Inner-Shell Photoionization in an Excited Atom: Many-Electron Effects and Partial Cross Sections in $2p^6 3p\ ^2P_{3/2}$ Sodium Atoms

D. Cubaynes, J. M. Bizau, and F. J. Wuilleumier
Laboratoire de Spectroscopie Atomique et Ionique, Université Paris-Sud, Bâtiment 350, 91405 Orsay CEDEX, France
and Laboratoire pour l'Utilisation du Rayonnement Electromagnétique, Université Paris-Sud, Bâtiment 209d, 91405 Orsay CEDEX, France

B. Carré and F. Gounand
Service de Physique des Atomes et des Surfaces, Centre d'Etudes Nucléaires de Saclay, 91191 Gif-sur-Yvette, France
(Received 31 July 1989)

Using synchrotron radiation, we have investigated, over an extended photon energy range, the full photoelectron spectrum following ionization in the $2p$ subshell of Na atoms laser excited into the $2p^6 3p\ ^2P_{3/2}$ state. We have determined the relative cross sections for leaving the positive ions in various final states, corresponding to the main line and to the satellite lines. In particular, we have observed a strong enhancement of the relative intensity of the shakeup satellites in the excited atom. Our measurements allow testing of the validity of a many-body calculation of the $2p$-photoionization cross section.

PACS numbers: 32.80.Fb, 32.80.Hd

We present in this Letter the results of a complete investigation of photoionization processes in an excited atom by electron spectrometry. We have measured an inner-shell photoionization cross section in the case of the $2p$ subshell of the $2p^6 3p\ ^2P_{3/2}$ excited sodium with a high enough accuracy to be able to test the theoretical prediction of a many-body calculation over an extended photon energy range. We have also observed, for the first time, a strong enhancement of correlation effects in an excited atom, namely an increased by a factor of 2 in the relative intensity of the $2p$-shakeup satellites as compared to the behavior of similar satellites in photoionization of sodium atoms in the ground state.

Advances in photoionization studies of excited atoms open new avenues for predicting the behavior of these systems in such media as plasmas of astrophysical interest or laser-produced plasmas. The first successful experiments[1-3] combining the use of laser beam and synchrotron radiation (SR) to study photoionization processes in an excited atom were achieved in 1981. Later on, owing to the large cross section of the resonant processes as compared to direct photoionization into the continuum, oscillator strengths for $2p^6 3p \rightarrow 2p^5 3s 3p$ resonant transitions in $2p^6 3p$ excited sodium atoms were measured.[4,5] More recently, it was possible to prepare large enough populations of sodium atoms in more highly excited states, using two lasers in cascade, to observe their resonant photoionization with SR.[6,7] In the mean time, photoionization processes in other laser-excited atoms, namely Ba, Li, and Ca, have also been investigated.[8-12]

Several theoretical predictions have been made about the behavior of photoionization cross sections in some classes of excited atoms,[13-16] but none have yet been checked experimentally because of the many difficulties in performing accurate measurements in a laser-synchrotron experiment. More specifically, the result of a many-body calculation[16,17] on the photoionization of the $2p$ subshell of the sodium atom with its valence electron either in its ground state or at different stages of excitation was that the photoionization cross section of a $2p$ electron at a fixed photon energy, i.e., its absolute magnitude and its photon energy dependence, was practically independent of the atomic orbit that the valence electron occupies.

Our first experiments combining the use of laser and ACO synchrotron radiation[1-3] did not allow us to check systematically the validity of this prediction over a wide photon energy range with a high accuracy. This aim required the availability of higher SR photon flux with a better resolution. These improved experimental conditions were made available to us when the new storage ring SuperACO was put into operation. For the experiments presented here, we transferred to a bending-magnet beam line of SuperACO the same experimental setup as previously used with ACO.[3] The increase in the photon flux, as compared to ACO, was about a factor of 3 (with 300-μm monochromator slits) in the 50–130-eV photon energy range. A nearly constant value of the monochromator bandwidth (0.30 to 0.35 eV) was maintained from 50 eV (with 300-μm slits) to 110 eV (with 200-μm slits). In these conditions, we have been able to obtain the full photoelectron spectrum from the $3p$ sodium atom.

