

## Dynamics of adsorbate core-hole decay. II. Lifetimes

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The carbon  $1s$ -to- $2\pi$  core-to-bound excitation energy and linewidth for CO adsorbed on Pt(111) are reported. A detailed comparison of these absorption data with the core-level photoionization and the electronic decay spectra shows that the optically excited  $C 1s \rightarrow 2\pi$  state decays to a fully screened core-hole state before the core hole decays. The mechanism of this relaxation is discussed. The lifetime contribution to the absorption linewidth for adsorbed CO is found to be equal to or larger than 0.25 eV.

The dynamics of the excitation and decay of a core electron of an adsorbed atom or molecule is still poorly understood, yet undoubtedly very important for understanding various spectroscopies.<sup>1-3</sup> The core-photoionization process is accompanied by vibrational or electronic excitations, charge transfer from the substrate, and internal charge rearrangement. This process can leave the adsorbate-substrate complex in a variety of possible excited states immediately after ionization. The lifetime of these excited states compared to the lifetime of the core hole will dictate the nature of the radiationless decay spectra. It is now possible using the tunability of synchrotron-radiation sources to begin probing the various lifetimes involved in the excitation and decay process.

Our previous study of the dynamics of adsorbate core-hole decay showed, for the system CO on Cu(110), that excited states (shakeup) created by ionization decay before the core hole decays.<sup>3-5</sup> In this paper a similar conclusion for CO on Pt(111) is made and the mechanism of the decay of these excited states is discussed. In addition, we present absorption and core-photoionization spectra for CO on Pt(111) to evaluate the relative lifetimes of the excited state created in absorption and the core-hole lifetime.

When a core electron is removed from an atom or molecule adsorbed on a metal surface, the metal tries to screen the hole by transferring charge into the lowest previously unoccupied molecular orbital. Depending upon how fast or efficient this charge transfer occurs, the photoelectron spectrum can be a single peak corresponding to a fully screened final state or a multitude of peaks corresponding to screened and unscreened final states. For the specific case of adsorbed CO the lowest-lying unoccupied molecular orbital is the  $2\pi$  state. All theoretical calculations agree that even in the most complicated core-level spectrum the lowest-binding-energy peak corre-

sponds to a CO molecule with a core hole and a screening electron in the  $2\pi$  orbital.<sup>6-9</sup>

Since the screened state of CO with a core hole is like an excited state of the molecule, it can be formed directly by tuning the photon energy to the core-to-bound absorption energy. This resonant photoabsorption creates one of the possible electronic excited states that result from photoionization and also allows one to investigate the lifetime and decay channels of this particular state. In Fig. 1 we compare photoabsorption spectra for the  $C 1s \rightarrow 2\pi$  transition in gas-phase CO (left) with CO adsorbed onto a Pt(111) surface at room temperature

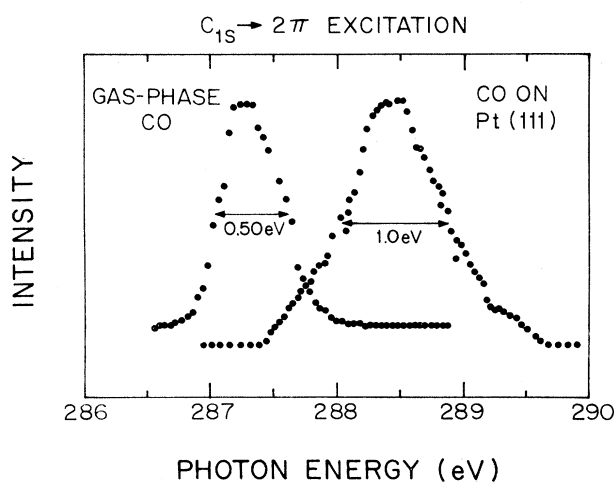


FIG. 1. Photoabsorption spectra of the  $C 1s \rightarrow 2\pi$  transition for gas-phase CO and CO adsorbed on Pt(111). The inherent widths of the gas-phase and adsorbed transitions are 0.1 and 0.98 eV, respectively.

