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Evolution of adsorbate core-hole states after bound and continuum primary excitation: Relaxation versus decay

W. Wurth, C. Schneider, R. Treichler, E. Umbach, and D. Menzel
Institut für Festkörperphysik E20, Technische Universität München,
D-8046 Garching, Federal Republic of Germany

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The core-hole decay in various CO adsorbates with different bonding, i.e., on Cu(100), Ni(111), and K/Ni(111), was studied after primary excitation into several bound and continuum states using soft-x-ray synchrotron radiation. The C and O *KLL* spectra of adsorbed CO following the resonant excitation $1s \rightarrow 2\pi$ are very similar to normal Auger spectra for all systems studied, whereas the respective primary energies (resonant absorption and x-ray photoemission binding energy) can be different, depending on the chemical environment. For a limited range of photon energies, marked changes are observed, particularly in the O *KLL* spectra. These changes coincide with a peak in the x-ray absorption spectra and are tentatively explained by primary excitation into Rydberg-like core-ionized states which interfere with the screening process.

The study of the core-hole decay in adsorbed molecules is of eminent interest not only for the physical understanding of one of the most frequently used analytical techniques, Auger spectroscopy, but also for unraveling the mechanism of the primary process (e.g., x-ray absorption, screening of the photoionized hole) and for the understanding of tertiary processes such as dissociation or desorption by bond breaking. One key question for the basic understanding of these processes concerns the time scale for the decay of the involved excited states or, in other words, the relative time scales for screening processes and for the delocalization of single or multiple holes in certain intermediate states. The influence of the primary excitation on the Auger decay is rather dramatic in the case of gas-phase molecules since after exciting the core electron into a bound-state resonance ("π^*" or "2π" resonance for most diatomic molecules) new, so-called "participant" and "spectator" Auger-decay channels appear or are strongly enhanced.[1] For coordination compounds (e.g., carbonyls) and for adsorbed molecules on metals this should be rather different since, in contrast to the gas phase, the initially unoccupied π^* orbital always becomes partially filled either by the excited electron or by charge-transfer screening from the substrate. Hence π^*-derived states (participants) can be directly observed in the Auger decay even for "sudden limit" excitation.[2] In the past, two experiments were published on the C *KLL* Auger decay of resonantly excited adsorbed CO.[3,4] While the data of Ref. 3 suffer from poor statistics, both show clearly the difference between adsorbate (or coordination compound) and gas-phase C 1*s* hole decay, but are considerably different in detail. Since this could well arise because two rather different adsorbate systems, strongly chemisorbed CO on Pt(111) (Ref. 3) and weakly chemisorbed CO on Cu(110),[4] had been chosen and because angular effects, which may be important,[2] had not been taken into account, we have performed an extensive investigation of these effects on three chemically very different CO adsorption systems, CO on Cu(100), Ni(111), and K/Ni(111), studying the O and C *KLL* decay spectra and their dependences on photon energy, polarization, and angle of emission.

The measurements were performed at the Berliner Elektronenspeicherring BESSY using the high-energy toroidial grating monochromator (HETGM)[5] in the ranges of 270 to 450 eV for the C 1*s* excitation and 520–650 eV for the O 1*s* excitation. The high-resolution Auger data (0.2 eV, ±6° acceptance angle) were taken with a Vacuum Generators CLAM analyzer at a fixed angle of 40° with respect to the photon beam. The photon energy was varied in 1 eV steps up to 30 eV above threshold and in larger steps up to approximately 150-eV kinetic energy of the photoelectron. Great care was taken in calibrating the energy analyzer to an accuracy of ±0.1 eV using a standard procedure[6] and subsequently the monochromator by measuring the position of the substrate Fermi edge and a substrate core level. The accuracy of the absolute photon energy scale achieved with this procedure was ±0.3 eV. The crystal was rotated for angle-resolved Auger spectra and for different photon polarizations in order to distinguish between σ- and π-like core-excited states. All data were taken on saturated CO layers. The crystals were prepared by standard techniques.

