

Adsorption of CO and NO on NiO and CoO: a comparison

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Abstract

Polar (111) and non-polar (100) thin epitaxial NiO and CoO films were prepared on suitable Ni and Co single-crystal metal surfaces. On these oxide films, CO and NO were adsorbed to probe the local electronic and geometric structure of the substrates using electron spectroscopic methods, especially HREELS and NEXAFS. On all oxide surfaces, the N–O stretching frequencies exhibit a red shift due to the chemical bonding to the surface, whereas the C–O stretching frequencies all lie in the vicinity of the C–O gas phase value with a tendency for a blue shift because of the purely electrostatic interaction with the substrates. An evaluation of these data together with NEXAFS data show that the NiO(111) film, which undergoes octopolar reconstruction upon heating, exhibits microfacets with fourfold sites tilted about 55° away from the surface normal even at room temperature. The situation on CoO(111), which cannot be heated sufficiently to prepare a reconstructed surface, seems to be somewhat different; a model of the possible structure of the unreconstructed CoO(111) surface is proposed.

Keywords: Carbon monoxide; Catalysis; Chemisorption; Cobalt oxides; Electron energy loss spectroscopy; Insulating films; Iron oxide; Near edge extended X-ray absorption fine structure (NEXAFS); Nickel oxides; Nitrogen oxides; Single crystal surfaces

1. Introduction

Both NiO and CoO are ionic oxides with rock-salt structure. The thermodynamically most stable surface is the non-polar (100) orientation. The (111) surfaces of these oxides are polar, which renders them thermodynamically unstable [1–3], and in turn leads to a diverging surface potential. It is, however, possible to prepare epitaxial (111) oxide films on Ni(111) and Co(0001) substrates [1,4] using two different routes of stabilization.

NiO(111)/Ni(111) exhibits a well ordered hexagonal (1 × 1) LEED pattern directly after prepara-

tion [1,5,6]. HREELS and XPS measurements indicate the presence of a considerable amount of OH at the surface [1,6]. The OH groups were desorbed by heating the sample to 600 K, which resulted in a p(2 × 2) pattern in SPA LEED measurements [1,5]. This superstructure can be attributed to the formation of an octopolar reconstruction [1,5,7], shown schematically in Fig. 1. The same reconstruction has been observed by Neddermeyer and his group with STM on even thinner films deposited on Au(111) [10]. Quantitative XPS analysis resulted in an oxide film thickness of about 30 Å.

NiO(100)/Ni(100) shows a broad (1 × 1) (100) pattern [11] with no or little OH present, and no

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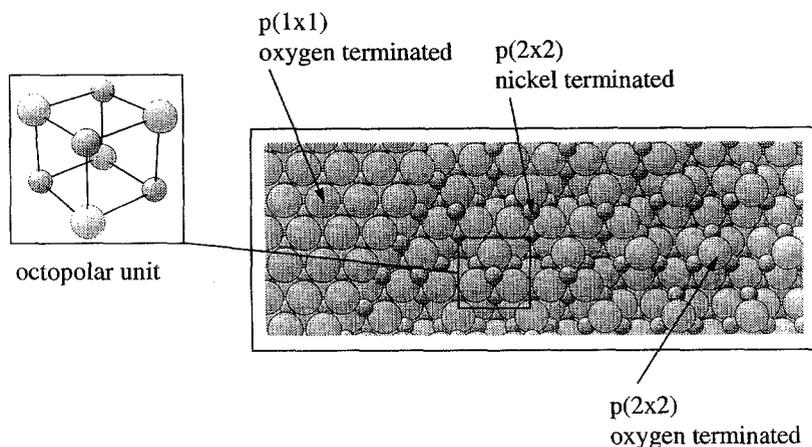


Fig. 1. Schematic representation of the $p(2 \times 2)$ reconstructed $\text{NiO}(111)$ surface.

tendency for reconstruction. $\text{CoO}(111)/\text{Co}(0001)$ also showed a well ordered hexagonal (1×1) LEED pattern after oxidation with OH present at the surface [9]. The film thickness was in the range of 30 Å. $\text{CoO}(100)/\text{Co}(11\bar{2}0)$ exhibited quite a sharp (1×1) LEED pattern and was about 15 Å thick.

