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Electron correlation in Xe $4d_{5/2}^{-1}6p \rightarrow 5p^{-2}6p$ resonant Auger transitions studied by utilizing the Auger resonant Raman effect

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The Auger resonant Raman effect provides a unique method to eliminate the lifetime broadening in resonant Auger spectra. The method is now used to resolve experimentally the fine structure of the Xe $4d_{5/2}^{-1}6p \rightarrow 5p^{-2}6p$ transitions. The strength of the electron correlation effects has been studied by comparing the observed intensity distribution with multiconfiguration Dirac-Fock predictions.

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In the Auger resonant Raman spectra [1], excited by a very narrow synchrotron radiation bandwidth, the width of the resonant Auger lines reflects only the combined broadening from the incident radiation and the electron spectrometer, and can be much narrower than the natural lifetime width of the initial hole state. This is a very important distinction from the normal Auger process. Until very recently [2] the use of the Auger resonant Raman effect was limited to few pilot studies performed in the x-ray region [3,4]. Recently a very significant development in high-intensity and high-brightness synchrotron radiation sources in the soft-x-ray region, as well as in the grazing incidence monochromators, has opened new possibilities of applying the Auger resonant Raman effect to studies of many interesting features in the dynamics of atoms and molecules. In order to have the full benefit of the improved photon energy resolution, the spectra should be recorded with an electron analyzer capable of a comparable kinetic-energy resolution.

By eliminating the lifetime broadening, the Auger resonant Raman spectroscopy offers a unique experimental method of determining the intensity distribution of the spectator Auger transitions with a far greater accuracy than has previously been possible. In this paper, the method is applied to study the Xe $4d^{-1}6p \rightarrow 5p^{-2}(^1S,^1D,^3P)6p$ spectator Auger transitions. The Xe $4d$ lifetime width is 111 meV [5], while the splitting of the $5p^4(^1D)6p$ levels is of the order of a few tens of meV. Such a splitting can be resolved only by using the Auger resonant Raman effect where the linewidth is limited only by the instrument (monochromator and electron spectrometer) resolution.

The final states of the resonant Auger transitions are split into a large number of daughter levels due to the coupling of the spectator electron with the electrons involved directly in the decay (spectator-core coupling).

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On a principal level the resonant Auger decay differs from the normal Auger decay in that the number of transitions is increased due to the larger number of final-state levels. Also the degree of ionization and the energies of Auger transitions are changed. The asymptotic field affecting a resonant Auger electron corresponds to a singly charged ion, in contrast to the doubly charged ion of the normal Auger decay. Due to the relatively low kinetic energies of Auger electrons the transition amplitudes are sensitive to the continuum orbital. For example, the exchange interaction with bound electrons may substantially alter the transition rates. The final ionic state configuration interaction, which is also very sensitive to the one-electron orbitals, may easily influence the branching ratios.

The sensitivity of the branching ratios of resonant Auger transitions to electron correlation is largely hidden if theoretical data have to be averaged over the various states belonging to a recorded peak with nonresolved transitions. This prevents the comparison of changes in the branching ratios of separate transitions. By applying Auger resonant Raman spectroscopy, the individual transitions have now been resolved for the first time, making it possible to study the importance of electron correlation effects in detail.

The measurements were performed on the Finnish beamline (BL 51) at the MAX laboratory in Lund, Sweden [6]. The beamline uses synchrotron radiation from an undulator operating in the photon energy range of 60–600 eV, and it has a modified SX-700 plane-grating monochromator with a plane elliptical focusing mirror [7]. The beamline contains a permanent differential pumping section designed to effectively isolate the high-pressure gas experiments from the ultrahigh vacuum of the monochromator. The exit slit width of 10 μm used in this study results in a photon energy resolution of about 8 meV at $h\nu = 65$ eV.

The electron spectrometer [8] has a hemispherical electron analyzer with a mean radius of 144 mm. The analyzer is provided with a position-sensitive microchannel plate detector and a differentially pumped electron lens system. The instrument is mounted with the principal axis of the electron lens in the pseudomagic angle of 54.7° versus the horizontal plane, allowing direct measurements of the branching ratios. The resolution of the electron spectrometer at a 5-eV pass energy is about 30 meV.

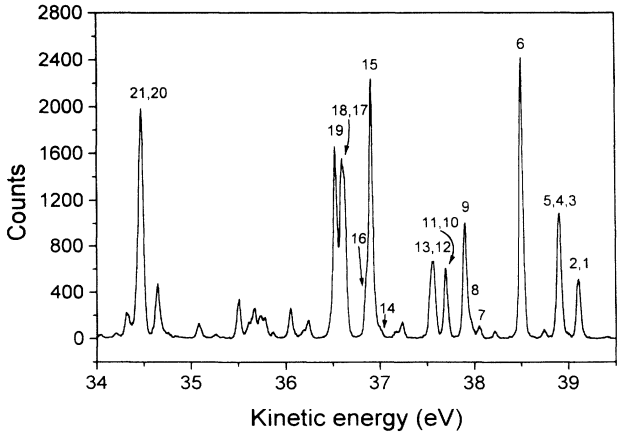

FIG. 1. The Xe $4d^{-1}6p \rightarrow 5p^{-2}(^1S,^1D,^3P)6p$ resonant Auger spectrum measured with a pass energy of 10 eV (corresponding to an electron spectrometer resolution of 40 meV). The numbers refer to those in Table I.

