Auger resonant Raman spectroscopy used to study the angular distributions of the Xe $4d_{5/2}\rightarrow 6p$ decay spectrum

B. Langer, N. Berrah, and A. Farhat
Physics Department, Western Michigan University, Kalamazoo, Michigan 49008

O. Hemmers
Chemistry Department, University of Nevada, Las Vegas, Nevada 89154-4003

J. D. Bozek
Lawrence Berkeley National Laboratory, Advanced Light Source, Mail Stop 2-400, Berkeley, California 94720
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The Auger resonant Raman effect can be used as a method to eliminate natural lifetime broadening in resonant Auger spectra. We have coupled this method with high-resolution photons from the Advanced Light Source to study angular distributions and decay rates of the Xe $4d_{5/2}\rightarrow 6p$ resonant Auger lines. The angular distribution parameters β of almost all possible final ionic $5p^4(^3P,^1D,^1S)6p$ states have been determined. Our data, which remove the discrepancy between previous lower-resolution experimental results, are compared to different theoretical results.

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Auger resonant Raman [1] spectroscopy is a powerful tool for studying the resonant Auger decay processes with a resolution narrower than the natural lifetime width of the initial inner-shell-hole state [2]. This effect has been used to analyze branching ratios of resonantly excited atoms [3,4] and molecules [5]. In this paper, we present results of a study of the angular distributions of the spectator decay lines of Xe following $4d_{5/2}\rightarrow 6p$ excitation using the Auger resonant Raman effect and highly resolved photons from the Advanced Light Source (ALS).

The resonant Auger decay spectrum of the Xe $4d_{5/2}\rightarrow 6p$ resonance was first reported by Eberhardt, Kalkhoffen, and Kunz in 1978 [6] and has been followed by other experimental and theoretical studies [7–12]. It took more than a decade after the first observation until measurements on the angular distribution were performed by Carlson *et al.* [13], who found anomalously negative β values in the decay spectrum. Such behavior was first explained theoretically for the decay of the Ar $2p\rightarrow 4s$ resonance by Cooper [14], who applied angular-momentum-transfer theory, treating the resonant decay as a single-step process. Kämmerling, Krässig, and Schmidt [15] compared resonant Auger and normal Auger angular distributions experimentally and theoretically. These experimental studies were limited by the low resolution of the photon sources as well as of the electron spectrometers, making it difficult to compare the results with the various theoretical calculations [14–19].

Recently, however, the development of new synchrotron sources and high-resolution monochromators in combination with high-resolution electron spectrometers has made it possible to study the energy positions and intensities of the peaks in the Xe $4d_{5/2}6p\rightarrow 5p^4 6p$ decay spectrum with a resolution better than the natural linewidth (106 meV [20]) of the $4d$ inner-shell hole by utilizing the Auger resonant Raman effect [3,4]. Using this technique, we are now able to determine the angular distribution parameters β of almost all of the possible final ionic $5p^4(^3P,^1D,^1S)6p$ states.

After a Xe $4d\rightarrow 6p$ excitation the decay process can involve (1) an excited electron (participator decay) resulting in an enhancement of the $5p^{-1}$ or $5s^{-1}$ main lines or (2) an excited $6p$ electron that remains in its state during the decay process (spectator decay) leaving the ion in a two-hole, one-electron (satellite) state. The spectator decay is the dominant process (57%), followed by simultaneous emission of two electrons (shake-off), leaving almost no intensity for the participator decay [11]. During the decay, the excited $6p$ electron can also move into the $7p$ orbital (shake-up) enhancing the $5p^4 7p$ final states. In this paper we focus on the strongest spectator decay channels, $5p^4(^3P,^1D,^1S)6p$.

Using elliptically polarized synchrotron light, the differential photoionization cross section $d\sigma_{if}/d\Omega$ measured perpendicular to the light's propagation direction can be written as [21]

$$\frac{d\sigma_{if}}{d\Omega}=\frac{\sigma_{if}}{4\pi}\left[1+\frac{\beta_{if}}{4}\,(1+3P_1\cos 2\theta)\right], \tag{1}$$

where σ_{if} and β_{if} are the partial photoionization cross section and the angular distribution anisotropy parameter, respectively, for the transition from the initial state $|i\rangle$ to the final state $|f\rangle$. P_1 is the degree of linear polarization [$P_1=0.991(2)$ in our case], and θ is the angle between the electric-field vector of the light and the propagation direction of the emitted electrons.

