Valence-shell photoionization of Ag-like Xe\(^{7+}\) ions: experiment and theory

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Received 9 July 2014, revised 1 September 2014
Accepted for publication 9 September 2014
Published 15 October 2014

**Abstract**

We report on experimental and theoretical results for the photoionization of Ag-like xenon ions, Xe\(^{7+}\), in the photon energy range 95–145 eV. The measurements were carried out at the Advanced Light Source at an energy resolution of \(\Delta E = 65\) meV with additional measurements made at \(\Delta E = 28\) meV and 39 meV. Small resonance features below the ground-state ionization threshold, at about 106 eV, are due to the presence of metastable Xe\(^{7+}(4d\, 4f\, F_{\frac{10}{2}, \frac{7}{2}})\) ions in the ion beam. On the basis of the accompanying theoretical calculations using the Dirac atomic R-matrix codes (DARC), an admixture of only a few percent of metastable ions in the parent ion beam is inferred, with almost 100% of the parent ions in the \(4d\, 5s\, S\) ground level. The cross section is dominated by a very strong resonance associated with \(4d \rightarrow 5f\) excitation and subsequent autoionization. This prominent feature in the measured spectrum is the \(4d^{10}5s\, ^1P_{\frac{9}{2}}\) resonance located at \((122.139 \pm 0.01)\) eV. An absolute peak cross section of 1.2 Gigabarns was measured at 38 meV energy resolution. The experimental natural width \(\Gamma = 76 \pm 3\) meV of this resonance compares well with the theoretical estimate of 88 meV obtained from the DARC calculation with 249 target states. Given the complexity of the system, overall satisfactory agreement between theory and experiment is obtained for the photon energy region investigated.

**Keywords:** photoionization, xenon ions, cross sections, experiment, theory

(Some figures may appear in colour only in the online journal)

1. Introduction

Collision processes with xenon ions are of interest for UV-radiation generation in plasma discharges [1], for fusion research [2] and also for spacecraft propulsion [3]. Photoionization of Xe ions in different charge states has been investigated previously in experiments with Xe\(^{+}\) [4–11], Xe\(^{2+}\) [6, 7, 11, 12], Xe\(^{3+}\) [6, 7, 11, 13, 14], Xe\(^{4+}\) [11, 14, 15], Xe\(^{5+}\) [11, 14, 15], Xe\(^{6+}\) [14, 15], and Xe\(^{7+}\) [16].

Here we report theoretical and experimental results for the photoionization of Ag-like Xe\(^{7+}\) ions which were measured at the ion photon beam (IPB) end station of AMO beamline 10.0.1.2 at the Advanced Light Source (ALS) in Berkeley, California. Xe\(^{7+}(4d^{10}5s\, ^2S_{\frac{1}{2}})\) is of particular interest because of its quasi-single-electron nature and, hence, its potential as a test case for understanding fundamental aspects of atomic processes. Compared with the only previous experimental study of single photoionization of Xe\(^{7+}\) carried out by Bizau and co-workers [16], the present cross sections were obtained at higher energy resolution (65 meV versus...
more than 700 meV) and on an absolute cross section scale. Preliminary experimental results from the present study were reported by Schippers et al [17]. In the photon energy range of 95–145 eV covered by the experiment the cross section is dominated by resonances associated with 4d → nl excitations with n = 5, 6, 7, ... and subsequent autoionization. The high-precision cross section measurements carried out at the ALS are compared with large-scale theoretical calculations within the confines of the Dirac Coulomb R-matrix approximation [18–21]. For the computations the Dirac atomic R-matrix codes (DARC) package was employed using progressively larger expansions in the close-coupling calculations. The results provide suitable representations of photoionization of the (4d105s 5p1/2) ground and metastable (4d104f 2F3/2,5/2) levels of Ag-like Xe7+ ions, the latter of which are excited by about 32.9 eV [22] above the ground state.

