Subnatural Linewidths in the Kr $M_5N_{2,3}N_{2,3}$ and Xe $N_5O_{2,3}O_{2,3}$ Resonant Auger Spectra

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The line sharpening effect, one of the characteristics of the Auger resonant Raman effect when the bandwidth of exciting photons is smaller than the lifetime widths of the corresponding core levels, has been observed with clarity for the first time. The kinetic energies of the resonant Auger lines following the $3d \rightarrow 5p$ and $4d \rightarrow 6p$ excitations in Kr and Xe, respectively, display also linear dispersion when photon energy is scanned over the resonances.

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The Auger resonant Raman effect was first observed by Brown *et al.* [1] in the $L_{2,3}M_{4,5}M_{4,5}$ Auger spectrum of Xe. They found that in the vicinity of the L_3 threshold the decay of the resonantly excited state $2p_{3/2}^{-1}5d$ to the final states $3d^{-2}(^1G_4)5d$, i.e., a spectator resonant Auger transition, exhibits linear dispersion as a function of photon energy. In a later study by Armen *et al.* [2] the same spectrum was measured with better resolution and also compared with quantum-mechanical calculations based on a resonant-scattering approach. The other characteristic of the Auger resonant Raman effect, hardly discovered in the Xe $L_3M_4M_5$ resonant Auger spectrum but well known from the analogous resonant Raman x-ray scattering effect [3], is that the observed linewidth reflects the width of the exciting radiation, if it is smaller than the natural lifetime width of the core hole. The Xe L_3 edge lies deep in the x-ray region at about 4786 eV. We have now observed the Auger resonant Raman effect for the first time in atoms in the vacuum ultraviolet (VUV) region, namely, at the Xe $4d \rightarrow 6p$ and Kr $3d \rightarrow 5p$ resonances at 65.11 and 91.20 eV, respectively. Our high resolution results allow us to clearly see the line sharpening effects. Very recently the Auger resonant Raman effect has been discovered in HBr molecule [4].

The resonant Auger spectra following the $3d \rightarrow 5p$ excitation in Kr and the $4d \rightarrow 6p$ excitation in Xe were first observed by Eberhardt *et al.* [5]. Several studies have been carried out on the subject during the last few years [6]. The spectra have been found to exhibit spectator resonant Auger lines accompanied by shakeup transitions. The photon and electron resolution were moderate in those earlier studies and therefore the fine structures of the spectra were only partly resolved. Recently Aksela *et al.* [7] published high-resolution resonant Auger spectra of Kr following $3d \rightarrow 5p$ and $6p$ excitations. The photon bandwidth was 90 meV or about the same as the reported value of 83 meV for the Kr $3d$ inherent lifetime width [8]. The electron resolution was estimated to be about 80 meV at 91 eV leading to experimental total linewidths of about 140 meV, which is still clearly larger than the lifetime width. In that study it was for the first time possible to resolve most of the multiplet components and determine their experimental intensities for comparison with theory. No comparable high-resolution studies of the resonant Auger spectra after $4d \rightarrow np$ excitations in Xe have been reported yet.

In the present investigation we have been able to improve considerably both the photon and the electron energy resolution resulting in a total instrumental resolution which is considerably smaller than the lifetime widths of the Kr $3d$ and Xe $4d$ (Γ=111 meV [8]) levels. In these experimental conditions the Auger resonant Raman effect has now been observed for the first time in the Kr $3d \rightarrow np$ and Xe $4d \rightarrow np$ decay spectra and with an accuracy that is considerably better than in the earlier studies.

The measurements have been performed at the MAX-synchrotron radiation laboratory in Lund, Sweden, using the new so-called Finnish beam line (BL 51) [9]. The radiation source is a short period undulator giving a reasonable photon flux in the important energy range of 60–600 eV. The radiation is monochromatized by a modified SX-700 plane grating monochromator [10] delivered by Zeiss. The monochromator bandwidth using a 50-μm exit slit is estimated to be 32 meV at the Kr excitation (91.20 eV) and 19 meV at the Xe excitation (65.11 eV). Then we can excite the resonance with a photon bandwidth that is only a small fraction of the inherent core level width. Our high-resolution electron spectrometer [11] has a hemispherical analyzer combined with an effective differentially pumped gas cell and a microchannel plate detector in order to increase count rate. Electrons are retarded to a low pass energy, typically 10 or 20 eV, by means of a modern four element electron lens. Kinetic energy resolution with 10-eV pass energy is about 50 meV and with 20 eV about 90 meV.

