High Resolution Polarization Analysis of the Fluorescence from $Ar^+[^3P]4p\,^2P^o_{3/2}$ Formed in Photoionization

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(Received 27 June 1997)

Using high resolution intensity and polarization measurements of radiation from the $[^3P]4p\,^2P^o_{3/2}$ excited state of Ar^+ formed by linearly polarized synchrotron radiation, one can trace how the one unit of angular momentum brought by the ionizing photon is shared between the bound state electrons and the photoelectron. A measured sharp change in polarization from 25% to -25% over a 7–8 meV energy interval of the ionizing radiation results from variations in the partial cross sections of the $|m_j| = 1/2$ and $3/2$ magnetic substates and is the signature of a rapid oscillation of the excited ionic charge cloud from prolate to oblate spheroid. [S0031-9007(97)04900-4]

PACS numbers: 32.80.Fb

In the photoionization of Ar, one often finds that Ar^+ is left in an excited state with varying values of total angular momentum, for example, from $J = 1/2$ to as high as $J = 9/2$, although the initial photon interacts with a single electron while giving up one unit of angular momentum [1]. This implies that the emitted photoelectron may also carry components of angular momenta larger than the one unit that was transmitted to the system. The description of the redistribution and sharing of this one unit of angular momentum between the bound atomic electrons and the continuum photoelectron depends very much on the dynamic electron-electron interactions during the photoionization process. One can gain insight into this angular momentum sharing from the knowledge of the total alignment A_0^c of the residual excited ionic state, which is a measure of the distribution of the total angular momentum-magnetic substate population of the excited satellite state. The alignment can be determined from a measurement of the polarization of the fluorescent radiation from the Ar^+ satellite states. Since we experimentally find that the formation of excited Ar^+ is dominated by the process in which doubly excited Rydberg states of Ar are formed, it is imperative that the intensity and polarization measurements, as a function of ionizing energy, be carried out at the highest possible resolution. This high resolution allows one to determine the energy and characterize the angular momentum quantum numbers of the Rydberg states. This initial characterization of the Rydberg states, in turn, allows one to determine the subsequent angular momentum sharing in the autoionization process in the formation of the excited Ar^+ and a free electron. Thus, by combining the characteristics of high resolution light sources with the added information that the polarization of the fluorescent radiation brings, one can obtain dynamical information about the energy and angular momentum sharing that cannot be obtained in any other way.

In previous studies by Kronast, Huster, and Melhorn [2], and by Goodman, Caldwell, and White [3], polarization measurements with the subsequent determination of the alignment, as a function of ionizing photon energy, of $^2D_{5/2}$ and $^2D_{3/2}$ satellite states of Cd^+ were shown to exhibit structure attributed to the coupling of discrete autoionizing states of Cd to the observed open channels $Cd^+(^2D_{5/2,3/2}) + e^-$. Samson *et al.* [4] observed variations in the fluorescence of satellite states of Ar^+ and attributed these to coupling of the open channels to discrete autoionizing states. However, no polarization measurement was performed and due to limited resolution of approximately 20 meV many features of the spectrum were unresolved. R. I. Hall *et al.* published the threshold photoelectron spectrum of Ar with an energy resolution of 50 meV for the ionizing photons over an energy range of 20–50 eV [5].

In this Letter, we present high resolution magnetic sublevel cross sections obtained from measurements of the polarization of the 476.5 nm fluorescent radiation from the fine-structure resolved $[^3P]4p\,^2P^o_{3/2}$ satellite state formed by linearly polarized ionizing photons of 35.6–36.25 eV energy. The reaction can be represented as

$$h\nu_0 + \mathrm{Ar} \rightarrow (\mathrm{Ar})^{**} \rightarrow \mathrm{Ar}^+(3p^4[^3P]4p\,^2P^o_{3/2}) + e^- \rightarrow \mathrm{Ar}^+(3p^4[^3P]4s\,^2P^o_{1/2}) + 476.5\ \mathrm{nm}.$$

A narrow band interference filter ($\Delta\lambda = 0.3$ nm) is used to isolate the 476.5 nm fluorescent radiation. The polarization $P(90)$ is determined by measuring the intensities of the fluorescent light polarized parallel ($I_\parallel$) and perpendicular ($I_\perp$) to the polarization axis of the incident synchrotron radiation with the axis of the optical system placed in a direction of 90° with respect to the polarization axis of the incident light. From these measurements we determined the intensity $I(90) = I_\parallel + I_\perp$ and the polarization $P(90) = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$ of the satellite line. The total intensity of the $^2P^o_{3/2}$ satellite line emitted to 4π solid angle is obtained from the intensity $I(90)$ and the polarization $P(90)$.