The polar (111) transition metal oxide surfaces are particularly interesting as the deviation from bulk termination due to the different stabilization mechanisms can result in an enhanced reactivity which is very interesting within the context of catalysis. In the case of $\text{NiO}(111)$, for example, the reconstructed surface adsorbs a factor of three more NO than the unreconstructed surface [4], and probably even some NO_2 is formed [8]. On $\text{CoO}(111)$, NO molecules adsorbed in the direct vicinity of the stabilizing OH molecules interact with the OH groups to form a more stable adsorbed species, probably a species similar to HNO_2 [9]. As the $\text{CoO}(111)$ surface suffers severe damage before the required temperature for OH desorption is reached, nothing can be said about the reactivity of a possibly reconstructed but adsorbate-free $\text{CoO}(111)$ film [9].

Although CO and NO are often adsorbed to probe the structure of surfaces, there have been few systematic studies of the adsorption behaviour of NO and CO on comparable substrates such as NiO and CoO . Here, an overview of the N–O and C–O stretching frequencies is given which shows

certain systematics regarding the shifts relative to the gas phase value. Furthermore, the local structure of CO and NO adsorbates on $\text{NiO}(111)$ and on $\text{CoO}(111)$ is investigated in this paper. Models are presented for the structure of both polar oxide surfaces based on HREELS and NEXAFS data.

2. Experimental

The samples have been studied in two different UHV systems by HREELS (high-resolution electron energy loss spectroscopy) and NEXAFS (near-edge X-ray absorption fine structure). The HREEL spectra were taken using a double-pass cylindrical electron monochromator and analyser that led to a resolution of about 8 meV. The NEXAFS measurements were performed at the HE TGM1 beamline at the synchrotron radiation centre BESSY (Berliner Elektronenspeicherring Gesellschaft für Synchrotronstrahlung mbH) in Berlin, Germany, with a resolution of about 1 eV. The procedure used for data accumulation and intensity calibration has been described in detail elsewhere [12]. The background has been removed from the spectra and the intensities have been normalized to the step edge using recipes from the literature [13].

Furthermore, both UHV systems were equipped with ion guns for sample preparation, quadrupole mass spectrometers and LEED (low-energy

electron diffraction) systems. The samples were spot-welded to tungsten rods that were connected to a liquid nitrogen reservoir. A temperature of 100 K could be reached. Behind the sample, a tungsten filament was mounted as a heating facility.

The metal single crystals were cleaned by repeated cycles of Ne ion bombardment and annealing. The oxide films were grown on Ni(100) and Ni(111), respectively, by cycles of oxidation with 1000 L ($1 \text{ L} = 10^{-6} \text{ Torr}\cdot\text{s}$) of O_2 at elevated temperatures ($T = 540 \text{ K}$), followed by annealing at $T = 650 \text{ K}$. The LEED patterns of the samples showed the formation of ordered oxide films.

3. Results and discussion

Fig. 2a shows HREEL spectra of NO adsorbed on the NiO(111) oxide film as prepared, the dehydroxylated (111) film and the (100) oxide film. All NiO HREEL spectra were taken at 80 K. The full HREEL spectra have been reported in detail before, where we discuss the substrate excitations [1] as well as the NO vibrations for NiO(100) [11]. Therefore, here only the range of the N–O stretching frequencies is shown, and all spectra are difference spectra of the adsorbate-covered and clean surfaces. Previous studies [11] showed that the N–O stretching frequency of NO on NiO(100) lies at 1797 cm^{-1} , and indicated that the NO molecule is adsorbed on NiO(100) with the nitrogen end towards the surface with a tilting angle of about 45° [11]. The N–O stretching frequency of NO on hydroxylated NiO(111) is found at 1772 cm^{-1} , whereas for NO on dehydroxylated NiO(111), the N–O stretching frequency can be seen at 1805 cm^{-1} , closer to the value of NO on NiO(100). This is compatible with the model of the (111) surface undergoing octopolar reconstruction upon heating in the following sense.

