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The bonding between NO and the NiO(100) surface*

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Summary. The interaction between NO and different possible adsorption sites of the NiO(100) surface is studied. The Ni^{2+} cation gives a bonding to NO in reasonable agreement with experiment, but only if a crystal potential corresponding to less than completely ionic charges is assumed. The computed angle of 43° is also in good agreement with experiment. O^{1-} sites in both weak and strong crystal potentials also give a strong interaction with NO, 1.3 and 0.5 eV, respectively. In this case the angle is larger or around 70°. The O^{2-} anion and Ni^{1+} sites do not give any significant bonding irrespective of assumed crystal potential and can be excluded as adsorption sites. The computed vibrational frequency for the adsorbed NO show shifts of $+50$, -85 and $-200\,\mathrm{cm}^{-1}$ for adsorption on Ni^{2+} in the weak potential, and O^{1-} in strong and weak potential, respectively. Only one, downwards shifted, frequency has been observed in the experiment but the most likely candidate for the experimentally observed adsorption site with a binding of 0.5 eV, is still the Ni^{2+} in a weak potential. Nitrogen core level shifts are also computed and discussed and the fully screened core-hole state is obtained for a cluster model, $NiF_4O + NO$, of Ni^{2+} in NiO with an ionicity lower than the standard ± 2.

Key words: NO – NiO(100) surface – Bonding

1 Introduction

The interaction between NO and transition metal oxide surfaces is of great importance in the context of catalysts, e.g., for reducing the NO_x content of exhaust gases. As a first step in such a reaction it may be assumed that a gas-phase NO molecule adsorbs at the surface before undergoing any reaction. However, in the case of NO the type of bonding and site at which the NO binds to the surface are largely unknown, both experimentally and theoretically. A particularly interesting case, where detailed experiments have been performed is the interaction between NO and the (100) surface of a cleaved NiO single crystal or a thin layer of NiO grown on nickel metal. For this system Kuhlenbeck et al. [1] have presented results

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* This work is dedicated to Prof. Inga Fischer–Hjalmars

from very nice experiments where the NO was found to adsorb at an angle of 45° against the surface and with a rather large binding energy. Through temperature programmed desorption the NO was found to desorb as a single peak at 220 K, which gives a binding energy to the surface of 0.52 eV. For the same surface CO is not observed at temperatures above 90 K which indicates that the binding energy in this case is less than 0.2 eV [2]. In a theoretical section of the experimental paper [1] Pöhlchen and Staemmler were able to demonstrate from cluster model calculations that the bent geometry originates from a weak interaction between the singly occupied π^*-orbital of the NO with the open $3d$-shells of the central Ni^{2+} ion of the cluster, though no chemical bond in the normal sense was obtained. They followed up this work by a separate study [3] of the NO/NiO(100) system comparing with earlier results for CO on NiO(100) [4]. Several different cluster-models were investigated, as were effects of basis set extensions and inclusion of dynamical correlation. However, the resulting computed binding energies for both species were found to be very similar and both less than 0.15 eV. The interaction that was found could be explained as originating from electrostatic interactions and no explanation of the strong interaction in the case of NO with NiO could be given. The computed interaction energy for the NiO_5 cluster model is in addition very likely an overestimate of the true adsorption energy for the cluster chosen. When the NiO_5 cluster was embedded in a surrounding of Mg^{2+} pseudopotentials the binding energy was seen to be strongly reduced [3]. The same effect has been found for CO on cluster models of the MgO(001) surface [5] and is the result of an increased repulsion against the O^{2-} anions obtained when these are not allowed to polarize towards a set of surrounding (nearest-neighbour) positive point-charges representing the crystal Madelung potential. Thus, if anything, the obtained theoretical binding energies are overestimates, both for CO and NO adsorption on NiO, and would very likely be reduced to close to zero if a proper embedding was used.

The comparison between CO and NO can be taken even further. On MgO(001) both species adsorb very weakly, with an experimental adsorption energy of 0.16 eV for CO. This is of the same order of magnitude in the case of CO as for adsorption on NiO. Furthermore, NO is known to dimerise in the gas-phase and NO dimers are observed on the MgO surface, but have not been observed on NiO [6].