The experiment was performed at the Advanced Light Source (ALS) in Berkeley under double bunch operation. Xenon atoms were ionized by monochromatic synchrotron radiation from an 8-cm, 55-period undulator and spherical grating monochromator on beamline 9.0.1. Figure 1 shows electron spectra taken simultaneously at different angles ($\theta=0°,54.7°$) by two time-of-flight spectrometers, which were mounted on a rotatable chamber. A retarding voltage could be applied to these spectrometers to increase the flight time of the electrons and therefore improve their energy

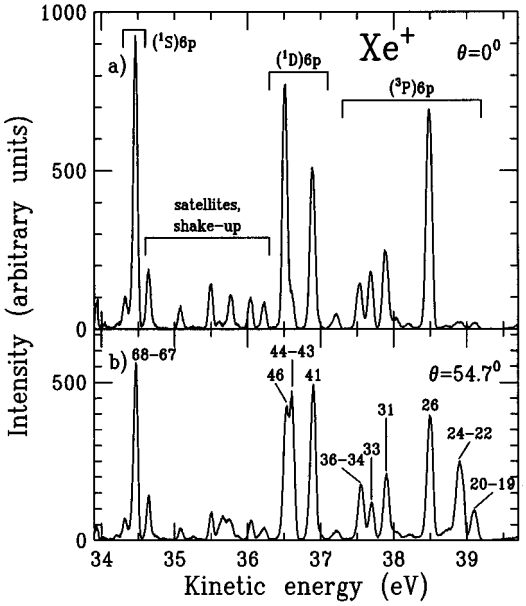

FIG. 1. Xe $5p^4nl$ decay spectra after $4d_{5/2}\rightarrow 6p$ resonant excitation at (a) 0° and (b) 54.7° with respect to the polarization of the incident photons. The spectra were recorded with a 30-V retarding potential, which corresponds to a spectrometer resolution of between 45 and 70 meV in the displayed region.

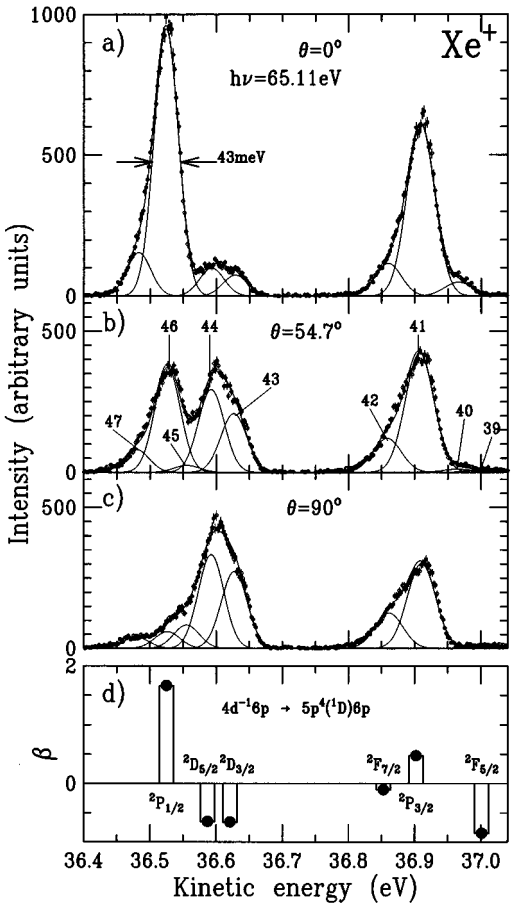

FIG. 2. Xe $5p^4nl$ decay spectra after $4d_{5/2}\rightarrow 6p$ resonant excitation in the kinetic-energy range of 36.4–37.1 eV at (a) 0°, (b) 54.7°, and (c) 90° with respect to the polarization of the incident photons. The spectra were measured with a 32-V retarding potential corresponding to a spectrometer resolution of between 43 and 50 meV in the displayed region. (d) shows the angular distribution parameter β for the $5p^4(^1D)6p$ spectator lines.

resolution. Figure 2 shows a section of the decay spectrum recorded with a 32-V retarding potential at three different angles (θ=0°,54.7°,90°). Areas of the peaks were determined by fitting Gaussian profiles to the data. In order to stabilize the fitting procedure the energy differences between overlapping peaks were fixed using experimental energy values from Aksela *et al.* [4]. With our time-of-flight spectrometers the linewidth is a nearly linear function of the electron kinetic energy. From the well separated $(^3P)6p(^2P_{3/2})$ peak (line 26 in Fig. 1) the kinetic-energy resolution for this experiment was found to be 1.1% and 1.0% of the final kinetic electron energy with retarding voltages of 30 and 32 V, respectively. We therefore fixed the linewidths of all peaks to these values.

