

## Alignment of Cd atoms by photoionization

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(Received 14 March 1977)

The  ${}^2D_{3/2}$  and  ${}^2D_{5/2}$  excited states of the cadmium ion are produced through photoionization of cadmium atoms by a beam of He I 584-Å radiation. The presence of alignment in the ions is detected by measuring the degree of linear polarization  $P$  of the resulting emission. It is found that  $P({}^2D_{5/2} \rightarrow {}^2P_{3/2}) = -0.052 \pm 0.005$  for the 4416-Å transition, and  $P({}^2D_{3/2} \rightarrow {}^2P_{3/2}) = +0.12 \pm 0.04$  for the 3536-Å transition, demonstrating that both  ${}^2D$  fine-structure components are aligned. A simple calculation is presented which ignores anisotropic final-state interactions. This calculation correctly predicts the sign of the degree of polarization, but fails to reproduce the experimental results.

### I. INTRODUCTION

Photoionization processes have long intrigued students of atomic structure but have only recently received extensive attention with development of superior light sources and electron energy analyzers. Most emphasis has been placed on the measurement of total ionization cross sections and the relative rate of production of different final-state ions. However, increasing attention is being focused on more subtle features of the photoionization dynamics. The process, by virtue of the transverse nature of radiation, is anisotropic when the ionizing light is unidirectional, even if it is not polarized. This spatial anisotropy can manifest itself in the angular distribution of the photoelectron and in the unequal  $M_J$  distribution of the target ion. The latter was first pointed out by Flüge, Mehlhorn, and Schmidt<sup>1</sup> and by Jacobs.<sup>2</sup> While in some cases measurements of the angular distribution of the photoelectron have been performed, to our knowledge target alignment has not been experimentally observed.

By alignment we refer to a particular inequality in the distribution of the projections along  $z$  ( $M_J$  values) of the resultant ion's total angular momentum  $\vec{J}$ . In a system characterized only by alignment, the positive ( $+M_J$ ) and negative ( $-M_J$ ) magnetic substates are equally populated, but there is a difference in the populations of the substates having unequal values of  $|M_J|$ . If the density matrix of the  $M_J$  distribution is expanded in spherical tensors,<sup>3</sup> then alignment corresponds to a nonvanishing  $T_0^2$  (quadrupole) term, where  $T_0^2$  is the tensor of rank 2 and projection 0. The coefficient of this term can be experimentally determined for an excited  $J$  state that can radiate a dipole photon by measuring the degree of linear polarization of the emitted radiation. If the system is one in which  $J \leq \frac{3}{2}$ , measurement of the  $T_0^2$  coefficient is sufficient to describe the  $M_J$  distribution, completely. For  $J > \frac{3}{2}$ , it provides information on the unequal

$|M_J|$  populations, but does not uniquely specify the  $M_J$  distribution.

We report alignment in the Cd II  ${}^2D_{5/2, 3/2}$  ions produced through the photoionization of Cd I  $1S_0$  atoms using a beam of unpolarized He I 584-Å radiation.<sup>4</sup> The presence of alignment is detected by measuring the degree of polarization of the  ${}^2D_{5/2} \rightarrow {}^2P_{3/2}$  (4416 Å) and  ${}^2D_{3/2} \rightarrow {}^2P_{3/2}$  (3536 Å) transitions. Following the description of the experiment and presentation of the results, we compare the observed polarizations with those predicted by a simple model which ignores anisotropic final-state interactions.

### II. EXPERIMENTAL

The apparatus consists of three basic parts: the atomic vapor source, the lamp, and the optical detection equipment.<sup>5</sup> Because the Cd II 4416- and 3536-Å transitions lie in different regions of the spectrum, and the former is an order of magnitude more intense than the latter, we found it necessary to make adjustments in the basic apparatus suitable to observation of each transition. Figures 1 and 2 depict the general arrangement of the apparatus as it has been set up to measure the 4416- and the 3536-Å transition, respectively. The principal alteration in the second case is to replace the aluminum window and collimators with a capillary tube and to change the optics for measuring the degree of polarization.

#### A. Atom source

To avoid systematic depolarization caused by collisions, an atomic beam of cadmium is used. The beam effuses from an oven, operated typically at a temperature of 445 °C. This corresponds to a cadmium vapor pressure of 3.5 Torr in the oven and gives rise to a beam intensity of  $\sim 10^{16}$  atoms  $\text{sr}^{-1} \text{sec}^{-1}$ . Water-cooled collimators maintain the beam divergence at 0.04 sr. Both the scattering chamber and the oven chamber are

