RAPID COMMUNICATIONS

PHYSICAL REVIEW A VOLUME 43, NUMBER 11 1 JUNE 1991

Circular dichroism in photoelectron angular distributions for the $7P_{3/2}$ level of cesium

L. E. Cuéllar
Department of Physics and Astronomy, University of Tennessee, Knoxville, Tennessee 37996

C. S. Feigerle
Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996

H. S. Carman, Jr. and R. N. Compton*
Chemical Physics Section, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831
(Received 13 November 1990; revised manuscript received 22 February 1991)

Circular dichroism in photoelectron angular distributions (CDAD) is used to examine the alignment of the $7P_{3/2}$ and $7P_{1/2}$ levels of cesium, prepared by absorption of linearly polarized laser radiation. As expected, the $7P_{1/2}$ level exhibits no CDAD, whereas the $7P_{3/2}$ level shows a significant CDAD signal, although smaller than that predicted by theory. The difference between experiment and theory is attributed to m_J mixing due to hyperfine coupling during the finite ionization time of the laser pulse.

INTRODUCTION

In this Rapid Communication, we report an experimental observation of circular dichroism in angular distributions (CDAD) of photoelectrons ejected from an atomic system. Circular dichroism occurs when the responses of a system to left and right circularly polarized light are different. It is often associated with the discrete (bound-bound) absorption of molecules[1,2] that lack a plane or point of symmetry (i.e., they have a chiral center) and is most commonly observed as a difference in the indices of refraction for left and right circularly polarized light. Studies of circular dichrosim are of considerable interest in physics, chemistry, and biology because of the frequent occurrence of chirality in molecules. Bound-continuum absorption has also been predicted to exhibit circular dichrosim,[3-7] providing insight into the dynamics of photoionization processes. Circular dichroic effects have been predicted for angular distributions of photoelectrons ejected from optically active[6,7] and oriented[5] molecules. More recently, Dubs, Dixit, and McKoy[8-10] have proposed that circular dichroism in angular distributions can be used to probe the alignment of atoms and molecules. Alignment (or orientation) of an atom or molecule frequently results from optical excitation using linearly (or circularly) polarized light. A convenient way of studying circular dichroism in angular distributions from aligned systems is to perform a two-color resonance-enhanced multiphoton ionization experiment in which excitation with linearly polarized light is used to produce an aligned intermediate level, which is then ionized using circularly polarized light. The photoelectron signal is measured as a function of the angle between the laser polarization used in the excitation step and the electron collection direction. CDAD is then the difference between photoelectron angular distributions obtained using left and right circularly polarized light for the ionization step. The observed CDAD signal contains information about the alignment of the system under study.[8-10]

Three recent CDAD experiments have been reported for molecular systems. Appling *et al.*[11] used CDAD to probe the alignment of NO molecules excited to the $A\,^2\Sigma^+$ state by linearly polarized light. In a related CDAD study, Winniczek *et al.*[12] probed the alignment of ground-state NO molecules produced by photodissociation of CH_3ONO. CDAD for a *fixed* molecule was reported by Westphal *et al.*,[13] who measured photoelectron angular distributions for CO molecules adsorbed on a Pd(111) crystal (where the CO is oriented with the C atom pointing toward the surface). To our knowledge, no experimental observations of CDAD for an atomic system have been previously reported.

Two groups[14,15] have reported photoelectron angular distributions for resonance-enhanced two-photon ionization (1+1) of cesium via the $7P_{1/2}$ and $7P_{3/2}$ levels, using linearly polarized light for both the excitation and ionization steps. In general, for linearly polarized light, a two-photon ionization process is expected to yield a photoelectron angular distribution of the form[16]

$$I(\theta)=(\sigma/4\pi)[1+\beta_2 P_2(\cos\theta)+\beta_4 P_4(\cos\theta)]\,, \qquad (1)$$

where σ is the total two-photon ionization cross section, P_n are nth-order Legendre polynomials, and β_n are the asymmetry parameters. The β_n coefficients are determined by the radial dipole matrix elements involved in the excitation and ionization transitions and thus contain detailed information about the photoionization process, including the alignment of the intermediate level. If the intermediate level is not aligned (i.e., if all m_J states are equally populated), only terms up to second order in the Legendre polynomial expansion will contribute to the angular distribution. In the case of (1+1) ionization of cesium via the $7P_{1/2}$ level, the $m_J=\pm 1/2$ states are equally populated by absorption of the linearly polarized light and the level is not aligned. For the $7P_{3/2}$ level, however, the $|m_J|=1/2,3/2$ states are unequally populated (only the $m_J=\pm 1/2$ states are excited) by absorption of linearly polarized light, resulting in an aligned level. It is expected therefore that higher-order Legendre polynomials will contribute to the photoelectron angular distribution for

