High-resolution study of the Xe $4d_{5/2}$:$4d_{3/2}$ branching ratio

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The Xe $4d_{5/2}$:$4d_{3/2}$ branching ratio has been determined in the photon energy range 80–250 eV using high-resolution electron spectroscopy and undulator radiation at the new Finnish beamline at the MAX I storage ring. The results were found to be in a satisfactory agreement with the calculated literature values obtained with the relativistic random-phase approximation. A few discrepancies between the theoretical predictions and our experimental results indicate additional correlation effects not accounted for in theory. The branching ratio is now shown to have a maximum of about 1.6 at around 230 eV. Lifetime widths of 114(4) and 121(4) meV are obtained for the $4d_{3/2}$ and $4d_{5/2}$ core hole states, respectively.

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Photoionization of the Xe $4d$ subshell has been of continuous interest to both experimentalists and theoreticians over the past decades [1]. The $4d$ photoionization gives the major contribution to the total absorption cross section in a wide photon-energy region, starting from the broad shape resonance that has a maximum around 100 eV, up to $3d$ ionization threshold around 700 eV. Above a threshold photon energy, the $4d$ core ionization process can be accompanied by a simultaneous transition of another electron either to a higher unoccupied orbital or to a continuum state, borrowing intensity from the $4d$ single ionization channel. Recently, a quantitative partition of the total cross section into its components has been achieved in the region of the shape resonance [2–6]. The partial cross sections and the angular-distribution asymmetry parameters of the photoelectrons have been determined with reasonable consistency across a large photon energy range [2–4,7,8]. Several sophisticated theoretical approaches [9–14] have given a fairly reasonable, though not excellent, agreement with the experimental findings. Even though present theory accounts for electron correlation at least to some extent, better consideration of the correlation effects is necessary.

A different situation holds for the experiments where the $4d_{5/2}$ and $4d_{3/2}$ spin-orbit split components are well resolved, relatively few data are available within a limited photon energy range. From the experimental point of view, the requirements on both intensity and resolution are stringent, which points towards the use of undulator radiation sources in conjunction with high-resolution monochromators and electron spectrometers. The Xe $4d_{5/2}$:$4d_{3/2}$ branching ratio (BR) as a function of photon energy has earlier been determined between $4d$ thresholds and 150 eV [7,15–17]. The only exception was Ref. [16], where the BR for a few photon energies above 150 eV was determined using x-ray line sources. Because the measurements were not performed at the magic angle, the accuracy of the BR values of Ref. [16] might suffer from angular-dependence effects. The rather moderate intensity and instrumental resolution in the earlier measurements made it difficult to determine the BR values with high accuracy. The experiments [7,15–17] have shown that the $4d_{5/2}$:$4d_{3/2}$ BR values strongly deviate from the statistical value of 1.5 in the whole photon energy region studied, leaving open the question of where the BR reaches its statistical value.

In this report, we present the Xe $4d_{5/2}$:$4d_{3/2}$ branching ratios at photon energies between 80 and 250 eV. The results are based on high-resolution gas-phase photoelectron spectra measured using monochromatized undulator radiation. The main purpose of the present study is to determine accurately the $4d$ BR values and to extend considerably the photon energy range compared to the previous studies. The experimental values of the BR will be compared with available theoretical results.

The experiments have been carried out at the Finnish beamline (BL 51) [18] at the MAX I storage ring in Lund, Sweden. Synchrotron radiation in the photon energy range of 60 to 600 eV obtained from a short period undulator is monochromatized by a modified Zeiss SX-700 plane grating monochromator [19]. The degree of linear polarization of undulator radiation in the case of the lower-order harmonics has been shown to be very high [5,20]. The gas-phase experiment is isolated from the ultrahigh vacuum of the monochromator by a permanent differential pumping section. This is equipped with a toroidal refocusing mirror that produces a small spot 1 mm in diameter at the source point in the sample compartment. The electron spectrometer SES-144 [21] is of the truncated hemispherical type with a mean radius of 144 mm. The analyzer is combined with a four element retarding or accelerating electron lens that focuses electrons onto the entrance slit of the analyzer. Electrons are retarded or accelerated to a constant pass energy. In the present study, pass energies of 10, 20, and 50 eV were

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used, giving an electron energy resolution of about 40, 60, and 130 meV, respectively. An efficient differential pumping of the gas cell allows gas pressures in the order of 10^{-3} – 10^{-4} mbar. The spectrometer is mounted with the principal axis of the electron lens in the pseudo-magic angle of about 55° versus the electric field vector of the photon beam, allowing direct angular independent measurements of the branching ratios.

