Photonization-produced alignment of Cd

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The degree of polarization of a target ion excited by (inner-shell) photoionization is shown to depend on only two parameters in Dill's angular-momentum-transfer formalism. The measured alignment of Cd*+ 2D5/2,3/2 is corrected for unresolved hyperfine structure, showing that anisotropic electron-ion interactions are substantially stronger than previously thought.

I. INTRODUCTION

The linear polarization of fluorescence emitted after an atom is photoionized can be a sensitive probe of electron correlations. Like the photoelectron angular distribution, the fluorescence polarization often reflects the photoionization dynamics more sharply than a total cross-section measurement. While there have been numerous photoelectron angular distribution studies, there appears to be only one atomic polarization measurement in photoionization, namely,

\[ \text{Cd} 4d^{10} 5s^2 1S_0 + h\nu \rightarrow \text{Cd}^+ 4d^9 5s^2 2D_{3/2,5/2} + e^- . \]

The polarization of the \( \text{Cd}^+ 2D_{5/2} \rightarrow 2P_{3/2} \) line \((P = -0.052 \pm 0.005)\) and of the \( \text{Cd}^+ 2D_{3/2} \rightarrow 2P_{3/2} \) line \((P = 0.12 \pm 0.04)\) have been measured by Caldwell and Zare\(^6\) using unpolarized incident photons with an energy of 21.2 eV. More recently Mauser and Mehlhorn\(^3\) have measured the polarization of the \( \frac{5}{2} \rightarrow \frac{3}{2} \) transition obtaining \( P = -0.054 \pm 0.004 \), in good agreement with Ref. 1.

The most striking result of these experiments has been their demonstration of the importance of anisotropic interactions between the photoion and photoelectron. A nonrelativistic model of photoionization formulated by Cooper and Zare (CZ),\(^3\) which ignores all such anisotropic interactions, predicts that for the \( \frac{5}{2} \rightarrow \frac{3}{2} \) transition the polarization must lie within the limits

\[ -0.226 \leq P_{\text{CZ}} \leq -0.061 , \]

which does not include the measured values of Refs. 1 and 2. Klar\(^4,5\) has recently derived a rigorous treatment which allows for anisotropic final-state interactions. He has obtained a three-parameter expression for the polarization of this line. This treatment predicts for the \( \frac{5}{2} \rightarrow \frac{3}{2} \) transition that

\[ -0.226 \leq P \leq 0.209 , \]

which is compatible with the experiments.

The main purpose of the present article is to show how the use of Dill's angular-momentum-transfer treatment of fluorescence polarization\(^6\) leads to a simpler, equivalent parametrization of \( P \) involving only two undetermined parameters.

Comparison of the Klar\(^4,5\) and Dill\(^6\) approaches amplifies the physical meaning of the angular-momentum-transfer formulation. The basic difficulty faced by any approach treating an anisotropy produced by photoionization is the great multiplicity of degenerate continuum channels contributing coherently to the anisotropy. In earlier work treating the photoelectron asymmetry parameter \( \beta \), Dill and Fano\(^7\) circumvented this problem by introducing a new set of continuum channels whose contributions to \( \beta \) add incoherently. These channels are characterized not by the usual \( jj \) coupling, but rather by \( \vec{j}_e \), the angular momentum transferred between unobserved photofragments,

\[ \vec{j}_e = \vec{j}_t + \vec{s} - \vec{j}_0 = \vec{j}_{\text{ph}} - \vec{l} . \]

Here \( \vec{j}_0 \) is the ground-state angular momentum of the atom or molecule, \( \vec{s} \) and \( \vec{l} \) are the spin and orbital angular momenta of the photoelectron, \( \vec{j}_{\text{ph}} \) is the unit angular momentum transferred to the target by the electric-dipole photon, and \( \vec{j}_t \) is the angular momentum of the ionic state after the photoionization. Using this set of continuum channels the expression for \( \beta \) is simply

\[ \beta = \sum_{\vec{j}_t} \left| S(j_t) \right|^2 \beta(j_t) \sum_{\vec{j}_t} \left| S(j_t) \right|^2 , \]

where \( S(j_t) \) is the amplitude for photoionization into the continuum channel characterized by the
angular-momentum-transfer quantum number \( j_i \), and expressions for \( \beta(j_i) \) are given in Ref. 7.

