Absolute Measurements and Theoretical Calculations of Photoionization Cross Sections along the Isonuclear Sequence of Multiply Charged Barium Ions

J.-M. Bizau, D. Cubaynes, J.-M. Esteva, and F. J. Wuilleumier
Laboratoire de Spectroscopie Atomique et Ionique, Unité Mixte du CNRS No. 8624, Université Paris-Sud, Bâtiment 350, 91405 Orsay, France

C. Blancard, J. Bruneau, J.-P. Champeaux, A. Compant La Fontaine, C. Couillaud, R. Marmoret, and C. Rémond
Commissariat à l'Energie Atomique, CEA-DAM/Ile-de-France, BP 12, 91680 Bruyères-le-Châtel, France

D. Hitz and M. Delaunay
CEA-Grenoble, Département de Recherches Fondamentales sur la Matière Condensée, 17 rue des Martyrs, 38054 Grenoble Cedex 9, France

N. Haque
Department of Physics, Morehouse College, Atlanta, Georgia 30314

P. C. Deshmukh,* H. L. Zhou, and S. T. Manson
Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia 30303
(Received 30 March 2001; published 12 December 2001)

Photoionization of multiply charged ions of the Ba isonuclear sequence up to Ba^{6+} has been studied in a beam-beam experiment. A very strong increase in the resonance structures was observed when moving from Ba^{2+} to Ba^{6+}. Absolute values of the photoionization cross sections were measured for Ba^{2+} and Ba^{3+} ions. The interpretation of the results is provided using theoretical multiconfiguration Dirac-Fock and relativistic random phase approximation calculations, showing that the collapse of the nf orbitals occurs for Ba^{4+}.

DOI: 10.1103/PhysRevLett.87.273002 PACS numbers: 32.80.Hd, 32.80.Fb

The response of positive ions to ionizing radiation is a dominant process in the universe. It is largely unexplored experimentally, however, due to the difficulty in producing and maintaining appropriate densities of multiply charged ions. Theory is the main source of information and remains untested in most of the cases. From a fundamental point of view, experimental information about photoionization of ions allows investigation of the dynamic interplay between many-body electron-electron correlation effects versus electron-nucleus interactions. Since significant changes in the behavior of photoionization processes may suddenly occur for particular ions, it is essential to have the capability of studying photoionization of ions along extended isonuclear as well as isoelectronic sequences. An important application of such experiments is in astrophysics since an accurate knowledge of photoionization cross sections for ions is a key point to interpret the stellar data. Recent measurements of such absolute cross sections [1–3] are an important step towards this goal.

In this Letter, we report the first combined theoretical and experimental investigation of photoionization of multiply charged ions along the Ba isonuclear sequence, up to Ba^{6+} ions, using an electron cyclotron resonance (ECR) ion source to produce highly charged ions of atomic vapors, and synchrotron radiation (SR) to study their photoionization. In comparison to our previous work on Xe ions [4], we have gone one step further in measuring, for the first time, absolute values of the photoionization cross sections, here for Ba^{2+} and Ba^{3+}. Multiconfiguration Dirac-Fock (MCDF) and relativistic random phase approximation (RRPA) calculations were performed to interpret the data. With these new results, we are able to answer long pending questions concerning the orbital collapse of the $nf/\varepsilon f$ wave functions for increasing charge states of Ba ions [5].

Photoionization of the inner $4d$ electrons in neutral Ba atoms has been long known to have a giant resonancelike structure in the continuum and very weak discrete resonance structure below the $4d$ ionization thresholds [6]. A large variety of theoretical methodologies have been used to explain the experimental data [7–11]. This behavior was finally understood in terms of the effective potential for f orbitals which has an inner well separated from an outer well by a potential barrier [5]. f orbitals are localized mainly in the outer well so that there is little overlap with the $4d$ orbitals, and the autoionization resonances arising from $4d \rightarrow nf$ discrete excitations are weak. As the photon energy increases, the εf orbitals eventually contract into the inner well, leading to a dramatic increase in the transition amplitudes of the $4d \rightarrow \varepsilon f$ channels.