We show, in Fig. 1, a typical set of photoelectron spectra from the cylindrical-mirror analyzer (CMA), taken at 75.6-eV photon energy. They have been corrected for the transmission of the CMA. The upper panel shows

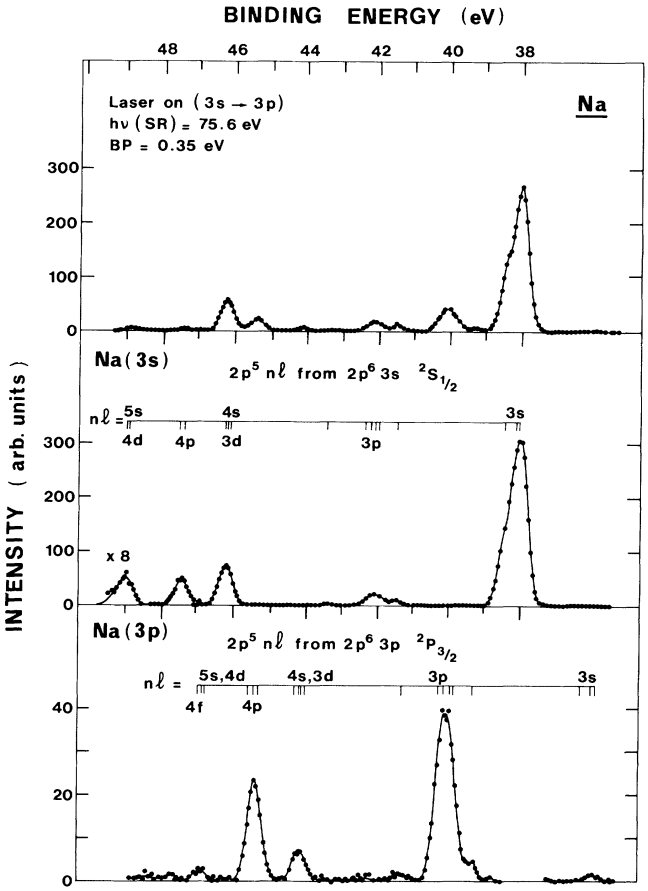

FIG. 1. Top: A photoelectron spectrum of sodium taken at $h\nu$=75.6 eV with the laser turned on. The lines at 38- and 40-eV binding energy are due to single photoionization of $2p$ electrons in sodium atoms in the ground state and in the $3p$ excited state, respectively. The other lines, at higher binding energies, are satellite lines. Middle: A spectrum taken at $h\nu$ =75.6 eV in the same experimental conditions, but with the laser turned off. The whole spectrum is due to photoionization of ground-state sodium atoms; the positions of the shakeup ($2p^5 4s$ and $2p^5 5s$ final ionic states) and of the conjugate shakeup ($2p^5 3p$ and $2p^5 4p$) satellites are shown by vertical marks on top of the spectrum. Bottom: The photoelectron spectrum following $2p$ photoionization in the $3p$ excited state; it has been obtained from subtraction of the two previous spectra, after proper corrections and normalizations. The arbitrary unit of the ordinate axis is identical for the three spectra.

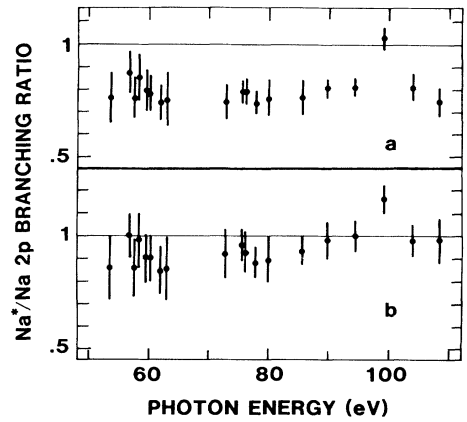

FIG. 2. (a) Variation, as a function of photon energy, of the ratio between single $2p$ photoionization in the $3p$ excited state (main line at 40.1-eV binding energy in the bottom spectrum of Fig. 1, $2p^5 3p$ final ionic states) and in the ground state (main line at 38.0-eV binding energy in the middle spectrum of Fig. 1, $2p^5 3s$ final ionic states) of atomic sodium, respectively. (b) Variation of the experimental ratio between the $2p$-photoionization cross sections (main line plus satellites) in the $3p$ excited and in the $3s$ ground states of atomic sodium, respectively.