In addition to the direct photoionization process removing the outermost 5s or 4f electron, the following indirect excitation processes can occur for the interaction of a photon with the 5s ground-state and the 4f metastable levels of the Xe7+ ion

\[ h\nu + Xe^{7+}(4d^{10}5s^25p_{1/2}) \rightarrow Xe^{7+}(4d^{10}5s5p_{1/2}L_{1/2},3/2), \]

\[ h\nu + Xe^{7+}(4d^{10}4f^25p_{3/2}) \rightarrow Xe^{7+}(4d^{10}4f^25p_{3/2}L_{3/2,5/2,7/2}), \]

\[ h\nu + Xe^{7+}(4d^{10}4f^25p_{1/2}) \rightarrow Xe^{7+}(4d^{10}4f^25p_{1/2}L_{5/2,7/2,9/2}), \]

where the term angular momentum L is 1, 2, 3, 4 or 5 (i.e. P, D, F, G or H) of the excited xenon ion. The contributing principal quantum numbers n (which can be as low as n = 4 for the metastable initial state) depend on the orbital quantum number ℓ (predominantly ℓ = 3 or 1) of the subshell to which the 4d electron is excited. The intermediate resonance states can then decay by autoionization to the ground state or other energy-accessible excited states of Xe8+.

The layout of this paper is as follows. Section 2 details the experimental procedure used. Section 3 gives an outline of the theoretical work. Section 4 presents and discusses the results obtained from both the experimental and theoretical methods. Finally in section 5 a summary is provided and conclusions are drawn from the present investigation.

2. Experiment

A detailed description of the experimental setup has been provided by Covington and co-workers [23]. The experimental procedures were similar to those used previously by Müller et al [24, 25]. The Xe7+ ions required for the present experiment were produced from natural xenon gas inside a compact 10 GHz all-permanent-magnet electron-cyclotron-resonance ion source placed at a positive potential of +6 kV. After extraction and acceleration of the ions to a kinetic energy of 42 keV the ion beam was deflected by a 60° dipole magnet selecting ions of the desired ratio of charge to mass. Collimated, isotope-resolved Xe7+ ion beams with electrical currents of up to 15 nA were passed through the photon-merged-beam interaction region. By applying appropriate voltages to several electrostatic steering and focusing devices the ion beam was aligned along the axis of the counter-propagating photon beam. Downstream of the interaction region, the ion beam was deflected out of the photon-beam direction by a second dipole magnet that also separated the ionized Xe8+ product ions from the Xe7+ parent ions. The Xe8+ ions were counted with a single-particle detector of nearly 100% efficiency [26, 27], and the Xe7+ ion beam was collected in a Faraday cup monitoring the ion current for normalization purposes. The measured Xe8+ count rate did not result completely from photoionization events. Although the interaction region was maintained at ultra-high vacuum, the product ion beam also contained Xe8+ ions produced by electron-loss collisions with residual gas molecules and surfaces. For the determination of absolute cross sections this background was subtracted by employing time modulation (mechanical chopping) of the photon beam.

Absolute cross sections were obtained by normalizing the background-subtracted Xe8+ photo-ion yield to the measured ion current, to the photon flux which was determined using a calibrated photodiode, and to the geometrical beam overlap. The latter was optimized by employing two commercial rotating-wire beam-profile monitors located in front of and behind the interaction region. The effective length of 29.4 cm of the interaction region is defined by a drift tube which, in the present experiment, was set to a potential of −1.5 kV with respect to the surrounding grounded electrodes and the vacuum vessel. By this potential, the Xe8+ ions produced inside the drift tube are energy-tagged. They emerge with a kinetic energy of 42 keV + 7e × 1.5 kV − 8e × 1.5 kV = 40.5 keV, where 7e is the electrical charge of the entering ions and 8e is the electrical charge of the exiting ions. Xe7+ ions born outside the interaction region maintain their original energy of 42 keV. The demerging magnet and a subsequent spherical electrostatic energy analyzer easily separate Xe7+ ions with energies of 40.5 and 42 keV from one another. The overlap of the merged beams is quantified by the form factor [28] which was determined by scanning narrow slits across the two beams at three positions along the beam axes, at the entrance, the middle and the exit of the interaction region. Due to the considerable effort required for carrying out reliable absolute cross section measurements, these were performed at only a few photon energies at selected resonance maxima. By comparison of these absolute measurements with the photo-ion-yield spectrum a constant normalization factor was determined matching the yield spectrum to the absolute cross sections. The scatter in the ratios of absolute cross sections and associated photo-ion-yields is much smaller than the relative systematic uncertainty of each absolute measurement.

