Interpretation of the N 1s photoelectron spectra of chemisorbed N₂ in terms of local molecule-metal interactions

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Results of *ab initio* generalized valence bond configuration interaction calculations on the N 1s photoelectron spectrum of a linear NiN₂ cluster with the geometry optimized for the neutral ground state are reported. The energy difference between the two inequivalent nitrogen-core ionizations is determined to vary between ~1.2 and ~0.9 eV depending on the Ni-N₂ internuclear distance and bond energy. We compare the calculated electron-binding-energy difference of the two N 1s ionizations with recent experimental results and show that the observed spectral function is determined primarily by the local bonding properties of the complex, i.e., by the inequivalency of the N 1s core holes.

I. INTRODUCTION

The present status of our understanding of the photoelectron spectra of chemisorbed molecules has profited substantially from the comparison between the spectra of adsorbates and the spectra of the corresponding transition-metal compounds.[1-7] It has been found, especially for CO adsorbates and the corresponding transition-metal carbonyls, that the core-photoelectron spectra are virtually identical.[6] This, in turn, has led to the conclusion that core-photoelectron spectroscopy basically probes the local metal-molecule interaction. Much of the theoretical and experimental attention has stemmed from two observations: (1) the core ionization energies of CO are shifted from the gas-phase values upon bonding to either a metal atom or to a surface by roughly comparable amounts; (2) new and intense satellite structure is found for the core ionizations upon coordination with metals, and the intensity of the satellite structure depends upon the coupling between the metal and molecule through π-orbital electron back donation.[5,7,8]

N₂ is known[9] to be a weaker π acceptor than CO and this is observed to lead to more intense satellite structure in the core-photoelectron spectra of N₂ adsorbates as compared to CO adsorbates. A comparison[10] between chemisorbed N₂ (Refs. 11-16) and N₂—transition-metal complexes[10,17,18] further substantiates the idea that the local metal-molecule interactions determine the spectral function as the spectra of N₂ complexes also exhibit much more intense satellite structure as compared to CO complexes. The fact that the N 1s electrons on the two atoms of N₂ are no longer equivalent after adsorption leads to a difference in electron-binding energy upon ionization, which may be observed spectroscopically as a line splitting in the N 1s ionization spectrum at lowest electron-binding energies.[11,12] However, recently a collection of N 1s spectra for N₂ adsorbed on transition metals has been

presented[13,14] [see Fig. 1 for the spectrum of N₂ on Ni(100) (Ref. 13)] and a different interpretation was of-
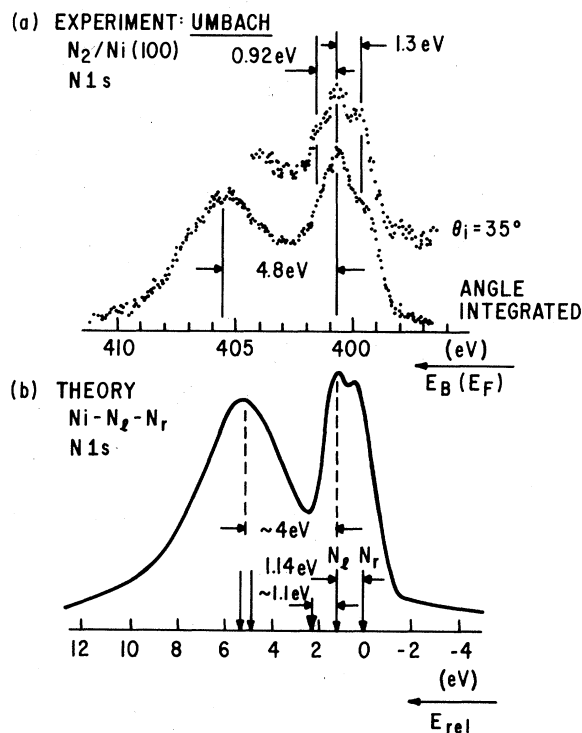

FIG. 1. Comparison of experimentally observed (a) N 1s spectral functions of Ni(100)/N₂ with the Gaussian-convoluted calculated line spectrum of NiN₂ (b). The calculated relative ionization energies are marked by arrows. The positions of the singlet coupled doublet states, resulting from different spin couplings as described in the text are indicated (↓). The full spectrum was taken in an angle-integrated mode, while the partially shown spectrum was taken in an angle-resolved mode.