The Xe 4*d* photoelectron spectra have been corrected for the spectrometer transmission using experimentally determined functions for each pass energy [22]. In order to obtain spectra of different electron energy resolutions and signal-to-background ratios for lower photon energies, several spectra with various spectrometer pass energies were recorded. This appeared to be rather crucial because the $4d_{5/2}$ and $4d_{3/2}$ photoelectron lines at kinetic energies below 37 eV overlap with the manifold of lines due to $N_{4,5}OO$ Auger transitions. In order to determine the peak areas the 4*d* photoelectron lines were fitted by the help of a computer code [23] using Voigt line shape and linear background subtraction. The full width at half maximum (FWHM) and the line position of the $4d_{5/2}$ and $4d_{3/2}$ photoelectron lines were allowed to vary independently. Also, different line shapes used in the preliminary fittings of the 4*d* photoelectron lines showed that the BR values are not very sensitive to a particular line shape. In Fig. 1 a photoelectron spectrum taken at photon energy of 83.1 eV is shown, where the 4*d* photoelectron lines overlap with the $4d^{-1} \rightarrow 5p^3 5d$ ($J = 1$) [24] Auger electron lines.

Figure 2 displays two Xe 4*d* photoelectron spectra recorded at photon energies 158.1 and 227.5 eV. The two spin-orbit components are well resolved, and the 4*d* spin-orbit splitting, as determined from several high photon energy (107 to 250 eV) spectra, was 1982(2) meV. This value agrees well with a previous estimate of 1979(7) meV [17]. For all the recorded 4*d* spectra, the FWHM ranged from 135 to 280 meV, depending on the pass energy and monochromator slit width (10 to 180 μm). A deconvolution procedure described in Ref. [25] enables an inherent Lorentzian width to be determined, if the presumably Gaussian instrumental contribution and Doppler broadening to the experimental Voigt line are known. The resolution of the monochromator and the spectrometer, respectively, has been determined on the basis of measurements of the Ar $2p_{3/2} \rightarrow 4s$ photoabsorption spectra and the Xe $5p_{3/2}$ photoelectron spectra. This procedure resulted in an estimate of 114(4) and 121(4) meV for the inherent lifetime width of the $4d_{3/2}$ and $4d_{5/2}$ core hole states, respectively. These values are slightly different from the lifetime widths of 119(8) and 111(4) meV as determined from the electron energy loss spectra for the $4d_{3/2}^{-1}6p$ and $4d_{5/2}^{-1}6p$ excited states, respectively [26].

The $4d_{5/2}$:$4d_{3/2}$ BR values are presented versus photon energy in Fig. 3. We omit here our BR values at lower photon energies because of uncertainties connected with strong post collision interaction [27] and increasing background in the spectra at very low kinetic energies. However, the values as high as about 3, observed at photon energies around 74 eV [17], could be confirmed semi-quantitatively. The error bars in Fig. 3 are mainly due to uncertainties in curve fitting and background subtraction. Some BR values from previous experimental studies by Banna *et al.* [16] and Yates *et al.* [17] are also shown. These experimental results are displayed together with BR values calculated in the relativistic random-phase approximation (RRPA) [9,28].

The overall agreement of the calculated BR values with the experimental ones in Fig. 3 is satisfactory. However, several discrepancies should be noted. First, at the first minimum the BR values of about 1.15 determined in the present work and by Yates *et al.* are higher than the calculated BR value of about 1. The experimental results show that the first minimum is shallower than the calculated shape of the BR curve. Second, the calculated minimum occurs at about 81 eV which is too low by a few eV in comparison with the experimental results. At higher photon energies, between 95 and 140 eV, our results agree rather well with the RRPA values, whereas those from Ref. [17] tend to be a little lower, supposedly due to differences in the experimental conditions or in the data treatment. Around the second broad mini-

