ADSORPTION OF NO ON AN OXYGEN PRECOVERED Ni(100) SURFACE

G. ODÖRFER, R. JAEGER, G. ILLING, H. KUHLENBECK and H.-J. FREUND

Lehrstuhl für Physikalische Chemie I, Ruhruniversität Bochum, Universitätsstrasse 150, 4630 Bochum, Fed. Rep. of Germany

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We have employed high resolution electron energy loss spectroscopy (HREELS), angle resolved photoelectron spectroscopy (ARUPS), and near edge X-ray absorption fine structure (NEXAFS) measurements to study the adsorption of nitric oxide (NO) on a clean and on oxygen precovered Ni(100) surfaces at T = 95 K. The adsorption behaviour on both the clean and the oxygen precovered surfaces is very complex. On the clean surface adsorption at low coverage starts in hollow sites with the NO axis oriented perpendicular to the surface. Consecutively, bridge sites are populated with both perpendicular and bent NO molecules. Finally, terminally bound, linear NO adsorbs on the surface. On the oxygen precovered surfaces we find the same adsorbate sites. Depending on whether we have chosen $p(2 \times 2)$ or $c(2 \times 2)$ oxygen precoverage we find a smaller percentage of molecules adsorbed in hollow sites, because oxygen occupies these sites in both layers but twice as many hollow sites in a $c(2 \times 2)$ layer. A particularly interesting observation concerns an oxygen influenced site in which the NO molecules are adsorbed with a bent orientation. This is corroborated via NEXAFS measurements. This NO species is more strongly bound to the surface than on the clean Ni surface. A section is included in the paper where we discuss some general aspects of NO bonding towards metal atoms in a linear versus bent orientation and the influence of coadsorbed species on the orientation of the molecular axis.

1. Introduction

The study of coadsorbates is the first step towards the study of reactions between molecules on surfaces because intermolecular interactions in coadsorbed molecular layers determine the reactivity of the system. Adsorption and reaction of nitric oxides on metal surfaces is particularly important because these molecules are very active in environmental chemistry [1]. This is one of the reasons why catalytic reactions of NO, e.g. with ammonia to form environmentally poisonless reaction products have become technologically important processes [2]. The interaction of NO with surfaces is thus an interesting subject for surface science studies.

NO adsorption has been studied on a variety of metal surfaces [3-49] including Ni(100) [4-21]. NO-oxygen interaction, however, which is interesting with respect to an understanding of the decomposition of higher oxides, e.g. NO₂, has only been studied occasionally [15,21,27,42]. Recently, an IRAS study has been reported for NO-oxygen interaction on Ni(111) [21]. Here we

report on the interaction of NO and oxygen on a Ni(100) surface. We shall show with the help of several surface sensitive techniques (high resolution electron energy loss spectroscopy, HREELS; angle resolved photoelectron spectroscopy, ARUPS; near edge X-ray absorption fine structure, NEXAFS; temperature progammed desorption, TPD) that NO on the clean surface adsorbs in several different surface sites as a function of coverage at 95 K. Within a rather complex adsorbate layer there exists a certain fraction of NO molecules oriented with its molecular axis perpendicular to the surface plane, and another fraction of NO molecules oriented with its molecular axis bent away from the surface normal. The linear and bent molecules may be bridge or terminally bonded.

On the oxygen precovered surface we find in addition to NO molecules with vibrational frequencies similar to the clean surface, an NO species whose vibrational properties are considerably modified by the presence of the coadsorbed oxygen. This NO species has a stretching frequency close to the gas phase value of NO and is, according to our NEXAFS data, characterized by a bent orientation of the molecular axis with respect to the metal surface.

2. Experimental details

The experiments were performed in two different ultra-high vacuum systems. The NEXAFS and ARUPS data were recorded using synchrotron radiation from the storage ring BESSY in Berlin. The HREELS data have been taken in a UHV system equipped with a Leybold ELS22 system with a typical resolution of 8 meV [50]. The preparation chamber of the system contains facilities for AES, low energy electron diffraction (LEED) and TDS. All EEL spectra were measured in specular geometry with a primary energy of 5 eV. Sample temperatures higher than 95 K were achieved by heating the crystal to this temperature for a short time. After heating the sample was allowed to cool down to 95 K.