the spectrum with the laser on. The sodium beam is then a mixture of sodium atoms in the $2p^6 3s\ ^2S_{1/2}$ ground state (GS) and in the $2p^6 3p\ ^2P_{3/2}$ excited states (ES), since at most 30% of the atoms in the ground state can be transferred into the $3p$ state. We observe photoelectron lines arising from photoionization in the $2p$ subshell of sodium in both atomic states. The main lines, corresponding to single ionization of the $2p$ electrons without additional transfer of energy to other electrons, appear at 38.0-eV ($2p^5 3s\ ^2P$ final states) and at 40.1-eV ($2p^5 3p$ final states) binding energy (BE) in the GS and in the ES, respectively. The closeness of these two lines makes clear why it was necessary to have as low a bandwidth of the monochromator as possible. Photoionization cross sections are evaluated from the integrated area under the photoelectron peaks; thus, it was necessary to have an accurate measurement of the true background between these two lines, because the determination of the background level is the main source of error in the values of the integrated area under low-intensity peaks. At higher binding energy, one can see several low-intensity lines, the so-called satellite lines corresponding to transitions in which the residual ion is left in higher excited states.

The photoelectron spectrum of the GS, taken in the same experimental conditions but with the laser off, is shown in the middle panel of Fig. 1. Lower-resolution examples of this spectrum have already been obtained,[18] but the high flux of photons available here makes it possible to observe some previously undetected satellite lines.

The lower panel of Fig. 1 shows the full photoelectron spectrum following photoionization in the $2p$ shell of $3p$-excited sodium atoms. It has been obtained by subtraction of the upper and middle spectra. This subtraction required some adjustments to account for the variation of the photon flux and for the shift of the apparent energy scale of the CMA arising from the plasma potential which develops in the beam via collisional ionization between excited atoms. In addition, the normalization factor was obtained from a comparison of the integrated area of the photoelectron line at 38-eV BE in both spectra. This factor gives the density of Na atoms brought to

the excited state, here about 17%. In the spectrum from the excited state, the so-called shakeup satellite lines, corresponding to the $2p^5 4p$ ($\Delta l = 0$ for the shaken electron) electronic configuration, appear around 45-eV BE; the conjugate shakeup satellites ($\Delta l = \pm 1$) have the $(2p^5)4s$ or $3d$ and $(2p^5)5s$ or $4d$ configurations and are visible around 44- and 47-eV BE, respectively. A detailed analysis of these photoelectron satellites will be given elsewhere.[19]

We turn now to the variation of the various $2p$-photoionization cross sections as a function of photon energy. Figure 2(a) shows the energy dependence, between 50- and 110-eV photon energy, of the ratio between the intensity of the $2p$ main lines in the ES and in the GS, respectively. No data are shown between 62- and 72-eV photon energy, because, in this energy range, resonant phenomena can occur below the $2s$-ionization threshold and strongly modify the relative intensity of the various photoelectron lines via selective autoionization. The same type of phenomenon can explain the small enhancement in the ratio, around 100-eV photon energy, near the $2p^4 3s$ double-ionization threshold. Otherwise, the ratio stays far below the 100% line and does not show, apparently, any photon energy dependence. The average value of this ratio is 0.78 ± 0.05, which demonstrates clearly that the single-$2p$-photoionization cross section in the ES is about 20% lower than in the GS. However, before drawing any definitive conclusion on the overall validity of the theoretical calculations, we should consider the other contributions to the total $2p$-photoionization cross section, namely the cross sections for simultaneous excitation and ionization corresponding to the various satellite lines. The theory does not explicitly calculate their individual contributions. Consequently, one must add them in the experimental ratio for a complete comparison with theory.

