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# Local and nonlocal effects in the core ionization of metal-molecule adsorbates and cluster systems

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An *ab initio* Green's function comparative study of the C1*s* ionization of PdCO and $Pd_3CO$ clusters has revealed distinct nonlocal effects in the spectrum of $Pd_3CO$. A good agreement with the experimental C1*s* spectrum of CO adsorbed on small Pd particles is achieved. A breakdown of individual charge transfer (CT) satellites associated with the basic PdCO unit of $Pd_3CO$ has been discovered. This breakdown is due to the coupling of the individual local CT states to a manifold of *nonlocal double* metal-adsorbate excitations and leads to a broadening of the giant satellites in adsorbate core-hole spectra.

Core ionization of small molecules adsorbed on *d*-metal surfaces is a most intriguing problem in the field of core-level spectroscopies. Unusually strong satellite structures which are observed in adsorbate core-ionization spectra of metal/adsorbate systems [for example, CO/Cu(100) and $N_2$/Ni(100)], but are absent in the spectra of the respective gas phase molecules have attracted wide interest to such systems for more than two decades (see Refs. 1–3 and references therein). The theoretical approaches employed to disclose the physical mechanisms responsible for the formation of the strong satellites ("giant satellites") can be divided in two groups. The first group is essentially based on model Hamiltonians that consider the interaction of discrete adsorbate levels with substrate metal bands.[4–8] The second group is based on the cluster approach, which takes into account only the local adsorbate-metal interaction.[3,9]

The general appearance of the spectral features in the adsorbate core-hole spectra can be described rather well already at the level of small cluster models that consider the adsorbate-metal interaction only within a basic unit representing a specific adsorption site (for example NiCO and $NiN_2$ clusters in the cases of the on-top adsorption of CO and $N_2$ on the Ni(100) surface).[3,10,11] This approach, however, due to its molecular (discrete) origin cannot reproduce *ab initio* the observed broadening of the giant satellites, nor the visible asymmetry of the lowest-energy lines in the spectrum (except maybe of the vibrational contribution to the broadening). The band approach, on the other hand, reproduces the overall spectral intensity distribution, but generally fails to describe fine structures observed in the spectra. This failure is due to a simplified representation of the adsorbate-related states.

Besides allowing the treatment of the core ionization of metal/adsorbate systems *ab initio*, i.e., without parameters, the cluster approach provides an opportunity to distinguish between *local* effects (i.e., those arising within the basic unit) and *nonlocal* ones (phenomena associated with the excitation of the rest of the system). Thus, in contrast to the band approach, which gives a *macroscopic* description where individual atomic contributions of the substrate cannot be separated, the cluster approach provides a more detailed *microscopic* picture. It is a primary aim of the present work to investigate precisely this aspect of the cluster approach, discussing in general terms its merits and the insights it can provide.

The *ab initio* cluster approach has been successfully used for studying the core ionization of adsorbates (see Ref. 3 and references therein). It has been shown that there are two different kinds of core-hole screening that are of equal significance for understanding the core ionization spectra: (i) statical screening due to the electrostatic interaction of the core hole with the valence electrons; and (ii) dynamical screening, which is due to many-electron relaxation and correlation effects.[3] The phenomenon of *partial localization of inequivalent core holes*[12] has also been discovered with the use of the *ab initio* cluster approach.

High-quality *ab initio* many-body size-consistent calculations usually require enormously large computer resources. This is the reason why only single-metal atom clusters have been considered (except of calculations on $Pd_2CO$ as a model for the bridge site adsorption[13]). The limitations of the cluster approach, however, have not been fully clarified. In particular, it seems very important to investigate the metal cluster size effects on calculated adsorbate core-hole spectra. Apart from an assessment of the reliability of the cluster approach, studies of larger clusters can give, as mentioned above, a microscopical view of physical processes contributing to the formation of core-hole spectral bandshapes in solid metal/adsorbate systems. The study of metal-molecule clusters is also interesting by itself since it is possible to create clusters consisting of a molecule and a few metal atoms in real experiments.[14]

In the present work, we study the adsorbate core ionization beyond the single-metal atom cluster approach by the

