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Deexcitation processes in adsorbates

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It is shown theoretically that there is competition between core-hole decay and delocalization of a resonantly excited electron from the adsorbate to the substrate metal with simultaneous substrate-to-ligand charge-transfer core-hole screening [relaxation from the resonantly core excited neutral state to the x-ray-photoemission-spectroscopy (XPS) core ionized state] or between the core-hole decay and the charge-transfer core-hole screening from the substrate metal to the adsorbate (relaxation from the XPS core ionized state to the resonantly core excited neutral state). In the former case a spectral feature due to the Auger decay from the ionic core-hole state appears in the autoionization spectrum, while in the latter case a spectral feature arising from the spectator and participant decay from the neutral screened core-hole state appears in the Auger spectrum measured high above the core ionization limit. The relaxation time can be determined from the relative Auger and autoionization spectral intensity. Applications of the Auger-photoelectron coincidence spectroscopy and x-ray-emission spectroscopy to adsorbates are also discussed.

I. INTRODUCTION

The resonantly core excited state is neutral and may decay by autoionization, namely, participant and spectator decays. In the former, the resonantly excited electron participates in the Auger decay of the resonantly excited one-hole–one-particle ($1h1p$) state, leading to a singly valence level ionized continuum state, identical to the main line state observed in the valence photoemission spectroscopy (PES) spectrum. At resonance, the final state created either by the participant decay channel or by direct photoionization becomes indistinguishable. This leads to interference and in general a large enhancement of the main line intensity. In spectator decay the excited electron remains as a spectator in the Auger decay and leads to the $2h1p$ state, corresponding to the shakeup satellite state observed in the PES spectrum. The spectral intensity of the final state is governed in the case of direct photoemission by the dipole excitation matrix element (and shakeup excitation matrix element), while in resonant photoemission, it is given by the Auger matrix element (Coulomb operator). Thus resonant photoemission can be used to identify weak satellite lines in the valence PES spectrum.

In contrast to the case of free molecules, for all studied CO adsorption systems (CO/Ni,CO/Pd, etc.), the deexcitation electron spectroscopy (DES) (resonant photoemission, resonant Auger emission) spectra are nearly identical to the normal Auger electron spectroscopy (AES) spectra, and no participant and spectator decay spectral features have been observed in the DES spectra.[1-9] Upon comparison between the DES and the AES spectra, the spectra are on the same kinetic-energy (KE) scale. So on a calibrated binding-energy (BE) scale, the two spectra are shifted relative to each other by the x-ray-photoemission-spectroscopy (XPS) ionization and x-ray-absorption-spectroscopy (XAS) resonance energy difference. The first explanation for this peculiar spectral behavior was that the core excited state in the photoabsorption process is a $^1\Pi$ state, which may then decay into the energetically more favorable $^3\Pi$ state (1.46 eV lower in the case of free CO) by exchange of electrons with the metal. The core excited state decays into the fully screened core-hole state before the deexcitation process, with the excess energy given up to the substrate.[9] A more acceptable recent explanation is as follows. In the case of physisorption, where the adsorbate and substrate are electronically isolated, unless the system becomes chemisorbed in the presence of a core hole, there is no charge transfer (CT) from the substrate to screen the core hole. Therefore there is no relationship between the resonant core excitation and the core ionization energies. However, for chemisorption systems, the energy onset in the XAS spectrum should correspond to the XPS BE. The XAS onset corresponds to the creation of a final state where a core electron is excited to the lowest unoccupied state, i.e., to the Fermi level. In the completely screened XPS final state, a charge redistribution takes place where one electron is taken from the Fermi level to locally screen the core hole. Thus those two final states should be indistinguishable.[10,11] The core-hole lifetime ($\sim 10^{-15}$ sec) is much longer than the time for the core excitation and ionization processes ($\sim 10^{-17}$ sec). The state created by the initial core ionization or excitation may not be energetically the most favorable state for the core hole. For chemisorbed systems, the strong coupling with the substrate allows for CT already on the time scale of the core ionization process. This leads to a complete screening of the core hole, which is seen as the lowest-energy state in the XPS core-hole spectrum. If the XAS state is energetically higher than the XPS lowest-energy state and unstable, the excited electron may delocalize from the adsorbate to the substrate and decay to the Fermi level. Simultaneously an electron from the Fermi level from the substrate may be transferred (CT) to locally screen the core hole.[2-5,11] Another possibility is that the excited electron makes a transition from the excited state to a state at the Fermi level.[11] Both the delocalization of the excited electron and the CT core-hole screening process are very fast and bring the system into the fully relaxed state with the screened core hole before the core-hole decay starts. In other words, the resonantly core level excited neutral state may relax to a state that could be considered as locally identical to the XPS lowest-energy state on the time scale of the core-hole decay. If this is possible, the initial state for the deexcitation process observed at the core resonance is not a core level excited neutral state but the core level ionized ionic state. Then the deexcitation process is a normal Auger decay process. Thus the DES spectrum becomes almost identical to the normal AES spectrum.[2–5,11]

For weakly coupled physisorption systems, adsorbate and substrate are electronically isolated in the ground state. However, in the presence of a core-hole CT screening from the substrate may occur because of the attractive core-hole potential, which may bring an empty adsorbate level closer to the Fermi level. In this case, the CT is much slower than in the case of chemisorption systems and comparable to the core-hole lifetime. In other words, within the time scale of the core-hole decay, the XPS core level ionized state relaxes further to the "well-screened" core-hole neutral state, which could be considered as locally identical to the resonantly core level excited neutral state. This relaxation occurs on the time scale of the core-hole decay. Therefore this relaxed state cannot be observed in the XPS core-hole spectrum. However, the state can be an initial state for the core-hole decay. If so, one can observe the decay from the resonantly excited state, namely, the spectator and participant decay spectral features in the Auger spectrum measured high above the core ionization limit. This was indeed observed for N_2 physisorbed on graphite.[12] The XPS N 1*s* ionic core-hole state (403.9 eV) lies above the N 1*s* to $^1\Pi_g$ resonance (401.0 eV).[12] This results in a CT screening from the substrate to neutralize the ionic state.

For a monolayer of Ar adsorbed on graphite, the XPS Ar $2p_{3/2}$ ionic core-hole state (242.6 eV) lies below the XAS Ar $2p_{3/2} \rightarrow 4s$ resonantly excited state (244.7 eV). For this system the excited electron has a certain probability of being delocalized to the substrate on the time scale of the core-hole lifetime. As a result a small portion (30%) of the DES spectrum for Ar/graphite recorded at the 4*s* resonance shows Auger spectral features due to a decay from an ionic core-hole state.[13] Whether the XPS core level ionized state or XAS resonantly core level excited neutral state has a possibility of further relaxation to the lowest core-hole state depends on their relative positions. The core electron excited into the resonance state may delocalize to the substrate (charge delocalization) and simultaneously metal-ligand CT core-hole screening occurs if the lowest core-hole state is ionic (XPS core level ionized state), and upon the core ionization the core-hole screening proceeds via CT from substrate to ligand if the lowest core-hole state is neutral (resonantly excited state or CT-screened core-hole state). If the relaxation to the lowest core-hole state occurs on the time scale of core-hole decay, the decay spectral features for the fully relaxed core-hole state will be manifested in the DES spectrum in the case when the lowest core-hole state is ionic and in the AES spectrum in the case when the lowest core-hole state is neutral.

The competition between the charge delocalization of the resonantly excited electron and the core-hole decay has been seen not only in adsorption systems but also in insulators such as CaF_2, and Sc_2O_3.[14] The time scale of the delocalization of the resonantly excited electron to the empty conduction band and simultaneous CT core-hole screening are faster than or comparable with the time scale of core-hole decay, so that in the DES spectra there is a competition between the spectator (participant) decay spectral intensity and normal Auger spectral intensity. In the present article we study theoretically the competition between the relaxation and the core-hole decay and its influences on the decay spectral features. We discuss also the possibility of application of Auger photoelectron coincidence spectroscopy (APECS) and interpretation of the recently measured x-ray emission spectroscopy (XES) spectrum of CO/Ni(100).

