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Theory of core-hole-decay dynamics of adsorbates on metal surfaces: Role of the $2\pi^*$ level of a chemisorbed CO molecule

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A comparative study of core-hole-decay dynamics is made for an adsorbate on a metal surface. On the basis of the available experimental results for a CO molecule chemisorbed on Cu(110) as a prototype system, we investigate the elementary processes of the core-hole decay via various new Auger channels open for adsorbates, i.e., the participation of an electron in the initially unoccupied level of the adsorbate is populated either by charge transfer from the substrate before core-hole decay or resonant core excitation and the crossed Auger transition involving a metal electron and valence electron of the adsorbate. We calculate the deexcitation spectrum following resonant core-to-bound excitation in the cases where the excited electron may become a spectator, or participate in, or escape before the Auger decay of the core hole. For a spectator decay leading to the final state composed of two valence holes and one electron in the initially occupied and empty levels, respectively, it is demonstrated that when the final-state configuration is unstable due to the decay into the metal the resultant deexcitation spectrum exhibits resonant-enhanced photoemission whose intensity is proportional to the population of the resonance state. We also calculated the deexcitation spectra due to a participant decay (autoionization) leading to a single valence-hole state and Auger spectra involving a screening electron transferred from the metal before the Auger decay of the core hole. These spectra are compared with the direct valence photoemission, in particular with a single valence-hole state screened by charge transfer from the metal. Absence of shakeup satellites in the deexcitation spectrum following resonant core-to-bound (e.g., C $1s \rightarrow 2\pi^*$ of a CO molecule) level excitation and the apparent mismatch of the binding energy of the screened final state between direct photoemission and normal Auger spectra and deexcitation spectra are explained in terms of the relaxation processes of the excited state before the Auger decay of the core hole.

I. INTRODUCTION

The electronic structures of an adsorbate on a metal surface, which is of eminent interest not only for its own right, but also for gaining deeper insight into the microscopic mechanisms of a wide variety of surface chemical reactions, have been studied using a variety of surface electronic spectroscopies, such as core [x-ray photoemission spectroscopy (XPS)] and valence [ultraviolet photoemission spectroscopy (UPS)] photoemission [photoemission spectroscopy (PES)] for the occupied states, inverse photoemission spectroscopy (IPS) for partially occupied or unoccupied states, and absorption spectroscopy (ABS) for the electronic transitions between the occupied and unoccupied states. Auger electron spectroscopy (AES), commonly used to probe the chemical species at or near surfaces, is also recognized as a useful tool to determine the energy levels and bonding configurations of adsorbates. A comparison of these surface electron spectroscopies has been presented in a review article of Plummer *et al.*[1] for a CO molecule on various metal surfaces as a prototype system.

Various theoretical works using the ABS,[2-4] PES,[5-7] and IPS (Refs. 8–10) processes of an adsorbate on a metal surface have revealed that the line shapes are characterized by the final-state relaxation due to the image potential and charge-transfer interaction between the adsorbate and metal. The complementary aspect of these electronic transitions has been clarified in detail,[11] which then allowed us to propose the semiqualitative energy diagram of a CO/Cu(110) system from a systematic analysis of the available experimental results.[12-15] Figure 1 shows the valence manifold of a CO/Cu(110) system for the present study of the core-hole-decay dynamics via the Auger transitions involving the 5σ or 4σ and empty $2\pi^*$ levels. In particular, the electronic properties of the $2\pi^*$ level have attracted interest because of their crucial roles in CO adsorption on metal surfaces.[16] The extent of the charge transfer of metal electrons into this level contributes to the determination of the CO-metal bonding strength. The electronic structure of the $2\pi^*$ level also plays a significant role in the vibrational properties of chemisorbed CO molecules, such as frequency shift,[17] vibrational damping,[18] and vibrational excitation via negative-ion resonances.[19] The correlation between the energy of the $2\pi^*$ level with adsorption bond strength[20] and C-O stretching frequency[21] for CO on various metal surfaces has also been reported.

The dynamics of adsorbate core-hole decay, via the Auger transition involving valence orbitals of chemisorbed molecules on metal surfaces, has recently attracted considerable interest. Loubriel *et al.*[22,23] reported that they observed resonantly enhanced photoemission for CO chemisorbed on Pt(111). According to their assignment, the resonant energy of a C $1s$ electron to the unoccupied $2\pi^*$ level (incident excitation energy $\nu = 288$

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eV) is followed by an Auger transition involving the valence manifold $n\sigma$ ($n=3$, 4, and 5) and 1π in the presence of an electron in the $2\pi^*$ level as a "spectator." They noted that most of the peak binding energies do not match those of either Auger or off-resonant photoemission. Accordingly, they claimed that the resonant photoemission near the C 1s threshold exists and assigned the resonance features to

$$(\mathrm{C}\ 1s^2)X^{10}2\pi^{*0} \rightarrow (\mathrm{C}\ 1s^1)X^{10}2\pi^{*1} \rightarrow (\mathrm{C}\ 1s^2)X^8 2\pi^{*1}\ ,$$

where X represents the $n\sigma$ ($n=3,4,5$), 1π, and $3d$ manifolds of levels. These final states can be understood as the photoemission shakeup state or as the Auger final state with a $2\pi^*$ spectator electron. Similar valence shakeup features of CO on Pt(100) were also observed by Grider, Purcell, and Richardson.[24] They reported that the weak structures, observed at the higher-energy side of the normal $5\sigma/1\pi$ and 4σ emissions, are associated with the creation of a Pt $4f$ core hole. The subsequent decay of the core hole via a direct recombination leads to Auger-like emission from the CO valence levels, which produces two holes and one electron in the final state of the adsorbate-metal system. Shortly after these observations, Johnson, Farrell, and Smith[25] reported the C KVV Auger contribution to the photoemission spectra for CO adsorbed on Pd(111) on passing through the resonance C $1s \rightarrow 2\pi^*$ excitation. In the spectral region of interest from a viewpoint of resonant-enhanced valence PES, they only observed the C KVV Auger peaks and photoemission from the substrate bands. This result showed no evidence for the resonantly enhanced PES involving a $2\pi^*$ spectator electron. Instead, they observed that the intensity of the Auger peak is enhanced as a result of the resonant C $1s \rightarrow 2\pi^*$ excitation at about 288 eV.

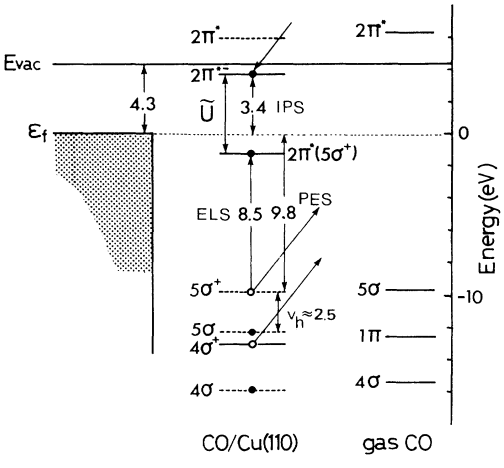

FIG. 1. Semiquantitative energy diagram of a CO/Cu(110) system on the basis of the available experimental data from IPS (Ref. 13), PES (Ref. 15), electron-energy-loss spectroscopy (EELS) (Ref. 14), where the superscripts + and − refer to the energy levels appropriate for the positive- and negative-charge final states, respectively, and $2\pi^*(5\sigma^+)$ stands for the $2\pi^*$ level in the presence of the 5σ hole. The ionization energies of the 5σ, 1π, and 4σ valence levels and the $2\pi^*$ affinity level of gas-phase CO are also shown for comparison. The ionization energy C 1s core level is 296.1 eV for gas-phase CO and the binding energy relative to the Fermi level is 286 eV for CO/Cu(100) (Ref. 12) (from Ref. 11).

A simple orbital picture describing the core-hole decay via various Auger processes following a resonant $|c\rangle \rightarrow |a\rangle$ excitation is schematically illustrated in Fig. 2. The electronic structure of the adsorbate consists of a core level $|c\rangle$ and two occupied valence levels $|v\rangle, |v'\rangle$ with energy ε_c and $\varepsilon_v, \varepsilon_{v'}$, respectively. The unoccupied level $|a\rangle$ reached by a resonant photoexcitation from the core level is located at ε_a above the Fermi level ε_F of the substrate. Such an initial-state configuration can be explicitly applied to a CO molecule on a metal surface, if one takes $|c\rangle = |1s\rangle$ and $|v\rangle$, $|v'\rangle = |5\sigma\rangle$, $|4\sigma\rangle$, or $|1\pi\rangle$, and $|a\rangle = |2\pi^*\rangle$. By absorbing the incident photon with energy ν, the core electron is excited to the unoccupied level $|a\rangle$ as shown in the upper panel. The system then relaxes to different final states via different Auger decay channels [Figs. 2(a)–2(e)] of the core hole. Process (a) of Fig. 2 corresponds to the case where the excited electron remains in $|a\rangle$ as a spectator for the valence Auger transition to reach the final-state configuration

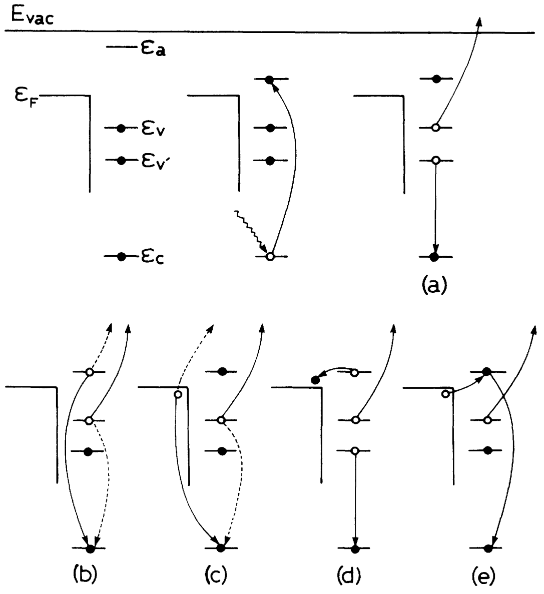

FIG. 2. Schematic orbital picture for core-hole decay via various Auger transitions following a resonant $|c\rangle \rightarrow |a\rangle$ excitation of an adsorbate on a metal surface. The electronic configuration of the ground state consists of the occupied core level with the energy ε_c, the valence levels $\varepsilon_v, \varepsilon_{v'}$, and the unoccupied level ε_a. Following the core-electron excitation by the incident photon, the system relaxes to the various final states via Auger decay of the core hole as illustrated in (a) two holes in $|v\rangle$ and $|v'\rangle$ and one electron in $|a\rangle$, (b) one valence hole in $|v\rangle$, and (c) two holes in $|v\rangle$ and in a substrate, and one electron in $|a\rangle$. The processes denoted by the dashed lines in (b) and (c) are the other processes leading to the equivalent final state, as far as the final-state energies are concerned. Process (d) shows a case where the excited electron decays into the metal continuum before core-hole decay, while in (e) the metal furnishes an electron to screen the valence hole, the screened counterpart of (b).

