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Theoretical Evidence for Delocalized Inequivalent Core Holes

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A phenomenon of partial localization of core holes has been discovered. Green's function calculations on a linear NiN_2 cluster used as a model of the weak chemisorption N_2/Ni(100)c(2×2) system show that the N1s core holes in the ionized states of the cluster are not fully localized on the inequivalent nitrogen atoms as has been previously believed. The core holes in some of the states are considerably delocalized. This leads to distinct interference effects in angularly resolved X-ray photoelectron spectra.

Introduction

It is a founding tenet in the field of core-level spectroscopies that core holes of systems with identical but chemically inequivalent atoms are localized on the respective sites. The localization originates from the fact that core levels do not strongly interact with each other. One example where even a slight inequivalence leads to localization of core holes is the CO_2 molecule. There is almost no direct interaction between the O1s core levels (the splitting between the O1s orbital energies is 0.001 eV), and at the $D_{\infty h}$ geometry, the O1s core orbitals are completely delocalized between the two oxygen sites only by virtue of the high symmetry itself. Vibronic coupling between these nearly degenerate delocalized levels leads to a strong excitation of the nontotally symmetric vibrational mode and to symmetry breaking upon ionization of the O1s electrons.[1] It is not evident a priori, however, that the interaction between core levels is always weak enough to result in localized core holes. Furthermore, core holes can also interact through many-electron excitations accompanying ionization.

The N_2/Ni(100) chemisorption system is examined here for the localization of the N1s core holes. This system is very relevant to the problem for several reasons: N_2 molecules are adsorbed vertically on Ni(100), and consequently, the nitrogen atoms are inequivalent; the interaction between the N1s levels in the N_2 molecule is not negligible (the splitting between the N1s orbitals is ∼0.06 eV); the N_2 molecules are very weakly bound to the Ni surface (the energy of desorption is 0.47 eV[2]); strong many-body effects accompany ionization of the N1s electrons.[3]

The experimental N1s X-ray photoelectron spectrum (XPS) of the N_2/Ni(100)c(2×2) system consists of two intense lines split by ∼1.3 eV and a broad intense structure at ∼6 eV above these lines.[4] The origin of these spectral features has been the subject of numerous and controversial discussions for more than 20 years (see ref 5 and references therein). By means of angle-resolved XPS, the splitting between the two lowest-energy lines has been attributed to the ionization of the two inequivalent nitrogen atoms.[2,4] The component with the lowest energy has been assigned to the ionization of the outermost nitrogen.[2,4] The authors of these experimental works used the fact that the amplitude of the electron wave emitted by an atom is strongly peaked in the forward direction due to the scattering by an atom in front of the emitting one.[6] This feature of the high-energy electron scattering has also been used to separate the N1s XPS of the inequivalent nitrogens.[4]

Because of strong many-body effects in the N1s XPS of N_2/Ni(100), a theoretical treatment of the N1s ionization has to properly account for electron correlation. In the literature one can find only few ab initio many-body calculations done on the core-hole states of the N_2/Ni system.[7,8] In these works the chemisorption system was modeled by a linear NiN_2 cluster. The use of the cluster approach for calculations of adsorbate core-hole spectra is justified to some extent by the local character of excitations forming the spectra of adsorbates, as is demonstrated by their similarity to the spectra of the corresponding transition-metal compounds.[9]

In previous studies it has been a priori assumed that core holes of inequivalent atoms must be localized, and the ionization was considered as two independent processes localized on the respective atoms. The experimental procedure to separate the spectra of the inner and outer nitrogens in N_2/Ni(100)c(2×2) is also based on this assumption.[4] Our present approach conceptually differs from previous treatments, in that we consider the simultaneous ionization of the two inequivalent nitrogen atoms of NiN_2.

Results and Discussion

The algebraic diagrammatic construction scheme for the one-particle Green's function consistent through fourth order in the Coulomb interaction (GF ADC(4))[10] has been used to calculate the energies and intensities of spectral lines. The calculations have been done using a contracted Gaussian basis set of size [8s,6p,3d] for Ni and [4s,2p,1d] for N, at the equilibrium geometry optimized at the CASSCF level. Full details of the calculations are given in ref 11.