II. CORE-HOLE DECAY AND RELAXATION FROM THE RESONANTLY CORE LEVEL EXCITED STATE

A. Theory

We consider a quasidiscrete molecular resonant excitation from a core level c to a localized (discrete) molecular empty level (a) which is coupled to a continuum of extended states, e.g., of a substrate metal. In chemisorption systems, the resonantly excited state $(c^{-1}a)$ is slightly above the core ionization limit, the CT-screened XPS core-hole state (c^{-1}). Thus there may be strong configuration interaction (CI) between the $c^{-1}a$ and $c^{-1}\varepsilon_k$ configurations (here ε_k denotes a photoelectron in the continuum of extended states of a substrate metal), which are coupled by the relaxation mechanism (charge delocalization and simultaneous CT screening). We focus particularly on competition between decay of the resonantly excited electron in the broadened affinity level (relaxation) and decay of the core hole, in other words, competition for the spectral intensity between decay from the resonantly core level excited neutral state $(c^{-1}a)$ and the normal Auger decay from the core level ionized ionic state (CT-screened core-hole state) $(c^{-1}\varepsilon_k)$. The intermediate resonant state $(c^{-1}a)$ may decay via different decay channels; participant decay, which leads primarily to single ionization, and decay of the core hole, which couples to decay to extended states by the electron in the affinity level (delocalization, ionization), leading to the double-ionization continuum. The latter decay of the core level takes place in the absence (normal Auger decay from the core ionized state) or presence of an electron in the affinity level (spectator decay from the resonantly core level excited neutral state). Both processes lead to the doubly ionized state. We denote by $|a\rangle$ the intermediate resonantly core level excited state $|a\rangle = c_a^\dagger c_c|\psi_0\rangle$ (here $c^\dagger$ and c are creation and annihilation operators, respectively, and Ψ_0 is the ground state), by $|c\rangle$ the core level ionized (CT-screened core-hole) state $|c\rangle = c_k^\dagger c_c|\Psi_0\rangle$

(here k is the delocalized excited electron ε_k), by $|f\rangle$ the doubly ionized final state $|f\rangle=c_\varepsilon^\dagger c_k^\dagger c_j c_l|\Psi_0\rangle$ (here j and l are the final-state valence holes and ε is the resonant or normal Auger electron), by $|s\rangle$ the singly valence level ionized final state from the spectator decay $|s\rangle=c_\varepsilon^\dagger c_a^\dagger c_j c_l|\Psi_0\rangle$, and by $|v\rangle$ the singly valence level ionized final state $|v\rangle=c_\varepsilon^\dagger c_v|\Psi_0\rangle$. Here ε is the resonant photoelectron and v is the valence level. We denote by $Z_{ac}(\omega)$ the dipole matrix element between $|\Psi_0\rangle$ and $|a\rangle$ (here ω is the photon energy), by V_{fc} the normal Auger matrix element (including exchange) between $|f\rangle$ and $|c\rangle$, by V_{ka} the relaxation matrix element between $|c\rangle$ and $|a\rangle$ or between $|f\rangle$ and $|s\rangle$, by V_{sa} the spectator decay matrix element between $|s\rangle$ and $a\rangle$, and by V_{va} the participant decay matrix element between $|v\rangle$ and $|a\rangle$. For the sake of simplicity, we neglect the interferences between different decay channels and we consider only one spectator, participant, and Auger decay channel. We neglect direct valence photoemission. In the present case the kinetic energy ε of the resonant or normal Auger electron is so high that the interaction between ε and ε_k (delocalized excited electron) is negligible. In other words, ε will not be influenced by the excited electron delocalized to the extended states. At or near the resonance, the resonant Auger and photoelectron emission amplitudes are given by

$$I(\varepsilon;\omega)\propto|V_{va}G_{aa}Z_{ac}(\omega)|^2\delta(\varepsilon-\varepsilon_v-\omega)+\int|V_{ka}G_{ss}V_{sa}G_{aa}Z_{ac}(\omega)|^2\delta(\varepsilon+\varepsilon_k-\varepsilon_{jl}-\omega)d\varepsilon_k$$
$$+\int|V_{fc}G_{cc}V_{ka}G_{aa}Z_{ac}(\omega)|^2\delta(\varepsilon+\varepsilon_k-\varepsilon_{jl}-\omega)d\varepsilon_k\ . \tag{1}$$

The first term in Eq. (1) describes the participant decay, the second term represents the spectator decay in the presence of an electron in the affinity level a (resonantly core level excited state), and the third term is the normal Auger decay in the absence of an electron in the affinity level a (screened core-hole state). G_{aa} is the one-hole–one-particle ($1h1p$) propagator of the state $|a\rangle$ given by

$$G_{aa}=[\omega-\omega_{ca}-i\,\mathrm{Im}\Sigma_a(\omega)]^{-1} \tag{2}$$

$$\omega_{ca}=\varepsilon_a-\varepsilon_c-U_{ca}\ . \tag{3}$$

ε_c, ε_a, ε_v, ε_{jl}, and U_{ca} are the ionization energy of level c, the affinity energy of level a, the ionization energy of valence level v, the ionization energy of the final two-hole (jl) state, and the effective core-hole–excited-electron Coulomb interaction, respectively.

The self-energy $\Sigma_a(\omega)$ consists of three components, and their corresponding decay widths (imaginary part of the self-energy) are given by

$$\Sigma_a(\omega)=\Sigma_{\mathrm{CT}}(\omega)+\Sigma_s(\omega)+\Sigma_v(\omega)\ , \tag{4}$$

$$\Gamma_a(\omega)=2\,\mathrm{Im}\Sigma_a(\omega)\ , \tag{5}$$

$$\Gamma_{\mathrm{CT}}(\omega)=2\,\mathrm{Im}\Sigma_{\mathrm{CT}}(\omega)=2\pi\sum_{k'>k_f}|V_{k'a}|^2\delta(\omega+\varepsilon_c-\varepsilon_{k'})\ , \tag{6}$$

$$\Gamma_s(\omega)=2\,\mathrm{Im}\Sigma_s(\omega)=2\pi\sum_{\varepsilon'}|V_{sa}(\varepsilon')|^2\delta(\omega+\varepsilon_s-\varepsilon')\ , \tag{7}$$

$$\Gamma_v(\omega)=2\,\mathrm{Im}\Sigma_v(\omega)=2\pi\sum_{\varepsilon'}|V_{va}(\varepsilon')|^2\delta(\omega+\varepsilon_v-\varepsilon')\ , \tag{8}$$

The self-energy Σ_{CT} describes the charge delocalization of an excited electron in $|a\rangle$ by hopping onto the unoccupied metal states above the Fermi level and simultaneous CT core-hole screening, by which $|a\rangle$ relaxes to $|c\rangle$. Charge delocalization becomes possible when the criterion $\omega+\varepsilon_c=\varepsilon_a-U_{ca}>\tilde{\varepsilon}_f$ is satisfied. Here $\tilde{\varepsilon}_f$ is the effective Fermi level shifted by the image potential. The self-energy Σ_s describes the spectator decay channel $c^{-1}a\rightarrow j^{-1}l^{-1}a\varepsilon$ of a core hole c in the presence of the spectator a in $|a\rangle$. Σ_v is due to the participant decay channel $c^{-1}a\rightarrow v^{-1}\varepsilon$ of $|a\rangle$. ε_s is the ionization energy of the final $2h1p$ ($j^{-1}l^{-1}a$) state by the spectator decay and is given by

$$\varepsilon_s=\varepsilon_{jl}-\varepsilon_a+U_{ja}+U_{la} \tag{9}$$

$$\varepsilon_{jl}=\varepsilon_j+\varepsilon_l-U_{jl} \tag{10}$$

G_{ss} is the propagator of the state $|s\rangle$, given by

$$G_{ss}=[\varepsilon-\omega-\varepsilon_s-i\,\mathrm{Im}\tilde{\Sigma}_{\mathrm{CT}}(\varepsilon-\omega)]^{-1}\ , \tag{11}$$

$$\Gamma_{\mathrm{CT}}(\varepsilon-\omega)=2\,\mathrm{Im}\tilde{\Sigma}_{\mathrm{CT}}(\varepsilon-\omega)$$
$$=2\pi\sum_{k'>k_F}|V_{k'a}|^2\delta(\varepsilon-\omega-\varepsilon_{jl}+\varepsilon_{k'})\ . \tag{12}$$

