Photoelectron Angular Distributions for *ns* ($n=8-12$) Subshells of Cesium: Relativistic Effects

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Photoelectron angular distributions for resonantly enhanced three-photon ionization (2+1) of cesium via the *ns* ($n=8-12$) states have been measured. The asymmetry parameter β is found to vary from +1.2 for the 8*s* state to −0.5 for the 12*s* state. These results provide the first clear experimental evidence for relativistic (spin-orbit) effects on the photoelectron angular distribution for an alkali-metal atom.

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The photoionization of an atom represents one of the most elementary collision processes. Photoionization of a randomly oriented ensemble of atoms is characterized by the total cross section σ and the asymmetry parameter β, which describes the angular distribution of photoelectrons. At low photon energies (wavelength of light much larger than the size of the atomic target) the electric dipole approximation is valid, and the differential cross section for photoionization by linearly polarized light is given by[1,2]

$$\frac{d\sigma(\epsilon)}{d\Omega}=\frac{\sigma(\epsilon)}{4\pi}[1+\beta(\epsilon)P_2(\cos\theta)]\,, \tag{1}$$

where θ is the direction of the photoelectron with respect to the electric-field vector of the incident light, and $P_2(\cos\theta)$ is the second-order Legendre polynomial. σ and β are dependent upon the photoelectron energy ϵ and the bound and continuum wave functions involved. For *LS* coupling of nonrelativistic single-particle wave functions, β is given by[2]

$$\beta(\epsilon)=\frac{l(l-1)R_{l-1}^2+(l+1)(l+2)R_{l+1}^2-6l(l+1)R_{l-1}R_{l+1}\cos\delta}{(2l+1)[lR_{l-1}^2+(l+1)R_{l+1}^2]}\,, \tag{2}$$

where R_{l-1} and R_{l+1} are the radial matrix elements between the bound and continuum wave functions for the $l-1$ and $l+1$ partial waves, respectively. $\delta=\delta_{l+1}-\delta_{l-1}$ is the difference in the phase shifts for the two possible continuum functions. The important point in the present context is that, for photoionization from a pure *s* orbital ($l=0$) and when the phase-shift difference is zero, Eq. (2) predicts that β is independent of energy and is identically equal to 2. It has been shown, however, that deviations from this expectation may result when (a) anisotropic electron-ion interactions are important (e.g., photoionization from open-shell systems)[3-6] or (b) relativistic (spin-orbit) interactions are appreciable.[7-12] Anisotropic electron-ion interactions are absent for photoionization of the *s* states of alkali-metal atoms (closed-shell core) and deviations from $\beta=2$ thus provide a direct test of relativistic interactions. In this Letter we report photoelectron angular distributions for resonantly enhanced three-photon ionization (2+1) of cesium atoms via the 8*s*, 9*s*, 10*s*, and 12*s* states. In general, multiphoton excitation can give rise to aligned (spatially anisotropic) target states for which the form of the differential cross section is more complicated than that given in Eq. (1). In the present case, excitation of an *ns* state ($J=\frac{1}{2}$) results in an isotropic target, and Eq. (1) is valid. Values of β are found to vary from +1.2 for the 8*s* state to −0.5 for the 12*s* state which we attribute to relativistic (spin-orbit) effects in the photoionization continuum.

The importance of spin-orbit interactions in the heavy alkali-metal atoms has been recognized for many years. In 1930, Fermi[13] showed that spin-orbit interactions are responsible for the anomalous doublet-line-strength ratios for cesium. Seaton[14] later showed that inclusion of spin-orbit effects can result in nonzero minima in the photoionization cross sections (the so-called Cooper minima[15]). Fano[16] predicted that spin-orbit effects would result in emission of spin-polarized electrons when circularly polarized light is used to ionize Cs atoms. Experimental observations of the Fano effect soon followed,[17-19] and it was shown that accurate values for the position of the Cooper minimum could be obtained from the spin-polarization measurements.[19] Several theoretical studies have addressed the effects of spin-orbit interactions on photoelectron angular distributions,[7-12] but experimental studies have been sparse.