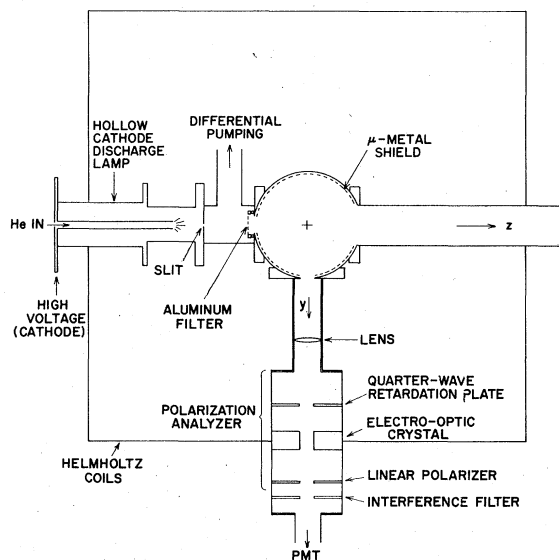


FIG. 1. Schematic diagram of the experimental setup for observing and analyzing the polarization of the Cd II 4416-Å transition.

evacuated by the same 6 in. diffusion pump. The pressure in the scattering chamber during a typical run is measured to be  $8 \times 10^{-6}$  Torr, corresponding to a background density of  $\sim 3 \times 10^{11}$  molecules  $\text{cm}^{-3}$ . At such a low pressure it may be estimated that a cadmium ion in the excited state ( $\tau = 773$  nsec) will make  $\sim 10^{-5}$  collisions before it radiates.

#### B. Ionization source

At the point marked "+" in the figures, the cadmium vapor is crossed with the He I 584-Å radiation from a hollow-cathode discharge lamp<sup>6</sup> of the type described by Newburgh, Heroux, and Hinteregger<sup>7</sup> with the modified cathode described by Newburgh.<sup>8</sup> When operated at pressures  $\geq 1$  Torr, the lamp produces principally the 584-Å line ( $\sim 70\%$ ) and the 304-Å He II resonance line is suppressed. We found that for the purpose of our work it was necessary to operate this basic lamp design in two modifications, one appropriate to each line observed. In obtaining the data for 4416-Å transition, the current to the lamp is drawn from a constant voltage power supply through a 4 k $\Omega$  ballast resistor. The lamp is operated at a pressure of 1.0 Torr, and the operating current is typically 190 mA at 1200 V. In order to obtain the higher light intensities necessary for viewing the 3536-Å transition, the lamp configuration is changed. The constant voltage supply is replaced by a constant current power supply, and the ballast resistor is removed from the circuit. The lamp is operated at a higher pressure,  $\sim 1.5$  Torr,

and a current of typically 300 mA.

At these higher currents and pressures we encounter a major difficulty in performing the experiment, namely that the discharge also produces large quantities of metastable helium atoms in both the  $^1S$  and  $^3S$  states. These states lie at 19.8 eV and 20.2 eV, respectively, above the ground state of the helium atom and can produce the Cd II  $^2D$  states by Penning ionization with a cross section<sup>9</sup> of  $4.5 \times 10^{-15}$   $\text{cm}^2$ , compared with a cross section<sup>4,10</sup> of  $7 \times 10^{-18}$   $\text{cm}^2$  for photoionization. As we only observe radiation from the ions, we have no way of determining whether this radiation is coming from an ion produced by photoionization or Penning ionization. To assure ourselves that no ions we observed were formed by the metastable atoms, we removed the latter from the scattering region by placing a thin aluminum filter behind the lamp and the chamber (see Fig. 1). This filter (Penn Spectra-Tech. Inc., Wallingford, Pa.) is  $\sim 1500$ -Å thick and has a transmission of 12% for the 584-Å line. It is 5.0 cm in diameter and fits into a special mount behind the light collimator. This mount allows the aluminum filter to be removed before evacuation and inserted when the entire system is at operating pressure. This is necessary because the filter will not withstand pressure differentials greater than 10 Torr. Once the aluminum filter is in place, it served as a vacuum-tight seal between the lamp and the scattering chamber, thus preventing flow of helium, both neutral and metastable, into the chamber. The filter not only removes metastable helium atoms, but it also prevents interference from impurity lines with wavelengths greater than 1000 Å and blocks transmission of visible light into the system, a fact which is especially helpful in re-

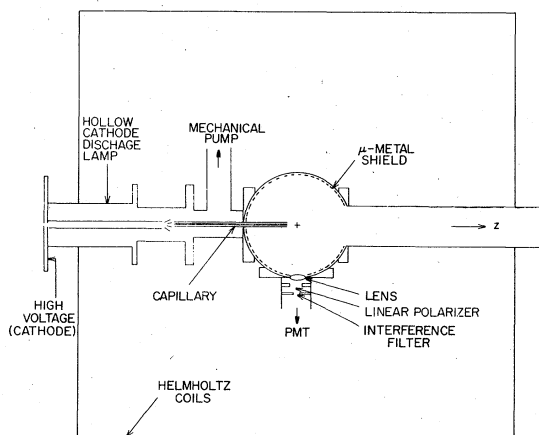


FIG. 2. Schematic diagram of the experimental setup for observing and analyzing the polarization of the Cd II 3536-Å transition.

ducing the background noise.