On the hydroxylated surface, only non-hydroxylated areas adsorb NO, exhibiting an NO frequency different from NiO(100). Upon reconstruction, the surface exposes mainly fourfold sites which are equivalent to the NiO(100) surface (Fig. 1). In the case where the reconstructed surface is nickel terminated, there is an extra site at the top of each octopolar unit where a Ni ion

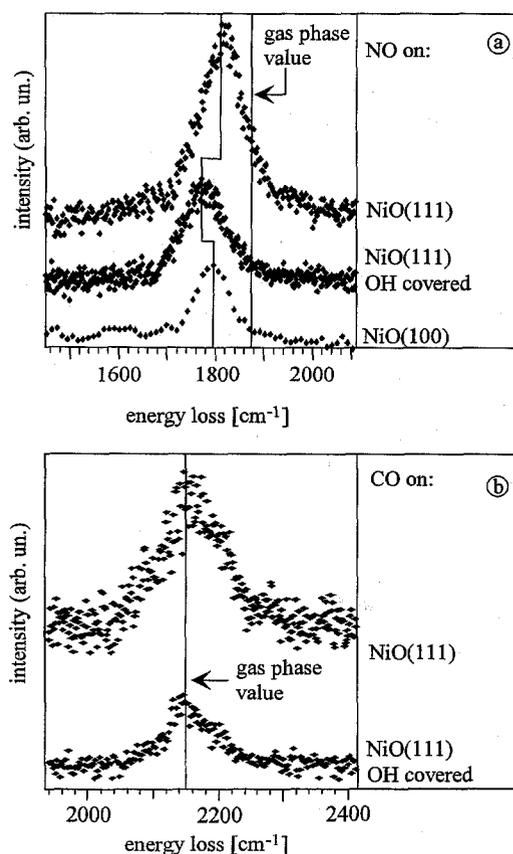


Fig. 2. HREEL spectra of NO adsorbed on NiO(100), NiO(111) OH covered and NiO(111) ($T = 80 \text{ K}$) (a), and of CO adsorbed on NiO(111) OH covered and NiO(111) (b). Close-up of the N–O- and C–O- stretching vibration regime.

in a threefold environment is exposed (Fig. 1). However, if the surface is oxygen terminated (Fig. 1), this site is occupied by the oxygen atom and is thus not available for NO bonding. Therefore we expect an envelope of the NO stretching band very close to those observed for NiO(100), in line with the experimental observations.

The HREEL spectra of CO on NiO(111) and dehydroxylated NiO(111), shown in Fig. 2b, do not differ significantly. On both substrates, the center of gravity of the band of C–O stretching frequencies is situated close to the gas phase value of 2151 cm^{-1} , indicating a rather weak interaction with the substrate. On NiO(100), the C–O stretch-

ing frequency has been found to be 2159 cm^{-1} [12], very close to this value. This finding suggests that the environment of the CO molecule is quite similar on both oxides or that the interaction is so weak that differences cannot be observed. Due to the results on NO adsorption the latter possibility is favoured.

Fig. 3a shows the N–O stretching vibration of NO adsorbed on CoO(111) and CoO(100). Again, all CoO HREEL spectra were taken at 80 K. In contrast with the NO adsorbate on the NiO(111) surface, the CoO(111) surface clearly exhibits two NO stretching vibrations, and there is also a weak second band for NO on CoO(100). For NO on CoO(111) one band is located at a frequency of