This intriguing and important problem has lead us to investigate in depth the interaction between NO and the NiO(100) surface. We have considered translations of the NO over the surface in search of more favorable adsorption sites, but the NO remains only weakly adsorbed and with very small energy barriers for the surface diffusion. Only by removing the assumption of a perfect ionicity of ± 2 at the surface do we obtain any significant binding. This corresponds to considering the interaction with ions having *unsatisfied ionicities* in the sense of not having the full ionic charge and/or being placed in a weaker or stronger Madelung potential. We have thus studied adsorption on both Ni^{n+} and O^{n-} with $n = 1, 2$ for both strong and weak ionic interactions with the remaining crystal. For ions with unsatisfied ionicities, such as O^{1-} in strong and weak potential and Ni^{2+} in a weak potential, the interaction with NO is quite strong with a binding energy of 0.5–1.3 eV resulting from a large degree of covalency and with a tilted NO molecule. The interaction with the closed-shell CO molecule remains completely electrostatic and is not affected by the electronic structure of the substrate atom. For each case we have obtained the equilibrium geometry, the adsorption energy, vibrational frequency of the NO stretch mode and in addition the N(1s) IP in order to provide enough data to determine by comparison with experiment which situations exist in the experimental situation.

The situations studied, i.e. the different ions in their different environments, can be regarded as model systems with predictive values for other oxides.

2 Methods

The calculations have been performed for a number of different models of different sites of the perfect NiO(100) surface. The experimental Ni–O distance of 2.08 Å for the bulk, rock salt structure was maintained throughout in the calculations. For each system the height above the surface and the tilt angle from the surface-normal towards a surface oxygen were optimized. For the most interesting cases the vibrational frequency of the NO stretch was computed for the adsorbed species. The simplest model consisted of a single ion, either oxygen or nickel, embedded in a set of point charges giving the Madelung potential from the remainder of the crystal for the assumed charge distribution. In order to include an approximate description of the repulsion against the surrounding positive ions, repulsive level-shift operators, $\hat{P}_c$, were included at these sites and given by:

$$\hat{P}_c = \sum_k |\phi_k^c > B_k < \phi_k^c|$$

The orbitals, $|\phi_k^c>$, of the level-shift operators in this model were taken from Mg^{2+} where the level-shifts, B_k, were optimized such that the O(1*s*) ionization potential computed for an O^{2-} ion in an all-electron Ni_5O cluster embedded in the surface Madelung potential was reproduced when the O^{2-} was surrounded by level-shift operators instead [7]. This resulted in a scaling factor of 0.487 applied to the original level-shifts that had been taken as the Mg^{2+} orbital energies. This procedure is expected to give the main effects of repulsion on the central ion.

These models were then extended in the case of adsorption on top of an Ni^{2+} ion in the weak crystal potential. The first extended cluster model used here contained also the nearest O^{1-} neighbours modelled by F^{1-} ions, so that the cluster was NiF_4 embedded in the Madelung potential from an assumed charge distribution of ± 1 and then further embedded in a surrounding of Mg^{2+} projectors. This model was extended to $Ni^{2+}F_4^{1-}O^{2-}$ by explicitly adding the oxygen directly beneath the central nickel ion. The charges assigned to each species in the notation used are not fixed in the calculations; the electrons are allowed to redistribute themselves freely over the cluster.

The calculations have been performed at the SCF or CASSCF levels and followed by a correlation treatment using either the Modified Coupled Pair Functional (MCPF) method [8] or internally contracted ACPF (IC-ACPF) [9, 10]. At the optimized equilibrium geometry the basis set superposition error (BSSE) was computed to eliminate this effect on the computed adsorption energies. The adsorption on the oxygen anions was described at the SCF level followed by an MCPF calculation to introduce correlation. The adsorption on nickel is somewhat more complicated to describe and CASSCF wave functions with basic active spaces including the open 3*d*-orbitals on Ni and the π and π^* orbitals on NO were used. In certain cases, such as Ni^{1+} in the strong potential, even larger active spaces had to be used in order to obtain a reliable zeroth-order wave function for the correlation treatment. The correlation treatment for Ni^{n+} adsorption was performed at the IC-ACPF level taking as reference all occupations from the CASSCF that generate some configuration with coefficient larger than 0.05 in the CASSCF wave function at long or short distance. All the valence electrons in the Ni^{n+} + NO system were correlated, e.g. 19 electrons for Ni^{2+} and 20 for Ni^{1+}.

In comparing the ionization potentials of the oxygen anions at the surface with the experimental work function, the effects of polarization of the crystal upon ionization have to be accounted for. In the present work we have used the Core Polarization Potential (CPP) method of Müller et al. [11] to give an estimate of this effect. The core-valence correlation and polarization effect is included using an attractive potential based on a classical description of the core as a polarizable charge distribution interacting with the fields, $\mathbf{f}_c$, generated by the valence electrons and surrounding cores. The additional operator to be included in the Hamiltonian and projected onto the valence space then becomes:

$$\hat{V}_{CPP} = -\tfrac{1}{2}\sum_{c} \alpha_c \mathbf{f}_c^2$$

where the polarizability, α_c, of the oxygen anions was taken as 12.15 a_0^3 [12] and a cutoff ρ_c of 0.7 a_0 was used.