Klar’s treatment of photoionization-produced alignment utilizes this same set of amplitudes, obtaining for the polarization, or for the equivalent Fano-Macek\(^8\) alignment parameter \( A_{0}^{\text{col}} \) [see Eq. (12) below for the relation between \( P \) and \( A_{0}^{\text{col}} \)] an expression of the form,

\[
A_{0}^{\text{col}} = \sum_{j_i,j_i'} \left| S(j_i)S(j_i')A_{0}^{\text{col}}(j_i,j_i') \right| \sum_{j_i} \left| S(j_i) \right|^{2},
\]

where \( A_{0}^{\text{col}}(j_i,j_i') \) is a complicated quantity given in Refs. 4 and 5. The presence of interference terms with \( j_i \neq j_i' \) illustrates the greater complexity of Eq. (5) for \( A_{0}^{\text{col}} \) compared with Eq. (4) for \( \beta \).

The Dill treatment of Ref. 6 introduces a different angular-momentum transfer \( \tilde{t} \) to calculate the alignment. Here \( \tilde{t} \) is the unobserved angular momentum that is transferred from the target to the photofragments. Since the ion is observed instead of the photoelectron, \( \tilde{t} \) is defined as

\[
\tilde{t} = \tilde{s} + \tilde{J} = \tilde{\rho}_{\text{h}} - \tilde{\rho}_{\text{i}}.
\]

Dill’s analysis thus results in the much simpler incoherent average,

\[
A_{0}^{\text{col}} = \sum_{l} \left| S(t) \right|^{2} A_{0}^{\text{col}}(t) / \sum_{l} \left| S(t) \right|^{2},
\]

where the \( S(t) \) are new photoionization amplitudes. We have extended the Dill treatment somewhat by evaluating the alignment \( A_{0}^{\text{col}} \) explicitly and showing the following:

(i) \( A_{0}^{\text{col}}(t) \) depends only on the angular-momentum quantum numbers of the excited ion \( j_i \) and the transfer \( t \). This is a simplification beyond Eq. (4) for \( \beta \) as \( \beta(j_i) \) depends on the dynamics.

(ii) The alignment of a target-ion state with angular momentum \( \tilde{J}_j \) depends generally on only three such terms in Eq. (7), and hence on two amplitude ratios only.

(iii) Parity-favored and parity-unfavored contributions\(^9\) to \( A_{0}^{\text{col}} \) have opposite signs.

Finally in this article, we reconsider the effect of unresolved hyperfine structure on the ionic alignment. It is important to treat this correctly, because theories of the ionic alignment generally address only the electronic contribution to the alignment, ignoring the precession of nuclear spin. Using the Percival-Seaton approach\(^10\) as reformulated by Fano and Macek\(^8\), we extract the “electronic” alignment. Reexamination of the experiments of Refs. 1 and 2 yields new values of the electronic polarization in the \( \text{Cd}^+ \rightarrow P_{3/2} \rightarrow P_{3/2} \) transitions. The revised values imply a substantially greater departure from the model of Cooper and Zare than originally thought.

II. ANGULAR-MOMENTUM-TRANSFER TREATMENT

Most treatments of atomic photoionization\(^11\) consider a photoelectron escaping with angular momentum \( \tilde{J}_e = \tilde{s} + \tilde{t} \) from an ion with angular momentum \( \tilde{J}_i \). The partial cross section for photoionization leaving the ion in the state \( |j_i \rangle \) is then an incoherent sum over all final-state angular momenta:

\[
\sigma(j_i) = C_0 \sum_{l,j_f} \left| \langle j_i l | \sum_{j_f} \sigma(j_f) | j_f \rangle \right|^2.
\]

Here we have introduced the reduced dipole matrix element between the ground-state and the energy-normalized final-state continuum wave function satisfying the usual incoming wave boundary condition at \( r \to \infty \). The constant \( C_0 \) is proportional to the photon energy and is given in Ref. 11. The polarization of light emitted during a dipole transition \( j_i \to j_f \) depends on the partial cross sections \( \sigma(j_f | m_i) \) for leaving the ion with alternative \( m_i \) quantum numbers. If the photoelectron escape direction is not detected, then the polarization and angular distribution of the radiation are completely specified in terms of the Fano-Macek\(^8\) alignment parameter \( A_{0}^{\text{col}}(j_i) \):

\[
I(\theta,\psi) = I_\theta \left[ 1 - \frac{1}{2} h^{(2)}(j_i,j_f) A_{0}^{\text{col}}(j_i) P_2(\cos \theta) + \frac{1}{2} h^{(2)}(j_i,j_f) A_{0}^{\text{col}}(j_i) \sin^2 \theta \cos 2\psi \right],
\]

where the alignment depends only on the excited ionic state,

\[
A_{0}^{\text{col}}(j_i) = \sum_{m_i} \sigma(j_i m_i) \left[ \frac{3m_i^2 - j_i(j_i + 1)}{j_i(j_i + 1)} \right] \sum_{m_i} \sigma(j_i m_i).
\]