To illustrate the absolute measurements, experimental form-factor data taken at a photon energy of 122.14 eV are shown in figure 1. For this specific measurement the monochromator slits were set to 59.9 μm at the entrance and 176.6 μm at the exit position resulting in a photon-energy resolution of 65 meV. The current measured at the photodiode was 81.75 μA corresponding to a photon flux of 3.37·1013 s⁻¹. The electrical ion current of 1.44 nA produced detector background of (39 ± 1) s⁻¹ mainly by
collisions of Xe7+ with residual gas particles resulting in the production of Xe8+ ions. The photoionization signal rate after background subtraction was \((1910 \pm 45) \text{s}^{-1}\). The cross section resulting from this particular measurement taken with a form factor \(F = 1244 \text{ cm}^{-1}\) is 965 Mb with a statistical uncertainty of 2.3%.

The error budget of absolute measurements at the IPB endstation has been previously discussed in detail by Covington et al [29]. Different from their experiment, a much more efficient single-particle detector [26, 27] was employed in the present measurements. Uncertainties associated with the product ion detection including product-ion collection were substantially reduced from a total of about 11% to a new total of only 5%. The resulting total systematic error of the present absolute cross section determination is estimated to be \(\pm 19\%\) at 90% confidence.

The energy scale was calibrated by first applying a Doppler correction to account for the motion of the Xe7+ parent ions. The monochromator calibration was determined by measurements of the photo-ions produced in photo-ionization of Ar gas in the vicinity of the Ar 2p\(3/2\) edge which was observed in second-and third-order light from the monochromator. The Ar photoabsorption spectrum covers characteristic and distinct features in the energy range from about 244 to 250 eV. Observations of these features with second-order light were made in the nominal energy range 122–124.5 eV and with third-order light in the energy range 82.1–82.9 eV. The resulting resonance positions were compared with the measurements carried out by King et al [30] and Ren et al [31]. King et al [30] employed electron-energy-loss spectroscopy with 1.5 keV electrons at about 70 meV resolution reaching an accuracy for the (2p\(5 2P^\circ_{3/2}\))4s resonance of 10 meV at 244.39 eV, that was unsurpassed for decades until a few years ago. Ren et al [31] also measured electron-energy-loss spectra with a resolution of 55 meV using 2500 eV electrons scattered from Ar at 0° and 4°. With improved energy resolution and better statistics they were able to provide the same energy of 244.390 eV for the (2p\(5 2P^\circ_{3/2}\))4s resonance but with an uncertainty of only 4 meV, i.e., a factor of two and a half better than King et al. The comparison of the present photoabsorption energies in second and third order with the literature values showed deviations between –23 meV near 82 eV and +53 meV near 122 eV. By applying a linear correction to the nominal photon energies of the present experiment an uncertainty of the overall energy calibration of \(\pm 10\) meV is estimated. Since the dominating Xe7+ photoionization resonance found in the present experiment is at an energy of 122.139 eV almost coincides in position with the energy to be expected in the second-order observation of the Ar (2p\(5 2P^\circ_{3/2}\))4s resonance, known to be at 122.195 eV, we conclude that the calibrated energy scale has a conservatively estimated uncertainty of better than \(\pm 5\) meV at the position of the Xe7+(4d\(5S5f\) 2P\(^\circ\)) resonance.

3. Theory

3.1. DARC calculations for Ag-like Xenon

For comparison with high-resolution measurements such as those carried out in the present study, state-of-the-art theoretical methods using highly correlated wavefunctions are required that include relativistic effects and thus provide quantitative results on fine-structure level splitting. An efficient parallel version [32] of the DARC [33–36] suite of codes has been developed [18–20] to address the challenge of

![Figure 1. Determination of the merged-beam form factor by slit scans of the beam profiles at different positions \(z_i\), \(i = 1,2,3\) along the axis of the overlapping photon and ion beams. Panels (a)–(c) show the measured beam profiles at \(z_1 = -10.11\) cm, \(z_2 = 0.88\) cm and \(z_3 = 11.88\) cm, respectively, where \(z = 0\) is in the center of the interaction region. Panel (d) shows the calculated overlap integrals, \(F(\zeta)\), at the measured positions (solid dots) and the solid line is a second-order polynomial fit to the data used for interpolating \(F(\zeta)\). The shaded area indicates the length of the interaction region. The resulting total form factor \(F\) is the integral of \(F(\zeta)\) over the length of the interaction region. The numerical values of the overlaps and the total form factor of the specific measurement are given in the respective panels.