The sample was spot welded to two tungsten rods which were connected with a liquid nitrogen reservoir such that the sample could be cooled below 95 K, and heated either directly or by electron bombardment on the reverse side of the crystal. The Ni(100) surface was prepared by repeated oxidation-reduction cycles (5×10^{-6} Torr O_2 at 800-900 K; 1×10^{-6} Torr H_2 at 900 K) and following cycles of Ne ion etching at 300-500 K and heating to 800-1000 K. Cleanliness and surface order were checked with Auger electron spectroscopy and low energy electron diffraction.

The NEXAF spectra were recorded by monitoring the nitrogen and oxygen K-edge Auger yields in a 12 eV wide window centered at 511 and 380 eV, respectively, as a function of photon energy. The Auger electron emission was detected at an angle of the incident plane so as to minimize direct photoemission features, and to allow maximum variation of the incidence angle. The latter was varied by rotating the sample relative to the light beam. With a dwell time of 0.5 s/data point and 400 data points per 60 eV typically two scans were taken to achieve reasonable signal to noise ratios at the nitrogen edge. The NEXAF spectra presented here are difference spectra and have been normalized to the absorption step height as was done previously [51].

3. Results and discussion

3.1. HREELS results

The absorption behaviour of NO on Ni(100) at low exposure is rather complicated, and we cannot give a complete and unambiguous interpretation on the basis of our data. However, the complexity of the adsorption behaviour outlined below may be one of the reasons why in LEED we did not find ordered molecular overlayers. This problem appears to be Ni(100) specific, because on other transition-metal(100)/NO systems, for example NO/Pd(100), various diffraction patterns have been observed [26]. Fig. 1a shows a series of spectra of NO on Ni(100) at T = 95 K with increasing exposure. At 0.3 L exposure we observe two NO induced features centered around 440 and 1330 cm^{-1} which are characterized by relatively large line widths, i.e. considerably larger than the spectrometer function (see the width of the elastic peak). We feel that the large widths are due to inhomogeneous line broadening possibly connected with defects on the surface. Even at 0.3 L exposure we find a slight indication of a peak close to 1600 cm^{-1} , which picks up intensity as we increase the exposure to 0.5 L NO. Furthermore the band at 1330 cm^{-1} shifts to 1430 cm^{-1} after adsorption of 0.5 L NO. If we heat a 0.5 L exposure to above 200 K the 1600 cm⁻¹ loss decreases and a partial structuring of the broad band centered at 1330 cm⁻¹ occurs as shown in fig. 1b. At least three components in the region of NO stretching vibrations can be identified near 1220, 1330, and 1430 cm^{-1} with the highest intensity in the 1330 cm^{-1} loss. Parallel with the structuring in the NO stretch region we register changes in the region of the metal-molecule vibrations. The broad loss centered at 440 cm⁻¹ shifts to lower energy, i.e. 360 cm^{-1} . A loss energy of 360 cm^{-1} is characteristic of a c(2 × 2) atomic oxygen overlayer on the surface. This shift appears together with a peak at 1840 cm^{-1} barely visible in the spectra which shall be discussed in more detail below. Therefore this implies that part of the adsorbed molecules dissociate upon heating. Upon increasing the coverage at T = 95 K the situation becomes even more complicated: At 1 L exposure two features in the stretch region dominate. Bands at 1480 and 1600 cm⁻¹ are the most intense ones. In addition the band at 1840 cm^{-1} mentioned above grows in. Starting with the 1 L exposure an extra feature at 690 cm^{-1} appears in the low energy region. A further increase in exposure from 1 to 8 L leads to considerable changes in the relative intensities, namely a strong increase in the 1600 cm^{-1} loss intensity connected with only a slight increase in loss energy. There is some indication that the peak centered around 1600 cm^{-1} is not due to a single species but rather the superposition of at least two bands centered at 1590 and 1650 cm^{-1} . There is even some indication for a third component at 1740 cm^{-1} . The situation at 8 L exposure seems to represent the situation at saturation coverage for T = 95 K because a considerable increase of the exposure to 12 L leads to no further changes in the vibrational spectrum. It is, however, interesting to note the changes in the loss spectrum when we heat the 8 L adsorbate to room temperature as shown in fig. 1c. The relative intensity of the peak at 1840 cm⁻¹ increases considerably. Simultaneously, the loss at 690 cm^{-1} is attenuated, and a loss at 610 cm⁻¹ remains. Also, the peak centered around 1600 cm^{-1} as well as the band at 1490 cm⁻¹ sharpens upon increase of the surface temperature. The loss with the lowest stretching frequencies around 1220 cm $^{-1}$ has disappeared. We have marked the mentioned loss positions by vertical lines in figs. 1a-1c in order to more easily reconcile the assignments.

