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On the measurement of molecular anisotropies using laser techniques. II. Differential absorption of circularly and linearly polarized light

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In this paper we describe a method which yields an unambiguous measure of the state multipolar moments of an anisotropic array of the angular momentum components of an assembly of ground state molecules. The method involves the measurement of circularly and linearly dichroic, single photon absorption and through such measurements, state moments having $K \leqslant 2$ may be directly obtained. The advantages of this technique over polarized laser fluorescence are discussed.

I. INTRODUCTION

In the previous paper in this series[1] we considered how the experimental polarization observables in a polarized laser fluorescence experiment transmit information on the anisotropy of the ground state of the species probed. We demonstrated however that such measurements are not unequivocal and that in general more than one ground state multipole may contribute to a given observable. Intuitively this can be seen in a qualitative fashion since the effect of polarized excitation on an anisotropic array is to increase the complexity of the information transmitted to the excited state by the light beam. The four main polarization observables in fluorescence, namely the intensities of emission of parallel and perpendicular linearly polarized, left and right circularly polarized light, will not be able in all circumstances to unscramble this information. In addition, the evolution in time of the excited state may bring increased complexities if cross relaxation occurs and for these reasons the laser fluorescence method suffers from serious problems for the most precise work.

Yet there is much to be learned from a precise and accurate experiment which can measure the full extent of the anisotropy of the distribution of gas phase species in a number of varied circumstances, as a test of the predictions of the transport equations for example in an ensemble of molecules possessing internal angular momentum. The Waldmann–Snider equation[2] predicts that molecules will become partially aligned when subjected to a gradient in concentration, say, and an experimental measure of this effect would yield insight into the dynamical behavior of fluid media. Molecules or fragments produced by chemical reactions or by light-induced processes[3–6] are known to emerge in the nascent state with anisotropic distributions, the nature of which give valuable evidence on the detailed mechanism of the fragmentation process.[7]

An alternative method exists, however, in which direct and unambiguous determination of the individual multipole moments characterizing an anisotropic ground state is possible. This is done by measuring the differences in *absorption* coefficient of linearly or circularly polarized light and the method may be made very sensitive to small anisotropies. A preliminary communication on this technique has already been submitted.[8] In this method, differences in polarized absorption relative to a particular z axis imposed by the light beam on the system are measured. The techniques and theory described will show some similarity to expressions derived and appropriate to chiroptical spectroscopy and to linear dichroism. These two effects are generally separated for theoretical treatment since in fluid media they do not often occur together. However, there are instances when linear dichroism intrudes into the measurements of circular dichroism and the techniques outlined here could in principle be used to deconvolute such data. In this treatment we deal with the case of rotationally resolved spectroscopic transitions of molecules in fluid media with particular reference to high resolution gas phase experiments. We consider the case of an anisotropic distribution of molecules characterized by multipole moment, $K \leqslant 2$, and our approach uses the tensor density matrix formalism which we have used in part I[1] of this series and in a number of recent publications.[9–11] Using this approach we derive the polarization observables of absorption in terms of the multipole moments of a generalized anisotropic ground state distribution. The direct relation between these will be demonstrated explicitly. The problem is nontrivial mainly because of the need to define the quantization axes appropriate to different types of polarization experiment using linearly and circularly polarized light. In part III of this series we discuss methods of determining anisotropies having multipole character of $K > 2$.

II. THEORY

The intensity of absorption, I^a, of light of polarization $\hat{e}$ defined with respect to the symmetry or quantization axis for the excitation process, is proportional to the trace of the excitation matrix defined in this geometry. For a rotationally resolved transition between lower state $\alpha''J''$ and upper state αJ, this is given by

$$I^a(\hat{e},z) = \sum_{M,M_1'',M_2''} \langle \alpha JM | \hat{e}\cdot d | \alpha''J''M_1'' \rangle$$

$$\times \langle \alpha JM | \hat{e}\cdot d | \alpha''J''M_2'' \rangle^{*J''J''} \rho_{M_1''M_2''}$$

$$= \sum_M {}^{JJ''}\rho_{MM}. \tag{1}$$

In Eq. (1), α stands for all quantum numbers not actually specified, d is the dipole moment operator, z is the axis of quantization for the particular excitation process, and $^{J''J''}\rho_{M_1''M_2''}$, $^{JJ}\rho_{MM}$ are the density matrix elements for ground and excited states, respectively.

In the multipolar expansion of the excited state density matrix,[1,9-11] it is the population monopole which is of most concern to us here. This is defined in the usual way as

$$^{JJ}\rho_0^0(\hat{e},z) = \sum_M (-1)^{J-M} \begin{pmatrix} J & J & 0 \\ M & -M & 0 \end{pmatrix} {}^{JJ}\rho_{MM}(\hat{e},z)$$

$$= \sum_M (-1)^{J-M+J-M} \delta_{JJ} \delta_{MM}$$

$$\times (2J+1)^{-1/2} \, {}^{JJ}\rho_{MM}(\hat{e},z). \quad (2)$$

Thus we can write

$$^{JJ}\rho_0^0(\hat{e},z) = (2J+1)^{-1/2} \sum_M {}^{JJ}\rho_{MM}(\hat{e},z) \quad (3)$$

and therefore the intensity of absorption is directly proportional to the excited state population ($K=0$) multipole. We now proceed in a manner similar to that described in our treatment of polarized laser fluorescence[1] and perform a multipole expansion of the ground state density matrix elements in terms of the state multipoles. We then consider how each multipole component in the ground state contributes to the excited state population monopole upon absorption of linearly and of circularly polarized light.

The absorption intensity is given by

$$I^a(z) = \sum_{\substack{M \\ M_1''M_2'' \\ K''Q''}} \langle \alpha JM | \hat{e} \cdot d | \alpha'' J'' M_1'' \rangle \langle \alpha JM | \hat{e} \cdot d | \alpha'' J'' M_2'' \rangle$$

$$\times (-1)^{J''-M_1''}(2K''+1)^{1/2}$$

$$\times \begin{pmatrix} J'' & J'' & K'' \\ M_1'' & -M_2'' & -Q'' \end{pmatrix} {}^{J''J''}\rho_{Q''}^{K''}(z). \quad (4)$$

The summations in Eq. (4) include off diagonal elements of the ground state density matrix, i.e., multipoles for which $Q'' \neq 0$. These quantities are retained for generality in circularly polarized absorption measurements though they vanish since a common z axis exists for both left and right circularly polarized light. For linearly polarized absorption a common axis is not retained and nonaxially symmetric multipoles in the ground state (with respect to z) can, if present, contribute to the absorption strength.