A simple two-level model provides a good starting point to analyze the localization phenomenon. Let us introduce a Hamiltonian matrix which describes the interaction of basis

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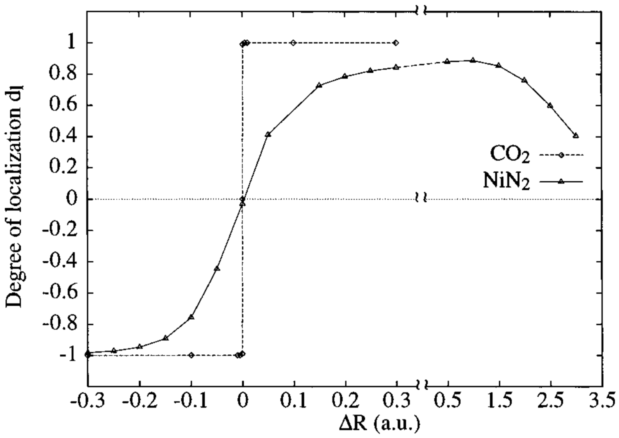

Figure 1. Degree of localization d_l as a function of the linear asymmetric displacement ΔR of the O_2 unit in the CO_2 molecule and as a function of the Ni−N_2 distance ΔR relative to the equilibrium position of the N_2 unit in the NiN_2 cluster. To get continuous curves we dropped the absolute signs in eq 2. Note the different scaling of the ΔR axis before and after the breaking point.

states localized on different centers

$$H = \begin{pmatrix} \epsilon_1 & U \\ U & \epsilon_2 \end{pmatrix} \qquad (1)$$

where the ϵ_1 and ϵ_2 are the energies of these states and the U is the (real) interaction between them. We now introduce a measure of localization, the *degree of localization*, given by

$$d_l = |C_1^2 - C_2^2|/(C_1^2 + C_2^2) = |\Delta|/\sqrt{\Delta^2 + 4U^2} \qquad (2)$$

where $\Delta = \epsilon_2 - \epsilon_1$ and C_1 and C_2 are the eigenvector components. The degree of localization is the difference of the probabilities for the eigenvectors of the Hamiltonian eq 1 to be localized on the different centers. It is seen from eq 2 that the range of energy splitting Δ where the eigenstates are considerably delocalized is dictated by the interaction matrix element U. When $\Delta = 0$ the degree of localization is exactly equal to 0 (completely delocalized states). When $U = 0$ the degree of localization is equal to 1 (completely localized states). We can generally expect $U \neq 0$, and the localization is only partial and depends on the interplay between the splitting Δ and interaction U.

The degree of localization for the O1s and N1s Hartree−Fock (HF) orbitals of CO_2 and NiN_2 is shown in Figure 1 as functions of ΔR, which is the linear asymmetric displacement of the O_2 unit in CO_2 and the displacement of the N_2 unit relative to the equilibrium Ni−N_2 distance in NiN_2. The very abrupt response in the case of CO_2 illustrates the immediate localization of the O1s orbitals when the symmetric geometry is slightly distorted. In the case of NiN_2, the N1s orbitals are almost completely delocalized at the equilibrium geometry ($d_l = 0.03$) despite the inequivalence. The region of Ni−N distance in which the N1s orbitals are still significantly delocalized is remarkably wide. This different behavior of CO_2 and NiN_2 is connected to the very different strength of the interaction between atomic core levels in these systems. Interestingly, the degree of localization for NiN_2 first increases when pulling the N_2 unit away from the Ni atom (Figure 1). At large Ni−N_2 distances the degree of localization decreases, asymptotically approaching the expected case of completely delocalized N1s orbitals of an isolated N_2 molecule. Thus, at the independent-particle level, the nitrogen core holes in NiN_2 are fully delocalized.