this level. Experimentally, however, it is found[14,15] that the angular distributions observed depend upon the laser-pulse duration. Using a long pulse length (≈ 400 ns) flashlamp-pumped dye laser, Kaminski, Kessler, and Kollath[14] reported angular distributions for the $7P_{1/2}$ and $7P_{3/2}$ levels which were very similar and adequately described by Eq. (1) including only the second-order term, with $\beta_2 \approx 1.4$. Subsequently, Compton *et al.*[15] measured angular distributions using a nitrogen-pumped dye laser with a shorter pulse duration (≈ 10 ns). Their results for the $7P_{1/2}$ level agreed well with the results of Kaminski, Kessler, and Kollath,[14] with $\beta_2 \approx 1.3$. However, their results for the $7P_{3/2}$ level differed remarkably from that of Kaminski, Kessler, and Kollath,[14] requiring up to fourth-order terms to fit the data, with $\beta_2 = 1.56$ and $\beta_4 = 0.69$. It was shown theoretically[15] that these differences could be explained by including the effects of hyperfine coupling, which causes a reduction in the alignment of the level during the finite time of the laser pulse.

In a vector model, hyperfine coupling results from the electronic angular momentum vector **J**, precessing about the total angular momentum vector, $\mathbf{F} = \mathbf{J} + \mathbf{I}$, where **I** is the nuclear-spin angular momentum. This precession occurs with a characteristic time of the order $\hbar$ divided by the hyperfine level separation. When the bandwidth of the laser used for excitation is greater than the separations of the relevant hyperfine levels, a nonstationary intermediate state is produced which is a superposition (partially coherent) of hyperfine levels. The time evolution of this nonstationary state results in a mixing of the m_J states, which reduces the initially prepared alignment. Such effects have been described in detail by Fano and Macek[17] and Greene and Zare.[18] The nuclear-spin angular momentum, I, of cesium is $7\hbar/2$ and the hyperfine coupling time is of the order of a few nanoseconds. The alignment measured experimentally will therefore depend upon the duration of the laser pulse. Varying degrees of disalignment thus provides an explanation for the differing results of Kaminski, Kessler, and Kollath[14] and Compton *et al.*[15] for the angular distribution of the $7P_{3/2}$ level of cesium.

In this paper, we present CDAD results for the $7P_{1/2}$ and $7P_{3/2}$ levels of cesium, using a Nd:YAG-pumped dye-laser system (YAG denotes ytrrium aluminum garnet) with ≈ 6-ns pulse duration. Our results are in qualitative agreement with the theoretical predictions of Dubs, Dixit, and McKoy.[9,19] Quantitative differences between experiment and theory are attributed to hyperfine coupling effects during the laser-pulse duration, which were not included in the theory.

EXPERIMENT

The experimental CDAD measurements were performed in an atomic beam apparatus with a base pressure $\approx 10^{-7}$ Torr. A pulsed Nd:YAG-pumped dye laser system (Quanta-Ray DCR,PDL) with a pulse duration of ≈ 6 ns provided the radiation for both the excitation and ionization steps. The output of the dye laser was linearly polarized to $\geq 98\%$ (using a Glan air prism) and was tuned to either the $6S_{1/2} \rightarrow 7P_{1/2}$ or $6S_{1/2} \rightarrow 7P_{3/2}$ transition of atomic cesium. A second laser beam (532 nm, second harmonic of the Nd:YAG) was circularly polarized (using a quarter-wave plate) and counterpropagated with the dye laser beam. In order to obtain a high purity of circular polarization, the polarization of the 532-nm laser beam (which was linearly polarized at the laser exit) was further purified using a Glan air prism, then rotated with a double Fresnel rhomb prior to entering the quarter-wave plate. Right (or left) circular polarization was obtained by rotating the input polarization 45° (or −45°) relative to the quarter-wave plate crystal axis. The two counterpropagating laser beams were crossed by a collimated effusive beam of cesium atoms (oven temperature ~130 °C) in the center of a time-of-flight electron-energy analyzer. The time delay between the two laser pulses could be varied with an adjustable optical delay line in the dye laser beam. The time delay was set such that atoms in the ionization volume experienced the full time duration of both laser pulses simultaneously.

