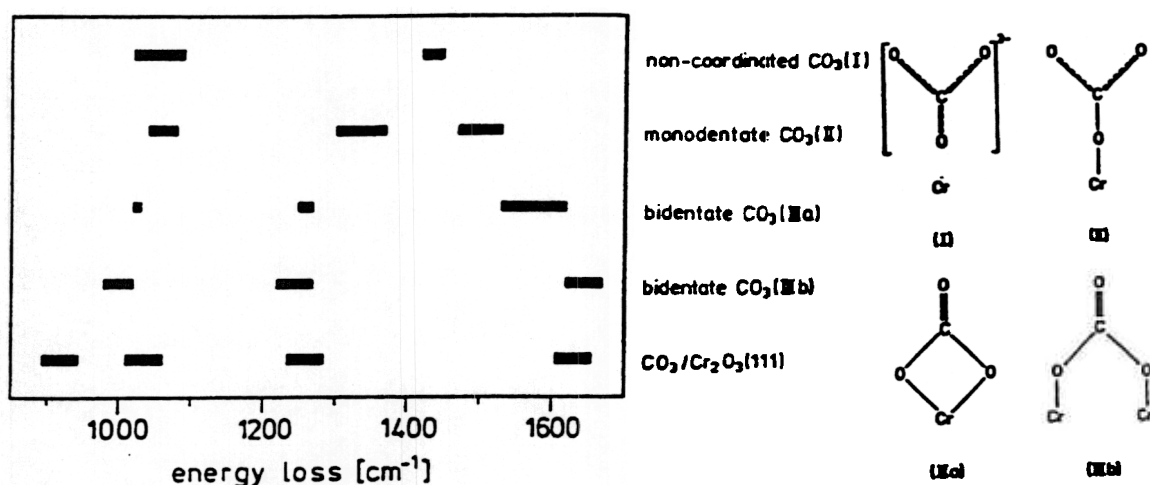


Figure 26. Left panel: Comparison of the vibrational loss energies of carbonate on $\text{Cr}_2\text{O}_3(111)$ obtained after exposing the surface to CO_2 at 100 K and subsequent annealing to 220 K with data from the literature [83] for different carbonate species on Cr_2O_3 . Right panel: Schematic diagram showing different surface coordinations of carbonate.

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