

Comments

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Dynamics of core-hole decay in adsorbates

M. Ohno*

*Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig,
W-3300 Braunschweig, Federal Republic of Germany*

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Wurth and co-workers [Phys. Rev. B **35**, 7741 (1987); **37**, 8725 (1988)] concluded that the deexcitation-electron-spectroscopy (DES) spectra of the adsorbates become identical to the Auger-electron-spectroscopy (AES) spectra. They interpreted the double-peak structure at the higher-kinetic-energy (KE) side of the AES spectrum of the CO/Cu system as due to two different ("partly" and "fully" screened) initial core-hole states. In the present Comment, the relation between the x-ray-photoelectron-spectroscopy lowest-energy state and the $1s$ to $2\pi^*$ resonantly excited state, and the possible mechanism by which the DES spectrum becomes very similar to the AES spectrum, are discussed. It is also proposed that the largest-KE peak of the double-peak structure corresponds to the double hole in the bonding orbital. For the CO/Cu system, the intensity of this peak is much more enhanced in comparison to the CO/Ni system because of the strong polarization of the bonding orbital toward the ligand in the presence of the core hole. The variation of the intensity of this double-peak structure reflects the degree of the polarization of the bonding orbital in the presence of the core hole.

Wurth *et al.*^{1,2} studied angle-resolved deexcitation-electron-spectroscopy (DES) spectra of adsorbed CO molecules and made the following remarks: (i) For strongly coupled systems such as the CO/Ni system, the DES spectrum becomes identical to the Auger-electron-spectroscopy (AES) spectrum because the $1s$ to 2π resonantly excited states relaxes to the x-ray-photoelectron-spectroscopy (XPS) core-hole lowest-energy state before the autoionization (participant and spectator Auger decay) starts. (ii) Then the final state of the participant Auger decay is the two-hole state and not identical to the photoelectron-spectroscopy single-hole state. (iii) For the CO/Cu system, two different ("partly" and "fully" screened) initial core-hole states are proposed to explain the double-peak structure observed in the participant (backbonding) Auger decay energy region. In this Comment, I would like to discuss points (i) and (iii).

First, the relation between the XPS lowest-energy state and the $1s$ to $2\pi^*$ resonantly excited state will be discussed. Recent high-resolution XPS core-hole spectra of the CO/Ni(100) and N_2 /Ni(100) systems show a number of resolved satellite lines including the 2.1-eV carbon (and outer nitrogen) satellite of a non-negligible intensity which were neither observed experimentally nor predicted theoretically.³ Furthermore, the main line and satellite line intensity ratios differ considerably from the previous experimental and theoretical results. All previous theoretical calculations of the core-hole spectra of a linear molecule such as NiCO based on molecular ap-

proaches fail to predict not only the additional satellite but also the main-line-satellite-line energy separations and intensity ratios. In those calculations, however, a large part of the important relaxation and correlations was entirely neglected or not treated in a proper manner by employing the inadequate approximations such as Δ (SCF) (self-consistent-field) and complete-neglect-of-differential-overlap approximations (see Ref. 4 for a summary of the theoretical results by different methods). Recent *ab initio* many-body calculations of the core-hole spectra of NiCO and NiN₂ by using an extended basis set can give a reasonably good description of the main-line-satellite-line energy separations, intensity ratios, and the energy splitting of the carbon and oxygen main-line peaks (the outer and inner nitrogen peaks) of the core-hole spectra of the CO/Ni and N₂/Ni systems.^{5,6} The lowest-energy state of the core-hole spectra of the CO/Ni system is still the one-hole state (closer to the Koopmans state) and not the two-hole, one-particle charge-transfer (CT) shake-down state.⁵ The π_M (here M denotes the metal-derived orbital) bonding orbital is more polarized toward the ligand; however, its character does not change much in the presence of the core hole. The 2-eV satellite is indeed predicted correctly and interpreted as the metal-ligand π shakeup satellite (excitation from the π_M bonding orbital to the $2\pi^*$ antibonding orbital; strong polarization toward the CO ligand).⁵ Then the $1s$ to $2\pi^*$ resonantly excited state should be similar to this satellite state. The difference between these two states is the pres-