The N(1*s*) core ionization potential was computed by restricting the excitations in the CASSCF to only allow configurations with a singly occupied N(1*s*) orbital and by furthermore not allowing this orbital to mix with the remaining orbital space. In a second step the N(1*s*) orbital was relaxed by freezing all other occupied orbitals and allowing it to mix with the virtual orbitals. In a third step, finally, the convergence of the procedure was checked by reoptimizing the occupied orbitals with the relaxed core hole frozen. This third step never had any effect on the computed IP's.

The basis set for Ni was the SDZC basis of Tatewaki and Huzinaga [13] extended with two diffuse *p*- and one diffuse *d*-functions, while nitrogen, oxygen and fluorine were described using the Dunning [4*s* 3*p*] contracted basis [14] extended with a diffuse *p*- and a *d*-function.

3 Results

The interaction between CO and NO and the NiO(100) surface has been studied theoretically in detail by Pöhlchen and Staemmler [3, 4] for a number of cluster models. They studied adsorption on top of Ni^{2+}, which is also the assumed adsorption site from experiment [1], and obtained the experimentally observed approximately 45° angle of the adsorbate to the substrate. However, the adsorption energy for both CO and NO were found to be very similar, 0.10–0.15 eV after correction for BSSE, which is much too small compared with the experimental 0.52 eV for NO obtained from TDS spectra of NO/NiO(100). We have extended the studies reported in Ref. [3] to a number of other possible and interesting situations for the NO interaction with the surface. Thus we have considered on-top adsorption both on Ni and on O and have furthermore varied both the charge-state of the substrate ion and also the potential in which it is located. This allows us then to draw more general conclusions about the types of interactions to expect on other metal oxide surfaces for different charge states and surrounding potentials.

The experiments of Kuhlenbeck and co-workers also included the N(1*s*) core level spectra for NO/NiO(100) and as a further comparison we have also computed the N(1*s*) ionization potential for each of the different cases. Before turning to the study of on-top adsorption we will, however, mention the results of a preliminary study of the diffusion of NO along the perfect NiO(100) surface performed in order to search for more favorable adsorption sites.

Here we investigated the possibility of a more favorable interaction between the NO and the surface at some position intermediate between the Ni^{2+} and the O^{2-} by calculations on a cluster model consisting of an O^{2-} ion embedded in the Madelung potential and surrounded by level-shift operators to mimic the repulsion against the nearest ions. The NO molecule was then allowed to move along the line connecting the O^{2-} and nearest Ni^{2+} ion. At each point the height above the surface and the tilt angle was optimized at the SCF and MCPF levels of approximation.

The surface was found to be very flat, however, with very small variations in the interaction energy as the NO is moved or tilted. Corrections for basis set superposition errors are important, but after these have been made only a weak interaction remains and thus it does not seem likely that a different adsorption site on the perfect NiO(100) surface should be responsible for the rather strong interaction observed experimentally.

3.1 Adsorption on oxygen

The adsorption on an oxygen anion was studied for a very simple model where a single central, surface oxygen ion was surrounded by level-shift operators (hard spheres) and embedded in a strong or weak Madelung potential. In this case the strong potential refers to that generated by an assumed ± 2 charge distribution for the remaining crystal while the weak potential corresponds to an ionicity of ± 1. These two were taken as limiting cases to study qualitatively the effects on the adsorption from reduced or increased environment ionicities or potential. For each of these cases the interaction of NO with the oxygen in the two different charge states was obtained. The surface-oxygen to nitrogen distance was optimized together with the tilt angle relative to the normal to the surface at the SCF or CASSCF level. The binding energy to the surface was then computed at the MCPF level and including the counterpoise correction for the basis set superposition errors. The results are given in Tables 1 and 2.

The interaction with oxygen results in a tilt angle around 70° in all cases and a height above the surface that decreases from 5.80 to 3.02 a_0 in going from the fully ionic O^{2-} ion in the strong potential to the O^{1-} ion in the weak potential. The SCF level binding energies show the corresponding increase, in particular after the BSSE correction. It should be noted that the superposition errors are rather large and, in particular for the ions which do not conform to the ionicity of the surrounding crystal, significant reductions of the computed binding energies are obtained. This is particularly evident from the results of the MCPF calculations where both for the weak and strong potential cases the O^{2-} ion is found to give a zero bonding to the NO once the BSSE has been corrected for (Table 2).