$\tilde{\Sigma}_{\mathrm{CT}}$ is the self-energy by which $|s\rangle$ relaxes to $|f\rangle$. We neglect the lifetime broadening of $|s\rangle$. G_{cc} is the propagator of the state $|c\rangle$ given by

$$G_{cc}=[\varepsilon_k-\omega-\varepsilon_c-i\,\mathrm{Im}\Sigma_c(\varepsilon_k-\omega)]^{-1}\ , \tag{13}$$

$$\Gamma_c(\varepsilon_k-\omega)=2\,\mathrm{Im}\Sigma_c(\varepsilon_k-\omega)$$
$$=2\pi\sum_{\varepsilon'}|V_{fc}(\varepsilon')|^2\delta(\varepsilon_k-\omega+\varepsilon'-\varepsilon_{jl})\ . \tag{14}$$

The self-energy Σ_c describes the Auger core-hole decay $c^{-1}\rightarrow j^{-1}l^{-1}\varepsilon$. $Z_{ac}(\omega)$ is given by

$$Z_{ac}(\omega)=Z_{ac}+\sum_{\varepsilon}\frac{V_{va}Z_{v\varepsilon}}{\varepsilon_v-\varepsilon+\omega+i\delta}\ . \tag{15}$$

Here the second term describes the CI between $|a\rangle$ and $|v\rangle$. Equation (1) can be written as

$$I(\varepsilon;\omega)\propto|Z_{ac}(\omega)|^2A_a(\omega)$$
$$\times\left[\frac{\Gamma_v}{\Gamma_a}\delta(\varepsilon-\varepsilon_v-\omega)+\frac{\Gamma_s}{\Gamma_a}A_s(\varepsilon-\varepsilon_s-\omega)\right.$$
$$\left.+\frac{\Gamma_{\mathrm{CT}}}{\Gamma_a}A_c(\varepsilon-\varepsilon_{jl}+\varepsilon_c)\right]\ . \tag{16}$$

The meanings of the terms in Eq. (16) are the same as those of Eq. (1). We note that the participant decay energy, the spectator decay energy, and the normal Auger decay energy are given by $\varepsilon_v+\omega$, $\varepsilon_s+\omega$, and $\varepsilon_{jl}-\varepsilon_c$, respectively. When we consider several spectator and Auger decays (channel indices i and m), we replace the second and third terms by

$$\sum_i \frac{\Gamma_s^i}{\Gamma_a} A_s(\varepsilon-\varepsilon_s^i-\omega)+\frac{\Gamma_{\mathrm{CT}}}{\Gamma_a}\sum_m \frac{\Gamma_c^m}{\Gamma_c} A_c(\varepsilon-\varepsilon_{jl}^m+\varepsilon_c) \; . \tag{17}$$

Here $\sum_m \Gamma_c^m=\Gamma_c$ and $\sum_i \Gamma_s^i=\Gamma_s$. $A_a(\omega)$ is the spectral function of the state $|a\rangle$ given by a Lorentzian profile with a width Γ_a

$$A_a(\omega)=\frac{1}{\pi}\frac{\Gamma_a/2}{(\omega-\omega_{ca})^2+(\Gamma_a/2)^2} \; . \tag{18}$$

$A_s(\varepsilon-\varepsilon_s-\omega)$ is the spectral function of the state $|s\rangle$ given by

$$A_s(\varepsilon-\varepsilon_s-\omega)=\frac{1}{\pi}\frac{\Gamma_{\mathrm{CT}}/2}{(\varepsilon-\varepsilon_s-\omega)^2+(\Gamma_{\mathrm{CT}}/2)^2} \; . \tag{19}$$

$A_c(\varepsilon-\varepsilon_{jl}+\varepsilon_c)$ is the spectral function of the state $|c\rangle$ given by

$$A_c(\varepsilon-\varepsilon_{jl}+\varepsilon_c)=\frac{1}{\pi}\frac{\Gamma_c/2}{(\varepsilon_{jl}-\varepsilon-\varepsilon_c)^2+(\Gamma_c/2)^2} \tag{20}$$

One many consider also the resonant x-ray emission spectrum. The resonant x-ray emission spectrum will be given by

$$\begin{aligned} I(\omega_x;\omega) \propto {} & |Z_{ac}(\omega)|^2 A_a(\omega) \\ & \times \left[\frac{\Gamma_x}{\Gamma_a}\delta(\omega_x-\omega)+\frac{\Gamma_x}{\Gamma_a} A_s(\omega_x-\tilde{\varepsilon}_v-\omega) \right. \\ & \left. + \frac{\Gamma_{\mathrm{CT}}}{\Gamma_a}\frac{\Gamma_x}{\Gamma_t} A_c(\omega_x-\varepsilon_v+\varepsilon_c) \right] \end{aligned} \tag{21}$$

The first term is the resonant radiative hole-particle recombination decay ($a\rightarrow c$), the second term describes the resonant spectator x-ray emission and the third term shows the normal x-ray emission. ω_x is the x-ray emission energy and Γ_x is the radiative decay width for the resonantly excited state (we assume that it is also the same for the core ionized state). $\tilde{\varepsilon}_v$ is the final $1h\,1p(v^{-1}a)$ state ionization energy. Γ_a is now given by a sum of Γ_{CT}, Γ_s, Γ_v, and Γ_x and the decay width of A_c is given by Γ_t which is a sum of Γ_x and Γ_c.

B. Discussion

One may consider the relaxation of the core excited state to the core ionized state within the molecular-cluster approach. Recent theoretical studies of the 1*s* core resonant excitation spectra of CO/Ni and N_2/Ni (Ref. 15) by an *ab initio* molecular-orbital many-body approach show that the local metal (substrate) *s*-*d* population in the resonantly excited state changes little from that in the neutral ground state, in constant to the case of core ionization. One may see the core excitation essentially as an intra-atomic process with modest relaxation effect because the core excitation leaves the molecule neutral. From the viewpoint of the cooperative core-hole screening mechanism (*s*-*d* promotion mechanism) recently proposed by the author (see Refs. 15–18 for a detailed account of the mechanism and its consistent description and successful predictions of the core-hole spectral features), the resonant excitation hinders the core-hole screening mechanism.[15] As a result, the *s*-*d* population remains almost the same as that in the neutral ground state. One may see the relaxation from the core excited state into the core ionized state as follows. The excited electron delocalizes to the empty substrate. This brings the system to a state very similar to the Koopmans state (frozen-core-hole state). However, the *s*-*d* promotion mechanism, which is hindered because of the presence of the resonantly excited electron (which acts as a screening electron), will be simultaneously switched on by the delocalization of the excited electron from the ligand to the substrate. As a result, metal-ligand CT occurs and the depletion of the *d* population by the metal-ligand CT reduces the *d*-*d* effective Coulomb interaction, so that an additional *d* electron can be supplied by the *s*-*d* promotion mechanism. Without the *s*-*d* promotion, which compensates the loss of *d* electrons to the ligand, the π CT will be suppressed.[15–18] The delocalization and CT screening processes occur simultaneously. They are very fast and bring the system to the fully relaxed state with a screened core hole. Thus Γ_{CT} should be interpreted as a time scale for this event. In the case of N_2/Ni, a recent numerical study which requires a state of the art calculation technique shows that, starting from the core-hole self-consistent-field (SCF) state, to reach the core excited SCF state, the system regains a large *s* contribution at the expense of the *d* participation, giving a situation much closer to that found in the ground state.[15] To achieve the reverse process, namely, from the core excited SCF state to the core ionized SCF state is certainly of great interest, but it is not an easy task. The reverse process is expected as described above.