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electron and photon interactions with atomic systems supporting the inclusion of hundreds of levels and thousands of scattering channels. Metastable states are populated in the Xe7+ ion beam experiments requiring additional theoretical calculations. Recent modifications to the DARC codes [18–20] facilitate high quality photoionization cross section calculations for heavy complex systems of interest to astrophysics and other plasma applications. Previously, cross section calculations for single photoionization of trans-Fe elements such as Xe+, Xe and Xe+ ions [19, 20, 37] have been made using this modified DARC code illustrating excellent agreement with the available experimental measurements.

Ag-like Xe7+ is a quasi-one-electron system with a single 4s electron outside filled sub-shells in the ground level or a single 4f electron in the first metastable excited level that contributes to the experimental cross section. Complexity emerges when a 4d electron is excited producing atomic configurations with typically three open sub-shells with relatively high angular momenta. Photoionization cross section calculations for Xe7+ were performed for the ground (4d10s5) and the excited metastable (4d10f4f) levels with a progressively larger number of states in our close-coupling work to benchmark our theoretical results with the present high resolution experimental measurements.

The atomic structure calculations were carried out using the GRASP code [38–40]. Initial atomic structure calculations were done for the target states using 249 levels arising from twelve configurations of the Pd-like (Xe8+) residual ion. The configurations 4d10, 4d2f, 4d5s, 4d5p, 4d5d, 4d5f, 4d6s, 4d6p, 4d6d, 4d6f, 4d5s2 and 4d5p2 were included in the close-coupling calculations. We investigated the convergence of this model by incorporating the additional configuration 4d5d2 which gave rise to a total of 526 levels. Models were also investigated, where we left out the 6d orbital in the ground and metastable states and incorporated a 4f2 configuration. Photoionization cross section calculations were then performed using the DARC codes for the different scattering models for the ground 4d10s5 2S12 state of the Xe7+ ion (with 249, 508 and 526 levels) in order to gauge convergence of the models. The DARC photoionization cross section calculations for the metastable (4d10f4f) levels were restricted to a 528-level model.

The R-matrix boundary radius of 12.03 Bohr radii was sufficient to envelop the radial extent of all the n = 6 atomic orbitals of the Xe7+ ion. A basis of 16 continuum orbitals was sufficient to span the incident experimental photon energy range from threshold up to 150 eV. Since dipole selection rules apply, total ground-state photoionization requires only the bound-free dipole matrices, 2Jf = 1 → 2Jf = 1, 3. For the excited metastable states, 2Jf = 5 → 2Jf = 3, 5, 7 and 2Jf = 7 → 2Jf = 5, 7, 9 are necessary.

For the ground and metastable initial states, the outer region electron-ion collision problem was solved (in the resonance region below and between all thresholds) using a suitably chosen fine energy mesh of 1.5 × 10−8 Rydbergs (≈0.2 μeV) to fully resolve all the extremely narrow resonance structure in the photoionization cross sections. The jj-coupled Hamiltonian diagonal matrices were adjusted so that the theoretical term energies matched the recommended NIST values [22]. We note that this energy adjustment ensures better positioning of certain resonances relative to all thresholds included in the calculation [19, 20]. The DARC photoionization cross sections for Ag-like xenon ions were convoluted with a Gaussian of 65 meV full-width-at-half-maximum (FWHM) in order to simulate the measurements. For a direct comparison with the ALS measurements an appropriate weighting of the cross sections from the ground and metastable state was made due to the presence of metastable states in the Xe7+ ion beam.

3.2. Assignment of the dominant resonance features

The DARC results do not provide detailed information about the intermediate excited states populated during the photoionization process unless a detailed resonance analysis is carried out. In order to gain some physical insight into the features observed in the spectra, separate calculations for the 4d10s5 ground level and the metastable 4d10f4f levels were carried out with the Cowan code [41] using the Los Alamos package of atomic physics codes [42]. Fine-structure mode was applied so that level-to-level transitions could be explored. For the 4d10s5 ground level nine 4d-excited configurations 4d5s5p, 4d5s6p, 4d5s7p, 4d5s8p, 4d5s9p, 4d5s5f, 4d5s6f, 4d5s7f, and 4d5s8f were considered giving rise to 272 energy levels. In a second step the oscillator strengths f of all dipole-allowed transitions from the ground level to excited levels within the above configurations were calculated. The resulting oscillator strengths were used to generate cross sections for photoabsorption. These are identical to the photoionization cross sections for each resonance, provided the branching ratios for single autoionization are all unity. Under this condition the photoionization cross section can be derived as

