One-Step and Two-Step Description of Deexcitation Processes in Weakly Interacting Systems

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The origin of one- and two-step behavior of core-hole decay processes is identified in connection with high resolution autoionization spectra for Ar/Pt(111). The spectra simultaneously show features of the two types (resonant Raman vs Auger-like behavior). The character of the process is determined by whether excitations in the intermediate state created in the scattering process are detected in the decay process or not. The consequences for phenomena like resonant Raman Auger, resonant inelastic x-ray scattering, and resonant photoemission are discussed.

Resonant spectroscopies such as resonant photoemission (RPES) (see, e.g., [1,2]) and resonant inelastic x-ray scattering (RIXS) (see, e.g., [3,4]) have been used as powerful tools for studying the electronic structure of matter. With the growing access to high resolution tunable x-ray excitation sources there is rapid progress in this field, leading to new and much improved possibilities to extract detailed information about the investigated systems.

The resonant process involves the (virtual) excitation and deexcitation (Auger or x-ray emission) of a core electron. The process ends up in a final state with one valence electron ionized or excited, i.e., the same type of final state as in valence electron photoemission or optical absorption [5]. In this way the valence electronic structure can be studied with the additional possibility of utilizing the unique features of a core level probe, such as element specificity, chemical shifts between different sites, etc. The excitation step can also be used to induce symmetry restrictions on the final states [6], or to make studies of selected vibrational states [7,8]. However, due to the complexity of the process, the information that can be extracted depends heavily on the extent of one's understanding of the process itself. One fundamental issue is to what extent the excitation and deexcitation steps in the process are truly coherent.

In the normal treatment of Auger decay and x-ray emission one usually uses a two-step language, i.e., the excitation and deexcitation steps are treated as consecutive and independent (incoherent) events [9]. However, a number of high resolution studies have clearly demonstrated that in general such an approach is not valid. Rather, a one-step treatment is required. Examples of this are the observations of the Auger resonant Raman effect [10,11] and effects of vibrational and state interference in autoionization decay [12]. In other cases, however, the two-step approach gives a satisfactory or even superior description of the process. The distinction between these two types of processes (one-step or two-step) is not at all clearcut,

and there is considerable debate on several of the key issues, in particular, when to use what approach.

For atoms and molecules one makes a separation between the Raman regime below and the Auger-like regime above the ionization threshold [5,13,14]. The latter regime is denoted the postcollision interaction (PCI) regime to emphasize that the two emitted electrons may be interacting. For solid systems, however, such a borderline provides no help at all. In the case of metallic solids, for instance, there is a continuum of states already starting from the Fermi level, and the resonant spectroscopies usually involve states well below the ionization limit. Furthermore, as will be seen below, there are cases where the same excitation leads to features with totally different behavior. In spite of the great importance of the resonance effects there have been no investigations which identified the mechanisms relating to the distinction between one-step and two-step behavior. There has been a well-known controversy on, for example, whether the so-called resonant photoemission in Ni really corresponds to a coherent process [15,16]. One also knows that there is a large fraction of incoherent intensity in RIXS, but there have been no detailed considerations of what causes this. It is therefore a most important issue in connection to the whole field of resonant spectroscopies to identify the mechanisms causing the loss of coherence.

We have addressed this problem in connection with high resolution autoionization measurements on Ar/Pt(111). The weak coupling between the Ar and the substrate [17] makes this system most suitable for investigating this problem. There are a number of reasons for this: (i) Both types of processes are simultaneously manifested in the spectra, (ii) the spectral features are narrow and well separated, (iii) the difference between the final states can be understood in intuitive ways, (iv) the intensities in the different "channels" are of the same order of magnitude, and (v) a whole range of intermediate states can be reached with varying character in terms of

wave function localization, and the consequences of this can be investigated.

The experiments were performed at beam line 8.0 at the *Advanced Light Source*. The beam line is an undulator beam line, using a modified "Dragon" monochromator with a calculated maximum resolving power of 10^4. The end station was designed at Uppsala University for surface science experiments and comprises a rotatable Scienta SES200 electron spectrometer [18]. The photon energy resolution was better than 100 meV in the present measurements, while the resolution of the spectrometer was set to 200 meV. The sample was cooled by a liquid He flow cryostat. The Ar monolayer was prepared by annealing multilayers to elevated temperatures. This procedure was monitored with the Ar $2p$ XP spectrum, utilizing the core level shifts between first and higher layers [17].

