

Dynamics of adsorbate core-hole decay

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We have measured the kinetic-energy distribution of the electrons emitted by the radiationless decay of the C_{1s} hole of CO adsorbed on Cu(110) as a function of the energy of the initial photon used to create the core hole. All excited core-hole configurations created by the initial photoionization process decay to the fully screened core-hole state before the core-hole decays. The Auger decay process appears to be "adiabatic," since both the initial- and final-state configurations are fully screened by charge transfer from the metal.

The radiationless decay of a core hole (Auger decay) on an atom or molecule near the surface of a solid has been used for many years as a technique to identify the elements at a surface and to make a qualitative estimate of each element's concentration. As experimental and theoretical techniques have been refined there has been a growing activity aimed at using the details of the Auger spectra as a probe of the local bonding configuration of chemisorbed molecules.¹⁻⁵ Any quantitative theoretical analysis of an Auger spectrum must be able to evaluate the Coulomb matrix element between the initial and final states. At the present time it appears that this part of the problem is tractable in several different theoretical schemes.^{1,5} What is unresolved at present is the time evolution of the various initial states into the manifold of possible final states.⁶ For example, in many adsorbate systems the photoionization process creates several core-hole configurations leading to a multiple-peak photoelectron spectrum. The excited core-hole configurations are referred to as shake-up peaks. Do these excited core-hole configurations decay into the lowest-energy core-hole state before the decay of the core hole, or should each one of these configurations be treated as a possible initial state? A similar question can be asked about the final states. Is the Auger decay so rapid that any theory must consider all possible excited states including multiple ionization?

We have chosen a system to study, CO adsorbed on Cu(110), that exhibits very intense satellite peaks in the photoelectron spectra of both the core and valence regions.⁷⁻¹⁰ By tuning the photon energy near the threshold for C_{1s} ionization we could selectively excite specific core-hole configurations and then monitor the changes in the *deexcitation electron spectra*.

Let us begin the discussion of the core-hole decay process by reiterating what is known about the initial ionization or excitation process. In 1978 Norton, Tapping, and Goodale⁷ showed that the spectra from both the C_{1s} and the O_{1s} regions for CO adsorbed on polycrystalline Cu exhibited very intense satellite lines. Since the Norton, Tapping, and Goodale⁷ measurements there have been spectra published for Cu(100) (Refs. 9 and 11) and Cu(111).¹⁰ All of these spec-

tra show qualitatively the same features, i.e., a lowest binding-energy peak at 286.5 ± 0.1 eV with two strong satellite peaks at 2.7 ± 0.3 - and 7.2 ± 0.5 -eV higher binding energy. The relative intensities (linewidths) of these three peaks are 1 (~ 1.2 eV), 2.4 ± 0.5 (3.8 ± 0.4 eV), and 1.4 ± 0.5 (3.6 ± 0.6 eV), respectively.¹² Everyone agrees that the lowest binding-energy peak at 286.5 eV is the fully screened core-hole state. The C_{1s} hole is screened by charge transfer from the metal into the first unoccupied molecular orbital of the neutral CO molecule, i.e., the 2π . The 2π level is pulled down below the Fermi energy by the attractive core hole.¹³ The assignment of the other two peaks depends upon the theoretical approach used to calculate the spectra,¹⁴⁻¹⁶ but one or more of the satellite peaks is an unscreened state. This multiplex spectrum is a consequence of the rapidity of the ionization process. The sudden approximation to photoionization leads to well-formulated sum rules on energy and intensity¹⁷ that have been tested experimentally.¹⁸

The question we addressed was whether all three of the core-hole states produced by photoionization participate directly in the Auger decay giving a complex spectrum, or do the higher-energy states decay into the fully screened configuration before the core-hole decays. This question is quite easy to answer with the tunability of a synchrotron light source.¹⁹ Figure 1 shows a partial yield absorption spectra near the C_{1s} threshold region. The sharp peak is the resonant $C_{1s} \rightarrow 2\pi$ excitation at $h\nu = 287.5$ eV, which is very close to the value of 287.3 eV measured for gas phase CO.²⁰ Therefore, if we tune the photon energy to 287.5 eV, we form the excited configuration of CO that is believed to be the fully screened core-hole state. There is not enough energy to create the two excited core-hole state configurations at 289 and 293 eV binding energy. Therefore, the deexcitation spectra at $h\nu = 287.5$ eV is from only one configuration, while the spectra at higher photon energy could be from all three states.²¹

Figure 2 shows the deexcitation electron spectra for both photoionization at $h\nu = 311$ eV (top)²¹ and for $C_{1s} \rightarrow 2\pi$ excitation (bottom). Except for small intensity changes the spectra are identical, proving that *all of the excited C_{1s} hole*