C *KLL* Auger spectra of CO/Ni(111) taken at a constant emission angle of 40° are shown in Fig. 1(a) for four different excitation energies corresponding to primary excitations into (a) the bound π resonance, (b) states near the vacuum level, (c) the quasibound σ-shape resonance, and (d) far above threshold. All spectra look nearly identical. This is also the case for the corresponding O *KLL* Auger spectra [Fig. 1(b)], with the exception of the photon energy range between the π and σ resonances (i.e., 535–544 eV) where the relative intensities of the peaks indicated by lines change quite markedly. We note that the equivalent sequences of O and C *KLL* spectra from CO/Cu(100) and CO+K/Ni(111) show exactly the same behavior, and that our data are in agreement with the two previously reported C *KLL* spectra of CO/Cu(110).[4] Thus we conclude that apart from the anomaly between the resonances for O *KLL*, the spectra of π- or σ-resonant

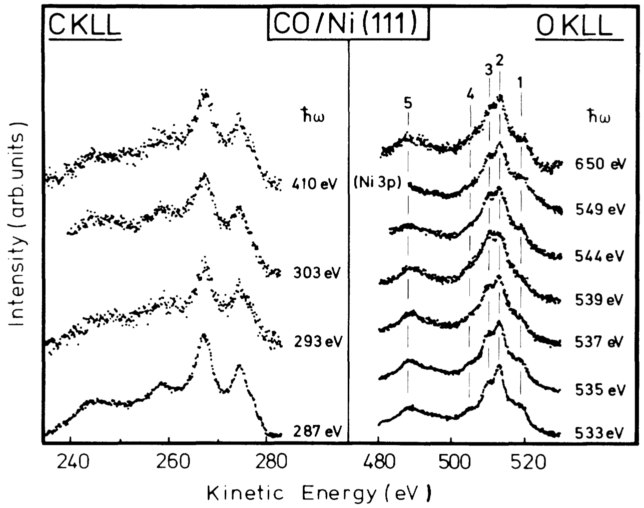

FIG. 1. (a) C *KLL* (left) and (b) O *KLL* (right) Auger-decay spectra for CO/Ni(111) obtained after primary excitation with various photon energies as indicated. Kinetic energies are referred to the Fermi level; angle of emission 4°.

excitation as well as those obtained with high-photon energy (sudden limit) are very similar, and that this is true for both C and O *KLL* spectra, and for the different adsorption bonds investigated.

At first glance this result seems to be unexpected not only because of the gas-phase data[1] but also because of the different excitation processes. Although both processes, the x-ray photoemission (XPS) excitation into the continuum ("sudden" case) and the resonant core-to-bound excitation ($1s \rightarrow 2\pi$), lead to a similar final state, namely, a partially filled 2π, there are obvious differences in binding and excitation energies, respectively, which are shown in Table I for various CO cases. Note that for all adsorbate systems the energy values for resonant absorption are very close to the gas-phase values,[8] and close to each other, while the XPS energies (peaks with lowest binding energy) differ considerably. Hence we derive that *the resonance energies are less dependent on the chemical environment than the XPS energies.* The reason is likely to be the local, internal nature of the absorption process in the CO molecule, which prevents major external screening contributions by the substrate, and hinders optimization of the charge distribution within the adsorbate complex on the time scale of the absorption process. The XPS process, on the other hand, leads to distinct binding energies, for instance, for the CO adsorbates on Cu(100) and Ru(001), due to their quite different screening properties.[9] We conclude that in the case of *strongly chemisorbed* molecules (CO/Ru, Ni, K+Ni) *the final state of the core-to-bound transition is different from the ionic ground state* that may be reached by the XPS process. Consequently, the XPS peak with the lowest binding energy corresponds to a better-screened final state, probably involving a different charge distribution of the valence (especially of the 2π-derived) orbitals. In the case of CO/Cu(100) the similarity of XPS and absorption energies, and small *differences* of the subsequent Auger decay spectra, indicate that for this system the low binding energy peak in XPS does *not* correspond to the fully relaxed final state even in the sudden limit. This is particularly obvious from the O $1s$ data (see Table I) which show a slightly *higher* XPS energy compared to the energy of resonant absorption. This finding will be discussed in more detail elsewhere.[10] Finally, we note that the previously suggested model for the photoemission/absorption energy difference in terms of a singlet-triplet splitting[4] which is indeed observed in the gas phase[11] is considered to be unlikely here because one would then expect smaller differences in energy for the O $1s$ than for the C $1s$ core hole due to a smaller exchange integral,[11,12] and one would expect about the same differences for CO/Cu compared to the other adsorbates, which is in disagreement with the results shown in Table I.

