

Extraction of alignment parameters from circular dichroic photoelectron angular distribution (CDAD) measurements

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In a previous paper, we showed that circular dichroism in photoelectron angular distributions (CDAD) can be used to probe alignment in gas phase atoms and linear molecules. Often this alignment is parametrized through the *moments* of alignment $A^{(2)}$, $A^{(4)}$, etc., which are commonly extracted from fluorescence polarization measurements. In this paper we show how these can be simply extracted from CDAD spectra. This technique can be used in principle to extract the moments to *any* order.

INTRODUCTION

Circular dichroism in photoelectron angular distributions (CDAD) involves photoionization with left and right circularly polarized light.¹⁻³ The CDAD spectrum is defined as the difference in the photoelectron angular distributions obtained for these two cases.¹⁻³ Recently we showed that CDAD can be used to probe alignment in gas phase atoms and linear molecules.¹ Alignment can arise in a variety of experimental situations, including photoabsorption,⁴ atom-diatom collisions,⁵ unimolecular processes,⁶ electron stimulated desorption of adsorbed molecules,⁷ and molecular scattering from surfaces.⁸ Often this alignment is parametrized through the *moments* of alignment $A^{(2)}$, $A^{(4)}$, etc., which are commonly extracted from fluorescence polarization experiments.⁹⁻¹² In this paper we show how these moments can be simply extracted from CDAD spectra. As in saturated laser optical pumping experiments,¹³ this technique can be used in principle to extract the moments to *any* order. This feature differs from that of a standard laser-induced fluorescence (LIF) experiment¹² in which $L_{\text{MAX}} = 2N + 2$, where N is the number of exciting photons. The reason for this difference is that in the angle-resolved photoionization process the electron can carry away an arbitrary amount of angular momentum from the system whereas in LIF the fluorescence photon can only carry away one unit.

In the experiment we consider here, linearly polarized light is used to pump the molecular sample to an aligned excited state (though we emphasize that CDAD can be used in principle to probe alignment created by any of the above methods). The light is polarized along the z axis of the laboratory frame and propagates along the x axis. After the alignment is created, circularly polarized light (left or right), copropagating with the original pump light, is used to photoionize the sample. The electrons are collected in the plane *at right angles* to the propagation direction of the light (Fig. 1). In our laboratory frame, the angles (θ_p, ϕ_p) for the propagation vector of the circularly polarized light are hence $(90^\circ, 0^\circ)$ and the electron collection angles (θ_k, ϕ_k) are $(\theta_k, 90^\circ)$.

THE ALIGNMENT

Consider a molecule in a $J = 5/2$ state. The state has six magnetic substates, $M_J = +5/2, +3/2, +1/2, -1/2, -3/2, -5/2$. If all the substates are equally populated, the state is considered *isotropic*. However, if the substates with different $|M_J|$ values have different populations, the state is considered *aligned*.¹¹ For example,

$J = 5/2$						
Relative population	0	2	3	3	2	0
M_J	5/2	3/2	1/2	-1/2	-3/2	-5/2

represents an aligned state. As shown in Ref. 1, molecules which are aligned exhibit CDAD.

The CDAD spectrum for a molecule in a given M_J state can be written^{1,14} as

$$I_{M_J}(\theta_k) = Y_{11}(\theta_p, \phi_p) \sum_{L'} \beta_{L'}^{M_J} Y_{L'-1}(\theta_k, \phi_k), \quad (1)$$

where $I(\theta)$ is the CDAD intensity and $Y_{LM}(\theta, \phi)$ is a spherical harmonic. The calculation of the $\beta_L^{M_J}$'s which contain all the dynamical information about the molecule of interest has been described in Ref. 1. (Here $\beta_L^{M_J} = 2\sqrt{2}\beta_{L11}^{M_J}$ of Ref. 1.) The details are not of interest here. The important point is that each M_J substate has a *different* CDAD spectrum (Fig. 2 of Ref. 1). The CDAD spectrum for an arbitrary alignment will be a sum of the spectra for given M_J 's weighted by the relative population of each substate:

$$I(\theta_k) = \sum_{M_J} N_{M_J} I_{M_J}(\theta_k), \quad (2)$$

where N_{M_J} represents the relative populations of the substates.¹⁵ These N_{M_J} 's are the values of interest for they contain all the alignment information. At this point, to extract the N_{M_J} 's, one would have to calculate the CDAD spectrum for each M_J and determine by fit which linear combination of spectra reproduces the experimental spectrum. We will now discuss a much cleaner method to determine the alignment.

