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Bonding of NH₃, CO, and NO to NiO and Ni-doped MgO: a problem for density functional theory

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Abstract

Recent experimental results (Hoeft *et al* 2001 *Phys. Rev. Lett.* **87** 086101) have questioned the capability of current theoretical methods for describing the bonding of NH₃, CO, and NO with the NiO(100) surface. We show that these systems do indeed represent a challenge to theory. For different reasons, density functional theory (DFT) fails in describing the bonding of these molecules to the NiO surface. The gradient-corrected functionals which work better for the properties of NH₃/NiO and CO/NiO (energies, geometries, vibrations) provide wrong answers for NO/NiO and vice versa. This is not due to the well-known difficulty as regards DFT describing the insulating character of NiO. In fact, exactly the same problem is found for isolated Ni²⁺ impurities in MgO. A correct description of the bonding of both closed-shell (NH₃ and CO) and open-shell (NO) molecules to Ni_xMg_{1-x}O is obtained only after inclusion of dynamical correlation and dispersion forces via wavefunction-based methods. However, even with correlated calculations some uncertainties exist regarding the predicted value of the energy of adsorption of NO on NiO. While CASPT2 calculations reach reasonable agreement with experiment, the results of approximate coupled-cluster calculations (the multi-configuration coupled-electron-pair approach) substantially underestimate the adsorption energy.

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1. Introduction

A correct description of the bonding of molecular complexes to transition metal oxide surfaces is of fundamental importance for the understanding of problems in catalysis, gas sensors, corrosion protection, etc. The bonding of simple molecules such as NH_3 , CO , and NO to metal oxides represents a serious challenge to theorists. A recent experimental paper on the structure of these molecules on $\text{NiO}(100)$ [1, 2] has highlighted the weakness of current theoretical descriptions of oxide–molecule bonding, in particular as regards the bond lengths (and hence the bond strengths). Nowadays, two basically different approaches are used to describe the bonding at surfaces. Wavefunction-based methods with explicit inclusion of correlation effects (e.g. through configuration interaction or perturbative treatments) were developed in the 1980s and 1990s and can be applied within the local cluster model approach. Their use is not straightforward and their application is restricted to relatively small systems. This is one reason for the wide use of density functional theory (DFT) in the description of the surface chemical bonding and of the electronic structure of solids and surfaces [3]. Historically, DFT was developed to perform band structure calculations where periodic boundary conditions are properly taken into account. Thanks to the introduction of hybrid exchange–correlation functionals, the description of bond dissociation energies in molecular complexes has also approached so-called ‘chemical accuracy’ (errors $< 1 \text{ kcal mol}^{-1}$). However, recent studies on some special problems (magnetic coupling [4], localized holes in insulators [5, 6], weakly interacting systems [7, 8], etc) have shown limitations of DFT which may lead to a physically incorrect picture or to a strong dependence of the results on the exchange–correlation functional.

The adsorption properties of NH_3 , CO , and NO on $\text{NiO}(100)$ and Ni-doped $\text{MgO}(100)$ have been determined experimentally in detail and represent a unique opportunity to test theory. Photoelectron diffraction studies of $\text{NiO}(100)$ thin films show that NO is bound with a Ni–N distance of 1.88 \AA and a tilt angle of 59° from the surface normal [1]; CO binds almost normal to the surface with a Ni–C distance of 2.07 \AA [1, 2]; a similar distance, 2.06 \AA , is measured for NH_3 [1, 2]. Thermally programmed desorption (TPD) studies on NiO single crystals show that the desorption energy of NO , 0.57 eV , is about twice that of CO , 0.30 eV [9]. According to a crude estimate from TPD spectra of NH_3 adsorbed on NiO thin films [10], this molecule is the most strongly bound, with a desorption energy of about 0.8 eV [1, 2]. Infra-red spectra of NiO powders show that while the frequency of adsorbed NO is red-shifted compared to that of the free molecule, $\Delta\omega = -71 \text{ cm}^{-1}$ [11], that of CO is slightly blue-shifted, $\Delta\omega = +9 \text{ cm}^{-1}$ [12]. Ni^{2+} ions diluted in a MgO matrix behave in a very similar way to Ni^{2+} ions in the extended NiO surface: the CO vibrational frequencies are virtually the same in the two systems [11, 13]; the desorption temperatures of NO adsorbed on Ni-doped MgO and NiO are very similar [14, 15]; for a more extended discussion see also [16]. The physical reason is that the bonding of CO and NO to the Ni ion is very local and only marginally depends on the matrix in which the ion is included. Electron spin resonance (ESR) measurements on NO adsorbed on NiO/MgO solid solutions show a single unpaired electron in the 3d shell of Ni (formally $\text{Ni}^+ 3d^9$) [17].