The O^{2-} ion is a closed-shell species and as such it is not expected that any significant interaction, apart from physisorption, with the NO should result. Somewhat more surprisingly this is also true for O^{2-} in the weaker, less electron-stabilizing, potential. In the latter case it might be expected that the O^{2-} ion would be able to share some of its excess charge with the incoming NO, but no such charge donation is seen from the wave function where the population analysis gives

Table 1. Results for NO adsorption on different sites of the NiO(100) surface including effects of different embedding potentials and different charge states of the ion and the cluster (Q). The SCF results for the height above the surface (R_e in a_0), tilt angle (ϕ in degrees) and binding energy (BE in eV) are given. NO bond distance fixed at the gas phase value of 2.17 a_0

Site	Charges	Q	R_e	ϕ	BE[a]	BSSE[b]
Ni^{2+}	± 2	0	4.28	42	0.30	0.14
Ni^{2+}	± 1	0	4.16	43	0.64	0.48
Ni^{1+}	± 2	0	6.12	76	0.05	− 0.03
Ni^{1+}	± 1	0	5.44	2	0.10	− 0.03
O^{2-}	± 2	0	5.80	70	0.08	0.00
O^{2-}	± 1	0	4.32	74	0.38	0.10
O^{1-}	± 2	0	3.47	72	0.37	0.24
O^{1-}	± 1	0	3.02	69	1.19	1.10
Ni^{2+}	± 1	+ 1	4.13	51	0.74	
Ni^{1+}	± 2	− 1			Unstable[a]	
O^{2-}	± 1	− 1	3.18	67	1.70	
O^{1-}	± 2	+ 1	3.39	69	0.67	

[a] Binding energy

[b] Binding energy after correction for BSSE

Table 2. Binding energies (in eV) including correlation. Computed at the respective optimized geometries. All clusters charge compensated

Site	Charges	BE[a]	BSSE[b]
Ni^{2+}	± 2	0.45	0.23
Ni^{2+}	± 1	0.80	0.57
Ni^{1+}	± 2	0.12	− 0.01
Ni^{1+}	± 1	0.03	− 0.16
O^{2-}	± 2	0.12	0.00
O^{2-}	± 1	0.42	0.00
O^{1-}	± 2	0.76	0.51
O^{1-}	± 1	1.57	1.30

[a] Binding energy

[b] Binding energy after correction for BSSE

a charge on the surface ion of − 1.95 to be compared with the − 1.96 from the strong-potential case. It should be noted here that the cluster has been made charge neutral by adding a charge + 2 in the layer immediately beneath the O^{2-} ion and this of course contributes to stabilize the obtained charge distribution.

The O^{1-} ion behaves quite differently, however, both in the weak and the strong potentials. In this case we have an open-shell radical species in the surface with an electronic structure having the open $2p_z$ orbital pointing out of the surface. This type of oxygen radical species has previously been shown to be active in e.g. the abstraction of hydrogen from methane leading to a gasphase methyl radical and a surface hydroxyl group [15]. Also in the present case a strong, covalent interaction with the open π^* orbital of the NO is possible and is indeed what is found from the calculations. The bond strength is highly dependent on the strength of the surrounding potential, even though in both cases the same type of electron-pair single bond between NO and the surface O^{1-} species is formed. In the strong-field case the binding energy to the surface is 0.5 eV at the MCPF level after correcting for the BSSE, which is in good agreement with the experimental value of 0.52 eV inferred from the desorption temperature. The binding becomes significantly stronger when the embedding potential becomes weaker; the radical character of the oxygen anion is enhanced and results in a significantly stronger interaction of the NO with the surface. In fact, the computed chemisorption energy now is as large as 1.3 eV. This is not associated with any large changes in the charge on the surface oxygen, where in the weak-field case the charge has decreased by only 0.13 e^-. For the closed-shell CO molecule this type of covalent interaction does not occur and the binding energy remains very small also in this case.