Along the Ba-isonuclear sequence, the inner well becomes deeper and deeper, and the potential barrier gradually disappears. Previous photoabsorption experiments on Ba, Ba^{+}, and Ba^{2+} [12,13] found that the absorption of

Ba^+ is similar to that of Ba while the absorption spectrum of Ba^{2+} is completely different [12], revealing a significant increase of the $4d$-oscillator strength for discrete transitions. Among several theoretical approximations [14–20] proposed to interpret the Ba^{2+} spectrum multiconfiguration Hartree-Fock calculations [15,16,19] have yielded the best agreement with the experimental results. Recently, a dual laser plasma experiment [21] confirmed the results for Ba^{2+}. Some pending questions were, however, unanswered. Absolute values of the partial photoionization cross sections were not known. It was not determined whether the Ba^{2+} excited states are autoionizing only in the single- or also in the double-photoionization continua. More important, for which ionic stage is the f-orbital collapse complete?

We studied photoionization of Ba^{2+} to Ba^{6+} ions over the energy range of $4d$ photoexcitation/photoionization (90 to 160 eV photon energy). The experiments were performed on the SU6 beam line of the Super-ACO SR light source by merging a 4-keV-per-charge collimated ion beam with the monochromatized photon beam, so that the ions and photons interacted over a distance of 20 cm. The multiply charged ions were produced in a 10 GhZ ECR ion source. In comparison to our previous work [4], we introduced two major enhancements in the experimental setup. First of all, a resistively heated oven was inserted into the ECR source to allow us to produce significant intensities of multiply charged ions of metallic vapors. Up to 100 nA were available in the interaction region for any Ba^{q+} ions. Second, three sets of movable wires were installed within the interaction region to determine the overlap of both ion and photon beams, in order to perform absolute measurements of the cross sections. After the interaction region, the resulting photoionization yield of $Ba^{(q+1)+}$ and $Ba^{(q+2)+}$ ions, and the primary beam of Ba^{q+} ions were separated from the photon beam by an electrostatic charge analyzer and measured by a particle detector and a Faraday cup, respectively. A calibrated photodiode served to measure the absolute photon flux. The absolute photoionization cross sections were determined from the $Ba^{(q+1)+}$ and $Ba^{(q+2)+}$ detector yields and their detection efficiency, the photodiode current and its efficiency, the Ba^{q+} beam current and energy, the interaction length, and the overlap of the beam profiles. Spectral resolution was limited to 500 meV by the need of high enough flux of monochromatic photons interacting with the multiply charged ion beams.

To interpret the measured data, we used two different theoretical methodologies. A MCDF formalism [4] served to calculate the photoexcitation spectra of the Ba^{q+} ions. We described the initial states by the following configurations: $[4d^{10}]\ -5s^25p^6$ for Ba^{2+}, $-5s^25p^5$ for Ba^{3+}, $-5s^25p^4$ for Ba^{4+}, $5s^25p^3$ for Ba^{5+}, and $5s^25p^2$ for Ba^{6+}. We constructed the excited states from the $4d^95s^25p^mn'p$ ($n' = 5$ to 7) and $4d^95s^25p^mnf$ ($n = 4$ to 7) configurations, with $m = 6, 5, 4, 3$, and 2, respectively, and assumed statistical populations of the initial levels of each ionic stage, neglecting the configuration mixing [4]. To compare theory with experiment, we also assumed a Lorentzian profile for the shape of each excitation line, and fixed a constant full width at half maximum of 100 meV, close to the value for neutral barium. In addition, the results of our theoretical calculations were convolved with our Gaussian experimental function. In the case of Ba^{2+}, we used the RRPA [14] to calculate the cross sections for photoionization of $4d$, $5s$, and $5p$ electrons. $5s$ and $5p$ photoionization of Ba^{2+} leads mainly to Ba^{3+}, and $4d$ photoionization to Ba^{4+} because the $4d$-core ionized Ba^{3+} ions Auger decay almost entirely into the $4d^{10}5s^25p^4$ states of Ba^{4+}.