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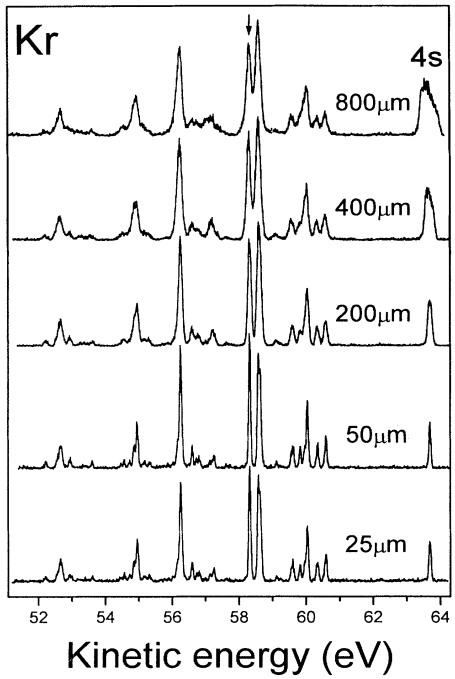

FIG. 1. The Kr $3d_{5/2} \rightarrow 5p$ resonant Auger spectrum taken with 10-eV pass energy of the electron analyzer and different exit slit widths of the monochromator.

Figure 1 shows spectra of the Kr $3d_{5/2} \rightarrow 5p$ resonance excitation measured using monochromator exit slit sizes of 25, 50, 200, 400, and 800 μm and a 10-eV pass energy. The width of the $4s$ photoelectron line, which lies in these spectra at 63.7-eV kinetic energy, directly shows the increase of the photon bandwidth with the slit width, growing from 67 meV to about 400 meV (FWHM). An inspection of the resonant Auger lines reveals also that their linewidths increase with the photon bandwidth. A comparison with the best spectra so far [7] shows a clear improvement in the resolution. The structure of the spectrum is complicated and almost every peak is composed of several close lying components (see Ref. [7] for details). As a reference line for the linewidth considerations we have used the peak indicated by an arrow in Fig. 1. This peak arises from the transitions to the $4p^4(^1D)5p(^2D_{3/2,5/2},^2P_{1/2})$ final states (peak 7 in Ref. [7]). This peak is the most suitable for the purpose, even though it is composed of three lines. Two of the lines have about the same intensities and are separated by about 11 meV [12] while the intensity of the third line is lower by an order of magnitude [13]. We observe the width of this peak to increase from 64 to 189 meV when the slit width goes from 25 to 800 μm. The widths of this Auger peak and the $4s$ photoelectron line are plotted versus the exit slit width of the monochromator in Fig. 2.

The fact that the $4s$ photoelectron line and the sharpest Auger features have very accurately the same

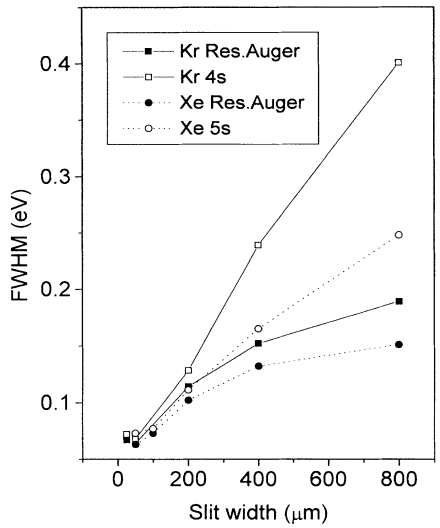

FIG. 2. The width of the Kr and Xe resonant Auger lines, Kr $4s$ and Xe $5s$ photolines as a function of slit size.

width for 25-, 50-, and 200-μm slits directly shows that the inherent broadening of these resonant Auger lines follows the width of the used photon band and does not depend on the lifetime width of the core level. As another illustration of the Auger resonant Raman effect we show in Fig. 3 the kinetic energy difference of the Kr $4s$ photoelectron line and the reference Auger line (marked by the arrow in Fig. 1) as a function of photon energy. The energy difference appears as a horizontal line demonstrating that the resonant Auger peak follows photon energy. For comparison we have plotted a line that represents the same energy difference calculated from optical data given

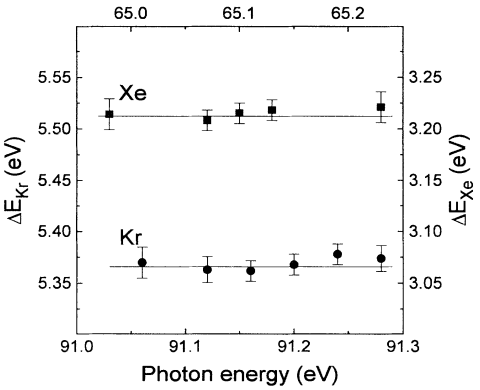

FIG. 3. The kinetic energy differences $\Delta E = E_k(\text{photo}) - E_k(\text{resonant Auger})$ when photon energy was scanned over the resonance. The photoelectron line is $4s$ in Kr and $5s$ in Xe. The resonant Auger lines used in the differences are indicated by the arrows in Figs. 1 and 4. Pass energy of the analyzer was 20 eV in this experiment. Slit size was set to 50 μm. Straight lines display the energy differences calculated from optical data.