ence of a hole in the substrate band in the latter state. Indeed the satellite energy [228 eV (Ref. 3)] is almost identical to the resonant excitation energy of 287.5 (Ref. 7) and 287.4 eV.^{8,9} For the CO/Ni system the resonantly excited (or excited by the shakeup process) 2π electron induces excessively large polarization in the CO ligand region because of a substantial amount of the 2π charge in the ligand region which already exists in the ground state. The resonantly excited state and the shakeup state eventually relax to the XPS lowest-energy state when the extra 2π charge flows toward the substrate. This is possible in the case of adsorbates because of the overlapping of the 2π orbital with the substrate band [as reflected in the near-edge x-ray-absorption fine structure (NEXAFS) width which is larger than the XPS lowest-energy state width;⁹ the latter is governed mainly by the core-hole lifetime and vibrational broadening³]. For the CO/Ni system it would be more reasonable to compare the NEXAFS energy with the resolved 2.1-eV satellite energy. This argument is also the case with the oxygen spectrum. The recent many-body calculation indeed shows that the oxygen satellite exists but the intensity is very small.⁵

For the CO/Cu system there seems to be some discrepancies among the $1s$ to 2π resonant energies measured by different groups.^{2,10,11} The recent NEXAFS measurement of the CO/Cu(100) [$c(2 \times 2)$] system shows that the $1s$ to 2π excitation energies for the carbon and oxygen are 287.45 and 533.75 eV, respectively,¹⁰ whereas the results by Wurth *et al.*^{2,11} are 286.4 and 532.9 eV, respectively. The former result shows that the NEXAFS energy is larger than the XPS energy, whereas the latter results show that the XPS energy is very close to or even slightly larger than the NEXAFS energy.

As an example of a weakly coupled system the N_2 /Ni(100) [$c(2 \times 2)$] system where the substrate is the same as the CO/Ni(100) [$c(2 \times 2)$] system will be discussed. For the N_2 /Ni(100) system the energy differences between the NEXAFS energy and the XPS lowest energy for the inner and outer nitrogen are 0.3 and 1.0 eV, respectively.^{8,9} Recent many-body calculations of NiN_2 show that the peak splitting of 1.3 eV is indeed due to the two inequivalent nitrogen atoms and that the inner nitrogen hole state is more weakly coupled than the outer nitrogen one.⁶ This is in accord with the conclusion drawn by others.³ The weaker the coupling of the hole state is, the weaker is the π bonding¹² (the σ bonding is as important as in the case of the CO/Ni system). For the inner nitrogen hole excitation in comparison to the outer one, in order to screen the core hole more screening charge has to be provided either by the CT from the substrate (according to the recent many-body calculation, the σ screening will be much more significant because of a weaker π bonding⁶), or by the 2π resonantly excited electron. This is represented in the much smaller difference between the NEXAFS energy and XPS energy for the inner nitrogen hole excitation than the outer one. The weaker the coupling of the hole state, the closer to the NEXAFS energy is the XPS lowest energy (for the same substrate).

Now we proceed to the discussion on the similarity of

the DES and AES spectra. For the CO/Ni system, if the 2π electron moves to the substrate band before the participant and spectator Auger decay starts, then the DES spectrum will become identical to the normal AES spectrum. However, if the 2π electron stays (spectator Auger decay) or decays by the participant Auger decay, then the DES spectrum will become the autoionization spectrum. When the spectator and participant Auger decay occur, is there any possibility that the Auger kinetic energy (KE) of the normal Auger decay and autoionization becomes identical so that the DES spectrum and the normal AES spectrum become very similar? For the CO/Ni system, the Auger KE difference between the normal Auger decay (the final state is two holes i and j) and the spectator Auger decay (the final states is two holes i and j and the spectator 2π electron) is given by $U_{1s,a} - U_{i,a} - U_{j,a}$ [here U is the effective Coulomb interaction between the hole and the 2π electron (a)]. Using the equivalent core approximation and relevant inverse photoemission and valence-hole photoemission data for the NO/Ni system (see references in Ref. 3), we find that $U_{1s,a}$ is almost zero. This implies that $U_{i,a}$ may also be negligible and the presence of the 2π electron will be negligible for the spectator decay. If so, then normal Auger decay KE and the spectator Auger decay KE become identical. In this case the Auger decay rates also become very similar. For the participant decay the same kind of analysis shows that it seems to be not possible that the participant Auger decay KE and the normal (backbonding) Auger decay KE become identical. If the 2π electron stays before the decay occurs, there is a possibility that between the DES and AES spectra one may see the spectral feature differences only in the participant Auger decay region.