\[ \sigma_{\text{PI}}(E) = 2\pi^2 a_0^2 R_\infty \frac{df}{dE} \]

\[ = 1.097 \times 10^{16} \frac{df}{dE} \text{ cm}^2, \]

where \( \alpha \) is the fine structure constant, \( a_0 \) is the Bohr radius, \( R_\infty \) is the Rydberg constant and \( \frac{df}{dE} \) is the differential oscillator strength per unit energy [41, 43]. Rearranging and integrating the equation relates the calculated oscillator strength \( f \) with the resonance strength \( \sigma_{\text{res}} \) (in Mb eV)

\[ f = 9.11 \times 10^{-3} \int_{-\infty}^{\infty} \sigma_{\text{PI}}(E) dE = 9.11 \times 10^{-3} \sigma_{\text{res}}, \]

where \( \sigma_{\text{PI}}(E) \) is the photoionization cross section in Mb (1 Mb = 1.0 × 10−18 cm2), and E is the photon energy in eV. The resulting cross section \( \sigma_{\text{res}}(E) = \sigma_{\text{res}} \delta(E - E_{\text{res}}) \), where \( \delta(x - x) \) is the standard Dirac \( \delta \) function [44] for a continuous variable) assumed to contribute only at resonance energy \( E_{\text{res}} \) was convoluted with a Gaussian of 65 meV FWHM in order to simulate the experimental resonance
widths. Further manipulations of the calculated photoionization spectrum are discussed in the results section.

Calculations with the Cowan code were also carried out for the metastable 4d105f levels of Xe7+. Ten excited configurations 4d4f5p, 4d4f6p, 4d4f7p, 4d4f8p, 4d4f9p, 4d4f42, 4d4f5f, 4d4f6f, 4d4f7f, and 4d4f8f were included which give rise to 1570 levels including the parent 2F levels. A total number of 1520 oscillator strengths $f$ of all dipole-allowed transitions from the two 2F5/2 and 2F7/2 ground levels to excited levels within the above configurations were calculated and cross sections determined.

4. Results and Discussion

An overview of the experimental cross section for single photoionization of Xe7+ ions is given in figure 2. The whole spectrum in the photon energy range 95–145 eV is dominated by a huge resonance at approximately 122 eV. It is associated with a 4d $\rightarrow$ 5f transition in ground-state Xe7+.

A plot of the energy dependence of $\sigma_{th}(E)$ obtained with the Cowan code (see section 3.2) shows many similarities with the experimental spectrum. In the calculations one can recognize the main features obtained in the experiment, however, the resonance energies for 4d105s $\rightarrow$ 4d95s1f transitions are not exactly matched. A linear transformation $E_{\text{obs}} = 9.081393$ eV $+ 0.936797 E_{\text{Cowan}}$ of the energies $E_{\text{Cowan}}$ calculated with the Cowan code and involving shifts of the order of 1–2 eV or less, nicely line up the calculated resonance positions $E_{\text{Cowan}}$ with those of the experiment, $E_{\text{obs}}$, with deviations around an average of 0.25 eV. The 4d105s $\rightarrow$ 4d95snp transitions do not require any shifts. Also for the 4d105f $\rightarrow$ 4d94fn transitions there is no obvious necessity to recalibrate the resonance energies. The relative sizes of the three groups of resonances discussed above were adjusted to the experiment. The result of this analysis is shown in (panel (b)) of figure 2, where assignments of calculated transitions to the dominant features are provided. The model (panel (b)) agrees remarkably well with the measured spectrum (panel (a)). This agreement provides confidence in the given assignments and their application to the resonance peaks observed in the experiment. Obviously, the dominant resonance is associated with 4d105s 2S1/2 $\rightarrow$ 4d95s5f 2P1/2, 3/2 transitions. Next in size are resonances associated with 4d105s 2S1/2 $\rightarrow$ 4d95s6f 2P1/2, 3/2 and 4d105s 2S1/2 $\rightarrow$ 4d95s7f 2P1/2, 3/2 transitions. However, with increasing principal quantum number $n$, the resonance heights also decrease. This is even more pronounced in the sequence of 4d105s $\rightarrow$ 4d95snp transitions, where the experiment does not show much evidence for $n \geq 7$ contributions.

