Decay of "autoionizing" core-hole states in adsorbed CO molecules

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The decay of resonantly excited $(1s \rightarrow 2\pi)$ C and O $1s$ core-hole states, called autoionization in the gas phase, was studied for absorbed CO molecules by means of angle-resolved Auger spectroscopy for three different systems [CO/Cu(100), CO/Ni(111), CO+K/Ni(111)] which represent rather different bonding configurations. It is shown that the final states resulting from the 2π-participant decay are, unlike the situation for the isolated molecule, *not* identical to the final states reached in valence photoemission. This is due to the coupling of the 2π level to the substrate valence band and to the dynamics of the screening process. For CO/Cu(100), whose decay spectra differ from those observed for other systems, a decay of two different initial states is proposed.

The autoionization of excited (neutral) core-hole states of simple *isolated molecules*[1,2] has recently attracted considerable interest because it provides information on the local valence density which can be obtained by comparing the participant autoionization decay of resonantly excited core-hole states with UV photoemission results. Autoionization is the Auger decay of a neutral system with a core electron excited into a bound (e.g., 2π) orbital, and participant decay means autoionization channels that lead to one-hole final states involving one valence electron and the excited 2π electron (participant). It is evident, and has been shown experimentally[1,2] and theoretically,[3] that, for an isolated system (free molecule), such autoionization final states are identical to the final states reached by valence photoemission although the observed intensities (and hence the information) are considerably different. This difference in intensity is expected because the Auger (autoionization) matrix element is very different from the photoemission matrix element and stresses the local overlap of the (participating) valence levels with the core hole. Hence, the intensity of the Auger transition becomes a measure of the local valence density at a specific atomic core of the molecule. The applicability of these considerations to *adsorbed* molecules is not yet quite clear although a first attempt has been made to identify valence photoemission [ultraviolet photoemission spectroscopy (UPS)] final states also in the C KLL decay spectra of adsorbed CO on Cu(110).[4]

One obvious difference between isolated (gas phase) and adsorbed molecules is the fact[4,5] that, in well-coupled adsorbates, an Auger process normally starts from a *neutral initial state,* despite the primary core hole, because screening of the primary hole leads to charge transfer from the substrate. Most likely, the decay process also leads to a *neutral final state,* due to charge-transfer screening, with two holes in valence orbitals and two additional electrons in initially (nearly) empty orbitals (2π-derived in the case of CO). Hence, the distinction be-

tween Auger and autoionization processes becomes meaningless in the case of strongly coupled adsorbates. The well-established notion "autoionization" is nevertheless also being used here, in analogy to equivalent gas-phase studies, in order to emphasize that only Auger channels with participation of 2π (screening or resonantly excited) electrons are considered here; there is, of course, the possibility of spectator (i.e., normal Auger) decay for these states also.

The important question, whether in the case of adsorbates autoionization (Auger) decay and valence photoemission (UPS) measure exactly the same final state still remains to be answered since, in contrast with the gas phase, strong screening interaction with the substrate takes place. This question is interesting not only with respect to the screening dynamics of the Auger and photoemission processes, respectively, but also because unambiguous identification of spectral features is the necessary prerequisite for utilizing the potential complementary information of Auger spectroscopy.

The present study of CO molecules adsorbed on Cu(100), Ni(111), and K/Ni(111) shows that the assumption of equal final states is at least not valid for adsorbate systems with a resonance-level coupling to the substrate valence band. Compared to a similar but less extensive previous study,[4] we come to a different assignment of the "autoionization" peaks in the O KLL and C KLL Auger spectra and also give a different interpretation of the occurring processes.

The experiments were performed at the Berliner Elektronenspeicherring (BESSY) using the high-energy toroidal grating monochromator (HETGM) in the photon energy range 270–450 eV for the C $1s$ excitation and 520–650 eV for the O $1s$ excitation. The high-resolution Auger data (0.2 eV, $\pm 6°$ acceptance angle) were taken with a VG CLAM analyzer at a fixed angle of 40° with respect to the photon beam. The polar angle of the measured Auger electrons was varied in steps of 5° and 10°

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from $-10°$ to $+70°$ with respect to the surface normal by rotating the crystal. Great care was taken in calibrating the energy scale of the electron analyzer to an accuracy of ± 0.1 eV using a standard procedure.[6] For pure CO, all data were taken on saturated CO layers while for the coadsorption system layers were prepared for which a ratio of 1:1 for K and CO was determined. The crystals were prepared using standard techniques.

