

Molecular Adsorption Bond Lengths at Metal Oxide Surfaces: Failure of Current Theoretical Methods

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New experimental structure determinations for molecular adsorbates on NiO(100) reveal much shorter Ni-C and Ni-N bond lengths for adsorbed CO and NH₃ as well as NO (2.07, 1.88, 2.07 Å) than previously computed theoretical values, with discrepancies up to 0.79 Å, highlighting a major weakness of current theoretical descriptions of oxide-molecule bonding. Comparisons with experimentally determined bond lengths of the same species adsorbed atop Ni on metallic Ni(111) show values on the oxide surface that are consistently larger (0.1–0.3 Å) than on the metal, indicating somewhat weaker bonding.

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Very substantial advances in computational density functional theory (DFT) during the past few years have shown that adsorbate bonding on metal surfaces can be described very precisely, achieving agreement with experimental results in local structural parameters within a few hundredths of an angstrom unit. There is now increasing interest in oxide surfaces, which are widely recognized as being of great importance in applications such as heterogeneous catalysis, but the state of knowledge concerning these surfaces is far more limited. In particular, there is a dearth of experimental structural data [1], especially for adsorbates on oxides, and theory-experiment comparison has had to concentrate on the molecular bonding energy (which is compared with the experimental thermal desorption energy) and the vibrational energies, especially of internal adsorbate vibrations, such as the C-O stretching frequency of adsorbed CO [2]. In an attempt to redress this balance we have performed quantitative structure determinations of the model systems of CO, NO, and NH₃ adsorbed on NiO(100). Our results show that the current theoretically derived adsorbate-substrate bond lengths on this surface are very seriously in error (by up to 0.79 Å), and they provide the first quantitative reference data against which future theoretical developments may be evaluated. In an attempt to identify some systematics of the bonding at NiO(100) based only on experimental structural information, we compare these bond lengths with those measured by the same experimental methods, in the same singly coordinated adsorption sites, on metallic Ni(111). Our results are consistent with adsorption on the oxide surface being significantly weaker than on the metal, but being much less weak than indicated by current theoretical treatments.

Our experiments use the technique of scanned-energy mode photoelectron diffraction (PhD) [3] which exploits the coherent interference between the directly emitted component of the photoelectron wave field from an adsorbate core level and other components of this wave field elastically scattered by nearby atoms in the substrate. By measuring the changes in the photoemission signal as a function of photon energy (and thus photoelectron kinetic energy and wavelength), modulations associated with specific scattering path lengths switching in and out of phase are observed. Multiple scattering simulations of this process for a series of model trial structures allow the local adsorbate structural environment to be determined. We have established the methodology of this technique [3] and used it to determine the structure of more than 60 adsorbate systems on metal and semiconductor surfaces. Using this same approach we have recently [4] used N 1s PhD to determine the adsorption geometry of NO adsorbed on a thin NiO(100) film grown *in situ* on Ni(100) using the approach of Kuhlbeck *et al.* [5] who characterized the adsorption characteristics of these films in detail and showed that their behavior is very similar to those of cleaved bulk NiO surfaces. We have now made new C 1s PhD measurements of adsorbed CO and N 1s PhD measurements of adsorbed NH₃ on NiO(100) thin films prepared in the same way. The experiments were conducted using the BESSY synchrotron radiation source in Berlin on a purpose-built beam line and surface-science end station described elsewhere (e.g., Ref. [4]). The general method of obtaining PhD modulation spectra from individual 1s photoelectron energy distribution curves recorded at 2 eV steps in photon energy was also described previously [3]. Measurements were made for

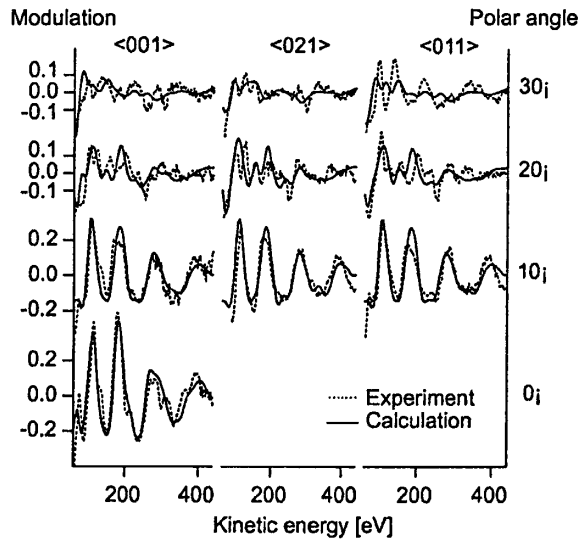


FIG. 1. Comparison of experimental (dashed lines) C 1s PhD modulation spectra from CO adsorbed on NiO(100) recorded at four different polar emission angles in three different azimuths with the results of multiple scattering simulations (solid lines) for the best-fit structure.