In this work we report a theoretical study where the bonding of the three molecules to NiO and Ni-doped MgO is treated using both DFT and wavefunction-based methods. The calculations have been done within the cluster approach and compared with results for periodic slabs in selected cases. We will show that the DFT results exhibit a strong dependence on the exchange–correlation functional used and that in some cases this results in a qualitatively wrong picture of the interaction. Functionals which provide the best answers for NH_3/NiO and CO/NiO are inadequate to describe the bonding in NO/NiO and vice versa. A correct solution requires explicitly correlated wavefunctions generated by complete-active-space SCF,

CASSCF, and second-order perturbation theory, CASPT2, approaches [18, 19] or the multi-configuration coupled-electron-pair approach (MC-CEPA) method [20]. In this case also, however, some uncertainties about the bonding properties remain, mainly due to the difficulty of approaching a full CI treatment and selecting the proper configurations involved in the differential electronic correlation effects.

2. Computational methods

Both spin-polarized and spin-restricted calculations have been performed. A spin-polarized DFT calculation corresponds to an unrestricted HF approach, UHF, and, as such, cannot rigorously describe the spin multiplicity of an open-shell system. In fact, the spin-polarized calculations resulted in severe spin-contamination problems, as will be discussed below. Therefore, the calculations have been performed also using the restricted open-shell (RO) formalism. In this case the corresponding electronic states are pure triplet states for the adsorption of a closed-shell molecule on an isolated Ni²⁺ impurity in MgO and pure doublet or pure quartet states for NO/NiO.

Correlation effects can be included, based on DFT. In the Kohn–Sham formulation of DFT, the exact non-local HF exchange for a single determinant is replaced by a general expression, the exchange–correlation functional, which can include both exchange and electron correlation energy terms. Here we used three different approaches; one of them is a pure DFT method and the other two are hybrid approaches where the exchange interaction is described partially or entirely by the HF exchange. In the pure DFT scheme, we used the approach based on the gradient-corrected exchange functional proposed by Becke [21] combined with the non-local expression of the correlation functional proposed by Lee, Yang, and Parr (BLYP) [22], which goes back to the original work of Colle and Salvetti [23, 24] on the correlation factor. In one hybrid approach the exchange term was entirely described at the HF level (100% HF exchange) while the correlation part made use of the LYP correlation functional described above; this approach is referred to as HFLYP. A second hybrid approach makes use of the hybrid B3LYP method where the HF exchange is mixed in with the DF exchange using the Becke three-parameter approach [25].

For CO/NiO the model of the NiO surface consists of a Ni₉O₉ cluster embedded in effective core potentials (ECP) and a 3 × 3 × 2 set of point charges (PC = ±2) to represent the crystalline Madelung potential; see table 1. The geometry was fixed to the ideal rock-salt structure of bulk NiO with a lattice constant of 4.16 Å [26]; no geometrical relaxation at the NiO(100) surface was allowed for. The calculations, performed with the GAUSSIAN98 program [27], have been compared with periodic calculations carried out with the CRYSTAL code [28] on three slabs of NiO for a CO coverage $\theta = 0.25$ monolayers. On Ni₉O₉ we assumed a ferromagnetic coupling of the spins on the Ni atoms; in the periodic calculation the correct antiferromagnetic ordering has been used [29]. The differences in CO/NiO properties obtained with cluster and slab are smaller than 0.03 Å for the bond lengths, 0.02 eV for the binding energy, and 7 cm⁻¹ for the frequencies; see table 1.

