Complete determination of the state multipoles of rotationally resolved polarized fluorescence using a single experimental geometry

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Complete determination of the state multipoles of rotationally resolved polarized fluorescence using a single experimental geometry

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When laser radiation is used to prepare single rovibronic levels in molecules, the excited state M_j distribution is invariably polarized. In many such experiments the polarization of the excited state is ignored, which is an inadequate basis for accurate work as much valuable detail is lost. A better approach is a completely polarization resolved experiment in which the preparation, dynamics, and detection of the excited state polarization components (the state multipoles $^{JJ}\rho_Q^K$) are fully described. A treatment of polarized excitation in terms of the state multipoles $^{JJ}\rho_Q^K$ is presented and consideration of excited state symmetry indicates that a common experimental geometry for linearly and circularly polarized excitation is feasible. A complete determination of the state multipoles ($K = 0,1,2$) is shown to be possible within a single experimental geometry. It is shown that neglect of polarization phenomena can lead to ambiguities in the interpretation of some experiments.

I. INTRODUCTION

Experiments in which laser radiation is used to excite single rotational levels in molecules are of considerable importance; in quantum resolved intramolecular dynamics or in intermolecular kinetics for example. In many experiments the use of polarized laser radiation is inadvertent[1,2] while in others it is utilized to increase the information available from the experiment[3,5] but in both instances an unsymmetrical distribution of M states is created in the excited level and the evolution in time of this distribution will be a complex function of the events which the excited molecular state undergoes. In a single photon process the excited M-state distribution may be fully described in terms of up to three tensor density matrix elements or multipoles ($^{JJ}\rho_Q^K$) where K the rank of the tensor may be 0, 1 or 2 and these are the state multipoles, population, orientation, and alignment, respectively. These have their own characteristic evolution in time depending on the experimental conditions.

In experiments where fully resolved fluorescence is detected, two situations are generally found. In the first, polarization of the excited state is ignored despite the highly polarized nature of laser radiation. The emission then passes through a detection system often having a complex and unpredictable polarization dependence. In this work the experimentor equates normalized detector response to population of the emitting level and although there is a rough equivalence, this is inadequate for accurate work and furthermore, much valuable detail is lost.

An alternative approach to this is to use exciting radiation of precisely defined polarization (linear or circular) and then to determine fully the polarization of emission. It is then possible to measure two of the state multipoles, the population, and the orientation by using circularly polarized light or the population and the alignment with linearly polarized light. Thus the excited array may be better characterized and a much more detailed physical picture of the interaction obtained. We have shown for example that cross sections for transfer of population and of orientation by rota-

tionally inelastic collisions and cross sections for reorientation by elastic collisions may be determined from circularly polarized fluorescence using simple pressure plots.[6,7]

This latter approach is clearly preferable as a means of describing laser excited states and their evolution in time in either a collision free regime or in the presence of colliding partners. Indeed we have shown that the neglect of unsymmetric M_j-state distributions may lead to erroneous conclusions in, for example, attempts to scale rotational transfer data.[8]

It is conventional to carry out linear polarization experiments (of a noninadvertent character) with the characteristic 90° geometry[3,9,10] while circular polarization work is generally done using a 180° (or 360°) configuration. (The angle specifies that between the exciting radiation direction and that of the detection.) Thus once an experiment is set up for one type of polarization it is difficult to reorient the laser or the monochromator to the other. As a result the complete determination of the tensor density matrix has rarely been attempted. In fact it is possible to do both experiments, linear and circular, using a single geometry and to thus determine the multipoles $K = 0$, 1, and 2 completely. This is the "straight through" or 180° geometry and in this paper we give a rigorous treatment of the fully rotationally resolved linear polarization problem in terms of the state multipoles of the excited array and demonstrate that it is invariant to rotation in the horizontal plane.

Similar considerations are implicit in the work of Fano and Macek (and, more recently, in that of Green and Zare)[11] particularly their treatment of the angular correlation of emission from atoms polarized as a result of collisional excitation.

This opens up the interesting possibility of a complete determination of the dynamical behavior of all three state multipoles in routine laser experiments on molecular systems, a task not hitherto attempted. This would have considerable application in the study of energy transfer processes in small molecules, the Π states of diatomics in particular since P, Q, and R transitions are seen in emission.

In this work we give a rigorous treatment of rotationally resolved polarization phenomena for the single photon case assuming an unpolarized ground state. The organization of the material is as follows. First we derive expressions for the excited state density matrix created by the absorption of light. The symmetry properties of this array are demonstrated and the equivalence of the multipoles to rotations which preserve axial symmetry is shown. The concept of a detection matrix is then introduced to emphasize the polarization dependence of a detected signal and finally explicit expressions are derived for the observables characteristic of a fully rotationally resolved polarization experiment.

