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On the measurement of molecular anisotropies using laser techniques. III. Detection of the higher multipoles

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In this paper we discuss the problem of measuring the higher moments ($K \geq 2$) of a generalized anisotropic distribution of molecular rotors. Two photon absorption techniques may be used to obtain these quantities and the appropriate expressions for linear and circular dichroism are derived.

I. INTRODUCTION

In previous papers in this series,^{1,2} we have considered the problems associated with the characterization of an anisotropic array of molecules in their electronic ground states but with single quantum level resolution. This anisotropy may arise in more than one way; through chemical reaction, via photofragmentation³ or as a result of flow in a concentration gradient⁴ to name some commonly occurring instances. In part I¹ we demonstrated that resonance fluorescence polarization ratios are not an unequivocal guide to ground state molecular polarizations since the experimental observables have contributions from more than one multipole component of the ground state. Perturbations during the excited state lifetime further reduce the value of the technique by introducing the possibility of cross relaxation between multipole components. Part II develops an alternative method, namely circular and linear differential *absorption* and we showed that unambiguous determination of ground state multipole moments of rank up to $K'' = 2$ was possible via these experiments by choosing the proper experimental geometry and probe polarization.

In part I [Eqs. (4) and (7)] it was shown that an arbitrary anisotropy in the ground state could be expressed as a multipolar series having moments, ${}^{J''J'}\rho_Q^{K''}$ with tensorial rank $K'' = 0, 1, 2, \dots$. The higher multipoles such as the octopolar ($K'' = 3$) and hexadecapolar ($K'' = 4$) may be nonzero and their measurement presents some difficulties. One solution may be to combine an absorption experiment yielding $K'' = 0, 1$, and 2 as outlined in part II with a full polarization analysis of the rotationally resolved fluorescence, the latter containing terms in $K'' > 2$. This method is implicit in the aforementioned papers^{1,2} and the evaluation of the higher moments is discussed by Greene and Zare³ in some detail.

Here however we consider an alternative method, namely, two photon linear and circular dichroism. Developments in laser technology have made high resolution two-photon spectroscopy a readily accessible spectroscopic technique⁵ and in this work we describe how the method may be used to obtain directly the higher moments of the ground state anisotropy.

In the first part of this series¹ we derived a relationship between the state multipolar moments of an excited state and those of an anisotropic ground state array:

$${}^{JJ'}\rho_Q^{K''}(\hat{e}, z) = \sum_{\substack{K''Q'' \\ M_1, M_2 \\ M_1'', M_2''}} (-1)^{J''-M_1+J'-M_1'} \\ \times \begin{pmatrix} J & J & K \\ M_1 & -M_2 & -Q \end{pmatrix} \begin{pmatrix} J'' & J'' & K'' \\ M_1'' & -M_2'' & -Q'' \end{pmatrix} \\ \times (2K+1)^{1/2} (2K''+1)^{1/2} \langle \alpha J M_1 | \hat{e} \cdot d | \alpha'' J'' M'' \rangle \\ \times \langle \alpha J M_2 | \hat{e} \cdot d | \alpha'' J'' M_2'' \rangle {}^{J''J'}\rho_{Q''}^{K''}(g, z), \quad (1)$$

where the symbols are defined in part I¹ and ${}^{J''J'}\rho_{Q''}^{K''}(g, z)$ is the K'' th multipolar moment (of component Q'') of the ground state molecular array.

In Eq. (18) of part I we showed that the individual ground state multipoles may contribute to the multipolar moments of the excited array in a manner which depends predictably on the way in which the excited state is formed. In this way the ground state multipolar moments influence the polarization of the fluorescence from the excited state and thus may in principle be determined.³ However, circumstances often mitigate against such a determination and the low light levels characteristic of fully resolved emission spectra and/or experimental complexities of the kind referred to in part II of this series² make an alternative probe of the higher multipole moments of the ground state desirable.

Below we present the theory of two photon linear and circular dichroism with particular reference to the measurement of the higher multipoles ($K'' > 2$) of the ground state array. It will be seen that this form of determination has a number of advantages over other methods.