For NH₃ and NO most of the calculations have been performed for a NiMg₈O₉ model of an isolated Ni²⁺ impurity on the MgO(100) surface; see figure 1 and tables 2 and 3. Here, an undistorted MgO rock-salt structure was used [26]. As already mentioned above, the behaviour of Ni²⁺ ions diluted in a MgO matrix is analogous to that of Ni²⁺ ions in the extended NiO surface. This has been verified theoretically by comparing CO on NiMg₈O₉ and Ni₉O₉ cluster models: within a given method, the results are the same within ≈0.05 eV for the energies and 0.03 Å for the distances; see table 1. For the specific case of NO we also performed periodic slab calculations; see table 3. Given the tilt angle of the NO molecule, the

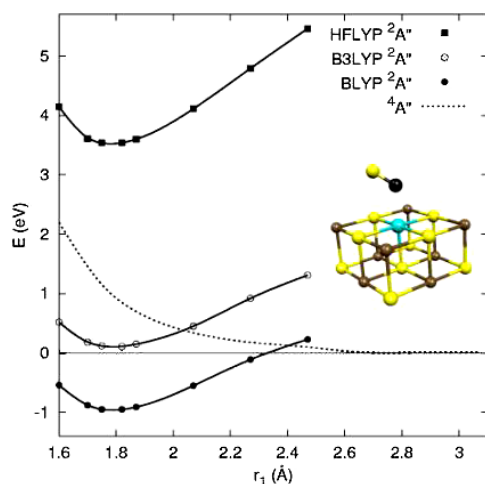


Figure 1. Potential energy curves for the $^2A''$ and $^4A''$ states of NO/NiMg₈O₉ computed at the RO HFLYP, B3LYP, and BLYP levels. The distance of NO from the Ni cation has been optimized, keeping fixed the N–O distance (1.17 Å), the tilt angle $\vartheta = 60^\circ$ (ϑ is the angle between the NO axis and the surface normal), and the O–N–Ni–O_{surface} polar angle $\varphi = 45^\circ$. In the inset we show the NiMg₈O₉ cluster used to model the surface. The cluster is embedded in ECPs and a large array of point charges (not shown).

(This figure is in colour only in the electronic version)

Table 1. Properties of CO adsorbed on NiO and Ni-doped MgO (D_e = dissociation energy, ω_e = vibrational frequency; U = spin unrestricted; RO = restricted open shell; in parentheses: values without BSSE correction).

Method	Model	D_e (eV)	$r_1(\text{Ni-C})$ (Å)	$r_2(\text{C-O})$ (Å)	$\Delta\omega_e$ (cm ⁻¹)
HFLYP	U Ni ₉ O ₉	0.15(0.22)	2.38	1.098	-10
HFLYP	U NiO slab	0.17(0.29)	2.40	1.095	-3
B3LYP	U Ni ₉ O ₉	0.02(0.12)	2.10	1.134	-73
B3LYP	U NiMg ₈ O ₉	0.06(0.16)	2.10	1.130	—
BLYP	U Ni ₉ O ₉	0.23(0.33)	1.87	1.161	-172
BLYP	U NiMg ₈ O ₉	0.30(0.41)	1.90	1.154	—
CASPT2	RO NiMg ₈ O ₉	0.13(0.30)	2.24	1.136	+16
Experiment		0.30 ± 0.04 [9]	2.07 ± 0.02 [1, 2]	1.15 ± 0.09 [1, 2]	+9 [12]

coverage dependence of the results has been analysed by considering two coverages, $\theta = 0.25$ and 0.125 monolayers. The properties computed for NO/NiO(100) slabs are similar to those obtained with the NO/NiMg₈O₉ cluster; see table 3. This justifies the use of NiMg₈O₉ instead of a Ni₉O₉ cluster. One practical advantage in using a NiMg₈O₉ model is that NO/Ni₉O₉ clusters result sometimes in severe convergence or spin-contamination problems due to the complex spin coupling (see below).

The cluster wavefunctions have been constructed using localized Gaussian-type basis sets of triple-zeta-plus-polarization quality. The basis set for NiMg₈O₉ is 6-31G for Mg, [16s8p2d/6s5p2d] for O [30], and [22s14p6d/7s6p3d] for Ni [31] (see also basis set B in [32]). The basis set for Ni₉O₉ is 6-311 + G for Ni [33], and 6-311 + G* [34] for O (see basis set C in [32]); this basis set has been used in a parallel study of CO adsorption at the NiO(100) surface [29], and is similar in quality to the basis set used for NiMg₈O₉. The 6-311 + G* [34]

Table 2. Properties of NH₃ adsorbed on Ni-doped MgO (D_e = dissociation energy; U = spin unrestricted; in parentheses: values without BSSE correction).