Figure 1 shows C KLL and O KLL Auger spectra for the three different adsorbate systems taken at an electron emission angle of $\theta=0°$ with respect to the surface normal after primary excitation of the respective $1s$ electron into the molecular 2π resonance. As pointed out before, these spectra are very similar to those obtained after "sudden limit" excitation (i.e., excitation into the continuum far above threshold)[4,5] indicating that the relevant initial state for the decay is the same in both cases. The consequence of this finding, together with the observed energy difference between resonance energy and x-ray photoemission spectroscopy (XPS) binding energy,[5] is that the resonantly excited $(1s \rightarrow 2\pi)$ state and the photoemission shake-up states relax before the Auger decay takes place.[5] Nevertheless, it is reasonable to compare autoionization or participant decay in the gas and adsorbate phase, respectively, because in both cases a partially filled 2π level is involved in the decay and even the relaxed state reached after "sudden limit" excitation has an extra electron in the formerly almost unoccupied CO-2π level due to charge-transfer screening.[7,8] The features resulting from the decay of the core hole under participation of this 2π level are clearly visible on the high kinetic energy side of the spectra in Fig. 1, since the kinetic energy of the spectator Auger peaks (i.e., the peaks representing "normal" Auger transitions that occur in the presence of a "spectator" 2π electron) should not exceed

$$E_{kin}(CV_1V_2) \leq E_B(1s) - E_B(V_1) - E_B(V_2) , \quad (1)$$

where $E_B(X)$ are the one-electron binding energies deter-

mined from photoemission experiments. Hence, the C KLL Auger peaks with kinetic energies above 270 eV and the shoulders in the O KLL spectra above 515 eV can be attributed solely to participant decay channels involving the 2π-screening electron. A closer look at the C KLL spectra in Fig. 1 reveals an obvious difference between CO/Cu(100) on the one hand, and CO on Ni(111) and K/Ni(111) on the other. The spectra of the latter two show only one peak (6) at 274.4 and 272.3 eV, respectively, in the energy range under consideration whereas on Cu(100), two distinct peaks (6 and 7) at 273.6 and 276.7 eV are observed, similar to the Cu(110) surface.[4] In the O KLL spectra, obtained at the same emission angle, a relatively broad shoulder (6) at 519 and 517 eV is observed for the Ni(111) and for the K/Ni(111) surface, respectively, while the spectrum for the Cu surface shows only one shoulder (5) at 516 eV and almost no intensity at higher kinetic energies.

The spectra in Figs. 2 and 3 were taken at electron emission angles of 45° and 70°, respectively, and show pronounced intensity changes compared to those obtained at normal emission. The participant channels in the C KLL spectra for 45°, and even more for 70°, are clearly enhanced with those from the Cu surface still showing two peaks and those from the two Ni surfaces one peak with an indication of a small shoulder on the high kinetic energy side. We note that peak 6 is much larger for the K/Ni(111) than for the pure Ni(111) surface relative to the spectator part of the spectrum, that on both Ni surfaces peak 6 shows a shoulder on the high-energy side, and that for Cu(100) peak 6 has increased relative to peak 7. As to the O KLL data, an increase of the observed shoulders 5 and 6 is seen leading to a small peak 6 at 519 eV, especially for the Ni(111) surface and 45°. The most pronounced difference in the O KLL spectra is seen for CO/Cu(100) at 70° (Fig. 3) where two new peaks (6 and 7) appear at 520.5 and 523.7 eV, respectively, together with the pronounced shoulder at 516 eV (peak 5).