In order to observe the weak Cd II 3536-Å transition, the aluminum filter and collimators were replaced with a long capillary tube.<sup>11</sup> This tube, 25 cm in length, is inserted through a vacuum tight seal between the lamp and the scattering chamber with one end about 2.5 cm from the discharge and the other about 2.5 cm from the scattering region. It has a bore of 2 mm, and the radiation from the discharge is channeled to the ionization zone by repeated small angle scattering. With this tube in place, we are able to see a signal, although it is still quite low in intensity. There is one possible disadvantage to the use of the capillary, however. With a passage now open for the metastable helium atoms to reach the scattering zone, we might experience interference from Penning ionization, although we expect that repeated collisions with the walls of the capillary should remove the metastable atoms from the system. To check this we repeated the 4416-Å measurement and obtained the same degree of polarization as measured with the foil in place. We feel that this proves that interference from metastable atoms is negligible.

### C. Detection optics

The radiation from the ionized cadmium is viewed along the  $y$  axis (see Fig. 1) perpendicular to the plane formed by the incoming radiation ( $z$  axis) and the atomic beam ( $x$  axis). The 4416-Å radiation is viewed through a 2.5-cm strain-free Pyrex window in the chamber wall followed by a lens with a focal length of 22 cm, placed such that the center of the scattering chamber is at the focal length of the lens. The 3536-Å radiation is viewed with a lens placed directly into the wall of the chamber, the focal length of the lens being such that the center of the chamber is at the focal point. Spectral isolation is accomplished in both cases with a narrow-band interference filter placed after the analyzing optics, the 4416-Å line with a filter (Corion Instrument Corporation), 10-Å FWHM, blocked into the  $x$  ray and the IR, and the 3536-Å radiation with a filter (Baird-Atomic Model S-121), 25-Å FWHM, blocked to the  $x$  ray and to the IR. Photon-counting techniques are used for both measurements because of the low-light levels.

The degree of linear polarization is defined by

$$P = (I_z - I_x) / (I_z + I_x). \quad (1)$$

Here  $I_z$  and  $I_x$  are the intensities of emitted radiation linearly polarized with electric vector pointing along the  $z$  axis and the  $x$  axis, respectively.

Measurement of  $P$  for the visible transition

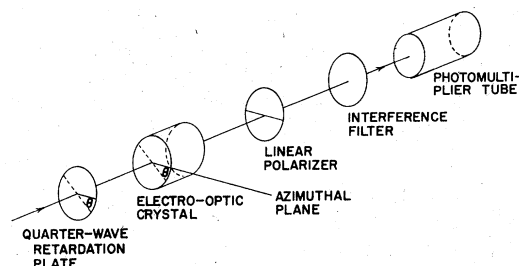


FIG. 3. Optical train of the polarization analyzer. The angle  $\theta$  which the principal axes of the quarter-wave retardation plate and the electro-optic crystal make with the azimuth is  $45^\circ$ .

(4416-Å) is accomplished with the help of a polarization analyzer based on a design of Illing.<sup>12</sup> The optical train consists of a quarter-wave retardation plate, an electro-optic crystal, and a linear polarizer (see Fig. 3). A voltage is applied across the crystal so that it functions as a quarter-wave retardation plate at the wavelength of interest. This voltage is rapidly reversed in direction permitting on alternate cycles the measurement of  $I_z$  and  $I_x$ , provided this instrument has been suitably calibrated. For linearly polarized light (no circular polarization present) the true degree of polarization,  $P$ , is related to the measured degree of polarization,  $P_m$ , by<sup>5</sup>

$$P = P_m / f(\Delta, \delta), \quad (2)$$

where  $f(\Delta, \delta)$  is a constant depending on the fixed retardation  $\Delta$  of the quarter-wave plate and the retardation  $\delta$  of the electro-optic crystal with voltage applied. Using the 100% linearly polarized output of a glan polarizer as a source, the result is obtained:  $f(\Delta, \delta) = 0.881 \pm 0.035$  for our polarization analyzer at the 4416-Å wavelength.

An additional correction to  $P$  is necessary to take into account the lack of parallelism of the radiation being analyzed. It may be shown that Eq. (2) then takes the form

$$P = \frac{a+b}{a-b} \frac{P_m}{f(\Delta, \delta)}, \quad (3)$$

where  $a/b$  is the extinction coefficient of the electro-optic crystal measured for the known divergence of the light source. In the present experiment, the divergence of the collected 4416-Å light is estimated to be  $3.5^\circ$ , leading to the correction  $(a+b)/(a-b) = 1.05$ .

The transmission of the above analyzer is limited to radiation with wavelengths greater than 3700 Å. Therefore, it is necessary for the polarization analysis of the uv transition (3536-Å) to return to the more conventional method of successively determining  $I_z$  and  $I_x$  with linear polarizers placed

with their transmission axes along the  $z$  axis and the  $x$  axis, respectively. The polarizers used in this instance are uv-transmitting sheet polarizers (Polaroid Corp. Model HNP'B). They have a transmission at 3536 Å of 28–30% and an extinction ratio in that region measured to be greater than 200:1. It is necessary to normalize the results to equal transmission of the two polarizers. For purposes of calibrating the transmission a zero-polarization source is used. This source consists of a pen lamp fixed in a mount rotating at 17 Hz followed by a diffuser and a pinhole. If  $S_1$  and  $S_2$  are the signals measured for the two directions of polarization and  $t_1$  and  $t_2$  the calibrated transmissions of the two polarizers, then for large extinction coefficients

