Experimental Verification of the Line-Shape Distortion in Resonance Auger Spectra

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When the mean excitation energy and the width of a broad photon band are varied the Kr $3d_{5/2}^{-1}5p \rightarrow 4p^{-2}5p$ resonance Auger electron lines show strong asymmetry and their average kinetic energies shift. Even extra peaks appear. Our results demonstrate experimentally, for the first time, that the incident photon energy distribution has very crucial importance on the resonance Auger line shape and thus on the reliable data analysis of complicated Auger spectra.

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The inherent line shapes in normal and resonance Auger spectra are commonly supposed to be Lorentzian and independent of the exciting photon energy distribution. The Auger resonance Raman effect, first observed in the x-ray energy range [1–3] and very recently also in the VUV range [4,5], forms a very important exception of this general rule. In an Auger resonance Raman spectrum, which is excited by synchrotron radiation with a very narrow bandwidth, the width of the resonance Auger lines is governed by the width of the incoming photon distribution function, and can be much narrower than the natural lifetime width of the core excited state. This important observation has opened completely new possibilities for the high resolution resonance Auger spectroscopy [6], e.g., to study the finest details of electron correlation.

However, the interplay between the measurement device and the inherent process is much more complex than has earlier been assumed. Consequences can be so dramatic that erroneous interpretations are possible if the interplay is not properly taken into account in the course of data handling. Theoretical studies of the line profiles in resonance Auger spectra were performed very recently by Gel'mukhanov and Ågren [7,8] and Armen and Want [9]. They showed that in certain cases a broad excitation band causes remarkable broadening, asymmetry, and even doubling of the resonance Auger lines. In this connection in analogy with optical spectroscopy also the term Stokes doubling was used. We will not use this terminology since the effect is purely a consequence from specific instrumental conditions, as will be shown here experimentally and by numerical simulations.

The line-shape distortion can be described on the basis of the energy conservation principle as follows. Initially the system consists of an incoming photon with the energy $h\nu_i$ and a target atom in its ground state. The photon is absorbed by the atom, and an Auger electron with the kinetic energy ϵ_K^i is ejected. Energy conservation holds when the kinetic energy of the Auger electron is measured. Thus

$$\epsilon_K^i(X) = h\nu_i - \epsilon_B(X), \tag{1}$$

where $\epsilon_B(X)$ is the binding energy of the discrete final state which contains two holes and an excited electron. X refers to a specific final state multiplet $^{2S+1}L_J$, which is for simplicity supposed not to decay further. Therefore, the linear energy dispersion of the Auger electron line is a direct consequence of the energy conservation exactly as in the photoemission. The role of the intermediate excited state in this picture is that it selects the suitable photon energies. The intermediate state, where the core electron is excited to a certain Rydberg state, is lifetime broadened allowing absorption of photons that have slightly different energies than the nominal resonance energy $h\nu_0$. If the photon energy deviates from $h\nu_0$, the absorption probability decreases according to the Lorentzian distribution L whose width Γ is determined by the lifetime of the intermediate excited state. Thus the relative intensity $I(\epsilon_K^i)$ of the resonance Auger electrons with the kinetic energy ϵ_K^i is proportional both to the intensity of incident radiation $\Phi(h\nu_i)$ at the energy $h\nu_i$ and to the absorption probability,

$$I(\epsilon_K^i) \propto \Phi(h\nu_i)L(h\nu_i - h\nu_0, \Gamma). \tag{2}$$

The shape of the resonance Auger electron line is thus simply given as the product of the photon energy distribution and the Lorentzian with lifetime broadening Γ. Some obvious consequences can be immediately stated. If the widths of the distribution functions are very different, then the width of the resonance Auger lines is roughly determined by the narrower one. Thus for a broad exciting photon band the resonance Auger line shape is close to a Lorentzian function with a width of Γ. In the case of a very narrow photon band, electron lines with subnatural narrow linewidths are created. Because $L(h\nu_i - h\nu_0, \Gamma)$ is symmetric around $h\nu_0$, the electron line shape is symmetric only if $\Phi(h\nu_i)$ is also symmetric with reference to $h\nu_0$. In all other cases the electron line shape is more or less asymmetric. Pure Lorentzian shape is created only

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with a constant photon energy distribution. Strong asymmetry is caused when the mean energy of the incident photons deviates from the nominal resonance energy $h\nu_0$ (for example, to lower energies). Then the corresponding side (lower energies) is enhanced in the product leading to asymmetry and in extreme cases also to an extra peak structure. Thus the exciting photon energy distribution has a very crucial importance to the resonance Auger line shape. In this Letter we demonstrate this effect experimentally for the first time.