As an alternative to the N_{M_J} description of alignment, we can express the alignment in a "spherical" basis¹¹:

$$N_{M_J} = \sum_L A^{(L)} T_L^{M_J}. \quad (3)$$

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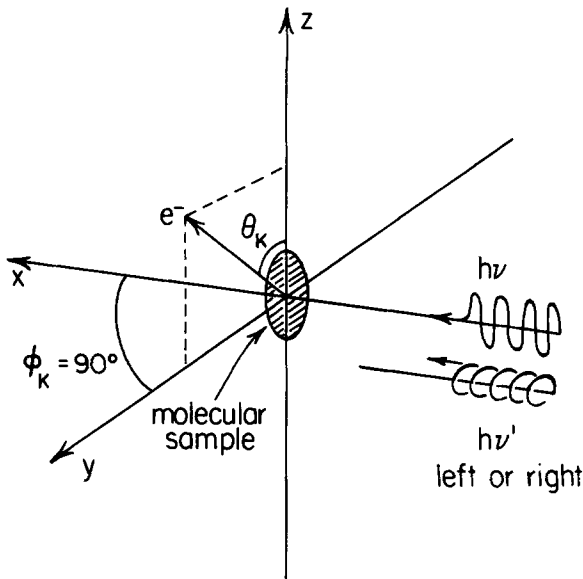


FIG. 1. Experimental configuration for measurement of CDAD spectra.

- 1) Creation of Alignment
- 2) Probe of Alignment

Here the $A^{(L)}$ are the state multipole moments of the alignment ($A^{(0)}$ is the monopole moment, $A^{(1)}$ is the dipole moment, etc.). The $T_L^{M_J}$ are spherical tensor operators defined as¹¹

$$T_L^{M_J} = (-1)^{J-M_J} \langle JJM_J - M_J | L 0 \rangle, \quad (4)$$

where $\langle JJM_J - M_J | L 0 \rangle$ is a Clebsch-Gordan coefficient. For example, for $J = 5/2$,

$$\begin{array}{l} T_0 = \left(\frac{1}{\sqrt{6}} \right) \times \begin{array}{cccccc} 1 & 1 & 1 & 1 & 1 & 1 \end{array}, \\ T_1 = \left(\frac{1}{\sqrt{70}} \right) \times \begin{array}{cccccc} 5 & 3 & 1 & -1 & -3 & -5 \end{array}, \\ T_2 = \left(\frac{1}{\sqrt{84}} \right) \times \begin{array}{cccccc} 5 & -1 & -4 & -4 & -1 & 5 \end{array}, \\ T_3 = \left(\frac{1}{\sqrt{180}} \right) \times \begin{array}{cccccc} 5 & -7 & -4 & 4 & 7 & -5 \end{array}, \\ T_4 = \left(\frac{1}{\sqrt{28}} \right) \times \begin{array}{cccccc} 1 & -3 & 2 & 2 & -3 & 1 \end{array}, \\ T_5 = \left(\frac{1}{\sqrt{252}} \right) \times \begin{array}{cccccc} 1 & -5 & 10 & -10 & 5 & -1 \end{array}, \\ M_J = \begin{array}{cccccc} 5/2 & 3/2 & 1/2 & -1/2 & -3/2 & -5/2 \end{array} \end{array}$$

For any distribution of N_{M_J} , an equivalent linear combination of $T_L^{M_J}$ can be found to describe the distribution. Because the $T_L^{M_J}$ are known, a knowledge of all $A^{(L)}$ is equivalent to a knowledge of all N_{M_J} .

The advantage of using the $T_L^{M_J}$ can be seen as follows. Substitution of Eqs. (1) and (3) into Eq. (2):

$$I(\theta_k) = Y_{11}(\theta_p, \phi_p) \sum_L A^{(L)} \sum_{M_J} T_L^{M_J} \times \sum_{L'} \beta_{L'}^{M_J} Y_{L'-1}(\theta_k, \phi_k). \quad (5)$$

On performing the sum over M_J in the above equation, one

obtains $L = L'$. Then

$$I(\theta_k) = Y_{11}(\theta_p, \phi_p) \sum_L A^{(L)} \bar{\beta}_L Y_{L-1}(\theta_k, \phi_k) \quad (6)$$

with

$$\bar{\beta}_L = \sum_{M_J} T_L^{M_J} \beta_L^{M_J}. \quad (7)$$

Equation (7) requires that only even L will contribute to CDAD. This result arises because $B_L^{M_J} = 0$ for L odd. Thus, CDAD only provides $A^{(2)}$, $A^{(4)}$, $A^{(6)}$, etc. CDAD from $A^{(0)}$, which represents equal population of all M_J levels, vanishes because this distribution lacks any alignment.¹

In an actual experiment, the photon direction (θ_p, ϕ_p) and the electron collection plane (ϕ_k) are both fixed. We will now specialize, Eq. (6) to the experimental configuration described earlier, i.e., $(\theta_p, \phi_p) = (90^\circ, 0^\circ)$ and $\phi_k = 90^\circ$. Then

$$I(\theta_k) = \sum_L A^{(L)} \bar{\beta}_L P_L^1(\cos \theta_k), \quad (8)$$

where

$$\bar{\beta}_L = \frac{i}{4\pi} \left[\frac{3(2L+1)}{2L(L+1)} \right]^{1/2} \beta_L. \quad (9)$$

