Coherent and Incoherent Processes in Resonant Photoemission

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In this contribution we present the distinction between coherent and incoherent processes in resonant photoemission. As a first step we determine whether an autoionization process is photoemission-like or Auger-like. The discussion is based on measurements for a weakly bonded adsorption system, Ar/Pt(111) [1]. This type of system is well adapted to investigate these effects since it yields distinctly shifted spectral features depending on the nature of the process. After this, the question of resonant photoemission in metallic systems is addressed. This is done in connection with measurements at the $2p$ edges for Ni metal. Ni has been one of the prototype systems for resonant photoemission. The resonances have been discussed in connection with the strong correlation and d -band localization effects in this system [2]. Based on the results some general comments about the appearance of resonant effects in metallic systems are made.

The experiments were performed using beamline 8.0 at the *Advanced Light Source*. This undulator beam-line is equipped with a modified 'Dragon' monochromator with a resolving power of up to 10^4 . The end-station was built at Uppsala University and comprises two rotatable spectrometers, a Scienta SES200 electron spectrometer [3] and a high-resolution grazing incidence grating spectrometer for x-ray fluorescence studies [4]. In the Ar measurements the resolution was set to 100 meV for the monochromator and to 200 meV for the spectrometer. In the Ni measurements the resolution was 100 eV for both the monochromator and the spectrometer. The spectra for Ar/Pt(111) were measured at low temperatures using a liquid He flow cryostat.

Fig. 1 shows electron emission (autoionization) spectra of Ar for a number of photon energies around the $2p_{3/2} \rightarrow 4s$ x-ray absorption spectroscopy (XAS) resonance. The overall spectral shape changes with photon energy. Two sets

Fig. 1: Ar/Pt(100) autoionization spectra for several photon energies around the $2p_{3/2} \rightarrow 4s$ resonance.

of spectral features can be identified, one which stays at constant kinetic energy and one which moves with the photon energy. The shapes of the two parts of the spectra seem to be independent of the excitation energy. The relative weights of the two parts, however, vary.

Fig. 2: A fit of the autoionization spectrum for an excitation energy at the resonance maximum.

mainly in the shake-up part of the autoionization spectrum. This is due to the interaction of the Ar orbitals with the substrate which modifies especially the extended orbitals involved in the shake-up processes. There may also be slight differences in the remaining parts of the spectra caused by small modifications of the splittings and relative intensities of the multiplet components. Similar decompositions have been performed for the decay spectra over the entire $4s$ resonance profile, reaching the same type of agreement. Each spectrum may thus be thought of as consisting of two parts, one with an Auger-like $3p^{-2}$ final state and one with a $3p^{-2}4s^1$ spectator-like final state.

Fig. 3 shows in detail Ni spectra recorded for photon energies around the $2p_{3/2}$ core-level threshold in the photoemission geometry. In this case the spectra are plotted on a binding energy scale. Below threshold, the whole spectrum stays at constant binding energy and the intensities of the different parts of the spectra changes. Immediately above threshold, we observe how the 6 eV feature starts to move to higher binding energies as the photon energy increases. This immediately shows that final states are produced which are not identical to the photoemission final states. This is completely analogous to the situation with the appearance of Auger-like features in Ar/Pt(111) as discussed above. We can also discuss this as an apparent loss of coherence in the process [1]. There are excitations in the system which we do not detect. Also in the valence band region we observe how a weak shoulder develops from the Fermi-level cut-off and starts to disperse with photon energy. This demonstrates the appearance of Auger-type features in the band-like part of the spectrum.

In order to probe the character of the resonant process we follow the photon energy dependence of the intensity for a region in the valence band spectrum close to the Fermi level and for an energy window around the 6 eV satellite. In Fig. 4 this has been done both for the 'Auger' and for the 'photoemission' geometries, i.e. with the E-vector in two different orientations.