We found no evidence of higher-order lines in the spectra. Since the photon resolution (about 15 meV) was much smaller than the resonance width, we did not have to subtract the nonresonant satellite background. The angular distribution of the $(^3P)6p(^2P_{3/2})$ peak (line 26) was determined by comparing its intensity to several groups of lines at different angles. This line was then used as an internal reference to which all other lines were compared.

The results for the relative intensities and the angular distribution parameters β are shown in Table I together with theoretical calculations from Tulkki, Aksela, and Kabachnik [19], Chen [18], and Hergenhahn *et al.* [16,17]. Chen [18], Tulkki, Aksela, and Kabachnik [19], and Hergenhahn *et al.* [17] used a multiconfiguration Dirac-Fock method in intermediate coupling with configuration interaction, whereas the older calculations of Hergenhahn, Kabachnik, and Lohmann [16] were carried out in jK coupling applying a strict spectator model. Only Tulkki, Aksela, and Kabachnik [19] include exchange with different continuum channels in their calculation. All the theoretical calculations have in common that both the direct photoionization and the participator decay are neglected, and these approximations have been verified experimentally [8,9].

Besides the $5p^46p$ spectator lines, Table I also includes some pure satellite lines. There is fair agreement between our intensities and those reported by Aksela *et al.* [4] (not shown) at least for the most intense lines. For small lines that are close to a strong line, our intensities tend to be larger than those of Aksela *et al.* [4]. This may be due to the fact that we used Gaussian profiles, which drop more rapidly than the Lorentzian profiles used by Aksela *et al.* [4].

Comparing our results to the different calculations, we find that the agreement varies between excellent and poor, depending on the configuration and method used. For some lines (20, 22, 31, 39) there is excellent agreement and for others (24, 43, 44) good agreement between our experimental anisotropy parameters and the results from all four calculations. For other lines (30, 34, 41, 65) the theoretical values are in disagreement with each other and with our experimental values. Finally, there are some configurations where our

TABLE I. Intensities and β parameters of the electron spectrum of Xe after $4d_{5/2}\rightarrow 6p_{3/2}$ excitation (65.110 eV). Intensities are normalized relative to the well separated $(^3P)6p(^2P_{3/2})$ line (line 26). The statistical uncertainty of the last digits is given in brackets. The identification of the peaks from Chen [18] was done with respect to their calculated energies. For Hergenhahn *et al.* [16,17] the energies of Hansen and Persson [22] were used. Peaks where the leading *LS* terms differ from that given by Aksela *et al.* [4] also used by Tulkki, Aksela, and Kabachnik [19] are marked with an asterisk (*).