In Fig. 1 the Ar $2p_{3/2} \rightarrow 4s$ x-ray absorption (XA) and $2p$ x-ray photoelectron (XP) spectra are shown on a common energy scale. The ionic x-ray photoelectron spectroscopy (XPS) final state is located 3.9 eV below the neutral x-ray absorption spectroscopy (XAS) final state. The lowest core excited state is thus ionic. The XAS spectrum shows a pronounced resonance due to excitations to the atomic $4s$ level. However, we also observe that the resonance is modified by the interaction with the substrate. It is broadened, and there is an asymmetric tail extending all the way to the Ar $2p_{3/2}$ binding energy.

Figure 2 shows nonradiative (electron emission) decay spectra for a number of photon energies over the XAS resonance. As can be seen the spectra vary considerably with photon energy. However, we immediately distinguish two sets of peaks in the spectra, one which stays at constant kinetic energy and one which moves as the excitation energy is varied. It is also seen that the relative intensities of these vary strongly with photon energy.

The spectral features can be identified as demonstrated in the lower part of Fig. 2. (B) is a $2p_{3/2}$ off-resonance Auger spectrum for the Ar/Pt sample. The different peaks correspond to the multiplet levels of the $3p^4$ configuration. (C) is a gas phase autoionization spectrum originating from the $2p_{3/2}^{-1}4s^1$ state, convoluted with a 0.3 eV Gaussian and shifted by an appropriate amount. The peaks in this spectrum have been assigned to the $3s$ photoemission line (223 eV) and the $^{2,4}P$ (219.5 eV), ^2D (218.5 eV), and ^2S (216.5 eV) terms of the $3p^4 4s^1$ configuration. The features that appear at lower kinetic energy are *shake-up* satellites primarily of the type $3p^4 5s^1$. By summing (B) and (C) with appropriate weight factors we obtain (A). As can be seen this curve mimics almost all features of the experimental Ar/Pt
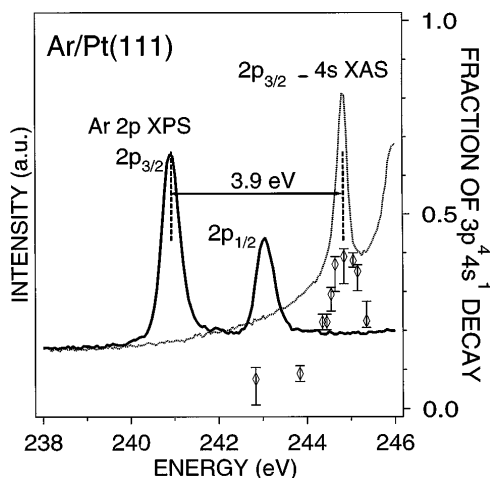

FIG. 1. The Ar $2p_{3/2} \rightarrow 4s$ XA and Ar $2p$ XP spectra are shown on a common energy scale. On the right-hand axis we plot the amount of $3p^{-2}4s$ ($\diamond$) intensity relative to the total integrated intensity, derived from a decomposition of the autoionization spectra, over the Ar $2p_{3/2} \rightarrow 4s$ resonance. The error limits are derived from a variation of parameters in the decomposition.
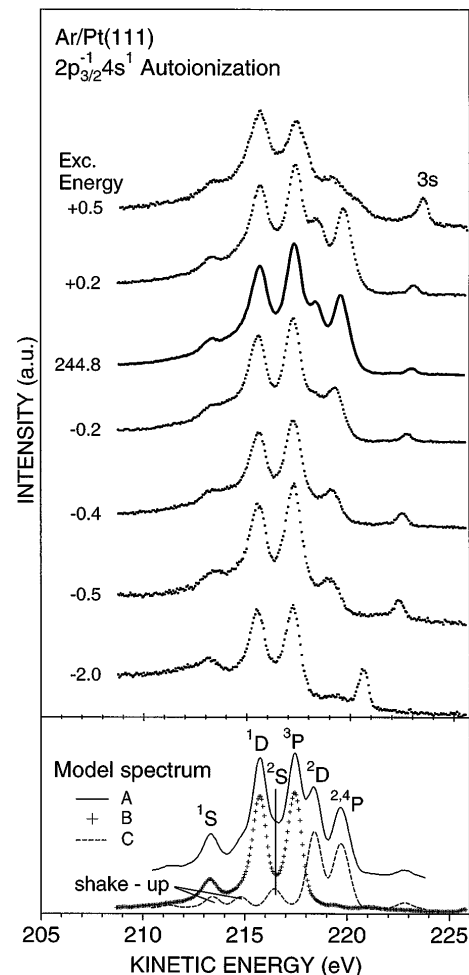