fered. A comparison of the experimental spectra with spectral functions calculated on the basis of a model Hamiltonian treatment[19,20] suggested that the structure of the density of states of the substrate exclusively determines the details of the experimental spectra. Experimental evidence from angle-resolved N 1s spectra[13] shows that there is extra structure which can be resolved in the leading peak of the spectrum for N_2 on Ni(100). These observations led to the conclusion that the peak splitting *cannot* be attributed to the ionization of two inequivalent nitrogen atoms.[13] In addition, theoretical evidence from Hartree-Fock calculations[8] on core holes of a linear NiN_2 cluster, predicting only a very small splitting between the two N 1s ionizations of the inequivalent nitrogen atoms, was used to support the argument that the splitting of the leading peak is not due to ionization of inequivalent nitrogen atoms.

We shall show in this paper that the small splitting predicted within a Hartree-Fock scheme is due to the neglect of important electronic correlation effects, and that by taking account of these effects,[21] splittings are obtained which are the same magnitude as those observed experimentally.[13] We study the magnitude of the splitting as a function of the bond energy and find that a change in the bond energy by ~ 25 kJ/mol (i.e., $\sim 40\%$ of the bond energy) only changes the splitting by approximately 0.2 eV (i.e., $\sim 20\%$ of the splitting). Furthermore, we propose that the extra structure in the leading peak[13] is due to ion states resulting from different spin couplings of the core and the valence electrons in the ion.

II. CALCULATIONAL DETAILS AND RESULTS

The ground state of NiN_2 has been shown[21] to be of $^1\Sigma^+$ symmetry. For the present calculations we apply procedures for the generalized valence bond (GVB) configuration-interaction calculations identical to those

used to determine the potential energy curve of the ground state.[21] In Table I the binding-energy differences for symmetry- and spin-adapted hole states are collected. In the final hole states the spin coupling of three electrons has to be considered, namely, the core electron and the two valence electrons resulting from the electron transfer between the metal and the N_2 molecule upon screening the hole. From three spins we can generate a quartet and two doublet states. The population of the quartet state is spin forbidden in a photoelectron experiment. The four spin eigenfunctions of the two doublet states (I and II) have the form:[5,22,24]

$$2^{-1/2}(\,|\,\alpha\beta\alpha\,\rangle - |\,\alpha\alpha\beta\,\rangle),$$
$$2^{-1/2}(\,|\,\beta\alpha\beta\,\rangle - |\,\beta\beta\alpha\,\rangle), \text{ for I}$$

and

$$6^{-1/2}(2\,|\,\beta\alpha\alpha\,\rangle - |\,\alpha\beta\alpha\,\rangle - |\,\alpha\alpha\beta\,\rangle),$$
$$6^{-1/2}(2\,|\,\alpha\beta\beta\,\rangle - |\,\beta\alpha\beta\,\rangle - |\,\beta\beta\alpha\,\rangle), \text{ for II}$$

where α and β represent the two spin states of an electron. The splitting between the two inequivalent N 1s hole states is found to be 0.71 eV after construction of proper spin eigenstates. The intensities given in Table I are calculated by projecting the final ion states on the frozen hole state built from the orbitals of the neutral ground state.[22,23] The intensity is mainly in the ion state at lowest binding energy (II). The other doublet state (I) has a relative intensity of only a few percent, and is not explicitly given.

This small intensity is mostly due to the strong orthogonality constraint inherent in the particular GVB approach used here. It biases the overlap of the properly spin-coupled ion states and the frozen hole state towards one doublet state (II) leaving the overlap of the other doublet state (I) significantly underestimated.

The fact that the construction of proper symmetry and spin eigenstates increases the splitting between the two

TABLE I. Relative binding energies and intensities for Ni-N_2 in comparison to experiment.