In a series of recent papers⁶⁻⁸ the consequences of linearly and circularly polarized nonresonant two photon excitation were discussed in terms of the state multipoles characterizing the polarization of the excited state ensemble. The high degree of polarization stored in the array as a result of the excitation process is reflected in the resonance fluorescence polarization. The theoretical polarization ratios for these transitions were seen to be significantly higher than for the analogous single photon processes. Two photon absorption (TPA) measurements should therefore prove a highly sensitive probe of ground state anisotropy in which all the ground state multipoles of rank $K'' = 0$ to $K'' = 4$ can contribute to the intensity. At present the theory of two photon circular dichroism has been restricted solely to solution studies of chiral molecules,⁹ however a recent theoretical treatment of polarized two photon absorption in relation to single photon circular and linear dichroism has been pre-

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sented by Nairn *et al.*¹⁰ Their approach uses one- and two-vector, density-of-states functions to describe the polarization of an arbitrarily ordered ensemble and does not extend to a full multipolar treatment nor to direct rotational resolution. In the following section we consider the nonresonant TPA for both circularly and linearly polarized photons and proceed to derive expressions for rotationally resolved two photon circular and linear absorption ratios. For simplicity we will restrict the discussion to rotational transitions in which $\Delta J = \pm 2$. The selection rules in this case permit the contribution of only one intermediate (virtual) rotational level J' to the transition moment thus:

$$\alpha'' J'' \xrightarrow{\omega_1 + \omega_2} \alpha J.$$

Here α represents all quantum numbers other than rotational and ω_1 and ω_2 are the frequencies of the two photons.

II. CIRCULARLY POLARIZED TWO PHOTON ABSORPTION

The absorption intensity I for two photons of the same circular polarization q_A is given by

$$I(2q_A, \hat{O}) = g(\omega) \sum_{\substack{M_1' M_2' \\ \alpha' J' M' \\ K'' Q''}} \langle \alpha J M | d_{q_A}^1 | \alpha' J' M' \rangle \\ \times \langle \alpha' J' M' | d_{q_A}^1 | \alpha'' J'' M'' \rangle \\ \times \langle \alpha J M | d_{q_A}^1 | \alpha' J' M' \rangle^* \langle \alpha' J' M' | d_{q_A}^1 | \alpha'' J'' M'' \rangle^*$$

$$\times D(\alpha' J' \omega_1 \omega_2) |\epsilon_{q_A}^1|^4 (-1) 4q_A \\ \times (-1)^{J'' - M''} \begin{pmatrix} J'' & J'' & K'' \\ M_1'' & M_2'' & -Q'' \end{pmatrix} \\ \times (2K'' + 1)^{1/2} J'' J'' \rho_0^{K''}(g, \hat{O}), \quad (2)$$

where $g(\omega)$ is the line shape function for the two photon transition and $D(\alpha' J' \omega_1 \omega_2)$ contains the detuning parameters for the transition. As is usual in circularly polarized excitation, the quantization axis is \hat{O} , the propagation vector of the light beam. Application of the Wigner-Eckart theorem in the space fixed frame defined by \hat{O} followed by some manipulation of the $3j$ symbols and summation over the magnetic quantum numbers using standard sum rules¹¹ gives

$$I(2q_A, \hat{O}) = g(\omega) \sum_{\substack{a_1 a_2 \\ \alpha' K''}} (2a_1 + 1)(2a_2 + 1) (-1)^{J'' + J' + q_A} \\ \times D(\alpha' J' \omega_1 \omega_2) \langle \alpha J || d^1 || \alpha' J' \rangle \langle \alpha' J' || d^1 || \alpha'' J'' \rangle^2 \\ \times \begin{Bmatrix} 1 & 1 & a_1 \\ J & J'' & J' \end{Bmatrix} \begin{Bmatrix} a_1 & 1 & a_2 \\ J' & J'' & J \end{Bmatrix} \begin{Bmatrix} a_2 & 1 & K'' \\ J'' & J'' & J' \end{Bmatrix} \\ \times \begin{pmatrix} 1 & 1 & a_1 \\ q_A & q_A & -q_A \end{pmatrix} \begin{pmatrix} a_1 & 1 & a_2 \\ 2q_A & -q_A & -q_A \end{pmatrix} \\ \times \begin{pmatrix} a_2 & 1 & K'' \\ q_A & -q_A & 0 \end{pmatrix} (2K'' + 1)^{1/2} J'' J'' \rho_0^{K''}(g, \hat{O}). \quad (3)$$

Here a_1, a_2 are summation parameters.