In light of the complexity of the outlined adsorption behaviour we have compared the observed loss energies with a larger variety of loss energies from other NO adsorbates [3-49] and vibrational frequencies from transition metal NO complexes [29,52-58]. Some of the data are shown in fig. 2, and are compared with the loss positions derived from figs. 1a-1c. The energetic positions of the stretching frequencies of coordinated NO reach from 1900 cm⁻¹, i.e. close to the NO gas phase value (1876 cm⁻¹, see fig. 2) [3] down to 1300 cm⁻¹ where NO is simultaneously coordinated to three metal atoms. This pattern, namely a decreasing stretching vibration with increasing number of metal atoms involved in the metal molecule bonding is very well known from CO adsorbate studies [59]. While, however, for CO the molecular CO axis is oriented perpendicular to the metal plane on close packed surfaces [60,61] – unless intermolecular interaction forces the molecules to bend [62] – in the case of NO another coordination mode with a bent metal molecule arrangement even for vanishing intermolecular interaction has to be considered. We have dedicated one of the following sections (section 3.4) of the paper to a detailed discussion of bent versus linear NO-metal bonding, and we postpone the discus-



Fig. 1. HREEL spectra of the system (a) NO/Ni(100) at 95 K for varying NO exposures; (b) NO/Ni(100) exposed to 0.5 L NO at 95 K and consecutively heated to 200 and 300 K; (c) NO/Ni(100) exposed to 8 L NO at 95 K and consecutively heated to 200 and 300 K.



Fig. 1. Continued.

sion at this point. Also, the tendency of NO to form dimers, in particular in the condensed phase, has to be considered when we discuss high coverage adsorbates. The vibrational spectrum of the dimer is well known [63] and the bands falling into the frequency range considered in our study are included in fig. 2. A key reference spectrum for a consistent interpretation of our loss spectra is the infra-red spectrum of ONCI [55]. ONCI may be considered as a system where a NO molecule is coordinated to a rather heavy mass (Cl) in a bent (116°) coordination. Therefore we can expect vibrational frequencies similar to NO coordinated in the on-top bent mode towards a transition metal surface. The frequency of the bending mode of this system should provide us with a reasonable estimate for the situation at the surface.

On the basis of this information it is clear that the losses below 1500 cm⁻¹ are not due to NO molecules adsorbed in on-top sites. The highly symmetric adsorption sites on a Ni(100) surface are either fourfold hollow or twofold bridges sites. Fig. 2 shows that two- and threefold coordinated nitrosyl complexes exhibit stretching frequencies between 1300 and 1550 cm⁻¹. Whether a fourfold coordinated NO molecule would lead to a stretching frequency close to 1200 cm^{-1} can only be speculated on.

Further clues towards a consistent interpretation of the data is provided by the results on NO/Ni(111) reported by Lehwald et al. [9], Erley [19] and Chen et al. [21] (fig. 2). Briefly, NO adsorption on Ni(111) leads at low coverage (i.e. exposures below 1 L) and low temperature (85 K) to adsorption in twofold bridge sites with the molecular axis bent with respect to the surface normal as indicated by the appearance of a bending mode at 740 cm⁻¹ and a stretching frequency of 1460 cm⁻¹ shifting to 1510 cm⁻¹ upon increasing coverage (still below 1 L). At exposures higher than 1 L, where the adsorbate exhibits a well ordered c(4 × 2) LEED pattern a new adsorbate

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Fig. 2. Comparison of loss energies observed in the present work with data from the literature as discussed in the text.

state develops (in full at 2.4 L) characterized by a stretching frequency of 1580 cm⁻¹ and the absence of the bending mode. This state has been attributed to bridge bonded NO with perpendicular orientation of the molecular axis. The orientation of the molecular axis in the $c(2 \times 2)$ overlayer has been corroborated by ARUPS measurements [20]. Only at higher exposures (20 L) and more elevated temperatures (200–275 K) an additional stretching frequency near 1680 cm⁻¹ is found and attributed to linearly bound NO in on-top sites. Coadsorbed oxygen induces an additional bonding site which shows a NO stretching frequency near 1870 cm⁻¹ [21].