A. Circularly polarized absorption

The quantization axis imposed in such measurements is the propagation vector $\hat{O}$ of the light beam. Expressing Eq. (4) in terms of the appropriate spherical components of the excitation operators we have

$$I^a(\hat{O}) = \sum_{\substack{M_1''M_2'' \\ M \\ K''Q''}} |\hat{e}_{q_A}^1|^2 (-1)^{q_A+q_A} \langle \alpha JM | d_{q_A}^1 | \alpha'' J'' M_1'' \rangle$$

$$\times \langle \alpha JM | d_{q_A}^1 | \alpha'' J'' M_2'' \rangle^* (-1)^{J''-M_2''}(2K''+1)^{1/2}$$

$$\times \begin{pmatrix} J'' & J'' & K'' \\ M_1'' & -M_2'' & -Q'' \end{pmatrix} {}^{J''J''}\rho_{Q''}^{K''}(\hat{O}), \quad (5)$$

where q_A is the projection of the photon angular momentum on the axis defined by the experiment.

Applying the Wigner–Eckart theorem in the space fixed frame defined by $\hat{O}$ we have

$$I^a(\hat{O}) = \sum_{\substack{M_1''M_2'' \\ K''Q''M}} |\epsilon_{q_A}^1|^2 (-1)^{q_A+q_A} |\langle \alpha J \| d^1 \| \alpha'' J'' \rangle|^2$$

$$\times (-1)^{J-M+J-M+J''-M_2''}(2K''+1)^{1/2} \, {}^{J''J''}\rho_{Q''}^{K''}(\hat{O})$$

$$\times \begin{pmatrix} J & 1 & J'' \\ -M & q_A & M_1'' \end{pmatrix} \begin{pmatrix} J & 1 & J'' \\ -M & q_A & M_2'' \end{pmatrix}$$

$$\times \begin{pmatrix} J'' & J'' & K'' \\ M_1'' & -M_2'' & -Q'' \end{pmatrix}, \quad (6)$$

where $|\epsilon_{q_A}^1|^2 = 1$.

After some slight rearrangement followed by application of a standard angular momentum sum rule for the contraction of three $3j$ symbols[12] we have

$$I^a(\hat{O}) = \sum_{K''Q''} (-1)^{J+J''+K''+q_A} \begin{pmatrix} K'' & 1 & 1 \\ Q'' & q_A & -q_A \end{pmatrix}$$

$$\times \begin{Bmatrix} 1 & 1 & K'' \\ J'' & J'' & J \end{Bmatrix} \times (2K''+1)^{1/2} \, {}^{J''J''}\rho_{Q''}^{K''}(\hat{O})$$

$$\times |\langle \alpha J \| d^1 \| \alpha'' J'' \rangle|^2. \quad (7)$$

As can be seen from the $3j$ and $6j$ symbols in Eq. (7), $K'' = 0,1,2$ can all contribute to the absorption intensity. As we are dealing with light of a well-defined polarization with respect to $\hat{O}$ we have only $Q'' = 0$ projection terms for any of the allowed multipoles. It is convenient to introduce a differential circular polarization absorption ratio C^a by

$$C^a = \left(\frac{I_{q_A} - I_{-q_A}}{I_{q_A} + I_{-q_A}} \right)^a (\hat{O}). \quad (8)$$

This is given by

$$C^a(\hat{O}) = \sum_{K''} (-1)^{J+J''+K''+q_A} \begin{Bmatrix} 1 & 1 & K'' \\ J'' & J'' & J \end{Bmatrix} (2K''+1)^{1/2} [1 + (-1)^{K''+1}]$$

$$\times \begin{pmatrix} K'' & 1 & 1 \\ 0 & q_A & -q_A \end{pmatrix} {}^{J''J''}\rho_0^{K''}(\hat{O}) \left[\sum_{K''} (-1)^{J+J''+K''+q_A} \begin{Bmatrix} 1 & 1 & K'' \\ J'' & J'' & J \end{Bmatrix} \right.$$

$$\left. \times (2K''+1)^{1/2} [1 + (-1)^{K''}] \begin{pmatrix} K'' & 1 & 1 \\ 0 & q_A & -q_A \end{pmatrix} {}^{J''J''}\rho_0^{K''}(\hat{O}) \right]^{-1}. \quad (9)$$

Note that the line strength factors given by the reduced matrix elements, together with any M-independent transition terms implicit in the above such as the line shape functions and pumping parameters, cancel in the ratio.

It can be seen from the symmetry properties of the $3j$ symbols governing the absorption that the numerator contains solely terms proportional to the ground state orientation while the denominator contains the population and alignment contributions to the intensity. Expanding Eq. (9) and inserting the numerical values for the $3j$ symbols yields

$$C^a(\hat{O}) = \frac{\begin{Bmatrix} 1 & 1 & 1 \\ J'' & J'' & J \end{Bmatrix}^{J'J''}\rho_0^1(\hat{O})}{\left(\frac{2}{3}\right)^{1/2}\begin{Bmatrix} 1 & 1 & 0 \\ J'' & J'' & J \end{Bmatrix}^{J'J''}\rho_0^0(\hat{O}) + \left(\frac{1}{3}\right)^{1/2}\begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix}^{J'J''}\rho_0^2(\hat{O})}. \tag{10}$$

Thus by measuring the differential absorption of left and right circularly polarized light in the common axis system defined by $\hat{O}$ it is possible to obtain a direct measurement of the ground state orientation in this frame.

We will now go on to consider the corresponding linear dichroism measurements and demonstrate how a combination of the two techniques can be used to provide a complete determination of the degree of alignment and orientation present in a given system in a totally unambiguous manner.

B. Linearly polarized absorption

We define the linear absorption ratio or P^a,

$$P^a = \left(\frac{I_\| - I_\perp}{I_\| + I_\perp}\right)^a, \tag{11}$$

where $I_\|$ and $I_\perp$ refer to the intensities of absorption of electric dipole radiation polarized parallel and perpendicular to a particular space fixed axis system. The symmetry or quantization axis for linearly polarized absorption is that of the polarization vector of the light beam, so in effect we are imposing two external z axes upon the system probed and are measuring the intensity of absorption with respect to each. This is somewhat different to the situation encountered in circular dichroism measurements in which a common z axis is maintained. The consequences of this become manifest if one tries to relate emission from the excited state to the absorption strength as will be discussed further on.

The treatment of linearly polarized absorption from a polarized array can be tackled in two ways; we can take a single z axis to be imposed upon the system along which we measure $I_\|$. Consequently, $I_\perp$ is I_x in this system. In this instance the state multipole moments for the ground state are defined in a common axis system but we have different expressions for our absorption operators.

The second approach is to treat $I_\|$ and $I_\perp$ as two separate processes each defining their own particular coordinate systems z_1 and z_2. Here the absorption operators are of the same form but in order to define the experimental observables it is necessary to rotate the state multipoles defined in z_1 into the z_2 axis system or vice versa. This is simply achieved by the Euler rotation $D(O,\pi/2,O)$ and is perhaps a better approach as it emphasizes that the asymmetry of the absorption process arises as a direct consequence of the rotationally noninvariant components of the ground state.

These two approaches are depicted in Fig. 1 and are outlined in the following section.

1. Common axis system

In this treatment we wish to calculate $I_z - I_x$ and $I_z + I_x$ defined in the z axis system (Fig. 1).