FIG. 2. The Ar/Pt(111) autoionization spectrum is shown for several photon energies around the $2p_{3/2} \rightarrow 4s$ resonance. At the bottom the 244.8 eV spectrum is modeled as described in the text.

autoionization spectrum measured at 244.8 eV photon energy (the maximum of the $4s$ resonance). Similar decompositions have been made for the decay spectra over the entire $4s$ resonance profile reaching the same type of agreement.

Each spectrum can thus be thought of as consisting of two parts, one with an Auger-like $3p^4$ final state and the other with a $3p^44s^1$ spectatorlike final state [17]. The difference in photon energy dependence of the two features is highlighted in Fig. 3. The figure displays the kinetic energy of (a) the $3p^{-2}(^3P)$ and (b) $3p^{-2}(^3P)4s$ features relative to that of the $3s$ photoemission line. From the slopes it is immediately clear that peak (a) tracks the photon energy, i.e., it stays at *constant kinetic* energy (like a normal Auger feature) while feature (b) stays at *constant binding* energy.

What is the difference between the two types of final states? First of all, we note that the intermediate state contains one hole in the $2p_{3/2}$ level and an extra electron in a $4s$-substrate hybrid state. The $3p^44s^1$ final state configuration corresponds to a two-hole one-particle state, where the spectator electron is fully localized to the adsorbate. This is a well-defined adsorbate state with little interaction with the substrate. The only influence of the substrate is an energy shift due to polarization effects. The spectral features corresponding to these states appear at constant binding energy over the complete $4s$ resonance. In this sense it can be viewed as the result of an Auger resonant Raman process involving scattering through the various intermediate $4s$-substrate hybrid states.

Also, the other set of states in the decay spectra must formally be of the spectator type since the photon energy is still below the $2p_{3/2}$ (vacuum level referenced) ionization energy. The spectra carry the signatures of an atomic $3p^4$-
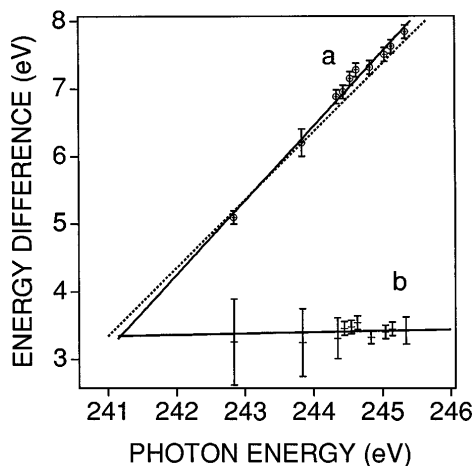

FIG. 3. The energy difference of the Ar $3s$ photoemission line to (a) the $3p^{-2}(^3P)$ line and (b) the $3p^{-2}4s^1(^{2,4}P)$ line is given. The dotted line corresponds to constant kinetic energy, while a horizontal line would correspond to constant binding energy.

like final state. This implies that the spectator electron is not located on the adsorbate. Since in the intermediate state the core electron was excited to a $4s$-substrate hybrid level, one can imagine a final state where the spectator electron is located in the substrate instead. If the exact energy of the spectator electron (which depends on the excitation energy) has a negligible influence on the energy of the adsorbate two-hole final state, the energy of this state can be viewed as the sum of two terms, the energy of the (polarization screened) two-hole final state of the adsorbate and the energy of the spectator electron (relative to the Fermi level) in the substrate. We can therefore describe the final state in terms of a factorized wave function. When the excitation energy is varied, the only effect of this is that the energy of the spectator electron changes while the features in the decay spectra remain at the same kinetic energies. This is exactly the behavior we expect if we would view the spectator electron as a photoelectron, which is emitted into the substrate, and the decay as a regular Auger process originating from a core ionized state as probed by XPS (referenced to the Fermi level). Even if the electron in the substrate is quite slow, the substrate screening prevents any significant PCI-like effects. A two-step description is thus fully adequate for this process.