The relative intensity of the conjugate shakeup satellites, with respect to the main line, is about the same in the GS and in the ES. It decreases slowly with increasing photon energy, varying from about 14% at 50 eV to 7% at 110 eV; thus, their contribution to the total $2p$ cross sections is about the same. This is not at all the case for the relative intensity of the shakeup satellites whose variation with photon energy is shown in Fig. 3 for the GS (squares) and for the ES (circles). The results for the GS are in good agreement with theoretical calculations.[20] Both results show the same energy behavior, i.e., a rather constant value. However, at all energies, the relative intensity of the shakeup satellites is strongly enhanced in the ES by about a factor of 2 (about 40%, against about 20%, at high photon energy). This can be understood when one considers that the $3p$ electron is more decoupled from the $2p$ core than the $3s$ electron, as already suggested by the higher binding energy of the $2p$ electrons in the ES, 40.1 eV against 38.0 eV in the GS. Since the $3p$ electron stays farther from the $2p$ core, their mutual screening is lowered. Thus the sudden relaxation of the core hole is more fully felt by the $3p$ electron; in addition, the overlap of its wave function with the wave function of the $4p$ orbital may be larger.

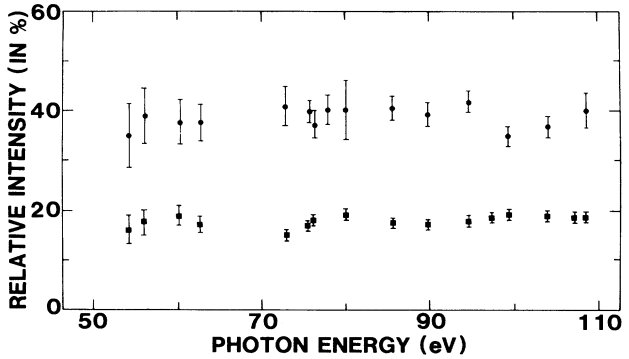

FIG. 3. Variation, as a function of photon energy, of the relative intensity of shakeup satellites for sodium atoms in the ground state (■, $2p^5 4s$ final ionic states) and in the $3p$ excited state (●, $2p^5 4p$ final ionic states), respectively.

When one adds in the ratio between the $2p$ main lines the contribution from the satellite states at each photon energy, one obtains the values shown in Fig. 2(b). They again do not suggest any photon energy dependence, but they are now much closer to 100%. The mean value of the data points, excluding the value at 100 eV, is 0.92 ± 0.07, which would bring the experiment and the theory in close agreement. However, it should be pointed out that one contribution is still missing in the $2p$-cross-section ratio of Fig. 3: the probability of double ionization, via the so-called shakeoff effect. This process would correspond to a simultaneous ionization of two electrons, namely one from the $2p$ subshell, the other one from the $3s$ (in the GS) or from the $3p$ (in the ES) subshell in the case of sodium. This process has never been directly studied for alkali-metal atoms, either theoretically, or experimentally. Adding into the $2p$-cross-section ratio the shakeoff contributions would continue to increase this ratio. But the present agreement between theory and experiment will remain over a large range of shakeoff probability, even though this probability would be as strongly enhanced in the ES as is the shakeup contribution.

To conclude, we have observed a strong enhancement of the correlation effects in the $2p$ inner-shell polarization of $3p$-excited sodium atoms, the relative intensity of correlation satellites reaching 50% of the main line. We have also checked the validity of a many-body calculation of the $2p$-photoionization cross section and shown that there is a satisfactory agreement between experiment and theory. However, it would be quite interesting to see whether the theory accounts also for the significant transfer of the oscillator strength from the main line to the shakeup satellites as observed experimentally in the excited state. Finally, our results demonstrate the need for measurement and calculation of double photo-

ionization for alkali-metal atoms, in the ground state as well as in the excited state.

The authors would like to thank M. Richter, B. Olson, T. Menzel, and P. d'Oliveira for their help in taking part of the data present here.

[1]J. M. Bizau, J. L. LeGouët, D. Ederer, P. Koch, F. J. Wuilleumier, J. L. Picqué, and P. Dhez, in *Proceedings of the Twelfth International Conference on Physics of Electronic and Atomic Collisions, Gatlinburg, 1981,* edited by S. Datz (XII ICDEAC, Gatlinburg, TN, 1981), post deadline papers, p. 1.