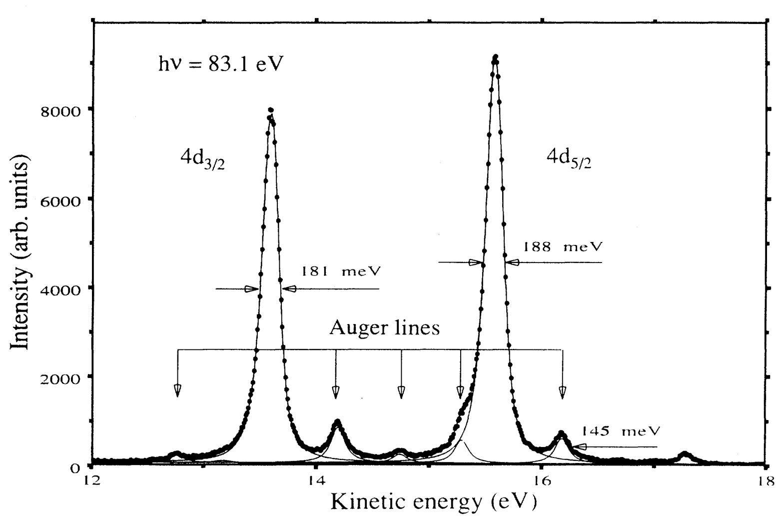

FIG. 1. The Xe $4d^{-1} \rightarrow 5p^3 5d$ ($J = 1$) Auger spectrum overlapping with the $4d_{5/2}$ and $4d_{3/2}$ photoelectron lines recorded at the photon energy of 83.1 eV. The spectrometer pass energy was set to 10 eV and the monochromator slit width to 180 μm.

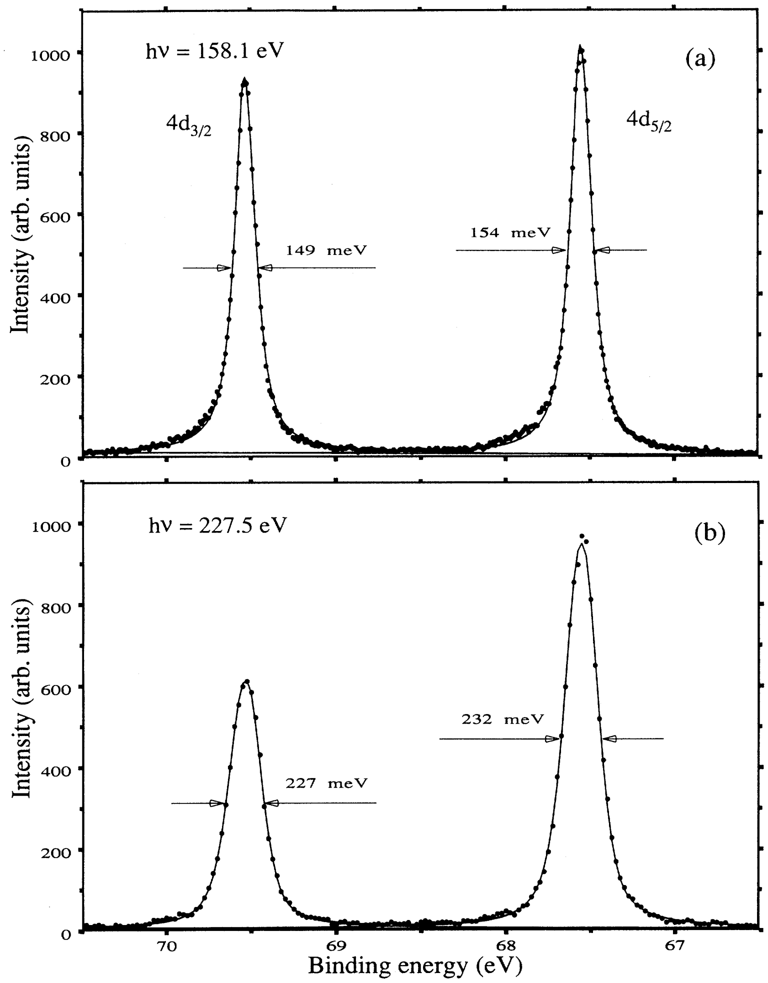

FIG. 2. $4d_{5/2}$ and $4d_{3/2}$ photoelectron spectra taken at photon energies of 158.1 eV (a) and 227.5 eV (b). The pass energy was set to 20 eV (a), 50 eV (b) and the monochromator slit width to 10 μm (a), 25 μm (b).