The corresponding expression for two photons each having polarization $-q_A$ is given by

$$I(-2q_A, \hat{O}) = g(\omega) \sum_{\substack{a_1 a_2 \\ \alpha' K''}} (2a_1 + 1)(2a_2 + 1) (-1)^{J'' + J' + q_A} D(\alpha' J' \omega_1 \omega_2) \langle \alpha J || d^1 || \alpha' J' \rangle \langle \alpha' J' || d^1 || \alpha'' J'' \rangle^2 \\ \times \begin{Bmatrix} 1 & 1 & a_1 \\ J & J'' & J' \end{Bmatrix} \begin{Bmatrix} a_1 & 1 & a_2 \\ J' & J'' & J \end{Bmatrix} \begin{Bmatrix} a_2 & 1 & K'' \\ J'' & J'' & J' \end{Bmatrix} \begin{pmatrix} 1 & 1 & a_1 \\ q_A & q_A & -2q_A \end{pmatrix} \begin{pmatrix} a_1 & 1 & a_2 \\ 2q_A & -q_A & -q_A \end{pmatrix} \\ \times \begin{pmatrix} a_2 & 1 & K'' \\ q_A & -q_A & 0 \end{pmatrix} (2K'' + 1)^{1/2} J'' J'' \rho_0^{K''}(g, \hat{O}) (-1)^{K''}. \quad (4)$$

The two photon circular absorption ratio is given by $(I_{2q_A} - I_{-2q_A}) / (I_{2q_A} + I_{-2q_A})$. Substituting Eqs. (3) and (4) into this expression gives

$$\frac{I_{2q_A} - I_{-2q_A}}{I_{2q_A} + I_{-2q_A}} = \sum_{\substack{a_1 a_2 \\ K''}} (2a_1 + 1)(2a_2 + 1) (-1)^{J'' + J' + q_A} \begin{Bmatrix} 1 & 1 & a_1 \\ J & J'' & J' \end{Bmatrix} \begin{Bmatrix} a_1 & 1 & a_2 \\ J' & J'' & J \end{Bmatrix} \begin{Bmatrix} a_2 & 1 & K'' \\ J'' & J'' & J' \end{Bmatrix} (2K'' + 1)^{1/2} \\ \times \begin{pmatrix} a_2 & 1 & K'' \\ J'' & J'' & J' \end{pmatrix} \begin{pmatrix} a & a & a_1 \\ q_A & q_A & -2q_A \end{pmatrix} \begin{pmatrix} a_1 & 1 & a_2 \\ 2q_A & -q_A & -q_A \end{pmatrix} \begin{pmatrix} a_2 & 1 & K'' \\ q_A & -q_A & 0 \end{pmatrix} \\ \times (1 + (-1)^{K'' + 1} J'' J'' \rho_0^{K''}(g, \hat{O})) \\ \left[\sum_{\substack{a_1 a_2 \\ K''}} (2a_1 + 1)(2a_2 + 1) (-1)^{J'' + J' + q_A} \begin{Bmatrix} 1 & 1 & a_1 \\ J & J'' & J' \end{Bmatrix} \begin{Bmatrix} a_1 & 1 & a_2 \\ J' & J'' & J \end{Bmatrix} \begin{Bmatrix} a_2 & 1 & K'' \\ J'' & J'' & J' \end{Bmatrix} \begin{pmatrix} 1 & 1 & a_1 \\ q_A & q_A & -2q_A \end{pmatrix} \right. \\ \left. \times \begin{pmatrix} a_1 & 1 & a_2 \\ 2q_A & -q_A & -q_A \end{pmatrix} \begin{pmatrix} a_2 & 1 & K'' \\ q_A & -q_A & 0 \end{pmatrix} (2K'' + 1)^{1/2} (1 + (-1)^{K''} J'' J'' \rho_0^{K''}(g, \hat{O})) \right]^{-1}, \quad (5)$$

all other quantities cancelling in the ratio.