These results may be partly compared with our results on Ni(100): The loss centered around 1330 cm^{-1} in fig. 1 should be due to fourfold hollow coordinated NO. The observed shift of this peak from 1330 to 1430 cm^{-1} after adsorption of 0.5 L NO could be explained by intermolecular interac-

tion within the NO layer. This effect has already been reported by other investigators [14]. The losses at even lower energy should be due to NO bound to undefined defect sites. Another possibility is to assign this peak to a NO-stretching mode of N₂O formed via N-NO interaction (gas phase: 1270 cm⁻¹) [29]. We have no clear indication for a bending vibration of any of those adsorption sites. We therefore assume that NO molecules adsorbed in these sites are oriented perpendicular to the surface. A clear indication for a bending vibration appears at an exposure of 1 L and higher together with an increase of the 1480 cm^{-1} loss. This correlates with the observed frequency for the bridge bonded bent NO on Ni(111). Parallel with the increase of the 1600 cm^{-1} loss above 1 L exposure the bending mode at 690 cm⁻¹ does not increase in intensity. The comparison with Ni(111) leads us therefore to assign this peak to bridge bonded linear NO. The increase in width and the



Fig. 3. HREEL spectra of the systems $NO/p(2 \times 2)O/Ni(100)$ (a) and $NO/c(2 \times 2)O/Ni(100)$ (b) exposed to 1 and 12 L NO at 95 K.

slight shift of the latter peak with higher exposure we explain with an on-top bound species giving rise to a loss at 1650 cm^{-1} , i.e. at a similar frequency (1685 cm^{-1}) found for the corresponding species on Ni(111) (fig. 2). We have investigated the adsorbate at this coverage with NEXAFS, as shall be discussed below, and find a nearly perpendicular orientation of the averaged molecular axis. At high (8, 12 L) NO exposures a loss at 1840 cm^{-1} is observed, and, additionally, there is a shoulder introduced at 1740 cm^{-1} . We may speculate that the latter is due to the formation of NO-dimers under these conditions, because the energy favourably compares with a dimer frequency (fig. 2). The former loss at 1840 cm^{-1} can, on the basis of the comparison with the Ni(111) data [9,19,21], as well as with the following experimental results of the present study, be assigned to NO adsorbed on Ni(100) modified by adsorbed atomic oxygen. This is supported by the

series of spectra shown in fig. 1c: as stated above we must assume that upon heating to room temperature NO dissociates and atomic oxygen is adsorbed on the surface (see for comparison also fig. 1b).

Better defined conditions are achieved when we preadsorb oxygen on the surface before we expose the surface to NO. Similar studies have been performed recently by Chen et al. [21], and we refer to those results via fig. 2. Fig. 3 shows our spectra of a Ni(100) surface on which a $p(2 \times 2)$ (fig. 3a), and a $c(2 \times 2)$ (fig. 3b) oxygen adlayer have been prepared, and which have been exposed to 1 and 12 L NO subsequently. Fig. 4 shows the corresponding sets of spectra where the coadsorbates have been heated to 200 and 300 K. We have again indicated in figs. 3 and 4 the positions of the losses derived from fig. 1 and transferred the information into fig. 2 in order to compare it with the previous results and with literature data. The



Fig. 4. HREEL spectra of the system (a) NO/c(2×2)O/Ni(100) exposed to 12 L NO at 95 K and consecutively heated to 200 and 300 K; (b) NO/p(2×2)O/Ni(100) exposed to 12 L NO at 95 K and consecutively heated to 200 K.

losses at lowest energies, i.e. at 360 and 410 cm^{-1} are due to oxygen-metal vibrations in the $c(2 \times 2)$ and $p(2 \times 2)$ [64–67] adsorbate layers respectively. Addition of NO to both oxygen adsorbate structures leads to populations of the same adsorbate sites as on the clean surface but with different probabilities. The following reasoning allows us to readily understand this observation. It is well known that oxygen in the $p(2 \times 2)$ as well as in the $c(2 \times 2)$ overlayer occupies the fourfold hollow sites. This blocks those sites for NO adsorption. Since in the $c(2 \times 2)$ two times as many sites are blocked as compared with the $p(2 \times 2)$ structure the losses at 1220 and 1330 cm⁻¹ are less populated in the former adlayer as can be seen from a comparison of figs. 3a and 3b. In turn this supports our assignment of the losses on the clean surface. Since we have assigned most of the losses to either bridge or terminal bonded NO (bent and linear) it is not too surprising that we still identify

these states on the surface in spite of the presence of the adsorbed atomic oxygen. While for high exposure, and also after heating to room temperature the loss spectra indicate very similar behaviour for both oxygen precoverages, the spectra taken after low NO exposure (1 L) exhibit characteristic differences. In particular, we find a reversal of the relative line intensities of the losses centered around 1600 and 1840 cm⁻¹ together with a slight energetic shift of the 1600 cm^{-1} loss and a smaller line width in the $p(2 \times 2)$ precoverage. It is not unreasonable that this is due to a blocking of sites that locally have the properties of pure Ni bridge and terminal sites when more oxygen is present on the surface. Therefore the oxygen modified surface sites exhibit higher populations. We believe this provides further support for the assignments put forward in the previous sections. It is important to realize, that in perfect agreement with the results on non-oxygen pre-