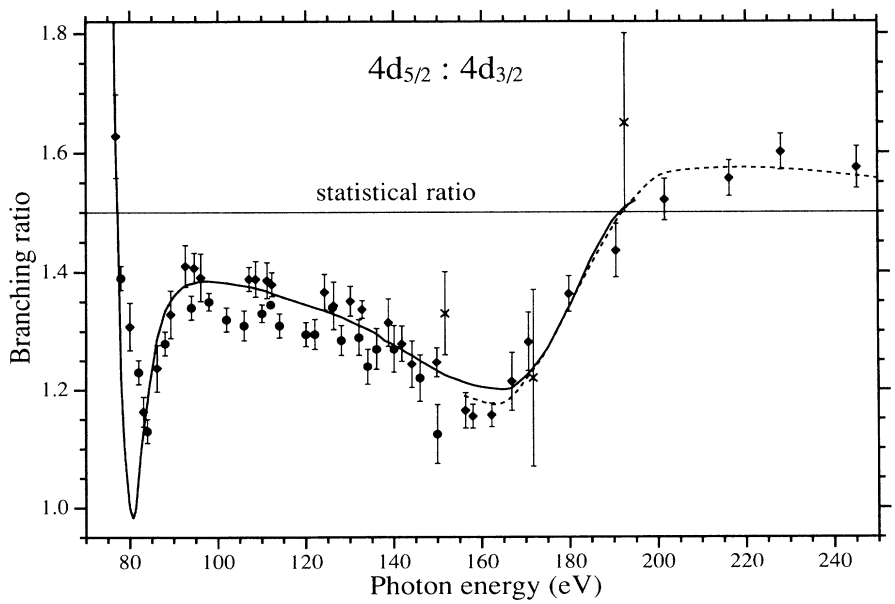

FIG. 3. The $4d_{5/2}$:$4d_{3/2}$ branching ratio as a function of photon energy. Experimental data: present work (diamonds); from Ref. [28] (circles); from Ref. [16] (crosses). The calculated values in the RRPA : Ref. [28] (solid line); Ref. [9] (dashed line).

mum at about 160 eV both the RRPA results are higher than ours, whereas at higher photon energies the accord with our experiment is better. At higher energies than those presented in Fig. 3, the calculated BR decreases slowly and reaches its statistical value at photon energies around 350 eV [9]. We have measured the $4d$ photoelectron spectrum at 365 eV photon energy with moderate resolution, and a new curve fitting was done to the x-ray photoelectron spectroscopy (1487 eV) spectrum of Ref. [29]. Both findings exhibited BR values of about 1.5.

Among the available theoretical predictions, the RRPA results in the most realistic match to the experimental $4d_{5/2}$:$4d_{3/2}$ BR for the whole photon energy range. A difference between the two RRPA calculations [9,28] is that in Ref. [9] five additional channels from the $4p$ subshell were included in the calculations contrary to Ref. [28] where only six channels from the $4d$ subshell were taken into account. Neither of the calculations included core relaxation effects. It should be stressed that the RRPA where the relaxation is omitted [9,28], used here for a comparison with the experimental results, is not the most up-to-date approach. Recently, the Xe $4d$ photoionization cross sections have been calculated applying more advanced approaches, for instance, the RRPA considering core relaxation [10,11] and including the coupling between channels from other subshells [10]. These studies have demonstrated the importance of relaxation and intershell coupling effects close to the thresholds. Unfortunately, no explicit data on the $4d_{5/2}$:$4d_{3/2}$ BR were given in these reports for the wide energy region. The $4d_{5/2}$ and $4d_{3/2}$ partial cross sections calculated in the RRPA with the inclusion of core relaxation [11] indicate that the BR values are considerably higher than the experimental ones between photon energies 80 and 90 eV. This shows that the calculated $4d_{5/2}$:$4d_{3/2}$ BR values are model dependent close to the $4d$ thresholds. Hopefully, the experimental results presented here will be useful in the verification of the capacity of the relativistic theoretical approaches to reproduce the experiment, in particular in the region of the $4d$ and $4p$ thresholds where the relaxation and intershell coupling effects manifest themselves as drastic changes in the calculated results.

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[1] V. Schmidt, Rep. Prog. Phys. **55**, 1483 (1992) and references therein.

[2] U. Becker, D. Szostak, H. G. Kerkhoff, M. Kupsch, B. Langer, R. Wehlitz, A. Yagishita, and T. Hayaishi, Phys. Rev. A **39**, 3902 (1989).