In Eq. (9) \( \theta \) is the angle between the detector and the quantization axis, while \( \psi \) is the angle between the
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detector polarization axis and the quantization axis. For linearly polarized incident photons the quantization axis is the photon polarization axis, while for unpolarized incident photons it is the photon propagation axis. The factor $h^{[2]}(j_l,j_f)$ isolates the effect of the final state on the distribution of emitted light. Explicit evaluation of $h^{[2]}(j_l,j_f)$ [see Eq. (8) of Ref. 8] gives

$$h^{[2]}(j_l,j_f) = \begin{cases} -j_l/(2j_l+3), & j_f = j_l+1 \\ 1, & j_f = j_l \\ -(j_l+1)/(2j_l-1), & j_f = j_l-1 \end{cases}$$

(11)

The polarization $P = (I||_1 - I_1)/(I||_1 + I_1)$ is related to the alignment by

$$P = 3h^{[2]}(j_l,j_f)A_0^{\text{col}}(j_l)/[4 + h^{[2]}(j_l,j_f)A_0^{\text{col}}(j_l)] .$$

(12)

Accordingly we need only to focus attention on the partial cross section $\sigma(j_l,m_l)$. Unlike Eq. (8) for $\sigma(j_l)$, however, $\sigma(j_l,m_l)$ involves a coherent summation over $J$, although the summation over $l$ and $j_e$ remains incoherent. Dill has shown how to remove this added complexity. By introducing $t$, the angular momentum transferred to the photoelectron [see Eq. (6)], Dill defines a new set of amplitudes

$$S(J_0,l,j_e,j_l;t) = \sum_{J} \left[ 2t + 1 \right]^{1/2} \left[ \begin{array}{c} J_l \\ J_e \\ J \\ J_0 \\ l \\ t \end{array} \right] (j_l sl j_l ||_1 t) (j_l ||_1 t) .$$

(13)

Within normalization, this results in the incoherent summation

$$\sigma(j_l,m_l) = \sum_{J_0,l_j_j_l} |S(J_0,l,j_e,j_l;t)|^2 (j_l m_l |q - m_l | |q)|^2 .$$

(14)

Here $q$ is the component of incident photon angular momentum along the quantization axis. For linearly polarized incident light we use $q = 0$, while for unpolarized incident light we average the $q = \pm 1$ results.

Equation (14) shows how the $m_l$ dependence of $\sigma(j_l,m_l)$ arises only through Wigner coefficients. Consequently, the separate contributions of each transfer $t$ to $A_0^{\text{col}}$ in Eq. (14) can be evaluated analytically. For linearly polarized incident photons Eq. (14) becomes

$$A_0^{\text{col}}(j_l) = \sum_{t} |S(j_l;t)|^2 A_0^{\text{col}}(j_l;t) ,$$

(15)

where $|S(j_l;t)|^2 = \sum_{J_0,l_j_j_l} |S(J_0,l,j_e,j_l;t)|^2$ and the summation over $t$ is restricted to the values $j_l - 1, j_l$, and $j_l + 1$. In Eq. (15) we have introduced the universal alignment function $A_0^{\text{col}}(j_l;t)$, whose nonvanishing values are

$$A_0^{\text{col}}(j_l;t) = \begin{cases} -\frac{2}{5} + \frac{3}{5(j_l+1)}, & t = j_l + 1 \text{(parity favored)} \\ -\frac{2}{5} - \frac{3}{5j_l}, & t = j_l - 1 \text{(parity favored)} \\ \frac{4}{5} - \frac{3}{5j_l(j_l+1)}, & t = j_l \text{(parity unfavored)} \end{cases}$$

(16)

For unpolarized incident light the right-hand side of Eq. (16) must be multiplied by $-\frac{1}{2}$.