In discussing the data we will first concentrate on the Ni data and then come back to the CO/Cu data which obviously show some distinct differences. In the UPS spec-
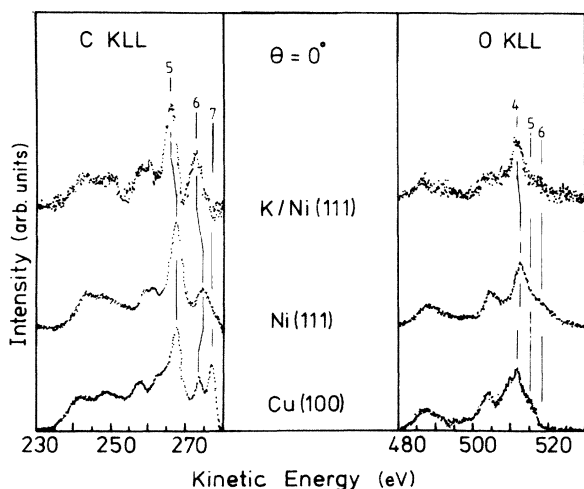

FIG. 1. C and O KLL spectra for CO on Cu(100), Ni(111) and K/Ni(111). The angle of emission $(\theta=0°)$ is referred to the surface normal; kinetic energies are given with respect to the Fermi level. Some intense lines are labeled.
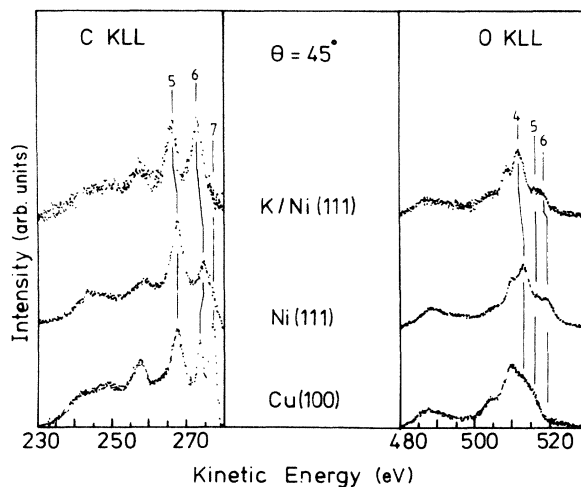
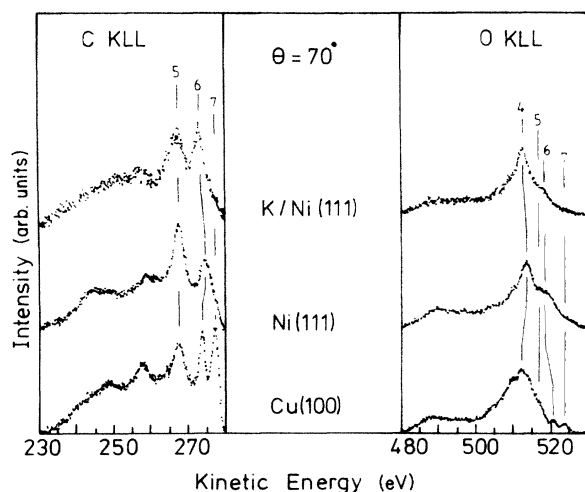

FIG. 2. Same as Fig. 1 but for emission angle $\theta=45°$.

FIG. 3. Same as Fig. 1 but for emission angle $\theta = 70°$.

tra for CO adsorbates, we normally observe two peaks, one at about 8 eV binding energy resulting from overlapping $5\sigma/1\pi$ emission and one (4σ peak) at about 11 eV. If the final states of autoionization and UV photoemission were identical, one should also observe at least two peaks as participant decay channels in the Auger spectra. Their expected energy values can be calculated by subtracting the respective UPS binding energies from the XPS $1s$ binding energy [see Eq. (1)] which gives values of 277.1 and 274.1 eV for the C KLL and 523.1 and 520.1 eV for the O KLL spectra, respectively, assuming that the participant 2π electron stems from near the Fermi level [$E_B(2\pi) = 0$] and that there is no effective interaction between the valence and the 2π hole ($U_{eff} = 0$).