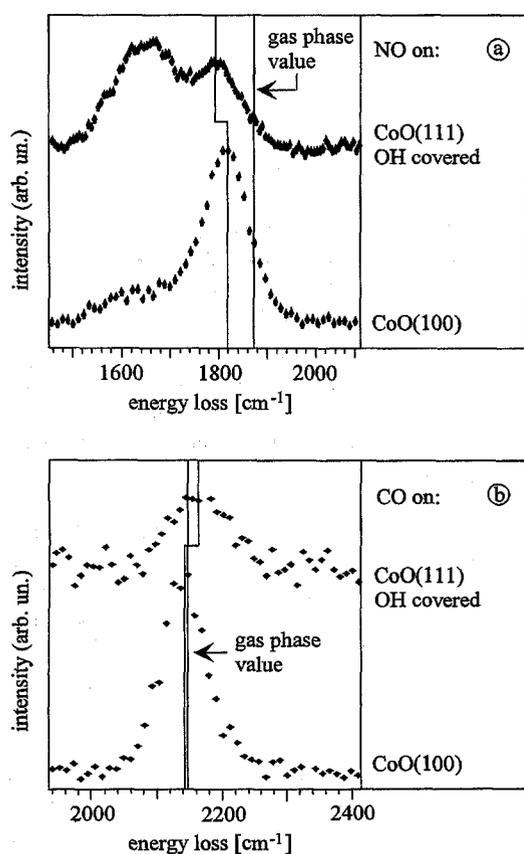


Fig. 3. HREEL spectra of NO adsorbed on CoO(100) and CoO(111) OH covered ($T=80\text{ K}$) (a) and of CO adsorbed on CoO(100) and CoO(111) OH covered (b). Close-up of the N–O and C–O stretching vibration regime.

1652 cm^{-1} and one at 1789 cm^{-1} , and for NO on CoO(100) the more intense band is located at 1813 cm^{-1} and the second one close to 1650 cm^{-1} . The vibration near 1800 cm^{-1} belongs to a species which is similar to the one on NiO, adsorbed with the nitrogen end towards the surface [9]. Just as on NiO, the frequency of this species on the CoO(100) surface lies about 25 cm^{-1} above the frequency of NO on the (111) surface. The vibration near 1650 cm^{-1} is very likely due to an NO species which interacts with the OH groups on the CoO surface as has been discussed in detail elsewhere [9]. Briefly, we have shown [9] that the species giving rise to the band near 1800 cm^{-1} desorbs at 180 K, i.e. only slightly below the desorption temperature observed for NO on NiO. Since Petterson's calculations [14] indicate a slightly weaker binding for NO on CoO as compared with NiO we assign this band to a "regular" NO adsorption. On the other hand, the frequency near 1650 cm^{-1} is very low for a regular NO species. However, it is near the NO stretching frequency in HNO_2 [9], which leads us to assign this frequency to an NO species interacting strongly with neighbouring OH groups. Two observations support this assignment. First, desorption of the species with low vibrational frequency takes place above 240 K, and secondly, the NO stretching frequency is shifted upon exchange of the OH coverage to an OD coverage. The shift upon isotopic labelling is 32 cm^{-1} , and is thus compatible with *cis*- HNO_2 (not with *trans*- HNO_2), a fact that is expected for two NO and OH molecules adsorbed parallel on a surface [9].

The HREEL spectra of CO on CoO(111) and CoO(100) (see Fig. 3b), also show a difference of 25 cm^{-1} in the C–O stretching vibration frequency, in contrast to the situation on the NiO surfaces. On CoO(111), the C–O stretching vibration even lies above the gas phase value. Such a frequency shift has been attributed to the so-called "wall effect" [15], the Pauli repulsion the adsorbed molecule experiences when vibrating near the diffuse bulky oxygen anions at the surface. The difference of 25 cm^{-1} suggests different environments on the two surfaces.

To give a systematic overview, Fig. 4 shows the N–O and C–O stretching vibration frequencies on