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The total alignment coefficient is related to the measured polarization $P(90)$ by [6,7]:

$$A_0^c = \frac{\langle 3J_z^2 - J^2\rangle}{J(J+1)} = \frac{\sum_{m_j}\sigma(j,m_j)[3m_j^2 - j(j+1)]}{j(j+1)\sum_{m_j}\sigma(j,m_j)} = \frac{4P(90)}{h^{(2)}[3 - P(90)]},$$

where $h^{(2)}$ is a constant depending on the total angular momenta of the initial and final fluorescent states. From the definition of the total alignment coefficient, for $j = 3/2$ states one readily finds that the magnetic substate cross sections $\sigma(|m_j| = 3/2)$ and $\sigma(|m_j| = 1/2)$, defined as the sum of the two $\pm m_j$ substate cross sections, are given by

$$\sigma(|m_j| = 3/2) \propto \frac{4 + 5A_0^c}{8} I_{\text{tot}} = \frac{2\pi}{3}[3 - 5P(90)]I(90),$$

$$\sigma(|m_j| = 1/2) \propto \frac{4 - 5A_0^c}{8} I_{\text{tot}} = \frac{2\pi}{3}[3 + 3P(90)]I(90).$$

Details of our experimental apparatus will be described in a future article, but briefly, photons from the 10-cm-period U-10 undulator of 9.0.1 beam line of the Advanced Light Source (ALS) in Lawrence-Berkeley Laboratory are monochromatized by a 385 lines/mm spherical diffraction grating monochromator at a resolution $E/\Delta E$ of 12 700 and collide with the target gas Ar from a needle jet. The monochromator is calibrated using $3s3p^6np\ ^1P_1^o$ series of window-type resonances [8] of Ar from $n = 6$ to $n = 20$, and the well-known threshold onsets [9,10] of the emission of radiation at 465.8, 476.5, 472.7, 488.0, 459.0, and 461.0 nm which are characteristic emission lines of satellite states of Ar^+. From this regression, the accuracy of the ionizing photon's energy is ± 2 meV.

Figure 1 shows the measured polarization of the fluorescent 476.5 nm radiation from the $[^3P]4p\ ^2P_{3/2}^o$ satellite state. Superimposed on these results are the locations of doubly excited Ar Rydberg states whose structure consists of an excited Ar^+ core and a nl Rydberg electron, hence the designations $[^1D]3d\ ^2F_{7/2}nf$, $[^1D]3d\ ^2F_{5/2}nf$, $[^1D]3d\ ^2F_{5/2}np$, and $[^1S]4s\ ^2S_{1/2}np$. The designation $[^1L]$ refers to the total orbital angular momentum of the $3p^4$ core electrons in LS coupling. One should note here that $[^1D]3d\ ^2F_{5/2}np$ series do not form $^1P_1^o$ levels. However, it is known from previous studies [8] that $[^1D]3d\ ^2F_{5/2}np$ series are populated. The identification of the energies of the Rydberg series shown in Figs. 1 and 2 is obtained by using the known ionization limits [10] and previously accepted quantum defects [8].

In Figure 2 we present the magnetic sublevel cross sections calculated from our polarization measurements. The open circles represent the $|m_j| = 1/2$ cross sections and the filled circles $|m_j| = 3/2$ cross sections. In both figures a step size of 1 meV and an energy resolution of 3 meV are used. The full measured spectra and the details of the spectroscopic assignments of the Rydberg states

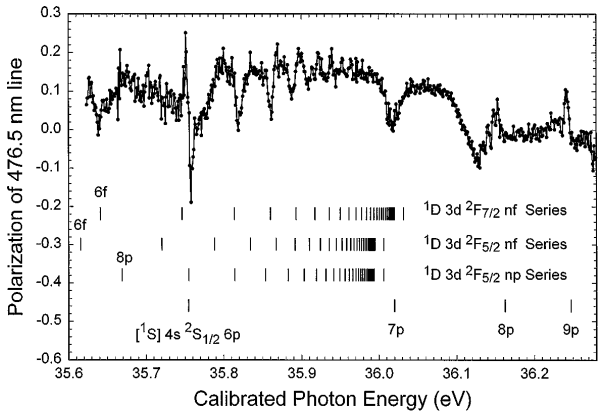

FIG. 1. Measured polarization of the 476.5 nm radiation from the $[^3P]4p\ ^2P_{3/2}^o$ satellite state of Ar^+ formed in the photoionization of Ar by linearly polarized synchrotron radiation with a nominal 3 meV resolution. The continuous line is to guide the eye. The 15–20 meV (energy full width) resonancelike variation near 35.76 eV originates from differences in the magnetic substate cross sections. The vertical lines correspond to the discrete doubly excited Rydberg series of Ar, as marked on the figure.

will be published elsewhere. We note the emission of the 476.5 nm radiation increases immediately at the threshold value of 35.627 eV. At threshold, the ionized electron has zero energy, but the detection efficiency of the satellite radiation is constant and independent of the energy of the emitted electron. This constant efficiency represents one of the strengths of fluorescence techniques for studying the details of photoionization phenomena at or near the thresholds of weak satellite states.