The two observables are given by

$$I_z^a = \sum_{\substack{M_1''M_2'' \\ MK''Q''}} \langle \alpha JM | \hat{e}_z \cdot d_z | \alpha''J''M_1'' \rangle$$

$$\times \langle \alpha JM | \hat{e}_z \cdot d_z | \alpha''J''M_2'' \rangle^*$$

$$\times (-1)^{J''-M_1''}(2K''+1)^{1/2}$$

$$\times \begin{pmatrix} J'' & J'' & K'' \\ M_1'' & -M_2'' & Q'' \end{pmatrix}^{J'J''}\rho_{Q''}^{K''}(z),$$

$$I_x^a = \sum_{\substack{M_1''M_2'' \\ MK''Q''}} \langle \alpha JM | \hat{e}_x \cdot d_x | \alpha''J''M_1'' \rangle$$

$$\times \langle \alpha JM | \hat{e}_x \cdot d_x | \alpha''J''M_2'' \rangle^*$$

$$\times (-1)^{J''-M_1''}(2K''+1)^{1/2}$$

$$\times \begin{pmatrix} J'' & J'' & K'' \\ M_1'' & -M_2'' & -Q'' \end{pmatrix}^{J'J''}\rho_{Q''}^{K''}(z). \tag{12}$$

We first consider I_z and expand the absorption operator in terms of its spherical components. Application of the Wigner–Eckart theorem in the space fixed frame defined by z, followed by some angular momentum manipulation gives

$$I_z^a(z) = \sum_{K''Q''}(-1)^{J+J''+K''}(2K''+1)^{1/2}$$

$$\times \begin{pmatrix} 1 & 1 & K'' \\ 0 & 0 & Q'' \end{pmatrix}\begin{Bmatrix} 1 & 1 & K'' \\ J'' & J'' & J \end{Bmatrix}$$

$$\times {}^{J'J''}\rho_{Q''}^{K''}(z)|\langle \alpha J\|d^1\|\alpha''J''\rangle|^2. \tag{13}$$

For $I_\perp(I_x)$ we can write absorption intensity in the following way:

$$I_x^a(z) = \sum_{\substack{M_1''M_2'' \\ K''Q''}}|\epsilon_x|^2 \tfrac{1}{2}[\langle \alpha JM | d_1^1 - d_{-1}^1 | \alpha''J''M_1'' \rangle$$

$$\times \langle \alpha JM | d_1^1 - d_{-1}^1 | \alpha''J''M_2'' \rangle^*]$$

$$\times (-1)^{J''-M_1''}\begin{pmatrix} J'' & J'' & K'' \\ M_1'' & -M_2'' & -Q'' \end{pmatrix}$$

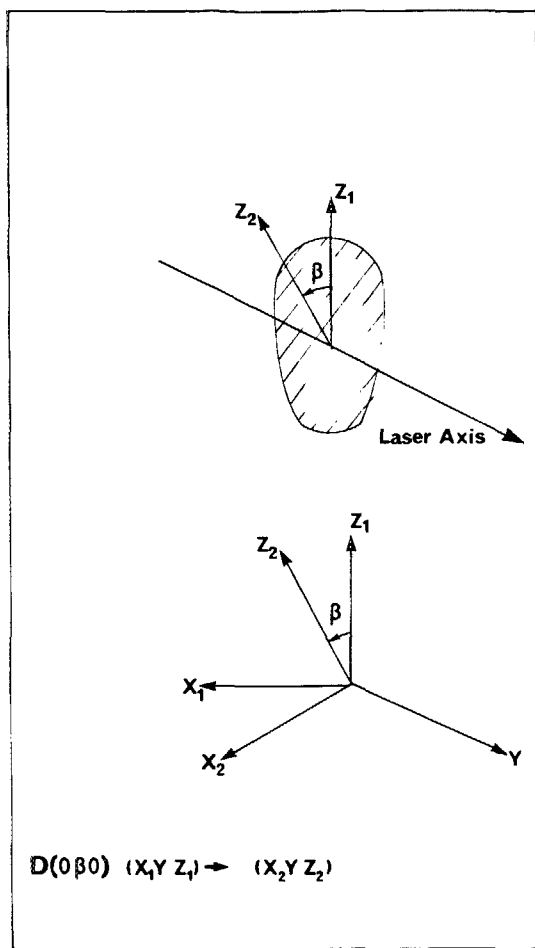$$\times (2K''+1)^{1/2}\,{}^{J'J''}\rho_{Q''}^{K''}(z). \tag{14}$$

FIG. 1. In the measurement of the differential absorption of two linearly polarized beams by a polarized array of molecules (shaded area), two sets of axes are imposed on the system and these are connected by an Euler rotation $D(O,\beta,O)$. For the measurement of $I_\perp$ and $I_\parallel$, $\beta = \pi/2$ and the two quantization axes z_1 and z_2 are orthogonal.

Treating this expression as before, i.e., applying the Wigner–Eckart theorem in the space fixed frame and then simplifying with some angular momentum algebra we obtain

$$I_x^a = I_1^a(z) = \sum_{K''Q''} \tfrac{1}{2} |\langle \alpha J \| d^1 \| \alpha'' J'' \rangle|^2 (2K'' + 1)^{1/2}$$

$$\times (-1)^{J+J''+K''+1} \begin{Bmatrix} 1 & 1 & K'' \\ J'' & J'' & J \end{Bmatrix} {}^{J''J''}\rho_{Q''}^{K''}(z)$$

$$\times \left[(1 + (-1)^{K''}) \begin{pmatrix} 1 & 1 & K'' \\ 1 & -1 & Q'' \end{pmatrix} \right.$$

$$\left. - \begin{pmatrix} 1 & 1 & K'' \\ -1 & -1 & Q'' \end{pmatrix} - \begin{pmatrix} 1 & 1 & K'' \\ 1 & 1 & Q'' \end{pmatrix} \right]. \quad (15)$$

From the symmetry requirements of the $3j$ symbols we can see that only the $K'' = 0,2$ and $Q' = 0 \pm 2$ terms contribute to the absorption intensity. Expanding Eq. (15) and inserting the numerical values of the $3j$ symbols gives

$$I_\perp(z) = |\langle \alpha J \| d^1 \| \alpha'' J'' \rangle|^2 (-1)^{J+J''+1}$$

$$\times \left[\frac{1}{\sqrt{3}} {}^{J''J''}\rho_0^0(z) \begin{Bmatrix} 1 & 1 & 0 \\ J'' & J'' & J \end{Bmatrix} \right.$$

$$+ \begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix} \frac{1}{\sqrt{6}} {}^{J''J''}\rho_0^2(z)$$

$$\left. + \frac{1}{2} \begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix} \left({}^{J''J''}\rho_2^2(z) + {}^{J''J''}\rho_{-2}^2(z) \right) \right].$$

$$(16)$$

Similarly for $I_\parallel^a(z)$ we have

$$I_\parallel^a(z) = |\langle \alpha J \| d^1 \| \alpha'' J'' \rangle|^2 \times (-1)^{J+J''+1}$$

$$\times \left[\frac{1}{\sqrt{3}} \begin{Bmatrix} 1 & 1 & 0 \\ J'' & J'' & J \end{Bmatrix} {}^{J''J''}\rho_0^0(z) + \left(\frac{2}{3} \right)^{1/2} \right.$$

$$\left. \times \begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix} {}^{J''J''}\rho_0^2(z) \right]. \quad (17)$$