$$P = \frac{(t_2/t_1)S_1 - S_2}{(t_2/t_1)S_1 + S_2}. \quad (4)$$

With the aluminum window in place there is no background scattering from the lamp in the chamber, but with the capillary there is some light leakage, especially through the 3536-Å filter. In order to be able to correct for this background signal, a beam flag is built into the system, and signals are recorded with the beam on and the beam off and subtracted. For the 4416-Å study, counts are taken for 100-sec periods, beam on and beam off, and for the 3536-Å study, counts are taken for 10-sec periods, alternating  $I_z$  and  $I_x$  and beam on and beam off for each  $I_z$  and  $I_x$  to take into account any possible polarization of the background. Counting is done for the duration of the beam, and the average counting rate is 200 counts/sec for the 4416-Å light and 20 counts/sec for the 3536-Å light.

#### D. Magnetic field effects

The  ${}^2D_{5/2}$  and  ${}^2D_{3/2}$  states of the cadmium ion have  $g$  values of 1.2 and 0.8 and lifetimes of 773<sup>13</sup> and 280 nsec,<sup>14</sup> respectively. For such large  $g$  values and long lifetimes, magnetic field depolarization (Hanle effect) becomes quite important. In particular, for the  ${}^2D_{5/2}$  level, a field of 60-mG perpendicular to the excitation direction is enough to reduce the degree of polarization of the transition by 50%. Thus the magnetic field of the earth is sufficient to cause significant depolarization of the 4416-Å transition. In order to reduce the effects of the Earth's field, the apparatus is surrounded by three orthogonal pairs of Helmholtz coils, which are adjusted to give zero field at the center of the chamber. In addition, all potentially magnetic parts have been removed from the region inside the coils, and the inside of the scattering chamber is lined with  $\mu$  metal. The oven pro-

duces a residual ac field of 5 mG. This, however, is deemed too small to warrant further attention. Before each run the field at the center of the scattering zone is measured with a temperature-compensated Hall-effect probe (Bell model T-6010), and in each case the residual field amounts to less than 10 mG. These fields cause a reduction in the degree of polarization given by<sup>15</sup>

$$P = \frac{P_0}{1 + (2g\mu\tau H/\hbar)^2}. \quad (5)$$

Here  $P$  is the measured degree of polarization,  $P_0$  the true polarization,  $g$  the atomic  $g$  factor,  $\tau$  the lifetime of the state, and  $\mu$  the Bohr magneton. For the 4416-Å transition  $2g\mu\tau/\hbar = 16.3 \text{ G}^{-1}$ , using the values of  $\tau = 773$  nsec and  $g = 1.2$ . This gives a correction for a 10-mG field of  $P/P_0 = 0.974$ . For the 3536-Å transition, since  $\tau = 280$  nsec and  $g = 0.8$ ,  $2g\mu\tau/\hbar = 3.937 \text{ G}^{-1}$ , and  $P/P_0 = 0.998$ . For this latter transition the effect of this correction on the result is negligible compared with the error in the counting statistics.

To check that the compensating fields were working correctly, one run was made with the  $\mu$  metal removed. During the run the Helmholtz coils were alternately adjusted between the following pair of conditions: (a) a net field of 1.0 G along the  $z$  axis (light propagation direction) with less than 10 mG along the  $x$  and  $y$  axes and (b) no compensation for the Earth's field in any direction (power supply to coils switched off). The magnitude of the polarization of the 4416-Å transition was observed to drop considerably, from  $-0.05$  with the former arrangement to  $-0.01$  with the latter. This test not only points out the sensitivity of our experiment to stray magnetic fields but demonstrates that the degree of polarization we observe is a property of the cadmium-ion excited state rather than being of instrumental origin.

### III. RESULTS

Using the experimental arrangement described in Sec. II, we have measured the degree of polarization,  $P$ , for the Cd II  ${}^2D_{5/2} \rightarrow {}^2P_{3/2}$  (4416-Å) and the Cd II  ${}^2D_{3/2} \rightarrow {}^2P_{3/2}$  (3536-Å) transitions. The availability of the polarization analyzer and the larger signal of the 4416-Å transition made the determination of  $P$  more accurate for this transition. Each value of  $P$  is a weighted average of three independent experimental runs according to the method outlined by Young.<sup>16</sup> Table I presents the results of each run along with error estimates. All data have been corrected for magnetic field depolarization and for the calibration of the optics, but the effect of the presence of hyperfine structure has not been taken into account. For the

TABLE I. Values  $P_h$  and  $\sigma$  for each individual run. ( $\sigma$  = one standard deviation).