Ni-N_1-N_r	N 1s		E_B^{rel} (eV)	Intensities (%) Screened	Unscreened
Ni(100)/N_2[a]	N_r	0.0	$(399.3)^b$	~ 15	
	N_1	1.3	$(400.6)^b$	~ 25	~ 60
Ni-N_2, EC[c]	N_r		0.0^d		
$(r_{Ni\text{-}N} = 1.64$ Å)	N_l		1.14^d		
Ni-N_2, DZP	N_r	0.0^d	$0.0(II)^e$	25	
$(r_{Ni\text{-}N} = 1.64$ Å)			$2.33(I)^e$		
	N_1	0.66^d	$0.707(II)^e$	18	57
			$1.83(I)^e$		
Ni-N_2[f]	N_r		0.34		
$(r_{Ni\text{-}N} = 1.93$ Å)	N_l		0.0	~ 74	~ 26

[a]Reference 13.
[b]Binding energies with respect to the Fermi level (Ref. 10).
[c]EC: equivalent-core calculation.
[d]Relative binding energies based on spatially symmetry-adapted wave functions.
[e]I and II refer to the different spin couplings as discussed in the text.
[f]Reference 8.

inequivalent N $1s$ ionizations by more than a factor of 2 with respect to the spin- and symmetry-averaged calculation (0.3 eV) (Ref. 21) indicates the importance of using proper space and spin eigenfunctions. However, an accurate description of the splitting may strongly depend on the quality of the basis set employed in the calculation, and our double zeta plus polarization (DZP) basis may not be adequate. In order to circumvent an expensive calculation using a triple zeta plus polarization (TZP) basis set we used instead an equivalent-core approach to explore basis set effects. We substituted the nitrogen atom to be ionized by an oxygen atom and minimized the total energy in the presence of a hole in the valence region (with a Ni $d \pi$ hole). The results are shown in Table I. The splitting has increased to a value of 1.14 eV, almost doubling the splitting with respect to the previous DZP calculation. We take this result as support for the statement made above about the sensitivity of the N $1s$ splitting to the quality of the basis set. We believe this splitting is close to that which would be obtained for an extended high-quality basis set. This is consistent with our experience that a proper description of the energy splitting of the $^1\Pi$ and $^3\Pi$ ion states resulting from N $1s$ ionization of free NO ($^2\Pi$), which is caused by core valence spin coupling, requires an extended basis set but can be well represented with an equivalent-core approach.[25] Obviously by using the equivalent-core concept we are able to globally account for subtle polarization effects in the valence region that are not properly described using DZP basis sets. In Fig. 1 the experimental spectrum of Ni(100)/N$_2$ (Ref. 13) is compared with a convolution of the calculated line spectrum using energy separations from equivalent-core calculations and intensities from Table I.

III. DISCUSSION

As alluded to in the Introduction there is at present some controversy concerning the interpretation of core-photoelectron spectra for weakly chemisorbed molecules, e.g., CO/Cu and N$_2$/Ni. One view[13,19,20] claims that the shape of the spectral function is completely determined by the shape of the surface density of states of the substrate while the other view[4-7] considers it as an indication of the nature of the local metal-molecule interaction.

The N $1s$ photoelectron spectra of N$_2$ chemisorbed on transition metals are especially well suited to test the two opposing points of view since the choice between them can be made by finding a consistent assignment of the N $1s$ ionization peak at lowest binding energy. This peak is split by ~ 1.5 eV (Ref. 13) and the simple question is the following: Is this splitting due to the inequivalency of the two nitrogen atoms of molecular N$_2$ bound linearly to a transition metal or is it caused by structure in the density of states of the substrate? A collection of N $1s$ spectra of N$_2$–transition-metal Ni(100), W(110), and Ru(0001) has been presented recently.[13,14] For example, the case of N$_2$/Ni(100) is shown in Fig. 1. Although the densities of states of the various substrates differ considerably from each other[26] the spectra are very similar. In particular, the splitting in the peak at lowest binding energy is 1.3, 1.3, and 1.5 eV,[13] respectively, for the three substrates

mentioned above. The heat of adsorption for N$_2$/Ru seems to be higher than those for the other two systems.[13] The shape of the peak at higher binding energy varies slightly in energy (position of the maximum) and full width at half maximum (FWHM) from Ni to Ru. The experimentally observed independence of the qualitative features of the spectral functions for the various substrates is already a hint that a local description in terms of inequivalent nitrogen ionizations is probably appropriate. More evidence can be gained by comparing the photoelectron spectra (PES) of chemisorbed N$_2$ with the PES of transition-metal complexes containing N$_2$ ligands. Very recently it was shown thermodynamically[27] that the energy of formation of a Ni—N$_2$ bond is ~ 0.5 eV which compares favorably with heat of adsorption for N$_2$/Ni(100), i.e., 0.45 eV.[15] A detailed comparison of photoelectron spectra has recently been presented,[10] as earlier suggested by Fuggle $et\ al.$[11,12] and it was found that the N $1s$ spectrum of a transition-metal complex is indeed very similar to the spectrum of chemisorbed N$_2$. The splitting of the leading peak in the transition-metal complex is very similar [i.e., 1.2 eV (Ref. 17)] to the adsorbate splitting. In the complex there is, of course, no extended metal substrate, and calculations of the spectral function of the complex[10] support the assignment of the splitting as being due to ionization of the two inequivalent nitrogen atoms.