The limiting case where the counter-charge is at a larger or infinite distance can also be of interest. This corresponds to the bottom entries in Table 1 where the excess charge has not been balanced by a corresponding reduction or increase of a nearby charge. The O^{2-} ion in the weak potential with an overall charge of -1 is now strongly destabilized and, as the NO approaches, one electron is transferred to the NO so that a purely ionic adsorption results. The strong binding is to be regarded as an artifact due to the unfavorable situation for the cluster oxygen, but it still indicates the possibility for yet another type of interaction with the oxygen once the potential becomes weak enough. A similar strong influence of the total charge on the system is also seen for the O^{1-} radical in a strong potential corresponding to an overall charge of $+1$. Here the ionicity is strongly unsatisfied and 0.2 electrons are transferred from the NO to the surface oxygen. The bond distance and the tilt angle remain very similar to the overall charge-neutral case, but the binding energy is increased by some 0.3 eV over the charge-neutral, oxygen anion radical in the weak potential.

The extra electron on the O^{2-} anions is very strongly stabilized by the embedding potential. The first ionization potential was computed (MCPF) as 9.6 eV for the strong and 6.0 eV for the weak potential cases, respectively. To compare this with the work function of 4.3 eV the polarization of the remaining crystal has to be considered. This was done by using the CPP formalism, as described in the methods section, assigning a polarizability of 12.15 a_0^3 to the oxygen anions [12] out to a distance of 7.2 Å, while the polarization of the cations was neglected. The resulting reduction of the IP was by 0.8 and 1.0 eV in the strong and weak potential cases, respectively, which probably underestimates the true effect of polarization. Thus, the resulting computed value for the work function, assuming ionization from O^{2-} and a weak potential, using this very simple computational model is 5.0 eV which is 0.7 eV larger than the experiment. The resulting ionization potentials, however, are such that even in the weaker potential there will be very little tendency of the O^{2-} to give up an electron to an incoming adsorbate. The electron affinities computed for the O^{1-} anions in the corresponding way, were found to be positive by 2.3 eV for the strong potential, while in the weak potential it was as strongly negative as -1.4 eV even when correlation is included. The ionization potentials were as large as 16.9 and 12.2 eV, respectively, so that charge transfer from the substrate to the adsorbate is very unlikely in these cases. Here it should be remembered that the crystal has been made charge neutral by adding a countercharge in the position directly beneath the central anion.

3.2 Adsorption on nickel

The adsorption on nickel can be qualitatively grouped into three classes according to the results of Table 1. The Ni^{1+} ion shows only a very weak interaction with the NO for both the strong and the weak potential. The interaction with Ni^{2+} in the strong potential, i.e. with a completely satisfied ionicity is somewhat stronger but still mostly of an electrostatic origin in agreement with the results of Pöhlchen and Staemmler [3]. The only interesting situation then is found for the Ni^{2+} ion in the weak potential, which constitutes the only case with any significant binding energy in the interaction between the nickel ion and the NO.

The bonding between NO and the Ni^{2+} d^8 ^3F-coupled ion has been described previously by Pöhlchen and Staemmler [1, 3]. It originates from an interaction between the NO singly occupied π^* orbital (a'-symmetry) and the two open $3d$-orbitals on Ni^{2+} lying in the same symmetry. These three orbitals are coupled to an overall doublet state and a CASSCF treatment becomes necessary as a zeroth order approximation. The qualitative character of the wave function is not dependent on the embedding potential so the above description of the bonding is correct for both the strong and the weak potentials. The difference that is found lies in the strength of the interaction among the three open-shell orbitals. In the case of Ni^{2+} in the strong potential (satisfied ionicity) the cation is situated at a strongly electron-repulsive position of the lattice and thus introducing additional electrons from the NO to interact with the Ni^{2+} becomes highly unfavourable. For the weaker potential this Madelung repulsion is diminished and a stronger, more covalent interaction can result.

The computed binding energy for the NO to Ni^{2+} (weak potential) is 0.48 eV at the SCF-level and 0.57 eV at the IC-ACPF level, including correction for BSSE. These results should be corrected for the repulsion against the surrounding oxygens, which in Tables 1 and 2 have simply been represented by the corresponding negative charges. The repulsion was estimated from SCF calculations on a $Ni^{2+}F_4^{\frac{1}{4}-}$ cluster embedded in the weak potential and resulted in a binding energy of 0.38 eV, i.e. a reduction by 0.26 eV relative to the uncorrected SCF value for the single ion. For the more extended $Ni^{2+}F_4^{\frac{1}{4}-}O^{2-}$ cluster the computed binding energy was very similar, 0.32 eV. These values are most likely overestimates since the correction for superposition errors has not been applied. However, correcting the IC-ACPF value by this effect of the repulsion we obtain as an estimated binding energy 0.3 eV, which is in reasonable agreement with the experimental value of 0.52 eV obtained from thermal desorption. Additional corrections should be applied to the theoretical value, however. The correlation contribution to the binding can be expected to increase somewhat with extensions of basis set and reference space.