Substituting these two expressions into our definition of the linear absorption ratio yields

$$\left(\frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} \right)^a = \frac{- \begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix} \left[{}^{J''J''}\rho_0^2(z) - \left(\frac{1}{6} \right)^{1/2} \left({}^{J''J''}\rho_2^2(z) + {}^{J''J''}\rho_{-2}^2(z) \right) \right]}{\frac{2}{3}\sqrt{2} \begin{Bmatrix} 1 & 1 & 0 \\ J'' & J'' & J \end{Bmatrix} {}^{J''J''}\rho_0^0(z) - \begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix} \left[\frac{1}{3} {}^{J''J''}\rho_0^2(z) + \left(\frac{1}{6} \right)^{1/2} ({}^{J''J''}\rho_2^2(z) + {}^{J''J''}\rho_{-2}^2(z)) \right]}. \quad (18)$$

2. Absorption measurements defined in z_1 and z_2

In this approach the absorption intensities are calculated in the z_1 and z_2 axis systems separately. The measurement made in z_2 is related to z_1 (or vice versa) by examining the transformation properties of the state multipoles when one frame is rotated into the other. The linear absorption ratio is given by

$$\left(\frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} \right)^a = \left(\frac{I_{z_1} - I_{z_2}}{I_{z_1} + I_{z_2}} \right)^a. \quad (19)$$

Following the procedure as before we obtain

$$I_{z_1} = \sum_{K''Q''} (-1)^{J+J''+K''} \begin{pmatrix} 1 & 1 & K'' \\ 0 & 0 & Q'' \end{pmatrix}$$

$$\times (2K'' + 1)^{J''J''}\rho_{Q''}^{K''}(z_1)$$

$$\times \begin{Bmatrix} 1 & 1 & K'' \\ J'' & J'' & J \end{Bmatrix} |\langle \alpha J \| d^1 \| \alpha'' J'' \rangle|^2, \quad (20)$$

$$I_{z_2} = \sum_{K''Q''} (-1)^{J+J''+K''} \begin{pmatrix} 1 & 1 & K'' \\ 0 & 0 & Q'' \end{pmatrix}$$

$$\times (2K'' + 1)^{1/2} \begin{Bmatrix} 1 & 1 & K'' \\ J'' & J'' & J \end{Bmatrix}$$

$$\times {}^{J''J''}\rho_{Q''}^{K''}(z_2) |\langle \alpha J \| d^1 \| \alpha'' J'' \rangle|^2. \quad (21)$$

From the symmetry constraints imposed by the $3j$ and $6j$ symbols only $^{J''J''}\rho_0^0(z_1)$ and $^{J''J''}\rho_0^2(z_1)$ contribute to I_z, and $^{J''J''}\rho_0^0(z_2)$ and $^{J''J''}\rho_0^2(z_2)$ to I_{z_2}.

In order to calculate the linear absorption ratio we transform the state multipoles defined in z_2 into their equivalent representation in z_1 by an Euler rotation of $D(O,\pi/2,0)$ which brings z_1 into coincidence with z_2.

The rotational transformation properties of the state multipoles are those of spherical tensors of rank K'' and projection Q''. Thus we can write

$$^{J''J''}\rho_{Q''}^{K''}(z_2) = \sum_{Q''} \mathscr{D}_{Q''-Q'}^{K} (O,\pi/2,O) \, ^{J''J''}\rho_{Q'}^{K''}(z_1), \quad (22)$$

where $\mathscr{D}_{Q''-Q'}^{K}(O,\pi/2,O)$ is the appropriate Euler rotation matrix element connecting the multipoles in the two axis systems as defined in Brink and Satchler.[13] Since an Euler rotation of $\beta = \pi/2$ alone connects the two frames, Eq. (21) can be rewritten in terms of the reduced rotation matrices:

$$d_{Q''-Q'}^{K''}(\beta = \pi/2),$$

$$^{J''J''}\rho_{Q''}^{K''}(z_2) = \sum_{Q''} d_{Q''-Q'}^{K}(\pi/2) \, ^{J''J''}\rho_{Q'}^{K''}(z_1). \quad (23)$$

The nonzero contributions to the absorption in z_2 are $^{J''J''}\rho_0^0$ and $^{J''J''}\rho_0^2$ ($Q''' = 0$) and thus we have

$$^{J''J''}\rho_0^0(z_2) = d_{00}^0(\pi/2) \, ^{J''J''}\rho_0^0(z)$$
$$= \,^{J''J''}\rho_0^0(z_1) \quad (24)$$

which is an obvious result as the population monopole is a scalar and hence rotationally invariant.

For the alignment in z_2 we have

$$^{J''J''}\rho_0^2(z_2) = \sum_{Q'} d_{0Q'}^2 \cdot(\pi/2) \, ^{J''J''}\rho_{Q'}^2 \cdot(z_1). \quad (25)$$

The algebraic expressions for the reduced rotation matrices are tabulated by Brink and Satchler[13] the appropriate nonzero elements being

$$d_{02}^2(\beta) = d_{0-2}^2(\beta) = (\tfrac{3}{8})^{1/2} \sin^2\beta,$$
$$d_{00}^2(\beta) = \tfrac{1}{2}(3\cos^2\beta - 1). \quad (26)$$

Hence,

$$^{J''J''}\rho_0^2(z_2) = -\tfrac{1}{2}\,^{J''J''}\rho_0^2(z_1) + (\tfrac{3}{8})^{1/2}$$
$$\times [\,^{J''J''}\rho_2^2(z_1) + \,^{J''J''}\rho_{-2}^2(z_1)]. \quad (27)$$

Substitution of Eq. (27) into Eq. (21) gives us the absorption intensity observed in z_2 in terms of the state multipoles defined in z_1,

$$I_{z_2} = |\langle\alpha J\|d^1\|\alpha''J''\rangle|^2 (-1)^{J+J''+1} \left\{ \left(\frac{1}{3}\right)^{1/2} \begin{Bmatrix} 1 & 1 & 0 \\ J'' & J'' & J \end{Bmatrix} \,^{J''J''}\rho_0^0(z_1) \right.$$
$$\left. - \begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix} \left(\frac{2}{3}\right)^{1/2} \left[\frac{1}{2}\,^{J''J''}\rho_0^2(z_1) - \left(\frac{3}{8}\right)^{1/2} (\,^{J''J''}\rho_2^2(z_1) + \,^{J''J''}\rho_{-2}^2(z_1))\right] \right\}. \quad (28)$$

Substituting Eqs. (20) and (28) into Eq. (19) which defines the linear absorption ratio gives, with some rearranging,

$$\left(\frac{I_{z_1} - I_{z_2}}{I_{z_1} + I_{z_2}}\right)^a = \frac{-\begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix} \left[\,^{J''J''}\rho_0^2(z_1) - \left(\frac{1}{6}\right)^{1/2} (\,^{J''J''}\rho_2^2(z_1) + \,^{J''J''}\rho_{-2}^2(z_1))\right]}{\frac{2}{3}\sqrt{2}\begin{Bmatrix} 1 & 1 & 0 \\ J'' & J'' & J \end{Bmatrix} \,^{J''J''}\rho_0^0(z_1) - \begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix} \left[\frac{1}{3}\,^{J''J''}\rho_0^2(z_1) + \left(\frac{1}{6}\right)^{1/2} (\,^{J''J''}\rho_2^2(z_1) + \,^{J''J''}\rho_{-2}^2(z_1))\right]} \quad (29)$$

which is exactly the same as Eq. (18).