The measured and calculated cross sections for single and double photoionization of Ba^{2+} ions are shown in the upper and lower panels of Fig. 1, respectively. The experimental cross section scale was calibrated absolutely at two photon energies (116 and 125 eV). The single photoionization spectrum of Ba^{2+} shows several discrete structures of strong intensity, followed by a weak continuum extending to the high-photon energy side. It results mainly from autoionization of core-excited states of the Ba^{2+} ions populated by discrete excitation of a $4d$ electron to a nf or $n'p$ orbital ($n \geq 4$, $n' \geq 5$). The small continuum represents the contribution of $5s$ and $5p$ single photoionization. The Ba^{2+} double photoionization spectrum shows also resonant structures, in addition to an intense continuum extending from the $4d$-ionization threshold towards the high-photon energy side. It results mainly, below the $4d$-ionization thresholds, from autoionization of the Ba^{2+} excited states proceeding via two-electron emission, and, above the $4d$-ionization thresholds, from single Auger decay of the $4d$-ionized Ba^{3+} ions. Energies of the resonances agree well with previous experimental results [12].

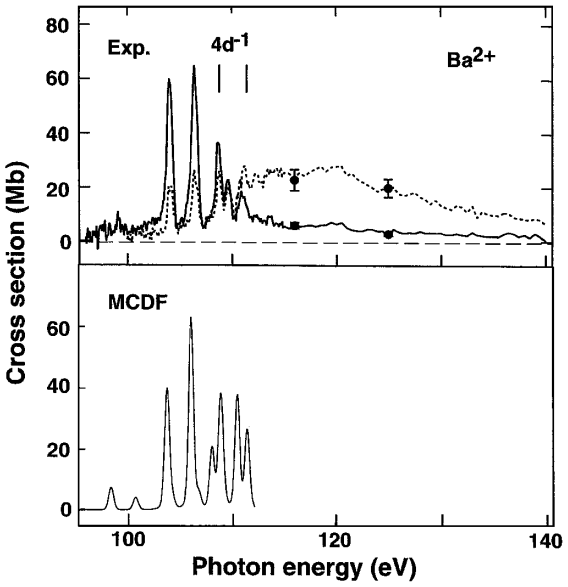

FIG. 1. Experimental (upper panel) and calculated (lower panel) photoionization spectra of Ba^{2+} ions. The full and dashed lines are the single and double photoionization spectra, respectively. The black dots are the results of our absolute measurements.

We note here that the excited states of Ba^{2+} ions do autoionize also with noticeable intensity into the Ba^{4+} continua, revealing for the first time that double Auger decay contributes significantly to the deexcitation of the Ba^{2+} resonantly excited states. In the lower panel of Fig. 1, we present the results of our MCDF calculations for single $4d$ photoexcitation of Ba^{2+}. The calculated spectrum is in rather good qualitative agreement with the experimental results, although significant differences exist in the absolute values of the cross sections. For example, the experimental cross section at the energy of the lowest-energy $4d \rightarrow 4f$ transition (80 Mb, including single and double photoionization) is twice as high as the calculated photoexcitation cross section.

In the experimental spectra, the double photoionization continuum (resulting mainly from single $4d$-photoionization followed by Auger decay) is higher than the single photoionization continuum ($5s$ and $5p$ cross sections) by a factor of 4 to 5. We show in Fig. 2 the results of our RRPA calculations (full lines) for the sum of the $5s$ and $5p$ photoionization (upper panel) and the $4d$ photoionization cross sections (lower panel) of Ba^{2+} ions, together with our experimental measurements. The measured $4d$ photoionization cross section is rather well reproduced by the theoretical calculations. Our results show that the major part of the oscillator strength is still in the continuum photoionization spectrum of Ba^{2+}, in agreement with theoretical predictions [21].