Fig. 5. NEXAF spectra of the systems NO/Ni(100) (a) and NO/ $c(2 \times 2)O/Ni(100)$ (b) at an exposure of 12 L NO at 90 K for two angles of incidence of the photons as indicated in the inset of (a).

covered Ni(100) the bending mode at 610 cm^{-1} survives the heat treatment and appears to correlate in intensity with the loss around 1840 cm⁻¹. We therefore are led to conclude that the NO molecule residing in the oxygen influenced adsorbate site is coordinated on-top of a metal atom with its molecular axis inclined with respect to the surface normal.

This assignment is further corroborated by a comparison with the reference molecules in fig. 2: We have assigned the bending mode at 690 cm^{-1} to a species adsorbed in a bridge site in line with the relatively high frequency of the bending mode observed for Ni(111) [9]; on the other hand the bending mode of the terminally bound NO molecule is close to the bending mode in ONCl [55] as well as in the bent transition metal complexes. This is basically what one would expect naively, namely that a bridge bonded species should exhibit a "harder" bending mode than a terminally bound molecule because more bonds have to be distorted upon bending in the bridge bound case. This analysis finally allows a reinterpretation of the very early IR investigations of Blyholder and Allen [4] studying NO adsorption on a polycrystalline Ni surface. The comparison with the frequencies observed in their experiments (see fig. 2)

are very close to our loss energies for the oxygen-NO co-adsorbate, and it is obvious that they had studied a partly oxygen covered Ni surface.

Summarizing the conclusions drawn based on the above discussion we may state:

(a) Adsorption on a clean Ni(100) surface begins by occupying fourfold hollow sites.

(b) Linear bridge and bent bridge sites as well as on-top sites are populated upon higher exposure.(c) If via heat treatment or high exposure the NO molecules are forced to dissociate a characteristic oxygen influenced NO species forms on the surface. The same species is observed when we preadsorb oxygen. In this configuration the NO molecule appears to be terminally bonded in a bent geometry.

We shall show in the following section that our NEXAFS results provide further evidence in favour of the above assignments.

3.2. NEXAFS results

In fig. 5 we have plotted some typical nitrogen K-edge NEXAF spectra of NO adsorbed on clean Ni(100) and $c(2 \times 2)$ oxygen precovered Ni(100). In both cases the substrate has been exposed to 12 L NO at 90 K. The dominant species present



Fig. 6. Evaluation of the angle dependent NEXAF spectra of NO/Ni(100) (\bullet) and NO/c(2×2) (\blacktriangle) according to the eq. given in the text. α : angle between electric field vector and surface normal. δ : angle between molecular axis and surface normal.

on the surface can be deduced from the HREEL spectra shown in figs. 1 and 3.

In the case of the clean Ni(100) substrate we have to consider the bridge and terminally bonded species giving rise to the loss peak centered around 1600 cm⁻¹. The NEXAF spectra shown in fig. 5a have been taken for normal (0°) and grazing (70°) light incidence. We see the strong attenuation of the π -signal at lower excitation energy and a considerable increase of the σ -signal due to the so-called σ -shape resonance as we move the angle of incidence towards grazing incidence. This is the typical signature of a situation where the molecular axis is nearly normal to the surface. A more quantitative analysis is given in fig. 6. The relative intensity of π/σ -signal has been plotted versus the angle between the light polarisation vector and the surface normal (\bullet) . If we know the degree of polarization of the light we may determine the orientation of the molecular axis by fitting the following equation to the experimental data [68]:

$$I_{\sigma}/I_{\pi} \propto \left[P(\sin^2\delta \, \sin^2\alpha + 2 \, \cos^2\delta \, \cos^2\alpha) + (1-P) \, \sin^2\delta \right] \left[1 - P \, \cos^2\alpha \right]^{-1},$$

in which P is the polarization.

The only remaining parameter of this equation is the angle between the molecular axis and the surface normal (δ). Fig. 6 shows a set of calculated curves where this parameter has been varied systematically as indicated. We find that the majority of molecules in the adsorbate under consideration must be oriented more or less perpendicular with respect to the metal surface, completely in line with our conclusions based on the HREELS data, and also in line with a previous NEXAFS study on the same system under comparable coverage conditions [13].