Examining Eq. (29) we can see that as a direct consequence of making two measurements in different axis systems there are direct contributions to the linear absorption ratio from multipoles with a nonzero projection on the z_1 axis. Off diagonal elements of the ground state density matrix $^{JJ}\rho_{M,M_2}(g,z)$ make no contribution to the circular absorption ratio in which cylindrically symmetric contributions to the absorption are taken with respect to the same axis. However, if we choose a geometry in which the ground-state multipoles are axially symmetric with the quantization axis, no nonzero Q'' terms exist and the linear absorption ratio simplifies somewhat:

$$\frac{I_\| - I_\perp}{I_\| + I_\perp} = \frac{\begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix} \,^{J''J''}\rho_0^2(g,z_1)}{\frac{2}{3}\sqrt{2}\begin{Bmatrix} 1 & 1 & 0 \\ J'' & J'' & J \end{Bmatrix} \,^{J''J''}\rho_0^0(g,z_1) + \frac{1}{3}\begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix} \,^{J''J''}\rho_0^2(g,z_1)}. \quad (30)$$

Such a situation is easily realized in processes possessing a well defined z axis with respect to the production of ground state anisotropy. Linearly or circularly polarized photodissociation and nozzle expansions in a molecular beam experiment are examples of processes which possess such an axis.

From Eqs. (17) and (28) we can see that when the multipoles are axially symmetric with respect to z_1, a combination of $I_\| + 2I_\perp$ will yield an expression in which only $K'' = 0$ terms contribute to the absorption intensity:

$$I_\| + 2I_\perp = |\langle\alpha J\|d^1\|\alpha''J''\rangle|^2 (-1)^{J+J''+1}\sqrt{3}$$
$$\times \begin{Bmatrix} 1 & 1 & 0 \\ J'' & J'' & J \end{Bmatrix} \,^{J''J''}\rho_0^0(g,z_1). \quad (31)$$

Thus the ratio $(I_\parallel - I_\perp)/(I_\parallel + 2I_\perp)$ is directly proportional to $^{J \cdot J \cdot}\rho_0^2(g,z_1)/^{J \cdot J \cdot}\rho_0^0(g,z_1) = [\alpha_2]$, the degree of alignment in the ground state:

$$\frac{I_\parallel - I_\perp}{I_\parallel + 2I_\perp} = \frac{-\begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix}\left(\frac{2}{3}\right)^{1/2}\left[\frac{3}{2}{}^{J \cdot J \cdot}\rho_0^2(g,z_1)\right]}{\sqrt{3}\begin{Bmatrix} 1 & 1 & 0 \\ J'' & J'' & J \end{Bmatrix}{}^{J \cdot J \cdot}\rho_0^0(g,z_1)}$$

$$= \frac{1}{\sqrt{2}}[\alpha_2]\begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix}\begin{Bmatrix} 1 & 1 & 0 \\ J'' & J'' & J \end{Bmatrix}^{-1}.$$

(32)

As will be discussed later these quantities are readily determined in a standard polarization–modulation experiment.

It is interesting to examine the situation where the two axis systems are not orthogonal and connected by an Euler rotation of $D(O,\beta,O)$ about their common y axis, Fig. 2. The absorption intensity in z_2 is given by

$$I_{z_2} = |\langle \alpha J \| d^1 \| \alpha'' J'' \rangle|^2 (-1)^{J+J''+1}$$

$$\times \left[\left(\frac{1}{3}\right)^{1/2}\begin{Bmatrix} 1 & 1 & 0 \\ J'' & J'' & J \end{Bmatrix}{}^{J \cdot J \cdot}\rho_0^0(g,z_2)\right.$$

$$\left. - \left(\frac{2}{3}\right)^{1/2}\begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix}{}^{J \cdot J \cdot}\rho_0^0(g,z_2)\right].$$

(33)

The state multipoles in z_2 are related to z_1 as in Eq. (25):

$$^{J \cdot J \cdot}\rho_0^0(g,z_2) = {}^{J \cdot J \cdot}\rho_0^0(g,z_1),$$

$$^{J \cdot J \cdot}\rho_0^2(g,z_2) = \sum_{Q'} d_{0Q'}^2(\beta){}^{J \cdot J \cdot}\rho_{Q'}^2(g,z_1).$$

(34)

Substituting into Eq. (33) gives us

$$I_{z_2} = |\langle \alpha J \| d^1 \| \alpha'' J'' \rangle|^2 (-1)^{J+J''+1}$$

$$\times \left[\left(\frac{1}{3}\right)^{1/2}\begin{Bmatrix} 1 & 1 & 0 \\ J'' & J'' & J \end{Bmatrix}{}^{J \cdot J \cdot}\rho_0^0(g,z_1)\right.$$

$$\left. - \left(\frac{2}{3}\right)^{1/2}\begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix}\sum_{Q'} d_{0Q'}^2(\beta){}^{J \cdot J \cdot}\rho_{Q'}^2(g,z_1)\right].$$
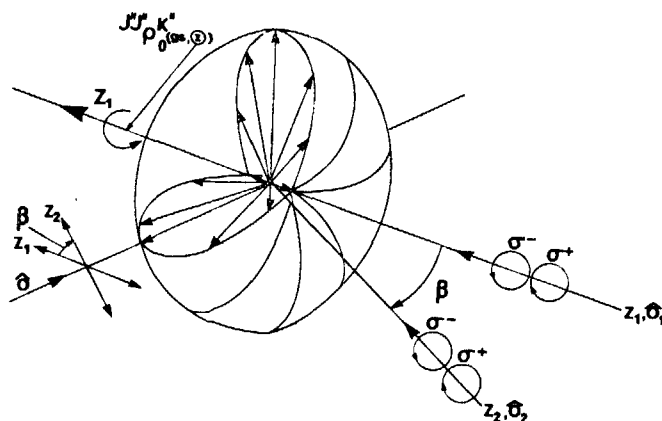
(35)

FIG. 2. In contrast to the linear polarization case (Fig. 1), the absorption of + and − circularly polarized light is made with respect to the propagation direction of the light beam $\hat{O}$ and thus a common z axis is retained for both measurements. A second quantization axis may be introduced by changing the propagation vector of light beam with respect to the ground state z axis, z_1. In this instance β is the angle between $\hat{O}_1$ and $\hat{O}_2$. The figure depicts both circularly and linearly polarized absorption geometries for a torroidal array of classical angular momentum vectors.