For the weakly coupled system (assuming that the XPS lowest-energy state is the π CT shakedown state) the Auger KE difference between the spectator and normal Auger decay will be $U_{d,1s} - U_{d,i} - U_{d,j}$. For the participant decay, it will be $U_{d,1s} - U_{d,i} - U_{d,a}$. Here d is the π_M hole. If the presence of the hole in the substrate in the screened core-hole state is negligible, the Auger KE will become identical and both spectra become very similar.

Wurth *et al.*² interpreted the double-peak structure in the carbon AES spectrum of the CO/Cu system and the DES spectrum of $Cr(CO)_6$ and the absence of one of the peaks in the AES spectrum of $Cr(CO)_6$ as due to two differently screened initial core-hole states for the CO/Cu system. First of all we consider the AES spectrum of $Cr(CO)_6$. The prominent peak around 268 eV (peak 2 in Fig. 12 in Ref. 13; in this paragraph, the spectra in Ref. 13 are referred to unless otherwise stated) is most likely the $5\sigma^{-1}\pi_M^{-1}$ state, in accord with the interpretation by Jenisson *et al.*¹⁴ This peak corresponds to peak 1 in the oxygen AES spectrum in Fig. 11. The intensity is much reduced in the oxygen spectrum, as it should be. The $4\sigma^{-1}\pi_M^{-1}$ state is seen on the shoulder of peak 2 in the oxygen AES spectrum (Fig. 11). Peak 1 of a small intensity in the carbon AES spectrum (Fig. 12) is most likely the π_M^{-2} state. As the polarization of the π_M bonding orbital toward the ligand in the presence of the core hole is small, the intensity of peak 1 is very small. The peak is

missing in the oxygen spectrum because of the greater localization of the π_M bonding orbital on the carbon site. The largest KE peak in the DES spectrum is the 5σ participant Auger decay (autoionization) peak and is not related to the largest KE peak (π_M^{-2} state) in the AES spectrum. The absence or the small intensity of the largest Auger KE peak in $\text{Cr}(\text{CO})_6$ data does not imply the existence of the two differently screened initial core-hole states for the CO/Cu system.

The AES spectrum of the CO/Ni system may be interpreted in the same way. The largest KE peak (peak 7 in Ref. 2) is most likely the π_M^{-2} states. The intensity of this peak is also very small because of a rather small polarization of the π_M bonding orbital toward the ligand in the presence of the initial core hole. This is in accord with the recent many-body calculation of the core-hole spectra of NiCO.⁴ Peak 6 (in Ref. 2) is the $5\sigma^{-1}\pi_M^{-1}$ state, in accord with others.^{2,15} As suggested by Wurth *et al.*, the $4\sigma^{-1}\pi_M^{-1}$ state is hidden on the shoulder of the prominent peak at 515 eV in the oxygen AES spectrum.² The SCF- $X\alpha$ -MS (multiple-scattering) calculations of the final-state two-hole spectra of NiCO by Laramore¹⁵ show that the energy difference between π_M^{-2} and $5\sigma^{-1}\pi_M^{-1}$ state (and $4\sigma^{-1}\pi_M^{-1}$ state) is 4.0 (and 8.6 eV), which agrees well with the experimental value of 3.6 eV (and 8 eV) for the CO/Ni system. For the CO/Cu system, the assignment of the double-peak structure is the same as for the CO/Ni system; however, the intensity of peaks 6 and 7 increases substantially in the CO/Cu system. Koel, White, and Loubriel¹⁶ also noticed a higher intensity of peaks 6 and 7 in comparison to those of the other systems. For the CO/Cu system, as the XPS lowest-energy state is most likely the CT shakedown state, the Auger