The high resolution monochromator used in the experiment gives one the capability to assign unambiguously discrete Rydberg states with well-identified angular momentum to certain resonance features in the cross section data. These assignments combined with the detailed polarization data enable one to describe the angular momentum redistribution and sharing in the photoionization process for selected doubly excited states. For example, the $|m_j| = 1/2$ and $3/2$ magnetic substate cross sections in the 36.16 eV range in Fig. 2 are equal and exhibit a large resonancelike behavior. This equality of magnetic sublevel cross sections implies that the $^2P_{3/2}^o$ satellite state has zero alignment, that is, a spherical charge distribution, at these particular energies of the ionizing photon. From Fig. 2, one notes that the identified doubly excited states found near 36.16 eV also have spherically symmetric $(Ar^+)^*$ cores. One of these doubly excited states has an excited $3p^4[^1S]4s\ ^2S_{1/2}$ core and a $8p$ Rydberg electron, and the other one has an excited $3p^4[^1D]4p\ ^2P_{1/2}$ core with a $6s$ Rydberg electron. Our measurements unambiguously show that in these cases, the spherical symmetry of the charge distribution of the core of the doubly excited state is maintained in the autoionization process. In the autoionization the spherically symmetric cores of the Rydberg states recouple to form a $3p^4[^3P]4p\ ^2P_{3/2}^o$ core while maintaining this spherical symmetry. All the anisotropy