Inclusion of relativistic (spin-orbit) effects results in radial matrix elements which depend upon the total angular momentum (j') of the continuum wave function. β for an s state then becomes[8,9,12]

$$\beta(\epsilon)=\frac{2R_{3/2}^2+4R_{1/2}R_{3/2}\cos(\delta_{3/2}-\delta_{1/2})}{2R_{3/2}^2+R_{1/2}^2}. \qquad (3)$$

It has been shown[8-11,16] that the phase-shift difference $\delta_{3/2}-\delta_{1/2}$ is generally close to zero. Under this condition note that when the matrix elements $R_{1/2}$ and $R_{3/2}$ are equal, β is again equal to 2. However, the two matrix elements go to zero at slightly different energies. In the energy region where the two matrix elements differ significantly, β is expected to differ from 2. In principle, β can have values between 2 and -1. A number of specific cases are worth noting: when $R_{3/2}=0$, $\beta=0$; when $R_{1/2}=0$, $\beta=1$; and when $R_{1/2}=-R_{3/2}$, $\beta=-\frac{2}{3}$.

Manson and Starace[20] have reviewed the subject of energy-dependent photoelectron angular distributions for s subshells. Deviations from $\beta=2$ have been observed in only a few cases. Niehaus and Ruf[21] measured angular distributions for ionization of the 6s electron in mercury. They found that β was energy dependent, varying from 2 to 1.25. More recently, several experimental and theoretical groups have studied the $5s\rightarrow\epsilon p$ photoionization of xenon.[22-31] Two of the experiments[28,29] suggest a small "dip" in β at a photon energy of ~ 32 eV, in the region of the Cooper minimum. Two of the theoretical calculations[24,25] include relativistic effects but only consider single-hole ionization channels and predict a much larger decrease in β from the value 2 than is found experimentally; a third such calculation[27] predicts a smaller decrease in β than is found experimentally. However, Tulkki[31] has recently calculated asymmetry parameters which are in excellent agreement with experiment. These calculations included double-excitation channels on equal footing with the important single-excitation channels using the multichannel multiconfigurational Dirac-Fock (MMCDF) method. Thus in this case, the relativistic (spin-orbit) effects are obscured by the effects of multielectron excitation which are known to be present from studies of satellite spectra in the region of the Xe 5s Cooper minimum.[30]

It is indeed surprising to find that, to our knowledge, only one solitary measurement of a photoelectron angular distribution exists for an alkali-metal s state. In 1931 Chaffee[32] reported β of approximately 2 for photoionization of ground-state potassium in the region of ~ 2400 Å, although he did detect a small residual signal when the light polarization was perpendicular to the electron detection direction. Samson[33] has performed a detailed analysis of these data and concluded that β was equal to 1.55. In 1979 Ong and Manson[10] reanalyzed the Chaffee data to obtain $\beta=1.5\pm0.3$. In order to more rigorously probe spin-orbit effects in the photoionization of the alkali metals, we have measured photoelectron angular distributions for several ns states of cesium.

Figure 1 shows the multiphoton ionization scheme. The photoionization cross sections versus photoelectron energy recently calculated by Lahiri and Manson[34] for the 8s and 9s states are also shown for illustration. The positions of the Cooper minima are very similar for different principal quantum numbers including the ground state ($n=6$) when plotted versus photoelectron energy.[34] The energy of the photoelectron in the continuum, ϵ, is determined by the photon energy and the ionization of cesium, $\epsilon=3h\nu-\mathrm{IP}$. Inspection of Fig. 1 shows that the outgoing electron energies are expected to be in the region of the calculated Cooper minima.

Experimentally, an Nd-doped yttrium aluminum garnet-pumped tunable dye laser (Quanta Ray DCR II, PDL2) is used to excite the 8s, 9s, 10s, and 12s states of cesium by nonresonant two-photon excitation. It was not possible to study the 11s state because of complications of nearby levels (see Ref. 35). A third photon from the same laser beam photoionizes the excited atom. Note that the two-photon excitation results in equal populations of the m_J sublevels, and thus the excited ns states are by definition randomly oriented. The photoelectron angular distributions are therefore not complicated by alignment of the intermediate states. The energy of the photoelectron is determined by its time of flight over a 7-cm path and is detected by a channel-plate charged-particle detector. The angular acceptance of the detection system is ±6.5°. The plane of polarization of the incident light is rotated with a double Fresnel rhomb which is controlled by a stepping motor. Each angular distribution was collected by averaging 100 laser shots at intervals of 9°. These measurements were difficult due to the small photoionization cross sections for the ns subshells of cesium.[35,36] The small cross section is a result of a Cooper minimum in the continuum, which of course