On the basis of these values which are marked in Fig. 4 by thick bars and compared to autoionization spectra taken at 70° on an expanded scale, one would probably associate peak 6 in the C KLL spectra with the $4\sigma2\pi$-Auger or 4σ-autoionization final state although bars and peaks do not coincide exactly. This assignment has been suggested previously by Chen et al.[4] based on their C KLL data for CO/Cu(110). However, we come to the conclusion that this assignment is not correct, for the following reasons. First, the same final state should show up in the O KLL data with an even higher intensity because one would expect the 4σ orbital to be mainly localized at the O end of the adsorbed CO molecule thus having larger overlap (and hence matrix element) with the O $1s$ hole than with the C $1s$ hole. This is obviously not the case as one observes only a very small peak at 519 eV in the O KLL spectra. Second, peak 6 in the C KLL decay spectra shows an angular distribution which is peaked around 60°; this does not fit well to a π-symmetric state like the $4\sigma2\pi$ final state.[8] Third, there is no reason why the $5\sigma2\pi$ and the $1\pi2\pi$ Auger (or 5σ and 1π autoionization) final states, which, according to their UPS binding energies, should appear in an energy range where almost no intensity is detected in the Auger spectra, should have only negligible spectral weight in both core-hole decay spectra, in contrast to the gas-phase results.[1,2] And finally, all theoretical predictions[3,9,10] would be at variance with such an assignment, considering the ratio of peaks 6 and 7 in

the C KLL as well as the ratio of peaks 6 in C KLL and O KLL spectra, respectively. Hence, we are led to the conclusion that the assumption of equal final states for valence photoemission and autoionization process is not correct in the case of most adsorbates.

Taking into account the relative intensity and the observed angular distribution of peak 6 in the C KLL spectra we come to the conclusion that this peak has to be associated with overlapping $5\sigma2\pi/1\pi2\pi$ decay channels with the $5\sigma2\pi$ channel probably a dominant contribution. Peak 6 in the O KLL decay is then mainly due to emission from the $1\pi2\pi$ final state; this assignment is indicated in Fig. 4 and corroborated by the angular distribution and the two-hole binding energy (see below). Our interpretation, which postulates that the $5\sigma2\pi$ participant channel is the most intense in the C KLL and the $1\pi2\pi$ channel in the O KLL autoionization spectra, is corroborated by the fact that the equivalent normal Auger (i.e., the $4\sigma1\pi$, $5\sigma1\pi$, and $1\pi1\pi$) decay channels show exactly the same quantitative trend.[8] Or in other words, since we cannot expect that the relative intensities of $X1\pi$ ($X = 1\pi$, 5σ, 4σ) and $X2\pi$ transitions are totally different, we must come to the above assignment. Of course, we now have to answer two questions, where the $4\sigma2\pi$ peak is hidden and why the UPS binding energies and the equivalent autoionization peak energies are separated by 2–3 eV. The first question is easy to answer. According to the same arguments, the $4\sigma2\pi$ final state should be most intense in the O KLL spectra; we associate it with shoulder 5 on the high-energy side of the spectator peak (4) at 515 eV which can be seen more clearly after deconvolution of a broadening function of 2 eV width. This argument has been suggested before.[8] It is further corroborated by calculations for NiCO clusters which yielded similar intensity relations and relative energy differences.[9,10]
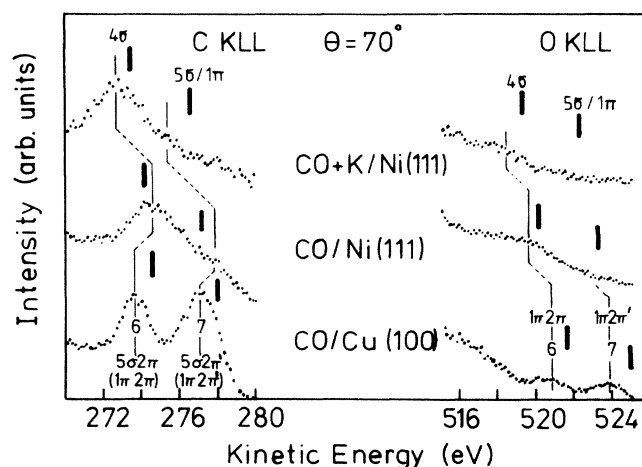
The other question concerns the obvious energy

FIG. 4. Comparison of autoionization peaks (high-energy part of Fig. 3 on an expanded scale) with one-electron binding energies (thick bars) derived from UPS measurements. UPS peak positions E_{kin} (labeled 4σ and $5\sigma/1\pi$, respectively) were obtained by subtracting measured UPS binding energies of valence orbitals (X) from respective XPS $1s$ binding energies: $E_{kin} = E_B(1s) - E_B(X)$. Our interpretation of participant structures is labeled in the figure and discussed in the text.