The charge delocalization and simultaneous CT core-hole screening due to the presence of the substrate render the core excited state the most favorable core-hole state on the time scale of core-hole decay. The relaxation time ($\Gamma_{\mathrm{CT}}^{-1}$) depends on a choice of substrate. When the metal-ligand (ML) coupling is strong, Γ_{CT} is much larger than Γ_s and Γ_v, so that the core-hole decay spectrum is dominated by normal Auger decay. This is the case with chemisorbed systems such as CO/Ni and CO/Pd, etc.[2–4] In this case there is no decay channel which leads to a final state the same as the main line direct valence photoemission state. As a result, there is no interference effect which may lead to Fano-type resonance or antiresonance behavior for the final state. The XAS spectrum will be given by $(Z_{ac})^2 A_a(\omega)$, representing the absorption from a discrete level broadened into a Lorentzian whose width is given predominantly by the charge delocalization of the excited electron. Γ_{CT} can be rewritten as $2\pi\rho|V_{ka}|^2$. Here ρ is the unoccupied density of states of the substrate band. V_{ka}, which is assumed to be k independent, describes the hybridization between an empty affinity level a (e.g., the $2\pi^*$ level) and the empty continuum states of the metal substrate $|k\rangle$. As a result of the hybridization with the substrate band, the empty affinity level is broadened. The stronger the hybridization between the empty level and the substrate band, the faster the delocalization of the excited electron from the adsorbate atomic site to the substrate. The rapid delocalization is manifested in a reduction of the core excited-state lifetime (a broader core resonance width with an increase of Γ_{CT}). Thus the increase of the XAS width indicates the stronger ML coupling in the core excited state and further broadening of the empty affinity level. The interpretation of the width of the XAS spectrum seems to be controversial. Whether the width should be interpreted as a lifetime width for the decay of the excited electron to the core-hole ground state,[19–21] or as the density of states for the core excited state,[10] appears to be more or less a problem of semantics rather than of physics.

When Γ_{CT} and $\Gamma_s(\Gamma_v)$ are comparable, the resonant spectrum splits into the spectral feature due to spectator (participant) decay from a neutral core excited state and that due to normal Auger decay from an ionic state. The total spectral intensity ratio of the spectator (or participant) decay spectrum to the normal Auger decay spectrum is given by $\Gamma_{s(v)}/\Gamma_{\mathrm{CT}}$. Such examples recently observed are the DES spectrum of Ar adsorbed on a number of substrates [graphite, Pt(111), Cu(100), Au(110), and Ag(110)], observed at the Ar $2p$-$4s$ resonance.[7,13] The presence of the substrate causes the core excited neutral state to relax to an ionic core-hole state, on the time scale of the core-hole lifetime, by the decay of the excited electron to the Fermi level of the substrate. In the DES spectrum, this is manifested in the increase of the portion of the Auger decay feature (see Table I).[13] Thus Γ_{CT} can be determined from the portion of the Auger decay in the spectrum, namely,

$$\Gamma_{\mathrm{CT}}/(\Gamma_{\mathrm{CT}}+\Gamma_s+\Gamma_v)\approx\Gamma_{\mathrm{CT}}/(\Gamma_c+\Gamma_{\mathrm{CT}})\ .$$

$\Gamma_c=0.12$ eV, which is the core-hole width of the Ar $2p$ hole [e.g., 5.5×10^{-15} sec (Ref. 22)] is used to determine Γ_{CT}.[13] Here it is assumed that Γ_V is very small and Γ_s is very close to Γ_c because the decay energy is so large that the presence of the spectator electron, which may screen the two final-state holes, will not be effective enough to influence the Auger electron wave function. However, this is not necessarily the case with the Coster-Kronig (CK) type of decay. Because of a small CK decay energy, the CK electron wave function is often sensitive to the final-state two-hole potential, which may be screened by the presence of an extra electron.[23] Γ_{CT} and Γ_a determined by the authors of Ref. 13 are also listed in Table I. The instrumental resolution is added in a quadratic to a linear sum for Γ_{CT} and Γ_c to evaluate Γ_a. As noted by the authors of Ref. 13, Γ_a deviates substantially from the XAS width for Ar on Cu and Ag, while for a more weakly coupled system (graphite, Pt), the agreement with the XAS width is much better. As noted by the authors of Ref. 13, the assumption of a Lorentzian profile for the XAS resonance peak is not valid for more strongly coupled systems (Ar/Cu, Ar/Ag). As already pointed out, strictly speaking, Γ_{CT} depends on the excitation energy through the density of states and the coupling matrix element (V_{ka}). This may explain the deviation from a Lorentzian profile and the inadequacy of determination of Γ_{CT} by the above-mentioned method. Moreover, in the present formulation, the interference effect between spectator and Auger decay channels which eventually end in the same doubly ionized final state is neglected. When the interference is strong, the spectral cannot be separated into Lorentzian profiles for different decay channels, and then the determination of the relaxation time by the present method may become inaccurate.

TABLE I. The contributions from ionic decay (Auger decay) in the DES spectra of Ar adsorbed on different substrates measured at the $2P_{3/2}\rightarrow 4s$ resonance. Γ_{CT} is the width due to the delocalization of the resonantly excited electron, Γ_{XAS} is the $2P_{3/2}\rightarrow 4s$ resonance width, and I_S/I_M is the XPS satellite/to main line intensity ratio obtained from δE (XAS-XPS energy difference) and Γ_{CT}. Γ_a is the calculated XAS width. $\delta\varepsilon$ is the spectator-Auger energy difference. The experimental data are from Ref. 13. (Quantities in units of eV, except for the Auger intensity ratios which are given in %.)

Substrate	Auger ratio	Γ_{CT}	Γ_a	Γ_{XAS}	I_S/I_M	δE	$\delta\varepsilon$
Graphite	30±5	0.05	0.31	0.28	0.0018	2.1	3.1
Pt(111)	54±5	0.14	0.33	0.30	0.0015	3.9	2.4
Au(110)	67±5	0.24			0.0033	3.4	2.0
Cu(100)	85±10	0.66	0.8	0.35	0.013	2.8	1.9
Ag(110)	85±10	0.66	0.8	0.48	0.017	2.5	1.2

One can estimate whether the substrate-to-adsorbate CT shakeup satellite state can be observed in the XPS spectrum. We take a local cluster approach by which the electronic structure is described by CI. In essence it is an Anderson-impurity Hamiltonian description of the substrate valence band hybridized to the ligand empty levels, but neglecting the substrate bandwidth. The Hamiltonian describing the metal-ligand CT in XPS is

$$H=\varepsilon_c c^\dagger c+\varepsilon_d d^\dagger d+(\varepsilon_d+\Delta-Uc^\dagger c)p^\dagger p$$
$$+V(d^\dagger p+p^\dagger d)\ . \qquad (22)$$

Here $p^\dagger$, $d^\dagger$, and $c^\dagger$ are the creation operators for valence ligand p, metal d, and core electrons, respectively. The orbital energies are $\varepsilon_d+\Delta$, ε_d, and ε_c, respectively. After photoemission the core hole pulls down the p level by an amount U, shifting it to about the same energy as in the $Z+1$ molecule (atom). The transfer integral responsible for the bonding between p and d is $V=\langle p|H|d\rangle$. Defining $\tan 2\theta=2V/\Delta$ and $\tan 2\theta'=2V/(\Delta-U)$, the initial state is $|i\rangle=\cos\theta|d\rangle-\sin\theta|p\rangle$, with energy $\varepsilon_d+\Delta/2-(\Delta^2+4v^2)^{1/2}/2$, whereas the final states are $|f_M\rangle=\cos\theta'|d\rangle-\sin\theta'|p\rangle$ and $|f_s\rangle=\sin\theta'|d\rangle+\cos\theta'|p\rangle$. The final-state energies are $E_{M,S}=\varepsilon_d+(\Delta-U\mp\delta E)/2$ with $\delta E=[(\Delta-U)^2+4V^2]^{1/2}$. Thus in the photoelectron spectrum a satellite line is seen at a distance δE from the (main) line. In the sudden approximation, the CT satellite (I_s) to main line