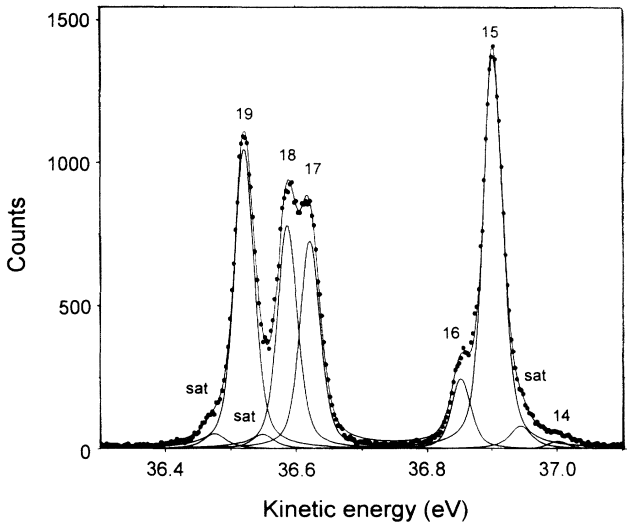

FIG. 2. The kinetic-energy range of 36.3–37.1 eV of the Xe $4d^{-1}6p$ resonant Auger spectrum measured with a pass energy of 5 eV (corresponding to an electron spectrometer resolution of 30 meV).

The photon energy was set to match the maximum of the resonance energy ($4d_{5/2} \rightarrow 6p$ at 65.110 eV [5]). Figure 1 shows the recorded spectrum in the kinetic-energy-region of 34.0–39.5 eV, containing the transitions to the $5p^4(^1S,^1D,^3P)6p$ final states. Figure 2 displays with higher resolution how the intensity is distributed between the daughter levels of the $5p^4(^1D)$ parent. Kinetic-energy calibration of the spectrum was achieved by determining the energies with the aid of the photoexcitation energy [5] and final-state binding energies from optical data [9]. The spectrum was corrected for the spectrometer transmission by using an experimentally determined correction function [10]. The intensities of different peaks in the spectrum were obtained by a least-squares fit of Voigt functions. The energy splitting of the Xe^+ states [9] was kept fixed during the fitting procedure. The linewidths obtained were 43 and 36 meV for the resonant Auger lines in Figs. 1 and 2, respectively.

In addition to the $4d_{5/2}^{-1}6p \rightarrow 5p^46p$ resonant Auger transitions, the spectrum of Fig. 1 also contains transitions where the spectator electron shakes up during the Auger decay. The $5s$ photoline accompanied by its satellite structure, resulting mainly from the direct photoionization, also appears at the same kinetic-energy region. In this work we will concentrate on the $4d_{5/2}^{-1}6p \rightarrow 5p^46p$ resonant Auger transitions only. The fitting results for the resonant Auger lines displayed in Fig. 1 are presented in Table I.

In order to check experimentally if the used subnatural bandwidth affects the intensity distribution, the spectrum was also measured with a photon bandwidth of 180

TABLE I. Calculated and experimental energies and intensities for Xe $4d_{5/2}^{-1}6p$ resonance Auger transitions. The intensities were calculated using final-state orbitals and excluding (F) or including (FE) the exchange for the continuum electron. Term is the leading LS term, which, due to a large mixing of the states, should be considered only as a tag of the transition. The results found from the F calculation agree well with the recent results published by Chen [15] and Fritzsche [16].

Final ionic state		Line	Energy (eV)		Intensity (%)		
Parent	Term	in expt.	Calc.	Expt.	Expt.	Calc.F	Calc.FE
$5p^4(^3P)6p$	$^4P_{3/2}$	1	39.86	39.12	1.03	0.86	0.69
	$^4P_{5/2}$	2	39.86	39.10	2.66	4.36	3.24
	$^4D_{7/2}$	5	39.64	38.88	1.36	1.80	2.48
	$^2D_{5/2}$	3	39.64	38.91	6.09	6.09	4.62
	$^2S_{1/2}$	4	39.60	38.89	0.65	0.69	0.87
	$^2P_{3/2}$	6	39.16	38.50	15.2	12.5	9.13
	$^2P_{1/2}$	7	38.78	38.05	0.62	0.93	0.69
	$^4P_{1/2}$	8	38.69	37.96	0.90	0.93	0.75
	$^2D_{3/2}$	9	38.65	37.90	6.57	7.02	5.60
	$^4D_{5/2}$	10	38.48	37.72	0.13	0.17	0.17
	$^4D_{3/2}$	12	38.37	37.57	2.84	2.87	2.14
	$^4S_{3/2}$	11	38.30	37.70	3.70	3.11	2.43
	$^4D_{1/2}$	13	38.22	37.54	2.54	2.49	1.91
$5p^4(^1D)6p$	$^2F_{5/2}$	14	37.40	37.00	0.25	0.59	0.58
	$^2F_{7/2}$	16	37.27	36.85	2.44	11.3	21.1
	$^2P_{3/2}$	15	37.25	36.90	13.6	13.9	13.1
	$^2D_{3/2}$	17	36.99	36.62	6.79	3.84	3.76
	$^2D_{5/2}$	18	36.98	36.59	7.48	6.88	6.99
	$^2P_{1/2}$	19	36.83	36.52	9.88	6.60	6.76
$5p^4(^1S)6p$	$^2P_{1/2}$	20	35.24	34.60	0.24	0.00	0.00
	$^2P_{3/2}$	21	35.19	34.48	15.0	13.1	13.0