(right). The gas-phase spectrum was recorded in a differentially pumped gas-phase chamber<sup>10</sup> as a calibration of the monochromator. The experimental linewidth of the gas-phase  $C\ 1s \rightarrow 2\pi$  transition is 0.5 eV compared to the inherent linewidth of  $\leq 0.1$  eV.<sup>11</sup> The absorption spectrum for adsorbed CO was acquired with an enhanced resolution of 0.25 eV. The gas-phase value of the absorption transition is 287.3 eV,<sup>11</sup> while there is a 1.2-eV shift to 288.5 eV for the adsorbed system with an increase in the linewidth to 1.0 eV. The inherent linewidth after removing the monochromator resolution is 0.98 eV. For comparison, the  $C\ 1s \rightarrow 2\pi$  transitions for CO on Ni(111), Ru(001), and Cu(100) occur at 287.0, 286.5, and 286.4 eV, respectively.<sup>3</sup> Therefore, compared to the only other data where the linewidth has been determined, the core-to-bound transition for CO on Pt(111) is anomalously large in energy.

Consider the origin of the linewidth of this absorption transition for gas-phase and adsorbed CO. The gas-phase line shape is proportional to the number of vibrational levels excited in the excitation from the CO ground state to the  $^1\Pi_u$  absorption state. The number of vibrational levels excited increases as the change in equilibrium bond length between the ground and excited states increases. High-resolution gas-phase absorption spectra<sup>11</sup> show vibrational excitations spaced 0.25 eV apart. Each of the excited  $^1\Pi_u$  vibrational levels has a width of less than 0.1 eV, which is proportional to the inverse of the excited-state lifetime. One possible explanation for the increase in the absorption linewidth for adsorbed CO could be based on the assumption that there is a larger difference between the ground state and  $^1\Pi_u$  equilibrium bond distances relative to the gas-phase difference, leading to more vibrational excitation in the absorption spectrum. The absorption linewidth could also be increased relative to the gas-phase value if there is significant lifetime broadening of the excited state. The broad 2.5-eV linewidth seen in the CO/Ni(111) absorption spectrum<sup>12</sup> has been attributed to lifetime broadening of the final state. The broadening is assumed to be a result of hybridization of the unoccupied  $2\pi$  state with the substrate states. Further methods that can increase the linewidth for the adsorbed species include the creation of phonons or electron-hole-pair excitations as a result of the absorption excitation. The absorption linewidth for adsorbed CO does not clearly show vibrational structure and the spectrum is relatively symmetric, while a molecular Franck-Condon envelope should be asymmetric. The lack of clear molecular vibrational structure in the high-resolution absorption spectrum indicates that *the lifetime contribution to the absorption linewidth is equal to or larger than the molecular vibrational spacing (0.25 eV)*. This analysis has neglected the effects of the phonon and electron-hole-pair excitations on the line shape. We also note that this line-shape analysis is complicated by the fact that CO is known to adsorb in two binding sites at these coverages<sup>13</sup> and, hence, the absorption spectrum could be composed of two peaks corresponding to the two absorption sites. The measured lifetime of  $\geq 0.25$  eV in chemisorbed CO is substantially larger than the lifetime of the equivalent state in the isolated gas-phase mol-

ecule, which is less than 0.1 eV.<sup>11</sup>

Our previous work<sup>5</sup> and this study indicate that the optically excited  $^1\Pi_u$  state of adsorbed CO decays to a lower-energy configuration before the core hole decays. The lifetime contribution to the linewidth is, therefore, proportional to the inverse lifetime of the state initially reached in absorption plus the inverse lifetime of the fully relaxed state.

The core-level photoelectron spectrum can provide information about the lifetime of the fully relaxed core-hole state reached following the decay of the state initially excited in absorption. The core-level photoelectron spectrum shown in Fig. 2 was acquired for a 10-L CO saturation coverage. [1 langmuir (L)  $\equiv 10^{-6}$  Torr sec.] A resolution of 0.65 eV was determined by measuring Pt 4f photoemission peak widths of 1.25 eV, which gives the instrument resolution when compared to the known inherent width.<sup>14</sup> We find that we can fit the spectrum with two Gaussian peaks of widths 1 and 0.8 eV separated by 0.8 eV as shown in Fig. 2. This gives inherent linewidths of 0.76 and 0.5 eV, respectively, to these transitions. Norton<sup>13</sup> has shown that these two peaks result from a bridged and terminally bound CO species and are not a result of a shakeup process. The core-photoelectron line shape is determined by the lifetime of the core hole and the molecular vibrational progression resulting from the excitation. The gas-phase core-photoelectron linewidth is 0.65 eV,<sup>15</sup> which is the envelope of five vibrational excitations of widths 0.32 eV separated by 0.33 eV. Thus the two deconvoluted peaks have widths similar to that seen in the gas-phase, which is reasonable, assuming that the molecular vibrational contribution to the line shape is similar in the gas phase and adsorbed phase.