The tilt angle of the NO against the surface is computed to be 43° in good agreement with the experimental estimates of 45° [1]. A very similar angle is obtained also for the Ni^{2+} ion in the strong potential, but here the interaction with the NO is so weak that this site must be excluded as a candidate for the adsorption site. The two Ni^{1+} sites show very different tilt angles for the NO. In the weak potential a very large angle of 76°, similar to those found for adsorption on oxygen, is obtained while the weak potential results in basically a linear adsorption. Both these cases merit further discussion even though they can be excluded as candidates on the basis of the very low binding energies.

As in the case of Ni^{2+} in the strong potential above, the Ni^{1+} ion is located at an electron-repulsive crystal site in the lattice. In the case of the strong potential the creation of the Ni^{1+} charge-state corresponds to a charge transfer against the Madelung potential of one electron from the site below Ni^{2+} (the cluster/crystal model is kept charge neutral). This is very unfavorable, and even though the additional electron remains bound to Ni even with the incoming NO, the electronic structure of Ni^{1+} is a d^8 $(sp)^1$ state with the additional electron in a strongly polarized orbital pointing out of the surface. To describe this state requires an accurate zeroth-order description with the Ni ($d_\sigma d_\delta 4s$) and NO ($5\sigma 1\pi 2\pi 6\sigma$) orbitals active, where the 2π is the π^* orbital. However, this is an atomic effect and the inclusion of a proper description of this state made it possible to converge the correlated calculation, but had no effect on the computed binding energy. Thus, the Ni^{1+} state shows no particular binding to the NO and only electrostatic and dispersive interactions will be present in these cases.

3.3 Vibrational frequency

To further characterize the adsorption site we have computed the vibrational frequency for the NO-stretch for the three different situations of interest (Table 3). The computed gas phase NO vibrational frequency of 1921 cm^{-1} compares very favourably with the experimental value of 1904 cm^{-1} so that the description of the NO molecule may be regarded as rather accurate. For NO adsorbed on Ni^{2+} in the weak potential we find a shift to higher frequency of + 50 cm^{-1}, while for both cases of adsorption on O^{1-} the shift is to lower frequency. In the strong potential the computed frequency of 1836 cm^{-1} is 85 cm^{-1} lower than the gasphase value, while in the weak potential case the shift is close to 200 cm^{-1} resulting in a frequency of 1724 cm^{-1}.

In the experiments only one frequency in addition to the phonon modes was found and this corresponds to the slightly upwards shifted frequency. This would indicate that the adsorption site is the Ni^{2+} ion, and that the potential in which it is embedded is weaker than for the fully ionic crystal. The vibration at 1724 cm^{-1} could in principle be masked by the third phonon vibration, but difference spectra with the substrate only and with the adsorbate show that there is no such loss in the HREEL spectrum of [1]. It is interesting to note that the computed frequencies for adsorption on O^{1-} are in very close agreement with the observed shifted frequencies for NO adsorption on Ni(100) and oxygen-precovered Ni(100) at high coverages [16]. In this case two frequencies appear at 1840 and 1740 cm^{-1}, but the close correspondence with the shifts found in the present investigation is probably coincidental, however. The peak at 1740 cm^{-1} for the high coverage case disappears when the temperature is raised to 300 K while the 1840 cm^{-1} peak remains.

Table 3. Computed bond distance, r_e in Å, and vibrational frequency, ω_e in cm^{-1}, for free and adsorbed NO. All results include correlation (see text). The gasphase experimental values are $r_e = 1.15077$ Å and $\omega_e = 1904$ cm^{-1}

Site	Charges	r_e	Δr_e	ω_e	$\Delta \omega_e$
Gasphase	–	1.156	0.000	1921	0
Ni^{2+}	5 ± 1	1.148	– 0.008	1971	+ 50
O^{1-}	± 2	1.161	0.005	1836	– 85
O^{1-}	± 1	1.185	0.024	1724	– 197

This would be opposite to the expected from the present case where the 1724 cm^{-1} peak corresponds to the most strongly adsorbed species.

3.4 Core ionization potentials

The experimental spectra for the N(1*s*) ionization potential upon adsorption show two very distinct peaks that are shifted by 0.8–1.1 eV upwards and 3.6–3.3 eV downwards with respect to gasphase NO. The intensities of the two peaks are very similar and, in fact, for the case of NO/NiO(100) cleaved in vacuo they have the same intensity. These peaks can in principle be explained by satellite structures as is also suggested in [1], but could also possibly arise from NO molecules adsorbed in similar amounts on different adsorption sites. To analyze this situation we have computed the lowest N(1*s*) hole states for NO adsorbed on the different sites studied above. In particular, it is of interest to see if the screened hole state can be obtained computationally. This would then provide a good indication that the interpretation of the double-peak structure as a shake-up is correct. The results are given in Tables 4 and 5.