$v^{-1}v'^{-1}2\pi^{*+1}$. This can be viewed as either a modified Auger or modified PES in the sense that it is Auger in the presence of the excited electron or a shake-up of PES with a single ionized final state. For a gas-phase molecule, the CVV Auger kinetic energy ε_K is given by $\varepsilon_K = \varepsilon_c - \varepsilon_v - \varepsilon_{v'} - U_{vv'}$, where $U_{vv'}$ is the Coulomb interaction between holes in $|v\rangle$ and $|v'\rangle$. The above relation then gives us a guide to study what happens in the adsorbate system. In addition to the change of binding energies, $U_{vv'}$ is significantly reduced by metallic screening. If ε_v is taken as the highest valence level of the adsorbate, any Auger kinetic energy greater than $\varepsilon_c - \varepsilon_v - \varepsilon_{v'}$ arises from the transition involving the electronic states not present in the gas phase.

In process (b) of Fig. 2 the excited electron participates in the Auger transition to fill the core hole and the excess energy will be taken by the valence electron in $|v\rangle$. This participant decay corresponds to the so-called autoionization in the gas phase where the neutral excited state with a core hole decays to a one-hole final state, identical to that reached by valence photoemission. However, in the case of adsorbates on a metal surface, it is an open question whether autoionizing Auger decay and valence photoemission result in the same final state, because of the screening dynamics involved in these processes. Another way that we look at this process leading to a one-hole final state is shown by the dotted line in Fig. 2(b), where the valence electron fills the core hole and the electron in the $|a\rangle$ level is ejected as an Auger electron. For a strongly coupled adsorbate the $|a\rangle$ level can be populated through charge transfer from the substrate to screen the primary hole. The Auger decay then starts from the neutral initial state, despite the presence of the core hole, and hence the distinction between Auger and autoionization becomes meaningless. As discussed later, such an Auger process involving the screening electron in the $2\pi^*$ has been observed for off-resonant electron-excited Auger spectra of CO/Cu(111) and Pt(111).[26]

Process (c) of Fig. 2 is another case where the excited electron remains in $|a\rangle$ as a spectator of the crossed Auger process where a valence electron falls into the core hole and the metal electron is emitted. This process can be viewed as a screened peak of PES where the valence hole is screened by the resonantly excited electron. Such a screened final state can also be created by direct PES as a result of charge transfer from the metal, provided that the initial unoccupied $|a\rangle$ is pulled down below ε_F as a result of the hole potential to allow the charge transfer from the metal. Loubriel *et al.*[2,23] assigned the weak structures in the resonance spectrum to $5d^{-1}5\sigma^{-1}(1\pi^{-1})2\pi^{*+1}$ along process (c) of Fig. 2.

In the deexcitation process following the resonant excitation, the excited electron screens the core hole as long as it remains in $|a\rangle$. However, such an excited state will be unstable because of the interaction with the substrate, and it may escape before the Auger decay of the core hole [Fig. 2(d)]. As mentioned above, Johnson, Farrell, and Smith[25] observed the photoelectron spectra in the vicinity of the K edge for CO/Pd(111). The C CVV Auger peaks remain at fixed kinetic energies, while the Pd core- and valence-level photoemission peaks shift linearly as a function of the excitation energy. Since the gross features of the photoelectron spectra are almost the same at and off resonance, they concluded that the interpretation of the spectra does not depend on the occupancy of the $2\pi^*$ level and the $2\pi^*$ spectator electron should be omitted in the assignment by Loubriel *et al.*[22,23] It is also possible under appropriate conditions that the escape of the resonant excited electron to the metal continuum is accompanied by simultaneous back donation to the $|a\rangle$ level, leading to the screened relaxed state of a core hole, as shown in Fig. 2(e). When the transferred electron participates in the Auger transition with a single valence electron, the resultant final state will be the screened or unscreened valence hole seen in PES.

These contradicting results or the different ways of interpretation have since stimulated extensive experimental efforts associated with the evolution of the core-hole decay after its resonant or off-resonant excitation.[27-32] Among others, Chen *et al.*[27] have measured the kinetic-energy distribution of the electron emitted by nonradiative decay of the C 1s hole of CO adsorbed on Cu(110) as a function of the photon energy to create the core hole. The comparison of the single valence portion (binding-energy scale relative to the Fermi level ε_F) of (a) the Auger spectrum (excitation energy $\nu=311$ eV), (b) deexcitation spectrum at resonant C $1s \rightarrow 2\pi^*$ excitation ($\nu=287.5$ eV), and (c) direct photoemission ($\nu=35$ eV) is reproduced in Fig. 3. Chen *et al.* pointed out several consequences of these spectra. When the binding energy of the fully screened C 1s state at 286.5 eV is used as the

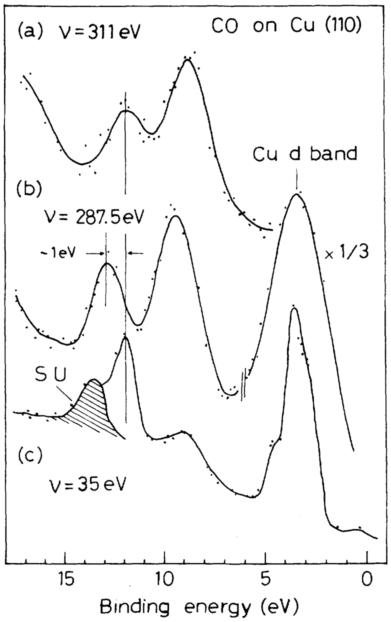

FIG. 3. Comparison of the binding energies for the single valence portions of (a) the Auger spectrum taken at primary excitation energy $\nu=311$ eV, but where the C 1s threshold 286.5 eV was used as the initial energy available for the Auger transition, (b) the deexcitation spectrum following C $1s \rightarrow 2\pi^*$ resonant excitation $\nu=287.5$ eV, and (c) direct photoemission at $\nu=35$ eV. The shaded peak (SU) in curve (c) is the 4σ shakeup (from Ref. 27).

effective initial energy instead of $\nu=311$ eV, or resonant excitation $\nu=287.5$ eV, the two main peaks corresponding to the screened $(1\pi+5\sigma)$ state at 8.4 eV and 4σ state at 11.8 eV in Auger and deexcitation spectra line up (Fig. 2 in Ref. 27). It is noted here that the deexcitation spectra were found to be nearly the same for $\nu=287-318$ eV, and they look similar to the electron-excited Auger spectra of CO/Cu(111).[26] This implies that the final state in the Auger decay is identical to the screened final state of the photoemission. Moreover, the system after primary core excitation relaxes to the fully screened core-hole state before the Auger transition takes places, so that the effective energy available for the Auger spectrum is not the apparent incident energy, but the screened core-hole binding energy. Consequently, Chen *et al.*[27] claimed that the excited state formed by resonant C $1s\rightarrow 2\pi^*$ optical absorption is an intermediate state in the core-hole-decay process, relaxing to the screened core-hole state before the core-hole decay. It is also important to note that Chen *et al.*[27] observed no satellite lines in the Auger spectrum or in the deexcitation spectrum taken at resonant excitation, whereas the direct valence PES observed at $\nu=35$ eV exhibits the shakeup satellite line on the 4σ peak, shaded peak SU in Fig. 3(c). The spectral shape of (a) and (b) of Fig. 3 are almost the same, except that the binding energies of the two valence peaks $(1\pi+5\sigma)$ and 4σ of the deexcitation spectrum are higher than those of the Auger [Fig. 3(a)] or photoemission [Fig. 3(c)] spectra. They claimed that the energy difference of about 1 eV between the excitation energy of 287.5 eV and the fully screened C 1s state at 286.5 eV is dissipated during the relaxation process of the resonant excited electron before the core-hole decay. A comparison of the PES at a photon energy 150 eV with the deexcitation spectrum following C $1s\rightarrow 2\pi^*$ excitation at 288.4 eV for CO/Pt(111) has also been made by Murphy *et al.*[28] The deexcitation spectrum was found to be the same as observed by Loubriel *et al.*[22,23] and is nearly identical to the Auger spectrum dominated by transitions involving the screening electron in the $2\pi^*$ level.

Wurth *et al.*[29,30] also investigated the decay of the resonantly excited C 1s core hole for CO/CU(100), Ni(111), and CO+K/Ni(111), which differ with each other in the bonding configuration and bonding strength. They showed that the final states resulting from the $2\pi^*$ participant Auger decay are not identical to that reached in valence PES, depending on the coupling strength between the $2\pi^*$ level and substrate and, more significantly, on the screening dynamics in the Auger and PES processes. For the C *KLL* spectrum of CO/Cu(100) at $1s\rightarrow 2\pi^*$ excitation, they observed a double-peak structure in the spectral region above 270 eV, which can be attributed to participant decay channels involving the $2\pi^*$ screening electron, in contrast to a single peak for CO/Ni(111). They interpreted the double peak as due to two different initial states from which the participant decay starts. One is the resonantly excited state with a $2\pi^*$ electron at ε_F, which represents a *partly* screened core hole, and the other is a *fully* relaxed final state before Auger decay occurs. Another experimental result to be mentioned here includes multielectron excitation in high-resolution PES of CO on Ni(100) by Nilsson and Martensson (NM).[31] They observed a number of additional resolved structures above the main C 1s and O 1s lines. In the C 1s spectrum, a low-energy satellite was interpreted as an excitation from bonding to antibonding $2\pi^*$-$3d$ combinations, not as due to the unscreened final state without charge transfer from the substrate to the $2\pi^*$ orbital.[6] In addition, they also observed new satellite peaks between the 3σ and 4σ valence PES peaks. According to their analysis based on the comparison of the C 1s and O 1s autoionization spectra, in which an intermediate neutral excited state decays into valence ionizated final states by Auger-like processes, the satellites are assigned to a mixture of the final states with two valence holes ($5\sigma^{-2}$, $5\sigma^{-1}1\pi^{-1}$, and $5\sigma^{-1}4\sigma^{-1}$) and one excited $2\pi^*$ electron. NM also commented that the above-described experimental results of Refs. 27 and 30 show the discrepancy in the kinetic-energy calibration of the spectra due to the different (Fermi and vacuum levels) reference levels and that the determined valence-electron binding energy depends on the accuracy of the used core-level binding energy.