This can be further simplified by noting that circularly polarized excitation for which $q_A \equiv \pm 1$ the a_1 parameter in the summation can only be 2. This gives

$$\frac{I_{2q_A} - I_{-2q_A}}{I_{2q_A} + I_{-2q_A}} = \sum_{a_2, K''} (2a_2 + 1) (-1)^{J'' + J' + q_A} \begin{Bmatrix} 2 & 1 & a_2 \\ J' & J'' & J \end{Bmatrix} \begin{Bmatrix} a_2 & 1 & K'' \\ J'' & J'' & J' \end{Bmatrix} \\ \times \frac{\begin{pmatrix} 2 & 1 & a_2 \\ 2q_A & -q_A & -q_A \end{pmatrix} \begin{pmatrix} a_2 & 1 & K'' \\ q_A & -q_A & 0 \end{pmatrix} (2K'' + 1) (1 + (-1)^{K'' + 1})^{J'' J'} \rho_0^{K''}(g, \hat{O})}{\sum_{a_2, K''} (2a_2 + 1) (-1)^{J'' + J' + q_A} \begin{Bmatrix} 2 & 1 & a_2 \\ J' & J'' & J \end{Bmatrix} \begin{Bmatrix} a_2 & 1 & K'' \\ J'' & J'' & J' \end{Bmatrix}} \\ \times \begin{pmatrix} 2 & 1 & a_2 \\ 2q_A & -q_A & -q_A \end{pmatrix} \begin{pmatrix} a_2 & 1 & K'' \\ q_A & -q_A & 0 \end{pmatrix} (2K'' + 1)^{1/2} (1 + (-1)^{K''})^{J'' J'} \rho_0^{K''}(g, \hat{O}). \quad (6)$$

The numerator contains solely the odd rank ground state multipoles $K'' = 1, 3$ while the denominator contains the even rank $K'' = 0, 2, 4$ components. As was shown in earlier papers⁶⁻⁸ the summations over the $6j$ symbols can be greatly simplified with reference to their algebraic forms for a particular excitation. The two photon circular absorption ratio will have the general form

$$\frac{I_{2q_A} - I_{-2q_A}}{I_{2q_A} + I_{-2q_A}} = \frac{[B_1]^{J'' J'} \rho_0^1(g, \hat{O}) + [B_3]^{J'' J'} \rho_0^3(g, \hat{O})}{[B_0]^{J'' J'} \rho_0^0(g, \hat{O}) + [B_2]^{J'' J'} \rho_0^2(g, \hat{O}) + [B_4]^{J'' J'} \rho_0^4(g, \hat{O})}, \quad (7)$$

where the B 's are determined by the symmetry of the excitation processes.

III. LINEARLY POLARIZED TWO PHOTON ABSORPTION

In calculating the two photon linear absorption ratio the most straightforward route is to calculate the absorption intensities in the two orthogonal axis systems z_1 and z_2 defined by I_{\parallel} and I_{\perp} , respectively. The measurement in z_2 is then related to that in z_1 by the appropriate rotational transformation, as in paper II on single photon linear dichroism.² For linearly polarized light the polarization vector ϵ_z is ϵ_0^1 in a spherical basis and we simply need to put $q_A = 0$ in Eq. (3). The absorption intensity in a_1 is thus