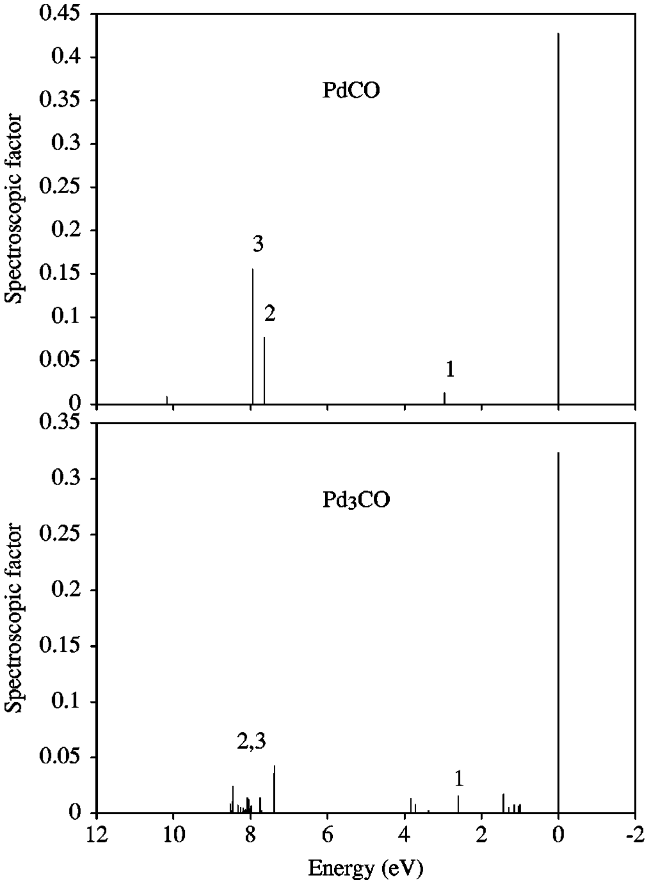

FIG. 1. The relative energies and intensities (spectroscopic factors) of the discrete spectral lines in the theoretical C1*s*-ionization spectrum of the PdCO and $Pd_3CO$ clusters calculated by the GF ADC(4) method. The spectra were aligned with respect to the position of the lowest-energy lines.

example of a CO/Pd system. The choice of the system is motivated by the recent experimental studies[15] where the adsorbate core-hole spectra were measured for CO adsorbed on relatively small Pd particles. This case, which is intermediate between the limiting cases of the solid-state system and a single-metal atom cluster, is well suited for our investigation.

The ionization potentials and intensities of spectral lines of PdCO and $Pd_3CO$ clusters have been calculated by means of the algebraic diagrammatic construction scheme for the one-particle Green's function consistent through fourth order in the Coulomb interaction [GF ADC(4)] (Ref. 16) and contains partial summations of diagrams to infinite order. The method is size-consistent, i.e., the results scale correctly with the size of the system. The maximal number of three Pd atoms was dictated by technical limitations. The geometry of the linear PdCO cluster ($R_{Pd-C}=3.569$, $R_{C-O}=2.123$ a.u.) has been optimized by the complete active space self-consistent field method.[17] Four electrons in the highest occupied $\pi$ orbital and two electrons in the highest occupied $\sigma$ orbital were correlated by allowing excitations to the lowest unoccupied two $\pi^*$ and two $\sigma^*$ orbitals. The $Pd_3CO$ cluster is a linear chain of three Pd atoms with CO situated vertically on top of the central Pd (the CO molecular axis is perpendicular to the line connecting the three Pd atoms). The interatomic distances within the PdCO basic unit of $Pd_3CO$ were kept as those in PdCO and the Pd-Pd distances were taken from the Pd bulk structure. Both clusters studied model the on-top CO adsorption on Pd(100). We should note that the on-top geometry is not favorable for regular CO structures on the Pd(100) surface, but at low-CO coverages and for the adsorption on small Pd particles this adsorption mode is dominant.[15] To make our calculations on $Pd_3CO$ technically possible we first restricted the orbital space of the self-consistent field calculations using the effective core potentials for the 1*s*-4*s*, 2*p*-4*p*, and 3*d* electrons of Pd and the respective Gaussian basis set.[18] The basis sets for C and O have been described in Ref. 11. The configuration space for the GF ADC(4) calculations was generated by allowing all single and double excitations of the $C1s^{-1}$ single-hole configuration of the respective clusters. Because of the very large number of configurations we further restricted the configuration space by freezing all virtual orbitals with energies $\geqslant 30$ eV. The final number of configurations amounts to 241,243 and 15,394 for $Pd_3CO$ and PdCO, respectively.