In comparison to Ba^{2+}, the measured and calculated photoionization spectra of Ba^{3+}, shown in the upper and lower panels of Fig. 3, respectively, look much simpler; at first sight, they are dominated by autoionization of the resonantly excited states. Double photoionization processes are significantly weaker. The spectra reveal that a larger part of the oscillator strength is now distributed into the discrete part of the spectrum, mainly in one dominant line due to autoionization of the $4d^9 5s^2 5p^5 4f(^1P)$ excited state. The results of our MCDF calculations for single photoexcitation are in qualitative agreement with the experimental data. The calculations predicting a strong increase of the cross section at the energy of the first transition ($4d \rightarrow 4f$) are validated by experiment, but the measured value (750 Mb) is again more than twice higher than the theoretical result (300 Mb). The weaker resonant lines result from autoionization of the $4d^9 5s^2 5p^5 nf$ or $n'p$ excited states of Ba^{3+} ($n \geq 5$, $n' \geq 6$). The calculated and measured spectra, however, do not reveal the classical intensity behavior expected from terms of Rydberg series. Theory spreads the total oscillator strength over more discrete transitions than observed in the experiment, which can explain the large difference between the calculated and experimental cross sections. In fact, calculations show a strong mixing of configurations in the Ba^{3+} excited states, invalidating any simple identification of the resonant lines. The value of the $4d$ cross section (17.6 ± 2.1 Mb), measured at 124 eV from the double ionization signal, is not much lower (by about 25% only), however, than the

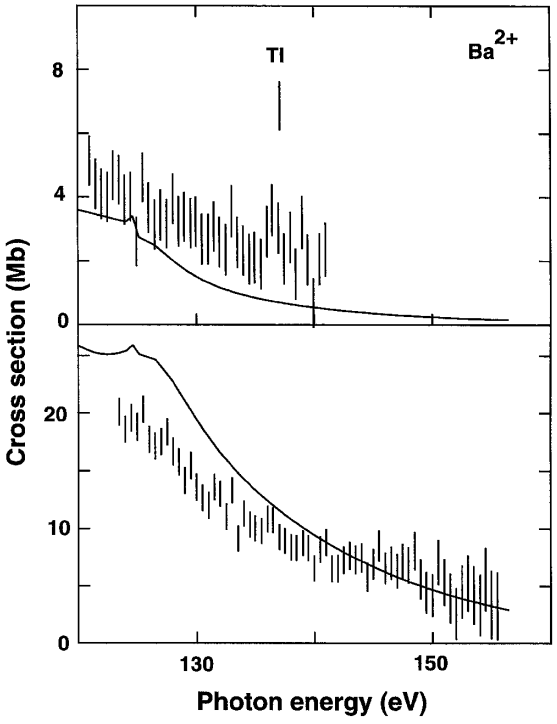

FIG. 2. Variation of the partial cross sections for photoionization of Ba^{2+} ions in the $5s + 5p$ (upper panel) and $4d$ (lower panel) subshells, respectively. Our RRPA theoretical results are shown as the full lines, the measurements are the data points with error bars. TI = triple ionization threshold.