The huge resonance due to 4d95sf 2P1/2, 3/2 intermediate levels in the photoionization of ground-state Xe7+ ions reaches a peak cross section of approximately 1 Gb at a photon energy resolution of 65 meV. Because of its relative importance and overwhelming dominance in the spectrum it has been investigated in special detail. Figure 3 shows three separate measurements of this resonance at energy resolutions 28 meV, 39 meV and 65 meV. None of these measurements provides direct evidence for a significant fine structure splitting of the 4d95sf 2P1/2, 3/2 levels. The theoretical calculations indicate the splitting between the 4d95sf 2P1/2, 3/2 levels is $\sim$15 meV which we determined from Fano-Beutler fits to cross section calculations for the individual 1/2 and 3/2 odd scattering symmetries. Since the resonances sit on top of each other no visible splitting is seen in the total cross section. As the splitting is much smaller than the natural widths of the two components we therefore fitted the data only with one-resonance Voigt profiles. The solid line in the figure represents the result of a global fit of Gaussian-convoluted Fano profiles
Figure 3. Analysis of the dominating 4d^55f^2P^o resonance formed during photoionization of ground-state Xe^{7+} ions. The three panels of this figure show measurements of the energy dependence of the resonance cross section taken at different bandwidths of the photon beam, namely, 28 meV, 39 meV and 65 meV. The solid lines result from a global simultaneous fit of all three measurements; see text for details.

[43, 45] to all three measurements simultaneously using the natural width and the Fano asymmetry parameter \( q \) of the resonance as fit parameters. The result of this analysis is a Lorentzian width \( \Gamma = 76 \pm 3 \) meV of the huge resonance. The asymmetry of the profile is small. The fit results in an asymmetry parameter \( q = -78 \pm 15 \). The 4d^55f^2P^o resonance energy is \( 122.139 \pm 0.005 \) eV and the line strength is \( 161 \pm 31 \) Mb eV. According to equation 2 this corresponds to an absorption oscillator strength \( f = 1.47 \pm 0.28 \) which is more than 1/7 of the total absorption oscillator strength of all the ten electrons in the 4d subshell. The dominance of the resonance in the experimental spectrum is illustrated by its relative contribution of about 40% to the total resonance strength observed in the experiment. This is in respectable agreement with the 47% contribution of the dominant resonance to the theoretical (DARC) spectrum in the same energy range.

The photoionization cross section results of the experiment and of the Dirac Coulomb R-matrix calculations for the Xe^{7+}(4d^105s^2S_1/2) ground level as well as the metastable Xe^{7+}(4d^104f^2F^3_3/2) and Xe^{7+}(4d^104f^2F^5_3/2) levels are provided in figure 4. The top (panel (a)) shows the experimental energy-scan results from figure 2 again with light (green online) shading and individual data points connected by straight lines. Because of the overwhelming dominance of the resonance at 122.14 eV the much smaller other resonances are barely visible on this scale. In order to visualize these more clearly, we have scaled them up in size. Panel (a) shows the same cross section multiplied by a factor of 5 with the zero line shifted up by 300 Mb. The resulting function is represented by the solid line (red online). The middle panel (b) displays the theoretical results for the Xe^{7+} ground level.

In order to check the convergence of the theoretical approach 249-level, 508-level and 526-level DARC photoionization cross section calculations were performed for the Xe^{7+}(4d^105s^2S_1/2) ground state. Panel (b) of figure 4 therefore includes the theoretical cross section results from all three multi-state models. The theoretical cross sections were convoluted with a 65 meV FWHM Gaussian. Obviously, the 526-level, the 508-level and the 249-level approximations yield similar results. Unexpectedly, though, the 526-level calculations are slightly shifted in energy from the experiment. Thus, the 249-state model gives marginally better agreement with experiment. Although the experimental data were obtained with a mixture of ground-level and metastable ions and the theoretical results displayed in panel (b) are only for ground-level ions, one can see here already that the DARC calculations overestimate the contribution of the 4d^55sf^2 resonance features relative to the strong 4d^55fsf^2 peak.