In order to understand the intensity ratios in the spectra we have to consider the time dependence of the process. The excitation can be regarded as the creation of a wave packet at the adsorbate site [9,19,20]. The wave packet is built from Ar $4s$-substrate hybrid orbitals. This wave packet will develop during the core-hole lifetime. The probability to end up in the Auger-like final state is given by the probability that the spectator electron becomes delocalized into the substrate on this time scale. To see how this works we start out by regarding the $4s$ resonant state as having very little mixing of substrate states. Furthermore, we assume that the $4s$ hybridization broadening has a Lorentzian shape and a width Δ. The probability for delocalization into the substrate is then described in terms of two competing exponential decay processes, the decay of the $4s$ electron into the substrate (with a rate proportional to Δ) and the core-hole decay rate (proportional to the lifetime width Γ). The probability is then given by the ratio $\Delta/(\Gamma + \Delta)$ [20,21].

This description is too simplistic in the general case. This is clearly seen from Fig. 2, where it is evident that the ratio of decay in the two channels changes as we move over the $4s$ resonance. This is illustrated more clearly in the lower part of Fig. 1 (right-hand axis), where the fraction of $3p^44s^1$ final states is shown. We observe a curve which qualitatively follows the shape of the resonance itself with the rate being the largest at the peak position of the $4s$ resonance. Close to E_f (3 eV below the resonance), almost no contribution from this channel can be seen. We estimate ~5% as an upper limit [22].

The fraction of decay leading to Auger-like features will qualitatively reflect the relative contribution of sub-

strate states in the wave function. The 4s resonance states will be more purely 4s-like at the center of the resonance, while the influence of substrate states will increase further away from the center. A quantitative interpretation of the results is, however, difficult. This is due to the fact that the energy dependence of the 4s-substrate hybrid orbitals will lead both to different original character of the created wave packet and to different behavior of the time evolution. These two effects are not easily separable, and a quantitative analysis would require detailed model calculations for the whole process.

The results in this Letter clearly demonstrate how different routes in a scattering process may lead to totally different behavior in terms of what is characteristic for one-step or two-step processes. On the fundamental level there is no such distinction. In practice, however, a process may appear as being of one type or the other. We note that the determining factor is whether the intermediate state creates an excitation in the system which remains during the decay process. Since this excitation is not detected, we will experience this as an apparent loss of coherence. In the present case we see that a two-step model describes all the essential physics for the Auger-like decay. A one-step treatment would require an integration and summation over the distribution of all possible (factorized) final states. Since each final state is distinct, this is done by summing probabilities rather than amplitudes. At the end, such a treatment would only give a broadening of the spectrum due to the core-hole lifetime. All the relevant physics is thus automatically included if the process is instead treated as an incoherent decay starting out from a lifetime broadened core-hole state. The applicability of a two-step description, however, requires that there is no strong energy dependence of the probability for delocalizing the spectator electron. Otherwise, a full evaluation of a Kramer-Heisenberg-type scattering formula [23,24] is required also for the Auger-like process.

We conclude that the remaining electron or vibrational excitations, not visible or controlled experimentally, may lead to the apparent loss of coherence and nonconservation of energy. Similarly Jahn-Teller-like excitations in the core excited state may leave an inaccessible signature, characteristic of a localized core-hole, which will be seen as a breakdown of symmetry selection rules (e.g., in RIXS), etc. Therefore, the question of coherence in RIXS is not related to the issue of core-hole localization [3], but rather to the excitations produced in the intermediate state that might lead to a distribution of final states. This emphasizes the need to explicitly consider the properties of the intermediate state in resonant spectroscopies in order to evaluate what final states can be reached.

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