The results of the GF calculations for the most intense lines in the N1s XPS of NiN_2 are presented in Table 1 together with the experimental data for the chemisorbed system. As one can see, *the core holes in all the states are only partially localized on the inequivalent nitrogen atoms*. Because of the partial localization, it is not possible to cleanly separate the spectra of the inner and outer nitrogens, and hence we listed in the same column the experimental energies of the lines in both the "inner" and "outer" nitrogen spectra.[4] For the same reason we show in the table, rather than the intensities, the computed spectroscopic amplitudes $x_c^{(n)} = \langle \Psi_n^{N-1} | \hat{a}_c | \Psi_0^N \rangle$, where Ψ_0^N and Ψ_n^{N-1} denote the ground state of the N electron system and the nth state of the ionized system, respectively, while $\hat{a}_c$ is the annihilation operator for the core orbital. The sudden removal of a core Hartree−Fock particle from the exact ground state $|\Psi_0^N\rangle$ of the system leads to $\hat{a}_c|\Psi_0^N\rangle$ which is not an eigenstate of the ion. The spectroscopic factor $|x_c^{(n)}|^2$ is the probability to find $\hat{a}_c|\Psi_0^N\rangle$ in the exact eigenstate $|\Psi_n^{N-1}\rangle$ of the ion. The actual spectral intensities obtained for the ionization of a core electron are related to the spectroscopic amplitudes and will be discussed later.

The lowest-energy core-hole state is mostly localized on the outer nitrogen and is separated by 1.47 eV from the next state, which is mainly localized on the inner nitrogen, in accord with previous theoretical treatments[7,8] and the experimental assignment.[2,4] According to our calculation these two states are $\pi \rightarrow \pi^*$ *shake-down* satellites. Despite their rather large splitting these states are not completely localized on the inequivalent atoms. The next two states, which are almost purely $\pi \rightarrow \pi^*$ shake-down, are perceptibly delocalized. The *main lines* of the spectrum correspond to the states computed at 6.48 and 6.90 eV. They are responsible for the intense and very broad band of the spectrum known as "giant satellite". The two nearly degenerate $\sigma \rightarrow \sigma^*$ states at 8.01 eV are pronouncedly delocalized.

To analyze the localization phenomenon quantitatively, in terms of eq 1, we used a technique for the block-diagonalization of Hermitian matrices.[12] With this method one can project the large configuration space of a secular problem onto a small subspace of "effective" or "dressed" configurations of interest, obtaining a small matrix of the effective interaction among them. This is in fact the exact effective Hamiltonian (EEH) which describes the coupling among the selected basis configurations "dressed" by the interaction with all the remaining configurations. In our case, we thus obtain the EEH matrix H, eq 1, of the interaction between the dressed core holes. We refer the reader to ref 12 for a thorough description of the formalism and to ref 11 for an explicit application.

It is convenient to transform all quantities to a representation where the N1s orbitals are localized on the inequivalent nitrogen atoms. This localized representation will be used throughout. Let us first briefly return to the Hartree−Fock treatment, where we consider dressed atomic core orbitals. The EEH calculation shows that the interaction between the $N_{in}1s$ and $N_{out}1s$ dressed orbitals of NiN_2 is significantly stronger than that of the O1s dressed orbitals in CO_2: the matrix element U of the interaction is 0.046 and 0.0006 eV, respectively. This matrix element is essentially independent of the displacement of the N_2 or O_2 units and is thus an inherent property of the unit itself. On the contrary, the splitting Δ between the dressed core orbitals is very sensitive to the displacement and hence constitutes the driving factor for the change in degree of localization as a

TABLE 1: Energies, Degrees of Localization $d_l^{(n)}$,[a] and Spectroscopic Amplitudes $x_c^{(n)}$ of the N_c1s Ionized States of the NiN_2 Cluster

Experiment N_2/Ni(100) [4]		GF ADC(4) results					
XPS band	ΔI_n	I_n	ΔI_n	$x_{in}^{(n)}$	$x_{out}^{(n)}$	State characterization[b]	$d_l^{(n)}$
1 Main line	0.0	409.00	0.0	−0.013	0.489	$\pi \to \pi^* + N1s^{-1}$, ($\sigma \to \sigma^*$)	0.998
2 Main line	1.3	410.47	1.47	0.456	0.014	$\pi \to \pi^* + N1s^{-1}$, ($\sigma \to \sigma^*$)	0.998
1 satellite, weak	2.1	411.93	2.93	−0.018	0.103	$\pi \to \pi^*$	0.940
		412.16	3.16	0.130	0.011	$\pi \to \pi^*$	0.985
2 satellite, strong	5.8	415.48	6.48	−0.628	0.051	$N1s^{-1} + \pi \to \pi^*$, ($\sigma \to \sigma^*$)	0.986
3 satellite, strong	6.6	415.90	6.90	−0.048	−0.602	$N1s^{-1} + \sigma \to \sigma^*$, ($\pi \to \pi^*$, N_2 $\pi \to \pi^*$)	0.987
4 satellite, weak	8.5	417.01	8.01	0.117	0.086	$\sigma \to \sigma^*$, ($\pi \to \pi^*$)	0.298
		417.09	8.09	−0.057	−0.134	$\sigma \to \sigma^*$, ($\pi \to \pi^*$)	0.693