Hartree-Fock calculations on small transition-metal—N$_2$ clusters,[8] on the other hand, showed that the expected splitting between the two nitrogen atoms was only of the order of 0.3 eV. However, it was shown recently by Rives and Fenske[28] that at the Hartree-Fock level the bonding between a transition-metal atom and a CO molecule cannot be described satisfactorily. Thus, it may be suspected that the same is true for N$_2$—metal bonding. Indeed, Kao and Messmer[21] have investigated in detail the reason for this failure and found the same problem to occur for the metal-N$_2$ interaction. Briefly, they found that for the metal—N$_2$ bonding the $3d^{10}$ configuration of the Ni atom is very important to adequately describe the back donation of electrons from the metal into the unoccupied N$_2$ 2π orbital. The energy of this configuration is much too high at the Hartree-Fock level.[21] Therefore within a description at the Hartree-Fock level the metal can only establish a bond to the molecule via its $3d^9 4s^1$ configuration. Due to the strong Pauli repulsion between the nitrogen lone pair and the $4s$ electron of the metal the resulting bond is rather weak (0.329 eV as compared to 0.779 eV using the d^{10} configuration[21]) and also much too long (1.94 Å as compared to 1.64 Å using the d^{10} configuration[21]). Previous Hartree-Fock calculations for a Ni-N$_2$ cluster have used bond distances that are consistent with a $d^9 s^1$ metal configuration, i.e., bond lengths between 1.93 and 2.12 Å.[8] Therefore it may be intuitively expected that at such long bond distances and the corresponding weak interactions the difference between the two nitrogen ionization energies is artificially reduced. The results of our calculations, summarized in Table I support this expectation. It is the lack of π back bonding in a Hartree-Fock calculation that artificially reduces the separation of the two inequivalent N $1s$ final hole states. Clearly, as shown

in Fig. 1 and in Table I, upon properly accounting for basis set deficiencies using the equivalent-core concept and including correlation effects as previously described[21] the calculated energy separation between the N $1s$ final states is in excellent agreement with the experimental findings. Figure 2 is a graphical summary of our calculations for various metal–N_2 bond lengths and the two metal-molecule interaction channels, namely, the $3d^{10}$-molecule (●) and $3d^9 4s^1$-molecule (▲) interaction channels. In the lower panel (b) the potential-energy curves $[\Delta R_{tot}(R)]$ in neutral NiN_2 for the strongly bonding $^1\Sigma^+(3d^{10})$ channel [bond energy 0.78 eV (Ref. 21)] and the weakly bonding $^3\Sigma^+$ $(4s\,3d^{10})$ channel [bond energy 0.35 eV (Ref. 21)] are shown. The upper panel (a) displays the variation of the binding-energy differences $(\Delta E_B N_{1,r})$ of the two inequivalent nitrogen ionizations for both channels using the equivalent-core concept. The separate entry (○) shows the result of the DZP basis set calculation. Obviously, as soon as we switch from the "strongly" bonding to the "weakly" bonding channel the splitting of the leading peak due to the inequivalency of the nitrogen atoms is dramatically reduced from 1.14 to 0.4 eV. This reduced splitting is in agreement with the results at the Hartree-Fock level. On the other hand, if we change the metal–molecule bond length from 1.64 to 1.8 Å within the strongly bonding channel, thus decreasing the total en-

ergy due to bond formation by about 40% from 0.78 eV to 0.5 eV, the splitting is only reduced by 0.2 eV (i.e., to 0.9 eV). This demonstrates, quantitatively, that although the bond energy may change considerably the splitting of the leading peak in the core-photoelectron spectrum changes only moderately. In particular, as the bond strength increases, i.e., from Ni to Ru, the splitting slightly increases.