Photoelectrons were collected at right angles to both the laser beams and the cesium beam and were energy analyzed by time of flight through a 7-cm drift tube. Stray magnetic fields were reduced to a value below 1 mG by a μ-metal shield lining the vacuum chamber. Electrons were detected with a dual channel-plate multiplier (18-mm diameter) with a concentric-ring anode collector (inner collector, 8-mm diameter; outer collector, 18-mm diameter). Data were obtained with the inner collector which provided a geometric acceptance angle of $\pm 2°$. The collector output signal was digitized using a 100-MHz transient digitizer (DSP Technologies 2001A) and transferred via a CAMAC (computer-automated measurement and control) interface to a laboratory computer (Compaq Deskpro 286).

Photoelectron angular distributions were measured by rotating the polarization of the excitation (dye) laser relative to the electron collection direction, while keeping the polarization of the 532-nm ionizing laser fixed. Typically, photoelectron signals were averaged over 100 laser shots and collected at 9° intervals. For the CDAD measurements, the dye laser was attenuated using neutral density filters in order to minimize the one-color (1+1) ionization signal. For all CDAD measurements reported here, the two-color (1+1′) ionization signal was ≥ 100 times that of the one-color (1+1) signal. In addition, the two processes could be distinguished by the difference in electron flight times (a difference of ≈ 30 ns or ≈ 0.39 eV). In order to obtain a CDAD signal, angular distributions were recorded for both left and right circular polarizations of the ionizing laser.

RESULTS AND DISCUSSION

The CDAD signal at a given photoelectron ejection angle (relative to the polarization direction of the excitation laser) is defined[9] as the difference in signals obtained for ionization with left (I_L) and right (I_R) circular polarizations: $I_{\mathrm{CDAD}}(\theta) = I_L(\theta) - I_R(\theta)$. Experimental angular distributions for the $7P_{1/2}$ level of cesium, using left and right circularly polarized light for ionization, are shown in Fig. 1(a). As described above, absorption of linearly polarized light by ground-state cesium atoms produces equal

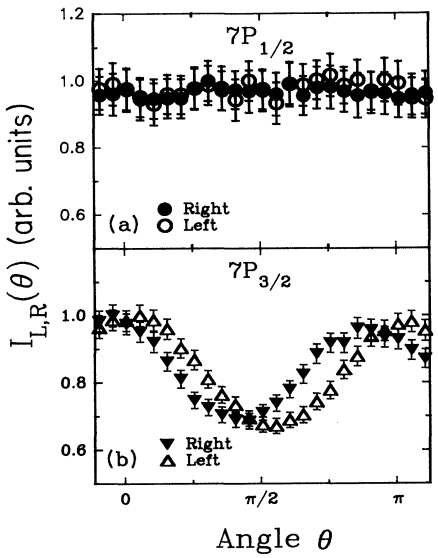

FIG. 1. Photoelectron angular distributions for the (a) $7P_{1/2}$ and (b) $7P_{3/2}$ levels of cesium, using left (L) and right (R) circularly polarized light for ionization. Error bars represent one standard deviation of the signal averaged over several hundred laser shots.

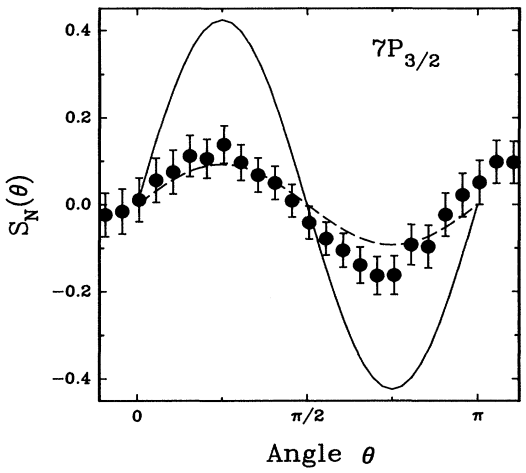

FIG. 2. Experimental and theoretical CDAD signals for the $7P_{3/2}$ level of cesium [normalized according to Eq. (2)]. (●) experimental (error bars represent one standard deviation of the signal averaged over several hundred laser shots); (——) theory (Ref. 19) (without hyperfine corrections); (---) theory including hyperfine corrections (as described in text).