Trial	Polarization	$\sigma$
4416-Å transition		
1	-0.045	0.010
2	-0.040	0.006
3	-0.048	0.012
3536-Å transition		
1	0.057	0.086
2	0.078	0.050
3	0.137	0.062

transition at 4416 Å ( ${}^2D_{5/2} \rightarrow {}^2P_{3/2}$ ) we find

$$P_h\left(\frac{5}{2} \rightarrow \frac{3}{2}\right) = -0.042 \pm 0.005. \quad (6)$$

For the 3536 Å ( ${}^2D_{3/2} \rightarrow {}^2P_{3/2}$ ) we find

$$P_h\left(\frac{3}{2} \rightarrow \frac{3}{2}\right) = +0.094 \pm 0.036. \quad (7)$$

The signs of the values of  $P_h$  refer to the definition of  $P$  in Eq. (1).

Having obtained  $P_h$ , hyperfine corrections are now made. Cadmium has eight isotopes; all have zero nuclear spin except for  ${}^{111}\text{Cd}$  and  ${}^{113}\text{Cd}$ , which have a spin of  $I = \frac{1}{2}$ . The abundance of the latter two is only 25.01% of the total. Therefore, one would expect that there would be a small depolarization caused by transitions involving these isotopes. Since this correction is quite involved but not major, we have made a crude estimate based on the depolarization of resonance fluorescence for the same transitions.<sup>5</sup> The final values for the degree of polarization corrected for hyperfine structure are for the transition  ${}^2D_{5/2} \rightarrow {}^2P_{3/2}$  (4416 Å)

$$P\left(\frac{5}{2} \rightarrow \frac{3}{2}\right) = -0.052 \pm 0.005, \quad (8)$$

and for the transition  ${}^2D_{3/2} \rightarrow {}^2P_{3/2}$  (3536 Å)

$$P\left(\frac{3}{2} \rightarrow \frac{3}{2}\right) = +0.12 \pm 0.04. \quad (9)$$

The errors quoted above are one standard deviation. With a 90% confidence limit both Cd II transitions are found to be polarized, but with opposite sign.

There is an additional effect which can give rise to errors in the polarization measurements, namely, the possibility that the  ${}^2D$  states observed may be produced by cascade. Between the  ${}^2D$  levels lying at 17.58 and 18.27 eV above the ground state of the atom and the 21.22 eV of the photon there are five states which can be produced: (1)

$4d^{10}6s {}^2S_{1/2}$  at 19.28 eV; (2)  $4d^{10}5d {}^2D_{3/2}$  at 20.11 eV; (3)  $4d^{10}5d {}^2D_{5/2}$  at 20.13 eV; (4)  $4d^{10}6p {}^2P_{1/2}$  at 20.73 eV; and (5)  $4d^{10}6p {}^2P_{3/2}$  at 20.81 eV. All of these states may be reached by a one-photon transition from configurations mixed into the ground state of the atom. Of these five states, however, only the  ${}^2P$  levels can be connected by an electric dipole transition to the  ${}^2D$  levels under consideration. Süzer and Shirley<sup>17</sup> have measured the photoelectron energy distribution of electrons from cadmium using the 584-Å He I resonance radiation. By far the most intense peaks correspond to direct production of the  ${}^2D_{5/2}$  and the  ${}^2D_{3/2}$  levels. While they do see production of the  $4d^{10}5p {}^2P_{1/2}$  and  ${}^2P_{3/2}$  states with an apparent relative intensity of 0.02, they do not see any indication of any of the states above the  ${}^2D$  levels. We conclude, therefore, that cascade effects can be ignored and that the  ${}^2D$  states we observe are produced by direct photoionization. This being the case, the experimental results indicate that there is alignment of both the  ${}^2D_{5/2}$  and the  ${}^2D_{3/2}$  states in the photoionization of cadmium with the radiation from the helium resonance line at 21.22 eV.

#### IV. SIMPLE MODEL FOR TARGET ALIGNMENT BY PHOTOIONIZATION

In what follows we calculate the alignment induced in the target ion by photoionization of the target atom with a unidirectional beam of unpolarized light. These calculations are carried out with the same assumptions as the Cooper-Zare<sup>18</sup> calculation for the asymmetry parameter  $\beta$  characterizing the angular distribution of the photoelectron. In particular, we use  $LS$  coupling to describe the initial and final states and we neglect anisotropic final-state interactions between the outgoing electron and the remaining target ion. At the outset, we cannot expect that such simple considerations will describe the photoionization of cadmium where the predicted values of  $\beta$  for the two fine-structure components  ${}^2D_{3/2}$  and  ${}^2D_{5/2}$  of the cadmium ion cannot be reconciled with the experimentally determined  $\beta$  values.<sup>19</sup> However, the motivation for this calculation is that it demonstrates that, in general, alignment can be expected in the target ion provided the outgoing electron is not removed from an  $s$  orbital, and it serves as a reference point for comparing more involved calculations that take into account anisotropic final-state electron-ion interactions.<sup>20</sup>

The initial state of the atom is described by the antisymmetrized wave function

$$|L_i S_i J_i M_i\rangle = \frac{1}{\sqrt{N!}} \sum_p \sum_{M_{Li}, M_{Si}} (-1)^p P[J_i]^{1/2} (-1)^{S_i - L_i - M_i} \begin{pmatrix} L_i & S_i & J_i \\ M_{Li} & M_{Si} & -M_i \end{pmatrix} \Psi(L_i M_{Li} S_i M_{Si}), \quad (10)$$

where the quantization axis is taken to be along the direction of the light beam.