Now we return to the observation that most Auger spectra of Fig. 1 look very similar despite the fact that different final states are reached by resonant absorption and sudden limit (XPS) excitation, respectively. Hence we must conclude that at least some of the various final states (e.g., the resonantly excited states $1s \rightarrow 2\pi,\sigma$) are not identical to the Auger initial state or, in other words, the adsorbate system relaxes to its ionic ground state before the core-hole decay takes place. The key to the understanding of this mechanism is the role of the CO 2π orbital in the relaxation process and its coupling to the metal.[9] In a simplified band picture, the initially nearly unoccupied 2π level is pulled below the Fermi level by the core hole and becomes partly filled by electron transfer from the metal, while in a molecular orbital picture the bonding orbital of the 2π-metal hybridization with mainly metal character in the ground state becomes more CO-like in the core-ionized state. These models describe a very effective screening by charge transfer, yielding an essentially neutral adsorbate and a positive charge delocalized in the metal.[9] The important point here is that this relax-

TABLE I. XPS (C $1s$, O $1s$) binding energies and energies for resonant core-to-bound excitation ($1s \rightarrow 2\pi$) for gas-phase CO and various CO adsorbates. Note that the XPS energies refer to the peak with the lowest binding energy with respect to the Fermi level except for gas-phase CO.

	CO_{gas}	CO/Cu(100)	CO/Ru(001)	CO/Ni(111)	CO+K/Ni(111)
C $1s$	296.2[a]	286.3	285.7	285.5	285.2
C $1s \rightarrow 2\pi$	287.3[b]	286.4	286.5	287.0	286.7
O $1s$	542.6[a]	533.3	532.0	531.1	531.0
O $1s \rightarrow 2\pi$	534.1[b]	532.9	532.6	532.6	532.2

[a] From Ref. 7 (referred to vacuum level). [b] From Ref. 8.

ation process is seen to be fast on the time scale of the Auger process. While for XPS excitation ("sudden" case) the (strongly bound) adsorbate system may reach the ionic ground state with a high probability even before the primary electron leaves ("adiabatic XPS peak"), our results show that charge rearrangement takes place for primary excitation into the bound 2π resonance before the core-hole decays (see above).

We now concentrate on the changes in the off-resonant Auger decay spectra which were observed around 6 eV above the π resonance for O 1*s* decay [see Fig. 1(b)]. In Fig. 2, resonant and off-resonant O *KLL* Auger spectra are compared for CO on Cu(100), Ni(111), and K/Ni(111). Quantitative evaluation of relative peak heights as a function of photon energy shows that for excitation energies 6 eV above the π resonance, Auger peak 1 of Fig 1(b) (double-hole final states with 2π participation; for a discussion of peak assignments see Ref. 6) goes through a minimum together with peak 2 (double-hole assignment: $1\pi 1\pi$) while peaks 3 ($4\sigma 1\pi$) and 5 ($3\sigma X$) remain nearly constant. The main features between 500 and 515 eV broaden, leading to a loss of structure around peak 4 ($4\sigma 4\sigma$). These observations can be attributed to two major changes. First, the intensity of the 2π-derived structures (515–522 eV range of Fig. 2) decrease markedly, and second, a significant amount of intensity is shifted to lower kinetic energies.[13] Both changes clearly indicate a significant probability for *incomplete* screening *before* the Auger decay occurs, since this should lead to lower kinetic energies of the spectator decay channels as well as to reduced occupancy of the 2π orbital in the Auger initial state and, hence, to a reduction of the participant channels.

