On core-hole screening in chemisorption systems

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Abstract

Core-hole screening in adsorbates was studied by the example of the CO/Ni(100) chemisorption system. The C Is and O Is core-hole spectra of a linear NiCO cluster used as a model of the system were obtained by large-scale ab-initio configuration interaction (CI) calculations. The computed spectra are consistent with the experimental ones of the CO/Ni(100)-c(2 × 2) system. Contrary to the previous restricted CI calculations (Surf. Sci. 258 (1991) 91; Chem. Phys. 156 (1991) 309), our results show that the screening mechanism of the core hole on the ligand atoms is dominantly metal–ligand π→π* charge transfer.

Keywords: Ab initio quantum chemical methods and calculations; Photoelectron emission

1. Introduction

The origin of the observed intense satellite structures in the core-level X-ray photoelectron spectra (XPS) of small molecules adsorbed on d-metal surfaces has been the subject of numerous discussions for about 20 years (see Refs. [1–3], and references therein). However, there is still no consensus on the interpretation of the spectral features. A variety of models for the adsorbate core-hole relaxation has been proposed. The central idea of the model proposed by Schönhammer and Gunnarsson (SG) [4] is that the adsorbate unoccupied level (the 2π* level in the case of CO adsorption) in the presence of the adsorbate core hole is pulled down below the Fermi level and is partially occupied by a charge transfer from the substrate d-bands. According to the model, the lowest energy state is the “fully screened” state, and the satellite structure is related to the “poorly screened” state, which is close to the Koopmans’ state. The ratio between the intensities of the main and satellite lines in the SG model depends on the degree of hybridization between adsorbate and substrate, i.e. on the strength of adsorption and on the position of the initially unoccupied adsorbate level in the core-ionized final state. This model, although based on a rather simple Hamiltonian and not including the intramolecular relaxation, is capable of describing qualitatively the band shapes of core-hole spectra which emerge when going from weakly adsorbed systems to cases of strong chemisorption.

Another model considers the dynamic image charge screening as a complementary mechanism of core-hole screening [5]. The authors of this model do not rule out, however, the importance of the charge transfer screening (CTS) mechanism for systems with strong chemisorption, in
particular for CO adsorbed on a Ni surface (CO/Ni system). Both these models treat the interaction of the discrete adsorbate levels with substrate bands.

A different way of approaching the problem of core-hole screening in adsorbates is to use cluster models in the calculations. The feasibility of the cluster approach for this case is based on the assumption that core-level XPS probes the local properties of the system under investigation. The local character of the excitations in the core-hole spectra of metal/CO adsorption systems has indeed been demonstrated by comparison with the spectra of carbonyl complexes [6]. The linear NiCO cluster is thought to be a rather good minimal model for the chemisorption system of interest here: carbon monoxide on Ni(100) surfaces [7–10]. The limitations of this model have not been fully clarified, but the experimental evidence of a local character of the excitations forming the spectra suggests that the essential physics of core-hole screening in the system considered is contained in this simple model. In the literature one can find many ab initio calculations performed on the core-hole states of NiCO [8–13]. Hartree–Fock (HF) ASCF [11] and generalized valence bond configuration interaction [10] calculations have shown the metal $d\pi \rightarrow$ ligand $\pi^*$ CT to be the main physical process responsible for core-hole screening in NiCO. According to the calculations on both the C 1s and O 1s XPS, the main line and the most prominent satellite at 5.5 eV are the CTS and Koopmans’ states, respectively. A different interpretation of the spectra was given in Ref. [9] using the diagonal Tamm–Dancoff two-particle–hole approximation: the most intense line is the Koopmans’ state, whereas the satellite is the $\pi \rightarrow \pi^*$ CT shake-up state.

Recent high-resolution experimental XPS data for the CO/Ni system [1] have revealed, in addition to the known satellite at 5.5 eV, other satellites which were neither detected experimentally nor predicted by any of the calculations before. According to the interpretation given by the authors of Ref. [1], the main line in the spectra is a CTS state and the satellites around 5.5 eV are related to excitations of the $2\pi^*$ orbital to the CO 3p and other CO Rydberg states in the presence of the CO core hole.

The previous calculations on the XPS did not include a great part of many-body effects accompanying ionization and, as a consequence, the results strongly depend on the computational method used. The necessity of using methods incorporating a large fraction of electron correlation to study core-hole screening in adsorbates is evident. Recently, restricted ab-initio configuration interaction (CI) calculations on the core-ionized states of NiCO have been performed [12,13]. As far as we can understand the statements of the authors of Refs. [12–14], the metal–ligand $\pi \rightarrow \pi^*$ CT excitations play a minor role in the relaxation of the core hole, whereas local metal $\sigma \rightarrow \sigma^*$ shake-up excitations were recognized to be mostly responsible for the screening. Based on the calculations for the series of molecules (NiCO [12,13], NiN$_2$ [13,15], PdCO [16] and PdN$_2$ [17]) a new model, the so-called "cooperative core-hole screening mechanism" [14] has been proposed.