[a] $d_l^{(n)} = |x_{in}^{(n)2} - x_{out}^{(n)2}|/x_{in}^{(n)2} + x_{out}^{(n)2})$. A localized representation is used; c refers to the inner and outer nitrogen atoms. Shown are the GF ADC(4) results obtained for the maximal dimension of the configuration space (114 414 configurations) in comparison to the experiment for the N_2/Ni(100)c(2×2) system. All energies in eV. [b] The contributions in parentheses denote small admixtures to the ionic states in order of decreasing importance.

function of the strength of the external perturbation (i.e., the interaction with the Ni atom for NiN_2 and with the C atom for CO_2).

The above treatment can be also applied to many-electron core-hole states. We computed the 2 × 2 EEH for the core-hole states corresponding to the most intense lines in the spectrum of NiN_2, the pair at 409.00, 410.47 eV and the pair at 415.48, 415.90 eV. This calculation yields values of the interaction between the dressed $N_{in}1s^{-1}$ and $N_{out}1s^{-1}$ configurations of 0.043 eV for the first pair and 0.034 eV for the second pair, which are surprisingly close to the value obtained at the HF level (0.046 eV). The splittings between the dressed configurations for the two pairs are however quite different: 1.46 and 0.42 eV, respectively. These results provide quantitative insight into the mechanisms of core-hole localization as a pure many-body effect: the interaction of the $N_{in}N1s^{-1}$ configuration with higher excitations differs considerably from that of the $N_{out}1s^{-1}$ configuration and results in a much larger effective splitting compared to the orbital picture.

We now turn to the calculation of XPS intensities. Here, one has to take into account possible interference effects due to partial localization. The intensity of the nth ionic state in the XPS reads[13]

$$I^{(n)} \sim |\sum_c \tau_c x_c{}^{(n)}|^2 \qquad c = \text{in, out} \qquad (3)$$

where τ_c denotes the photoionization amplitude of the N1s level of the inner (c = in) and outer (c = out) nitrogens and $x_c(n)$ are the spectroscopic amplitudes of the single hole N_c1s^{-1} states. In the dipole approximation the photoionization amplitudes are given by $\tau_c = \vec{A} < \vec{k}|\vec{r}|c>$, where $|c\rangle$ is the core orbital to be ionized, $|\vec{k}\rangle$ is the wave function of the photoelectron, and $\vec{A}$ is the polarization of the ionizing photon.

Assuming that the wave function of the photoelectron is essentially a plane wave, assuming that the core orbital ionization cross sections of the two atoms are equal if the scattering by the other atom is neglected, and taking into account the forward peaking of the scattering amplitude,[6] we write

$$\tau_{in} = \tau[1 + \alpha(1 + e^{-\gamma\theta^2})e^{ikR(1-\cos\theta)}]$$

$$\tau_{out} = \tau[e^{ikR\cos\theta} + \beta(1 + e^{-\gamma(\theta-\pi)^2})e^{ikR(1+\cos\theta)}] \qquad (4)$$

where α and β are parameters controlling the amount of electron scattering in the photoionization of the inner and outer nitrogen cores, respectively, and γ controls the forward peaking of the scattering amplitude. θ is the polar angle of emission from the N−N axis, k is the electron wavenumber, and R is the N−N distance.