populations of the $m_J = \pm 1/2$ states of the $7P_{1/2}$ level and the atom is therefore (by definition) not aligned. As expected for a system which is not aligned, the angular distributions for ionization with left and right circularly polarized light are found to be identical and $I_{\mathrm{CDAD}}(\theta)$ equals zero at all angles (i.e., there is no circular dichroism). This result, while expected, provided confidence that (i) a high purity of circular polarization of the ionization laser was maintained, (ii) spatial overlap of the two laser beams remained constant during rotation of the excitation-beam polarization, and (iii) the $(1+1)$ contribution to the photoelectron signal was negligible compared to the $(1+1')$ signal.

A similar plot of angular distributions for the $7P_{3/2}$ level is shown in Fig. 1(b). In this case, absorption of linearly polarized light produces an aligned atom (the $|m_J| = 3/2$ and $|m_J| = 1/2$ states are not equally populated) and the angular distributions for ionization by left and right circularly polarized light are clearly different. Figure 2 shows the resulting CDAD signal, which has been normalized to the average of the signals at $\theta = 0$ and $\pi/2$:

$$S_N(\theta) = \frac{I_L(\theta) - I_R(\theta)}{\frac{1}{2}[I(0) + I(\pi/2)]} . \tag{2}$$

Note that, by symmetry, $I_L(\theta) = I_R(\theta) = I(\theta)$ at $\theta = 0$ and $\pi/2$. Also shown in Fig. 2 (solid line) are the theoretical CDAD results of Dubs, Dixit, and McKoy[19] (using the same normalization procedure) for ionization with 532-nm light, based upon the theory of Ref. 9. Qualitatively, the experimental results are consistent with the theoretical predictions: the CDAD signal vanishes at $\theta = 0$ and $\pi/2$ and has a characteristic $\sin(2\theta)$ angular dependence. However, the magnitude of the experimental CDAD signal is considerably smaller than that of the theoretical calculations. Theoretically, the CDAD intensity, $I_{\mathrm{CDAD}}(\theta)$, is given by [10]

$$I_{\mathrm{CDAD}}(\theta) = \sum_L a_L P_L^1(\cos\theta) , \tag{3}$$

where $P_L^1(\cos\theta)$ are associated Legendre polynomials and $a_L = A_L \bar{\bar{\beta}}_L$. Here, A_L are the state multipole moments of the angular momentum distribution (which describe the alignment of the atom) and $\bar{\bar{\beta}}_L$ describe the dynamics of the photoionization event, including the matrix elements and phase shifts of the continuum partial waves.[9,10] For one-photon excitation from an unaligned ground state, only A_2 (the quadrupole moment of the angular momentum distribution) contributes to the alignment of the intermediate level and Eq. (3) reduces to

$$I_{\mathrm{CDAD}}(\theta) = \tfrac{3}{2} A_2 \bar{\bar{\beta}}_2 \sin(2\theta) . \tag{4}$$

The theoretical result of Dubs, Dixit, and McKoy[19] shown in Fig. 2 (solid line) is based upon Eq. (4) with the assumption that no time elapses between excitation and ionization and hence the alignment (A_2) does not change. In the present experiments, as much as ≈ 6 ns can elapse between excitation and ionization. As described above and discussed by Fano and Macek[17] and Greene and Zare,[18] the presence of unresolved hyperfine levels (which are coherently excited) induces a time dependence in the multipole moments of the electronic angular momentum distribution. In general, the hyperfine coupling reduces the alignment initially produced in the excitation step. In the present experiments, the bandwidth of the excitation laser is greater than the splitting of the hyperfine levels of the $7P_{3/2}$ level and a superposition of these hyperfine levels ($F = 5, 4, 3, 2$) is excited. A decrease in alignment caused by hyperfine coupling may therefore affect the CDAD results.