If we then set β to be the so called "magic angle" of 54.73° we have

$$d_{00}^2 = 0,$$

$$d_{01}^2 = -d_{0-1}^2 = (\tfrac{1}{3})^{1/2}, \quad d_{0\pm2}^2 = (\tfrac{1}{6})^{1/2}.$$

(36)

Thus,

$$I_{z_2} = |\langle \alpha J \| d^1 \| \alpha'' J'' \rangle|^2 (-1)^{J+J''+1}$$

$$\times \left[\left(\frac{1}{3}\right)\begin{Bmatrix} 1 & 1 & 0 \\ J'' & J'' & J \end{Bmatrix}{}^{J \cdot J \cdot}\rho_0^0(g,z_1)\right.$$

$$- \left(\frac{2}{3}\right)^{1/2}\begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix}\left[\left(\frac{1}{3}\right)^{1/2}\right.$$

$$\times [^{J \cdot J \cdot}\rho_1^2(gs,z_1) - {}^{J \cdot J \cdot}\rho_{-1}^2(g,z_1)]$$

$$\left.\left. + (\tfrac{1}{6})^{1/2}[^{J \cdot J \cdot}\rho_2^2(g,z_1) + {}^{J \cdot J \cdot}\rho_{-2}^2(g,z_1)]\right]\right].$$

(37)

The lack of axial symmetry means that as in fluorescence there is no unique absorption direction along which linear polarization measurements will yield the population monopole.[1] In the case of $I_\perp$ if we rotate the probe beam in the xy plane through an angle $\gamma = 90°$, $I_\perp$ is now equivalent to I_y and we have imposed a third z axis, z_3 on the system which is related to z_1 by the composite Euler rotation $D(O,\pi/2,\pi/2)$. Proceeding as above we have

$$^{J \cdot J \cdot}\rho_0^K(z_3) = \sum_{Q'} D_{0Q'}^K(O,\pi/2,\pi/2){}^{J \cdot J \cdot}\rho_{Q'}^K(z_1)$$

$$= \sum_{Q'} d_{0Q'}^K(\pi/2)e^{-iQ'\pi/2}{}^{J \cdot J \cdot}\rho_{Q'}^K(z_1).$$

(38)

Expanding Eq. (38) and inserting the numerical values of the rotation matrix elements appropriate to the Euler angles $\beta = \gamma = \pi/2$ we have

$$^{J \cdot J \cdot}\rho_0^0(z_3) = {}^{J \cdot J \cdot}\rho_0^0(z_1),$$

$$^{J \cdot J \cdot}\rho_0^2(z_3) = -\frac{1}{2}{}^{J \cdot J \cdot}\rho_0^2(z_1)$$

$$- \left(\frac{3}{8}\right)^{1/2}[^{J \cdot J \cdot}\rho_2^2(z_1) + {}^{J \cdot J \cdot}\rho_{-2}^2(z_1)].$$

(39)

Comparison of Eq. (39) with Eq. (27) shows that in the z_3 axis system the $Q'' = \pm 2$ contributions to the absorption intensity (I_y) will be equal in magnitude but opposite in sign to those in z_2 (I_x):

$$I_{(z_3)} = I_y = |\langle J \| d^1 \| \alpha'' J'' \rangle|^2 (-)^{J+J''+1}$$

$$\times \left\{\left(\frac{1}{3}\right)^{1/2}\begin{Bmatrix} 1 & 1 & 0 \\ J'' & J'' & J \end{Bmatrix}{}^{J \cdot J \cdot}\rho_0^0(z_1)\right.$$

$$- \frac{1}{2}\begin{Bmatrix} 1 & 1 & 2 \\ J'' & J'' & J \end{Bmatrix}\left[\left(\frac{2}{3}\right)^{1/2}\left[\frac{1}{2}{}^{J \cdot J \cdot}\rho_0^2(z_1)\right.\right.$$

$$\left.\left.\left. + \left(\frac{3}{8}\right)^{1/2}(^{J \cdot J \cdot}\rho_2^2(z_1) + {}^{J \cdot J \cdot}\rho_{-2}^2(z_1))\right]\right]\right\}.$$

(40)

From Eqs. (40), (28), and (21) it follows that the combination of absorption measurements $(I_{z_1} + I_{z_2} + I_{z_3})(I_z + I_x + I_y)$ is equivalent to $I_\parallel + 2I_\perp$ in axially symmetric systems being directly proportional to the population monopole. The absorption ratio $[I_z - \frac{1}{2}(I_x + I_y)][I_z + I_x + I_y]^{-1}$ is equivalent to Eq. (32) and yields the degree of ground state axial

alignment $[\alpha_{20}]$. Furthermore, the difference between I_x and I_y gives the absorption intensity solely in terms of $Q'' = \pm 2$ terms thus $(I_x - I_y)[I_z + I_x + I_y]^{-1}$ is directly proportional to the degree of axially asymmetric alignment $[\alpha_{2\pm2}]$. If the ground state is axially symmetric with respect to z_1 there are no alignment terms in Eq. (37) which gives an expression analogous to that for $I_{\parallel} + 2I_{\perp}$ shown in Eq. (31). An absorption measurement using this geometry therefore contains solely the ground state population. There are similar geometries which can be employed in two-photon absorption measurements to remove the contributions from higher multipoles, and we shall consider these in more detail in a forthcoming publication.[14]

III. EXPERIMENTAL REALIZATION

The preceding sections have outlined how linear and circular dichroism measurements can provide an unequivocal test for and a method of determining the first three state multipoles of an anisotropic array of molecules. Equation (10) relates the ground state orientation directly to an experimental observable and Eq. (30) makes this relation for the alignment when axial symmetry prevails. The off-diagonal elements are obtained by rotating the probe geometry to obtain equations such as (18). The population multipole is easily obtained either as $I_{\parallel} + 2I_{\perp}$ [Eq. (31)] or by the magic angle method [Eq. (37)]. Measurement of the linear and circular absorption ratios (P^a and C^a) for a particular rotational transition $\alpha''J'' \rightarrow \alpha J$ yields direct polarization information, decoupled from the scalar properties of the transition as contained in the reduced matrix elements and the line shape function.

The techniques available for measuring circular and linear dichroism are well known from the field of chiroptical spectroscopy and are summarized in a recent book by Mason.[15] It is relatively straightforward to obtain both the difference (Δ) and the sum (Σ) of absorption coefficients for left and right circularly or for parallel and perpendicularly polarized light using standard absorption techniques. An alternative method is to use fluorescence detection and we discuss this below. Equation (32) demonstrates that the absorption ratio $(I_{\parallel} - I_{\perp})(I_{\parallel} + 2I_{\perp})^{-1}$ is directly proportional to the degree of alignment in the ground state $[\alpha_2]$ provided the multipoles are axially symmetric with respect to z_1. Using the standard techniques referred to above we may determine this quantity directly from the combination $(2\Sigma)(3\Sigma - \Delta)^{-1}$ using linearly polarized light.