We have not yet addressed the question: which of the two ionization energies (of the split leading peak) is to be assigned to the nitrogen atom close to the surface (N_1)? Again referring to the comparison between adsorbates and transition-metal complexes,[10] it was shown there, that in the neutral ground state the nitrogen molecule accumulates a small negative charge due to back donation and polarization in the π channel.[10,17,18] Upon ionization of the N $1s$ levels the hole is screened[4−8] and the distribution of valence electrons looks like Ni^+–NO and Ni^+–ON depending on the position of the hole on the adsorbed N_2 molecule, according to the equivalent-core concept. It is the binding-energy difference of NO bound with its oxygen or nitrogen end to a Ni ion in the geometry of the neutral ground state that determines the energy separation between the two ion states. The more stable configuration is achieved when "NO" binds with the nitrogen atom to the surface. In terms of hole states therefore, we conclude that the hole on the nitrogen atom remote from the surface (i.e., N_r) has the lower binding energy. This picture is completely consistent with the present calculations. A corresponding assignment of the adsorbate spectrum has been put forward on the basis of Green's-function calculations for a linear Ni-N_2 cluster.[29] Recently, Egelhoff[30,31] discussed the interpretation of N $1s$ spectra of adsorbed N_2 in terms of the equivalent-core concept on the basis of an analysis of Born-Haber cycles[30] to estimate the binding energies of the core ionization. He uses transition energies of core-to-bound excitations (not ionization energies) of N_2 in combination with the difference in the heats of adsorption between NO adsorbed on Ni(100) with the oxygen and nitrogen end down to estimate the difference in ionization energies of the two inequivalent nitrogen atoms.[30] In addition, Egelhoff has provided independent experimental evidence[31] for this assignment by determining the angular dependence of the intensities of the two lines. He shows that the subpeak at lowest binding energy follows a pattern similar to that of O $1s$ for CO adsorbates while the one at higher binding energy behaves analogously to the C $1s$ ionization for CO adsorption. Since the CO molecule is known to be bound through the carbon end to the surface he takes the observed behavior of the N $1s$ ionizations as evidence for the proposed assignment.[29] A Hartree-Fock calculation, however, would lead to the opposite assignment,[8] namely, a larger binding energy for the nitrogen atom remote from the surface, in contradiction to the accumulated evidence. The reason for this failure of a Hartree-Fock calculation is, again, the lack of back bonding in the $d^9 s^1$ configuration employed. Figure 1 shows a comparison between a convolution of our calculated line spectrum and the measured spectrum of chemisorbed N_2 on Ni(100). In our convolution we used the linewidths of the two unscreened components as
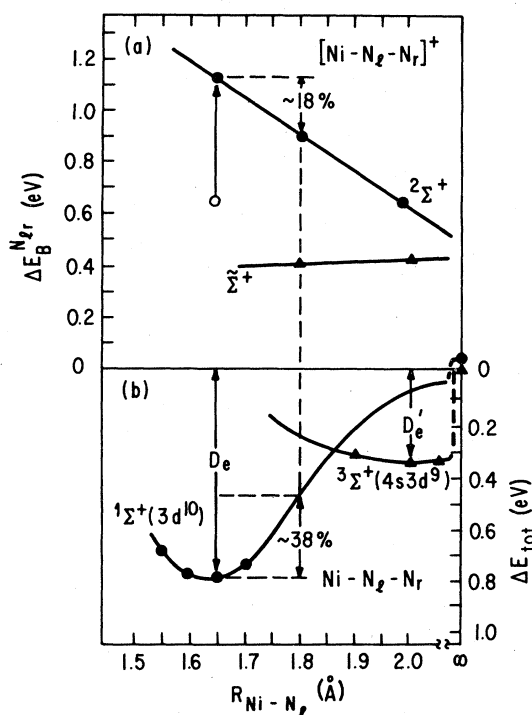

FIG. 2. (a) Upper panel: binding-energy difference between the inequivalent nitrogen atoms N_1 and N_r as a function of metal-molecule separation. (●) represents the equivalent-core calculations in the $3d^{10}$ configuration; (○), nonequivalent-core calculation in $3d^{10}$ configuration; (▲), equivalent-core calculation in $4s\,3d^9$ configuration. (b) Lower panel: potential energy curves for the ground state $(3d^{10})$ and the lowest triplet excited state $(4s\,3d^{10})$ of neutral NiN_2. D_e and D_e' denote the heats of adsorption of these states.