meV. This spectrum was compared with the spectrum of Fig. 1 convoluted with a Lorenzian function in order to broaden it to the same width. The spectra were found to agree very well, and also a least-squares fit of both original spectra gave the same branching ratios for the main resonant Auger peaks, thus confirming the assumption that their intensities are independent of the photon bandwidth used.

The experimental energies and intensities can be compared with theoretical results obtained using a single-channel multiconfiguration Dirac-Fock (MCDF) method. A full account of the theoretical approach will be given elsewhere [11] and here we will only briefly introduce the results of actual calculations.

In all calculations, the initial and final states of resonant Auger decay were described by multiconfiguration wave functions accounting for the initial- and final-state configuration interaction. For the initial photoexcited state we included three jj-coupled configurations $4d_{5/2}^{-1}6p_{3/2}, J=1$, $4d_{3/2}^{-1}6p_{1/2}, J=1$, and $4d_{3/2}^{-1}6p_{3/2}, J=1$. For the final state all the jj-coupled configurations, resulting from the nonrelativistic configurations $5s^{-2}6p, 5s^{-1}5p^{-1}6p, 5p^{-2}6p$, $5s^{-1}$, and $5p^{-1}$, were included. The continuum orbital was optimized in a jj-average field of the final ion. The Lagrangian multipliers were included to orthogonalize the continuum orbital to the bound orbitals (FE), except in the calculation (F) which excludes the exchange interaction.

A comparison between experiment and theory indicates that theory predicts the intensity distribution fairly well, apart from a few transitions. Here we will focus on the transitions to the daughter levels of the $5p^4(^1D)$ parent, displayed in Fig. 2, where the discrepancies are most noticeable. Theory seems to overestimate the relative intensity of line 16, the overestimation being even larger when the exchange interaction is included (FE) The transition to the $5p^4(^1D)6p, J=7/2$ state (line 16) is dominated by the $\epsilon g_{9/2}$ transition amplitude which is sensitive to the exchange interaction according to the calculations. Another discrepancy is in the intensities of lines 17 and 19, which are clearly underestimated by theory. The rate of these lines was found to vary remarkably, depending on whether the mixing of the final ionic states was predicted with initial- or final-state orbitals. Energy splitting is not correctly reproduced by theory, indicating that the inclusion of only the final-state configurations of the resonant Auger transitions and the use of an average level optimization scheme [12] do not give accurate transition energies. This may be explained by the strong interaction of the $(5s5p)^6 6p$ configurations with the $(5s5p)^6 7p, (5s5p)^6 4f$ and $(5s5p)^6 5f$ configurations [9], which may result in changes in the eigenvectors and energies.

Although the overall agreement between experiment and theory is good, the discrepancies in the branching ratios of some lines indicate that the many-electron correlation effects, ignored in the present calculations, play an important role. Due to the near degeneracy of several levels, making a pronounced mixing of configurations and channels possible, the resonant Auger transitions are more easily affected by electron correlation effects than the normal Auger transitions. The theoretical description may be improved by including the electron relaxation and the interaction of the various continuum chan-

nels in a way similar to that done in the recent studies of normal Auger electron spectra [13,14].

In conclusion, by using the Auger resonant Raman effect, we have been able to eliminate the lifetime broadening in the Xe $4d^{-1}6p \rightarrow 5p^{-2}6p$ resonant Auger spectrum. This has allowed us to determine the relative intensities of separate resonant Auger transitions with an accuracy that makes a detailed comparison with theory possible. The results indicate that correlation effects, beyond the present MCDF calculations, play a prominent role in the resonant Auger decay. From the present work it is clear that the resonant Auger transitions are extremely sensitive to electron correlation and are therefore very well suited to test the capacity of the theory in accounting for correlation effects. By utilizing the Auger resonant Raman effect it is possible to enhance the experimental resolution and resolve the fine structure of the resonant Auger transitions in much more detail than ever before, and thus pinpoint finer details of electron correlation.

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