Method	Model	D_e (eV)	r_1 (Ni–N) (Å)	r_2 (N–H) (Å)
HFLYP	U NiMg ₈ O ₉	0.49(0.55)	2.169	0.992
B3LYP	U NiMg ₈ O ₉	0.23(0.31)	2.189	1.015
BLYP	U NiMg ₈ O ₉	0.16(0.24)	2.166	1.024
Experiment		0.80 [1, 2]	2.06 ± 0.02 [1, 2]	

Table 3. Properties of NO adsorbed on NiO and Ni-doped MgO (D_e = dissociation energy; θ = angle between the NO axis and the surface normal; ω_e = vibrational frequency; U = spin unrestricted; RO = restricted open shell; in parentheses: values without BSSE correction).

Method	Model	Spin on Ni	D_e (eV)	r_1 (Ni–N) (Å)	r_2 (N–O) (Å)	θ (deg)	$\Delta\omega_e$ (cm ⁻¹)
HFLYP	RO NiMg ₈ O ₉	0.94	-3.53(-3.42)	1.82	1.148	64.1	-404
HFLYP	RO NiO slab	0.95	-3.90(-3.80)	1.78	1.170	60.0 ^a	—
B3LYP	RO NiMg ₈ O ₉	0.79	-0.11 (0.00)	1.85	1.164	61.2	-209
B3LYP	U NiMg ₈ O ₉	≈3 ^b	0.25(0.36)	2.02	1.153	57.1	-110
B3LYP	U NiO slab	≈3 ^b	0.07(0.33) ^c	2.07	1.186	60.0 ^a	—
BLYP	RO NiMg ₈ O ₉	0.68	0.96(1.10)	1.84	1.191	59.6	-292
CASPT2-A ^d	RO NiMg ₈ O ₉	≈1	0.48(0.65)	2.03	1.185	62.6	-101
CASPT2-B ^e	RO NiMg ₈ O ₉	≈1	0.17(0.65) ^f	2.03	1.173	62.6	—
			0.31(0.78) ^g				
MC-CEPA ^d	RO NiMg ₈ O ₉	≈1	-0.18 (0.12) ^h	2.03 ^a	1.170 ^a	60.0 ^a	—
CEPA-0 ^d	RO NiMg ₈ O ₉	≈1	0.00(0.33) ^h	2.03 ^a	1.170 ^a	60.0 ^a	—
MC-CEPA ⁱ	RO NiMg ₈ O ₉	≈1	0.02(0.24) ^h	2.03 ^a	1.170 ^a	60.0 ^a	—
CEPA-0 ⁱ	RO NiMg ₈ O ₉	≈1	0.34(0.57) ^h	2.03 ^a	1.170 ^a	60.0 ^a	—
Experiment		≈1	0.57 ± 0.04 [9]	1.88 ± 0.02 [1]	—	59 [1]	-71 [11]

^a Not optimized.^b Strongly spin-contaminated solution (two spins up and one spin down).^c The calculation refers to a coverage $\theta = 0.25$; for a lower coverage, $\theta = 0.125$, and assuming the same geometry, $D_e = 0.16$ eV (0.41 eV before BSSE).^d Calculations done with the same basis set as used for the DFT calculations (see the text).^e Calculations done with the ANO basis set (see the text).^f State-averaged CASSCF/CASPT-2 for an isolated NO molecule.^g State-optimized CASSCF/CASPT-2 for an isolated NO molecule.^h State-optimized CASSCF/MC-CEPA for an isolated NO molecule.ⁱ Extended basis.

basis set was used for the NH₃, CO, and NO molecules. The adsorption energies have been corrected using the counterpoise method to remove the basis set superposition error (BSSE) inherent to the use of localized basis functions [35].

The DFT results have been complemented by wavefunction-based calculations with explicit inclusion of correlation effects employing the CASSCF, CASPT2, and MC-CEPA approaches. Clusters and basis sets are the same as for DFT. However, we restricted the CASPT2 analysis to CO and NO adsorbates and to NiMg₈O₉ models, since calculations on a Ni₉O₉ cluster, possible in principle, are quite complex because of the large number of possible spin couplings in the 3d manifold all within a very small energy interval.