The circular polarization ratio C^a may be expressed as

$$C^a = \left[(-1)^{q_A} \frac{\left\{ \begin{matrix} 1 & 1 & 1 \\ J'' & J'' & J \end{matrix} \right\}}{\left\{ \begin{matrix} 1 & 1 & 0 \\ J'' & J'' & J \end{matrix} \right\}} [\alpha_1] \right]$$

$$\times \left[\left(\frac{2}{3}\right)^{1/2} + \left(\frac{1}{3}\right)^{1/2} \frac{\left\{ \begin{matrix} 1 & 1 & 2 \\ J'' & J'' & J \end{matrix} \right\}}{\left\{ \begin{matrix} 1 & 1 & 0 \\ J'' & J'' & J \end{matrix} \right\}} [\alpha_2] \right]^{-1} ,$$

$$\tag{41}$$

where $[\alpha_1] = [^{J''J}\rho_0^1(g,\hat{O})][^{J''J}\rho_0^0(g,\hat{O})]^{-1}$.

Having previously determined $[\alpha_2]$ in z_1 as described we may substitute the result into Eq. (38), providing that $\hat{O}$ defines the same axis, and thus determine $[\alpha_1]$ from the measured value of C^a. This will always entail two measurements in a right angled geometry as $\hat{O}$ and z_1 are orthogonal as Fig. 3 shows.

IV. FLUORESCENCE DETECTION METHODS

It is well known that the measurement of fluorescence intensity is an excellent method of determining absorption strengths and in many instances, may be a more viable technique than absorption spectroscopy. This might apply particularly to the case of two-photon absorption measurements, which we discuss in part III of this series.[14] Unfortunately it is a common fallacy to relate fluorescence intensity (whether spectrally dispersed or undispersed) directly to the excited state population. As we have shown in earlier papers,[11] the emission intensity contains a contribution from the alignment and proper account must be taken of this polarization and anisotropy of the emission in order to obtain unambiguous results.

Fluorescence detection of circular dichroism from optically active molecular species has been discussed by Turner,

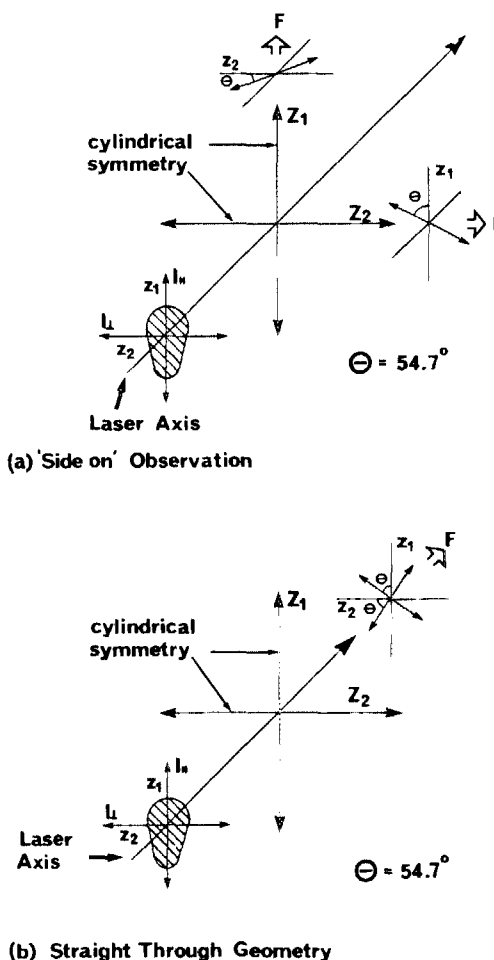(a) 'Side on' Observation

(b) Straight Through Geometry

FIG. 3. Experimental geometries for unresolved fluorescence detection of the population component of the excited state using the magic angle polarizer setting of 54.7° to the excited state symmetry axis for linearly polarized excitation in "side on" and "straight through" configurations.

Maestre, and Tinoco[16] for systems which reorient rapidly compared to the lifetime of the emitting state as do the species we consider here. Their treatment is somewhat different to that presented here and is concerned with a particular form of anisotropy. We now present a very general treatment of the problem of determining an arbitrary anisotropic distribution of angular momentum states using fluorescence detection in a one- or a two-photon process.

It has been demonstrated above that the absorption intensity is directly proportional to the population monopole for the excited state. Under isotropic or collision free conditions, encountered in cell and molecular beam environments, respectively, there is no interconversion of the excited state multipoles.[17] In these circumstances, with the knowledge that only the population orientation, and alignment multipoles ($K = 0,1,2$) for the excited state can contribute to electric dipole emission, the predominant contribution to the fluorescence, the measurement procedure must be such that the monopole component is the sole contributor to the fluorescence signal. We will now consider both circularly and linearly polarized excitation and demonstrate how this can be achieved.

A. Circularly polarized excitation (single and two photon)

In circularly polarized absorption the excitation process is symmetric to $\widehat{O}$. The orientation contribution to the fluorescence signal may be removed by measuring the *linearly* polarized component of the signal in the forward direction. However, in axially symmetric systems all linear polarizer settings are equivalent (i.e., $I_x \equiv I_y$). If the fluorescence is observed at right angles to the z axis ($\widehat{O}$), along y in a side on configuration this is not so. The plane polarized components of the fluorescence can be measured parallel and perpendicular to $\widehat{O}$ yielding exactly analogous quantities to $I_{\parallel}$ and $I_{\perp}$ encountered in linearly polarized fluorescence.

In this side on configuration we can write expressions for the total unresolved fluorescence intensity as follows:

$$I. = \sum_{M_1 M_2} {}^{JJ}\rho_{M_1 M_2}(q_A, \widehat{O}) \, \mathbb{D}_{M_2 M_1}(\hat{\epsilon}_z, \widehat{O})$$

$$= \sum_{\substack{M_1 M_2 M''' \\ \alpha''' J'''}} {}^{JJ}\rho_{M_1 M_2}) q_A, \widehat{O}) \langle \alpha''' J''' M''' | d_0^1 | \alpha J M_1 \rangle$$

$$\times \langle \alpha''' J''' M''' | d_0^1 | \alpha J M_2 \rangle^*, \tag{42}$$

where the sum over $\alpha''' J'''$ is to all rovibronic levels accessible in the ground state.