The lowest (panel (c)) of figure 4 shows the results of 528-level DARC calculations for the metastable Xe^{7+}(4d^104f^2F^3_3/2) and Xe^{7+}(4d^104f^2F^5_3/2) levels. At least as far as the dominant resonance features are concerned the two spectra are very similar to one another. According to the calculations with the Cowan code and on the basis of the assignments given in figure 2 the lower-energy features are due to 4d^104f \( \rightarrow \) 4d^9f^2 excitations with possible contributions from states within the 4d^4f^2 configuration. Due to the presence of three open subshells in this configuration, all with high angular momenta, a high number of possible couplings and associated energy levels are to be expected. The numerous resulting resonances are spread out over a very broad energy range. Nevertheless a very distinct feature can again be associated with the 4d \( \rightarrow \) 5f excitation of metastable Xe^{7+} which theory finds at around 121 eV close to, where the huge resonance due to 4d^55sf^2P^o_{1/2} intermediate levels in the photoionization of ground-state Xe^{7+} ions is located. In comparison with the theoretical data for photoionization of metastable ions the experiment shows very small cross sections. This is particularly true for the region below the ground-state ionization threshold which is indicated by vertical bars in (panel (b)) of figure 4. In this discussion one has to keep in mind that the experimental cross section is determined under the \textit{a priori} assumption of only one primary-beam component. \textit{A posteriori}, the discussion shows that a small fraction \( a \) of metastable ions accompanied the large fraction \( 1 - a \) of ground-state ions in the parent ion beam. So, in fact the apparent experimental cross section is that for a mixture of ionic levels. The real cross section for metastable ions can in principle be obtained by normalizing the apparent cross section for signal arising from the metastable ions to the fraction \( a \). Thus, the present discussion addresses the size of that fraction \( a \).
The total oscillator strength found in the experiment in the energy range 95–105 eV is only 2.4% of what theory finds in that same range. A comparably small fraction of metastable ions in the parent ion beam must be concluded. For further comparison between theory and experiment fractions of 97.6% ground-level and 2.4% metastable Xe7+ ions in the parent ion beam are assumed. The metastable fraction is divided into 3/7 for the °F2 and 4/7 for the °F2 contributions assuming level population proportional to the statistical weights.

Figure 5 compares the present experimental cross sections with the initial-fractions weighted theoretical 249-level DARC results except for the overwhelmingly dominant resonance peak. As figure 4 already shows, the height of the dominating peak that results from excitation of the Xe7+ (4d8s5f P92) ground state to Xe7+ (4d8s5f P12,32) levels with a vacancy in the 4d sub-shell is overestimated by theory. Considering the ±19% total experimental uncertainty, the theoretical peak cross section is still about 28% above the maximum experimental limit. This is partly due to the fact that theory finds an additional resonance feature of unknown origin near the position of the °P2 term. The Lorentzian width of the dominant excited °P2 term deduced from the theoretical data is 88 meV which compares favorably with the experimental width of (76 ± 3) meV. The resonance strength predicted for the °P2 term, however, is 279 Mb eV, more than 70% above the experimental result. It is worth mentioning at this point that the theoretical multi-configuration Dirac–Fock (MCDF) result accompanying the previous study of photoionization by Bizau et al [16] is a little more than 10% below the present experimental result (see figure 6). The simple calculations carried out with the Cowan code for finding assignments of resonances underestimates the experimental finding by 80%. These examples clearly show the difficulty to predict the correct resonance parameters for this three-open-subshells resonance feature.

It should be noted that the cross section axis in figure 5 for the theoretical cross sections is different from that of the experimental data indicating differences in absolute height of
resonance features. Nevertheless, resonance groups seen in the experiment can be clearly recognized in the theoretical spectrum with reasonable agreement in relative peak heights. Theory and experiment agree in that they both show negligible contributions of direct photoionization of the outermost electron in Xe$^{7+}$. The cross section is dominated by inner-shell excitations with subsequent Auger or Coster–Kronig decays. Given the complexity of Ag-like Xe$^{7+}$ arising from opening the 4d sub-shell, the present study shows reasonable agreement of theory and experiment over the photon energy region investigated.