CASPT2 is a generalization of the well-known MP2 method based on HF wavefunctions to CASSCF wavefunctions and reduces rigorously to MP2 for CAS containing a single closed-shell Slater determinant (i.e. for a single HF wavefunction). Some part of the electron correlation effect is treated in a variational way in the CASSCF step, and the remainder,

mainly dynamical electron correlation, is estimated by second-order perturbation theory with the CASSCF as the zeroth-order wavefunction. This strategy combines the accuracy of a multi-reference CI treatment and the low computational cost of a perturbational approach. Over the last few years the CASPT2 method has been proven to be a fruitful approach for studying, analysing, and predicting the spectroscopy of a wide range of organic and inorganic molecules [36–39]. The method has also been successfully applied for studying excited states in solid-state compounds [40–42].

CASSCF and CASPT2 interaction energy curves have been determined by single-point calculations as functions of the distance of CO or NO from the Ni cation (the C–O or N–O distances have been kept fixed at 1.13 and 1.17 Å, respectively; a tilt angle $\vartheta = 60^\circ$ has been assumed for NO while CO is normal to the surface). In a first set of CASSCF calculations on NO/NiMg₈O₉ (CASSCF-A) the active space includes the Ni 3d(z^2) and 3d($x^2 - y^2$) orbitals, two diffuse Ni 4d(z^2) and 4d($x^2 - y^2$) orbitals, and the $\pi^*(x)$ and $\pi^*(y)$ antibonding orbitals on NO and three active electrons. For CO/NiMg₈O₉, the active space includes the CO 5 σ , 6 σ^* , 1 π , 2 π^* and the Ni 3d(z^2), 3d($x^2 - y^2$), 3d(xz)3d(yz) orbitals and twelve electrons. In CASPT2, a second-order estimate of the total energy is calculated by correlating a total of 162 (CO) and 163 (NO) valence electrons (CASPT2-A). The bonding of NO to NiO represents a particularly complex case so another calculation has been performed on NO/NiMg₈O₉ using a larger basis set (CASPT2-B). In particular, we used the atomic natural orbitals (ANO) basis set given by Roos *et al* [43, 44]. The contraction scheme of the basis used for the NiMg₈O₉ is as follows: [17s12p/3s2p] for Mg, [14s9p4d/6s5p2d] for O, and [21s15p10d6f/8s6p3d1f] for Ni. For the NO molecule the contraction scheme is [14s9p4d/5s4p2d]. For the CASSCF–CASPT2 calculations we used the MOLCAS 5 package [45].

A less approximate way of including dynamical correlation effects on top of a HF or CASSCF calculation is to employ a coupled-cluster method. In the present study, we have used the MC-CEPA scheme developed by Fink and Staemmler [19] which is an approximate multi-configuration coupled-cluster method. It is, in contrast to CISD methods, exactly size consistent, but contains certain approximations for complicated matrix elements [20]. The present implementation can make use of three variants: the genuine MC-CEPA approximation, a variant-averaged coupled-pair functional (ACPF) as proposed by Gdanitz and Ahlrichs [46], and a linearized version, CEPA-0, in which all matrix elements not necessary to ensure size consistency are completely neglected. In all applications so far we found that MC-CEPA and ACPF correlation energies are quite similar and rather close to full CI results as well, whenever a comparison was possible, while CEPA-0 generally overestimates correlation effects. Similar observations have been made by other authors using related approaches [47].

In the present study, we have performed single point MC-CEPA calculations for NO/NiO employing the same cluster geometry and nearly the same basis sets as in the DFT and CASPT2 calculations. However, in order to keep the computer time low, we identified all doubly occupied orbitals in the cluster and included only the valence orbitals at Ni, at the O atoms adjacent to the Ni adsorption site, and at the NO molecule in the correlation treatment.

3. Results and discussion

NH₃, CO, and NO bind to the NiO surface through completely different mechanisms. NH₃ and CO interact mainly electrostatically with the Ni²⁺3d⁸ surface cation (the ³B₂ ground state in C_{4v}), with very small covalent bonding contributions [48]; the bonding arises from polarization and dispersion forces with no change of Ni²⁺ spin state. The bonding in NO/NiO and NO/NiMg₈O₉ implies interaction of the paramagnetic NO molecule, the ²Π ground state, with a magnetic Ni²⁺ ion in an open-shell 3d⁸, ³B₂, configuration. The coupling of the

unpaired electrons on the two fragments results in four electronic states, $^2A'$, $^2A''$, $^4A'$, $^4A''$ (C_s symmetry) [49]. Only one of them, $^2A''$, is bonding, in agreement with ESR measurements [17]; the other three states exhibit purely repulsive potential energy curves, figure 1.