Expanding in terms of the state multipoles, applying the Wigner–Eckart theorem to the emission matrix elements and the standard angular momentum manipulations we have

$$I.(\epsilon_z, \widehat{O}) = \sum_{\substack{KQ \\ J''' \alpha'''}} (-1)^{J + J''' + K}(2K+1)^{1/2}\,{}^{JJ}\rho_Q^K(q_A)$$

$$\times \begin{pmatrix} 1 & 1 & K \\ 0 & 0 & Q \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ J & J & J''' \end{Bmatrix}$$

$$\times |\langle \alpha''' J''' \| d^1 \| \alpha J \rangle|^2. \tag{43}$$

Only the population and alignment multipoles contribute to the emission intensity in this arrangement giving

$$I.(\epsilon_z, \widehat{O}) = \sum_{J''' \alpha'''} (-1)^{J + J''' + 1} |\langle \alpha''' J''' \| d^1 \| \alpha J \rangle|^2$$

$$\times \left[\left(\frac{1}{3}\right)^{1/2} \begin{Bmatrix} 1 & 1 & 0 \\ J & J & J''' \end{Bmatrix} {}^{JJ}\rho_0^0 \right.$$

$$\left. - \left(\frac{2}{3}\right)^{1/2} \begin{Bmatrix} 1 & 1 & 2 \\ J & J & J''' \end{Bmatrix} {}^{JJ}\rho_0^2 \right]. \tag{44}$$

The corresponding expression for $I_{\perp}$ is

$$I_{\perp} = \sum_{\substack{M_1, M_2 \\ M''' J''' \alpha'''}} {}^{JJ}\rho_{M_1, M_2}(q_A, \widehat{O}) \, \mathbb{D}_{M_2 M_1}(\hat{\epsilon}_x, \widehat{O}). \tag{45}$$

Proceeding as before the nonzero elements of this in terms of the state multipoles and the tensor moments of the detection matrix are given by

$$I_{\perp} = \sum_{J''' \alpha'''} (-1)^{J + J''' + 1}$$

$$\times \left[\left(\frac{1}{3}\right)^{1/2} \begin{Bmatrix} 1 & 1 & 0 \\ J & J & J''' \end{Bmatrix} {}^{JJ}\rho_0^0(q_A, \widehat{O}) \right.$$

$$\left. \times - \left(\frac{1}{6}\right)^{1/2} \begin{Bmatrix} 1 & 1 & 2 \\ J & J & J''' \end{Bmatrix} {}^{JJ}\rho_0^2(q_A, \widehat{O}) \right] \tag{46}$$

$$\times |\langle \alpha''' J''' \| d^1 \| \alpha J \rangle|^2.$$

A combination of $I_{\parallel} + 2I_{\perp}$ will yield a signal which contains solely the population monopole. This is achieved in an exactly analogous manner to linearly polarized excitation and emission by measuring the fluorescence intensity of plane polarized light at the so called magic angle of 54.7° to the z axis, $\widehat{O}$.

It should be remembered that here the magic angle setting of 54.7° is between the propagation vector of the laser and the polarizer axis. The necessary geometry is shown in Fig. 3.

In axially asymmetric systems the equivalent measurements for the determination of the excited state population ($K = 0$) are $I_z + I_x + I_y$ which requires both straight through and side on fluorescence measurements with respect to $\widehat{O}$. The two polarizations may be related to the same quantization axis. The excited state population components ${}^{JJ}\rho_0^0(q_A)$ and ${}^{JJ}\rho_0^0(-q_A)$ can therefore be determined from undispersed fluorescence in a common geometry with a single linear polarizer setting.

However, with linearly polarized absorption using two orthogonal polarizations the situation is more complex if one wishes to relate fluorescence intensity to absorption. From the geometry of the system two excited state ensembles are created with orthogonal z axes. The spatial anisotropy of emission from a dipole oscillator ensures that a common geometry for the determination of ${}^{JJ}\rho_0^0(z_1)$ and ${}^{JJ}\rho_0^0(z_2)$ is not feasible.

The possible geometries for the fluorescence measurements are illustrated in Figs. 3 and 4. The population components are measured as before using linear polarizers set at 54.746° to the respective z axes. It can be seen that a "side on" measurement of fluorescence requires a separate geometrical arrangement of polarizer and detector for each compo-
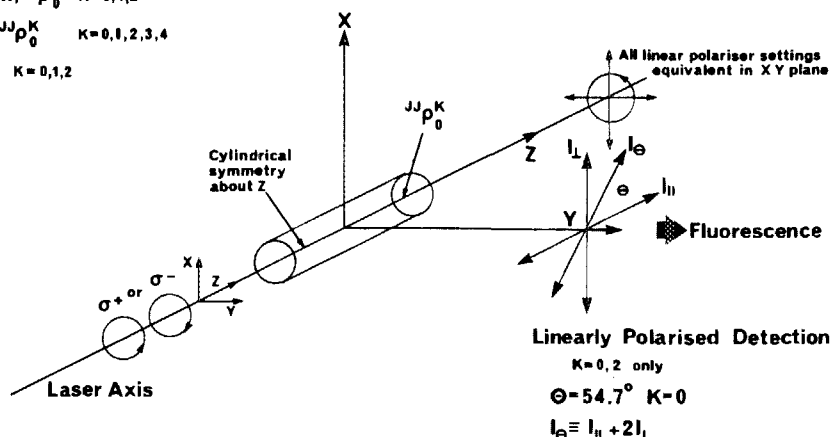
Circularly Polarised Excitation ($K''=0$)

a. Single Photon, $^{JJ}\rho_0^K$ $K=0,1,2$

b. Two Photon, $^{JJ}\rho_0^K$ $K=0,1,2,3,4$

E1 detection $K=0,1,2$

FIG. 4. As for Fig. 3 but here circularly polarized excitation is used.

Linearly Polarised Detection

$K=0,2$ only

$\Theta=54.7°$ $K=0$

$I_\Theta \equiv I_{||} + 2I_\perp$

nent. A straight through geometry is feasible, the only difference in determining the two intensities being the relative polarizer settings with respect to z_1 and z_2.

For axially asymmetric arrays the geometry is further complicated in that it is necessary to measure three fluorescence signals $(I_z + I_x + I_y)$ only two of which can be collinear. In such instances a direct measurement of the absorption intensity as previously outlined by us is perhaps preferable.

V. CONCLUSIONS

We have shown in this and a preceding work[1] that the problems which arise in determining in full the multipole moments of a generalized anisotropy $(K<2)$ by the technique of fluorescence polarization may be overcome by the use of differential absorption techniques using both circularly and linearly polarized light. The intensity of absorption is proportional to the excited state population and in a single photon process, multipoles, K, of magnitude 0, 1, and 2 may contribute to the production of an excited state population. Hence the problem reduces to a calculation of the contribution of each K'' value upon absorption of circularly and linearly polarized light. Circular polarization measurements yield the orientation multipole directly with no cross terms in $^{J''J''}\rho_Q^{K''}$. Linear polarization is considerably more complex since a common axis is not maintained for the two polarizations. Thus in general cross terms (i.e., those with $Q \neq 0$) intrude but we show that it is possible to choose an experimental geometry in which these vanish. Linear dichroism experiments yield the alignment $(K=2)$ multipole directly and simple manipulation of this data can be made to give the population monopole $(K=0)$ contribution. Detection of ab-

sorption by induced fluorescence is shown to have a number of pitfalls but useful results may be extracted. Higher multipoles of the ground state contribute to the excited state orientation and alignment and hence to the fluorescence. In a third paper in this series[14] we describe techniques for obtaining these higher moments via two-photon absorption experiments.

ACKNOWLEDGMENT

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