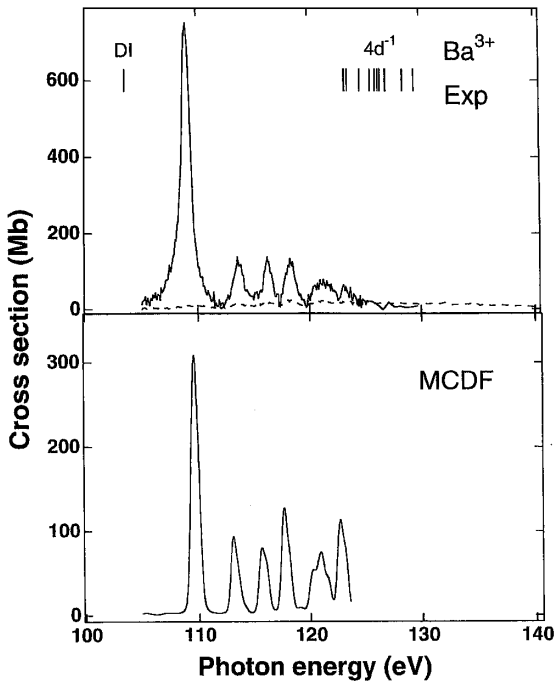

FIG. 3. Experimental (upper panel) and calculated (lower panel) photoionization spectra of Ba^{3+} ions. The full and dashed lines are the single and double photoionization spectra, respectively. DI = double ionization threshold. The black dots at 125 eV are the results of our absolute measurements.

threshold value of the $4d$ cross section determined for Ba^{2+} (22.8 ± 2.9 Mb at 116 eV), confirming our theoretical results showing that the overlap of the εf wave function with the $4d$ wave function does not vary strongly when moving from Ba^{2+} to Ba^{3+}. In spite of the strong increase in the intensity of the first $4d \rightarrow 4f$ discrete transition for Ba^{3+}, a significant part of the total $4d$-oscillator strength is still in the continuum, revealing that the collapse of the nf wave functions is not yet complete for Ba^{3+}. It occurs only for Ba^{4+}, as indicated by our results for Ba^{4+} and Ba^{5+} ions shown in Fig. 4. The two upper (experiment and theory) and the two lower panels show the single photoionization spectra of Ba^{4+} and Ba^{5+}, respectively. For Ba^{4+} and Ba^{5+}, the continuum transitions have virtually vanished and the total oscillator strength is almost fully concentrated into the first excitation line $4d^{10} \rightarrow 4d^9 4f\ ^1P$. Experiment and theory are again in good qualitative agreement. We note the extremely high value of the calculated cross section (about 6000 and 12 000 Mb for Ba^{4+} and Ba^{5+}, respectively) at the maximum of this line for both ions. The measured photoionization spectrum of Ba^{6+} (not shown here) confirms these trends. Comparing the change in the photoionization spectra when moving from Ba^{2+} to Ba^{6+} ions establishes clearly that the collapse of the nf orbitals is fully achieved only for Ba^{4+} with an increasing predominance of the first autoionization line ($4d^{10} \rightarrow 4d^9 4f\ ^1P$) with increasing charge state of the multiply charged ions along the isonuclear series.