First we consider the bonding of the three molecules as described by the popular hybrid B3LYP approach. At the U-B3LYP level CO/Ni₉O₉ and CO/NiMg₈O₉ are almost unbound complexes, with $D_e = 0.02$ and 0.06 eV, respectively, despite a distance from the surface, 2.10 Å, close to the experimental one; see table 1. For NH₃/NiMg₈O₉ we found at the same level a weak bonding, $D_e = 0.23$ eV, much lower than in the experiment, and a distance from the surface, 2.19 Å, which is ≈ 0.13 Å longer than the measured one [1, 2]; see table 2. It is important to note that the spin contamination is small for both NH₃ and CO surface complexes and the expectation value of $\langle S^2 \rangle$ is within 0.02 of the nominal value for a triplet state. This is indicative of the single-reference nature of the ground state. For NO/NiMg₈O₉ the U-B3LYP approach gives $D_e = 0.25$ eV (BSSE corrected), a Ni–N distance of 2.02 Å, but a spin distribution which is contrary to experiment; see table 3. $\langle S^2 \rangle$ is 1.41 instead of that expected for a doublet state, 0.75 , indicating a substantial spin contamination. The spin distribution shows the presence of three unpaired electrons, two with spin up on Ni and one with spin down on NO, at variance with the ESR experiment [17]. This is indicative of a multi-reference character of the ground state [32, 49]. Similar results are obtained when we model the NiO surface by a NiO slab; see the NO/NiO U-B3LYP results for $\theta = 0.25$ in table 3. The binding energy, however, is considerably smaller, $D_e = 0.07$ eV after BSSE. This is due in part to adsorbate–adsorbate repulsions. In fact, repeating the calculation for $\theta = 0.125$ (the geometry has not been reoptimized), D_e becomes 0.16 eV. Apart from the slightly different energy, the NiMg₈O₉ cluster and the NiO slab give similar properties and incorrect spin distributions, showing that the problem cannot be treated properly within this DFT approach. If the B3LYP calculation is repeated using the RO formalism so that the corresponding solution is forced to be an eigenfunction of the $\langle S^2 \rangle$ spin operator (pure $^2A''$ state; figure 1), then the geometry is similar to the spin-polarized solution but the interaction energy is close to zero; see table 3. The other wrong prediction of the B3LYP approach is for the vibrational shifts of adsorbed CO and NO. For NO/NiMg₈O₉, $\Delta\omega$ (RO-B3LYP) = -209 cm⁻¹ is three times the experimental value, -71 cm⁻¹; $\Delta\omega$ (U-B3LYP) = -110 cm⁻¹ is better but still overestimated; see table 3. For CO/Ni₉O₉ even the direction of the shift is wrong (theory: $\Delta\omega = -73$ cm⁻¹; experiment: $\Delta\omega = +9$ cm⁻¹ [12]; see table 1). Clearly, the B3LYP method does not provide a satisfactory description of the three bonds.

We have further considered the ‘pure’ BLYP gradient-corrected exchange–correlation functional. At the BLYP level, NH₃/NiMg₈O₉ with $D_e = 0.16$ eV is underbound—table 2; CO/NiMg₈O₉ with $D_e = 0.30$ eV matches the experimental result perfectly—table 1; while NO/NiMg₈O₉ is overbound, $D_e = 0.96$ eV—table 3. Probably BLYP underestimates the dispersion contribution to the bonding of NH₃ to ionic substrates, while it overestimates the covalent contribution in NO/NiO. For NO and especially for CO, the distance from the surface is too short. This results in a strong overlap with the Ni 3d orbitals and in an excessive back-donation of charge into the antibonding levels of the adsorbed molecule. The consequence is that the CO vibrational shift is -172 cm⁻¹, instead of $+9$ cm⁻¹—table 1; for NO, $\Delta\omega$ is -292 cm⁻¹ instead of -71 cm⁻¹—table 3. Thus, the BLYP method is also completely inadequate for describing the bonding at the NiO surface. Notice that the Perdew–Wang GGA approach provides results (not reported here for brevity) similar to the BLYP ones. LDA appears to be totally inadequate since it fails even to correctly predict NiO as an insulator [50].