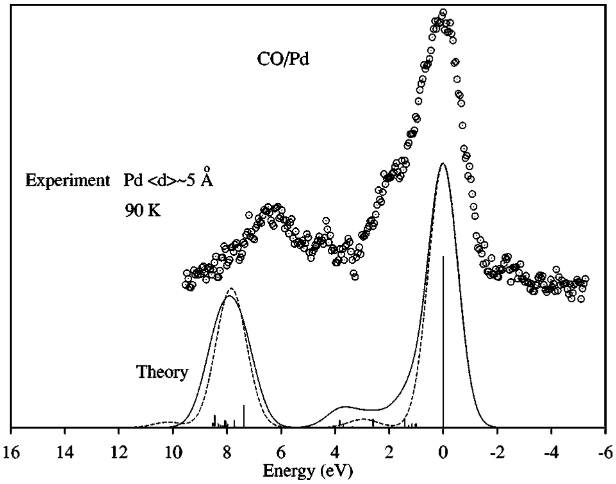

FIG. 2. The theoretical C1*s* ionization spectra of PdCO (dashed line) and $Pd_3CO$ (solid line) calculated by the GF ADC(4) method in comparison with the experimental spectrum measured for CO adsorbed on small Pd particles (Ref. 15). The spectra were aligned with respect to the position of the lowest-energy line. The vertical lines represent the intensities (spectroscopic factors) and energies of the discrete spectral lines obtained for the $Pd_3CO$ cluster.

We first describe the results on the PdCO basic unit (Fig. 1). The lowest-energy C1*s*-ionized state of PdCO is dominated by the C1*s* single-hole configuration and is, therefore, the main state. The spectroscopic factor[19] (SF) for this state is 0.427 indicating that more than 50% of the total spectral intensity is borrowed by satellites. The first satellite (labeled 1 in the figure) appears in the spectrum at 2.96 eV above the main line. This satellite is almost purely a $\pi\rightarrow\pi^*$, metal $\rightarrow$ molecule charge transfer (CT) state with the SF of 0.013. Two states (2) and (3) at 7.64 and 7.94 eV acquire considerable intensity (SF is 0.077 and 0.156, respectively) and are both shake-up satellites (''giant satellites''). They have different characters. The state (2) is mostly a metal $\rightarrow$ metal $\sigma\rightarrow\sigma^*$ state with a small admixture of $\pi\rightarrow\pi^*$ configurations, whereas the state (3) is mostly a $\pi\rightarrow\pi^*$ metal $\rightarrow$ molecule CT satellite with a small admixture of metal $\rightarrow$ metal $\sigma\rightarrow\sigma^*$ excitations. The satellite observed at 10.17 eV above the main line has SF of 0.008 and is a $\pi\rightarrow\pi^*$ CT state. The comparison of our theoretical band shape with the experimental C1*s* spectrum of CO adsorbed on three-dimensional (3D)-Pd islands of estimated diameter about 5 Å (approximately 10 Pd atoms)[15] is presented in Fig. 2 (dashed line). The theoretical bandshape has been obtained by Gaussian broadening of the discrete lines in the spectrum with the uniform half-width of 0.6 eV for all the lines. The overall agreement is rather good. Some distinct features are, however, absent in the theoretical spectrum. First, the shoulder at ~2 eV observed in the experiment is not reproduced by the calculation. Second, the features at 4-5 eV in the experimental spectrum are absent in the theoretical one. The ''giant satellite'' in the experimental spectrum is considerably broader and is situated at ~6 eV above the main line. The energy of the respective peak in the theoretical spectrum is about 2 eV higher than in the experiment. These differences are mainly to be ascribed to the minimal size of the cluster. Here, we should note that the configuration space restriction imposed also affects the energy of the ''giant satellite'' and we expect this influence to be stronger for larger clusters.