We now turn to an analysis of the core-to-bound-state electronic decay spectrum to substantiate the claim above that the optically excited state created in absorption decays to a relaxed state before the core hole decays.

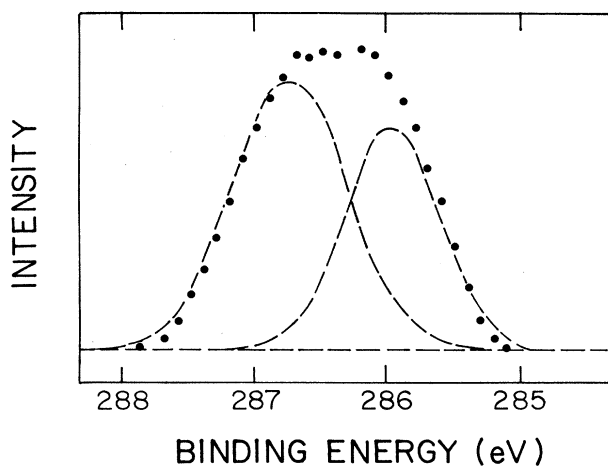


FIG. 2. Core-photoelectron spectrum for adsorbed CO taken at a photon energy of 370 eV. The inherent linewidths of the two peaks corresponding to the two binding sites are 0.76 and 0.5 eV.

The excited molecule decays predominantly by an Auger process with a neutral initial state. If the  $2\pi$  electron participates in the decay, the final state has one hole in the valence states of CO. If the  $2\pi$  is a spectator in the decay, there will be two holes in the valence states of CO. These two final states correspond, in general, to the ordinary and shakeup peaks in the photoemission spectrum of CO. Previous work has shown that the deexcitation spectra accentuate the two-hole-type states; however, the single-hole states are visible in the spectra.<sup>3,5,16,17</sup> In Fig. 3 we show a comparison of the photoemission spectrum [panel (a)] taken at a photon energy of 150 eV with the deexcitation spectrum following C  $1s \rightarrow 2\pi$  excitation [panels (b) and (c)]. These spectra were taken with a 30-L exposure of CO at room temperature. They are all plotted on a binding-energy scale ( $E_b = \hbar\omega - E_{\text{kinetic}}$ ). The scale at the top of Figs. 3(b) and 3(c) is the kinetic energy. The single-hole states from the adsorbed CO are shaded in Fig. 3(a). It should be noted that there never is a clear single-hole peak from the  $3\sigma$  state, presumably due to many-body interactions. In our spectrum the  $4\sigma$  peak has a binding energy of 11.7 eV and the  $1\pi+5\sigma$  peak appears at 8.6 eV. This is to be compared to the binding energies obtained by Norton *et al.*<sup>13</sup> of 12 and 8.9 eV, respectively. The difference is undoubtedly caused by our poorer resolution and consequent error in defining the Fermi energy. The inherent core-to-bound absorption

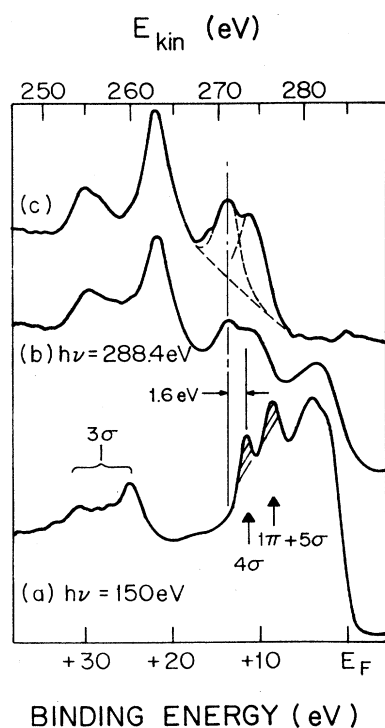


FIG. 3. (a) Photoemission spectrum of CO on Pt(111),  $h\nu = 150$  eV. (b) Deexcitation spectrum following C  $1s \rightarrow 2\pi$  excitation at  $h\nu = 288.4$  eV. (c) Deexcitation spectrum, (b), with a clean Pt(111) photoemission background for  $h\nu = 288.4$  eV subtracted.