Figure 6 provides a comparison of the present experimental data with experimental and theoretical results of Bizau et al [16]. The inset focuses on the dominant Xe$^{7+}$ (4d$^4$5s5f $^2$P$_{1,2,3}$) resonance feature. For the comparison, the relative results of Bizau et al were normalized so as to match the peak area of the dominant $^3$P$^+$ resonance. Due to the larger width ($\approx 750$ meV instead of 65 meV) the normalized $^3$P$^+$-peak cross section is much smaller in height than the present absolute measurement. For a meaningful comparison of the MCDF theory result with the experimental data displayed in Figure 5.
figure 6 the theory curve displayed in [16] for the $2^3P^o$ resonance was digitized and the resonance parameters were determined. With the peak area (147 Mb eV) and the resonance energy (122.98 eV) thus obtained plus assuming a Lorentzian width of 76 meV as found in the present study, the MCDF resonance was convoluted with Gaussians of 65 meV and 750 meV FWHM, respectively, to be compared with the present and the previous experiments. While very good agreement is found in terms of peak height the experimental and theoretical resonance energies found in [16] differ from one another and from the present measurement. As mentioned above, calculating the correct resonance energies in an ion with three open subshells is difficult. The present 249-level R-matrix calculation finds the $3^+\text{Xe}^{7+}(4d^35s5f\, 2^3P^o)$ resonance at 123.89 eV, the MCDF result is 122.98 eV while the present experiment finds 122.139 eV. Also the experiment by Bizau et al with a resonance energy of 121.36 eV differs from the present result by 0.779 eV. While this difference is of the order of the experimental energy spread of the previous measurement, the absolute calibration could be substantially better than the resolution. However, in the letter format of their publication [16] Bizau et al did not provide an estimate for the uncertainty of their photon-energy axis. In contrast to that, the present experiment involved an extremely careful energy calibration with an estimated uncertainty of the $3^+\text{Xe}^{7+}(4d^35s5f\, 2^3P^o)$ resonance energy of only 5 meV.

5. Summary and conclusions

High-resolution absolute cross section measurements for single photoionization of Ag-like $\text{Xe}^{7+}$ ions forming $\text{Xe}^{8+}$ products were obtained at the ALS. Compared to a previous experiment, the cross sections are now on an absolute scale and the energy resolution and statistical precision have been vastly improved. The experimental results are compared with large-scale close-coupling calculations within the Dirac Coulomb R-matrix approximation. Calculations using different basis sets and incorporating a progressively larger number of levels (respectively 249, 508 and 526 levels) in the close-coupling calculations, show no significant improvement. This would indicate that convergence is already obtained with the 249-level calculation. However, differences still exist between theory and experiment with respect to level energies (resonance positions and resonance strengths). Nevertheless, the main features in the experimental spectrum are reproduced reasonably well by theory. While the $\text{Xe}^{7+}$ parent ion in this study is a quasi-one-electron system with a 5s or a 4f electron outside fully occupied electronic sub-shells, the intermediate excited states (which then decay by autoionization) comprise mainly three open sub-shells with relatively high angular momenta and the appropriate coupling of the active electrons renders this problem quite complex. Including many more target configurations and levels in the close-coupling calculations makes the theoretical treatment extremely challenging. Given the complexity of the system and the available finite computational resources, the comparison of the present experimental high-resolution photoionization cross sections with the large-scale close-coupling calculations in the present study shows overall agreement.

Acknowledgments

We acknowledge support by Deutsche Forschungsgemeinschaft under project number Mu 1068/10 as well as by the US Department of Energy (DOE) under contract DE-AC03–76SF-00098 and grant DE-FG02-03ER15424. C P Ballance was supported by US Department of Energy (DoE) grants through Auburn University. B M McLaughlin acknowledges support by the US National Science Foundation through a grant to ITAMP at the Harvard-Smithsonian Center for Astrophysics, a visiting research fellowship (VRF) from Queen’s University Belfast and the hospitality of AM, SS and the University of Giessen. The computational work was carried out at the National Energy Research Scientific Computing Center in Oakland, CA, USA, the Kraken XT5 facility at the National Institute for Computational Science (NICS) in Knoxville, TN, USA and at the High Performance Computing Center Stuttgart (HLRS) of the University of Stuttgart, Stuttgart, Germany. The Kraken XT5 facility is a resource of the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation grant number OCI-1053575. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the US Department of Energy under Contract No. DE-AC02-05CH11231.
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