In Eq. (8), $P_L^M(\cos \theta)$ is an associated Legendre polynomial. The imaginary factor "i" in Eq. (9) is a necessary result since, as pointed out in Ref. 1, the $\beta_L^{M_J}$ are pure imaginary and $I(\theta_k)$ must be real. Equation (8) is the key result of this paper. It shows that the quadrupole moment of the alignment $A^{(2)}$ will make a $P_2^1(\cos \theta_k)$ contribution to the shape of the CDAD spectra, the hexadecapole moment a $P_4^1(\cos \theta_k)$ contribution, and so on. The relative weights of these contributions depend on the molecular details of the problem. From the orthogonality of the P_L^m , the moments of

the alignment can be written as

$$A^{(L)}\bar{\beta}_L = \frac{(2L+1)}{2(L+1)(L)} \int_0^\pi I(\theta_k) \times P_L^1(\cos\theta_k)\sin\theta_k d\theta_k \quad (10)$$

$$= \frac{(2L+1)}{(L+1)(L)} \int_0^{\pi/2} I(\theta_k) \times P_L^1(\cos\theta_k)\sin\theta_k d\theta_k, \quad (11)$$

where Eq. (11) follows from Eq. (10) because L is even as described earlier.

Using Eq. (11), the alignment parameters $A^{(L)}$ (L even) can be easily obtained once the $\bar{\beta}_L$ are known.¹⁶ These $\bar{\beta}_L$ can be calculated in a straightforward way by *ab initio* methods.¹⁻³ Alternatively, if the molecules can be prepared in a state of *known* alignment (i.e., known $A^{(L)}$), the $\bar{\beta}_L$ can be experimentally determined. These values can then be used to probe unknown alignments. Note that Eq. (11) puts no upper limit on the value of L .

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¹R. L. Dubs, S. N. Dixit, and V. McKoy, *J. Chem. Phys.* **85**, 656 (1986).

²R. L. Dubs, S. N. Dixit, and V. McKoy, *Phys. Rev. Lett.* **54**, 1249 (1985).

³R. L. Dubs, S. N. Dixit, and V. McKoy, *Phys. Rev. B* **32**, 8389 (1985).

⁴R. N. Zare, *Ber. Bunsenges. Phys. Chem.* **86**, 422 (1982); S. N. Dixit and V. McKoy, *J. Chem. Phys.* **82**, 3546 (1985); M. G. White, W. A. Chupka, M. Seaver, A. Woodward, and S. D. Colson, *ibid.* **80**, 678 (1984); W. J. Kessler and E. D. Poliakoff, *ibid.* **84**, 3647 (1986).

⁵See, for example, E. Marinero, C. T. Rettner, and R. N. Zare, *J. Chem. Phys.* **80**, 4142 (1984).

⁶See, for example, R. Vasudev, R. N. Zare, and R. N. Dixon, *J. Chem. Phys.* **80**, 4863 (1984); I. Hadler, J. Pfab, H. Reisler, and C. Wittig, *ibid.* **81**, 653 (1984); S. Beulow, G. Radhakrishnan, J. Catanzarite, and C. Wittig, *ibid.* **83**, 444 (1985).

⁷See, for example, A. R. Burns, *Phys. Rev. Lett.* **55**, 525 (1985).

⁸See, for example, G. M. McClelland, G. D. Kubiak, H. G. Rennagel, and R. N. Zare, *Phys. Rev. Lett.* **46**, 831 (1981); F. Frenkel, J. Häger, H. Krieger, H. Walther, C. T. Campbell, G. Ertl, H. Kuipers, and J. Segner, *ibid.* **46**, 152 (1981).

⁹(a) U. Fano and J. H. Macek, *Rev. Mod. Phys.* **45**, 553 (1973); (b) D. A. Case, G. M. McClelland, and D. R. Herschbach, *Mol. Phys.* **35**, 541 (1978).

¹⁰G. E. Hall, N. Sivakumar, and P. L. Houston, *J. Chem. Phys.* **84**, 2120 (1986).

¹¹C. H. Greene and R. N. Zare, *Annu. Rev. Phys. Chem.* **33**, 119 (1982).

¹²C. H. Greene and R. N. Zare, *J. Chem. Phys.* **78**, 6741 (1983).

¹³U. Hefter, G. Ziegler, A. Mattheus, A. Fischer, and K. Bergmann, *J. Chem. Phys.* **85**, 286 (1986).

¹⁴Generally, one must take the real part of the right-hand side of Eq. (1). However, in this letter we only consider cases for which $\sin(\phi_k - \phi_p) = \pm 1$, i.e., right angle collection—the configuration for which CDAD is a maximum. For this case, Eq. (1) is correct as it stands.

¹⁵These N_{M_j} are normalized such that $\sum_{M_j} N_{M_j} = 1$ for any value of J .

¹⁶U. Hefer *et al.* (Ref. 13) have found, using saturated laser optical pumping, that for highly aligned molecules, direct solution of an equation similar to Eq. (8) (as a set of linear equations for different values of θ_k) is numerically more stable than integration [Eq. (11)]. They find integration preferred, however, if only a few moments are necessary to characterize the alignment.