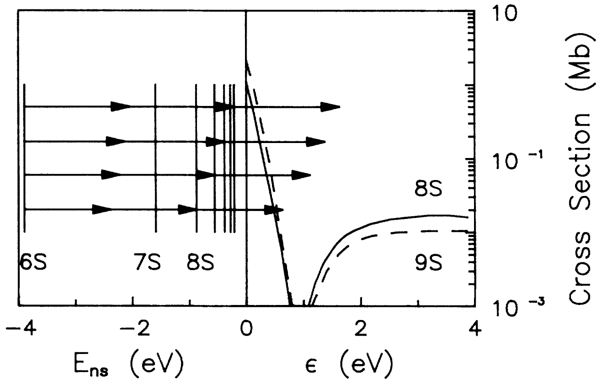

FIG. 1. Illustration of resonantly enhanced three-photon ionization scheme used to study photoelectron angular distributions for ns ($n=8$–12) states of cesium. Also shown are the theoretical photoionization cross sections vs photoelectron energy ϵ of Lahiri and Manson (Ref. 34) for the 8s and 9s states.

makes the present problem interesting. Several angular-distribution measurements were averaged for each state in order to obtain good signal-to-noise ratios. We should point out that since a signal is only observed when the laser wavelength is in two-photon resonance with an *ns* state, the contribution due to photoionization of dimers should be close to zero. Electron-energy analysis also assures this fact. We note parenthetically that the results of Chaffee[32] were probably affected somewhat by photoionization dimers.

Photoelectron angular distributions for photoionization of *ns* ($n=8-12$) subshells of cesium are shown in Fig. 2. The asymmetry parameters for each angular distribution are obtained using a least-squares method to fit the experimental data by the equation [see Eq. (1)],

$$I(\theta)=1+\beta P_2(\cos\theta)\,. \tag{4}$$

Note that since $-1\leq\beta\leq 2$ and $P_2(\cos\theta)=\frac{1}{2}(3\cos^2\theta-1)$, Eq. (4) gives $0\leq I(\theta)\leq 3$. The β values thus obtained for each state are also indicated in Fig. 2. Identical β values are obtained from $\beta=(R-1)/(1+R/2)$, where R is the ratio of the electron signal recorded at $\theta=0°$ to that at $\theta=90°$. The linear polarization of the laser was $>99.8\%$.

Pindzola[12] has calculated β parameters using the Dirac-Fock approximation in order to obtain the radial-dipole matrix elements used in Eq. (3) for photoionization from the 6*s*, 7*s*, and 8*s* subshells of cesium. When his results for β are plotted versus photoelectron energy, β decreases from 2 to -1 as ϵ goes from 0 to $\sim$2 eV. Our measurements for the 8*s* state agree exactly with the theoretical value calculated using the velocity form of the wave function but is $\sim$15% lower than that calculated using the length form.

This study represents the first measurements of photoelectron angular distributions for excited *s* states of an alkali-metal atom. The data clearly show the importance of spin-orbit effects in the photoionization continuum and support the previous theoretical predictions[34] of a Cooper minimum at photoelectron energies just above the threshold for ionization. Further theoretical calculations for the simple case of photoionization of *s* subshells of alkali metals are encouraged. Experimentally, our program is to use two lasers, one to pump the *ns* states and the second to photoionize the *ns* levels at different energies in the continuum. Energy-dependent β parameters for an isolated *ns* state can then be determined as well as the energy dependence of the photoionization cross section. We are also in the process of performing experimental measurements on one-photon ionization of ground state (6*s*) cesium atoms in order to obtain $\sigma(\epsilon)$ and $\beta(\epsilon)$.

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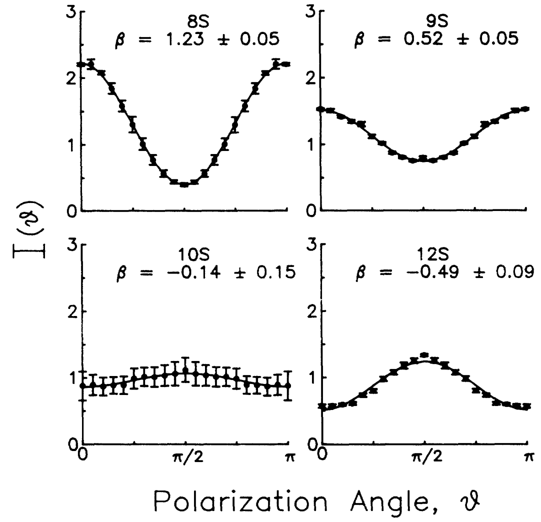

FIG. 2. Photoelectron angular distributions for *ns* ($n=8,9,10,12$) states of cesium. Distributions were measured from 0 to 2π; however, the data from π to 2π are averaged with that from 0 to π and shown here. Solid lines are best fits of data by Eq. (4). Error bars are 1 standard deviation for the average of several angular distributions. The errors in β are $\pm 1\sigma$ from the statistical variance of fit.

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