(I_M) intensity ratio is given by

$$I_s/I_M=\tan^2(\theta'-\theta)\ . \quad (23)$$

In the present case,

$$\Gamma_{CT}(=2\pi|V|^2)\ll|\Delta-U|\approx|\delta E|$$

and $\theta\approx 0$ [the hybridization in the initial state is very weak, and V(initial state) differs from V(final state)]. Thus we obtain

$$I_s/I_M\simeq\frac{|V|^2}{(\delta E)^2}\ . \quad (24)$$

The calculated I_s/I_M are listed in Table I. The satellite intensity is too small to be observable by XPS, although the intensity increases for a more strongly coupled system. We may consider the case of CO/Ni(100). The C 1s XPS width is 0.7 eV, while the C 1s-to-π^* XAS width is 1.7 eV.[10,24] Assuming that the width difference 1.0 eV is approximately equal to Γ_{CT}, one obtains the satellite intensity of 0.04 at 2.1 eV where the π shakeup satellite is observed in the C 1s XPS spectrum. This is in accord with experiment and a recent many-body calculation.[16,24]

The authors of Ref. 13 noted that the spectator–Auger-decay energy difference ($\delta\varepsilon$ in Table I) decreases in the order of Pt, Au, Cu, and Ag. At resonance, the kinetic-energy separation between the spectator decay ($\varepsilon_s+\omega_{ca}$) and the normal Auger decay ($\varepsilon_A=\varepsilon_{jl}-\varepsilon_c$) is given by $U_{ja}+U_{la}-U_{ca}$. Thus the energy difference $\delta\varepsilon$ is given by $2U_{3p4s}-U_{2p4s}\approx U_{2p4s}$. The XPS-XAS energy deference (δE in Table I) is given by $\varepsilon_{4s}-U_{2p4s}$which decreases also in the same order. This can be interpreted as the further screening of U and the lowering of the 4s empty level in both core excited state ($\varepsilon_{4s}-U_{2p4s}$) and ground state ($\varepsilon_{4s}$). As noted also by the authors of Ref. 13, the closer the empty level is to the Fermi level, the larger is the probability of the delocalization of the excited electron.

An indication of chemisorption in the core excited state could be the effect of the core hole which could perturb the properties of the adsorption system. The attractive potential of the core hole may bring the empty adsorbate level closer to the Fermi level, so that chemical binding between the adsorbate and substrate will occur. In that case, if the integrated intensity of the XAS resonance peak does not change in comparison to the gas-phase data, this is an indication of chemisorption in the core excited state, despite the physisorption in the ground state.[13]

At the resonance the spectral intensity ratio of the normal x-ray emission to the resonant x-ray emission is given by Γ_{CT}/Γ_t. For a more strongly coupled system such as CO/Ni, $\Gamma_{CT}\gg\Gamma_t$. Thus the normal x-ray emission peak dominates. When $\Gamma_{CT}\approx\Gamma_t$ ($\approx\Gamma_c$), the spectral intensities of normal x-ray emission and resonant x-ray emission become comparable. The emission energy difference between these two lines will be $U_{va}-U_{ca}$.

It is not only the DES spectra of molecules (atoms) adsorbed on metals surfaces which show spectral features due to the competition between the delocalization of a resonantly excited electron with the simultaneous CT core-hole screening and core-hole decay. Recently, Elango *et al.*[14] measured the DES spectra of NaCl, KCl, $CaCl_2$, CaF_2, and Sc_2O_3 in the vicinity of the L_{23} absorption edges. The DES spectra show both spectator (participant) decay and normal Auger decay spectral features, whose spectral intensity depends on the degree of localization of the resonantly excited d electron or delocalization of the d electron to an empty conduction band, reflecting the covalency of the system. Equation (16) is also applicable for those spectra to determine the relaxation time. In these systems, the L_2-M_{45} resonantly excited state can decay also to the L_3 ionized state by the $L_2L_3M_{45}$ Coster-Kronig decay, whose decay width is the difference between the L_2 and L_3 XAS (or XPS) widths. The L_3 ionized state eventually decays by L_3MM Auger decay. At the L_2 resonance, both L_2MM and L_3MM Auger spectral features appear as well as the spectator (participant) decay spectral features. The CK decay width can be determined also from the L_3MM Auger spectral intensity. Such an analysis would be useful for the study of deexcitation spectra, together with the XAS (XPS) width analysis.

As a consequence of the infinite degrees of freedom in the substrate-band electronic levels, a hole left in the substrate metal band by CT does not play any role in the electron (x-ray) emission, as if it were frozen. This is reflected in the emission energy. The Auger (radiative) decay energy from the π CT shakeup state will be the same as that from the resonantly core level excited state, if the shakeup electron does not delocalize before the Auger decay starts. Otherwise, the Auger decay energy from the shakeup state becomes the same as that from the core ionized one-hole state. The participant decay energy of the π shakeup state will be the same as that of the resonantly excited state, if both processes are possible.

In this section it is pointed out that the resonantly excited electron can delocalize on the time scale of the core-hole decay. The question which should be raised now is about the competition between the core-hole decay and the relaxation of the π shakeup satellite state, whose energy is very close to the resonantly excited state (for the C 1s shakeup satellite state of CO/Ni, only 0.5 eV larger than the resonant energy [24]). Within the framework of an Anderson-impurity-model calculation, the possibility of the appearance of Auger spectral features originating from the initial shakeup satellite state was proposed by Gunnarsson and Schönhammer.[25] However, such a possibility was experimentally denied by Wurth *et al.*[2] The CT shakeup states relax before the core-hole decay. This is not unexpected, because the shakeup excitation energy (2.1 and 8.0 eV for the C 1s shakeup satellite state of CO/Ni system[16,24] is much larger than the core-level width [0.7 eV for the C 1s main line state of CO/Ni (Ref. 24)].[26] The recently measured O KLL AES spectrum of CO/Ni(100) was found to be broader relative to the DES spectrum recorded around the O 1s XPS ionization energy.[8] This is even more pronounced for weak-chemisorption systems such as CO/Cu(100) and CO/Ag(110).[8] This spectral broadening was interpreted as due to decay from the shakeup states.[8] To study the possibility of incomplete relaxation, Auger photoelectron coincidence spectroscopy would be useful. The APECS spectrum is given by

$$I(\varepsilon_A,\varepsilon_k,\omega)\propto\sum_{c,i}|V^i_{fc}G_{cc}Z_{ck}(\omega)|^2\delta(\varepsilon_A+\varepsilon_k-\varepsilon^i_{jl}-\omega)\ . \tag{25}$$

Here indices c and i denote initial core-hole states and Auger decay channels, respectively. $Z_{ck}(\omega)$ is the dipole excitation matrix element for the core ionization. G_{cc} is given by Eq. (13). Equation (25) can be written as

$$I(\varepsilon_A,\varepsilon_{k,}\omega)\propto\sum_{c,i}|Z_{ck}(\omega)|^2\frac{\Gamma^i_c}{\Gamma_c}A_c(\varepsilon_k-\omega)$$
$$\times\delta(\varepsilon_A+\varepsilon_k-\varepsilon^i_{jl}-\omega)\ . \tag{26}$$

Here Γ_c is the total decay width of the core hole c and is given by a sum of the partial decay width Γ^i_c. The APECS can be used to assign the initial core-hole state for a particular Auger final state.[27] By fixing the Auger energy ε_A for a particular final state, the APECS spectrum (a function of the primary photoelectron energy ε_k at fixed photon excitation energy ω) is a partial XPS core-hole spectrum, which is a core-hole spectral function weighted by the partial decay ratio. If the APECS spectral intensity is not negligible also for the core-hole shakeup satellite state, the shakeup satellite state can relax to the lowest XPS core-hole state before the Auger decay starts. Note that if the Auger decay occurs directly from the shakeup state, the Auger KE differs. On the other hand, when the primary photoelectron energy ε_k is fixed at a particular XPS core-hole state, the APECS spectrum is an Auger spectrum without the initial core-hole lifetime broadening, as long as the uncertainty in the core-hole energy (given by the resolution of the photoelectron spectrometer and the bandpass of the exciting radiation) is small compared with Γ_c. A preliminary APECS spectrum of CO/Cu(100) was measured at fixed Auger energy.[28] The spectrum implies that the shakeup states relax to the lowest core-hole state by a "shakedown" process before the Auger decay starts. Further experimental studies with better statistics are needed.