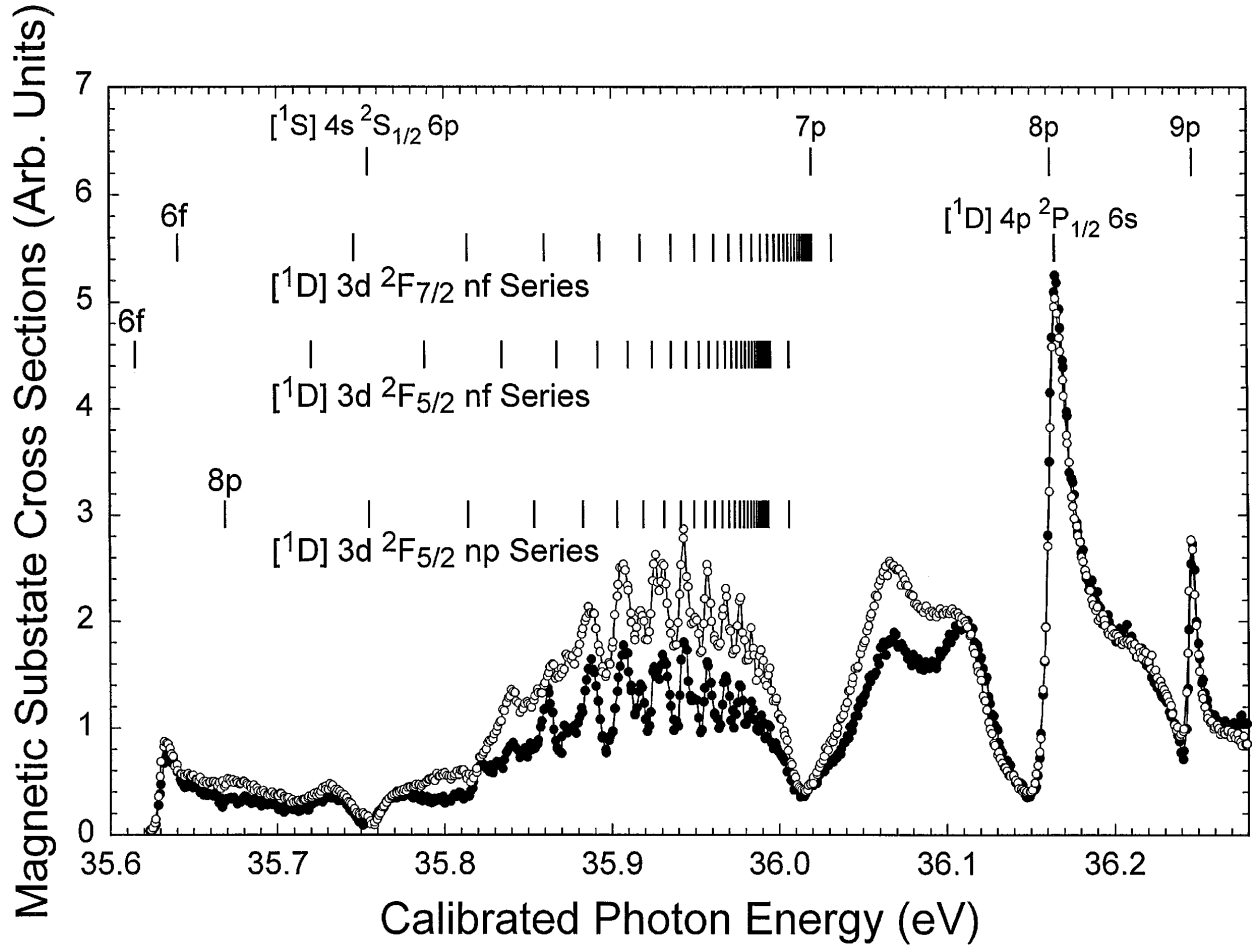

FIG. 2. Magnetic substate cross sections for the $[^3P]4p\,^2P^o_{3/2}$ satellite state of Ar^+ calculated from the polarization measurements, the open circles for $|m_j| = 1/2$ and the filled circles for the $|m_j| = 3/2$ cross sections. The differences in the magnetic substate cross sections causing the sharp variation in polarization near 35.76 eV can barely be seen at this scale. The vertical lines correspond to the discrete doubly excited Rydberg series of Ar, as marked on the figure.

brought by the initial polarized photon is carried away by the free electron, in this case, into $s_{1/2}$, $d_{3/2}$, and $d_{5/2}$ partial waves. In the process, the coupling of the $3p^4$ electrons changes from ^1S or ^1D to ^3P, giving energy to the emitted electron.

Similarly, for the peak at 36.24 eV, shown in Fig. 2, the magnetic sublevel cross sections coincide once more, implying a nonaligned residual ion. Indeed, the spherically symmetric charge distribution of the core of the $[^1S]4s\,^2S_{1/2}9p$ Rydberg state is again maintained in the autoionization process.

In addition, the linear polarization of the incident photon provides information about the charge distribution of the doubly excited state and its angular momentum properties. It implies that the Ar^{**} is aligned. For specific $[^1S]4s\,^2S_{1/2}8p$ and $9p$ Rydberg states discussed here, the implication of an aligned doubly excited state with a nonaligned core is that the Rydberg electron contains all the alignment and is in magnetic sublevel $m = 0$ which is aligned along the incident photon's polarization axis. Then the $[^1S]4s\,^2S_{1/2}8p$ Rydberg state at these ionizing energies is described by a spherically symmetric core with a mean radius $\langle R\rangle \cong 4a_0$ as can be estimated from hydrogenic wave functions, and an elongated charge distribution along the incident photon's polarization axis, having six radial nodes and a mean radius $\langle r\rangle \cong 94a_0$.

As we have shown above, the high resolution intensity information combined with high resolution polarization measurements makes it possible to depict a physical picture of the cases where there is a large variation in intensity while the corresponding polarization is zero. On the other extreme, the data show also that it is possible to have a slowly varying intensity pattern while the corresponding polarization changes rapidly and substantially. This is exemplified by the polarization data of Fig. 1 which displays an unusually sharp resonancelike variation near 35.76 eV where the polarization changes very rapidly from approximately $+25\%$ to -25% over a range of 7–8 meV. Figure 3 shows the details of the polarization from 35.700 to 35.890 eV with the energy resolution improved from 3 to 2 meV and with longer counting times for better statistics.

This resonancelike behavior reflects the dependence of the polarization on the magnetic substate populations as a function of the ionizing photon energy. From the

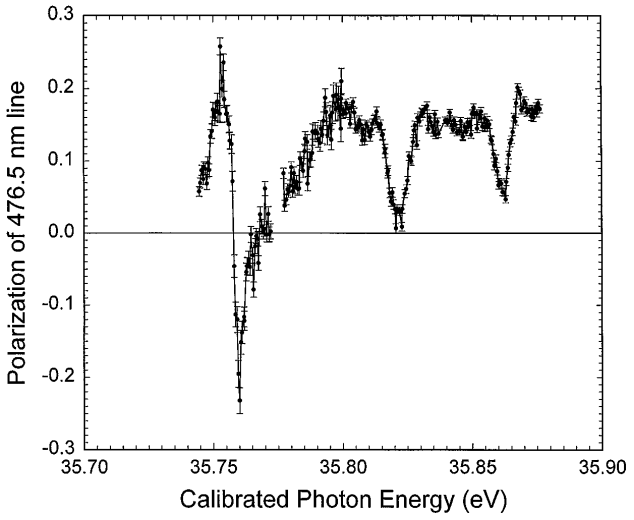

FIG. 3. Details of the polarization measurements near 35.76 eV with the resolution improved to 2 meV. The error bars are the statistical uncertainties.