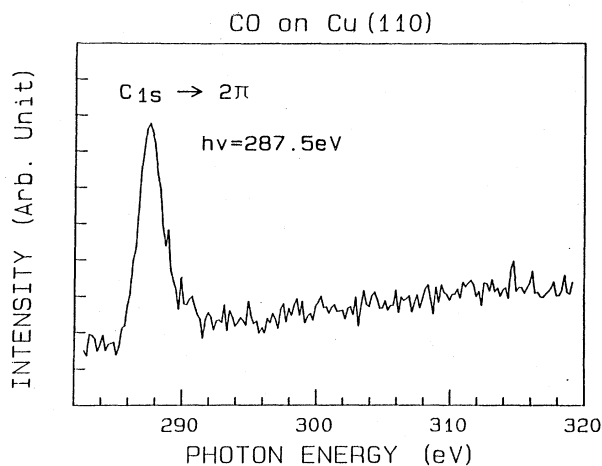


FIG. 1. The "absorption" spectrum for CO adsorbed onto Cu(110) at 100 K. The spectrum was measured by monitoring the partial yield of low-energy electrons.

configurations produced by photoionization decay into the fully screened state before the C_{1s} hole decays. We find that the deexcitation spectra are nearly the same for a range of $h\nu$ from 287 → 318 eV and the data of Baker, Canning, and Chesters¹⁰ for the electron- (> 2 keV) induced Auger spectrum of CO on Cu(111) look very similar to ours, especially considering that they are integrating a differentiated spectra.

To proceed from this point it is necessary to transform the kinetic-energy scale shown on the bottom of Fig. 2 into a binding-energy scale. Normally the binding energy of a peak is defined as the energy difference between the energy

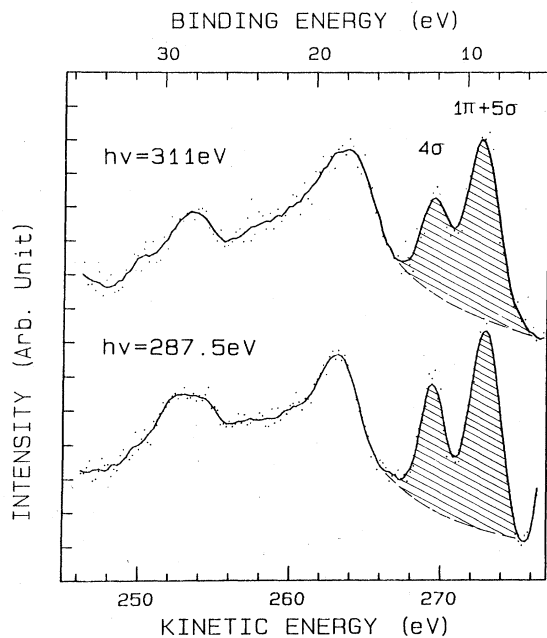


FIG. 2. A comparison of the deexcitation spectra following the decay of the C_{1s} hole for CO on Cu(110). The kinetic-energy scale is measured with respect to the vacuum.

put into the system and the kinetic energy extracted by the emitted electron; i.e., $E_B(i) = E_{IN} - E_{kin}(i)$. On the top of Fig. 2 we show the Auger binding-energy scale (referenced to the Fermi energy), where the binding energy of the C_{1s} fully screened state (286.5 ± 0.1 eV) is used as the initial energy E_{in} . Using this binding-energy scale we immediately see that the two high-energy peaks (shaded) are at the same binding energy as we recorded for the valence 4σ (11.8 eV) and $1\pi + 5\sigma$ (8.4 eV) states in photoemission. This fact has already been pointed out for the Auger spectra of CO on Cu(111).¹⁰ There are several important consequences of these data. (1) Since the binding energies in the Auger spectra agree with photoemission data for the single-valence hole states, the final state in the Auger decay is identical to the photoemission final state, which is a screened configuration. For example, the molecular-orbital configuration for the peak at ~ 12 eV in Fig. 2 is a hole in the 4σ and an extra electron in the 2π . But the CO molecule started with a configuration of a hole in the C_{1s} and an extra electron in the 2π . In the gas phase this 2π electron in the initial state would be an active participant in the decay, so the metal must furnish another electron to screen the valence hole. (2) There are no satellite lines present in the single-valence hole portion of the Auger spectra,⁸ and (3) the intensity of the $(4\sigma^{-1}, 2\pi)$ peak is large, while the 4σ molecular orbital is a lone pair on the oxygen end of the molecule and should have very small overlap with the C_{1s} hole. In the gas phase deexcitation spectra of CO, excited $C_{1s} \rightarrow 2\pi$, the 1π single-hole state is ten times bigger than the 4σ .^{22,23} The first two observations indicate that the Auger decay is considerably slower than the photoemission process, allowing time for screening without any shake-up lines. The final observation about the intensity variation is, we believe, also a consequence of the time evolution of the process. In a longer paper we will present a new empirical model for determining the intensities in the deexcitation spectra based on data from diatomic and triatomic molecules, carbonyl complexes, and adsorbed CO.