III. CT CORE-HOLE SCREENING AND CORE-HOLE DECAY

A. Theory

So far we have considered the case when the lowest core-hole state is the ionic state, not a neutral core excited state. We now consider the case when the lowest core-hole state is a neutral core excited state, not an ionic state. In this case there will be competition between the normal Auger decay from an ionic state and the CT core-hole screening process from substrate to adsorbate. The latter leads to a neutral core excited state and eventually to the appearance of the spectator and participant decay features in the Auger spectrum measured above the ionization limit.[12] Moreover, the spectral and participant decay energies are the same as those at resonance (independent of the excitation energy).

We treat the problem within the sudden approximation. We denote by $|c\rangle$ the initial core-hole state $|c\rangle=c_c|\Psi_0\rangle$ and by $|a\rangle$ the CT-screened (neutral) core-hole state $|a\rangle=c^\dagger_a c_m c_c|\Psi_0\rangle$. Here an electron in the metal is transferred into an empty affinity level a to screen a core hole c (m is a hole left in the metal substrate which will be delocalized within the time scale of the core-hole decay). We denote by $|s\rangle$ the singly ionized final state formed by the spectator decay from $|a\rangle$, $|s\rangle=c^\dagger_\varepsilon c^\dagger_a c_j c_l c_m|\Psi_0\rangle$, and by $|v\rangle$ the singly ionized final state formed by participant decay from $|a\rangle$, $|v\rangle=c^\dagger_\varepsilon c_v c_m|\Psi_0\rangle$. We denote by Z_{ck} the dipole matrix element between $|\Psi_0\rangle$ and $|c\rangle$ and by V_{ca} the CT screening matrix element between $|c\rangle$ and $|a\rangle$. The rest of the notation is the same as before. For the sake of simplicity, we consider only one decay channel for each Auger, spectator, and participant decay. It is also assumed that the coupling matrix elements such as V_{ca}, V_{sa}, and V_{fc} are energy independent. Upon core ionization, the emission amplitudes will be given by

$$I(\varepsilon)\propto\int|V_{fc}G_{cc}Z_{ck}|^2\delta(\varepsilon+E-\varepsilon_{jl})dE+\int|V_{sa}G_{aa}V_{ca}G_{cc}Z_{ck}|^2\delta(\varepsilon+E-\varepsilon_s-\varepsilon_m)dE\,d\varepsilon_m$$
$$+\int|V_{va}G_{aa}V_{ca}G_{cc}Z_{ck}|^2\delta(\varepsilon+E-\varepsilon_v-\varepsilon_m)dE\,d\varepsilon_m\ . \tag{27}$$

Here E is the core-hole energy parameter. The first term describes the normal Auger decay ($c^{-1}\to j^{-1}l^{-1}\varepsilon$) from the "unscreened" core-hole state, the second term represents the spectator decay ($c^{-1}am^{-1}\to j^{-1}l^{-1}a\varepsilon m^{-1}$) from the CT-screened neutral state, and the third term is the participant decay ($c^{-1}am^{-1}\to v^{-1}m^{-1}\varepsilon$) from the CT-screened state. G_{cc} and G_{aa} are given by

$$G_{cc}=(E-\varepsilon_c-i\Gamma_t/2)^{-1}\ , \tag{28}$$

$$\Gamma_t=\Gamma_{\mathrm{CT}}+\Gamma_c\ , \tag{29}$$

$$\Gamma_{\mathrm{CT}}=2\pi|V_{ca}|^2\ , \tag{30}$$

$$\Gamma_c=2\pi|V_{fc}|^2\ , \tag{31}$$

$$G_{aa}=(E+\omega_{ca}-\varepsilon_m-i\Gamma_a/2)^{-1}\ . \tag{32}$$

$$\Gamma_a=\Gamma_s+\Gamma_v\ , \tag{33}$$

$$\Gamma_s=2\pi|V_{sa}|^2\ , \tag{34}$$

$$\Gamma_v=2\pi|V_{va}|^2\ . \tag{35}$$

Equation (27) can be rewritten as

$$I(\varepsilon)\propto|Z_{ck}|^2\left\{\frac{\Gamma_c}{\Gamma_t}A_c(\varepsilon_{jl}-\varepsilon)+\frac{\Gamma_{\mathrm{CT}}}{\Gamma_t}\frac{\Gamma_s}{\Gamma_a}A_a(\varepsilon_s-\varepsilon+\omega_{ca})+\frac{\Gamma_{\mathrm{CT}}}{\Gamma_t}\frac{\Gamma_v}{\Gamma_a}A_a(\varepsilon_v-\varepsilon+\omega_{ca})\right\}. \tag{36}$$

The meanings of the terms are the same as those of Eq. (27). The spectral function $A_c(\varepsilon_{jl}-\varepsilon)$ of the "unscreened" state $|c\rangle$ is given by the imaginary part of G_{cc}. It is represented by a Lorentzian profile with a width Γ_t, giving rise to a finite lifetime of the state $|c\rangle$ by both CT relaxation (Γ_{CT}) and Auger decay (Γ_c):

$$A_c(\varepsilon_{jl}-\varepsilon)=\frac{1}{\pi}\frac{\Gamma_t/2}{(\varepsilon_{jl}-\varepsilon-\varepsilon_c)^2+(\Gamma_t/2)^2}. \tag{37}$$

The spectral function A_a of the "screened" state $|a\rangle$ is given by the imaginary part of G_{aa} and a profile with a width Γ_a, giving rise to a finite lifetime of the state $|a\rangle$ by both spectator decay (Γ_s) and participant decay (Γ_v):

$$A_s(\varepsilon_{s(v)}-\varepsilon+\omega_{ca})=\frac{1}{\pi}\frac{\Gamma_a/2}{(\varepsilon_{s(v)}-\varepsilon+\omega_{ca})^2+(\Gamma_a/2)^2}. \tag{38}$$

B. Discussion

If the "unscreened" core-hole state can relax to the "screened" core-hole state on the time scale of core-hole decay, the XPS width of the "unscreened" core-hole state of the adsorbate, Γ_t, is given by a sum of Γ_{CT} and Γ_c, instead of Γ_c. It is larger than that of the free atom or molecule by Γ_{CT}. The widths of the spectator and participant decay spectra are given by Γ_a, the sum of the spectator and participant decay widths. The decay energy is given by $\varepsilon=\varepsilon_{s(v)}+\omega_{ca}$ which is constant and independent of the excitation energy (when the excitation energy is far above the ionization limit). These energies are the same as those at resonance. At resonance (below the ionization limit), the resonant photoemission spectrum is given by

$$I(\varepsilon;\omega)\propto|Z_{ac}(\omega)|^2A_a|(\omega)\left\{\frac{\Gamma_v}{\Gamma_a}A_v(\varepsilon-\varepsilon_v-\omega)+\frac{\Gamma_s}{\Gamma_a}A_s(\varepsilon-\varepsilon_s-\omega)\right\}, \tag{39}$$

$$A_a(\omega)=\frac{1}{\pi}\frac{\Gamma_a/2}{(\omega-\omega_{ca})^2+(\Gamma_a/2)^2}, \tag{40}$$

$$A_{s(v)}(\varepsilon-\varepsilon_{s(v)}-\omega)=\frac{1}{\pi}\frac{\Gamma_{fs(v)}/2}{(\varepsilon-\varepsilon_{s(v)}-\omega)^2+(\Gamma_{fs(v)}/2)^2}. \tag{41}$$

Equation (39) is the same as the first and second terms of Eq. (16) except for the definitions of $A_{s(v)}$ which are different. At the resonance the width of the spectator (participant) decay spectrum is given by the lifetime $\Gamma_{fs(v)}$ of the final state reached by the spectator (participant) decay from the resonantly excited state. Thus the width of the spectator (participant) decay spectrum is identical to that of the valence photoemission satellite (main) line. As a result, there should be a difference in width between the decay spectrum observed at resonance and that upon the core ionization.