The intensity angular dependence for two of the line pairs in the spectrum, calculated using the above model, is shown in Figure 2. The parameters have been chosen to fit the relative intensity and halfwidth of the small angle peak in the respective experimental data[4] (shown in the inset in Figure 2a). As the figure shows, the intensity of the 410.47 eV line has a distinct interference pattern. The angular distribution of the 409.00 eV line is instead close to uniform, but still one can clearly see a modulation of the intensity due to the interference caused by the partial localization. For *all* the other spectral lines listed in Table 1, the angular dependence of the intensity considerably deviates from a uniform distribution. Particularly pronounced are the interference patterns for the pair of $\sigma \to \sigma^*$ shake-up satellites at 417.01 and 417.09 eV (Figure 2b). If the core holes were localized, one line from each pair would exhibit an essentially isotropic angular distribution of the intensity.

To validate and generalize our finding of partial localization of core holes, we also computed by the same methods and quality of basis set[11] the P2s XPS of a linear NiP_2 molecule at the SCF optimized geometry. The 2s level of phosphorus is a (shallow) core level. The direct interaction of the P2s orbitals in NiP_2 is much stronger than that of the N1s orbitals in NiN_2 (the splittings between the orbitals are 0.9 and 0.1 eV, respectively). The GF computed ionization energies of the two lowest-energy states in NiP_2 are 188.24 and 189.71 eV, and their degree of localization (0.886 and 0.945) is substantially smaller than in NiN_2, although their splitting is very similar.

To further illuminate the role of the direct interaction in the core-hole localization−delocalization phenomenon, we have

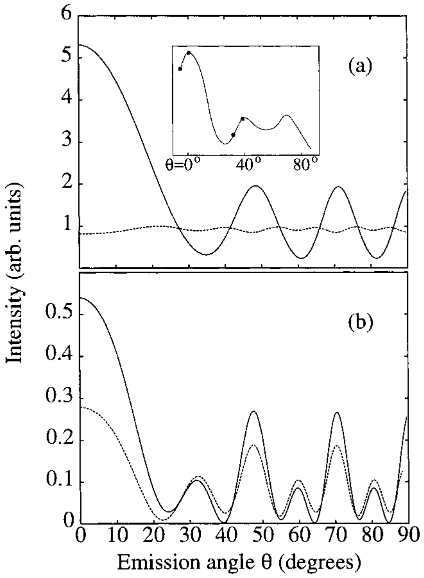

Figure 2. Angular dependences of the intensities I_n of two pairs of lines in the N1s spectrum of the NiN$_2$ cluster. (a) $I_{410.47}$ and $I_{409.00}$ are the solid and dashed lines, respectively. Shown in the inset is the experimental angular dependence of the intensity ratio of the lowest-energy lines in the C1s and O1s XPS of CO/Ni(100)c(2×2) (solid line) and of the 400.7 and 399.4 eV lines in the N1s XPS of N$_2$/Ni(100)-c(2×2) (dots).[4] (b) $I_{417.01}$ (solid line) and $I_{417.09}$ (dashed line). The angular dependence was calculated using the following values of the parameters in the model eq 4: $\alpha = 2.0$, $\beta = 1.0$, $\gamma = 6.56$, and $R = 2.069$ au. The ionization by photons of energy 1486 eV (Al Kα) has been assumed.

calculated the N1s XPS of a linear NiN$_2$ cluster with an artificially short N−N distance of 1.5 au. At this N−N distance the N1s core orbitals are split by 1.1 eV and they are considerably delocalized ($d_l = 0.38$). The direct interaction between the dressed N1s orbitals obtained by the EEH method is 0.51 eV, and their splitting is 0.42 eV. This strong interaction is the main reason why the core holes remain rather delocalized also at the level of the GF ADC(4) approach which incorporates a great part of electron correlation in calculations of ionized states (see Table 2). Many-body effects although increasing the degree of localization for most of the states are not strong enough to make the core-hole states localized to the extent seen for the case of the equilibrium N−N distance in NiN$_2$. What is important is that the core holes in some of the ionized states (the states at 419.00, 419.29, and 420.30 eV) are even more delocalized (the degree of localization is 0.238, 0.290, and 0.205, respectively) than the N1s core *orbitals*. This implies that many-body effects, in principle, must not necessarily favor localization of inequivalent core holes but can even strengthen their delocalization compared to that obtained at the independent-particle level. The two lowest-energy intense lines in the N1s XPS of the NiN$_2$ cluster with the short N−N distance are split by 1.69 eV and exhibit reasonably delocalized core holes in these states ($d_l = 0.837$ and 0.896, respectively). The splitting is comparable to that in the spectrum of the NiN$_2$ cluster calculated at the equilibrium geometry (1.47 eV), but the core holes are substantially more delocalized than in the latter case. This example clearly intimates that a large splitting of core level lines observed in a particular XPS is not indicative itself of core holes localized on inequivalent atoms.