equations defining A_0^c the polarization is directly proportional to the difference between the $|m_j| = 1/2$ and $3/2$ cross sections and inversely proportional to the weighted sum. Thus, rapid changes in polarization reflect rapid changes in the difference of the substate cross sections. These differences are amplified as the total cross section becomes smaller. The magnetic substate cross sections, calculated from the polarization shown in Fig. 3, are displayed in Fig. 4 with an expanded scale. From Fig. 4 one notes that the difference in the substate cross sections is a significant fraction of the total cross section. The total cross section $\sigma(j = 3/2)$ is the sum of the two magnetic substate cross sections shown in Figs. 2 and 4. Its magnitude in the vicinity of 35.76 eV is small and the line profile suggests the presence of a window resonance. Coupled with the fact that the magnetic substate cross sections intersect near 35.76 eV, this leads to the amplified resonancelike behavior of Figs. 1 and 3. This amplification illustrates how polarization analysis of radiation from satellite states can be used as an additional sensitive tool to study subtle variations and differences in the magnetic sublevel cross sections even when the individual substate cross sections vary relatively slowly with the energy of the ionizing photon. Near 35.76 eV, the polarization shows a 15–20 meV resonancelike variation which can be unambiguously attributed to the differences in the magnetic substate cross sections, suggesting magnetic sublevel dependent coupling between the partial open channels and the discrete doubly excited Rydberg states. The rapid change from $+25\%$ to -25% in polarization indicates that the excited ionic charge distribution oscillates from prolate to oblate spheroid within 7–8 meV of energy interval describing an unexplored dynamical aspect of the photoionization.

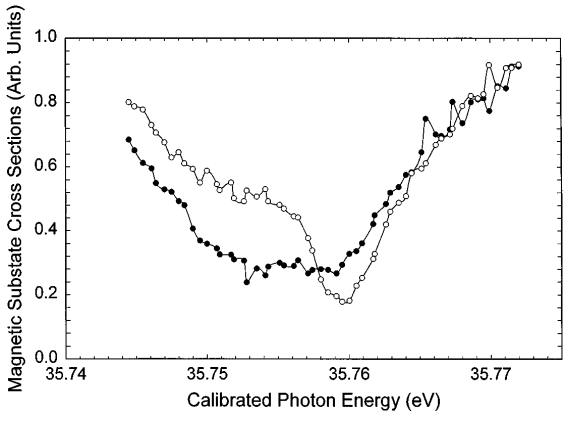

FIG. 4. Magnetic substate cross sections for the $[^3P]4p\,^2P^o_{3/2}$ satellite state of Ar^+ corresponding to the sharp variation near 35.76 eV in Fig. 3. The open circles for $|m_j| = 1/2$ and the filled circles for the $|m_j| = 3/2$ cross sections. Since the polarization $P = [\sigma(1/2) - \sigma(3/2)]/[\frac{5}{3}\sigma(1/2) + \sigma(3/2)]$, the subtle differences between the $|m_j| = 1/2$ and $|m_j| = 3/2$ cross sections are amplified to produce the sharp resonancelike variation in the polarization presented in Figs. 1 and 3.

High spectral resolution combined with polarization measurements provide us with a visual description and interpretation of diverse photoionization phenomena that cannot be extracted by any other means. On one extreme, when the polarization is zero but the intensity displays a large variation associated with the formation of a doubly excited Rydberg state, we have presented evidence for a propensity to conserve the spherical symmetry of the core during the autoionization process following the absorption of the ionizing photon. On the other extreme, when the polarization changes rapidly from a positive value to a negative value, even though the corresponding intensity may vary slowly, we have shown that the charge distribution of the excited residual ion varies rapidly changing its shape from a prolate spheroid to an oblate shape over small changes in the energy of the ionizing radiation.

This work is supported by the National Science Foundation under Grant No. PHY-9419505. We thank the entire staff of the Advanced Light Source, Berkeley, CA for their support. We thank Professor James A. R. Samson, Professor Chris H. Greene, Professor Joseph H. Macek, and Professor Anthony F. Starace for insightful discussions.

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