$$I_{\parallel} = I_{z_1} = g(\omega) \sum_{a_1, a_2} (2a_1 + 1) (2a_2 + 1) (-1)^{J'' + J' + q_A} \\ \times \begin{Bmatrix} 1 & 1 & a_1 \\ J & J'' & J' \end{Bmatrix} \begin{Bmatrix} a_1 & 1 & a_2 \\ J' & J'' & J \end{Bmatrix} \begin{Bmatrix} a_2 & 1 & K'' \\ J'' & J'' & J' \end{Bmatrix} \\ \times \begin{pmatrix} 1 & 1 & a_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_2 & 1 & a_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_2 & 1 & K'' \\ 0 & 0 & 0 \end{pmatrix} \\ \times (2K'' + 1)^{1/2} J'' J' \rho_0^{K''}(g, z_1) [D(\alpha' J', \omega_1 \omega_2)] \\ \times |\langle \alpha J \| d^1 \| \alpha' J' \rangle \langle \alpha' J' \| d^1 \| \alpha'' J'' \rangle|^2. \quad (8)$$

We have an identical expression for I_{z_2} (I_{\perp}) though of course it refers to a different coordinate frame. From the restrictions imposed by the $3j$ and $6j$ symbols, only $J'' J' \rho_0^0$, $J'' J' \rho_0^2$, and $J'' J' \rho_0^4$ can contribute to the absorption intensity with respect to each frame. The multipoles in z_2 are related to those in z_1 by the standard Euler rotation of $\beta = \Pi/2$ about their common y axis in the usual way:

$$J'' J' \rho_0^{K''}(g, z_2) = \sum_Q d_{0Q}^K(\Pi/2) J'' J' \rho_Q^{K''}(g, z_1). \quad (9)$$

Algebraic expressions for $d_{0Q}^K(\beta)$ were given earlier.² For higher tensors the algebraic expressions are complex and

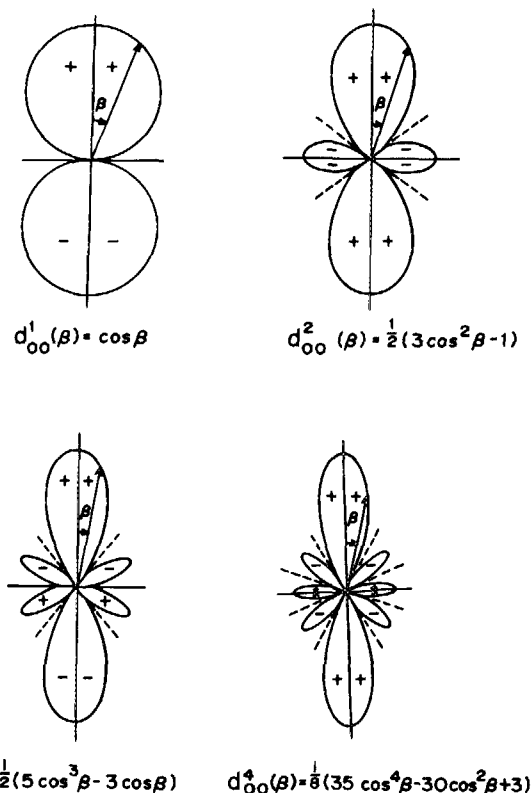


FIG. 1. Angular plots of $d_{0Q}^K(\beta)$ where $K = 1, 2, 3, 4$. The angles for which $d_{0Q}^K(\beta) = 0$ correspond to geometries between the ground state symmetry axis and the probe quantization axis for which the particular multipole K does not contribute to the absorption strength.

extensive tables are given by Buckmaster and Chiu.¹² The relevant numerical values of $d_{0Q}^4(\Pi/2)$ are

$$\begin{aligned} d_{00}^4(\Pi/2) &= 3/8, & d_{0\pm 1}^4(\Pi/2) &= d_{0\pm 3}^4(\Pi/2) = 0, \\ d_{0\pm 2}^4(\Pi/2) &= -\sqrt{10}/8, \\ d_{0\pm 4}^4(\Pi/2) &= \sqrt{20}/8. \end{aligned} \quad (10)$$

Thus if the ground state multipole distribution is not axially symmetric about z_1 , there will be contributions to the absorption measured in z_2 from ${}^{J''J''}\rho_{\pm 2}^2(g, z_1)$, ${}^{J''J''}\rho_{\pm 4}^4(g, z_1)$ as well as the axially symmetric components ${}^{J''J''}\rho_0^K(g, z_1)$.