parameters to fit the experimental spectrum (FWHM of 3.6 eV). The linewidths of the two screened components were chosen according to the experimental resolution [FWHM of 1.2 eV (Ref. 13)]. The physical justification to use different linewidths comes from the expected difference in dynamical behavior (lifetime) of the screened and unscreened ion states. If one wanted to theoretically describe the different dynamical behavior of the different ion states properly by an *ab initio* calculation one would have to invoke the electronic structure of the extended substrate. However, given the simplicity of the local model using a single metal atom to describe a transition-metal surface we consider the agreement between calculated and measured spectral function, shown in Fig. 1, as excellent, and believe that the essential physics is contained in this approach.

There is another interesting point. Recording the angular dependence of the intensity of the peak at lowest binding energy an indication of a third peak in addition to the two so far observed peaks is found.[13] It has been interpreted in terms of substrate band structure.[13] We will propose in the following that this peak is due to a different spin coupling in the final ion state of the nitrogen atoms.

It has been shown by many groups that the dominating mechanism leading to the appearance of shake-up satellites in the core-photoelectron spectra of CO and N_2 adsorbates is the screening of the core hole on the adsorbate.[4−8,19,20] The screening occurs through transfer of an electron from the metal substrate to the coordinated molecule. The transferred unpaired electron resides in the unoccupied 2π orbital of the coordinated molecule. The coupling between this electron, the electron spin on the metal, and the spin of the core electron allows for two final doublet states which distributes the ionization probability over several states (lines in the spectrum) of each N $1s$ ionization. The separation of the two doublet states is different for the two inequivalent nitrogen ionizations (see Table I). The energy splitting produced by the two spin couplings for the ionization of N_r is 2.3 eV as compared to 1.2 eV for the ionization of N_1. The reason is that upon ionization of the $1s$ electron of N_r, the resulting electron distribution (Ni^+-NO) increases the tendency to spin pair the electrons in the metal-molecule π back-donating channel, and thus increases the energy separation of the singlet and triplet coupled doublet states as compared to that which occurs for the ionization of N_1 (Ni^+-ON). Since the binding-energy difference between the inequivalent ionizations is only 1.2 eV the two extra lines due to spin coupling overlap in the same binding-energy range, about 1.1 eV below the two main lines. The combination of the two lines low in intensity therefore lead to moderate intensity at that particular binding energy and very likely causes the third line.[13] Table I shows the re-

sults of our calculations and Fig. 1 illustrates the comparison to the experimental findings. Simulations of the spectrum shows that a relative intensity of 8−10 % in the spin-coupled doublet state with respect to the screened peaks is sufficient to reproduce the shape of the angle-resolved spectrum in Fig. 1. It is therefore very likely that the third peak is due to local-spin coupling of the screening electron transferred to the molecule and the spin of the core electron of the molecule.

IV. SUMMARY AND CONCLUSION

We have shown that the splitting observed in the N $1s$ ionization line at lowest binding energy for N_2 adsorbates on transition metals is caused by the inequivalency of the two nitrogen atoms of the N_2 molecule after coordination to the surface. The splitting found for N_2 adsorption on transition metals is fully consistent with the splittings observed for molecular nitrogen in transition-metal complexes. Our calculations indicate that the splitting is not very sensitive to the strength of the coupling between metal and adsorbed N_2, although it does slightly increase as the interaction increases. A possible explanation of a recently observed third peak in the energy region of the lowest N $1s$ ionization is given in terms of different spin coupling between the screening electron and the electron in the core of the molecule, i.e., the local-spin coupling on the molecule.

In summary our study is a complete corroboration of the interpretation of the N $1s$ spectra of N_2 adsorbates in terms of local metal-molecule interactions. The same local cluster model can be used to determine the vibrational properties of the same adsorbates and also explains the observed local dipole moment as recently shown by Kao and Messmer.[21] As it turns out, a local description of the spectroscopic properties of an adsorbate can be carried much farther than previously expected. On the other hand, we are quite aware that this approach is not a panacea for all problems of surface physics as there are a number of properties and situations where this approach is *a priori* inappropriate. Nonetheless, there is a wide variety of properties, as demonstrated here and elsewhere,[21] for which the local metal-molecule interactions are dominant and the local cluster approach is a very good first-order approximation to investigate the underlying physics.

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