A corresponding analysis for the oxygen precovered Ni(100) surface is presented in fig. 5b where the nitrogen K-edge spectra are shown, and in fig. 6 which also contains the more quantitative intensity information for the complete series of angles of incidence of the oxygen precovered system (\blacktriangle). It is already obvious from the pure experimental data (fig. 5b) that the situation is different from the NO adsorbate on the clean Ni surface. The variation of the relative intensity ratio between π - and σ -signal is much less pronounced as compared with fig. 5a. A corresponding fit results in an angle between the molecular axis and the surface normal of roughly 40°. In other words, the majority of NO molecules on the oxygen precovered surface are tilted. Again, this is in accord with our conclusions from the HREELS data: the dominant species on the surface under the chosen conditions is the oxygen influenced terminally bound bent NO species giving rise to losses at 1840 cm^{-1} (stretching mode) and 610 cm^{-1} (bending mode). We have shown elsewhere [69] that NO also assumes a bent geometry on a completely oxidized, i.e. NiO(100) surface. It is therefore necessary to assure in situ that the surface is not oxidized when we carry out the NEXAFS experiments. Fortunately, this can easily be done by recording the oxygen K-edge NEXAF spectrum of the adsorbate because NiO exhibits characteristic features very different, and easy to differentiate from an oxygen adsorbed layer [70].

3.3. ARUPS and TPD results

In order to check to what extent the coadsorption of oxygen changes the electronic structure of the adsorbed molecules we have performed photoemission studies on the same systems for which we



Fig. 7. ARUPS data for NO/Ni(100) and NO/c(2×2)O/Ni(100) at 90 K and 37.5 eV photon energy. The parameters of the measurements are given in the figure and are defined in the inset.

presented our NEXAFS results, i.e. the clean and the oxygen precovered surface at 90 K and saturation coverage. Fig. 7 shows normal emission spectra at near grazing incidence with light polarized near normal to the surface for both the clean and the oxygen precovered system. If we disregard the very slight differences in the region around 6 eV the spectra are very similar indicating that the electronic structure of the two systems is still very similar. The similarity observed for normal emission is also observed at off-normal emission (fig. 7). The comparison of photoelectron spectra taken in the so-called allowed and forbidden geometry is not conclusive. Our results on the NO adsorbate on the clean Ni(100) surface favourably compare with those reported by Loubriel [7]. However, the surface temperature was T = 200 K in their experiments. We know from our HREELS study that at 200 K some bent NO and of oxygen influenced NO is present on the surface. It is therefore not surprising that Loubriel deduces a bent orientation of NO on the Ni(100) surface ion states because, as in the case in our experiments the σ -ion states do not completely disappear in the forbidden geometry. Another indication that at saturation coverage we have bent and linear NO molecules on the surface is the behaviour of the shape resonance in different geometries. Fig. 8 shows 4σ - (fig. 8a) and 5σ - (fig. 8b) shape resonances taken with z-polarised light and electron emission angles of 0° and 40°. The attenuation of the 5σ -resonance at off normal emission angles is considerably less than in systems with linear adsorbed NO [20].

Why there is so little difference in the photoelectron spectra of the oxygen-free and the oxygen-precovered surface, except for the small



Fig. 8. Intensities of the 4σ - (a) and 5σ - (b) ion states as a function of photon energies for normal electron emission (**A**) and emission 40° off-normal (**O**).



Fig. 9. 5σ - and 4σ -dispersion in the system NO/Ni(100) as a function of the wave-vector parallel to the surface determined via ARUPS applying the formula $k_{\parallel} = 0.512 (E_{\rm kin})^{1/2} \sin \theta$.

shift of the peaks, is not completely clear. Since we know that on the oxygen-free surface we also have to expect bent *and* linear molecules we cannot expect a textbook behaviour of the σ - and π -states in forbidden and allowed geometry.

The peaks in the spectrum which can be assigned to the 4σ and the $5\sigma/1\pi$ ion states show pronounced *E* versus k_{\parallel} dispersions as shown for the clean surface in fig. 9. The size of the dispersions is close to the expectation for an adsorbate with 0.5 coverage as is indicated via tight-binding calculations. The observed dispersion is larger as compared with the dispersion reported by Steinrück et al. [20] for the NO c(2 × 4)/Ni(111) overlayer.