width determines the energy resolution for the deexcitation process. The  $d$  bands are not resolved because they are from the direct photoemission process and the spectrum was accumulated with rather poor photon-energy resolution. A photoemission spectrum for clean Pt at 288.4 eV photon energy was obtained and subtracted from curve (b) to produce (c), which is the spectrum created by the core-hole decay.

The deexcitation spectrum shown in Fig. 3(b) is exactly the same as the spectrum previously reported by Loubriel *et al.*,<sup>17</sup> for this system and the difference curve (c) is nearly identical to the Auger spectrum published by Baker *et al.*<sup>18</sup> The fact that the deexcitation spectrum is similar to the Auger spectrum supports the assumption that the fully screened deexcitation and Auger initial states are the same. The two peaks in the (8–15)-eV binding-energy region of Fig. 3(c) are the  $4\sigma$  and  $1\pi+5\sigma$  hole states<sup>18</sup> seen in the photoemission spectrum at 1.6 eV lower binding energy. The 1.6-eV energy shift between the deexcitation spectrum [Figs. 3(b) and 3(c)] and the photoemission spectrum [Fig. 3(a)] is a consequence of the relaxation of the optically excited C  $1s \rightarrow 2\pi$  ( $^1\Pi_u$ ) state before core-hole decay occurs.<sup>5</sup> The fully screened C  $1s$  hole configuration is 1.6 eV lower in energy than the optically excited state. There are at least three processes that could account for this energy change. There is a  $^3\Pi$  state which is 1.4 eV lower in energy for gas-phase CO,<sup>19</sup> which could be reached from the  $^1\Pi$  state by exchange of electrons with the metal. Secondly, there could be charge redistribution following the sudden excitation.<sup>3,4</sup> Thirdly, there could be intramolecular vibrational relaxation from the vibrational state reached in the initial Franck-Condon absorption to the lowest vibrational state of the  $^1\Pi$  potential surface. The data show that the totally screened state of the CO molecule on the surface has an energy of  $288.4 - 1.6$  eV = 286.8 eV, which is identical to the value for the higher-binding-energy peak that we find in the C  $1s$  photoelectron spectrum in Fig. 2. This result proves that the optically excited  $^1\Pi_u$  state decays to a fully relaxed state before the core hole decays. The absorption and core-photoelectron spectra have indicated that the combined lifetimes of these two states is  $\geq 0.25$  eV.

The results above present the problem of firmly defining the mechanism for the relaxation from the state initially excited in absorption to the “fully relaxed core-hole state” lying 1.6 eV below the state initially reached following absorption. Is the relaxation a result of an intramolecular relaxation, or can the relaxation be explained by some substrate screening mechanism?<sup>3</sup> The observation of only the unrelaxed core-hole state in the absorption spectrum is an important point to consider. The fact that the relaxed core-hole state is not reached in the absorption process can be explained by the singlet-to-triplet conversion mechanism, since the lower-lying triplet state is optically inaccessible from the singlet ground state. If the relaxation mechanism is due to substrate screening, then we must explain why we do not observe the relaxed and unrelaxed states in absorption, given that it is well known that analogous relaxed and “shakeup” states are observed in the core-photoemission process for other systems.<sup>3</sup> This raises the possibility for