Fig. 2 shows an analysis of the spectrum recorded at the resonance maximum (244.8 eV). The spectrum can be accurately reproduced by a summation of two model spectra. The curve denoted by (+) corresponds to a $2p_{3/2}$ Auger spectrum recorded for the Ar/Pt sample using a photon energy well above the XAS resonance. The different peaks in the spectrum are due to the multiplet levels of the $3p^4$ final state configuration as denoted in the figure. The dashed curve is a gas phase autoionization spectrum following the excitation of the $2p_{3/2}4s^1$ state. The identification of the peaks is given in the figure. The spectrum has been convoluted with a Gaussian of width 0.3 eV and shifted to achieve the best possible fit. By summing these spectra with appropriate weight factors we obtain a model spectrum given by the solid line. As can be seen this curve mimics all essential features of the experimental Ar/Pt autoionization spectrum. The remaining small differences appear

Fig. 3: Valence electron spectra around the $2p_{3/2}$ core-level threshold on a binding energy scale measured in the 'photoemission geometry'. The photon energy increment is about 0.2 eV except for the lower set of data (844.2, 848.0, 849.0, 849.8, 850.3, 850.5, 850.7).

more pronounced Fano-like profiles corresponding to smaller q -values (e.g. $q \sim 0.5$ for the valence band in the 'photoemission' geometry) as expected due to the weaker absorption and larger lifetime width of the $2p_{1/2}$ level. The trends are fully consistent with the expectations from the Fano model and we therefore conclude that the shapes of the resonance profiles are due to interference.

To summarize, we have investigated the basis for resonant photoemission for two prototype systems, one weakly bonded adsorption system and one transition metal. We find that for Ar/Pt(111) there are two types of features in the spectator autoionization spectra. One of these shows resonant Raman behavior and has to be treated in a one-step picture. The other one shows a normal Auger-like behavior and can be described in a two-step picture. This branching is due to the quasi-localized character of the intermediate state. The intermediate state is localized enough to yield a constant binding energy feature for excitation energies over the entire resonance, although of varying relative strength. The Auger-like feature dominates at most energies and corresponds to final states in which the spectator electron is located in the substrate. The spectator electron may have a distribution of energies and the scattering process can be viewed as the creation of two particles which share energy. Since we observe only one of these we recognize this as a loss of coherence and as an apparent loss of conservation of energy.

We have also performed measurements of the resonant photoemission for a Ni(100) sample with special emphasis on the possible interference between the autoionization and the direct photoemission channels. We observe clear signatures of interference both for the main valence

The two top curves show the valence band intensity in the 'photoemission' (top) and 'Auger' (middle) geometries. It is immediately seen that the intensities show characteristic Fano-like profiles [5, 6]. The results for the 6 eV satellite is shown at the bottom. The curves for the 'Auger'- and 'photoemission' geometries are plotted together. Looking at the individual curves there is no clear indication of a resonance line-shape. However, when comparing the measurements for the two geometries (see inset) differences in the profiles are observed which are characteristic of Fano profiles with different q . This shows that there are interference effects also in these spectra. The interference term is small but this is due to the fact that the autoionization channel is dominating so strongly. We have therefore demonstrated that the absence of visible interference effects is not a good criterion for the absence of interference. This may instead be due to the total dominance of one of the spectroscopic channels.

It is found that q is smallest for the valence band, in particular in the 'photoemission' geometry ($q \sim 1.5$ at the $2p_{3/2}$ resonance). This channel is the majority channel in photoemission and the minority one in autoionization. For the satellite, the opposite situation is true and consequently much larger q -values are found ($q \gtrsim 20$ and $q \sim 9$ in the 'Auger' and 'photoemission' geometries, respectively). Going to the $2p_{1/2}$ edge, we find in all cases

Fig. 4: Intensity of the valence-band emission (top two curves) and the 6 eV satellite (bottom set of curves, plotted together) as function of photon energy in the 'photoemission' and 'Auger' geometries.

band emission and for the 6 eV satellite. The spectra show resonantly enhanced photoemission-like spectral features only in the region before threshold. For photon energies above threshold the emission features rapidly transform into features which appear at constant kinetic energy. In terms of the possible interference with the direct photoemission process this corresponds to a loss of coherence. This implies furthermore that a large fraction of the totally observed resonantly enhanced intensity is incoherent. The results indicate that the resonance behavior is not explained by any strongly localized intermediate state in the resonant scattering process. This also implies that resonance phenomena and especially the interference effects may occur also in systems with very delocalized excited states.

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