CO adsorbed at temperatures of 60–90 K, and for NH₃ adsorbed at 140 K. A representative data set of PhD spectra recorded in ten different emission directions for the NiO(100)/CO system is shown in Fig. 1. Strong modulations with a single period are characteristic of a 180° scattering geometry from a near neighbor [3], so the fact that these data show such modulations at normal emission, and that the amplitude decays with increasing polar emission angle, is characteristic of an atop adsorption geometry. Multiple scattering simulations [3] confirm this conclusion, and after structural optimization we obtain the best-fit curves of Fig. 1. The optimized geometry gave a PhD reliability (*R*) factor [6] value of 0.19 for the set of ten spectra, indicating a good quality fit, and corresponds to CO adsorbed atop a surface Ni atom via the C atom with the C-O axis approximately perpendicular to the surface. Tests on models based on different adsorption sites and geometries (including CO bonded through the O atom and adsorption atop O atoms in the NiO surface) led to far higher *R*-factor values (>0.4) and can clearly be excluded. The adsorbed NH₃ molecules were also found to occupy sites atop a surface Ni atom. Table I summarizes the structural parameter values found for CO

TABLE I. Optimum values of the structural parameters found in this experimental study of NiO(100)/CO and NiO(100)/NH₃.

Adsorbate	CO	NH ₃
$d_{\text{Ni-C}}, d_{\text{Ni-N}}$	$2.07 \pm 0.02 \text{ \AA}$	$2.06 \pm 0.02 \text{ \AA}$
$d_{\text{O-C}}, d_{\text{O-N}}$	$1.15(+0.10/-0.08) \text{ \AA}$...
$\theta_{\text{Ni-C}}, \theta_{\text{Ni-N}}$	$7(+5/-3)^\circ$	$7 \pm 6^\circ$
$\theta_{\text{O-C}}, \theta_{\text{O-N}}$	$12 \pm 12^\circ$...
Δz_{Ni}	$0.03(+0.06/-0.08) \text{ \AA}$	$0.11 \pm 0.02 \text{ \AA}$

and NH₃ adsorption; for CO adsorption the local site and molecular orientation (Fig. 2) are consistent with previous theoretical treatments [7,8]. Notice that any local expansion of the outermost Ni atom layer (Δz_{Ni}) is either negligible or very small, as are any tilts of the Ni-N, Ni-C, or C-O bonds (θ parameters).

While the local adsorption site for CO (and for NO) is in good qualitative agreement with the results of the previous theoretical studies [5,7,8], the quantitative values of the local Ni-molecule bond lengths are in very poor agreement. These are shown for all three adsorbate systems in Table II. The theoretical Ni-N bond length for NO adsorption [5] is 0.22 Å longer than the experimental value, while the Ni-C distances found in the two theoretical treatments are 0.42 Å [7] and 0.79 Å [8] longer than the experimental value. Differences of this scale indicate gross errors in the description of the bonding by the theoretical calculations. Another manifestation of this misdescription, which is already recognized, is the bonding energy of CO and NO on NiO(100); the theoretical calculations yield values for CO of 0.25 eV [7] and 0.08 eV [8] and for NO of 0.17 eV [5], while the corresponding experimental values from thermal desorption are 0.30 and 0.57 eV [9].

The general problem of accurately describing oxide-molecule bonding has been the subject of recent debates [10–12]. In the case of MgO(100)/CO, standard local density approximation calculations significantly underestimate the adsorption energy of this very weak adsorption system, and while stronger bonding occurs if one does not include generalized gradient correction [11] this solution is not generally regarded as acceptable [10]. The case of NiO is potentially even more difficult, because standard DFT methods fail to give a proper description of the electronic structure, including the band gap, and in particular do not properly describe the occupation of the Ni 3*d* states [13]; as such they are ill-suited to describe adsorbate bonding. Potentially more fruitful for NiO adsorption are the SCF (self-consistent field) methods, including various correction terms and configuration interaction. However, while the citations given here for this type of calculation on NiO

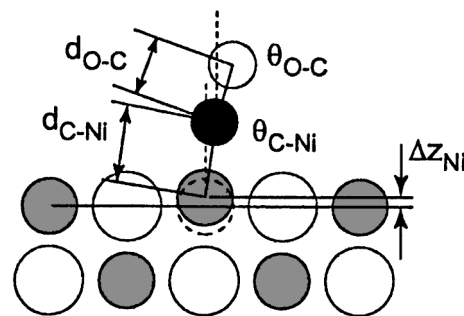


FIG. 2. Schematic side view of the best-fit adsorption geometry of CO on NiO(100), including a definition of the structural parameters given in Table I. The shaded and open circles correspond to Ni and O atoms, respectively.

TABLE II. Comparison of Ni-C and Ni-N nearest neighbor distances obtained from PhD studies of CO, NO, and NH₃ adsorption on NiO(100) and Ni surfaces, and of theoretical values of the same parameters for CO and NO adsorption on NiO(100).