[2]J. M. Bizau, F. J. Wuilleumier, P. Dhez, D. L. Ederer, J. L. LeGouët, J. L. Picqué, and P. Koch, in *Laser Techniques for Extreme Ultraviolet Spectroscopy,* edited by T. J. McIlrath and R. R. Freeman, AIP Conference Proceedings No. 90 (American Institute of Physics, New York, 1982), p. 331.

[3]F. J. Wuilleumier, J. Phys. (Paris), Colloq. **43**, C2-347 (1982).

[4]F. J. Wuilleumier, in *Laser Techniques in the Extreme Ultraviolet,* edited by S. E. Harris and T. B. Lucatorto, AIP Conference Proceedings No. 119 (American Institute of Physics, New York, 1984).

[5]J. M. Bizau, F. J. Wuilleumier, D. L. Ederer, J. C. Keller, J. L. LeGouët, J. L. Picqué, B. Carré, and P. Koch, Phys. Rev. Lett. **55**, 1281 (1985).

[6]M. Ferray, F. Gounand, P. d'Oliveira, P. R. Fournier, D. Cubaynes, J. M. Bizau, T. J. Morgan, and F. J. Wuilleumier, Phys. Rev. Lett. **59**, 2040 (1987).

[7]D. Cubaynes, J. M. Bizau, T. J. Morgan, F. J. Wuilleumier, M. Ferray, F. Gounand, P. d'Oliveira, and P. R. Fournier, J. Phys. (Paris), Colloq. **48**, C9-453 (1987).

[8]J. M. Bizau, B. Carré, P. Dhez, D. Ederer, P. Gerard, J. C. Keller, P. Koch, J. L. LeGouët, J. L. Picqué, G Wendin, and F. J. Wuilleumier, in *Proceedings of the Thirteenth International Conference on the Physics of Electronic and Atomic Collisions, Berlin, 1983,* edited by J. Eichler, W. Fritsch, I. V. Hertel, N. Stolterfoht, and U. Wille (North-Holland, Amsterdam, 1983), p. 27.

[9]A. Numemann, T. Prescher, M. Richter, M. Schmidt, B. Sonntag, and P. Zimmermann, J. Phys. B **18**, L337 (1985).

[10]J. M. Bizau, D. Cubaynes, P. Gérard, F. J. Wuilleumier, J. L. Picqué, D. L. Ederer, B. Carré, and G. Wendin, Phys. Rev. Lett. **57**, 306 (1986).

[11]M. Meyer, B. Müller, A. Nunnemann, T. Prescher, E. V. Raven, M. Richter, M. Schmidt, B. Sonntag, and P. Zimmermann, Phys. Rev. Lett. **59**, 2963 (1987).

[12]M. Meyer, T. Prescher, E. V. Raven, M. Richter, B. Sonntag, B. R. Müller, W. Fiedler, and P. Zimmermann, J. Phys. (Paris), Colloq. **48**, C9-547 (1987).

[13]A. Msezane and S. T. Manson, Phys. Rev. Lett. **35**, 364 (1975).

[14]A. Msezane and S. T. Manson, Phys. Rev. Lett. **48**, 473 (1982).

[15]J. Lahiri and S. T. Manson, Phys. Rev. Lett. **48**, 614 (1982).

[16]T. N. Chang and Y. S. Kim, J. Phys. B **15**, L835 (1982).

[17]T. N. Chang and Y. S. Kim, in *X-Ray and Atomic Inner-Shell Physics—1982,* edited by B. Crasemann, AIP Conference Proceedings No. 94 (American Institute of Physics, New York, 1982), p. 633.

[18]S. Krummacher, V. Schmidt, J. M. Bizau, D. L. Ederer, P. Dhez, and F. J. Wuilleumier, J. Phys. B **15**, 4363 (1982).

[19]D. Dubayanes *et al.* (unpublished).

[20]I. P. Craig and F. P. Larkins, J. Phys. B **18**, 3713 (1985).