The results of our calculations on the C1*s* ionization spectrum of $Pd_3CO$ are presented in Figs. 1 (lower panel) and 2 (solid line) in comparison with the spectrum of the basic PdCO cluster and the experimental one. The theoretical band shape has been obtained as was done above in the case of PdCO. The band shapes of the C1*s*-spectrum of both clusters are similar in their general appearance. The lowest-energy state in the spectrum of $Pd_3CO$ is the main state. The SF of this state (0.323) is appreciably smaller than that of PdCO (0.427). This is an expected result because the number of the metal *d* electrons available for the C1*s* hole screening is larger for $Pd_3CO$ and, consequently, relaxation of the core hole is stronger than in the case of PdCO. In contrast to PdCO where the first satellite appears at 2.96 eV, the C1*s* spectrum of $Pd_3CO$ exhibits a group of satellites situated at 1.-1.5 eV above the main line. These satellites are almost purely *single* $\pi\rightarrow\pi^*$ *excitations* associated with the terminal Pd atoms and are, therefore, nonlocal in character. They form a wing at the high-energy side of the main line resulting in the visible asymmetry of this line in the spectrum. We relate these wing satellites to the shoulder at ~2 eV in the experimental spectrum. Clearly, the number and, consequently, the total intensity of the wing satellites should increase reaching saturation when increasing the number of metal atoms in the cluster. The next satellite in the spectrum of $Pd_3CO$ appears at 2.59 eV. This state is purely a $\pi\rightarrow\pi^*$ CT state associated with the *single excitations* of the central Pd atom and is, therefore, *local* in character. A group of satellites at 3.4-3.9 eV consists of three $\sigma\rightarrow\sigma^*$ satellites. These states are dominated by *single excitations* of the highest occupied $\sigma$ orbital of the cluster to the lowest virtual $\sigma^*$ orbital. These orbitals have a mixed character with comparable contributions of the central and terminal Pd atoms. The satellites do not have counterparts in the relevant part of the spectrum of PdCO and are thus *nonlocal* single excitations. It seems clear that these nonlocal $\sigma\rightarrow\sigma^*$ satellites are responsible for the experimentally resolved structure at ~4 eV.

A most interesting result of our calculations on the C1*s* ionization of the $Pd_3CO$ cluster is a ''forest'' of satellite lines situated at 7.4-8.5 eV. We computed ~100 satellite states situated in this region, with no individual SF exceeding 0.042. The location and the total intensity of this dense satellite ''forest'' are almost identical to those of the corresponding structure, made up of essentially two lines, in the spectrum of PdCO. Thus, we associate this region of satellite states with the shake-up giant satellites in the spectrum of PdCO [satellites (2) and (3)]. This phenomenon is nothing but a *breakdown* of the giant satellites which are formed locally by single CT excitations within the basic PdCO unit of the $Pd_3CO$ cluster. As Fig. 1 shows, the breakdown leads to a considerable broadening of the giant satellite.

It may be expected that the origin of the line breakdown in the giant satellite region lies in the interaction between the local excitations and nonlocal ones. Indeed, an analysis of the structure of the satellite state ''forest'' reveals two very interesting features. First, the weights of the single excitations of the basic PdCO unit in these states are very small (almost negligible) compared to those of the terminal metal atoms. Second, the contributions of double excitations (mostly the excitations of electrons of the terminal Pd atoms to screening $\pi^*$ orbitals) are dominant in all the states. The two discrete $\sigma\rightarrow\sigma^*$ and $\pi\rightarrow\pi^*$ states of the PdCO basic unit are broken down and redistributed within the manifold of *doubly excited* states essentially associated with CT excitations from the terminal Pd atoms to the molecule. The coupling between the *individual states* of the basic unit and the manifold of doubly excited terminal atom states leads to the observed intensity redistribution over this rather dense manifold. In other words, the giant satellite states of the PdCO basic unit are dissolved in the ''sea'' of the doubly excited nonlocal CT states and, therefore, lose their individual (local) character. The appearance of a manifold of relatively weak satellites instead of a few intense ones when enlarging the cluster size has been reported in a cluster model Hamiltonian investigation of the Ni2p ionization spectrum of the solid NiO.[20]