The linear absorption ratio under these circumstances is given by

$$\begin{aligned} \left(\frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \right)_{\text{TPA}} &= \sum_{a, a_2, K''} (-1)^{J''+J'} (2a_1+1)(2a_2+1) \begin{Bmatrix} 1 & 1 & a_1 \\ J & J'' & J' \end{Bmatrix} \begin{Bmatrix} a_1 & 1 & a_2 \\ J' & J'' & J \end{Bmatrix} \\ &\quad \times \begin{Bmatrix} a_2 & 1 & K'' \\ J'' & J'' & J' \end{Bmatrix} \begin{pmatrix} 1 & 1 & a_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_1 & 1 & a_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_2 & 1 & K'' \\ 0 & 0 & 0 \end{pmatrix} (2K''+1)^{1/2} \\ &\quad \times \left[{}^{J''J''}\rho_0^{K''}(g, z_1) - \sum_Q d_{0Q}^{K''}(\Pi/2) {}^{J''J''}\rho_Q^{K''}(g, z_1) \right] \\ &\quad \left[\sum_{a, a_2, K''} (-1)^{J''+J'} (2a_1+1)(2a_2+1) \begin{Bmatrix} 1 & 1 & a_1 \\ J & J'' & J' \end{Bmatrix} \begin{Bmatrix} a_1 & 1 & a_2 \\ J' & J'' & J \end{Bmatrix} \right. \\ &\quad \times \begin{Bmatrix} a_2 & 1 & K'' \\ J'' & J'' & J' \end{Bmatrix} \begin{pmatrix} 1 & 1 & a_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_1 & 1 & a_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_2 & 1 & K'' \\ 0 & 0 & 0 \end{pmatrix} (2K''+1)^{1/2} \\ &\quad \left. \times {}^{J''J''}\rho_0^{K''}(g, z_1) + \sum_Q d_{0Q}^{K''}(\Pi/2) {}^{J''J''}\rho_Q^{K''}(g, z_1) \right]^{-1}. \end{aligned} \quad (11)$$

When the ground state ensemble possesses axial symmetry about z_1 we have

$$\begin{aligned} \left(\frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \right)_{\text{TPA}} &= \sum_{a, a_2, K''} (-1)^{J''+J'} (2a_1+1)(2a_2+1) \begin{Bmatrix} 1 & 1 & a_1 \\ J & J'' & J' \end{Bmatrix} \begin{Bmatrix} a_1 & 1 & a_2 \\ J' & J'' & J \end{Bmatrix} \\ &\quad \times \begin{Bmatrix} a_2 & 1 & K'' \\ J'' & J'' & J' \end{Bmatrix} \begin{pmatrix} 1 & 1 & a_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_1 & 1 & a_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_2 & 1 & K'' \\ 0 & 0 & 0 \end{pmatrix} \\ &\quad \times (2K''+1)^{1/2} {}^{J''J''}\rho_0^{K''}(g, z_1) [1 - d_{00}^{K''}(\Pi/2)] \\ &\quad \left[\sum_{a, a_2, K''} (-1)^{J''+J'} (2a_1+1)(2a_2+1) \begin{Bmatrix} 1 & 1 & a_1 \\ J & J'' & J' \end{Bmatrix} \begin{Bmatrix} a_1 & 1 & a_2 \\ J' & J'' & J \end{Bmatrix} \begin{Bmatrix} a_2 & 1 & K'' \\ J'' & J'' & J' \end{Bmatrix} \right. \\ &\quad \left. \times \begin{pmatrix} 1 & 1 & a_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_1 & 1 & a_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} a_2 & 1 & K'' \\ 0 & 0 & 0 \end{pmatrix} (2K''+1)^{1/2} {}^{J''J''}\rho_0^{K''}(g, z_1) [1 + d_{00}^{K''}(\Pi/2)] \right], \end{aligned} \quad (12)$$

where

$$\begin{aligned} d_{00}^0(\beta) &= 1, \\ d_{00}^2(\beta) &= \frac{1}{2}(3 \cos^2 \beta - 1), \\ d_{00}^4(\beta) &= \frac{1}{8}(35 \cos^4 \beta - 30 \cos^2 \beta + 3). \end{aligned} \quad (13)$$