It is important to understand the consequence of the discussion concerning binding energy present in the previous paragraphs, so we present in Fig. 3 an expanded view of the deexcitation spectra compared to the direct photoemission spectra. Curve *a* is a photoemission spectra for CO adsorbed on Cu at 100 K, taken at a photon energy of $h\nu = 35$ eV, so that E_{IN} is 35 eV. Curve *c* is the Auger spectrum run using a photon energy of 311 eV, but E_{in} is the energy stored in the totally screened C_{1s} hole configuration, i.e., 286.5 eV. Notice that the two main peaks in both the photoemission spectrum and the Auger spectrum line up. However, there are no satellite lines on the Auger spectrum, while the satellite line on the 4σ is quite visible in the photoemission spectrum. Now in curve *b* we plot the deexcitation spectra from the resonant absorption experiment ($C_{1s} \rightarrow 2\pi$). The apparent value for the energy E_{IN} is 287.5 eV (Fig. 1). However, with use of this value the two valence peaks are both ~ 1 eV higher in binding energy than in either the Auger spectra or photoemission spectra. Obviously what happens is that the CO molecule excited $C_{1s} \rightarrow 2\pi$ is not in the fully screened state. It gives up the energy difference between the excitation energy 287.5 eV and the fully screened state 286.5 eV to the solid before the core-hole decays. Therefore the state formed by optical absorption $C_{1s} \rightarrow 2\pi$ is an intermediate state in the core-hole decay

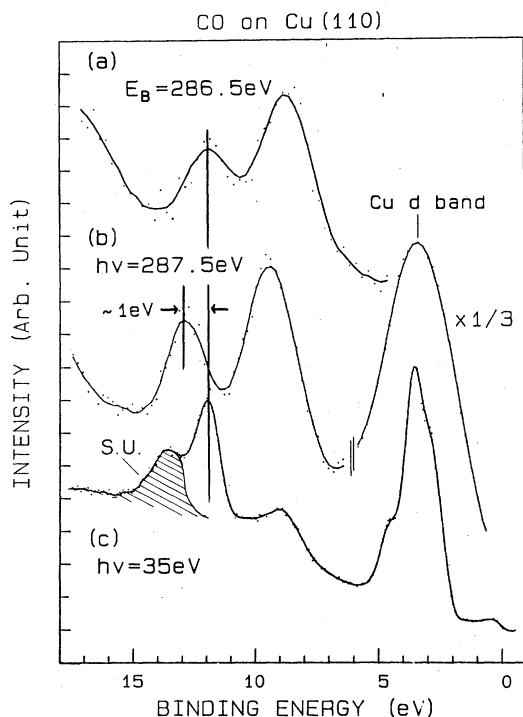


FIG. 3. A comparison of the binding energies for the single-hole valence portions of (a) the Auger spectrum, (c) the direct photoemission, and (b) the deexcitation spectrum following $C_{1s} \rightarrow 2\pi$ excitation. The Cu 3d bands seen in (b) are excited by direct photoemission not by the core-hole decay process. The shaded peak (S.U.) in curve (c) is the $4s$ shake-up.

process, relaxing into the fully screened core-hole state before the core-hole decays. This means that we should not use the $C_{1s} \rightarrow 2\pi$ photon energy to calculate binding energies, but instead the binding energy of the screened core-hole states.

This observation immediately explains one of the puzzles existing in the literature. In 1982 Loubriel, Gustafsson,

Johansson, and Oh²⁴ measured the deexcitation spectra for CO in Pt(111). Their conclusions, based on the assumption that the binding energy for the spectrum should be calculated using the measured 288 eV $C_{1s} \rightarrow 2\pi$ energy, led to contradictions with subsequent work.²⁵ If you use the screened core-level binding energy of 285.8 eV (Ref. 26) for Loubriel's data²⁴ there is no problem. This is the explanation offered earlier by Matthew, Ramaker, and Chesters.²⁷

There are two processes that may contribute to the energy difference between the excited ($C_{1s} \rightarrow 2\pi$) and the fully screened configurations. First, the optical absorption may be sudden in the sense that the excited configuration reorganizes itself after the excitation to minimize the energy. The time scale is too short for nuclear motion. Second, it is known from gas phase studies on CO that the lowest energy configuration of the $C_{1s} \rightarrow 2\pi$ state is the $^3\Pi$.²⁸ This state is 1.4 eV lower in energy than the optically allowed $^1\Pi$ state. The initially excited $^1\Pi$ state could decay into the $^3\Pi$ by exchange of electrons with the metal. The existing data indicate that the $^1\Pi$ -to- $^3\Pi$ exchange is probably not the major part of the energy difference. Stohr and Jaeger's data for adsorbed molecules indicate ~ 1 -eV differences between the core-hole binding energy and the resonant excitation energy,²⁹ independent of the core-hole identity. For the O_{1s} hole of CO the $^1\Pi \rightarrow ^3\Pi$ splitting is only ~ 0.6 eV.²⁸

These measurements show that core-hole decay for the low- z first-row elements is slow compared to the photoionization process. In fact, in the language of photoionization the Auger decay seems to be adiabatic. The intensity seen in the valence hole portion of the deexcitation spectra is quite different than would have been expected by looking at the overlap of the valence state with the core hole.

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