difference. The reason for this is the energetic position of the hole in the 2π orbital. The model which describes autoionization and UPS final states as equivalent[4] assumes the 2π orbital to be located at the Fermi level in both cases. Hence, there should be just one valence hole, and an equally relaxed (screened) system, in both cases. However, this picture is too simple since the Auger (or autoionization) process starts from a (relaxed) core-hole state. In the presence of a core hole, the bonding metal-2π hybrid orbital gains weight on the CO molecule (compared to the ground state) and is pulled below the Fermi level. A rough estimate comparing the ground-state position of the 2π orbital of the equivalent core molecule NO on Ni(111) (Ref. 11) yields a 2π binding energy of about 2 eV. Taking this E_B value and the two-hole interaction ($U_{\mathrm{eff}} \geq 0$) into account, we obtain an autoionization peak energy,

$$E_{\mathrm{kin}} = E_B(1s) - E_B(X) - E_B(2\pi) - U_{\mathrm{eff}}$$

(with X any valence orbital), that is shifted to lower kinetic energies by more than 2 eV compared to the (previously suggested) one-hole final state with

$$E_{\mathrm{kin}} = E_B(1s) - E_B(X) \ .$$

Hence, the difference between both processes is that the UPS process ends in a screened (i.e., neutral) *one-hole* final state while the autoionization process ends in a screened *two-hole* final state (with one 2π hole more than 2 eV below E_F). It is important to realize that in the latter case, the screening process does not "immediately" (i.e., *during* the decay process) fill the participant 2π hole that is created by the Auger decay itself or, in other words, that the 2π hole does not immediately delocalize into the metal and "bubble" up to the Fermi edge. If such a process were possible, we should also see it for each UPS process or for other Auger decay channels, in particular those involving 5σ electrons, since the 5σ orbital couples as well with the substrate bands as the 2π. However, this is not the case; the binding energy for *each* 5σ hole in Auger processes is equal to (or larger by U_{eff} than) the one-hole UPS binding energy.[8]

We emphasize that the autoionization final state is then identical to a UPS *"shake-up"* final state, i.e., a screened final state that involves two holes in the valence orbitals, one X ($X = 5\sigma$, 4σ, and 1π) hole and one 2π hole, and screening electrons at the Fermi level. In principle, such final states could be seen in valence photoemission spectra as satellites to the main UPS peaks, but will, of course, have rather low intensity in most cases. This interpretation is corroborated by very recent calculations.[12] The intensity difference of such states in autoionization and UPS spectra, respectively, is caused by the very different matrix elements in both cases, as pointed out above. Hence, both spectroscopies give different but complementary information on an adsorbate, as previously emphasized.[4,5]

The given assignment and the same arguments equally apply to both Ni(111) adsorbates, CO and CO+K. The comparison of both sets of spectra reveals two more aspects. One is that the dominant autoionization peak and the UPS 4σ bar do not coincide and have also switched their relative energy positions, as seen in Fig. 4. In gen-

eral, all participant structures in the CO+K spectra are shifted to lower kinetic energies with respect to the UPS peaks which indicates an increased binding energy for the 2π level in the core-ionized state of coadsorbed CO+K. This fits to the second aspect, the above-mentioned relative intensity increase of the C KLL participant structures for the CO+K layer which is compatible with an enhanced population and bonding contribution of the 2π in the ground state due to coadsorbed K.

The last question to address is whether the pronounced double-peak participant structure in the case of weakly chemisorbed CO on Cu can be understood within the same model or whether the previous interpretation for CO/Cu(110) (Ref. 4) is applicable in this case. In the light of our discussion of the Ni results, it also appears unlikely that for CO/Cu the assignment of both prominent autoionization peaks (6 and 7) as 4σ and $5\sigma/1\pi$ one-electron peaks is correct. Again, the arguments on energy position, angular dependence, and relative intensities are the same as given above, although the relative intensity of peaks 6 and 7 in O KLL and C KLL is now in favor of peak 7, and hence, would fit better to its identification as 5σ final state.[4] However, the weak intensity of peak 7 in O KLL (high 1π overlap with O $1s$ hole) and the relative intensity of peak 6 in C KLL and O KLL clearly argue against the one-hole assignment, peak 6 $\hat{=} 4\sigma$, peak 7 $\hat{=} 5\sigma/1\pi$. We therefore come to the conclusion that even in the weakly chemisorbed case the interpretation of corresponding UPS final states and participant channels in the Auger decay is not correct. But if this is so, we have to explain the obvious differences in the participant decay structures for CO on Cu and on Ni.