Even though the vibrational spectra indicate a rather complex adsorption behaviour, the ARUP spectra do not mirror image the complexity in the electronic structure. The same is true for the temperature programmed desorption. Fig. 10 shows TPD spectra of the NO covered clean Ni(100)

surface in comparison with the oxygen-precovered surface. The results for the clean surface are basically identical with the results gained by Peebles et al. [16] some time ago. They are characteristic for chemisorbed NO. Most of the NO dissociates before desorption so that the flux of molecular NO from the surface is rather small. The peak maximum indicates [71] an adsorption enthalpy of around 0.93 eV. The interesting result revealed by fig. 10 is that the NO molecules on the oxygen precovered surface exhibit a higher desorption temperature as compared with the clean surface. The position of the peak maximum coincides with the high temperature shoulder for the clean surface, which may be connected with desorption from sites near adsorbed oxygen atoms formed via dissociation of NO molecules [16]. From the peak maximum we can estimate an adsorption enthalpy of about 1.06 eV. This explains why for the oxygen precovered surface even for rather small coverages a considerable fraction of the adsorbed molecules resides near the oxygen atoms: it is the energetically favourable site. This situation is different from the situation on other surfaces, e.g. on Pt(111) [42] and Ni(111) [15], where the NO bonding becomes weaker in the presence of coadsorbed oxygen [42].



Fig. 10. Thermal desorption spectra taken at 2 K s⁻¹ heating rate for NO/Ni(100) (a) and NO/c(2×2)O/Ni(100) (b).

3.4. On the bonding of NO to metal atoms

The discussion of bonding between CO and a metal surface has been the subject of many papers during the last decade. It is not the aim of this section to review and evaluate this discussion. Instead, we shall adopt at this point the old-fashioned Blyholder model of CO bonding [72] and try to evaluate whether this model allows us to understand why and under which conditions a molecule like CO or NO is going to bind in a linear or a bent geometry. We shall proceed at this point basically at a one-electron level and consider the effects of σ -donation and π -backdonation as a function of the angle between a metal atom, fixed in space by the surface, with a configuration of electrons determined by the metal surface of which it is part, and by possibly present coadsorbates that may or may not influence the electronic structure of the metal atom under consideration. Very similar considerations apply for nitrosyl complexes [73]. Bonding of NO on transition metal surfaces has been discussed before [7,74-77].

Fig. 11 shows on the left a schematic diagram of the d-orbitals of a Ni atom in a square pyramidal environment as adopted from ref. [73]. On the right we have indicated the position of a doubly occupied non-bonding lone pair of a diatomic molecule as well as the positions of a non or partly occupied doubly degenerated π^* -level of a diatomic molecule like CO or NO. The coordinate system has been chosen as indicated in the figure. Let us first consider the situation in a linear molecule-metal bond. In such a situation the Blyholder model predicts a σ -interaction, i.e. between the d_{z^2} metal level and the molecule lone pair orbital, and a π -interaction between the metal d_{xz} , d_{yz} levels and the two π^* -components (π_x^*, π_y^*) . If the d_{z²} and the lone pair are both doubly occupied there will be a Pauli repulsion between the two orbitals and the net effect of this interaction for the metal-molecule bond will be repulsive. However, the Ni atom still has unoccupied 4s-levels available in which the lone pair may donate its electrons, and thus establish a bonding σ -donor interaction. Since the configuration of a Ni atom within a Ni(100) surface is close to $4s^{1}3d^{9}$, the bonding of the molecule may, if the



Fig. 11. Schematic molecular orbital diagram for the interaction of the nitrogen lone-pair (n) and the antibonding $2\pi^*$ NO orbitals (right) with a set of atomic d-orbitals which have been energetically arranged such as to represent a square planar environment of ligands (left) (ref. [73]).

interaction is strong enough, help to change the configuration to $3d^{10}4s^0$ and establish a σ -donor interaction [78]. Simultaneously, there will be a strongly bonding metal-molecule π -interaction as long as the π *-levels of the molecule are empty, and the metal π -levels are occupied. If the π *-levels of the molecule become occupied this interaction becomes more and more repulsive.