The calculations have been performed allowing for a relaxation of the N(1*s*) core hole and allowing charge transfer from the substrate ion or ions to the NO. Only in the most interesting case of Ni^{2+} in the weak potential have we extended the treatment to include the nearest anions explicitly to allow for additional charge transfer and polarization around the adsorption site. The resulting larger clusters, $Ni^{2+}F_4^-$ and $Ni^{2+}F_4^-O^{2-}$, will be discussed separately. It should already here be pointed out, however, that the computed core IP's should only be interpreted qualitatively, in particular for the smallest cluster models.

The final core hole states for NO adsorbed on the different oxygen sites are all more or less screened by charge transfer from the substrate to the adsorbate. The largest charge transfer is 0.74 electrons in the case of O^{1-} in the strong potential, but the resulting shift is still to higher energy. The O^{1-} ion in this model is surrounded by four pointcharges of plus two at the surface which generate an attractive potential for the N(1*s*) electron. However, there is a possibility that a shake-up structure could be obtained, but it would probably be located at higher energy than what was observed in the experiment. The next largest charge transfers

Table 4. Nitrogen 1*s* ionization potential (IP in eV) for different adsorption sites, substrate, electronic structures and charge states. Relaxation of both core hole and valence included. *ΔIP* (in eV) denotes the difference from the gas phase computed value of 411.8 eV

Site	Charges	*Q*	IP	*ΔIP*
Ni^{2+}	± 2	0	410.7	− 1.1
Ni^{2+}	± 1	0	413.6	+ 1.8
Ni^{1+}	± 2	0	403.0	− 8.8
Ni^{1+}	± 1	0	407.9	− 3.9
O^{2-}	± 2	0	411.6	− 0.2
O^{2-}	± 1	0	408.1	− 3.7
O^{1-}	± 2	0	414.0	+ 2.2
O^{1-}	± 1	0	411.2	− 0.6

Table 5. Charge distribution for neutral and core-ionized NO in gasphase and adsorbed on Ni^{2+} in weak potential using different models

Gasphase NO

	N–O				N*–O			
	O	N	Ni	F	O	N	Ni	F
Charge	-0.13	0.13	–	–	0.52	0.48	–	–
s-pop	3.84	3.85	–	–	3.88	2.85	–	–
p-pop	4.26	2.96	–	–	3.56	3.60	–	–
d-pop	0.03	0.07	–	–	0.04	0.07	–	–

Ni^{2+}–NO

	N–O				N*–O			
	O	N	Ni	F	O	N	Ni	F
Charge	0.09	0.06	1.86	–	0.62	0.40	1.98	–
s-pop	3.86	3.76	6.06	–	3.91	2.83	6.01	–
p-pop	4.02	3.12	12.06	–	3.43	3.72	12.02	–
d-pop	0.03	0.06	8.02	–	0.04	0.06	7.99	–

$Ni^{2+}F_4^-$–NO

	N–O				N*–O			
	O	N	Ni	F	O	N	Ni	F
Charge	0.06	0.09	1.35	-0.87	0.57	0.44	1.33	-0.84
s-pop	3.86	3.75	6.21	3.96	3.91	2.81	6.22	3.96
p-pop	4.05	3.10	12.31	5.91	3.48	3.69	12.34	5.87
d-pop	0.03	0.06	8.13	0.00	0.04	0.06	8.12	0.00

$Ni^{2+}F_4^-O^{2-}$–NO

N–O

	O	N	Ni	F	O^{2-}
Charge	0.04	0.09	0.92	-0.87	-1.57
s-pop	3.86	3.75	6.34	3.96	3.91
p-pop	4.07	3.09	12.49	5.91	5.66
d-pop	0.03	0.06	8.26	0.00	0.00

N*–O

	O	N	Ni	F	O^{2-}
Charge	0.14	0.00	1.06	-0.83	-0.87
s-pop	3.88	2.78	6.28	3.96	3.97
p-pop	3.94	4.16	12.42	5.87	4.90
d-pop	0.03	0.06	8.25	0.00	0.00

occur for the O^{2-} and O^{1-} both in the weak potential. In both cases somewhat more than half an electron is transferred to the adsorbate. Since no binding was found to the O^{2-} ion it will not be discussed further. The O^{1-} ion gives a small shift to lower energy which could conceivably increase somewhat if polarization of the crystal is included. The smallest charge transfer, less than 0.2 electrons, is found for the O^{2-} ion in the strong potential. This is also the site with the largest distance to the NO, but again the NO would only be physisorbed at this site and it thus has to be discarded from the discussion.