The XPS core-level spectra of chemisorbed CO, exhibiting substantially different structures from free CO, have been one of the central issues associated with dynamic relaxation processes upon core-hole excitation. As an example of a strong CO chemisorption, the C 1s peak on Ni(111) exhibits an asymmetric Lorentzian shape.[32] The asymmetry of the peak, which is indicative of the threshold, was interpreted as a manifestation of the Anderson *orthogonality catastrophe*[33] or *infrared divergence*[34] due to low-energy electron-hole pair shakeup excitation within the fractionally occupied $2\pi^*$-derived resonance formed by charge transfer from the substrate.[5] The core-level threshold energy is then determined by the final-state relaxation shift by the hole-image potential and chemical shift associated with the change in the occupation in the resonance state induced by the core-hole potential. The dynamical screening model based on the $2\pi^*$ resonance has been recently extended by Lovric, Gumhalter, and Wandelt[35] to explain the satellite structure in the C 1s XPS spectra of the weak chemisorption system CO/Cu(100).[14,36–38] However, a number of observations which contradict this picture have been reported[31,39–41] and the existence of the $2\pi^*$ resonance for chemisorbed CO still remains an open question.[16] In the absence of hybridization of the $2\pi^*$ orbital with broad substrate bands leading to the resonance state in the initial state, the XPS core-level spectra are characterized by the position of the $2\pi^*$ level pulled down by U_{ac} from ε_a in the presence of a core hole, relative to ε_F. In an analogous problem of metals with incomplete shells,[42] the photoelectron spectra of a core electron exhibit an edge singularity *ca*: $\varepsilon_a-U_{ac}-\varepsilon_c$ for $\varepsilon_a-U_{ac}<\varepsilon_F$, while at ε_F for $\varepsilon_a-U_{ac}>\varepsilon_F$.[7,11] In real systems the edge singularity is round off by the finite lifetime of the core hole into skew Lorentzian shape.[43,44] On the other hand, the broader and asymmetric core-level spectra of CO on Ni(100) and Cu(100) have been recently explained in terms of vibrational excitation in the final core-ionized state.[38,45] Core-level binding energy was shown to be sensitive to the adsorption site, and the temperature-dependent line shape was reproduced by the model calculation using the potential-energy curve for a CO/Ni system. Further experimental and theoretical works need to be directed at the line shape of the core-level spectra not only from its own interest, but also in conjunction with the deexcitation and autoionization processes after resonant core-to-bound excitation for chemisorbed CO.

In a preceding work[46] we have studied the elementary processes of the core-hole decay via various Auger transitions involving the creation of valence holes in the adsorbate-metal system. A central issue of this problem is that the electron, resonantly excited to a highly localized state, may escape before, participate in, or serve as a spectator to the Auger decay of the core hole.[47] The relaxation processes toward the valence final states after resonant excitation of a core hole are crucially dependent on the residence time scale of the excited electron in the $|a\rangle$ state, relative to the core-hole lifetime due to the various Auger processes. The key to clarifying this mechanism is the role of the $|a\rangle$ state in the relaxation process and its coupling to the substrate. There are two types of participant decay of the core hole. One is the excited state with the $|a\rangle$ electron slightly above the Fermi level, which represents an incomplete screened core-hole state because of the finite lifetime effect. The other is the complete screening of the core hole before Auger decay occurs. A similar argument also holds for the characteristic difference of the XPS spectra and of the decay of autoionizing core-hole states between weakly and strongly chemisorbed CO molecules. These aspects have been incorporated into the treatment by the position of the $|a\rangle$ level in the presence of the core hole. When the $|a\rangle$ level is pulled down below ε_F, the excited electron cannot escape before the core-hole decay and it participates in or becomes a spectator of the core-hole decay. In the opposite situation there are three channels, as mentioned above. When it decays before the core-hole decay via the Auger transition involving the two valence levels, the resultant photoelectron can be interpreted as the Auger electron in the sense that it has a fixed kinetic energy. In other words, the primary excitation process and subsequent Auger decay can be viewed as two independent processes. Only when the excited electron is fairly localized in the $|a\rangle$ state, with small decay probability into the substrate continuum, may it participate in the core-hole decay and be responsible for the resonantly enhanced valence shakeup satellite. If it is directly involved in the Auger transition, the final state reached by this process is identical to that by direct ionization from the valence level.

In this paper we present a comparative study of core-hole-decay dynamics of an adsorbate on a metal surface. We study the valence photoelectron composed of Auger and photoemission via the Auger decay of the photoinduced core hole. The Auger electron can be distinguished from photoemission because the energy of the photoemission peak increases with that of the incoming photon (in a binding-energy scale, it remains fixed), while the energy of the Auger electron does not depend on the excitation energy. This is analogous to the distinction between Raman scattering and luminescence. On the basis of the experimental results for a CO/Cu discussed above, we study the elementary processes of a core-hole-decay dynamics via various Auger channels open for adsorbates. We focus our interest on the participation of an electron in the initially unoccupied level created by either direct core excitation or charge transfer from the substrate and the crossed Auger transition involving a metal electron. The deexcitation spectrum following resonant core-to-bound excitation is calculated for the cases where the excited electron may become a spectator, participate in, or escape before Auger decay of the core hole. In these processes an intermediate neutral excited state with a core hole decays to into various valence-ionized states by Auger transitions. We clarify under which conditions a spectator decay gives rise to resonant enhanced photoemission. We also calculate the deexcitation spectrum due to participate decay (autoionization) leading to the final state having one valence hole. This is then compared to a direct valence photoemission and Auger spectra involving a screening electron transferred from the metal in the Auger decay of a core hole, in conjunction with the experimental results of Chen *et al.*[27]

II. DEEXCITATION SPECTRUM FOLLOWING RESONANT EXCITATION

We consider the following model Hamiltonian of the adsorbate-metal system:

$$\begin{aligned} H = {} & \left[\varepsilon_a - U_{ac}(1-n_c) - \sum_{i=v,v'} U_{ai}(1-n_i) \right] n_a \\ & + \varepsilon_c n_c + \sum_{i=v,v'} \varepsilon_i n_i + U_{vv'} n_v n_{v'} \\ & + \sum_k \varepsilon_k n_k + \sum_k (V_a c_a^\dagger c_k + \text{H.c.}) \,, \end{aligned} \tag{1}$$

where ε_a is the initially unoccupied level $|a\rangle$ which is pulled down by U_{ac} (U_{av}) in the presence of a core (valence) hole, $\varepsilon_{v(v')}$ is the energy of the valence levels, and $U_{vv'}$ represents the intra-atomic Coulomb interaction between them. The energy levels of the adsorbate are measured with respect to the Fermi level ε_F. The adsorbate interacts with the metal state ε_k via V_a. The core-level number operator n_c takes 1 in the initial and final states, and becomes zero in the intermediate state, while $n_v = n_{v'} = 1$, $n_a = 0$ in the initial state, and their final-state occupations depend on the Auger-decay processes defined below.

The deexcitation or photoelectron spectrum via the Auger transition H_A following radiative core excitation H_R is calculated by the formula

$$P(\nu,\varepsilon) = \sum_p \sum_f \left| \left\langle f \left| H_A \frac{1}{\nu + E_i - H - H_A} H_R \right| i \right\rangle \right|^2 \delta(\omega + E_i - E_f)\, \delta(\varepsilon - \varepsilon_P) \,, \tag{2}$$

where $\omega=\nu-\varepsilon$ is the binding energy of the photoelectron. We consider resonant excitation in which the core electron is excited to the unoccupied level $|a\rangle$ by $H_R=M_{ac}c_a^\dagger c_c+\text{H.c.}$ Equation (2) is rewritten as

$$P(\nu,\varepsilon)=\frac{|M_{ac}|^2}{\pi}\operatorname{Im}\sum_p\langle i|c_c^\dagger c_a A^*(\nu)H_A R(z)H_A A(\nu)c_a^\dagger c_c|i\rangle\delta(\varepsilon-\varepsilon_p)\ , \tag{3}$$

where

$$A(\nu)=\frac{1}{\nu+E_i-H(n_c=0)-i\Gamma_c}\ , \tag{4}$$

$$R(z)=\frac{1}{z+E_i-H(n_c=1)},\quad z=\nu-\varepsilon-i\zeta,\quad \zeta\to0+\ , \tag{5}$$

and Γ_c is introduced to describe the core-hole lifetime due to virtual Auger transitions. When a core electron is excited to a highly localized state, the excited electron may be (1) a spectator [Fig. 2(a)], (2) participate in [Fig. 2(b)], or (3) escape before [Fig. 2(d)] Auger decay of the core hole. We first study the former two processes, viz.,

$$H_A=M_{vv'}c_c^\dagger c_p^\dagger c_v c_{v'}+M_{av}c_c^\dagger c_p^\dagger c_v c_a+\text{H.c.}, \tag{6}$$

where $c_p^\dagger$ is the creation operator of a photoelectron. We then obtain, from Eq. (3),

$$P(\nu,\varepsilon)=\frac{|M_{ac}|^2}{\pi}|A_{ac}(\nu)|^2\operatorname{Im}[M_{vv'}^2R_{avv'}(z)+M_{av}^2R_v(z)]\ , \tag{7}$$

$$A_{ac}(\nu)=\langle i|c_c^\dagger c_a A(\nu)c_a^\dagger c_c|i\rangle\ , \tag{8}$$