The question we have to answer next is: how do these interaction change a we change the angle between the fixed Ni atom and the molecular axis? This problem can be solved on the basis of a Walsh-diagram shown in fig. 12 [73]. As is indicated by the molecular orbital diagrams within fig. 12 the metal-lone-pair repulsion, and the bonding metal-molecule π -interaction is largest for linear bonding. In other words, if the π -bonding is the dominant interaction and the σ -repulsion can be minimized the molecule will be bound in a linear geometry as is CO in most cases. Upon bending the metal-molecule bond the σ -repulsion is going



Fig. 12. Schematic Walsh-diagram for four one-electron orbitals shown in fig. 11. The energies of the molecular orbitals are plotted as a function of the M-N-O angle.

to decrease because the lone-pair-metal d₂ overlap decreases. Also the overlap of the π^* -levels of the molecule with the metal d_{xz}/d_{yz} levels decreases. However, the overlap of the π^* -levels with the d_{z^2} levels increases upon bending the bond. Therefore, bending the bond is stabilized by minimizing the σ -repulsion and maximizing the $\pi^* - d_{z^2}$ overlap. In other words whether a NO molecule is bent bond to a metal atom depends on two opposing factors: the slope of the d_{2} level, which favours bending, and the slope of the d_{xz} level, which favours linearity. Of course, these statements apply only if the corresponding metal orbitals are occupied, that is the configuration of the metal atom is at least d⁷, because in the case of a d^6 configuration the d_{z^2} orbital is no longer occupied. Also, the higher the energetic position of the d₂ level is before interaction with the NO molecule, the stronger its stabilizing interaction, as it bends, with π_{xz}^* . This effect is stronger than the

linearity favouring less stronger destabilizing interaction between d_{z^2} and the molecular lone-pair. Synergetically, the higher the energetic position of the d_{xz} , the less its destabilizing interaction with the molecular lone-pair, and the greater its stabilizing interaction with π_{xz}^* . Consequently, a higher position of the d_{xz} level will lessen the preference of that orbital for the linear geometry. In conclusion, the net result of raising the energy of the d_{z^2} and d_{xz} levels is to favour bending of the molecule-metal bond.

These qualitative arguments may help to rationalize the experimental result, that very many different types of NO coordinations are observed. The balance of the above discussed contributions to the relative stability of linear or bent bonding is very likely to change when we change the NO coverage or if we introduce electronegative adatoms on the surface. Probably also lateral intermolecular interaction is an additional factor that determines the orientation of the molecular axis. It appears that in the case of coadsorbed oxygen we find one type of oxygen influenced NO species, namely a terminally bound bent NO. If we disregard lateral interactions in this case for the moment we may conclude that it is the above discussed increase of d-level energies at the Ni atom adjacent to the adsorbed oxygen that leads to stabilization of a bent NO-metal bond. In order to draw more detailed conclusions one would need more information about the site. It would be very helpful to try to prepare an ordered O + NOcoadsorbate structure and perform a detailed LEED study on such a system. Unfortunately, the present system does not seem to be the proper choice, but possibly the O + NO/Ni(111) system is a more interesting candidate for such a study.

4. Summary and conclusions

We have shown in the present study that chemisorption of NO on Ni(100) is rather complex. On the clean surface NO adsorbs in hollow sites at low coverage and T = 95 K with perpendicular orientation of the molecular axis relative to the surface plane, followed by adsorption in bridge sites where both linear and bent species may be present upon increase of exposure. Simultaneously, terminally bound molecules with perpendicular orientation are present on the surface, and at saturation coverage we cannot exclude the existence of $(NO)_2$ dimers on the surface.

If the surface is precovered with oxygen a fraction of the adsorbed molecules still occupy the same sites as on the oxygen-free surface but there is a new oxygen influenced NO species present on the surface that is characterized by a relatively high NO stretching frequency, close to the gas phase value. Similar species have been observed recently on Ni(111) by Chen et al. [21]. We show via the analysis of NEXAFS data that this species is adsorbed in a bent geometry. This species is bound to the Ni(100) surface stronger than any species on the clean Ni(100) surface, as indicated by a higher desorption temperature in the TDS spectrum. The electronic structure of this species is not significantly different from NO on the clean surface as suggested by the very similar photoelectron spectra in both cases.

We present a general discussion of NO bonding towards metal surfaces with particular emphasis on the question under which conditions one may expect a linear versus a bent orientation of the molecular axis. This discussion is based on qualitative arguments and is supported by semi-empirical calculations. We show that bending of the metal-molecule bond depends on two opposing factors: the avoiding of σ -repulsion, and the attenuation of π -back-donation as a function of the bond angle. Another factor is the energetic position of the metal level involved in the σ -repulsion: the higher its energy the steeper the energetic stabilization upon bending and the stronger the stabilization upon bending. Since the energy of this level will increase if the Ni atom is close to an oxygen atom the NO molecule bound to this Ni atom will assume a bent configuration.

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