Equations (15) and (16) constitute the key results of this article. They show how the alignment $A_0^{\text{col}}(j_l)$ is the incoherent average of three alternative values of the transfer $t$. Moreover, Eq. (15) fully disentangles the dynamical considerations, contained in $S(j_l;t)$, from the geometrical, contained in the universal alignment function $A_0^{\text{col}}(j_l;t)$, which depends solely on the values of $t$ and $j_l$. The universal alignment function of Eq. (16) is plotted in Fig. 1. Note that the parity-favored terms ($t \neq j_l$) are negative, while the parity-unfavored term ($t = j_l$) is positive (except for the trivial cases with
$j_l < 1$, for which $A_{0}^{\text{col}} \equiv 0$). Though not identical, this is analogous to the difference between parity-favored and parity-unfavored contributions to the angular distribution asymmetry parameter $\beta$. The parity-unfavored contributions to $\beta$ are always identically $-1$, while parity-favored contributions may range from $-1$ to $2$, depending on the dynamics. Reference 7(a) also showed that an unfavored photoelectron angular distribution reflects the presence of internal torques in the photoelectron-photoion dynamics. Such torques imply the presence of pseudotensor dynamical elements, as amplified in Refs. 12 and 13. This observation should apply as well to unfavored contributions to the alignment.

Consider once again the processes

$$\text{Cd}^+ (^1S_0) + h\nu \rightarrow \text{Cd}^+ (^2D_{5/2;3/2}) + e^- \quad \rightarrow \quad \text{Cd}^+ (^2P_{3/2}) + h\nu$$

Using Eqs. (15) and (16) it is now straightforward to express the alignment in terms of two unknown dynamical parameters. We take these to be

$$a = \frac{|S(\frac{5}{2}; \frac{7}{2})|^2}{|S(\frac{5}{2}; \frac{5}{2})|^2}; \quad b = \frac{|S(\frac{5}{2}; \frac{5}{2})|^2}{|S(\frac{5}{2}; \frac{5}{2})|^2}; \quad \text{for } j_l = \frac{5}{2},$$

and

$$c = \frac{|S(\frac{5}{2}; \frac{1}{2})|^2}{|S(\frac{5}{2}; \frac{5}{2})|^2}; \quad d = \frac{|S(\frac{5}{2}; \frac{5}{2})|^2}{|S(\frac{5}{2}; \frac{5}{2})|^2}; \quad \text{for } j_l = \frac{3}{2}.$$

Then the most general possible expressions for the electronic alignment $A_0^{\text{col}} (j_l)$ (as generated by unpolarized incident photons) in these two cases are

$$A_0^{\text{col}} (\frac{5}{2}) = \frac{-64 + 56a + 20b}{175(1+a+b)};$$

$$A_0^{\text{col}} (\frac{3}{2}) = \frac{-8 + 10c + 2d}{25(1+c+d)};$$

$$P(\frac{3}{2} \rightarrow \frac{1}{2}) = (16 - 14a - 5b)/(72 + 62a + 65b);$$

$$P(\frac{1}{2} \rightarrow \frac{3}{2}) = (-12 + 15c + 3d)/(46 + 55c + 51d).$$

These expressions imply that $P$ must lie within the ranges

$$-0.226 \leq P(\frac{3}{2} \rightarrow \frac{1}{2}) \leq 0.222;$$

$$-0.261 \leq P(\frac{1}{2} \rightarrow \frac{3}{2}) \leq 0.273.$$
However, this weak interaction causes a precession of \( \vec{I} \) and \( \vec{j} \) about their resultant \( \vec{F} \), affecting the nuclear and electronic multipole moments far more dramatically. Because theoretical analyses of the alignment usually consider only the electronic degrees of freedom, it is important to extract from a given measurement the net effect of this precession. This problem has been treated previously in a variety of contexts, and for more details we recommend the formulation of Fano and Macek. We reproduce their result here to clarify some confusion regarding this effect which has caused errors in interpreting recent experiments.

The main result derived in Ref. 8 is that in the absence of collisions the alignment \( A_{0}^{\text{col}} \) of an electronic state with angular momentum \( \vec{j} \) oscillates in the time \( t \) after the photoionization according to

\[
A_{0}^{\text{col}}(t) = A_{0}^{\text{col}}(0)g^{(2)}(t),
\]

where

\[
g^{(2)}(t) = \sum_{F,F'} \frac{(2F+1)(2F'+1)}{(2I+1)} \left[ \frac{F'}{F} \right]^{2} \cos \omega_{FF} t.
\]