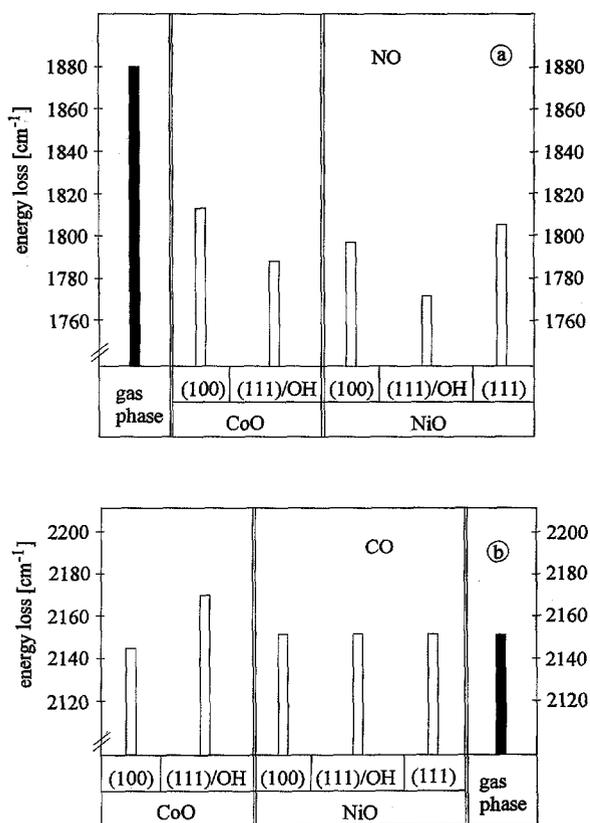


Fig. 4. Overview over the stretching vibration frequencies of (a) NO and (b) CO on all investigated NiO and CoO surfaces plus the gas phase values.

all the surfaces investigated in this work. First, it can be seen that all N–O frequencies are shifted towards lower frequencies compared to the gas phase value, whereas all C–O frequencies lie at or close to the gas phase value. This can be understood in terms of bond character. For CO on NiO(100), calculations show that the interaction of CO with the surface is purely electrostatic [15–17]. The bond is weak, and the frequency of the C–O stretching vibration lies at the gas phase value or slightly above (wall effect) [15]. Fig. 4 shows that this obviously also holds for the other NiO and CoO surfaces. The situation is different for NO on NiO(100). Here, calculations show that there is a chemical bond between NO and the surface [11]. According to these calculations, there is an interaction between the Ni 3d electrons and

the NO 2π -orbital which weakens the N–O bond. Therefore, the N–O stretching frequency is chemically shifted towards lower frequencies compared to the gas phase value. This also seems to be the case for NO on the other surfaces, as can be seen in Fig. 4.

Another similarity between NiO and CoO is found when the differences in the N–O stretching vibration frequencies for NO on the (111) and (100) surfaces are compared. For both NiO and CoO, the N–O stretching vibration is shifted 25 cm^{-1} towards higher frequencies for NO on the (100) surface compared to the hydroxylated (111) surface.

The vibrational frequencies may be compared with data reported in the literature for thin-film systems [18,19] and for powder samples [20,21]. A direct comparison of NO and CO adsorption has recently been reported by King and his group [18] for a NiO film grown on a Ni(110) surface. Also, Goodman and collaborators have systematically studied oxide films [22–24] and in particular important for the present work, CO adsorption on a NiO(100) film grown on Mo(100) [19]. The other important body of references may be found in the work from the Torino group around Zecchina [20,21], who have studied CO and NO adsorption on many oxides including NiO. Both Sanders et al. [18] and Vesecky et al. [19] report CO stretching frequencies (2148 cm^{-1} [18] and 2156 cm^{-1} [19]) that are compatible with the present results for the terrace sites of the NiO(100) surface. This interpretation is also in agreement with Escalano-Platero [19,20]. Corresponding conclusions may be drawn for NO adsorption, for which Sanders et al. [18], as well as Escalano-Platero [20,21] report stretching frequencies (1805 cm^{-1}) [18] that are in line with the present values. While the values reported in the literature have been determined from IRAS spectra which could be recorded with better resolution than the present data, in the present case structural information could be obtained parallel to the vibrational studies, as we shall show in the following.