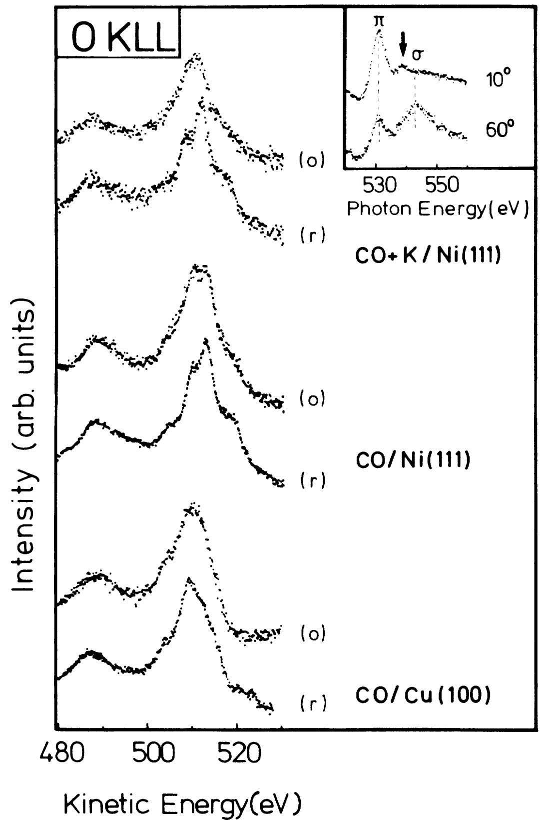

FIG. 2. O *KLL* decay spectra for CO on three different substrates after $1s \rightarrow 2\pi$ resonant (r) and off-resonant (o) (6 eV above the resonance) excitation. The inset shows near-edge x-ray absorption fine-structure (NEXAFS) spectra for CO+K/Ni(111) at two different angles of polarization (angle between electric field vector and surface plane).

Next we have to ask why incomplete screening occurs mainly for excited states at about 6 eV above the 2π resonance and not for states closer to threshold. This is simply because excitation into the 2π resonance leads to rapid charge rearrangement for optimum screening, since the 2π orbital is hybridized with the metal as discussed above. For off-resonant excitation into states near threshold, the excited electron is no longer in an adsorbate orbital but "moves slowly away." As long as it is still near the adsorbate it interferes with the relaxation process since it partially screens the core hole and thus hinders the normal screening process via the 2π orbital. In particular, if the primary electron is captured in a quasibound resonance like a Rydberg state it could be sufficiently long lived to influence the Auger initial state. This model is supported by the observation that the maximum change occurs at the approximate energy position of Rydberg-like core-ionized states near the vacuum level. Moreover, we indeed observed a small structure in most absorption [near-edge x-ray-absorption fine structure (NEXAFS)] spectra of adsorbed CO at about 6 eV above the π resonance (see arrow in inset of Fig. 2) which is consistent with enhanced absorption into Rydberg-like states that are contracted and fairly localized by the presence of a core hole.[14] The fact that the observed changes are much smaller for the carbon than for the oxygen core-hole decay (see Fig. 1) further corroborates such a model, since Rydberg levels contracted around a carbon hole should have a better overlap with the metal and hence the electron should delocalize much faster.

Finally, we briefly discuss other possible explanations for the observed changes. For instance, the influence of a resonantly enhanced shake-up excitation in the primary process (most likely a $1\pi \rightarrow 2\pi$ shake up) could lead to different screening properties of the core hole or to additional structures. However, the π symmetry of the two-electron matrix element for such a shake-up excitation should lead to a much stronger polarization dependence than that observed experimentally.[13] Second, gas-phase data[15] show that the resonance of this shake-up process is fairly weak and broad (15–20 eV) in disagreement with our data. And third, such a shake-up process should lead to an enhanced population of the 2π orbital and hence to an increase rather than a decrease of the participant structures. An alternative explanation could be the influence of a totally unscreened Auger initial state where the primary electron is delocalized and the charge rearrangement has not yet taken place. This process, however, appears to be unlikely in view of the fast charge rearrangement discussed above and of the small 4 eV shift of the extra part of the "spectator" Auger spectrum[16] compared to the large shift (10 eV) observed in the gas phase.[1]

In conclusion, our comparative studies of x-ray absorption and subsequent core hole decay of CO molecules in different chemisorption bonds show that (a) resonant absorption ($1s \rightarrow 2\pi$) is less dependent on the chemical environment than the XPS process and (b) leads to a less-screened final state compared to XPS in the case of strong chemisorption, and that (c) the relaxation process of a core hole is fast compared to the following Auger decay for most of the excited final states, but (d) apparently not fast enough for excitation energies 6 eV above the 2π resonance for which quasibound Rydberg-type states are suggested. Observation (c) indicates a very large delocalization probability, i.e., a short lifetime of the ($1s \rightarrow 2\pi$) excited electron, due to the coupling of the adsorbate orbitals to the metal substrate. Only if the excited electron is fairly localized (d), with a small hopping probability away from the core-hole site, an influence of the primary process in the Auger decay spectra is seen. Finally, on one hand our results show clearly that for most excitation energies primary ionization process and subsequent Auger decay can be viewed as two fairly independent processes and that the influence of the primary process on the Auger line shape can be neglected.[17] On the other hand, our results also prove for the same system that under certain circumstances initial excitation and hole decay cannot be considered separately.

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