$$R_{avv'}(z)=\langle i|c_p c_a c_v^\dagger c_{v'}^\dagger R(z)c_p^\dagger c_a^\dagger c_v c_{v'}|i\rangle\ , \tag{9}$$

$$R_v(z)=\langle i|c_v c_p^\dagger R(z)c_p^\dagger c_v|i\rangle\ . \tag{10}$$

Equation (8) determines the excitation profile of the photoelectron spectrum, and Eqs. (9) and (10) describe the final states of two valence holes with a spectator electron and single valence hole, respectively. For a gas-phase molecule ($V_a=0$), we immediately obtain the deexcitation (Auger) spectrum

$$P_A(\varepsilon)=|M_{ac}|^2\left[\frac{|M_{vv'}|^2}{[\varepsilon+(\varepsilon_c+U_{ac})-(\varepsilon_{vv'}+U_{av}+U_{av'})]^2+\Gamma_c^2}+\frac{|M_{av}|^2}{[\varepsilon+\varepsilon_c-(\varepsilon_v+U_{vv'})-(\varepsilon_a-U_{ac})]^2+\Gamma_c^2)}\right], \tag{11}$$

peaked at

$$\begin{aligned}\varepsilon&=-(\varepsilon_c+U_{ac})+(\varepsilon_{vv'}+U_{av}+U_{av'})\ ,\\ \varepsilon_{vv'}&=\varepsilon_v+\varepsilon_{v'}+U_{vv'}\ ,\end{aligned} \tag{12}$$

$$\varepsilon=-\varepsilon_c+(\varepsilon_v+U_{vv'})+(\varepsilon_a-U_{ac})\ , \tag{13}$$

where the terms in the parentheses of Eq. (12) represent the binding energy of core and valence electrons in the presence of the spectator electron in the $|a\rangle$ level. For the gas-phase CO molecule at resonant C $1s\rightarrow2\pi^*$ excitation at 287.3 eV,[48] the first term may correspond to the final-state configuration with $1\pi^{-1}5\sigma^{-1}2\pi^{*+1}$ at $\varepsilon_K=264.3$ eV, $4\sigma^{-1}5\sigma^{-1}2\pi^{*+1}$ at $\varepsilon_K=259.9$ eV, and so on, while the second one to $5\sigma^{-1}$, $1\pi^{-1}$, and $4\sigma^{-1}$ at $\varepsilon_K=273.3$, 270.5, and 267.5 eV, respectively, which are absent at off-resonant excitation. In a binding-energy scale taking $\nu=(\varepsilon_a-U_{ac})-\varepsilon_c$ as the excitation energy, Eq. (13) leads to $\omega=\nu-\varepsilon=-(\varepsilon_v+U_{vv'})$, corresponding to a single valence hole. This means that, for a free molecule, autoionization (Auger decay with participation of a resonantly excited electron) final states are identical to the final states reached by direct photoemission.

For an adsorbed molecule the interaction with the substrate occurs at every stage. In particular, a resonant excited electron is no longer stable against its decay to the substrate continuum, and the screening electron as well as the resonant-excited one may participate in deexcitation (Auger) processes. In what follows we investigate possible elementary processes of a core-hole decay which result in single- and double-hole final states of the valence manifold. For spectator decay, when the final-state interaction is taken into account, Eq. (9) is calculated as

$$R_{avv'}(z)=\frac{1}{z+\varepsilon_{vv'}-\varepsilon_{avv'}-\Sigma_{vv'}(z)}\ , \tag{14}$$

where $\varepsilon_{avv'}=\varepsilon_a-U_{av}-U_{av'}$ and the self-energy

$$\Sigma_{vv'}(z)=\sum_{k>k_F}\frac{|V_a|^2}{z+\varepsilon_{vv'}-\varepsilon_k} \tag{15}$$

has a finite imaginary part $\Gamma_{vv'}$ when ω approaches $\omega_B=\varepsilon_{avv'}-\varepsilon_{vv'}$ for $\varepsilon_{avv'}>\varepsilon_F$, viz., the excited electron in the presence of the two valence holes is unstable because of the decay to the substrate. We then obtain, from Eqs. (8) and (14),

$$P_{avv'}(\nu,\varepsilon;\omega)=\frac{|M_{ac}|^2|M_{vv'}|^2}{\pi}|A_{ac}(\nu)|^2 \times\frac{\Gamma_{vv'}(\omega)}{(\omega-\omega_B)^2+\Gamma^2_{vv'}(\omega)}\ , \tag{16}$$

where the real part of the self-energy is neglected for simplicity. It is obvious that $P_{avv'}$ shows a peak at $\omega=\omega_B$, irrespective of ν. In this sense Eq. (16) represents a valence shakeup PES with a singly ionized final state, although having two valence holes and one spectator electron. If we use the resonant excitation energy $\nu_{\text{res}}=(\varepsilon_a-U_{ac})-\varepsilon_c$, Eq. (16) shows the same peak as Eq. (12) in a kinetic-energy scale. Hence the distinction between PES and Auger processes becomes meaningless at resonant excitation.

As shown above, the electron excited into $|a\rangle$ may decay to the substrate with a rate given by $\pi\rho|V_a|^2$, ρ being the constant density of states of the metal. When this occurs before the decay of core hole [Fig. 3(d)], it is appropriate to expand Eq. (4) with respect to V_a and we obtain

$$P(\nu,\varepsilon;\omega)=\frac{|M_{ac}|^2|M_{vv'}|^2|V_a|^2}{\pi}|A_{ac}(\nu)|^2 \times\sum_{k>k_F}|\langle i|c_c^\dagger c_k A(\nu)c_k^\dagger c_c|i\rangle|^2 \times\text{Im}[\langle i|c_{v'}^\dagger c_v^\dagger c_k c_p R(z)c_p^\dagger c_k^\dagger c_v c_{v'}|i\rangle]\ , \tag{17}$$

where the second factor $\langle i|c_c^\dagger c_k A(\nu)c_k^\dagger c_c|i\rangle$ describes the process where the core electron is indirectly excited to the metal via $|a\rangle$. The last term, corresponding to the final state with two holes in the valence levels and one electron in the metal, is calculated as

$$R_{kvv'}(z)=\frac{1}{z-\varepsilon_k+\varepsilon_{vv'}-\Sigma_{vv'k}(z)}\ , \tag{18}$$

where the self-energy

$$\Sigma_{vv'k}(z)=\sum_{k'<k_F}\frac{|V_a|^2}{z-\varepsilon_k+\varepsilon_{k'}+\varepsilon_{vv'}-\varepsilon_{avv'}} \tag{19}$$

has no imaginary part for $\varepsilon_{avv'}>\varepsilon_F$. In this case Eq. (17) gives the so-called *CVV* Auger spectrum

$$P_{CVV}(\nu,\varepsilon;\omega)=|M_{ac}|^2|M_{vv'}|^2|A_{ac}(\nu)|^2 \times\frac{\rho|V_a|^2}{[\varepsilon+\varepsilon_c-(\varepsilon_v+\varepsilon_{v'}+U_{vv'})]^2+\Gamma_c^2} \times\Theta(\nu+\varepsilon_c-\varepsilon_F)\ , \tag{20}$$

where the step function Θ describes the threshold of a core-electron excitation into the continuum above ε_F.

In addition to the intra-Auger transition given by Eq. (4), there is a crossed Auger transition involving an electron in the substrate, viz.,

$$H_A=M_{vm}\sum_{k<k_F}c_c^\dagger c_p^\dagger c_k c_v+\text{H.c.} \tag{21}$$

We then obtain, from Eq. (3),

$$P(\nu,\varepsilon;\omega)=\frac{|M_{ac}|^2|M_{vm}|^2}{\pi}|A_{ac}(\nu)|^2 \times\text{Im}\sum_{k<k_F}\langle i|c_v^\dagger c_k^\dagger c_a c_p R(z)c_p^\dagger c_a^\dagger c_k c_v|i\rangle\ . \tag{22}$$

If we assume the Lorentzian density of states for d electrons, characterized by the central energy ε_d, width γ_d, and maximum ρ_d/γ_d^2, Eq. (22) gives the resonance PES corresponding to the $d^{-1}v^{-1}a^{+1}$ final state:

$$P(\nu,\varepsilon;\omega)=\frac{|M_{ac}|^2|M_{vm}|^2}{\pi}|A_{ac}(\nu)|^2 \times\frac{\rho_d}{[\omega-(\varepsilon_a-U_{av})+(\varepsilon_v+U_{vv'})+\varepsilon_d]^2+\gamma_d^2}\ . \tag{23}$$

Since the central energy of the d band is located above the valence levels of the adsorbate, the binding energy of Eq. (23) is lower than that of the $v^{-1}v'^{-1}a^{+1}$ final state. Figure 4 shows an example of the evolution of the total photoelectron $P(\nu,\varepsilon;\omega)$ spectra in the binding-energy scale [sums of Eqs. (16), (20), and (23)] and their excitation profile $|A(\nu)|^2$, where the Auger peak of Eq. (20) shifts as $\omega=\nu+\varepsilon_c-\varepsilon_{vv'}$. Here we used a set of parameters $\varepsilon_a=3.5$ eV, $U_{ac}=1.5$ eV, $\varepsilon_v=-10.0$ eV, $\varepsilon_{v'}=-12.5$ eV, $U_{vv'}=1.2$ eV, $U_{av}=U_{av'}=0$, $\varepsilon_d=3.0$ eV, $\varepsilon_c=-285.5$ eV, $\rho|V_a|^2=1.0$ eV, $\Gamma_c=2.0$ eV, and $\gamma_d=1.0$ eV. The reason for this choice has been described in detail elsewhere.[46] Also shown in Fig. 4 are the final-state configurations corresponding to the Auger and PES peaks. Figure 4 exhibits two PES peaks for $\nu<\varepsilon_F-\varepsilon_c$, and the envelope of these peaks follows the excitation profile. For $\nu>\varepsilon_F-\varepsilon_c$ the Auger peak begins to appear and shifts as a function of ν. The Auger and PES peaks are almost amalgamated into a single peak at $\nu=289$ eV, i.e., $\nu=\varepsilon_a-\varepsilon_c-(U_{av}+U_{av'})$, beyond which