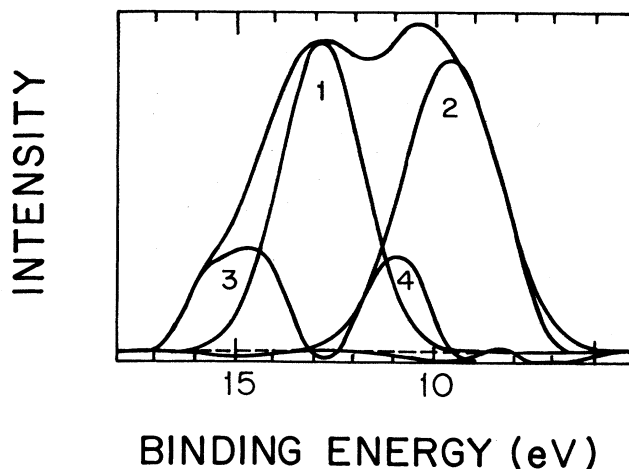


FIG. 4. Expansion of the  $4\sigma$  and  $1\pi+5\sigma$  region of the deexcitation spectrum [Fig. 3(c)]. Peaks 1,2 and 3,4 correspond to the  $4\sigma$ ,  $1\pi+5\sigma$  single-hole final states of the more and less populated CO binding configurations, respectively.

some dynamical difference in the time evolution of an absorption process versus a core-photoemission process.

Assume that the two binding configurations of CO create the two states seen in the core-photoelectron spectrum, and that these two states are the fully relaxed core-hole initial states for the Auger decay. Since the two binding sites have energetically different initial states, we should expect to see a doubling of the number of deexcitation final states. Figure 4 is an expanded view of the  $4\sigma$  and  $1\pi+5\sigma$  regions of the deexcitation spectrum, Fig. 3(c), following a background subtraction. Peaks 1 and 2 were required to have a separation seen in the photoemission spectrum with adjustable Gaussian amplitudes and widths, while peaks 3 and 4 are the result of subtracting peaks 1 and 2 from the spectrum. Peaks 3 and 4 are approximately 35% of the main intensity and are 1.3 eV higher in binding energy. These peaks are assumed to be the  $4\sigma$  and  $1\pi+5\sigma$  single-hole final states resulting from the decay of the less populated CO state seen in the core-photoelectron spectrum. The 0.8-eV splitting of the CO states in the core-photoelectron spectrum can partially explain the 1.3-eV rise of the binding energy of these weaker states. The 0.5-eV deficit in the binding-energy shift must be distributed between a difference in the core-to-bound excitation energies of the two binding

states and the single-hole binding energies of the two binding states. The C  $1s \rightarrow 2\pi$  transition energies are known to vary up to 1 eV depending on the substrate; hence, it is quite plausible that the absorption spectrum is composed of two peaks corresponding to the two binding configurations. The absorption spectrum can be fitted with two peaks spaced 0.2 eV apart with the peak corresponding to the less populated state shifted to a higher transition energy, consistent with the observed shift to higher binding energy in the deexcitation spectrum. The remaining (0.2–0.3)-eV energy shift needed to explain the 1.3-eV shift of the weaker CO deexcitation final states could be obtained from the difference in the single-hole binding energies for the two binding sites.

The widths of the Gaussians fitted to the deexcitation spectrum are approximately 2.5 eV compared to about 1.5 eV for the photoemission spectrum. Baker *et al.*<sup>18</sup> observed the same width in their Auger spectrum. The lifetime broadening of the peaks in this Auger spectrum should be the sum of the core lifetime and the valence hole lifetime. A 2.5-eV width is too large to be explained as a lifetime broadening. It is more likely that this width is caused by molecular vibrational excitations. Correia *et al.*<sup>20,21</sup> have demonstrated theoretically that vibrational excitations can considerably broaden the CO C  $1s$  deexcitation line shapes.

This work has defined two important issues in the study of the core-hole decay of adsorbates. The lifetime and vibrational contributions to the observed linewidths contain the essential information regarding the dynamics of core-hole-decay processes. We have shown that the lifetime contribution to the absorption linewidth is composed of contributions from the state initially excited in absorption and the fully relaxed core-hole state, resulting in a total absorption lifetime of  $\geq 0.25$  eV. Secondly, further work needs to be directed at understanding possible differences between the dynamics of a core-to-bound absorption process and the dynamics of a core-photoemission process. The problem is to explain why only a single final state is seen in the absorption process, while a multitude of relaxed and shakeup states can be seen in core-photoemission spectra. Further progress on this issue will provide more insight into the mechanism of the decay of the state initially excited in the core-to-bound transition.

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