Here \( \omega_{FF} \) is the frequency splitting between two hyperfine levels whose total angular momenta are \( \vec{F} \) and \( \vec{F'} \), respectively. Clearly \( A_{0}^{\text{col}}(t) \) attains its maximum absolute value at \( t = 0 \). Since the photoionization aligns only the electronic charge distribution, we interpret \( A_{0}^{\text{col}}(0) \) as the electronic alignment which then oscillates as \( \vec{j} \) and \( \vec{I} \) precess about \( \vec{F} \). In keeping with this point of view we will denote \( A_{0}^{\text{col}}(0) \) by \( A_{0}^{\text{col}}(\text{elec}) \) in what follows. To apply Eq. (22) to the more usual time-unresolved experiments, we integrate over time including an exponential decay factor for the total intensity \( \exp(-t/\tau) \). This gives

\[
\langle A_{0}^{\text{col}}(t) \rangle \equiv A_{0}^{\text{col}}(\text{obs}) = A_{0}^{\text{col}}(\text{elec})g^{(2)},
\]

where

\[
g^{(2)} = \sum_{F,F'} \frac{(2F'+1)(2F'+1)}{(2I+1)} \left[ \frac{F'}{F} \right]^{2} \frac{1}{1 + \omega_{FF}^{2} \tau^{2}}.
\]

Equation (24) has two interesting limits. First, when the radiative lifetime is much smaller than all reciprocal hyperfine frequencies (\( \omega_{FF} \tau << 1 \)), then the \( \vec{j} \) and \( \vec{I} \) do not have time to precess before the photon is emitted. In this limit \( g^{(2)} \approx 1 \) and no hyperfine depolarization occurs. In the opposite limit of a relatively long fluorescence life-

### Table I. Depolarization factors for Cd\(^{+}\).

<table>
<thead>
<tr>
<th>( I )</th>
<th>( j_i )</th>
<th>( g^{(2)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3/2</td>
<td>1</td>
</tr>
<tr>
<td>1/2</td>
<td>3/2</td>
<td>5/8</td>
</tr>
<tr>
<td>0</td>
<td>5/2</td>
<td>1</td>
</tr>
<tr>
<td>1/2</td>
<td>5/2</td>
<td>5/6</td>
</tr>
</tbody>
</table>

Using these correction factors and Eqs. (11), (12), and (23), we now deduce the electronic alignment of Cd\(^{+}\) implied by the measurements of Refs. 1 and 2. These are shown in Table II. Note that the values of \( P(\text{elec}) \) for the \( \frac{5}{2} \rightarrow \frac{3}{2} \) transition imply a breakdown of the model of Ref. 3 more than twice as great as previously thought, because of an overcorrection for hyperfine depolarization.

The alignment thus has the same sign for both the \( j_i = \frac{3}{2} \) and \( j_i = \frac{5}{2} \) states of Cd\(^{+}\), although the measured polarizations are of opposite sign owing to the factor \( h^{(2)}(j_i,j_f) \) in Eq. (11). The positive sign of \( A_{0}^{\text{col}} \) implies a flattening of the excited-state charge density along the incidence axis of the unpolarized photons. This is the sign expected from simple arguments, in the absence of strong anisotropic interactions having pseudotensor character.

**IV. CONCLUDING REMARKS**

For this particular example the hyperfine correction factor \( g_{av}^{(2)} \) turned out to be very close to unity for both \( j_i = \frac{3}{2} \) and \( j_i = \frac{5}{2} \). The crude correction
TABLE II. Hyperfine corrections in Cd$^+$.  

<table>
<thead>
<tr>
<th>Transition</th>
<th>$J_t$</th>
<th>Photon energy (eV)</th>
<th>$P_{\text{obs}}$</th>
<th>$P_{\text{elec}}$</th>
<th>$A_0^{(0)}(\text{elec})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^2D_{3/2} \rightarrow ^2P_{3/2}$</td>
<td>$\frac{3}{2}$</td>
<td>21.2$^a$</td>
<td>0.094</td>
<td>0.104</td>
<td>0.143</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\pm 0.036$</td>
<td>$\pm 0.035$</td>
<td>$\pm 0.049$</td>
</tr>
<tr>
<td></td>
<td>$\frac{5}{2}$</td>
<td>21.2$^a$</td>
<td>$-0.042$</td>
<td>$-0.044$</td>
<td>0.066</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\pm 0.005$</td>
<td>$\pm 0.005$</td>
<td>$\pm 0.005$</td>
</tr>
<tr>
<td>$^2D_{5/2} \rightarrow ^2P_{3/2}$</td>
<td>$\frac{3}{2}$</td>
<td>21.2$^b$</td>
<td>$-0.043$</td>
<td>$-0.045$</td>
<td>0.067</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\pm 0.003$</td>
<td>$\pm 0.003$</td>
<td>$\pm 0.005$</td>
</tr>
<tr>
<td>$^2D_{5/2} \rightarrow ^2P_{3/2}$</td>
<td>$\frac{5}{2}$</td>
<td>26.9$^b$</td>
<td>$-0.034$</td>
<td>$-0.035$</td>
<td>0.053</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\pm 0.002$</td>
<td>$\pm 0.002$</td>
<td>$\pm 0.004$</td>
</tr>
</tbody>
</table>