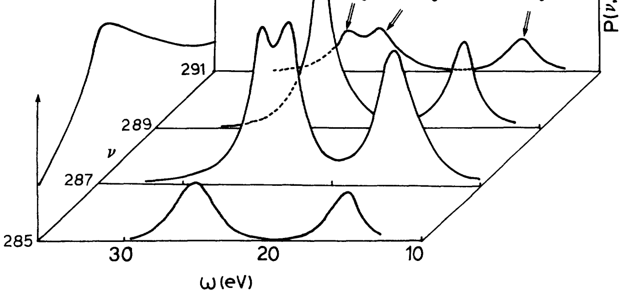

FIG. 4. Evolution of the photoelectron spectra $P(\nu,\varepsilon;\omega)$ in a binding energy scale ω as a function of the incident photon energy ν and the excitation profile $A_{ac}(\nu)$. See the text for the parameters used in this calculation. Also shown are the final-state configuration of the $v^{-1}v'^{-1}$ Auger, $v^{-1}v'^{-1}a^{+1}$, and $d^{-1}v^{-1}a^{+1}$ photoemission.

they are again separated. Loubriel *et al.*[22,23] assigned the peaks at 23 and 14 eV as resonant-enhanced PES of $5\sigma^{-1}1\pi^{-1}2\pi^{*+1}$, respectively. However, there is no reason to be convinced that the resonant-excited electron does not escape before Auger decay of the core hole. When it decays to the continuum of the substrate before Auger decay, we obtain the normal crossed Auger transition, which gives rise to a final-state configuration $d^{-1}v^{-1}$. It has been argued by Matthew *et al.*[47] that the prominent peaks postulated as resonant-enhanced PES by Loubriel *et al.*[22,23] agree closely with the electron-excited Auger-yield curve for CO/Pt(111) (Ref. 49) and with the estimated energies for $1s \rightarrow 1s^{+2}5d^{-1}(5\sigma^{-1},1\pi^{-1})$ and $1s^{+2}5d^{-1}4\sigma^{-1}$. It is important to remark that a clear distinction between resonant PES and Auger emission should be made by tuning the incident photon energy ν in the vicinity of a core excitation to the $|a\rangle$ level and ε_F. For a CO/Pd(111) system, the photoelectron spectra were taken at $\nu = 283-303$ eV,[25] which covers the energy region of interest; namely, the C 1*s* binding energy with respect to ε_F is 285.6 eV and the C $1s \rightarrow 2\pi^*$ excitation energy is estimated to be about 288 eV from the photon energy dependence of the intensity of the Auger peak. According to this observation, C *CVV* Auger peaks start to appear at and above $\nu = 288$ eV, below which the spectrum only exhibits the Pd valence photoemission whose peak positions shift to the higher-kinetic-energy side with an increase of ν. This seems to suggest that the decay of a resonant-excited electron to the substrate takes place before Auger decay of core hole, and the process described by Eq. (16) is unlikely for a CO/Pd(111) system, where the resonantly excited electron may become an active participant in Auger decay.

A possibility of spectator decay following resonant excitation has been demonstrated for a CO/Ni(110) system.[39] The photoemission spectra in the valence-ion region exhibited interesting evolution as a function of photon energies. Below C $1s \rightarrow 2\pi^*$ excitation at 288 eV, the spectrum showed $5\sigma + 1\pi$ and 4σ features at the expected binding energies. At the resonance several intense peaks appeared at higher energies. Such resonance-enhanced features were also observed at the same binding energy for O $1s \rightarrow 2\pi^*$ resonance at 535.0 eV. For excitations between these resonances, the spectra were composed of the normal valence photoemission peaks at fixed binding energies and two-valence-hole Auger peaks shifted for different photon energies. The observed resonance feature is clear evidence that the intensity is proportional to the population of the $2\pi^*$ level, and the most intense peak was assigned as a superposition of $5\sigma^{-1}1\pi^{-1}2\pi^{*+1}$ and $1\pi^{-2}2\pi^{*+1}$ configurations. Both CO/Ni and CO/Pd belong to a strongly chemisorbed system and show similar valence PES spectra characterized by the well-screened configuration $M^{-1}5\sigma^{-1}/1\pi^{-1}2\pi^{*+1}$ and $M^{-1}4\sigma^{-1}2\pi^{*+1}$, where M denotes the metal level. It remains to be answered why the former exhibits the resonance-enhanced PES due to a spectator Auger decay of the core hole, while the latter does not.

Let us next study participant decay leading to a single-valence-hole state given by Eq. (10). This final state is reached by the process in which the excited electron fills the core hole and the excess energy is taken by a valence electron (and vice versa). The binding energy of this photoelectron is exactly the same as that from the direct PES process at off resonance. It is well understood that the valence PES of a chemisorbed CO molecule exhibits a multitude of satellite lines due to multielectron excitation in which the photoinduced valence hole is screened by charge transfer from the metal to the $2\pi^*$ level.[50] For strongly chemisorbed CO the spectral weight is almost dominated by the fully screened final state, while it is shared by the screened and unscreened states for weakly chemisorbed CO. As studied in detail before,[7,11] Eq. (10) gives an unscreened spectrum with a Lorentzian shape centered at $\omega \sim -\varepsilon_v - U_{vv'}$ and a screened one characterized by a skewed Lorentzian shape at $\omega \sim -(\varepsilon_v + U_{vv'}) + (\varepsilon_a - U_{av}) - \varepsilon_F$. Deexcitation spectra observed at resonant C $1s \rightarrow 2\pi^*$ excitation of CO/Cu(110) and Pt(111) exhibited only the screened peak, while the normal PES of the former system shows a shakeup satellite [the photoemission final state of CO/Pt(111) is a screened configuration at off-resonant excitation]. This finding implies that the final valence-hole state via resonant excitation always has a screened configuration irrespective of the strength of the adsorbate-metal coupling. There are two possible pathways through which the resonant excitation causes the screened final state of the valence hole. First is a case where the excited electron remains in the $|a\rangle$ level as a spectator of the crossed Auger transition of Eq. (21). If we assume an *s* electron with a rectangular density of states ρ within the energy range from $\varepsilon_F - D$ to $\varepsilon_F + D$ in Eq. (22), we obtain

$$
\begin{aligned}
R_{av}(z) &= \sum_{k<k_F} \langle i | c_v^\dagger c_k^\dagger c_a c_p R(z) c_p^\dagger c_a^\dagger c_k c_v | i \rangle \\
&= \sum_{k<k_F} \frac{1}{z - (\varepsilon_a - U_{av}) + (\varepsilon_v + U_{vv'}) + \varepsilon_k} \\
&= \rho \left[\ln \left| \frac{\omega'}{\omega' - D} \right| + i\pi [\Theta(\omega') - \Theta(\omega' - D)] \right], \\
&\qquad \omega' = \omega - (\varepsilon_a - U_{av}) + (\varepsilon_v + U_{vv'}) + \varepsilon_F \;, \qquad (24)
\end{aligned}
$$

showing a logarithmic singularity at

$$\omega = (\varepsilon_a - U_{av}) - (\varepsilon_v + U_{vv'}) - \varepsilon_F \;. \qquad (25)$$

This is nothing but the lowest-order contribution to a screened final state of the valence PES for $\varepsilon_a - U_{av} < \varepsilon_F$. A collection of the higher-order singularities leads to the screened peak, which diverges in a power law[7] or an asymmetric Lorentzian in the presence of a lifetime broadening.[43,44] It is important to note that the screening charge for the valence hole is directly created by a resonant photoexcitation from the core level, not by the charge transfer from the substrate. The same screened valence-hole state can also be reached by the final-state interaction of a single-valence-hole state given by Eq. (10) as

$$R_v(z) = \left| \frac{V_a}{\omega + \varepsilon_v + U_{vv'}} \right|^2 R_{av}(z) \;. \qquad (26)$$

Adding the unscreened PES spectrum given by a simple Lorentzian shape centered at $\omega=-\varepsilon_v-U_{vv'}$, we obtain the valence PES spectrum, from Eq. (10),

$$P(\omega)=\frac{1}{\pi}\operatorname{Im}R_v(z)$$
$$=\rho|V_a|^2\left[\frac{1}{(\omega+\varepsilon_v+U_{vv'})^2+(\pi\rho V_a^2)^2}+\frac{1}{(\omega+\varepsilon_v+U_{vv'})^2}\left[\frac{\omega'}{D}\right]^{-\alpha}\Theta(\omega')\right], \quad (27)$$

where $\alpha=2g-g^2$, $g=\rho|V_a|^2/(\varepsilon_F-\varepsilon_a-U_{av})$. Consequently, when the photoexcited electron directly participates in Auger decay of the core hole, we expect a resonantly enhanced valence PES whose structure is the same as that observed at off-resonant excitation. Equation (26) also suggests that the intensity of the screened peak via the direct photoionization of the valence electron followed by the nonadiabatic charge transfer from the substrate is weaker than that via the Auger process, leaving the photoexcited electron in the $|a\rangle$ level as a screening charge. This is simply because in the latter case the screening charge is directly created by resonant excitation, not by charge transfer from the metal. We then expect that no satellite line will appear in resonant PES, even when it appears in the normal PES. It is important to understand the consequence of this finding. Chen *et al.*[27] found that there are no satellite lines in the deexcitation spectrum of the valence hole following C $1s\rightarrow2\pi^*$ excitation ($\nu=287.5$ eV), while it is seen in the direct photoemission ($\nu=35$ eV). As shown in Eq. (27), the relative intensity between the screened and unscreened peaks of the valence PES is determined by the degree of charge-transfer screening. For strongly chemisorbed CO molecules, such as on Pd or Ru, the valence PES spectra exhibit only a screened peak as a result of the complete screening of a valence hole. For weakly chemisorbed systems, such as CO on Cu, incomplete screening gives rise to the satellite lines due to multielectron excitation in the presence of the valence hole. We postulate that a resonantly excited state of a weakly chemisorbed CO is somewhat like the ground state of a strongly chemisorbed CO having a significant back donation from the substrate into the $2\pi^*$ level or NO having one electron in the $2\pi^*$ level in the gas phase. By this reasoning no satellite lines are expected in the valence PES observed at resonant excitation.