As has been shown previously [25], CO is adsorbed perpendicularly with the carbon atom directed toward the surface on NiO(100). For the (111) surface the situation is more complicated due

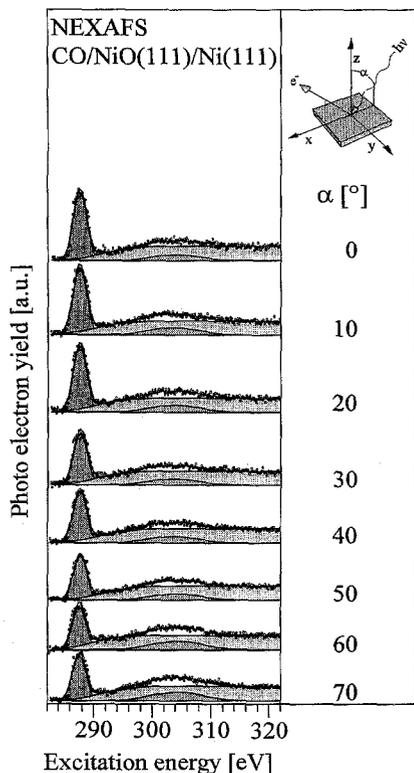


Fig. 5. NEXAFS spectra of CO adsorbed on NiO(111) OH covered in the range of the carbon K-edge. The π -resonance is located below 290 eV photon energy, and the broad, very low σ -resonance between 300 and 310 eV.

to the reconstruction as will be discussed below. Fig. 5 shows the NEXAFS spectra of CO on NiO(111), as-prepared, in the range of the carbon K-edge. Background subtraction and normalization of the spectra have been performed using well-known procedures [12,13]. The spectra show a rather large π -resonance and a very weak σ -resonance, comparable to the data of gas phase CO [25]. Fig. 6 shows a plot of the normalized π -resonance intensity versus the angle of light incidence. As can be seen, there is no significant intensity variation. Fig. 6 also shows the calculated π -resonance intensity variations for various tilting angles δ of the molecule [11]:

$$I_{\sigma} \approx -P \sin^2 \alpha + 1 - [1 - 3P \sin^2 \alpha] \cos^2 \delta, \quad (1a)$$

$$I_{\pi} \approx P \sin^2 \alpha + 1 + [1 - 3P \sin^2 \alpha] \cos^2 \delta, \quad (1b)$$

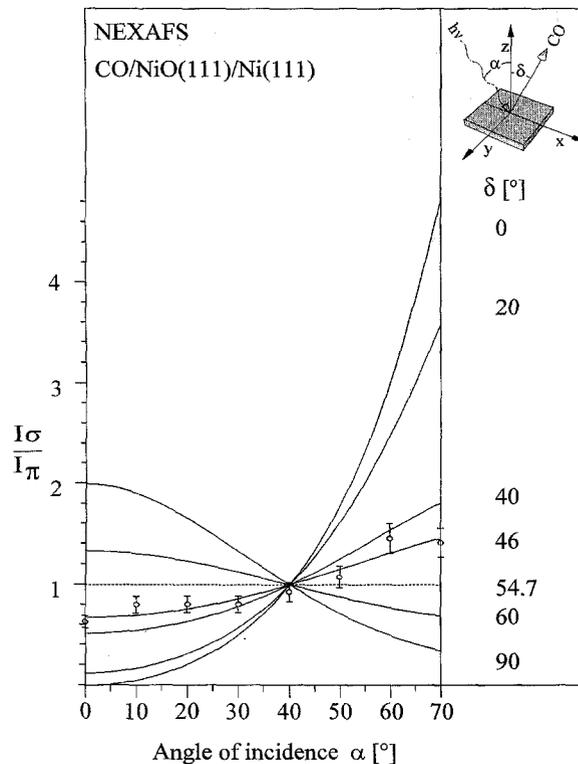


Fig. 6. π -resonance intensity as a function of light incidence angle. The data of Fig. 5 as well as results from calculations (Eq. (1a)) are shown (see text).

where α is the light incidence angle and P is the degree of linear polarization. The data are consistent with a tilting angle of about 46° , in the range of the “magic angle” of 54.7° , where no dependence of the intensity on light polarization direction is expected.