Following photoionization, the system (ion plus photoelectron) is described by

$$|L_\alpha S_\alpha J_\alpha M_\alpha\rangle = \frac{1}{\sqrt{N!}} \sum_p (-1)^p P |L'S'J'M'\rangle |\bar{k}, s, m_s\rangle. \quad (11)$$

Here  $|L'S'J'M'\rangle$  represents the excited ion and  $|\bar{k}, s, m_s\rangle$  the outgoing electron. We expand the latter in partial waves,

$$|\bar{k}, s, m_s\rangle = \sum_{l', m'} a(l', m') Y_{l', m'}(\hat{r}) G_{kl'}(r) |s m_s\rangle, \quad (12)$$

where

$$a(l', m') = 4\pi(i)^{l'} e^{-i\delta_{l'}} Y_{l', m'}^*(\hat{k}). \quad (13)$$

In Eqs. (12) and (13)  $\delta_{l'}$  is the phase shift of the  $l'$ th partial wave and  $G_{kl'}(r)$  is the continuum radial wave function.

Subsequently, the excited system makes a radiative transition to the final state

Equation (14) assumes that the transition is between the ion states  $J'M'$  and  $J''M''$  and that the photoelectron plays only the role of a spectator. The justification for this approximation is that for the problems we are considering the characteristic time for the electron to "escape" from the target is very short compared to the radiative lifetime of the transition. Note that this may not hold for photoionization near threshold or for autoionizing states.

$$|L_f S_f J_f M_f\rangle = \frac{1}{\sqrt{N!}} \sum_p (-1)^p P |L'' S'' J'' M''\rangle |\bar{k}, s, m_s\rangle. \quad (14)$$

Let us further suppose that the photoionization occurs by an electric dipole transition as does the subsequent ion emission. Then the emitted intensity of polarization  $q$  from the excited ion produced by a beam of unpolarized light will be proportional to<sup>5</sup>

$$I(q) = [J_i]^{-1} \sum_{M_i, M_f} \int d\bar{k} \sum_{q'=\pm 1, -1} \left| \sum_{M_\alpha} \langle J_i M_i | r C_q^1 | J_\alpha M_\alpha \rangle \langle J_\alpha M_\alpha | r C_q^1 | J_f M_f \rangle \right|^2, \quad (15)$$

where  $C_q^1 = (3/4\pi)^{-1/2} Y_{1q}$ . In Eq. (15) we average over all initial magnetic substates (since the target is unpolarized) and sum over all final magnetic substates of the ion and photoelectron. In addition, we integrate over the unobserved photoelectron angular distribution. Note that the summation over different intermediate states connecting the same initial and final state must be performed before squaring the probability amplitudes. We treat the unpolarized ionizing radiation as an incoherent superposition of left and right circularly polarized light.

In the present experiment we measure the degree of linear polarization,  $P$ , from which information

about the extent of alignment can be inferred. We define  $P$  by

$$P = \frac{I_z - I_x}{I_z + I_x}, \quad (16)$$

where

$$I_z = I(0) \quad (17)$$

and

$$I_x = \frac{1}{2} [I(+1) + I(-1)]. \quad (18)$$

The evaluation of Eq. (15) for  $I(q)$  is straightforward. The key matrix elements are of the form (omitting constant factors):

$$\begin{aligned} \langle J_i M_i | r C_q^1 | J_\alpha M_\alpha \rangle &= \sum_{l', m'} \sum_{M_L', M_S'} \sum_{M_{Li}, M_{Si}} \sum_m a(l', m') l^{1/2} \sigma_{l'} [J']^{1/2} [S_i]^{1/2} [J_i]^{1/2} [L_i]^{1/2} \\ &\times (-1)^K \begin{pmatrix} L_i & S_i & J_i \\ M_{Li} & M_{Si} & -M_i \end{pmatrix} \begin{pmatrix} L' & S' & J' \\ M_L' & M_S' & -M' \end{pmatrix} \begin{pmatrix} S' & s & S_i \\ M_S' & m_s & -M_{Si} \end{pmatrix} \\ &\times \begin{pmatrix} L_i & L' & l \\ -M_{Li} & M_L' & -m \end{pmatrix} \begin{pmatrix} l' & 1 & l \\ m' & q' & m \end{pmatrix} \end{aligned} \quad (19)$$

and

$$\langle J_\alpha M_\alpha | r C_q^1 | J_f M_f \rangle = (-1)^{J' - M'} \begin{pmatrix} J' & 1 & J'' \\ -M' & q & M'' \end{pmatrix}, \quad (20)$$

where  $l_>$  is the greater value of  $l$  and  $l'$ ,

$$\kappa = -M' + q' + s - M_{S_i} + S_i - M_i + L_i + 1 + \frac{1}{2}(l' - l + 1) + l + l' - m' + M'_L + m \quad (21)$$

and

$$\sigma_{l'} = \int_0^\infty P_{nl}(r) r G_{kl'}(r) dr \quad (22)$$

is the reduced radial matrix element of the electric dipole operator connecting the bound electron  $nl$  to the outgoing electron  $kl'$ .

