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

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(Received 11 January 1996)

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}→6p resonant Auger lines. The angular distribution parameters $\beta$ of almost all possible final ionic $5p^{i}(3P, 1D, 1S)6p$ states have been determined. Our data, which remove the discrepancy between previous lower-resolution experimental results, are compared to different theoretical results.

PACS number(s): 32.80.Dz, 32.80.Fb, 32.80.Hd

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}→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}→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 $\beta$ values in the decay spectrum. Such behavior was first explained theoretically for the decay of the Ar 2p→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 by 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→5p^{i}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 $\beta$ of almost all of the possible final ionic $5p^{i}(3P, 1D, 1S)6p$ states.

After a Xe 4d→6p excitation the decay process can involve (1) an excited electron (participant 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 participant decay [11]. During the decay, the excited 6p electron can also move into the 7p orbital (shake-up) enhancing the $5p^{i}7p$ final states. In this paper we focus on the strongest spectator decay channels, $5p^{i}(3P, 1D, 1S)6p$.

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]

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

(1)

where $\sigma_{if}$ and $\beta_{if}$ 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 $\theta$ 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 ($\theta = 0^\circ, 54.7^\circ$) 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...
resonant Ramon spectroscopy used to study... the theoretical calculations from Tulkki, Aksela, and Kabachnik. Ping peaks were fixed using experimental energy values from the fitting procedure the energy differences between overlap-by fitting Gaussian profiles to the data. In order to stabilize energy. From the well separated (3 linewidth is a nearly linear function of the electron kinetic angles recorded with a 32-V retarding potential at three different 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(4P3/2) 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(4P3/2) 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 5p6p 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
data agree with one or the other calculation. For instance, Chen [18] comes close to our $\beta$ value for the \( ^3P_6p(7S_{3/2}) \) 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 \( ^3P_6p(7D_{3/2}) \) peak (line 36), Tulkki, Aksela, and Kabachnik [19] give almost the same $\beta$ value as the experiment but the other calculations are off. Interestingly, there is almost perfect agreement between all theories for our reference peak \( ^3P_6p(7P_{3/2}) \) (line 26), but the experimental $\beta$ value is significantly larger. We were able to observe the splitting of the \( ^1S_6p(7P_{3/2}) \) 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 $\beta$ for those lines. In Table II we compare our $\beta$ 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
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.

We wish to thank the ALS for providing an excellent source of photons. B.L. is indebted to the Alexander von Humboldt Foundation for partial financial support. This work was supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Chemical Science, under Contract No. DE-FG02-92ER14299.

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

<table>
<thead>
<tr>
<th>No.</th>
<th>Present work</th>
<th>I</th>
<th>II$^d$</th>
<th>III$^e$</th>
</tr>
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<tbody>
<tr>
<td>19.20</td>
<td>1a</td>
<td>-0.66(6)</td>
<td>-0.60(3)</td>
<td>-0.67(5)</td>
</tr>
<tr>
<td>22–24</td>
<td>1b</td>
<td>-0.88(2)</td>
<td>-0.90(2)</td>
<td>-0.93(3)</td>
</tr>
<tr>
<td>26</td>
<td>1c</td>
<td>1.30(2)</td>
<td>1.31(2)</td>
<td>1.35(6)</td>
</tr>
<tr>
<td>28–31</td>
<td>2a</td>
<td>0.65(4)</td>
<td>0.58(2)</td>
<td>0.89(6)</td>
</tr>
<tr>
<td>32–36</td>
<td>2b</td>
<td>0.52(5)</td>
<td>0.54(3)</td>
<td>0.45(6)</td>
</tr>
<tr>
<td>39–42</td>
<td>3a</td>
<td>0.36(4)</td>
<td>0.23(2)</td>
<td>0.55(5)</td>
</tr>
<tr>
<td>43–47</td>
<td>3b</td>
<td>0.28(3)</td>
<td>0.33(5)</td>
<td>0.46(5)</td>
</tr>
<tr>
<td>67,68</td>
<td>5</td>
<td>1.17(4)</td>
<td>0.83(5)</td>
<td>1.09(6)</td>
</tr>
</tbody>
</table>

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

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