As we have studied above, when the resonant-excited electron remains in the $|a\rangle$ level as a spectator of the Auger transition involving a single valence hole, the resultant deexcitation spectrum corresponding to a screened valence-hole state should have the same binding energy as that observed in direct photoemission. However, this is not the case for CO/Cu(110), as shown in Fig. 3. In addition to the absence of satellite lines, we note that the two valence peaks in the deexcitation spectrum [Fig. 3(b)], following resonant $1s\rightarrow2\pi^*$ excitation with $\nu=287.5$ eV, are about 1 eV higher in binding energy than in either the Auger [Fig. 3(a), $\nu=311$ eV] or photoemission spectra [Fig. 3(c), $\nu=35$ eV]. The characteristic features of these spectroscopic results have been qualitatively studied by Gumhalter, Wandelt, and Avouris[51] on the basis of the $2\pi^*$ resonance model as shown in Fig. 5. In the deexcitation process after a core electron is ejected above the vacuum level [Fig. 5(a)], an electron supplied either from a state at ε_F of the metal or from a state in the partially filled $2\pi^*$ resonance pulled down by $U_{1s,2\pi^*}$, fills the core in the fully relaxed final state. The available Auger energy from such a transition is not the apparent incident energy ($\nu=311$ eV), but the core-hole threshold energy ε_T for C 1s at 286.5 eV relative to ε_F. A similar deexcitation process can be expected for resonant excitation into the $2\pi^*$ resonance state [Fig. 5(b)]. The excited electron relaxes to ε_F either by intraresonance transition (wiggly line) or by tunneling out and into the $2\pi^*$ resonance (dashed arrows). Both processes leading to the screened core-hole state are faster than the core-hole decay, so that the effective excitation energy for a valence Auger transition equals ε_T, as in photoionization.

We propose here a slightly different interpretation which does not necessarily require the CO $2\pi^*$ resonance in the initial and final states (i.e., before and after the core-hole creation). A resonantly excited electron remains in the $|a\rangle$ level for $\varepsilon_a-U_{ac}<\varepsilon_F$, where ABS (XPS) spectrum is characterized by the infrared divergence at $\nu(\omega)\sim\varepsilon_a-U_{ac}-\varepsilon_c$. For $\varepsilon_a-U_{ac}>\varepsilon_F$ it decays into the continuum of the metal; simultaneously, an electron near ε_F of the substrate may tunnel into the $|a\rangle$ level before the core-hole decay, and the core-level threshold appears at $\omega\sim\varepsilon_F-\varepsilon_c$. Such a process can be calculated by expanding $A_{ac}(\nu)$ of Eq. (8) as

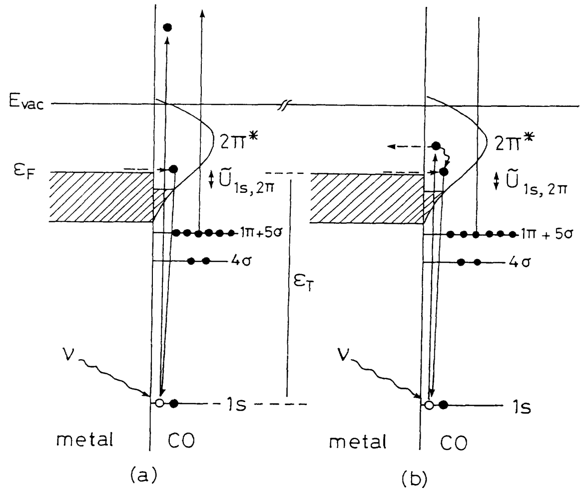

FIG. 5. Schematic energy-level diagram for core-hole deexcitation following (a) photoionization in XPS and (b) $1s\rightarrow2\pi^*$ excitation. In (a) a core electron is ejected above the vacuum level E_{vac} and core-hole screening proceeds via electron transfer from the substrate Fermi level into the resonance level (dashed arrow pointing right). In (b) a core electron excited into the resonance either tunnels out (dashed arrow pointing left) or makes an intraresonance transition to the Fermi level (wiggly arrow). In both cases the Auger energy released in the core deexcitation equals the core-hole threshold ε_T and may lead to the emission of an Auger electron out of $1\pi+5\sigma$ and 4σ levels (from Ref. 51).

$$P(\nu,\varepsilon)=\frac{|M_{ac}|^2|V_a|^4}{\pi}\sum_{k>k_F,k'<k_F}|A_{ac}(\nu)|^2|A_{kc}(\nu)|^2|A_{ackk'}(\nu)|^2\mathrm{Im}[\langle i|c_c^\dagger c_a c_{k'}^\dagger c_k H_A R(z) H_A c_k^\dagger c_{k'} c_a^\dagger c_c|i\rangle], \tag{28}$$

where

$$A_{kc}(\nu)=\langle i|c_c^\dagger c_k A(\nu) c_k^\dagger c_c|i\rangle\ , \tag{29}$$

$$A_{ackk'}(\nu)=\langle i|c_c^\dagger c_a c_{k'}^\dagger c_k A(\nu) c_k^\dagger c_{k'} c_a^\dagger c_c|i\rangle \tag{30}$$

describe the excitation of the core electron into the metal states above ε_F and into the $|a\rangle$ level accompanying the electron-hole pair excitation in the metal, respectively. Using Eq. (21) for H_A and assuming that the electrons from ε_F are involved in both charge transfer and the Auger transition, Eq. (28) can be approximately calculated as

$$P(\nu,\varepsilon)=|M_{ac}|^2|M_{vm}|^2\frac{|V_a|^2}{(\varepsilon_a-U_{ac}-\varepsilon_F)^2+\Gamma_c^2}\,\frac{|V_a|^2}{[\nu+\varepsilon_c-(\varepsilon_a-U_{ac})]^2+\Gamma_c^2}$$
$$\times\frac{1}{[\varepsilon+\varepsilon_c-(\varepsilon_v+U_{vv'})+(\varepsilon_a-U_{av})-2\varepsilon_F]^2+\Gamma_c^2}\ , \tag{31}$$

where the first factor represents the charge-transfer probability of an electron at ε_F to the $2\pi^*$ level in the presence of a core hole. The binding energy of this Auger electron following resonant excitation $\nu=(\varepsilon_a-U_{ac})-\varepsilon_c$ is then given by

$$\omega=-(\varepsilon_v+U_{vv'})+(\varepsilon_a-U_{av}-\varepsilon_F)+(\varepsilon_a-U_{ac}-\varepsilon_F)\ , \tag{32}$$

which is larger by $\varepsilon_a-U_{ac}-\varepsilon_F$ than that of the screened final state [Eq. (25)] of the valence hole observed at direct photoemission. This may explain the apparent energy mismatch of the screened valence hole in a binding-energy scale between the direct photoemission and resonant deexcitation spectra shown in Fig. 3. For CO/Cu(110), IPS revealed the $2\pi^*$ state about 3.4 eV above ε_F,[13] while ABS places ε_a-U_{ac} at about 1 eV above ε_F.[27,51] This explains the above-mentioned mismatch of the binding energy. When $\nu_T=\varepsilon_F-\varepsilon_c$ is used for the effective excitation, we obtain Eq. (25), so that the peak positions corresponding to the screened valence hole in direct PES and resonant deexcitation spectra coincide in a binding-energy scale. These findings seem to support the prediction by Chen *et al.*:[27] (1) the Auger decay is considerably slower than the photoemission process, allowing time for screening without any shakeup time, and (2) the state formed by optical absorption C 1$s\rightarrow 2\pi^*$ is an intermediate state in the core-hole-decay process.

However, a different situation appears for $\varepsilon_a-U_{ac}<\varepsilon_F$. In this case the resonant-excited electron in $|a\rangle$ no longer decays into the continuum of the substrate, so that the screened valence-hole state can be created either by the crossed Auger transition or final-state charge transfer when the excited electron participates in the Auger transition. In the former case we obtain

$$P(\nu,\varepsilon)=\frac{|M_{ac}|^2|M_{vm}|^2}{\pi}\sum_{k<k_F}|A_{ac}(\nu)|^2\mathrm{Im}[\langle i|c_a c_v^\dagger c_k^\dagger c_p R(z) c_p^\dagger c_k c_v c_a^\dagger|i\rangle$$
$$=|M_{ac}|^2|M_{vm}|^2\frac{1}{[\varepsilon+(\varepsilon_c+U_{ac})-(\varepsilon_v+U_{vv'}+U_{av})-\varepsilon_F]^2+\Gamma_c^2}\ . \tag{33}$$

In the latter case we also obtain

$$P(\nu,\varepsilon)=\frac{|M_{ac}|^2|M_{av}|^2|V_a|^2}{\pi}\sum_{k<k_F}|A_{ac}(\nu)|^2|R_v(\omega)|^2\mathrm{Im}[\langle i|c_a c_v^\dagger c_k^\dagger c_p R(z) c_p^\dagger c_k c_v c_a^\dagger|i\rangle]$$
$$=|M_{ac}|^2|M_{vm}|^2\frac{|V_a|^2}{(\varepsilon_a-U_{av}-\varepsilon_F)^2}\,\frac{1}{[\varepsilon+(\varepsilon_c+U_{ac})-(\varepsilon_v+U_{vv'}+U_{av})-\varepsilon_F]^2+\Gamma_c^2}\ . \tag{34}$$

Both Eqs. (33) and (34) give the Auger electron out of the $|v\rangle$ level with kinetic energy

$$\varepsilon=-(\varepsilon_c+U_{ac})+(\varepsilon_v+U_{vv'}+U_{av})+\varepsilon_F\ , \tag{35}$$

where the first two terms in parentheses denote the binding energy of core and valence electrons in the presence of an electron in the $|a\rangle$ level, respectively. When resonant energy $\nu=(\varepsilon_a-U_{ac})-\varepsilon_c$ is used, Eq. (35) gives the binding energy of the screened valence state given by Eq. (25). This reveals that the excited state formed by optical absorption C 1$s\rightarrow 2\pi^*$ in the case $\varepsilon_a-U_{ac}<\varepsilon_F$ is a fully relaxed state in the core-hole decay, so that we can use the excitation energy to calculate the binding energies. This is also true for the off-resonant Auger process studied below.