The summations over the $6j$ symbols are greatly simplified if the appropriate algebraic forms are used. The linear absorption ratio can be written in a general form which is analogous to the circular absorption ratio, Eq. (7),

$$\left(\frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \right)_{\text{TPA}} = \frac{[B_2]{}^{J''J''}\rho_0^2(g, z_1) + [B_4]{}^{J''J''}\rho_0^4(g, z_1)}{[B_0]{}^{J''J''}\rho_0^0(g, z_1) + \frac{1}{3}[B_2]{}^{J''J''}\rho_0^2(g, z_1) + \frac{1}{11}[B_4]{}^{J''J''}\rho_0^4(g, z_1)}. \quad (14)$$

As can be seen the $K'' = 3$ state moment does not contribute to the linear TPA ratio.

IV. "MAGIC ANGLE" CONSIDERATIONS

An examination of Eq. (13) shows that in addition to the well known settings of $\beta = 54.7^\circ$ to remove the alignment contribution,³ there are analogous geometries for which the absorption will contain no hexadecapole term. These are the

values of β for which $d_{00}^4(\beta)$ is zero; these being,

$$\beta_4 = 30.556^\circ, 70.124^\circ, 109.875^\circ, 149.444^\circ. \quad (15)$$

Thus if we perform a two photon linearly polarized absorption measurement at a polarization setting of β_4 to the

ground state symmetry axis it will contain solely $J''J''\rho_0^0(g,z)$ and $J''J''\rho_0^2(g,z)$ terms:

$$\begin{aligned} I_{\beta_4} &= C [[B_0]^{J''J''}\rho_0^0(g,z) + d_{00}^2(\beta_4)[B_2]^{J''J''}\rho_0^2(g,z)], \\ I_{\parallel} &= C [[B_0]^{J''J''}\rho_0^0(g,z) + [B_2]^{J''J''}\rho_0^2(g,z) \\ &\quad + [B_4]^{J''J''}\rho_0^4(g,z)]. \end{aligned} \quad (16)$$

Here C contains the line shape function, the reduced matrix elements, and the relevant defining parameters for the transition; while $[B_K]$ represents the degree to which each multipole moment in the ground state is coupled to the excited state population monopole as in 7 and 14.

Similar considerations apply to circularly polarized two photon absorption measurements in which β is now the angle between O , the propagation direction, and the ground state symmetry axis. We have

$$\begin{aligned} d_{00}^1(\beta) &= \cos \beta, \quad \beta = 90^\circ, \\ d_{00}^3(\beta) &= \frac{1}{2}(5 \cos^3 \beta - 3 \cos \beta), \\ \beta_3 &= 39.231^\circ, 90^\circ, 140.768^\circ. \end{aligned}$$

The relevant geometries of the ground state symmetry axis and the quantization axis imposed by the probe for which the various multipolar components of the ground state are removed are given in Fig. 1 as a plot of $d_{00}^K(\beta)$ vs β .

Thus a combination of the measurements outlined above can be used to obtain a complete multipolar picture of the ground state density matrix.

V. CONCLUSIONS

This series of papers has covered the various possibilities of using polarized laser excitation as a method by which the full information contained in the ground state density matrix can be unraveled.

It was shown that dispersed laser fluorescence studies while probing the $K'' = 0$ to $K'' = 4$ multipole components of the ground state did not necessarily lead to their determination in an unambiguous manner. However, by performing an experiment in which these multipoles (scalar, vector, and tensor quantities) are coupled solely to a scalar observable (the excited state population), such a measurement can be obtained. Single and two photon laser dichroism measurements of this type will hopefully prove important techniques, applicable to a wide range of dynamical studies such as product state analysis in molecular beam laser experiments, pump-probe studies of rotational energy transfer and the determination of photofragment polarization.

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⁵See, for example, E. Riedle, H. J. Neusser, and E. W. Schlag, *J. Chem. Phys.* **75**, 4231 (1981).

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