The relative spectral intensity of the neutral (spectator and participant) to ionic (Auger) decay processes in the "Auger" spectrum is given by $\Gamma_{\mathrm{CT}}/\Gamma_c$. Thus the neutralization rate Γ_{CT} can be determined from the relative spectral intensity. The spectral intensity ratio of the Auger and spectator (participant) decay spectra is reversed when the relative positions of the XPS and XAS maxima are reversed.

Recently the DES spectrum of N_2 physisorbed on graphite was measured. The spectrum shows both Auger and autoionization spectral features. Using $\Gamma_c=0.12$ eV, $\Gamma_{\mathrm{CT}}=0.07$ eV is determined from the autoionization spectral intensity of 0.38 ± 0.05.[12] One can estimate also whether the CT-screened neutral core-hole state can be observed in the XPS spectrum by using Eqs. (23) and (24). We obtain $I_sI_M\approx0.001$, so the probability that one observes the CT shakedown state in the XPS spectrum is beyond the resolution of XPS. Indeed, the N 1*s* XPS spectrum of N_2/graphite does not show such a state.[12]

IV. XAS SPECTRUM AND DES SPECTRUM

As Eq. (16) shows, near or at the resonance, the total intensity of the DES spectrum measured at a certain excitation energy is the XAS spectrum intensity at that energy. Thus the total intensity of DES spectra recorded at several photon excitation energies can be used to monitor the XAS spectrum. By collecting the emitted electrons at a constant binding energy $\varepsilon_{s(v)}=\omega-\varepsilon$, where ω is the photon energy and ε the kinetic energy, one obtains the constant ionic (final) -state spectroscopy (CISS) spectrum. By assuming that the lifetime broadening of the final state $s(v)$ is negligible [i.e., replacing $A_{s(v)}(\varepsilon-\varepsilon_{s(v)}-\omega)$ by $\delta(\varepsilon-\varepsilon_{s(v)}-\omega)$, the CISS spectrum will be given by

$$I(\omega)\propto|Z_{ac}(\omega)|^2A_a(\omega)\frac{\Gamma_{s(v)}}{\Gamma_a}. \tag{42}$$

The CISS spectrum integrated over the whole BE range gives the XAS spectrum in total electron yield. Thus CISS can be interpreted as the partial electron yield at constant binding energy. By the CISS spectrum one can determine also the partial decay rate of the resonantly excited state. When the XAS spectrum consists of more than two resonant excitations (e.g., N_2/Ni due to the inequivalent N atoms[4]) the XAS spectrum can be separated into each excitation component in terms of the CISS spectrum for the final state which can be reached only from a particular resonantly excited state.

V. XES SPECTRA OF ADSORBATES

The O 1*s* XES spectrum of CO/Ni(100) shows an interesting spectral feature in comparison to that of free CO.[29] The spectrum shows a strong satellite feature at

1.8 eV above the main line. The satellite intensity is comparable to the main line intensity. The transition from the O 1s core main line state to the final 1π hole state is assigned to the main line. The satellite is interpreted as due to the initial core-hole shakeup state.[15,29] The main line corresponds to the transition $1s^{-1} \rightarrow 1\pi^{-1}$ and the satellite line to $1s^{-1}\pi_m^{-1}\pi^* \rightarrow 1\pi^{-1}\pi_m^{-1}\pi^*$ (here π_m is the bonding orbital of mainly metal character). The energy of the latter transition is larger than that of the former by $U_{1\pi 2\pi} - U_{1s2\pi}$ [we obtain $U_{1s2\pi} = 2$ eV from inverse photoemission data ($\varepsilon_{2\pi} = 3-4$ eV) (Ref. 30) and the XPS-XAS energy difference (1.5 eV) (Ref. 31)]. As $U_{1\pi 2\pi} < U_{1s2\pi}$, it is unlikely that the satellite energy is larger than that of the main line by 1.8 eV. If the final state for the satellite is the same as that of the main line, the initial shakeup state must be 1.8 eV higher than the initial main line state. The C 1s XPS spectrum shows the π CT shakeup satellite of a small intensity at 2.1 eV above the main line,[24] whereas the O 1s spectrum does not show such a satellite. However, the CI calculation predicts it at 1.6 eV.[16] Moreover, a Green's function calculation shows the breakdown of the one-electron picture of the 1π ionization due to strong CI between $1\pi^{-1}$ and $1\pi^{-1}\pi_m^{1}\pi^*$ configurations.[32] Then the main line corresponds to $1s^{-1}$ to $1\pi^{-1}\pi_m^{-1}\pi^*$, while the satellite corresponds to $1s^{-1}\pi_m^{-1}\pi^*$ to $1_\pi^{-1}\pi_m^{-1}\pi^*$.[15] This explains at least the energy separation of 1.8 eV. However, it appears to be difficult to explain the enhanced satellite intensity because the initial π CT shakeup state has a very small intensity. For a qualitative interpretation of the spectrum, we take a local cluster approach. The ground state $|\psi_0\rangle$ is a linear combination of properly symmetrized d^n and $d^{n-1}L$ configurations,

$$|\Psi_0\rangle = \cos\theta_0 |d^n\rangle - \sin\theta_0 |d^{n-1}L\rangle \ .$$

Here L denotes a ligand electron of appropriate symmetry relative to empty metal d states. The core-hole state is determined by a linear combination of the same valence-electron combinations as those describing the ground state. The main line core-hole state $|M\rangle$ and the satellite core-hole state $|S\rangle$ are given by

$$|M\rangle = \cos\theta_c |\underline{c}d^n\rangle - \sin\theta_c |\underline{c}d^{n-1}L\rangle$$

and

$$|S\rangle = \sin\theta_c |\underline{c}d^n\rangle + \cos\theta_c |\underline{c}d^{n-1}L\rangle \ ,$$

respectively. Here $\underline{c}$ denotes a core hole. The same is the case for the valence ionized final state $|v(M)\rangle$ and $|v(S)\rangle$, $\underline{c}$ and θ_c being replaced by $\underline{v}$ and θ_v, respectively. The x-ray emission spectrum is given by

$$I(\omega) \propto \int \Big|\sum_{f,i} Z_{fi} \langle f|vc^\dagger|i\rangle G_{ii}(E) \langle i|c|\Psi_0\rangle\Big|^2 \times \delta(E+\omega-\varepsilon_f)\,dE \ . \tag{43}$$

Here $c, c^\dagger$, and v are the core-electron annihilation and creation and the valence annihilation operators, respectively. $|i\rangle$ and $|f\rangle$ are the initial core-hole and final valence-hole states, respectively. G_{ii} is the core-hole propagator, ω is the photon energy, and ε_f and E are the final- and initial-state energy parameters, respectively. When the interference between different decay channels is neglected, the intensities of four different decay channels are given as follows:

$$\begin{aligned}
&(\mathrm{A})\quad |M\rangle \rightarrow |v(M)\rangle; \quad \propto \cos^2(\theta_c - \theta_v) I_M \ ,\\
&(\mathrm{B})\quad |S\rangle \rightarrow |v(M)\rangle; \quad \propto \sin^2(\theta_c - \theta_v) I_S \ ,\\
&(\mathrm{C})\quad |M\rangle \rightarrow |v(S)\rangle; \quad \propto \sin^2(\theta_c - \theta_v) I_M \ ,\\
&(\mathrm{D})\quad |S\rangle \rightarrow |v(S)\rangle; \quad \propto \cos^2(\theta_c - \theta_v) I_S \ .
\end{aligned} \tag{44}$$