This is compatible with the existence of patches exposing the reconstructed surface even on the OH-covered NiO(111) surface onto which CO is adsorbed, as the angle between the surface normals of a microfacet (see Fig. 7a) in the reconstructed phase and the unreconstructed (111) surface is 54.7° . A CO molecule adsorbed on a NiO (100) microfacet would be oriented perpendicular to this microfacet (Fig. 7) and thus be strongly inclined with respect to the average (111) orientation. The NEXAFS data are therefore compatible with the hypothesis that CO is adsorbed perpendicularly on the microfacets present even on OH-covered

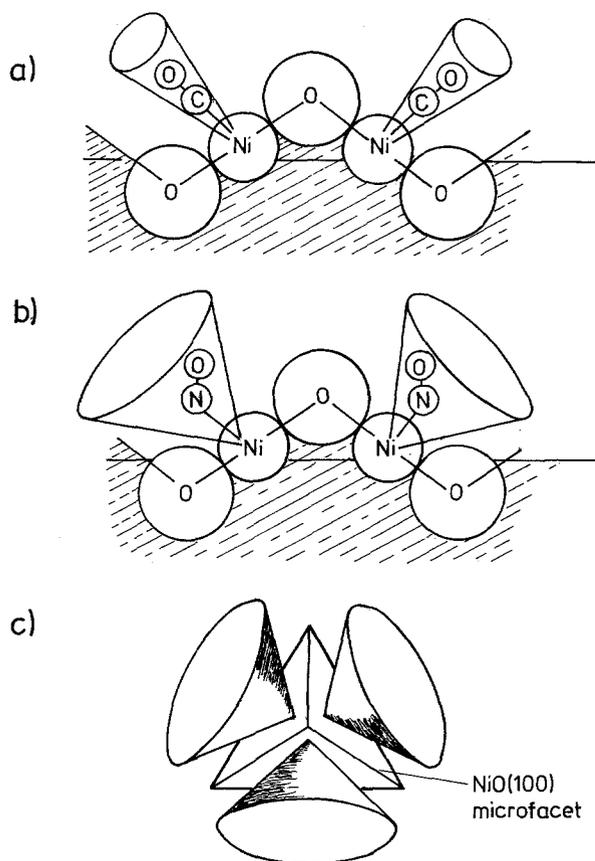


Fig. 7. Schematic representation of the surface orientation of (100) microfacets on a (111) surface plane. The orientation and motional cones of adsorbed CO and NO are indicated. (a) CO adsorption, (b) NO adsorption, viewed perpendicular to the (111) surface plane, (c) NO adsorption as looked down upon along the (111) direction.

NiO(111), which results in an overall tilting angle of $\sim 45^\circ$ – 55° .

Fig. 8 shows NEXAFS spectra of NO on OH-covered NiO(111) in the nitrogen K-edge range. The σ -resonance and π -resonance are of about the same magnitude now. As mentioned before, on NiO(100) the NO molecule is adsorbed with the nitrogen end towards the surface with a tilting angle of about 45° [11]. The NEXAFS data in Fig. 8 show no significant intensity variation with varying light incidence angle. In fig. 9, the intensity ratio of σ -resonance to π -resonance versus the light incidence angle is shown together

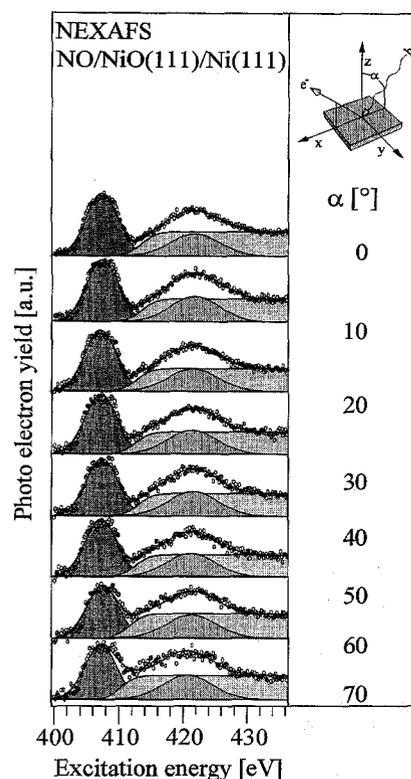


Fig. 8. NEXAFS spectra of NO adsorbed on NiO(111) OH covered in the range of the nitrogen K-edge.