In order to quantitatively estimate the effect of hyperfine coupling on the CDAD results, the time dependence of A_2 was calculated using the theory of Fano and Macek.[17,18] In the actual CDAD experiment, each Cs atom will undergo a different amount of depolarization depending on the time between excitation and ionization, and the measured alignment will be a convolution of the time dependence of the depolarization, the ionization rate, and the laser power and pulse shape. In order to simplify the calculation considerably, we calculated the average value of A_2 in the "long-time limit,"[18] which is applicable when ionization occurs over a time period which is much longer than the time of precession of **J** about **F**. In this limit, the average value of A_2 is given by[18]

$$\langle A_2(t)\rangle = A_2(0)\sum_{F=2}^{5}\frac{(2F+1)^2}{(2I+1)}\begin{Bmatrix} F & F & 2 \\ J & J & I \end{Bmatrix}^2 . \quad (5)$$

Evaluation of the $6j$-symbols and summation over F yields $\langle A_2(t)\rangle = 0.219A_2(0)$. Therefore the theoretical CDAD results of Dubs, Dixit, and McKoy,[19] which were calculated assuming $A_2 = A_2(0)$, were multiplied by 0.219 to give the dashed curve shown in Fig. 2. As can be seen, the inclusion of hyperfine depolarization (even in the approximation of the long-time limit) results in much better, although not statistically perfect, agreement between theory and experiment. The remaining discrepancy is not suprising in view of the fact that the long-time limit used to obtain Eq. (5) only roughly approximates the 6-ns laser pulse duration used for the experiments.

We conclude that CDAD is indeed a sensitive method for measuring the alignment of atomic systems and should be a useful technique in many areas of atomic and molecular physics. Further experiments are planned to measure CDAD in the absence of hyperfine depolarization using high-resolution diode lasers to excite single hyperfine levels of heavy atoms.

ACKNOWLEDGMENTS

This research is sponsored by a grant from the U.S. Office of Naval Research, Grant No. ONR N-00014-87-K-0065 and by the Office of Health and Environmental Research, U.S. Department of Energy, under Contract No. DE-AC05-840R21400 with Martin Marietta Energy Systems, Inc. We would like to thank R. L. Dubs, S. N. Dixit, and V. McKoy for helpful discussions and for providing the results of their calculations prior to publication.

*Also at Department of Chemistry, University of Tennessee, Knoxville, TN 37996.

[1]E. U. Condon, W. Altar, and H. Eyring, J. Chem. Phys. **5**, 753 (1937).
[2]E. U. Condon, Rev. Mod. Phys. **9**, 432 (1937).
[3]N. A. Cherepkov, Chem. Phys. Lett. **87**, 344 (1982).
[4]R. Parzyński, Acta Phys. Polonica **A57**, 49 (1980).
[5]B. Ritchie, Phys. Rev. A **12**, 567 (1975).
[6]B. Ritchie, Phys. Rev. A **13**, 1411 (1976).
[7]B. Ritchie, Phys. Rev. A **14**, 359 (1976).
[8]R. L. Dubs, S. N. Dixit, and V. McKoy, Phys. Rev. Lett. **54**, 1249 (1985).
[9]R. L. Dubs, S. N. Dixit, and V. McKoy, J. Chem. Phys. **85**, 656 (1986).
[10]R. L. Dubs, S. N. Dixit, and V. McKoy, J. Chem. Phys. **85**, 6267 (1986).
[11]J. R. Appling, M. G. White, T. M. Orlando, and S. L. Anderson, J. Chem. Phys. **85**, 6803 (1986); J. R. Appling, M. G. White, R. L. Dubs, S. N. Dixit, and V. McKoy, J. Chem. Phys. **87**, 6927 (1987).
[12]J. W. Winniczek, R. L. Dubs, J. R. Appling, V. McKoy, and M. G. White, J. Chem. Phys. **90**, 949 (1989).
[13]C. Westphal, J. Bansmann, M. Getzlaff, and G. Schönhense, Phys. Rev. Lett. **63**, 151 (1989).
[14]H. Kaminski, J. Kessler, and K. J. Kollath, Phys. Rev. Lett. **45**, 1161 (1980).
[15]R. N. Compton, J. A. D. Stockdale, C. D. Cooper, X. Tang, and P. Lambropoulos, Phys. Rev. A **30**, 1766 (1984).
[16]P. Lambropoulos, Adv. At. Mol. Opt. Phys. **12**, 87 (1976).
[17]U. Fano and J. H. Macek, Rev. Mod. Phys. **45**, 553 (1973).
[18]C. H. Greene and R. N. Zare, Annu. Rev. Phys. Chem. **33**, 119 (1982).
[19]R. L. Dubs, S. N. Dixit, and V. McKoy (unpublished).