Here I_M and I_s are the XPS spectral intensity of $|M\rangle$ and $|S\rangle$, respectively. The relative spectral intensity for the emission processes B and C, A and D are given by I_s/I_M which is smaller than 0.05 for CO/Ni. For a case similar to CO/Ni(100), where the ground state is dominated by $|d^n\rangle$ and $I_s/I_M = 0.05$, the enhanced satellite intensity is due to the final-state effect rather than the initial-state effect. The initial state is the XPS lowest-energy state. The main line (C) and the satellite line (A) in the XES spectrum correspond to the transition to the final main line state dominated by $\underline{v}d^n$ and that to the final CT shakedown shakedown dominated by $\underline{v}d^{n-1}L$, respectively. The former spectral intensity is 0.55 and the latter is 0.45, if the spectral intensity of the shakedown state $\underline{v}d^{n-1}L$ is 0.25. The satellite intensity (0.45) is larger than that of the final shakedown state (0.25). This is because the spectral intensities are not simply given by the sum of products of the weights of the basis states in the initial and final states, but also contain the cross term $\sim 2\sin\theta_c \cos\theta_c \sin\theta_v \cos\theta_v$ and this is added to the satellite line (A) and subtracted from the main line (C). The shakedown satellite for the 1π ionization has not been observed so far but the present result indicates the strong CI between $1\pi^{-1}$ and $1\pi^{-1}\pi_m^{-1}\pi^*$ configurations. The time scale of the radiative decay process is much longer than that for the Auger decay process, so that the π CT shakeup state relaxes to the main line state before the x-ray emission starts. XES studies of adsorbates above the core ionization limit and below the π CT shakeup excitation energy would be interesting.

VI. CONCLUSION

It is shown that if the time scale of the relaxation from the resonantly core level excited state to the lowest core-hole state is comparable to the core-hole decay time, there is a competition between the relaxation and the core-hole decay. As a result one observes Auger spectral features (decay from the ionic state) in the DES spectrum of an adsorbed molecule (atom). If the relaxation occurs much faster than the core-hole decay, the DES spectrum of the adsorbate at the resonance (which is above the XPS ionization limit) becomes very similar to the AES spectrum. This is the case with strongly chemisorbed systems. On the other hand, if the XPS ionized limit is above the resonance, the presence of a core hole pulls an empty affinity level below the Fermi level so that CT from the substrate to the adsorbate may occur on the time scale of the core-hole decay. As a result there is a competition between the core-hole decay and the CT screening (neutralization). An autoionization spectral feature appears in the AES spectrum. A more interesting case which should be investigated is the case of a Coster-Kronig-type decay spectrum, where the decay energy is much smaller than the Auger decay energy. In the case of *KVV* Auger (spectator) decay of CO adsorbants, the decay energy is larger and the relaxation is fast so that the interaction between the decay electron and the excited electron which moves out from the excited atomic site is negligible. However, if the decay energy is small and the relaxation is slow, there may be a post collision interaction kind of effect on the decay spectrum. One may also study the competition between the core-hole decay and the relaxation by selecting different initial core-level excitations so that the core-hole decay time can be varied.

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[1] C. T. Chen, R. A. DiDo, W. K. Ford, E. W. Plummer, and W. Eberhardt, Phys. Rev. B **32**, 8434 (1985).

[2] W. Wurth, C. Schneider, R. Treichler, E. Umbach, and D. Menzel, Phys. Rev. B **35**, 7741 (1987).

[3] W. Wurth, C. Schneider, R. Treichler, D. Menzel, and E. Umbach, Phys. Rev. B **37**, 8725 (1988).

[4] O. Björneholm, A. Sandell, A. Nilsson, N. Mårtensson, and J. N. Andersen, Phys. Scr. **T41**, 217 (1992).

[5] M. Ohno, Phys. Rev. B **45**, 3865 (1992).

[6] G. Illing, T. Porwol, I. Hemmerich, G. Dömötör, H. Kuhlenbeck, H.-J. Freund, C.-M. Liegner, and W. von Niessen, J. Electron. Spectros. Relat. Phenom. **51**, 149 (1992).

[7] W. Wurth, P. Feulner, and D. Menzel, Phys. Scr. **T41**, 213 (1992).

[8] A. Sandell, O. Björneholm, A. Nilsson, J. N. Andersen, B. Hernnäs, and N. Mårtensson (unpublished).

[9] W. Eberhard, E. W. Plummer, C. T. Chen, and W. K. Ford, Aust. J. Phys. **39**, 853 (1986).

[10] A. Nilsson, O. Björneholm, E. O. F. Zdansky, H. Tillborg, N. Mårtensson, J. N. Andersen, and R. Nyholm, Chem. Phys. Lett. **197**, 12 (1992).

[11] B. Gumhalter, K. Wandelt, and Ph. Avouris, Phys. Rev. B **37**, 8048 (1988).

[12] O. Björneholm, A. Nilsson, A. Sandell, B. Hernnäs, and N. Mårtensson, Phys. Rev. Lett. **68**, 1892 (1992).

[13] A. Sandell, A. Nilsson, O. Björneholm, B. Hernnäs, P. Benich, and N. Mårtensson (unpublished); A. Sandell, Ph.D. thesis, Uppsala University, 1993.

[14] M. Elango, A. Ausmees, A. Kikas, E. Nõmmiste, R. Ruus, A. Saar, J. F. van Acker, J. N. Andersen, R. Nyholm, and I. Martinsen, Phys. Rev. B **47**, 11 736 (1993).

[15] M. Ohno and P. Decleva, Surf. Sci. **284**, 372 (1993); **296**, 87 (1993); Chem. Phys. **171**, 9 (1993); J. Chem. Phys. **98**, 8070 (1993).

[16] M. Ohno and P. Decleva, Surf. Sci. **258**, 91 (1991); **269/270**, 264 (1992); Chem. Phys. **156**, 309 (1991).

[17] P. Decleva and M. Ohno, Chem. Phys. **160**, 341 (1992); **160**, 353 (1992); **164**, 73 (1992).

[18] M. Ohno, J. Electron Spectrosc. Relat. Phenom. (to be published).

[19] R. Murphy, E. W. Plummer, C. T. Chen, W. Eberhardt, and R. Carr, Phys. Rev. B **39**, 7517 (1989).

[20] D. Menzel, P. Feulner, R. Treichler, E. Umbach, and W. Wurth, Phys. Scr. **T17**, 166 (1987).

[21] H. Rabus, D. Arvantis, M. Domke, A. Puschmann, and K. Baberschke, Phys. Scr. **T31**, 131 (1990).

[22] D. A. Shaw, G. C. King, F. H. Read, and D. Crejanovic, J. Phys. B **15**, 1785 (1982).

[23] M. Ohno, Phys. Rev. A **49**, 4430 (1994).

[24] A. Nilsson and N. Mårtensson, Phys. Rev. B **40**, 10 249 (1989).

[25] O. Gunnarsson and K. Schönhammer, Phys. Rev. B **22**, 3710 (1980).

[26] J. W. Gadzuk and M. Sunjic, Phys. Rev. B **12**, 524 (1975).

[27] H. Haak, G. A. Sawatzky, and T. D. Thomas, Phys. Rev. Lett. **41**, 1825 (1978).

[28] R. A. Bartynski, E. Jensen, C.-C. Kao, S. Hulbert, R. Garrett, and F. Curti (unpublished).

[29] N. Wassdahl, A. Nilsson, T. Wiell, H. Tillborg, L.-C. Duda, J. H. Guo, N. Mårtensson, J. Nordgren, J. N. Andersen, and R. Nyholm, Phys. Rev. Lett. **69**, 812 (1992).

[30] P. D. Johnson and S. L. Hulbert, Phys. Rev. B **35**, 9427 (1987).

[31] O. Björneholm, A. Nilsson, E. O. F. Zdansky, A. Sandell, B. Hernnäs, H. Tillborg, J.-N. Andersen, and N. Mårtensson, Phys. Rev. B **46**, 10 353 (1992).

[32] M. Ohno and W. von Niessen, Phys. Rev. B **42**, 7370 (1990); **44**, 1896 (1991); **45**, 1851 (1992); **45**, 9382 (1992).