III. VALENCE AUGER SPECTRUM

We calculate the Auger spectrum where the core electron is excited above the vacuum level by $H_R = M_{pc} c_p^\dagger c_c + \mathrm{H.c.}$, $c_p^\dagger$ being the creation operator of photoelectron ejected above the vacuum level. It is appropriate to start with a general formula for the Auger spectrum given by Gunnarsson and Schönhammer:[52]

$$P_A(\nu,\varepsilon) = \frac{1}{\pi} \sum_p |M_{pc}|^2 \mathrm{Im}[\langle i | c_c^\dagger c_p A(\nu) H_A R(z) H_A A(\nu) c_p^\dagger c_c | i \rangle] . \tag{36}$$

In the case of a free molecule, the available Auger transition H_A involves two valence levels [first term of Eq. (6)], so that we obtain from Eq. (36) the CVV Auger spectrum

$$P_A(\nu,\varepsilon) = \frac{1}{\pi} \sum_p |M_{pc}|^2 \frac{|M_{vv'}|^2}{(\nu+\varepsilon_c-\varepsilon_p)^2+\Gamma_c^2} \mathrm{Im}\left[\frac{1}{z-\varepsilon_p+\varepsilon_{vv'}} \right] = |M_{pc}|^2 \frac{|M_{vv'}|^2}{(\varepsilon+\varepsilon_c-\varepsilon_{vv'})^2+\Gamma_c^2} . \tag{37}$$

In the case of a gas-phase CO ionized by $\nu = 296.1$ eV, the highest Auger kinetic energy $\varepsilon_K = 253.9$ eV was assigned as resulting from the $1\pi^{-1}5\sigma^{-1}$ configuration[43,44] with a double-hold binding energy 42.2 eV (see Fig. 1; $\varepsilon_{5\sigma} = 14.0$ eV, $\varepsilon_{1\pi} = 16.9$ eV, and $U_{5\sigma,1\pi} = 11.3$ eV).

When a molecule is chemisorbed on a metal surface, there appears Auger decay channels M_{av} involving the electron transferred from the metal before core-hole decay. We first consider the cases where the transferred electron serves as a spectator of the Auger transition of two valence electrons $M_{vv'}$ [Fig. 6(a)] or participates as a partner of a single valence electron M_{av} [Fig. 6(b)]. Putting Eq. (6) into Eq. (36) and expanding $A(\nu)$ with respect to V_a lead to

$$P_A(\varepsilon) = \frac{1}{\pi} |M_{pc}|^2 \sum_p \sum_{k<k_F} |V_a|^2 |A_{pc}(\nu)|^2 |A_{ak}(\nu)|^2 \mathrm{Im}[|M_{vv'}|^2 R_{vv'ak}(z) + |M_{av}|^2 R_{vk}(z)] , \tag{38}$$

$$A_{pc}(\nu) = \langle i | c_c^\dagger c_p A(\nu) c_p^\dagger c_c | i \rangle = \frac{1}{\nu+\varepsilon_c-\varepsilon_p+i\Gamma_c} , \tag{39}$$

$$A_{ak}(\nu) = \langle i | c_c^\dagger c_k^\dagger c_a c_p A(\nu) c_p^\dagger c_a^\dagger c_k c_c | i \rangle = \frac{1}{\nu+\varepsilon_c-\varepsilon_p-(\varepsilon_a-U_{ac})+\varepsilon_k+i\Gamma_c} , \tag{40}$$

$$R_{vv'ak}(z) = \langle i | c_k^\dagger c_v^\dagger c_{v'}^\dagger c_a c_A c_p R(z) c_p^\dagger c_A^\dagger c_a^\dagger c_v c_{v'} c_k | i \rangle = \frac{1}{z-\varepsilon_p-\varepsilon_{avv'}+\varepsilon_{vv'}+\varepsilon_k} , \tag{41}$$

$$R_{vk}(z) = \langle i | c_k^\dagger c_v^\dagger c_A c_p R(z) c_p^\dagger c_A^\dagger c_v c_k | i \rangle = \frac{1}{z-\varepsilon_p-(\varepsilon_a-U_{av})+(\varepsilon_v+U_{vv'}+\varepsilon_k)} , \tag{42}$$

where $A_{ak}(\nu)$ describes the electron transfer from the metal before core-hole decay. After the p integration we obtain

$$P_A(\varepsilon) = |M_{pc}|^2 \sum_{k<k_F} \frac{|V_a|^2}{(\varepsilon_a-U_{ac}-\varepsilon_k)^2+\Gamma_c^2} \times \left[\frac{|M_{vv'}|^2}{[\varepsilon+(\varepsilon_c+U_{ac})-(\varepsilon_{vv'}+U_{av}+U_{av'})]^2+\Gamma_c^2} + \frac{|M_{av}|^2}{[\varepsilon+\varepsilon_c-(\varepsilon_v+U_{vv'})-(\varepsilon_a-U_{ac})]^2+\Gamma_c^2} \right] , \tag{43}$$

where the first factor describes the transition probability that an electron is transferred from the metal to the $|a\rangle$ level in the presence of the core hole.

The first term of Eq. (43) corresponds to the $v^{-1}v'^{-1}a^{+1}$ final-state configuration, which can also be reached when the resonant-excited electron remains as a spectator, as explicitly shown in the preceding section. This means that the initial state for Auger decay of the core hole is the same as the excited neutral state. The final state of this Auger decay is photoemissionlike in the sense that it is singly ionized, although having two valence holes and one electron. Normally, the binding energy of a photoelectron spectrum (Auger and PES) is defined as the energy difference between the incident energy to the system and kinetic energy extracted by the emitted electron. However, if we assume the resonant $|c\rangle \rightarrow |a\rangle$ excitation energy $\nu_{\mathrm{res}} = (\varepsilon_a - U_{ac} - \varepsilon_c)$ as an effective energy available for this Auger decay, the first term of Eq. (43) shows the peak in a binding energy scale ω,

$$\begin{aligned} \omega(v^{-1}v'^{-1}a^{+1}) &= \nu_{\mathrm{res}} - \varepsilon(v^{-1}v'^{-1}a^{+1}) \\ &= (\varepsilon_a - U_{av} - U_{av'}) - \varepsilon_{vv'} , \end{aligned} \tag{44}$$

and coincides with that of the $v^{-1}v'^{-1}a^{+1}$ final state of resonant photoemission given by ω_B in Eq. (16).

The second term of Eq. (43) represents the Auger process involving the valence electron in the $|v\rangle$ level and the electron in $|a\rangle$, which is transferred from the metal to screen the core hole, as shown in Fig. 6(b). The kinetic energy of the Auger electron emitted via this process,

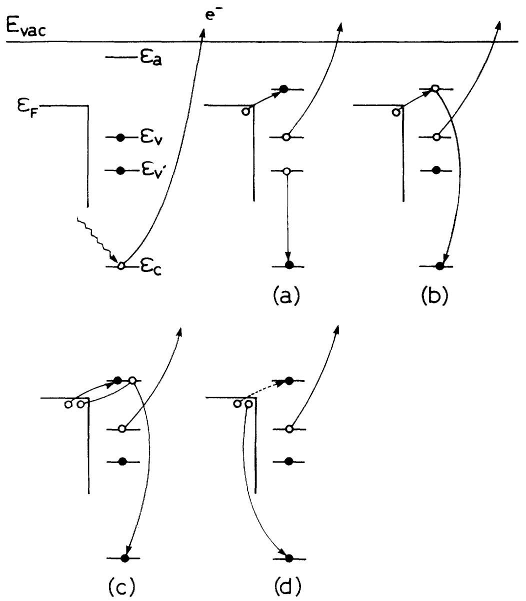

FIG. 6. Schematic orbital picture for core-hole decay via the Auger transition following core excitation above vacuum. The electronic configuration of the ground state consists of the occupied core level with energy ε_c, valence levels $\varepsilon_v, \varepsilon_{v'}$, and the unoccupied level ε_a. After core-electron excitation the system relaxes to the various final states via Auger decay of the core hole: (a) an electron transferred from near the Fermi level into the $|a\rangle$ level to screen the core hole becomes a spectator of the Auger transition involving two valence electrons; (b) the transferred electron participates in the Auger transition with a valence electron; (c) another electron is supplied near the Fermi level to screen the valence hole in the final state; (d) the crossed Auger transition involving a metal electron. $\hbar\omega$ should read ν in the text.

$$\varepsilon_K(v^{-1}a^{-1}) = -\varepsilon_c + (\varepsilon_v + U_{vv'}) + (\varepsilon_a - U_{ac}) \ , \tag{45}$$

is not the same as Eq. (13) because of the bonding shift of ε_v or the metallic screening of U_v and U_{ac}. Since $\varepsilon_c - U_{ac} > \varepsilon_{v'}$, Eq. (45) is higher than that of any Auger electron from a free molecule. As mentioned above, the highest Auger kinetic energy of gas-phase CO is due to the $1\pi^{-1}5\sigma^{-1}$ configuration of 253.9 eV.[53,54] Baker, Canning, and Chesters[26] observed *CVV* Auger spectra for CO/Cu(111) and Pt(111) systems. From a comparison of the Auger spectra between CO/Cu(111) and gas-phase CO, they found that high-energy peaks of the adsorbed CO do not correlate with any other lines in the gas phase. They assigned peaks at 278 and 275 eV to the Auger process involving $(1s, 5\sigma, 2\pi^*)$ and $(1s, 4\sigma, 2\pi^*)$, respectively. They also noted that the separation of 3 eV between these lines correlates with the 5σ and 4σ separation in the valence PES spectrum and the final states involved would be the same as in PES. A similar participation of the screening level in the Auger decay has also been reported for CO/Ni(100) (Ref. 55) and transition-metal carbonyls.[56] When the screening electron participates in the Auger transition, there is a single valence hole in the final state, so that Eq. (45) gives the binding energy of the *unscreened* valence level seen in normal PES:

$$\omega(v^{-1}) = \nu_{\mathrm{res}} - \varepsilon(v^{-1}a^{-1}) = -(\varepsilon_v + U_{vv'}) \ . \tag{46}$$