Final ionic state Term[b]		Line in experiment[b]	Kinetic energy (eV)[b]	Relative intensity	β	β theory[a]			
						Ref. [19]	Ref. [18]	Ref. [17]	Ref. [16]
$5p^4(^3P)6p$	$^4P_{3/2}$	19	39.119	2.0(5)	1.4(6)	1.045	0.984	0.061	1.014
$(^3P)6p$	$^4P_{5/2}$	20	39.098	23.2(7)	−0.85(3)	−0.994	−1.000	−0.999	−0.998
$(^3P)6s$	$^2D_{3/2}$	21[c]	38.975	0.82(12)	2.0(3)				
$(^3P)6p$	$^2D_{5/2}$	22	38.906	37.5(8)	−0.967(12)	−0.994	−1.000	−1.000	−0.998
$(^3P)6p$	$^2S_{1/2}$	23	38.886	17.1(6)	−0.69(3)	−0.448	0.215*	0.157*	0.451*
$(^3P)6p$	$^4D_{7/2}$	24	38.882			−0.588	−0.974	−0.923	−0.932
$(^1D)5d$	$^2G_{9/2,7/2}$	25[c]	38.738	4.0(2)	−0.16(3)				
$(^3P)6p$	$^2P_{3/2}$	26	38.501	100	1.30(2)	1.030	1.018	0.972	1.014
$(^1D)5d$	$^2F_{5/2}$	27[c]	38.216	2.9(2)	0.60(11)				
$(^3P)6p$	$^2P_{1/2}$	28	37.988	5.0(2)	1.03(7)	0.984	0.962*	0.749*	NA[d]*
$(^3P)6p$	$^4P_{1/2}$	30	37.955	7.1(3)	−0.13(6)	0.233	0.774*	0.927	1.000
$(^3P)6p$	$^2D_{3/2}$	31	37.899	42.8(5)	0.73(3)	0.656	0.653*	0.910*	0.800*
$(^3P)6p$	$^4D_{5/2}$	32	37.716	1.3(4)	0.3(6)	−0.188	−0.331	−0.323	0.737
$(^3P)6p$	$^4S_{3/2}$	33	37.627	24.0(6)	1.13(5)	0.745*	0.955	0.557	−0.861
$(^3P)6p$	$^4D_{3/2}$	34	37.570	22.1(5)	−0.14(3)	−0.536*	−0.860*	−0.764*	−0.861*
$(^3P)5d$	$^2G_{5/2}$	35[c]	37.567						
$(^3P)6p$	$^2D_{1/2}$	36	37.535	19.5(4)	0.52(3)	0.593	0.935*	0.817*	1.000*
$(^1D)5d$	$^2P_{1/2}$	37[c]	37.232	5.6(2)	1.36(6)				
$(^1D)5d$	$^2D_{3/2}$	38[c]	37.169	2.7(2)	0.69(11)				
$(^1D)6p$	$^2F_{5/2}$	39	37.001	2.10(14)	−0.85(10)	−0.875	−0.860	−0.914	−0.928
$(^1D)6s$	$^2S_{1/2}$	40[c]	36.959[e]	3.0(2)	2.0(3)				
$(^1D)6p$	$^2P_{3/2}$	41	36.902	82.7(10)	0.47(2)	0.175	0.073	−0.319	−0.399
$(^1D)6p$	$^2F_{7/2}$	42	36.853	24.3(5)	−0.11(3)	0.246	0.052	0.116	0.112
$(^1D)6p$	$^2D_{3/2}$	43	36.621	39.0(7)	−0.66(2)	−0.553	−0.529	−0.375	−0.399
$(^1D)6p$	$^2D_{5/2}$	44	36.587	51.0(8)	−0.65(2)	−0.888	−0.882	−0.930	−0.928
$(^3P)7s$	$^4P_{5/2}$	45[c]	36.550	6(1)	SN[f]				
$(^1D)6p$	$^2P_{1/2}$	46	36.521	63.1(6)	1.66(2)	1.503	1.307	0.550	0.373
$(^3P)7s$	$^2P_{3/2}$	47[c]	36.232	13.9(3)	0.94(4)				
$(^1S)6p$	$^2P_{1/2}$	65	34.602	1.6(3)	0.73(4)	0.130	−0.139	−0.035	NA[d]
$(^1S)6p$	$^2P_{3/2}$	67 68	34.479 34.456	98.9(6)	1.17(4)	0.829	0.847	0.754	0.800

[a]The originally given σ_2 values are multiplied by $-\sqrt{2}$.
[b]According to Aksela *et al.* [4].
[c]Satellite line.
[d]Not allowed.
[e]Energy taken from Hansen and Persson [22].
[f]Strongly negative.

data agree with one or the other calculation. For instance, Chen [18] comes close to our β value for the $(^3P)6p(^4S_{3/2})$ state (line 33), whereas Tulkki, Aksela, and Kabachnik [19] and Hergenhahn, Kabachnik, and Lohmann [16] do not even have the correct sign. However, for the $(^3P)6p(^4D_{1/2})$ peak (line 36), Tulkki, Aksela, and Kabachnik [19] give almost the same β value as the experiment but the other calculations are off. Interestingly, there is almost perfect agreement between all theories for our reference peak $(^3P)6p(^4P_{3/2})$ (line 26), but the experimental β value is significantly larger. We were able to observe the splitting of the $(^1S)6p(^2P_{3/2})$ state (lines 67 and 68), as Aksela *et al.* [4] did, but the fitting procedure was very sensitive to even small changes in the positions and widths of the peaks. Therefore, in Table I we give only the average β for those lines. In Table II we compare our β results with previous experimental data from Carlson *et al.* [13], Becker *et al.* [23], and Kämmerling, Krässig, and Schmidt [15]. There is, in general, good agreement between the latter experiment and these results.

In summary, we have reported high-resolution angular

TABLE II. β parameters of the electron spectrum of Xe after $4d_{5/2} \rightarrow 6p_{3/2}$ excitation: a comparison with previous, lower-resolution data.