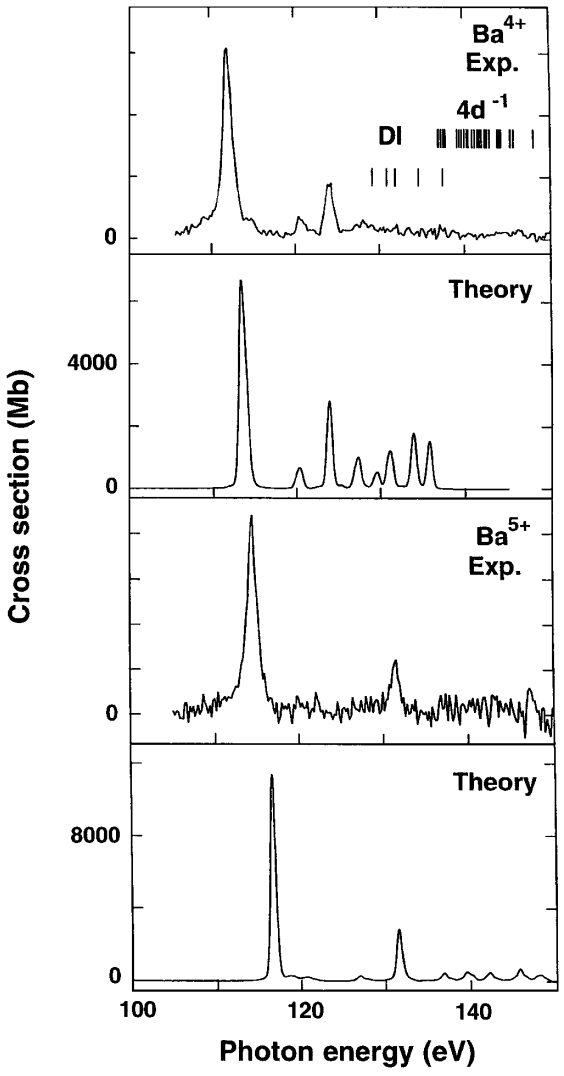

FIG. 4. Single photoionization spectra for Ba^{4+} (two upper panels) and Ba^{5+} (two lower panels) ions. For each ion are shown, from top to bottom, the experimental results and the MCDF theoretical results, respectively.

To summarize, we have achieved the first extensive study of photoionization processes along an isonuclear series of multiply charged ions in an atomic vapor, including the evolution of the single-to-double photoionization ratio with absolute measurements of the cross sections, thus opening a wide range of new possibilities. Our results for the Ba^{q+} ions demonstrate the physics that can be elucidated by being able to vary the ionic stage of the multiply charged ions step by step. Together with our MCDF and RRPA theoretical calculations, our measurements bring definite answers to the remaining questions concerning the collapse of the f orbitals along the Ba^{q+} ionic series. To provide these answers, it was crucial for the measurements to extend over both the autoionizing region and the open continuum.

*Present address: Department of Physics, Indian Institute of Technology-Madras, Chennai 600036, India.

[1] H. Kjeldsen *et al.,* Astrophys. J. **524**, L143 (1999).
[2] H. Kjeldsen *et al.,* J. Phys. B **32**, 4457 (1999).
[3] H. Kjeldsen *et al.,* Phys. Rev. A **62**, 020702(R) (2000).
[4] J.-M. Bizau *et al.,* Phys. Rev. Lett. **84**, 435 (2000).
[5] *Giant Resonances in Atoms, Molecules and Solids,* edited by J.-P. Connerade, J.-M. Esteva, and R. C. Karnatak (Plenum Press, New York, 1987).
[6] R. Haensel, G. Keitel, P. Schreiber, and C. Kunz, Phys. Rev. **188**, 1375 (1969).
[7] G. Wendin, Phys. Lett. **46A**, 119 (1973); J. Phys. B **9**, L297 (1976).
[8] M. Ya Amusia and S. I. Sheftel, Phys. Lett. **55A**, 469 (1976).
[9] G. Wendin and A. F. Starace, J. Phys. B **11**, 4119 (1978).
[10] J.-P. Connerade, J. Phys. B **11**, L381 (1978).
[11] A. Zangwill and P. Soven, Phys. Rev. A **21**, 1561 (1980).
[12] T. B. Lucatorto, T. J. McIlrath, J. Sugar, and S. M. Younger, Phys. Rev. Lett. **47**, 1124 (1981).
[13] T. Koizumi *et al.,* J. Phys. B **28**, 609 (1995).
[14] K. Nuroh, M. J. Stott, and E. Zarembahn, Phys. Rev. Lett. **49**, 862 (1982).
[15] K. T. Cheng and W. R. Johnson, Phys. Rev. A **28**, 2820 (1983).
[16] K. T. Cheng and C. Froese-Fischer, Phys. Rev. A **28**, 2811 (1983).
[17] J.-P. Connerade and M. W. D. Mansfield, Phys. Rev. Lett. **48**, 131 (1982).
[18] J. P. Connerade, J. Phys. B **16**, L257 (1983).
[19] C. Clark, J. Opt. Soc. Am. B **1**, 626 (1984).
[20] C. Clark and T. B. Lucatorto, in Ref. [5], p. 137.
[21] U. Köble *et al.,* Phys. Rev. Lett. **74**, 2188 (1995).