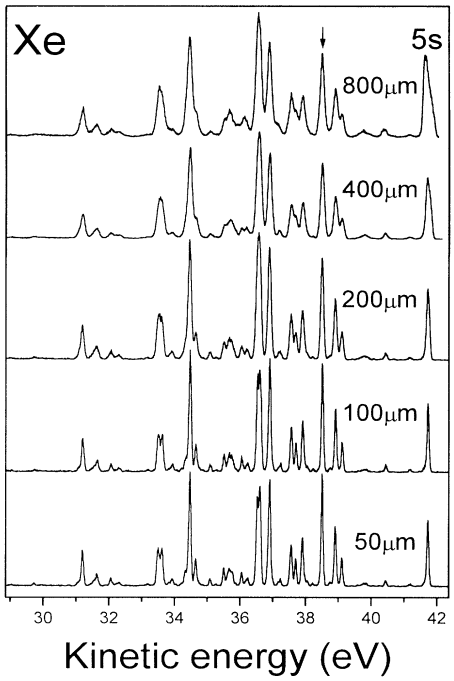

FIG. 4. The Xe $4d_{5/2} \rightarrow 6p$ resonant Auger spectrum taken with 10-eV pass energy of the electron analyzer and different exit slit widths of the monochromator.

by Moore [12]. The average energy of the two dominating final states was used for the reference resonant Auger peak. Other resonant Auger peaks display similar linear dispersion with photon incident energy. This is, as far as we know, the first very-high-resolution observation of the Auger resonant Raman effect for atoms in the VUV and soft x-ray region where the lifetime widths are small, typically of the order of 100 meV, and grazing incidence grating monochromators have to be used.

The way Fig. 3 is displayed eliminates the possible drifts of the spectrometer. Actually, we observed that the positions of the Kr 4*s* photoelectron and resonant Auger lines do not vary exactly linearly with photon energy. This is most probably due to the increased plasma potential at the resonance. Electrons leave the collision region instantaneously whereas ions are left behind. Therefore a positive plasma potential, that is proportional to absorption, builds up in the sample compartment and electrons get somewhat lower kinetic energies at the resonance.

In Fig. 4 we show the Xe $4d_{5/2} \rightarrow 6p$ resonant Auger spectra measured with different slit widths. These are the first published very-high-resolution resonant Auger spectra of Xe. The analyzer was also in this case set to a 10-eV pass energy. A similar behavior of the linewidths as in Fig. 1 can be observed. The resonant Auger peak used as a reference is again shown by an arrow. This peak was chosen since it originates from the transitions to only one final state $[5p^4(^3P)6p(^2P_{3/2})]$ [14]. The linewidths for this peak and the 5*s* photoelectron peak are also plotted in Fig. 2. The widths for 50 and 100 μm are about the same (60–70 meV), which means that the electron analyzer has the most significant contribution in the total linewidth. With a 200-μm slit the lines are about twice as broad, indicating that now the photon bandwidth becomes the dominating factor. The linewidths of Kr are slightly larger due to the larger bandwidth at higher photon energy. For wider slits the photoelectron peaks follow closely the bandwidth whereas the Auger electron linewidths show a saturating trend towards the limit which corresponds to the convolution of the inherent core hole lifetime width with the electron spectrometer broadening. These convolutions should be about 110 and 135 meV wide for Kr and Xe Auger lines, respectively. The fact that our Auger lines are broader for 400- and 800-μm slits is probably explained by charging effects that broaden the lines.

In Fig. 3 we also display the energy difference between the Xe 5*s* photoelectron line and the reference resonant Auger line when scanning photon energy over the Xe $4d_{5/2} \rightarrow 6p$ resonance. The same general observation as for Kr can be made. The energy difference between the peaks obtained from optical data [14] is also plotted in Fig. 3.

In conclusion, we have for the first time been able to observe the Auger resonant Raman effect in very high resolution for free atoms in the VUV region. Apart from the interesting physics of the resonant Raman effect itself, we would like to point out the important practical consequences of this observation. The resonant Auger spectroscopy is one important tool to study the correlation effects in atoms and molecules. Utilizing the Auger resonant Raman effect it is possible to enhance the experimental resolution of resonant Auger spectra and resolve all the spectral fine structure in much more detail and thus pinpoint finer details of the electron correlation.

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