For the special case of photoionization of the target initially in a  $^1S_0$  state, Eq. (19) reduces to

$$\langle 00 | r C_q^1 | J_\alpha M_\alpha \rangle = \sum_{l', m'} a(l', m') l_{>}^{1/2} (-1)^{-M' + l' + m_s + (l' - l + 1)/2} \times [J']^{1/2} [S']^{-1/2} [L']^{-1/2} \begin{pmatrix} L' & S' & J' \\ -m' - q' & -m_s & -M' \end{pmatrix} \begin{pmatrix} l' & 1 & l \\ m' & q' & -m' - q' \end{pmatrix}, \quad (23)$$

and Eq. (15) becomes

$$I(q) = \sum_{q' = +1, -1} \sum_{l'} f(q', q, l') l_{>} \sigma_{l'}^2, \quad (24)$$

where

$$f(q', q, l') = \sum_{m', m_s} \left[ \begin{pmatrix} l' & 1 & l \\ m' & q' & -m' - q' \end{pmatrix} \begin{pmatrix} L' & S' & J' \\ -m' - q' & -m_s & m' + q' + m_s \end{pmatrix} \begin{pmatrix} J' & 1 & J'' \\ m' + q' + m_s & q & -m' - q' - m_s - q \end{pmatrix} \right]^2. \quad (25)$$

Thus the degree of linear polarization has the form

$$P = \frac{A + BR}{C + DR}, \quad (26)$$

where

$$R = \sigma_{l+1}^2 / \sigma_{l-1}^2, \quad (27)$$

and the coefficients  $A$ ,  $B$ ,  $C$ , and  $D$  are linear combinations of  $f(q', q, l')$ .  $P$  ranges from  $A/C$  to  $B/D$  as  $R$  varies from zero to infinity. For the case where an  $s$  electron is removed,  $P=0$ , corresponding to the vanishing of  $B$ . As first shown by Flügge, Mehlhorn, and Schmidt,<sup>1</sup> this is to be expected.

For the photoionization of Cd by the direct removal of a  $d$  electron, the coefficients  $A$ ,  $B$ ,  $C$ , and  $D$  are given in Table II for the various possible fine-structure transitions. In Fig. 4 we present

TABLE II. Values of the polarization coefficients for ejection of a  $d$  electron from a closed-shell atom.

Coefficient	Transition		
	$^2D_{5/2} \rightarrow ^2P_{3/2}$	$^2D_{3/2} \rightarrow ^2P_{3/2}$	$^2D_{3/2} \rightarrow ^2P_{1/2}$
$A$	$-\frac{7}{3}$	$\frac{7}{3}$	$-\frac{7}{3}$
$B$	$-1$	$1$	$-1$
$C$	$\frac{31}{3}$	$\frac{107}{9}$	$\frac{73}{9}$
$D$	$\frac{49}{3}$	$17$	$13$

the variation of  $P$  with  $R$ . We see that this calculation predicts each transition is polarized, but  $P$  becomes an insensitive function of  $R$  for increasing  $R$ . On comparing these values of  $P$  with the experimentally determined values, we observe that

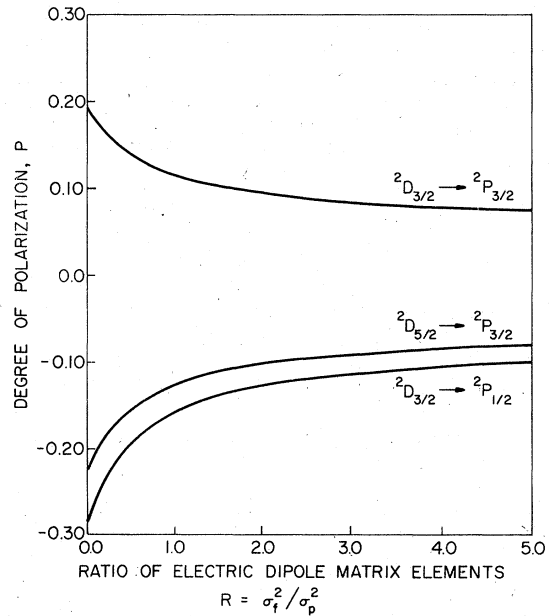


FIG. 4. Plot of the calculated degree of polarization,  $P$ , as a function of the ratio,  $R = \sigma_d^2 / \sigma_p^2$ , for the transitions Cd II  $^2D \rightarrow ^2P$  following photoionization of Cd atoms by an unpolarized light beam.

this model correctly predicts the sign of  $P$  for the two transitions we have measured, but it is not possible to find any value of  $R$  that matches the observed values of  $P$  within the experimental error. This failure of the model suggests that a more sophisticated treatment will be necessary to describe the target alignment by photoionization of cadmium with the He I 584-Å resonance line.