As a last example of exchange–correlation functionals, we have considered the HFLYP approach. Notice that hybrid DFT approaches such as HFLYP give a rather good description

of the properties of bulk NiO [51, 52]. In HFLYP, for CO/Ni₉O₉, $D_e = 0.15$ eV is somewhat smaller than the experimental value; the Ni–C distance, 2.38 Å, is 0.21 Å longer than in the experiment; and $\Delta\omega$ is -10 cm⁻¹ instead of $+9$ cm⁻¹—table 1. For NH₃/NiMg₈O₉, $D_e = 0.49$ eV is slightly smaller than the experimental estimate and the Ni–N bond distance is 0.1 Å too long—table 2. These results are far from being satisfactory. Still, HFLYP provides the best overall description of the bonding characteristics of CO/NiO and NH₃/NiO among the functionals considered. Unfortunately, the same HFLYP approach gives a completely wrong description of NO/NiO; see table 3. The calculations are done at the RO level to avoid spin-contamination problems. Only the bond length, 1.82 Å for NiMg₈O₉ and 1.78 Å for a NiO slab, is reproduced with an acceptable error. The minimum of the ²A'' curve for NiMg₈O₉—see figure 1—lies 3.53 eV above the dissociation limit (3.90 eV with a NiO slab) and $\Delta\omega$, -404 cm⁻¹, is five times larger than the experimental one! The reason for this failure lies in the description of the on-site Coulomb repulsion in Ni²⁺. The coupling of the NO spin with the Ni²⁺ unpaired electrons results formally in a change of Ni configuration from 3d⁸ to 3d⁹. This can be related to the electron affinity (EA) of the Ni²⁺ cation in NiO, a key parameter in determining the Hubbard U -parameter in magnetic insulators. EA for the process NiMg₈O₉ + e⁻ → [NiMg₈O₉]⁻ changes dramatically as a function of the amount of HF exchange which is mixed in with the DFT exchange and goes from -2.7 eV in BLYP to -6 eV in HFLYP! The ordering of the ²A'' curves follows the same trend; see figure 1. Thus, the 3d intra-shell Coulomb repulsion is substantially overestimated when the exchange is treated at the HF level. This is associated also with the level of spin localization: in HFLYP the spin is localized by 94% on the Ni 3d orbital; in BLYP the localization is reduced to 68%; see table 3.

These results show unambiguously the problems of the DFT approach for describing the bonding of NH₃, CO, and NO to NiO or Ni-doped MgO surfaces. Therefore, we made use of wavefunction-based methods where the dynamical correlation, spin state, and multi-reference character of the wavefunction are treated explicitly on an equal footing by means of the CASSCF, CASPT2, and MC-CEPA approaches.

The ³B₂ curves of CO/NiMg₈O₉ and the ²A'' and ⁴A'' curves of NO/NiMg₈O₉ have been determined by considering several single-point geometries. The only geometrical parameter which has been varied is the distance of CO or NO from the Ni cation. The bonding of CO to NiMg₈O₉ is dominated by electrostatic and dispersion terms and does not involve any spin change in the surface complex. At the CASSCF level the complex is unbound while in CASPT2 the minimum is found for $r(\text{Ni-C}) = 2.24$ Å, with a $D_e = 0.13$ eV; see table 1. This means that the distance is overestimated and that the bonding is about 50% of the experimental one. The CO vibrational frequency exhibits a shift, $\Delta\omega = +16$ cm⁻¹, with the right sign and an absolute value close to the measured one, $+9$ cm⁻¹; see table 1. In this respect, CASPT2 represents a clear improvement in the description of the complex, since all properties are determined with acceptable errors. The case of NO is somewhat more complex.