Line(s)		β			
No.[a]	No.[b]	Present work	I[c]	II[d]	III[b]
19,20	1a	−0.66(6)	−0.60(3)	−0.67(5)	−0.88
22–24	1b	−0.88(2)	−0.90(2)	−0.93(3)	−0.93
26	1c	1.30(2)	1.31(2)	1.35(6)	0.82
28–31	2a	0.65(4)	0.58(2)	0.89(6)	0.26
32–36	2b	0.52(5)	0.54(3)	0.45(6)	0.16
39–42	3a	0.36(4)	0.23(2)	0.55(5)	−0.02
43–47	3b	0.28(3)	0.33(5)	0.46(5)	−0.09
67,68	5	1.17(4)	0.83(5)	1.09(6)	0.51

[a]According to Aksela *et al.* [4].
[b]Carlson *et al.* [13].
[c]Kämmerling, Krässig, and Schmidt [15].
[d]Becker *et al.* [23].

distribution measurements of the Xe spectator lines following Xe $4d_{5/2} \rightarrow 6p$ excitation. The Auger resonant Raman effect was utilized to obtain energy resolutions well below the natural linewidth of the $4d$ inner-shell hole. Our results appear to remove the existing experimental discrepancy. Comparisons with different theoretical calculations show partly good agreement, but there is room for improvement for some lines.

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[1] G. S. Brown, M. H. Chen, and B. Crasemann, Phys. Rev. Lett. **45**, 1937 (1980).
[2] B. Crasemann, in *Proceedings of the XVII International Conference on the Physics of Electronic and Atomic Collisions, Brisbane, Australia, 1991*, edited by I. E. McCarthy, W. R. MacGillivray, and M. C. Standage (AIP, New York, 1992), p. 69.
[3] H. Aksela, S. Aksela, O.-P. Sairanen, A. Kivimäki, A. Naves de Brio, E. Nõmmiste, J. Tulkki, S. Svenson, A. Ausmees, and S. J. Osborne, Phys. Rev. A **49**, R4269 (1994).
[4] H. Aksela *et al.*, Phys. Rev. A **51**, 1291 (1995).
[5] Z. F. Liu *et al.*, Phys. Rev. Lett. **72**, 621 (1994).
[6] W. Eberhardt, G. Kalkhoffen, and C. Kunz, Phys. Rev. Lett. **41**, 156 (1978).
[7] V. Schmidt *et al.*, Phys. Rev. A **24**, 1803 (1981).
[8] H. Aksela *et al.*, Phys. Rev. A **33**, 3867 (1986).
[9] U. Becker *et al.*, Phys. Rev. A **33**, 3891 (1986).
[10] P. A. Heimann *et al.*, J. Phys. B **20**, 5005 (1987).
[11] U. Becker *et al.*, J. Phys. B **22**, 749 (1989).
[12] C. D. Caldwell, in *15th International Conference on X-Ray and Inner-Shell Processes*, edited by T. A. Carlsson, M. O. Krause, and S. T. Manson, AIP Conf. Proc. No. 215 (AIP, New York, 1990), p. 685.
[13] T. A. Carlson *et al.*, Phys. Rev. A **39**, 1170 (1989).
[14] J. W. Cooper, Phys. Rev. A **39**, 3714 (1989).
[15] B. Kämmerling, B. Krässig, and V. Schmidt, J. Phys. B **23**, 4487 (1990).
[16] U. Hergenhahn, N. M. Kabachnik, and B. Lohmann, J. Phys. B **24**, 4750 (1991).
[17] U. Hergenhahn *et al.*, J. Phys. B **26**, L117 (1993); nonaveraged β values: U. Hergenhahn (private communication).
[18] M. H. Chen, Phys. Rev. A **47**, 3733 (1993).
[19] J. Tulkki, H. Aksela, and N. M. Kabachnik, Phys. Rev. A **50**, 2366 (1994).
[20] S. Masui *et al.*, J. Phys. B **28**, 4529 (1995).
[21] H. Derenbach and V. Schmidt, J. Phys. B **17**, 83 (1984).
[22] J. E. Hansen and W. Persson, Phys. Scr. **36**, 602 (1987).
[23] U. Becker *et al.*, quoted in Ref. [16]; R. Weckwerth, Diplomarbeit (Diploma thesis), Technical University Berlin, 1991 (unpublished).