Chen *et al.*[27] and Murphy *et al.*[28] demonstrated for CO/Cu(111) and Pt(111) that, when the binding energy of the C 1*s* threshold is used as the effective initial energy for the Auger transition, the binding energies of the high-energy Auger peaks are the same as that of the screened final states of the valence photoemission. For example, the peak at about 12 eV in a binding energy scale [Fig. 3(a)] was assigned to the molecular-orbital configuration composed of a hole in 4σ and a screening electron in the $2\pi^*$ level. If the electron transferred to the $|a\rangle$ level becomes an active participant in the Auger decay, another electron must be supplied from the metal in order to screen the final valence-hole state, as shown in Fig. 6(c). Within the present model this screening process can be treated by the final-state interaction of $R_{vk}(z)$ in Eq. (38) as

$$P_A(\varepsilon) = \frac{|M_{pc}|^2}{\pi} \sum_p \sum_{k,k'<k_F} |V_a|^4 |A_{pc}(\nu)|^2 |A_{ak}(\nu)|^2 \mathrm{Im}[|M_{av}|^2 R_{vk}^2(z) R_{vakk'}(z)] \ , \tag{47}$$

$$\begin{aligned} R_{vakk'}(\nu) &= \langle i | c_{k'}^\dagger c_k^\dagger c_v^\dagger c_a c_A c_p R(z) c_p^\dagger c_A^\dagger c_a^\dagger c_v c_k c_{k'} | i \rangle \\ &= \frac{1}{z - \varepsilon_p - (\varepsilon_a - U_{av}) + (\varepsilon_v + U_{vv'}) + \varepsilon_k + \varepsilon_{k'}} \ . \end{aligned} \tag{48}$$

If electrons at ε_F of the metal are involved in the valence relaxation process after core excitation, Eq. (47) can be approximated to yield

$$P_A(\varepsilon) = |M_{pc}|^2 |M_{av}|^2 \frac{|V_a|^2}{(\varepsilon_a - U_{ac} - \varepsilon_F)^2 + \Gamma_c^2} \frac{|V_a|^2}{[(\varepsilon_a - U_{av}) - \varepsilon_F]^2} \frac{1}{[\varepsilon + \varepsilon_c - (\varepsilon_v + U_{vv'}) + (\varepsilon_a - U_{av}) - 2\varepsilon_F]^2 + \Gamma_c^2} \ , \tag{49}$$

which gives the same Auger kinetic energy as Eq. (31). Since an electron transferred from a state at ε_F screens the photoinduced core hole and becomes an active participant of the Auger transition, the available Auger energy from such a transition is then given by the core-hole threshold at $\nu \sim \varepsilon_F - \varepsilon_c$ or $\nu \sim (\varepsilon_a - U_{ac}) - \varepsilon_c$, depending on $(\varepsilon_a - U_{ac}) \gtrless \varepsilon_F$. For

CO/Cu(111) we should use $v_T = \varepsilon_F - \varepsilon_c$ as the effective initial energy and obtain from Eq. (48) the binding energy of the screened final state given by Eq. (25). The same final state can also be reached when the crossed Auger transition M_{vm} is accompanied by charge transfer to screen the valence hole [Fig. 6(d)]. From Eqs. (21) and (36) we obtain

$$\begin{aligned} P_A(\varepsilon) &= \frac{|M_{pc}|^2 M|_{vm}|^2}{\pi} \sum_p \sum_{k,k'<k_F} |A_{pc}(\nu)|^2 |V_a|^2 \mathrm{Im}[\,|A_{ak}(\nu)|^2 R_{vakk'}(z)] \,, \\ &= |M_{pc}|^2 |M_{vm}|^2 \frac{|V_a|^2}{(\varepsilon_a - U_{ac} - \varepsilon_F)^2 + \Gamma_c^2} \, \frac{1}{[\varepsilon + \varepsilon_c - (\varepsilon_v + U_{vv'}) + (\varepsilon_a - U_{av}) - 2\varepsilon_F]^2 + \Gamma_c^2} \,. \end{aligned} \tag{50}$$

From a comparison of Eqs. (31), (49), and (50), we have clearly demonstrated that both the participant decay in the deexcitation process following resonant core-to-bound excitation and the Auger transition involving the screening electron populated in the $|a\rangle$ level via charge transfer result in the same screened valence-hole-state reached in valence photoemission. This is valid only when the excited state created by resonant or off-resonant excitation fully relaxes before Auger decay of a core hole takes places.

IV. CONCLUDING REMARKS

We have studied the elementary processes of the core-hole decay dynamics of an adsorbate via the various Auger decay channels available on a metal surface. We calculated the deexcitation spectrum via valence Auger transitions following resonant core excitation to the initially empty level of the adsorbate. We considered three different processes where the excited electron either participates or remains as a spectator in the Auger decay of the core hole, or it decays into the substrate. We have clearly demonstrated that when the spectator electron is unstable as a result of the decay to the substrate, the resultant deexcitation spectrum exhibits the resonant-enhanced satellite corresponding to the $v^{-1}v'^{-1}a^{+1}$ configuration, such as the $5\sigma^{-1}1\pi^{-1}2\pi^{*+1}$ state observed for a CO/Ni system.[31,39] This should be distinguished from the Auger spectrum due to two valence holes in the presence of the spectator electron.

We also studied the participant decay in which an intermediate neutral excited state decays into valence-ionized final states by the Auger-like processes (autoionization). In contrast to the gas phase where the final state of autoionization is the same as that seen by photoemission, the dynamics of core- and valence-hole screening in the Auger and photoemission processes is a key to interpreting and/or understanding the spectral features associated with participant decay channels involving the screening electron in the initially unoccupied level populated either by resonant core excitation or charge transfer from the substrate before core-hole decay. The assignment of the autoionization spectra of a CO/Cu system has been made in different manners,[27,30] partly because of discrepancies in the energy calibration of the spectra. Although these spectra in kinetic-energy scales seem to differ by a few eV, the peak positions (as well as the relative intensities), assigned as the screened 4σ and $1\pi+5\sigma$ final states[27] or $5\sigma 2\pi^*$ decay channel starting from partially and fully related core-hole states,[30] are almost the same on a binding-energy scale. We have presented a qualitative explanation in favor of the former interpretation. The absence of shakeup satellites (observed in photoemission spectra) in both the deexcitation spectrum associated with participant decay following resonant excitation and the normal Auger spectra at off-resonant Auger spectra suggests that complete relaxation of the excited state occurs before Auger decay of the core hole. This means that the initial state for Auger decay of the core hole is identical to the fully relaxed core-hole state seen in C 1s core XPS spectra. As a consequence of faster relaxation than the Auger decay time, the *effective* excitation energy available for the Auger transition is not the apparent incident photon energy, but the core threshold either at $\omega_T \sim \varepsilon_F - \varepsilon_c$ or $\varepsilon_a - U_{ac} - \varepsilon_c$, depending on $\varepsilon_a - U_{ac} \gtrless \varepsilon_F$. This explains the binding-energy mismatch of the screened valence-hole state between direct photoemission or normal Auger and deexcitation spectra for CO/Cu(110) shown in Fig. 3. Such a mismatch will not occur in a case where the core-hole threshold appears at $\varepsilon_a - U_{ac} - \varepsilon_c < \varepsilon_F$, since the binding energy of the screened core-hole state is the same as the absorption threshold. Thus the key to understanding the core-hole decay dynamics is the role of the $|a\rangle$ level and its coupling to the metal in the relaxation process following core excitation. Only when the excited electron remains localized in the $|a\rangle$ level with a small hopping probability into the metal is it involved in the primary process in Auger decay of the core hole.

In addition to the obvious implication of a role of the $2\pi^*$ level for a better understanding of the core-hole decay dynamics of a CO molecule, a final remark is addressed on important ramifications for photon-stimulated desorption (PSD) of CO and NO molecules on metal surfaces. For ion desorption such as CO$^+$(NO$^+$) and O$^+$, adsorbate core excitations followed by the creation of a double-hole–one-electron state have shown to enhance the PSD cross section.[57–59] From the response of the desorption yield to energy and symmetry of the primary excitation, the Auger (participant or spectator) decay involving resonance $2\pi^*$ electron has been proved to be responsible for the observed resonance features of ion PSD. The single-hole state v^{-1} created by the participant decay is rapidly delocalized and ineffective for desorption. On the other hand, the spectator transition giving rise to the Auger final state having two valence holes in the bonding orbitals and an additional electron in the $2\pi^*$ orbital, viz., $v^{-1}v'^{-1}2\pi^{*+1}$, leads to a longer lifetime of a double-hole state due to Coulomb localization and the highly repulsive character with respect to the C(N)-O bond, thereby causing fragmentation. The critical role of the $2\pi^*$ occupancy has also been demonstrated in PSD of NO induced by valence electronic excitation.[60]

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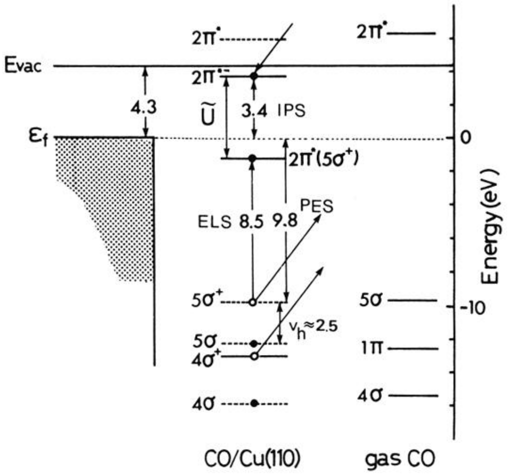

FIG. 1. Semiquantitative energy diagram of a CO/Cu(110) system on the basis of the available experimental data from IPS (Ref. 13), PES (Ref. 15), electron-energy-loss spectroscopy (EELS) (Ref. 14), where the superscripts + and − refer to the energy levels appropriate for the positive- and negative-charge final states, respectively, and $2\pi^*(5\sigma^+)$ stands for the $2\pi^*$ level in the presence of the 5σ hole. The ionization energies of the 5σ, 1π, and 4σ valence levels and the $2\pi^*$ affinity level of gas-phase CO are also shown for comparison. The ionization energy C 1s core level is 296.1 eV for gas-phase CO and the binding energy relative to the Fermi level is 286 eV for CO/Cu(100) (Ref. 12) (from Ref. 11).