The fact that the C1*s* ionization spectra obtained for PdCO and $Pd_3CO$ are consistent with each other and with experiment, largely justifies the validity of the cluster approach for studying core-hole spectra of metal/adsorbate systems. It is conceptually important to start from a basic representative unit of a chemisorption system as the minimal cluster. Indeed, by analyzing the ionized states of $Pd_3CO$ (or a larger cluster) alone, one is likely to arrive at the misleading idea that the Pd atom adjacent to the CO molecule almost does not contribute to the charge transfer and that this charge transfer is dominated by nonlocal double excitations. As we have seen above, the contrary is true for the giant satellite: its intensity originates from the local CT at the absorption site, while the nonlocal excitations just lead to a redistribution of this intensity.

In summary, our *ab initio* GF ADC(4) comparative study of the C1*s* ionization spectrum of PdCO and $Pd_3CO$ reveals four groups of low-lying shake-up satellites, which are energetically separated and have distinctly different character: (i) the wing satellites which are the single $\pi\rightarrow\pi^*$ CT excitations of the terminal Pd atoms and, consequently, are nonlocal; (ii) the local $\pi\rightarrow\pi^*$ CT satellite at 2.59 eV; (iii) the group of the $\sigma\rightarrow\sigma^*$ satellites at 3.4-3.9 eV which are nonlocal single excitations; (iv) the $\pi\rightarrow\pi^*$ and $\sigma\rightarrow\sigma^*$ giant satellites associated with the PdCO basic unit and its breakdown in Pd$_3$CO, which is of purely many-body nature. The physical mechanism responsible for the breakdown is the coupling between these local CT states and the manifold of the nonlocal CT double excitations. This breakdown is mostly responsible for the broadening of the giant satellite observed in the experimental spectrum.

The good agreement of the C1*s* ionization spectrum computed for the Pd$_3$CO cluster with the experimental spectrum and, in particular, the clear picture of local and nonlocal effects obtained in our comparative study allows us to generalize our findings to solid-state substrates. For the wing satellites the finite substrate *d*-band width should result in a satellite band of a comparable width. This leads to an asymmetric high-energy broadening of the main line. In some cases the main line might be embedded in the manifold of these nonlocal satellite states, leading to a breakdown of the main line and, consequently, to an approximately symmetrically broadened band shape. In still other cases, the nonlocal CT satellites may appear below the main line (nonlocal shake-down) leading also to a broadening of the main line, but with a low-energy asymmetry. The nonlocal $\sigma\rightarrow\sigma^*$ satellites should also form a band in the solid state case. The width of this band should be of the order of the substrate $d\sigma$-$s$ band. The local $\pi\rightarrow\pi^*$ CT satellite [state (1) in the spectrum of PdCO and its counterpart in the spectrum of Pd$_3$CO] should keep its local character also in the solid state case and can be detected as a narrow distinct feature (when its intensity is large enough to be detected) in the experiment. According to our results the mechanism leading to the breakdown and broadening of the giant satellite is the coupling to the CT nonlocal double excitations. In the case of a solid substrate this should result in a giant satellite band roughly twice as broad as the substrate *d*-band width.

Here we should mention that local and nonlocal effects in the core ionization of metal-molecule adsorbates have already been discussed in the literature. The fact that the ligand core-hole spectra of the Cr(CO)$_6$ carbonyl complex are similar to those of the solid-state CO/Ni(100) chemisorption system is usually referred to as a proof of the local character of the major features in the spectra of solid adsorbates.[21] It is, however, hardly possible to clearly distinguish between local and nonlocal effects in the spectra of adsorbates by just comparing the experimental spectra of completely different systems such as $d-$metal carbonyls and solid adsorbates. Moreover, the experimental comparison of the spectra of Cr(CO)$_6$ and CO/Ni(100) cannot give any details on the nature of nonlocal effects. In contrast, our *ab initio* calculations tell definitely what are nonlocal effects in the spectra and what are local.

Finally, we would like to mention that clusters Pd$_n$CO exist and are of interest by themselves. Our calculations take into account all the electronic effects contributing to the formation of the spectral band shapes. For a more accurate discussion, vibrational broadening should be considered as well. Because of the rather general nature of the local and nonlocal effects disclosed in the present paper we expect them also in other clusters, solid state, and large molecular systems.

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