The measurements were carried out at the Finnish beam line in MAX-laboratory, Lund, Sweden. The beam line is equipped with a modified Zeiss SX-700 plane grating monochromator [10] having a plane elliptical focusing mirror. The resonance Auger spectra were collected with a high resolution SES-144 spherical mirror electron spectrometer [11] equipped with a position sensitive detector system. In order to keep the lineshape modifications caused by the electron spectrometer as small as possible with a reasonable count rate, a pass energy of 10 eV was used. This corresponds to an electron spectrometer resolution of about 40 meV. The shape of the spectrometer broadening function should be close to a Gaussian line profile.

The $3d_{5/2}^{-1}5p \rightarrow 4p^{-2}5p$ resonance Auger spectrum is a good test object, because it has some rather well-isolated lines in the kinetic energy range from 55.5 to about 59 eV. Especially, we like to focus on the double peak structure between 58 and 59 eV. It corresponds to the $3d_{5/2}^{-1} \rightarrow 4p^{-2}(^1D_2)$ normal Auger transition, which splits due to the coupling with the $5p$ spectator electron to the $3d_{5/2}^{-1}5p \rightarrow 4p^{-2}(^1D)5p(^2D_{3/2,5/2},^2P_{1/2})$ and $3d_{5/2}^{-1}5p \rightarrow 4p^{-2}(^1D)5p(^2F_{5/2,7/2},^2P_{1/2})$ transitions. Figure 1 shows the experimental spectra in this energy range taken with an exit slit width of 400 μm which corresponds to a photon bandwidth of about 280 meV. The spectrum B is taken with the average photon energy tuned exactly to the nominal resonance energy $h\nu_0 = 91.20$ eV

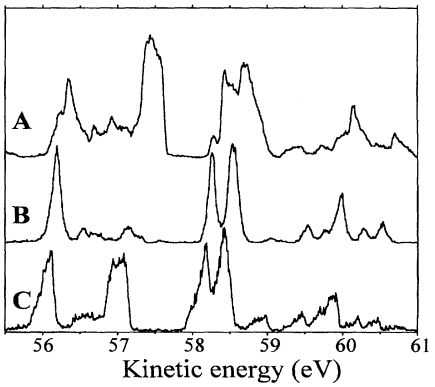

FIG. 1. Kr $3d_{5/2}^{-1}5p \rightarrow 4p^{-2}5p$ resonance Auger spectra, excited at 91.45 eV (A), 91.20 eV (B), and 90.91 eV (C) mean photon energy.

of the $3d_{5/2} \rightarrow 5p$ excitation. The two peaks between 58 and 59 eV are well separated, whereas the splitting of the higher energy peak into two components is unresolved. The curve fitting gives the linewidth of 105 meV for all the three line components. The uppermost spectrum A is obtained when the average photon energy is 0.25 eV higher than the nominal resonance energy $h\nu_0$. In this case only the photons in the low energy part of the exciting photon energy distribution can excite the $3d_{5/2}^{-1}5p$ resonance state. The number of photons that can be absorbed by the target atoms is now decreased by about a factor of 10. The shape of the Auger electron lines is dramatically changed and the maxima are shifted to higher energies. It is important to note that with the decreased excitation probability (and thus decreased Auger emission probability) the relative strength of $4s$ photoelectron line and its satellites correspondingly increases. Thus the highest structure in spectrum A around 57.5 eV is caused by the $4s$ satellite lines. The spectrum C is obtained when the mean photon energy is 0.29 eV lower than the nominal resonance energy $h\nu_0$. Again strong distortion of the electron line shape is observed and the peak maxima are found to shift to lower energies.

Inspection of the spectra A and C (Fig. 1) shows that the line-shape distortion is essentially different. In spectrum A even a small extra peak appears on the low energy side at the kinetic energy of the nominal resonance Auger line of spectrum B. The fact that the extra peak appears in spectrum A but not in C is obviously connected to the asymmetric shape of the photon band and its low energy tail.

In order to clarify the origin of the observed features, a numerical simulation was carried out. The $4s$ photoelectron line provides a good measure for the photon energy distribution, because the lifetime broadening of the $4s$ line is negligible and also the spectrometer broadening is relatively small for the applied large photon bandwidths. The distortion effect can be simulated by multiplying the measured $4s$ photoelectron line profile with the Lorentzian function (FWHM, 83 meV [12,13]) and by varying the energy shift between the two profiles. In the following we first consider the behavior of the photon energy distribution. Second, we compare the results of computer simulation and experiment.