$^a$ Measured in Ref. 1.
$^b$ Measured in Ref. 2.

used in Ref. 1 greatly overestimated the hyperfine depolarization effect, and consequently the electronic polarization previously reported$^{1, 2}$ was too large in absolute value, $P(\text{Ref. 1}) = -0.054 \pm 0.004$ for $\frac{1}{2} \rightarrow \frac{3}{2}$. Our present results indicate a smaller absolute polarization for this transition, $P(\text{present}) = -0.044 \pm 0.005$, which implies that the experiments are even less compatible with the simple model of Cooper and Zare$^3$ than previously thought (recall $-0.226 \leq P_{\text{CZ}} \leq -0.061$). We stress the importance of treating the depolarization correctly, however, as in other cases the correction is known to be quite significant.$^6$

Cadmium offers an opportunity to compare ionic alignment with the angular distribution of photoelectrons. The asymmetry parameter $\beta$ was measured several years ago by Harrison,$^1$ and reinvestigated by Schönhense$^8$ who obtained quite different values. Recent Dirac-Fock calculations$^9$ of the cadmium continuum eigenfunctions using the angular-momentum-transfer formulation$^{10}$ have resulted in reasonably good agreement with Schönhense's measurements of $\beta$, though the comparison with measured values of the fluorescence polarization is less satisfactory. Actually, the agreement with Schönhense's value of $\beta$ at 58.4 nm may be somewhat fortuitous as the recent measurements of Shirley and coworkers$^{21}$ show a sharp variation of $\beta$ with energy. This is attributed to a broad autoionizing state $4d^9(5s 5p^3P)6s$ at 58.8 nm, first identified in absorption by Mansfield.$^{22}$ This autoionizing state may well provide the mechanism for the strong parity-unfavored contributions to the alignment which make the observed value of $P$ lie outside the Cooper-Zare limits.

ACKNOWLEDGMENTS

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As discussed in Ref. 7(a), the parity-favoredness quantum number $\pi_f$ is defined by

$$\pi_f = (-1)^{l - l_{\text{obs}} + l_{\text{ph}}} = (-1)^{l - l_{\text{obs}} + 1},$$

where $l_{\text{obs}}$ is the angular-momentum quantum number associated with the observed anisotropy. For measurements of the photoelectron angular distribution $J_{\text{obs}}$ is $J_z$, the photoelectron orbital angular momentum. For fluorescent polarization measurements, $J_{\text{obs}}$ coincides instead with $J_z$, the excited-state angular momentum of the ion. The contribution to the anisotropy associated with a given $j_z$ is termed parity favored or parity unfavored according to whether $\pi_f = +1$ or $-1$, respectively.


14It should be noted that the upper bound on $P(\frac{1}{2} \rightarrow \frac{1}{2})$ given in Eq. (20) differs from that given by Klar in Eq. (2) above. This discrepancy has been traced to Klar’s more complicated three-parameter expression for $P$, which does not lend itself easily to a determination of extrema. Proper consideration of Klar’s parametrization results in the same upper bound as given in Eq. (20). Reference to Eq. (6) shows that when the target angular momentum $J_0$ is zero as for cadmium, then $\pi_f$ reduces simply to the photoelectron angular momentum $j_z$. Thus in this case, the angular-momentum-transfer amplitudes $S(J_0, j_z, j_z; t)$ coincide with the amplitudes specified in $jj$ coupling. The explicit connection between Klar’s parametrization of the alignment and that obtained in this work can be found in Table I of Ref. 19 for cadmium photoionization. It is also interesting to note that Eq. (19) is equivalent to Eqs. (10) and (14a) of Ref. 19.

15This result follows because the alignment parameter $A_0^\text{col}$ is equal to the mean value (expectation value) of $(3j_z^2 - J_z^2)/J_z^2$, which is the quadrupole moment of the excited-state charge distribution.