with calculated intensity ratio variations [11] for various tilting angles. These data suggest a tilting angle of $\sim 53^\circ$. This is not compatible with a spatially fixed adsorption geometry of NO on the microfacets, because NO is tilted by about 45° with respect to the facet (Fig. 7b), which should result in a tilting angle of about 10° with respect to the global surface plane. If, however, the NO molecule rotates about the microfacet normal (Fig. 7c), the NEXAFS signals would also become more or less independent of the light polarization direction because the molecules would then be azimuthally disordered. This could also account for the fact that the stretching frequency of NO on NiO(111) differs from that of NO on NiO(100). Such a model would be fully consistent with the observations.

As for CoO(111), the situation appears to be different from that on NiO. Although the HREELS

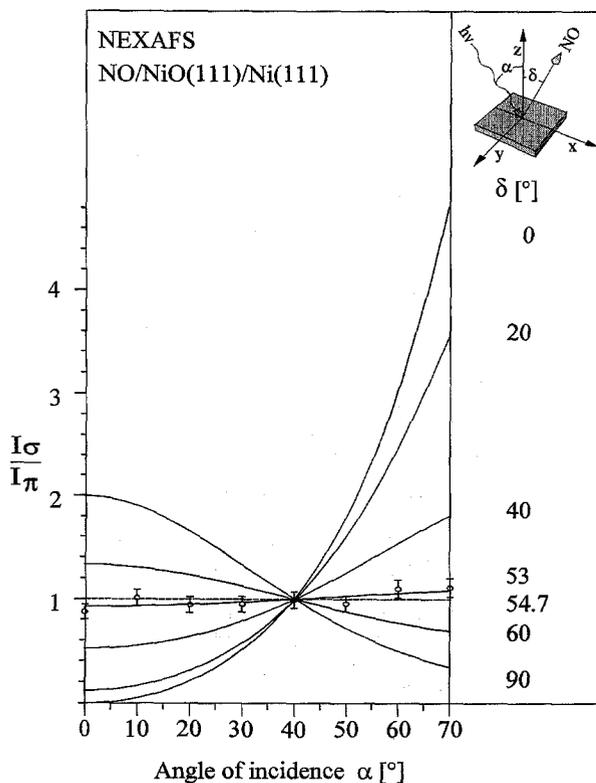


Fig. 9. σ/π -resonance intensity ratio as a function of light incidence angle. The data of Fig. 8 as well as results from calculations (Eqs. (1a) and (1b) with the ratio plotted) are shown (see text).

data point towards a similar situation, since the difference in N–O stretching vibration frequencies is comparable to that of NO on NiO, the CO data need further comment. The difference in C–O stretching vibration frequencies on CoO(100) and CoO(111), and also the fact that CO on the (111) surface has a stretching vibration frequency above the gas phase value, suggests a different environment for CO adsorption on CoO(100) and CoO(111). One possible picture would be that on CoO(111), the reconstructed patches are not oxygen terminated, as suggested for NiO(111), but cation terminated (see Fig. 1), possibly because of the lower ionicity of CoO compared to NiO. This would result in different additional adsorption sites, as both CO and NO only adsorb on cationic sites [8,9,11,26]. For CoO, however, further inves-

tigations are necessary to clarify this point, possibly with IRAS.

4. Synopsis

We have compared the vibrational spectra of NO and CO adsorbates on non-polar and polar oxide surfaces in order to probe the local geometry and bonding characteristic of the adsorption sites. The information gained from the vibrational spectra were augmented by structural information from NEXAFS analysis. We find that the two sets are compatible if we take into account the so-called octopolar reconstruction of the polar surfaces.

Although the present study provides some systematics on CO and NO bonding on the different substrate orientation, a full understanding, including the trends across the series of the transition metal oxides with rock salt structure, will require considerable more work in the future including iron oxide and manganese oxide.

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