Substrate	$d_{\text{Ni-C}}(\text{CO})/\text{\AA}$	$d_{\text{Ni-N}}(\text{NO})/\text{\AA}$	$d_{\text{Ni-N}}(\text{NH}_3)/\text{\AA}$
NiO(100)	2.07 ± 0.02	1.88 ± 0.02	2.06 ± 0.02
NiO(100) theory	2.49 [7], 2.86 [8]	2.1 [5]	...
Ni(111) atop	1.77 ± 0.02 [15]	...	1.97 ± 0.03 [16]
	(coadsorbed with O)		
Ni(111) hollow	1.93 ± 0.03 [17]	1.84 ± 0.07 [18]	...

are for work which is some ten years old, very recent attempts to reinvestigate this situation with the latest methods have so far failed to yield any improvement [12]. One possible underlying problem is the use of small clusters in these calculations, which will fail to describe the electronic band properties, and may not be properly converged. In this regard we note that the other SCF calculations of this type showed that CO and NO bonding strengths on NiO could be increased by using a "weak potential," effectively lowering the ionicity [14]. This idea can only be evaluated effectively, however, through the use of larger clusters to eliminate the effects of the assumed charge distribution.

While it is not possible to infer the details of bonding from measured bond length alone, the values of this parameter are expected to follow some general trends with bonding character. Table II includes a comparison of the local Ni-C and Ni-N bond lengths for adsorption of the three species on the NiO(100) surface and on metallic Ni(111) (the only Ni surface on which the local structure of all three species have been studied) [15–18]. In constructing this table we used only values for the metal surfaces obtained by the same PhD technique, as this ensures that any systematic errors of the method should be common to all measurements. Note, however, that for those systems investigated by other methods [notably Ni(111)/CO and Ni(111)/NO by low-energy electron diffraction [1]] there is excellent quantitative agreement between the methods. One complication in making these comparisons is that a chemical bond length depends not only on the character of the bonding but also on the coordination [19]. All three molecules are singly coordinated in atop sites on NiO(100), so ideally one should compare these bond lengths with similar atop site adsorption on metallic Ni. For NH₃ adsorption on Ni(111), atop site adsorption is standard. On clean Ni(111) both CO and NO occupy threefold coordinated hollow sites at all coverages studied up to 0.5 monolayer, and the bond lengths corresponding to these sites are also given in Table II. In the case of CO adsorption, however, preadsorption of atomic O leads to the CO occupying atop sites, and the bond length for this coadsorption situation is given in the table. Clearly the presence of the coadsorbed O may influence the character of the Ni-CO bonding, but the reduction in Ni-CO bond length in the singly coordinated site relative to that in the threefold coordinated site does follow the expected trend for the

coordination change [19]. This singly coordinated Ni-C bond length on Ni(111) of 1.77 Å is also similar to that found for atop adsorption on Ni(100) [1]. For CO and NH₃ adsorption the table shows a clear trend for Ni-C and Ni-N distances to be longer on the NiO surface by approximately 0.1–0.3 Å.

The situation is less clear for the case of NO because on Ni(111) this species has only been found in the threefold coordinated site, and the difference in bond lengths shown in the table between NiO(100) and Ni(111) is smaller than the estimated precision. Although quantitative structural information is available for singly coordinated NO adsorption on Ni(111), the results shown in Table II for CO adsorption in the two different coordinations certainly suggest that we might expect atop NO on metallic Ni to have a Ni-N distance shorter than the value of 1.84 Å found for the threefold coordinated site. There is also some relevant comparative data for NO for the case of a saturated (2 × 2) layer of NO on Ru(0001) in which atop and threefold coordinated hollows are both occupied; in this system the Ru-C bond lengths are 1.72 and 2.08 Å for single and threefold coordination, respectively [20]. This clearly reinforces the view that the Ni-N bond length found for NO adsorbed on NiO(100) is significantly longer than that which would correspond to NO in a singly coordinated bond on metallic Ni.

The fact that the local bond lengths are shorter for CO, NO, and NH₃ adsorption on Ni(111), relative to adsorption on NiO(100), is consistent with the higher desorption temperature and higher implied bonding energies on the metal surface. Nevertheless, the adsorption bond lengths measured on NiO(100) are sufficiently short to indicate true bond formation, and not simply electrostatic interaction as has been concluded for CO adsorption on NiO(100) on the basis of current theoretical treatments. Indeed, while the shorter Ni-molecule bond lengths obtained on metallic Ni surfaces are generally consistent with expectations for covalent bonding, the bond lengths on NiO are very much smaller than those which may be estimated from a sum of van der Waals radii [21] of 3.18 and 3.33 Å for Ni-N and Ni-C, respectively. Clearly there is a need for further theoretical work, but our results provide the first quantitative structural information by which the results of these calculations may be judged.

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