According to this mechanism, the metal–ligand $\pi \rightarrow \pi^*$ CT actually takes place upon ionization, but the depletion of the d population due to the $\pi \rightarrow \pi^*$ CT makes it possible for an additional d electron to be supplied by the s–d hybridization and promotion. Thus, the authors of this mechanism consider the local metal s d population change in the metal–ligand system, associated with metal $\pi \rightarrow \pi^*$ excitations, as the origin of many-body effects in the XPS of adsorbates. The interpretation of the spectral features which emerges from these CI calculations differs significantly from that of all the previous models: the satellite at 5.5 eV is the local metal $\sigma \rightarrow \sigma^*$ shake-up state, and the main line is close to the Koopmans’ state. The dimension of the configuration space used in these calculations was severely limited (about 8000 configurations). Core-ionized SCF relaxed orbitals were used as basis in the CI.

Let us briefly discuss general aspects of using relaxed versus unrelaxed (i.e. ground state (GS)) orbitals in the calculation. Using a relaxed orbital basis has the advantage that the static relaxation is incorporated a priori into the calculation. On the other hand, this can lead to a loss of flexibility of the computation to converge properly if strong final state correlation effects are present. In this case, very high excitations must be considered in
the CI calculation to restore the balance between relaxation and correlation and to achieve convergence (see, e.g., Ref. [18]). Using the relaxed basis for many-body calculations also makes the calculation of spectral intensities difficult, because different basis sets for the ground and ionic states are used.

What is important in the present context is, in particular, that use of the unrelaxed orbital basis in the CI affords an immediate interpretation of the nature of the core-hole screening mechanism. This mechanism is described by the change in the wavefunction upon ionization, and one can read it straightforwardly from the CI wavefunction of the ionized states, since the ground state of NiCO, although not the lowest Hartree–Fock state, is well described by the HF determinant. On the other hand, a large and unknown fraction of wavefunction change is hidden in the basis set when the CI calculation on the core-hole states is carried out in the relaxed orbital basis. The authors of Refs. [12–17] used relaxed ionic orbitals, which makes it difficult to arrive at a clear picture of core-hole screening. The hidden fraction of wavefunction change is substantial and is lost for the disclosure of the underlying mechanism. This probably explains why the authors of Refs. [12–17] obtained such an unusual picture of core-hole screening in adsorbates.

2. Results and discussion

The importance of high-order valence excitations in the presence of a core hole, particularly double excitations (demonstrated in Refs. [12,13]), prompted us to perform very large-scale CI calculations without substantial limitations on the size of the CI space and using the unrelaxed orbital basis set to make both the calculations and the interpretation of the results more transparent. The dimension of the configuration space for our multi-reference direct CI (MRDCI) calculations was about 2,500,000. The set of HF orbitals for the CI calculations was obtained from an SCF calculation of the $^1\Sigma^+$ closed-shell state of linear NiCO ($R_{\text{Ni-C}} = 3.5$ a.u., $R_{\text{C-O}} = 2.179$ a.u.). Details of the calculations will be reported elsewhere [19].

The results of our large-scale MRDCI calculations on the C 1s and O 1s XPS of the NiCO cluster are listed in Table 1, together with the literature CI results [12,13] and experimental XPS data [1]. According to our calculations the state corresponding to the most intense line in both the C 1s and O 1s spectra is a strong mixture of the single-hole state ($C 1s^{-1}$ and $O 1s^{-1}$, respectively) and $\pi \rightarrow \pi^*$ CT configurations, with small admixtures of the local metal $\sigma \rightarrow \sigma^*$ shake-up configurations. The relative intensities of the main line in both spectra are 0.48, and differ considerably from the experimental estimates (0.29 for the C 1s XPS and 0.36 for the O 1s XPS). We relate this discrepancy to the limitations of the cluster model used: CTS in the real chemisorption system should be larger than that of the cluster, resulting in a more intense screening of the core hole, which reduces the intensity. The first computed satellites appear in the spectra at 2.77 eV (C 1s XPS) and at 2.53 eV (O 1s XPS) and are nearly pure $\pi \rightarrow \pi^*$ CTS excitations. The position of this low-intensity satellite in the C 1s XPS coincides rather well with that of the experimental spectrum, where it appears at 2.1 eV. The satellite in the O 1s spectrum is very weak and cannot be detected, explaining why there is no peak in the experimental O 1s spectrum corresponding to the first satellite in the experimental C 1s spectrum. The second satellite in each spectrum (at 7.64 eV in the C 1s XPS and at 7.41 eV in the O 1s XPS) is intense and mainly a $\pi \rightarrow \pi^*$ CTS state. The positions of these satellites differ by ~2 eV from the intense satellites observed experimentally at 5.5 eV in both spectra. Although the experimentalists do not report estimates of the relative intensities of these satellites, the calculated intensities are consistent with the experimental data. Our calculations also reproduce the experimentally observed smaller intensity of the 5.5 eV satellite in the O 1s spectrum relative to that in the C 1s spectrum. The local metal $\sigma \rightarrow \sigma^*$ shake-up satellites having small intensities are predicted to be at 10.21 and 9.14 eV in the C 1s and O 1s XPS, respectively. These satellites are identified as the satellites at 9.5 and 8.5 eV in the corresponding experimental spectra.