To shed light on the role of many-body interactions in the core-hole localization−delocalization phenomenon, we constructed an 8 × 8 EEH for all the states listed in Table 2. The basis of two c_{in}^{-1} and c_{out}^{-1} single-hole dressed configurations and six satellite dressed configurations ($c_{\text{in}}^{-1}\ \sigma \rightarrow \sigma^*$, $c_{\text{out}}^{-1}\ \sigma \rightarrow \sigma^*$, $c_{\text{in}}^{-1}\ \pi \rightarrow 1\pi^*$, $c_{\text{out}}^{-1}\ \pi \rightarrow 1\pi^*$, $c_{\text{in}}^{-1}\ \pi \rightarrow 2\pi^*$, $c_{\text{out}}^{-1}\ \pi \rightarrow 2\pi^*$) has been chosen for the EEH analysis ($1\pi^*$ and $2\pi^*$ denote the two lowest in energy unoccupied π orbitals). The interaction between the c_{in}^{-1} and c_{out}^{-1} dressed single-hole configurations obtained by the EEH method for this many-body case is very close to that of the Hartree−Fock case (the matrix element in both cases is 0.51 eV). All the dressed satellite configurations localized on the inner and outer nitrogens are closely spaced within an energy interval of 0.6 eV, and they strongly interact with each other. This explains why the satellites do not enter the spectrum as pairs, in contrast to the case of the equilibrium geometry where the pairwise character is observed for all the states listed in Table 1. Very important is that the interaction between the single-hole and some of the dressed satellite configurations localized on *different* atomic sites is even stronger than the interaction between the dressed N1s orbitals. For example, the matrix element of the interaction between the c_{out}^{-1} and $c_{\text{in}}^{-1}\ \pi \rightarrow 1\pi^*$ dressed configurations is 0.71. Thus, the delocalization of inequivalent core holes can be enhanced by many-body effects not only due to decreasing the splitting between states but also due to strengthening the interaction between configurations. This suggests existence of systems where many-body excitations significantly enhance the delocalization of core holes.

Interestingly, the two lowest-energy lines in the N1s XPS of NiN$_2$ with the short N−N distance are the main lines, in contrast to the case of the equilibrium geometry where the lowest-energy lines are shake-down satellites. Thus, the perturbation of the

TABLE 2: Energies, Degrees of Localization $d_l^{(n)}$,[a] and Spectroscopic Amplitudes $x_c^{(n)}$ of the N$_c$1s Ionized States of the NiN$_2$ Cluster Calculated for the N−N Distance of 1.5 au

I_n	ΔI_n	$x_{in}^{(n)}$	$x_{out}^{(n)}$	$d_l^{(n)}$
413.59	0.0	0.189	-0.636	0.837
415.28	1.69	-0.695	-0.162	0.896
417.20	3.61	0.038	-0.196	0.927
417.81	4.22	0.198	-0.418	0.633
418.77	5.18	0.335	0.196	0.492
419.00	5.41	-0.190	-0.149	0.238
419.29	5.70	0.090	-0.122	0.290
420.30	6.71	0.093	0.076	0.205

[a] $d_l^{(n)} = |x_{\text{in}}^{(n)2} - x_{\text{out}}^{(n)2}|/x_{\text{in}}^{(n)2} + x_{\text{out}}^{(n)2})$. A localized representation is used; *c* refers to the inner and outer nitrogen atoms. Shown are the GF ADC(4) results for reasonably intense lines obtained for the maximal dimension of the configuration space (114 414 configurations). All energies in eV.