The shifts for the Ni^{1+} adsorption are large and towards lower IP's and in this case there are substantial effects of charge transfer from the metal ion to the NO. This is particularly true for the Ni^{1+} in the strong potential in which case the ion already has a tendency to go to the $d^8(sp)^1$ atomic state, where the $4sp$-hybrid is strongly polarized away from the surface. However, in neither of the Ni^{1+} cases was any appreciable adsorption energy obtained and thus the observed peaks cannot be attributed to NO adsorbed on these species.

Very little charge transfer is seen for the Ni^{2+} systems in the simple model with just a single ion, but this is still the most likely adsorption site in the experiment. The most interesting case for cation adsorption then is the Ni^{2+} ion in the weak potential. Here the computed shift is 1.8 eV to higher energy (unscreened core hole), while should be compared to the 1.1 eV observed experimentally for the high-energy peak. Improving the description to include also a representation of the nearest anion neighbours, taken as F^- ions, leads to somewhat lower shifts. In this case we obtain an N(1*s*) binding energy of 412.7 eV which corresponds to a shift relative to the computed gas-phase value of 0.9 eV. This is still an unscreened state without any appreciable charge transfer from the substrate to the adsorbate. The charge distributions within the cluster before and after the core ionization are given in Table 5 for each of the cluster models studied. For the NiF_4 cluster the charge on the central Ni^{2+} ion has been somewhat reduced, mainly by a higher charge density in the 4(*sp*) orbitals. This, however, is basically unaffected by the creation of the core hole on the NO adsorbate.

In order for the cluster to remain charge neutral a nearby O^{2-} ion must be present. In a weaker potential this would have an IP that would make it a reasonable candidate for the charge transfer. Thus we extend the cluster model to also include this O^{2-} ion located directly beneath the Ni^{2+} which proved to have dramatic effects on the computed N(1*s*) IP leading to a reduction of 7.2 eV down to an IP of 405.5 eV. The wave function corresponds to the screened core hole state with one electron transferred from the oxygen anion to the adsorbate which is very likely to be the origin of the lower energy peak in the spectrum. The charge distribution within this cluster model before and after the ionization process corresponds more closely to a singly charged nickel ion. The nickel ion thus only seems to act as a mediator for the electron from the O^{2-} and is in itself hardly affected by the screening. Additional polarization of the surface is likely to increase the computed value somewhat, since the polarization contribution should be higher for the unscreened state.

Thus it is very likely that the two peaks observed experimentally correspond to the unscreened and screened states computed above and that the observed adsorption really is on top of a Ni^{2+} ion, but that the potential in which it is embedded must be assumed to be substantially weaker than that corresponding to a completely ionic crystal.

4 Conclusions

Adsorption of NO on NiO(100) is experimentally found to occur with a tilt angle of approximately 45° to the surface normal and a binding energy to the surface of 0.52 eV. For NO adsorbing on Ni^{2+} embedded in the Madelung potential from a fully ionic crystal only weak adsorption is found and this site has to be excluded as the adsorption site. When the ionicity of the remaining crystal is reduced, however, the binding energy increases to a value in reasonable agreement with experiment. The tilt angle is near the experimental one for both cases. Adsorption on Ni^{1+} does not occur, neither for the weak nor for the strong Madelung potential embedding.

Adsorption on the anion is also considered and it is shown that the closed-shell character of the O^{2-} species always leads to a very weak interaction with the incoming NO. Reducing the charge on the oxygen again leads to a stronger interaction with a binding energy of 0.5 eV for O^{1-} in a strong potential and 1.3 eV for adsorption on O^{1-} in a weak potential. Here the interaction is strongly covalent between the O^{1-} radical and the NO π^* open-shell orbital. The strong potential case could lead to a desorption peak coinciding with that for desorption from Ni^{2+} in a weak potential, but the existence of only one shifted vibrational frequency in the experiment, the unlikeliness of having oxygen radical species available at the perfect NiO(100) surface combined with the computed frequency shifts and N(1*s*) core-level shifts would seem to exclude that this is a site that is present under the experimental conditions. However, the model calculations clearly indicate that this and the corresponding weak potential O^{1-} sites should also be considered when discussing adsorption on NiO. In particular, the present work raises the question of what is the true ionicity of nickel oxide.

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