Our interpretation of the double-peak structure in CO/Cu is that the participant decay starts from two different initial states. One is the resonantly excited state with a 2π electron at the Fermi level which represents a *partly* screened core-hole state, and the other is a *fully* relaxed final state which is also observed for strongly coupled CO adsorbates such as CO/Ni(111). The difference between CO/Cu and CO/Ni is that for CO/Ni the resonantly filled 2π state near the Fermi edge fully relaxes to the core-hole ground state *before* the Auger/autoionization decay occurs while it does not relax completely for CO/Cu. Thus, the relative intensities of peaks 6 and 7 indicate the probability for the relaxation process to happen on the time scale of the decay process. The observation that excitation into final states far above resonance ("sudden" excitation) yields essentially the same Auger/autoionization spectra is *not* at variance with this interpretation since core photoemission (XPS) does *not* lead to a fully screened final state in the case of CO/Cu.[5,13] This conclusion has been derived from the significant difference between CO/Cu and other strongly bound CO adsorbates when comparing the core-to-bound ($1s \rightarrow 2\pi$) excitation energy and the energy of the lowest binding-energy peak in XPS spectra.[5,13]

A similar two-peak structure has recently been observed for resonantly excited metal carbonyl films.[2] We interpret these results in the same way as arising from two different initial states, in contrast with the authors of Ref. 2. However, two main differences between the CO/Cu

and the carbonyl spectra need to be explained: The disappearance of one autoionization peak 7 far above threshold and a shift of the spectator (normal) Auger spectrum by about 3 eV for the carbonyls. Both of these observations can easily be understood by different screening in the metal carbonyl and CO/Cu system, respectively. The substrate metal in the latter case provides enough screening charge to end up with an essentially neutral adsorbate for each one- or two-hole final state. This is apparently not the case for the carbonyls, for which the XPS process leads to a (partly) ionic state, and hence to a shifted spectator spectrum, while the resonance excitation, of course, ends in a neutral state with one electron in the 2π orbital (similar to any CO/Cu excitation). In the carbonyl case, this 2π state can only be populated by resonant excitation, and hence be observed as peak 7 in the autoionization spectra, while for adsorbates it is also filled by charge-transfer screening in the XPS (sudden) excitation process.

In conclusion, we stress that for the three different CO systems investigated we can clearly show that the final states observed in the autoionization (i.e., 2π participant decay) process are *not* equal to the final states reached after valence photoemission. We explain the observed energy differences with the appreciable binding energy (>2 eV) of the 2π electron in the core-hole state and the interaction energy of the two holes in the final state. Thus, the autoionization peaks should be compared to (probably very weak) satellite structures in the UPS spectra rather than to the dominant one-electron peaks. This observation is especially important for the assignment of partici-pant channels in Auger spectra and hence for the interpretation of changes in the local electronic structure of molecules in different adsorption systems. For CO on Cu, we propose a participant decay of two different initial states corresponding to different degrees of relaxation of the core-ionized state to explain the observed two-peak structure which is different compared to strongly coupled systems. The two initial states are likely to be a fully relaxed state similar to the adiabatic state observed for strongly coupled systems, and a partially screened state which is similar to the near-edge x-ray absorption fine-structure (NEXAFS) final state. The observation of both initial states arises because of the small coupling of the 2π orbital to the Cu substrate, and hence a smaller probability for the system to arrive at the fully relaxed state before the decay. We point out that there is *no* indication for a role of the "giant satellite"[14] XPS final state as initial state in the sudden case (for the core-to-bound excitation it can be excluded anyway, since energy does not suffice to excite this state). This implies that such states decay fast on the time scale of Auger processes.

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