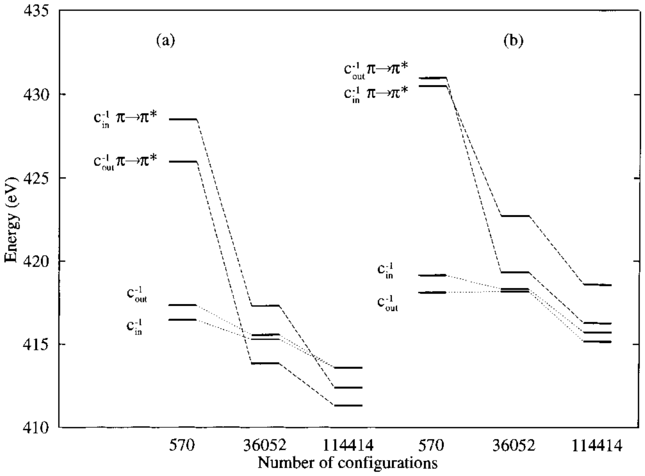

Figure 3. Energies of the dressed $c^{-1}{}_{\text{in,out}}$ single-hole and $c^{-1}{}_{\text{in,out}}\pi \rightarrow \pi^*$ CT configurations as a function of the number of the basis configurations used in the GF ADC(4) calculations of the N1s ionized states of the NiN_2 cluster taken at two different N−N distances: (a) $R_{N-N} = 2.069$ au; (b) $R_{N-N} = 1.5$ au.

electronic subsystem of the NiN_2 cluster due to shortening the N−N distance significantly changes the efficiency of the core-hole screening. The EEH technique allows us to extract some important details of the difference between the core-hole screening in the NiN_2 cluster taken at its equilibrium geometry and the cluster with the artificially short N−N distance. In a manner used in our recent work[14] for the analysis of the core-hole screening in weak and strong chemisorption systems, we constructed the 2 × 2 exact effective Hamiltonians for the most intense lines in the N1s XPS in the basis of dressed single-hole ($c_{\text{in}}{}^{-1}$, $c_{\text{out}}{}^{-1}$) and charge-transfer ($c_{\text{in}}{}^{-1}\ \pi \rightarrow \pi^*$, $c_{\text{out}}{}^{-1}\ \pi \rightarrow \pi^*$) configurations using the computed ionization potentials and spectroscopic amplitudes. Extending the configuration space step by step (starting from the space comprising all single excitations of the two N1s^{-1} single-hole configurations) by allowing double excitations in increasing number of virtual orbitals, we were able to monitor the increase of dynamical screening contributions to the ionic states. The relaxation patterns for the dressed configurations obtained for the two geometries of the NiN_2 cluster are shown in Figure 3. It is clearly seen that the dressed $c^{-1}\pi \rightarrow \pi^*$ configurations relax stronger in the case of the equilibrium N−N distance. These configurations become lowest in energy at the dimension of the space about 114.000 for the case of the equilibrium geometry. Contrary to that the relaxation of the dressed $c^{-1}\pi \rightarrow \pi^*$ configurations for the case of the short N−N distance is not so efficient, and the dressed single-hole configurations remain lowest in energy up to the maximal dimension of the configuration space. The character of the π and π^* orbitals has substantially changed upon shortening of the N−N distance, and this leads to a different behavior of the ionized states.

Conclusions

Our accurate *ab initio* calculations show that the adsorbate core holes in the ionized states of nonsymmetrical molecular systems are not completely localized on the inequivalent atoms as has been generally believed. The degree of localization is different for different states, and the core holes in some satellite states are considerably delocalized. The good agreement between the N1s spectrum computed for the NiN_2 molecule and the experimental spectrum of the N_2/Ni(100)c(2×2) solid-state system makes clear that the partial localization phenomenon is also to be expected for this system. The presence of a surface rather than a single Ni atom could even strengthen the effect. There are no reasons to anticipate the opposite. This partial localization, which is of interest by itself, leads to distinct interference effects in the angularly resolved core-hole spectra, and in principle, this phenomenon can be detected experimentally. The EEH analysis carried out here will be a very useful and simple tool to interpret further data in this light. We surmise that the partial localization of core holes can be observed also in some physisorbed systems. The EEH analysis also shows that many-body effects can enhance delocalization of inequivalent core holes. Thus a search for systems where inequivalent core holes are delocalized due to many-body excitations is of special interest for further understanding of the localization−delocalization phenomena.

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