Figure 2 shows the measured $4s$ photoelectron lines with the mean photon energy $\overline{h\nu} = 91.20$ eV, for exit slit widths of 20, 200, 400, and 600 μm. The photoelectron line becomes more and more squarelike with increasing slit width as expected. The SX-700 monochromator has only one slit: the exit slit. For wider slit widths the slit contribution, which has in the first approximation a squarelike shape, dominates in the convolution of partial broadenings from slit width, source size, and slope errors [9]. The last two contributions are supposed to be close to a Gaussian shape. In the observed photoelectron spectrum

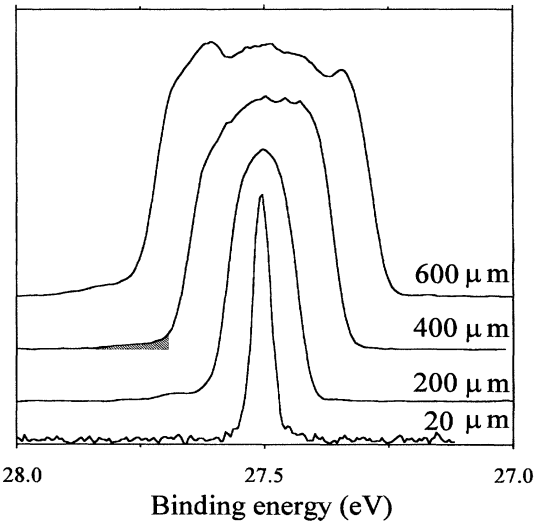

FIG. 2. Kr 4*s* photoelectron spectra, recorded using different monochromator exit slit widths (marked next to the spectra). The tail at low photon energy for 400 μm slit width is shadowed. For further details see the text.

the photon band is further convoluted by the spectrometer function of the electron energy analyzer.

It is important to notice that our experimental 4*s* photoelectron lines in Fig. 2 show some weak tail structure on the low kinetic energy side. Such tails can lead to drastically emphasized line-shape distortions. They are dangerous if distortions are unwanted but advantageous for the demonstration of the effect discussed here.

The experimental spectrum in the kinetic energy range 58.1–59.1 eV, taken at the mean photon energy

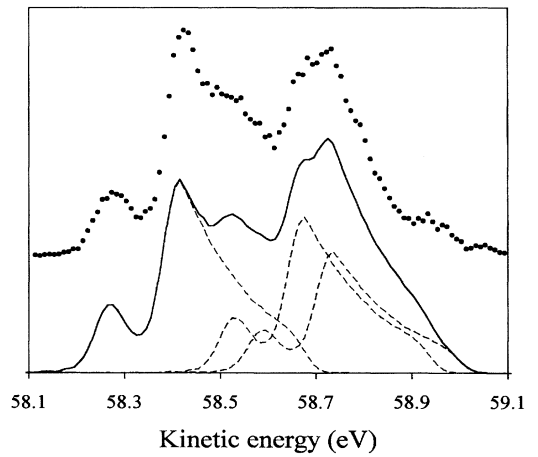

FIG. 3. Computer simulated resonance Auger spectrum with its individual components (solid lines), together with an experimental spectrum (dotted line). See the text for further details.

$\overline{h\nu}$ = 91.45 eV (detuning equal to 0.25 eV) and with the monochromator exit slit width of 400 μm is given by the dotted line in Fig. 3. The normalized 4*s* photoelectron spectrum excited by 88.5 eV photons just below any resonance has been subtracted from this spectrum. The solid curves in Fig. 3 display the results of the computer simulation. The Auger line energies and the intensity ratios of the three peaks were taken from a high resolution Auger resonance Raman spectrum recorded at the photon energy $h\nu_0$. The best fit between the simulated and experimental results was achieved when $\overline{h\nu} - h\nu_0 = 0.28$ eV. Both observed features—the double-peak structure (e.g., peaks at 58.27 and 58.41 eV) and strongly reduced intensity of the Auger electron lines (10 times in the simulated spectrum as compared to the spectrum taken at $h\nu_0$)—are reproduced quite well. According to the simulation, the double-peak structure appears only if the detuning is in the range 0.25–0.4 eV ($\overline{h\nu}$ = 91.45–91.6 eV). In other cases only heavily asymmetric profiles are seen. The result is also supported by the experiment, where the double-peak structures appear in even narrower detuning ranges, most probably because the additional line broadening caused by the electron spectrometer smears out weaker-double peak structures. The slight difference in the values of detuning between experimental and simulated spectra is within the error limits.

Similar, but more subtle, line-shape distortions can also be seen in the resonance Auger spectra, excited by much narrower photon bands. These results will be published elsewhere.

Our results show that the distortion depends strongly on the actual energy distribution of the exciting photon beam. Therefore the corresponding distortions of the resonant Auger spectra may look very different when using other monochromator designs that generate different photon energy distributions. The main feature, strong asymmetry or even the double-peak structure when the mean photon energy is detuned from the resonance, should still appear. The detuning can lead to very artificial results in the case of several close-lying resonances. It may result in a superposition of spectra with different line shapes making the deconvolution very difficult.

In conclusion, we have for the first time demonstrated the drastic line-shape distortion effect of detuning the exciting photon beam with respect to the resonance maximum. Moreover, the effect is strongly dependent on the properties of the monochromator design. These line-shape distortions may have very serious consequences for the data handling.

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