The key aspect of the bonding mechanism in NO/NiMg₈O₉ is the coupling of the unpaired electrons in the Ni 3d(z^2) orbital with that in the NO $2\pi^*$ antibonding level [49]. First of all we notice that the CASSCF wavefunction does indeed result from a mixing of configurations, confirming the multi-reference character of the doublet state. However, no bonding is found at the CASSCF level. The ²A'' curve is in fact purely repulsive, as is the ⁴A'' one. Since a CASSCF wavefunction includes mainly non-dynamical correlation, one can deduce that the dynamical correlation is essential for the description of the bonding. This has been included by means of CASPT2; see table 3. The result is a distance, $r(\text{Ni-N}) = 2.03$ Å, and a $D_e = 0.65$ eV before BSSE correction and 0.48 eV after (CASPT2-A). It should be mentioned that the BSSE was estimated using the same correction as used for CO. Since most of this error is due to the

description of the cluster, and considering that the distances of CO and NO from the surface are not too different, a similar BSSE can be expected. The calculation of the vibrational shift, $\Delta\omega = -101 \text{ cm}^{-1}$, is also in line with the measured one, -71 cm^{-1} ; see table 3. Thus, the bond strength is somewhat underestimated. This important point has been considered in more detail by performing a calculation with a larger basis set, CASPT2-B. In principle, the CASPT2 result can be systematically improved by increasing the size of the basis set and of the active space. The results—table 3—show that the geometrical parameters and the binding energy are reasonably converged with respect to the basis set. Here we applied a full counterpoise correction to determine the BSSE-corrected value. This is 0.31 eV, i.e. slightly smaller than the CASPT2-A result, and about 0.3 eV smaller than the experimental value. Therefore, we can conclude that CASPT2 is able to provide a correct description of all the properties of the NO/NiO bond.

Finally, we have performed single-point calculations for NO/NiMg₈O₉ using the MC-CEPA approximation [20] on top of a CASSCF reference wavefunction. The BSSE was corrected both at the CASSCF and at the MC-CEPA level. In addition to the basis set used for the DFT and CASPT2 calculations, we have also employed a more extended one which contains several semidiffuse polarization functions for a better description of dispersion effects and a reduction of the BSSE. The results are also included in table 3. They show that the MC-CEPA approach, as well as ACPF which is not documented here, yields only a very small binding energy of 0.02 eV (0.24 eV without BSSE correction), even with the more flexible basis set. This is much less than obtained at the CASPT2 level and observed in experiment. On the other hand, our CEPA-0 result, 0.34 eV (0.57 without BSSE correction), is rather close to the corresponding result at the CASPT2 level, calculated for the same adsorption geometry.

Apparently, the two ways of describing the NO/NiO interaction by wavefunction-based correlated *ab initio* methods differ substantially. At the CASPT2 level, a moderately strong chemical bond is obtained and most of the calculated properties are in fair agreement with experiment. The approximate coupled-cluster (MC-CEPA) approach, on the other hand, yields only a very small binding energy, much lower than the experimental value. (Several additional MC-CEPA calculations with different cluster models, basis sets, and embeddings led to the very same picture and resulted in binding energies of only 0.05–0.10 eV at equilibrium geometries with rather long Ni–N distances of about 2.3–2.5 Å [53].) The question is still open of which one of these two approaches is more reliable. It is well established that the CASPT2 method very often leads to reasonable results because of error cancellations between an overestimation of correlation effects and basis set deficiencies. By proceeding to extended basis sets, one might obtain too large binding energies at the CASPT2 level; a recent example has been given by Persson and Taylor [54]. MC-CEPA might slightly underestimate correlation effects, but hardly so much that the calculated adsorption energy is too low by about 0.5 eV. Of course, there are other effects, e.g. surface relaxation, which were not included in the present study and which might also have some influence on the precise value for the adsorption energy: the importance of triples and of the antiferromagnetic structure of NiO for the bonding between NiO and the open-shell molecule NO has yet to be investigated.

4. Conclusions

The description of the bonding of NH₃, CO, or NO to a Ni²⁺ cation embedded in an oxide matrix (either MgO or NiO) represents a challenge to theory. DFT methods provide very different answers, often qualitatively incorrect, depending on the exchange–correlation functional used, reflecting the different natures of the bonding of NH₃, CO, and NO to NiO. For NH₃ and CO the failure is connected in part to the well-known limitations of DFT for describing dispersion

forces; for NO the problem is related to the description of the on-site Coulomb repulsion in the Ni 3d shell and to the multi-reference character of the ground state [49]. Explicitly correlated methods give an acceptable, although not perfect, description of all the properties of both systems. However, there are still rather large discrepancies between perturbational and variational ways for taking care of correlation effects (CASPT2 versus MC-CEPA). This shows the importance of quantum-chemical methods in combination with cluster models for describing surface bonds of some kinds. In this respect, the recent development of density-based embedding cluster approaches seems particularly important [55].

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