decay for peaks 6 and 7 can be seen as the participant Auger decay in the presence of the hole in the substrate. The 2π electron fills the core hole and the π_M electron is emitted from the bonding orbital (peak 7). For peak 6 the 5σ electron is emitted instead of the π_M electron. The participant decay rate is much larger than the normal Auger decay rate. One expects, then, a substantial intensity increase in both peaks for the CO/Cu system in comparison to the CO/Ni system. One may also see peak 7 as the final state two holes created in the 2π character bonding orbital. The variation of the double-peak intensity according to the different systems reflects the degree of the polarization of the bonding orbital in the presence of the initial core hole. Baker, Canning, and Chesters¹⁷ suggested that narrower and relatively more intense lines reflect that the screening electron density of states is sharper and more localized to the ligand for the CO/Cu system. The intensity of peak 7 is higher than that of 6 because the Auger decay for peak 7 dominantly "consists" of the intra-atomic Auger decay which involves the two p ($l=1$) hole and the d ($l=2$) continuum atomic orbitals. This atomic Auger decay is very large in comparison to other decays.¹⁸ If the double-peak structure is due to two different initial core-hole states, then we should be able to see the double-peak structure for the $4\sigma^{-1}\pi_M^{-1}$ state in the oxygen AE spectrum. No corresponding extra peak has been seen in the spectrum.

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*Present address: Department of Physics, Uppsala University, Box 530, S75121 Uppsala, Sweden.

¹W. Wurth, C. Schneider, R. Treichler, E. Umbach, and D. Menzel, *Phys. Rev. B* **35**, 7741 (1987).

²W. Wurth, C. Schneider, R. Treichler, D. Menzel, and E. Umbach, *Phys. Rev. B* **37**, 8725 (1988).

³N. Mårtensson and A. Nilsson, *J. Electron Spectrosc. Relat. Phenom.* **52**, 1 (1990); *Phys. Rev. B* **40**, 10249 (1989), and references therein.

⁴M. Ohno and W. von Niessen, *Phys. Rev. B* **42**, 7370 (1990).

⁵M. Ohno and P. Decleva, *Chem. Phys.* **156**, 309 (1991); *Surf. Sci.* **258**, 91 (1991).

⁶P. Decleva and M. Ohno, *Chem. Phys.* (to be published).

⁷J. Stöhr and R. Jaeger, *Phys. Rev. B* **26**, 4111 (1982).

⁸O. Björneholm, A. Nilsson, E. Zdansky, H. Antonsson, N. Mårtensson, J. N. Andersen, and R. Nyholm (unpublished).

⁹A. Nilsson, E. Zdansky, H. Antonsson, O. Björneholm, N. Mårtensson, J. N. Andersen, and R. Nyholm (unpublished).

¹⁰O. Björneholm, A. Nilsson, A. Sandell, E. Zdansky, H. Antonsson, B. Hernäs, M. Karolewski, N. Mårtensson, J. N. Andersen, and R. Nyholm (unpublished).

¹¹W. Wurth, D. Coulman, A. Puschnann, D. Menzel, and E. Umbach, *Phys. Rev. B* **41**, 12933 (1990), and references therein.

¹²C. W. Bauschlicher, Jr., S. R. Langhoff, and L. A. Barnes, *Chem. Phys.* **129**, 431 (1989).

¹³E. W. Plummer, W. R. Salaneck, and J. S. Miller, *Phys. Rev. B* **18**, 1673 (1978).

¹⁴D. R. Jennison, G. D. Stucky, R. R. Rye, and J. A. Kelber, *Phys. Rev. Lett.* **46**, 911 (1981).

¹⁵G. E. Laramore, *J. Vac. Sci. Technol. A* **3**, 1618, (1985).

¹⁶B. E. Koel, J. M. White, and G. M. Loubriel, *J. Chem. Phys.* **77**, 2665 (1982).

¹⁷M. D. Baker, N. D. S. Canning, and M. A. Chesters, *Surf. Sci.* **111**, 452 (1981).

¹⁸M. Ohno (unpublished).