In closing, it is worthwhile to inquire whether the measurement of target-ion alignment contains information about the photoionization dynamics which is different from that contained in the photo-

electron angular distribution. First, we examine this question in light of the above model. For unpolarized light the angular distribution may be written as<sup>21</sup>

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{tot}}}{4\pi} \left[ 1 - \frac{1}{2}\beta P_2(\cos\theta) \right], \quad (28)$$

where  $\theta$  is the angle the photoelectron makes with the direction of the light beam,  $P_2$  is the Legendre polynomial of order two,  $\sigma_{\text{tot}}$  is the total cross section, and  $\beta$  is the asymmetry parameter. The calculation of  $\beta$  by Cooper and Zare<sup>18</sup> yields

$$\beta = \frac{l(l-1)\sigma_{i-1}^2 + (l+1)(l+2)\sigma_{i+1}^2 - 6l(l+1)\sigma_{i+1}\sigma_{i-1} \cos(\delta_{i+1} - \delta_{i-1})}{(2l+1)[l\sigma_{i-1}^2 + (l+1)\sigma_{i+1}^2]}. \quad (29)$$

On comparing Eq. (29) for  $\beta$  with Eq. (17) for  $P$  it may be seen that  $\beta$  depends on the radial matrix elements  $\sigma_{i-1}$  and  $\sigma_{i+1}$  as well as on the phase-shift difference ( $\delta_{i+1} - \delta_{i-1}$ ) whereas  $P$  depends only on the ratio of  $\sigma_{i+1}^2$  to  $\sigma_{i-1}^2$  and is independent of the phase-shift difference. The absence of phase-shift dependence in the formula for  $P$  results from the average over the unobserved electron. Similarly the absence of alignment dependence in  $\beta$  arises from the average over the unobserved tar-

get ion magnetic substates. This suggests that the measurement of both  $P$  and  $\beta$  for the same system will yield complementary information.

#### ACKNOWLEDGMENTS

We thank Professor H. M. Foley and Professor W. Happer for helpful discussions in the course of this work. Support by the National Science Foundation is gratefully acknowledged.

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<sup>1</sup>S. Flügge, W. Mehlhorn, and V. Schmidt, Phys. Rev. Lett. **29**, 7 (1972).

<sup>2</sup>V. L. Jacobs, J. Phys. B **5**, 2257 (1972).

<sup>3</sup>J. F. Papp and F. A. Franz, Phys. Rev. A **5**, 1763 (1972).

<sup>4</sup>R. B. Cairns, H. Harrison, and R. I. Schoen, J. Chem. Phys. **51**, 5440 (1969).

<sup>5</sup>C. D. Caldwell, thesis (Columbia University, 1976) (unpublished).

<sup>6</sup>The particular lamp we used was designed and built by Dr. Henry Tang, presently at Bell Telephone Laboratories. We thank Dr. Tang for his permission to use the lamp and for his assistance in adjusting it to optimum operating efficiency.

<sup>7</sup>R. G. Newburgh, L. Heroux, and H. E. Hinteregger, Appl. Opt. **1**, 733 (1962).

<sup>8</sup>R. G. Newburgh, Appl. Opt. **2**, 864 (1963).

<sup>9</sup>L. D. Shearer and F. A. Padovani, J. Chem. Phys. **52**, 1618 (1970).

<sup>10</sup>G. V. Marr and J. M. Austin, Proc. R. Soc. A **310**, 137 (1969).

<sup>11</sup>J. L. Dehmer and J. Berkowitz, Phys. Rev. A **10**, 484

(1974). We thank Dr. Dehmer for his suggestions regarding the use of this capillary.

<sup>12</sup>R. M. E. Illing, thesis (Columbia University, 1973) (unpublished).

<sup>13</sup>L. D. Shearer and W. C. Holton, Phys. Rev. Lett. **24**, 1214 (1970).

<sup>14</sup>J. Hamel, J. Margene, and J.-P. Barrat, Opt. Commun. **12**, 409 (1974).

<sup>15</sup>R. N. Zare, Acc. Chem. Res. **4**, 361 (1971).

<sup>16</sup>H. D. Young, *Statistical Treatment of Experimental Data* (McGraw-Hill, New York, 1962).

<sup>17</sup>S. Süzer and D. A. Shirley, J. Chem. Phys. **61**, 2481 (1974).

<sup>18</sup>J. Cooper and R. N. Zare, J. Chem. Phys. **48**, 942 (1968); J. Cooper and R. N. Zare, *Lectures in Theoretical Physics*, edited by S. Geltman, K. Mahanthappa, and N. Brittin (Gordon and Breach, New York, 1969), Vol. 11c, p. 317.

<sup>19</sup>H. Harrison, J. Chem. Phys. **52**, 901 (1970).

<sup>20</sup>Prof. D. Dill, Department of Chemistry, Boston University, has communicated to us that the calculation of target polarization can be analyzed in terms of different angular momentum transfers, in the same manner as in the calculation of the photoelectron angular distribution [see D. Dill, Phys. Rev. A **7**, 1976 (1973)].

<sup>21</sup>C. N. Yang, Phys. Rev. **74**, 764 (1948).