Our results show that $\pi \rightarrow \pi^*$ excitations play a dominant role in the C 1s and O 1s XPS of NiCO.
Table 1
The C 1s and O 1s XPS of the NiCO cluster calculated by the CI method in comparison to the experiment for the CO/Ni(100)-c(2×2) chemisorption system, and the results of previous CI calculations.

<table>
<thead>
<tr>
<th>XPS band intensity</th>
<th>Present results</th>
<th>Previous results [12,13]</th>
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<tbody>
<tr>
<td></td>
<td>$\Delta E_h$</td>
<td>$E_{int}$</td>
</tr>
<tr>
<td>C 1s XPS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Main line, strong</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1 satellite, weak</td>
<td>2.1</td>
<td>2.77</td>
</tr>
<tr>
<td>2 satellite, strong</td>
<td>5.5</td>
<td>7.64</td>
</tr>
<tr>
<td>3 satellite, weak</td>
<td>9.5</td>
<td>10.21</td>
</tr>
<tr>
<td>O 1s XPS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Main line, strong</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1 satellite, strong</td>
<td>5.5</td>
<td>7.41</td>
</tr>
<tr>
<td>2 satellite, weak</td>
<td>8.5</td>
<td>9.14</td>
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$^a$ The contributions in parentheses denote small admixtures to the ionic states in order decreasing importance.

Note: all energies are in eV.
The results rule out the interpretation of the low-energy satellites given by the authors of the experiment in Refs. [1,2], who attribute the satellites to excitations of the CO 2π* orbital to the CO 3p and other CO Rydberg states in the presence of the CO core hole. Also, our 2.5 million CI results strongly contradict the very restricted CI results of Refs. [12,13]. Apart from the basic interpretation problem discussed above, the different physical picture emerging from our calculations originates from the very much larger space of double excitations used here. Indeed, we found that restricting the configuration space in our calculations enhances the strength of the σ→σ* excitations. Furthermore, according to the results reported in Refs. [12,13], one could expect another intense feature around 10 eV in the C 1s spectrum and around 9 eV in the O 1s spectrum, exhibiting a total intensity comparable to that of the intense structure observed at 5.5 eV. The experimental spectra do not show such features (see Table 1).

The commonly accepted picture of chemical bonding in 3d metal carbynyls [20] assumes two interconnected channels of bonding: a σ channel responsible for donation of an electron from a ligand to a metal and forming metal s−dσ, s+dσ hybrids, and a π channel responsible for backdonation from the metal to the ligand (π→π* CT). A perturbation of one channel immediately causes a response of the other channel. The perturbation caused by ionizing the system leads to a mixing of excitations in the final states. The σ→σ* and π→π* excitations are indeed mixed in most of the C 1s and O 1s ionic states of the NiCO. Furthermore, the CT from the metal to the ligand can lead to a dehybridization of the occupied s−dσ and unoccupied s+dσ hybrids. As a result of such dehybridization, the σ hybrid acquires a more spatially compact dσ character, whereas the σ* becomes a more diffuse s-type level. Thus one can expect the balance between the contributions of the σ→σ* and π→π* in the final ionic states to depend on the strength of the π→π* backdonation in the GS. In the case of C 1s ionization, the π→π* CT is slightly weaker than in the C 1s spectrum, mainly because of the fact that the 2π* orbital is mostly localized on the C atom. Here, one can expect an increase of the σ→σ* admixture to the final states. From Table 1 it can be seen that this is actually the case: the intensity of the local σ→σ* satellite at 9.14 eV in the O 1s XPS increases relative to the satellite at 9.5 eV in the C 1s spectrum, and the contributions of the σ→σ* excitation to the ionic states are larger in the case of O 1s ionization.

3. Summary

The results of the present large-scale MRDCI calculations on the C 1s and O 1s XPS of a NiCO cluster support the physical picture that core-hole screening in molecule/transition-metal chemisorption systems is dominated by the metal−adsorbate π→π* CT mechanism. Metal σ→σ* transitions can be non-negligible, but our calculations make clear, at least in strong chemisorption situations, that they do not dominate.

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References