[3] D. W. Lindle, T. A. Ferret, P. A. Heimann, and D. A. Shirley, Phys. Rev. A **37**, 3808 (1988).

[4] B. Kämmerling, H. Kossmann, and V. Schmidt, J. Phys. B **22**, 841 (1989).

[5] B. Kämmerling and V. Schmidt, J. Phys. B **26**, 1141 (1993).

[6] N. Saito and I. H. Suzuki, Phys. Scr. **49**, 80 (1994).

[7] S. P. Shannon, K. Codling, and J. B. West, J. Phys. B **10**, 825 (1977).

[8] S. Southworth, P. H. Kobrin, C. M. Truesdale, D. W. Lindle, S. Owaki, and D. A. Shirley, Phys. Rev. A **24**, 2257 (1981).

[9] N. Shanti and P. C. Desmukh, Phys. Rev. A **40**, 2400 (1989).

[10] M. Kutzner, V. Radojevič, and H. P. Kelly, Phys. Rev. A **40**, 5052 (1989).

[11] W. R. Johnson and K. T. Cheng, Phys. Rev. A **46**, 2952 (1992).

[12] F. A. Parpia, W. R. Johnson, and V. Radojevič, Phys. Rev. A **29**, 3173 (1984).

[13] Z. Altun, M. Kutzner, and H. P. Kelly, Phys. Rev. A **37**, 4671 (1988).

[14] M. Ya. Amusia, L. V. Chernysheva, G. F. Gribakin, and K. L. Tsemekhman, J. Phys. B **23**, 393 (1990).

[15] M. Y. Adam, F. Wuilleumier, S. Krummacher, N. Sandner, V. Schmidt, and W. Mehlhorn, J. Electron Spectrosc. Relat. Phenom. **15**, 211 (1979).

[16] M. S. Banna, M. O. Krause, and F. Wuilleumier, J. Phys. B **12**, L125 (1979).

[17] B. W. Yates, K. H. Tan, L. L. Coatsworth, and G. M. Bancroft, Phys. Rev. A **31**, 1529 (1985).

[18] S. Aksela, A. Kivimäki, A. Naves de Brito, O.-P. Sairanen, S. Svensson, and J. Väyrynen, Rev. Sci. Instrum. **65**, 831 (1994).

[19] R. Nyholm, S. Svensson, J. Nordgren, and A. Flodström, Nucl. Instrum. Methods A **267** (1986); S. Aksela, A. Kivimäki, R. Nyholm, and S. Svensson, Rev. Sci. Instrum. **63**, 1252 (1992).

[20] M. O. Krause, S. B. Whitfield, C. D. Caldwell, J.-Z. Wu, P. van der Meulen, C. A. de Lange, and R. W. C. Hansen, J. Electron Spectrosc. Relat. Phenom. **58**, 79 (1992).

[21] S. J. Osborne, A. Ausmees, J. O. Forsell, B. Wannberg, G. Bray, L. B. Dantas, S. Svensson, A. Naves de Brito, A. Kivimäki, and S. Aksela, Synch. Rad. News **7**(1), 25 (1994).

[22] J. Jauhiainen, A. Ausmees, A. Kivimäki, S. J. Osborne, A. Naves de Brito, S. Aksela, S. Svensson, and H. Aksela, J. Electron Spectrosc. Relat. Phenom. **69**, 181 (1994).

[23] ESCA-300 program, Scienta Instrument AB, Uppsala, Sweden.

[24] H. Aksela, S. Aksela, and H. Pulkkinen, Phys. Rev. A **30**, 865 (1984).

[25] G. K. Wertheim, M. A. Butler, K. W. West, and D. N. E. Buchanan, Rev. Sci. Instrum. **45**, 1369 (1974).

[26] G. C. King, M. Tronc, F. H. Read, and R. C. Bradford, J. Phys. B **10**, 2479 (1977).

[27] T. Åberg, Phys. Scr. **T41**, 71 (1992) and references therein.

[28] K. T. Cheng and W. R. Johnson, Phys. Rev. A **28**, 2820 (1983).

[29] S. Svensson, B. Eriksson, N. Mårtensson, G. Wendin, and U. Gelius, J. Electron Spectrosc. Relat. Phenom. **47**, 327 (1988).