II. THEORY

A. The excitation process

The excitation of a molecular ensemble by laser radiation is a process which will possess axial symmetry with respect to a particular axis. This symmetry axis is taken as the Z or quantization axis of the coordinate system within which the excitation process is described. We consider three limiting polarization cases, those of circular polarized, linearly polarized, and unpolarized light and we show that in each case the excited state is invariably polarized.

The treatment given here is in terms of the state multipoles of the excited array. This method has numerous advantages, one being that the inherent symmetries of the excited state density matrix are fully exploited. We take the ground state to be unpolarized and assume negligible relaxation of the excited state by isotropic or anisotropic perturbations prior to emission. The consequences of polarization in the ground state together with anisotropic relaxation mechanisms will be discussed in a later paper.

1. Circularly polarized excitation

A treatment of circularly polarized excitation in terms of the state multipoles has been presented in earlier work by us[6] and thus is given only in outline here. For circularly polarized excitation, the z axis is that of the *propagation direction* of the light beam $\hat{O}$ (Fig. 1). We define circularly polarized electric dipole (E1) radiation by the spherical polarization vector $\epsilon^1_{q_A}$, where $q_A = \pm 1$, and we take the excitation process to be $q_A = +1$.

The excited state density matrix elements $^{JJ}\rho_{M_1 M_2}$ are given by linear combinations of excitation matrix elements thus

$$^{JJ}\rho_{M_1 M_2}(\hat{O}, q_A)$$

$$= \sum_{M''} \langle \alpha J M_1 | \epsilon^1_{-q_A} \cdot d^1_{+q_A} | \alpha'' j'' M'' \rangle (-1)^{q_A}$$

$$\times \langle \alpha J M_2 | \epsilon^1_{-q_A} \cdot d^1_{+q_A} | \alpha'' J'' M'' \rangle^* (-1)^{q_A}. \qquad (1)$$

The scalar product may be expressed in spherical vector components as follows:

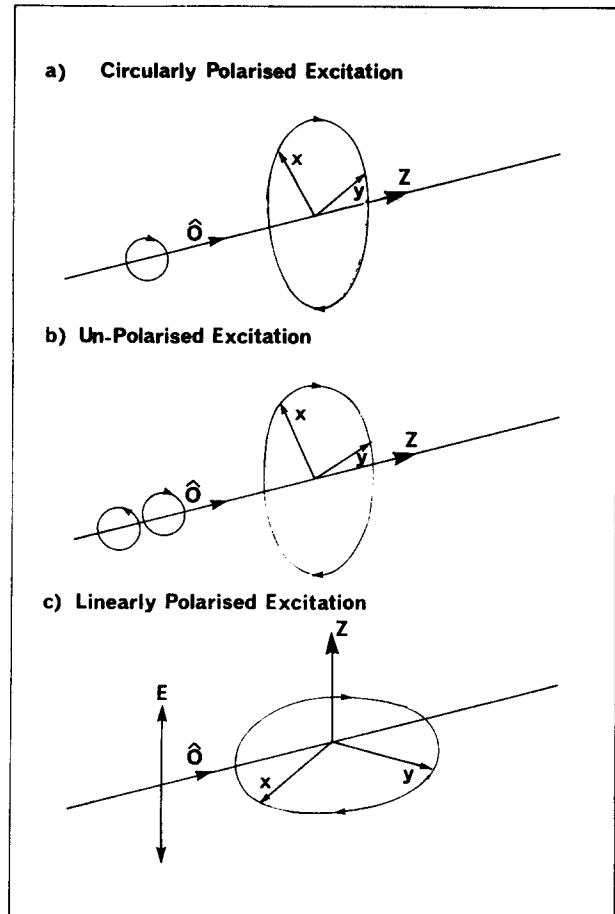$$\hat{\epsilon} \cdot d = (-1)^{q_A} \epsilon^1_{q_A} d^1_{q_A}, \quad q_A = \pm 1.$$

Thus

FIG. 1. Quantization axes for (a) circularly polarized excitation, (b) unpolarized excitation, and (c) linearly polarized excitation.

$$^{JJ}\rho_{M_1 M_2}(\hat{O}, q_A)$$

$$= \sum_{M''} (\epsilon^1_{-q_A})(\epsilon^1_{-q_A})^* (-1)^{q_A + q_A}$$

$$\times \langle \alpha J M_1 | d^1_{q_A} | \alpha'' J'' M'' \rangle \langle \alpha J M_2 | d^1_{q_A} | \alpha'' J'' M'' \rangle^*. \qquad (2)$$

The tensor density matrix elements (or state multipoles) are linear combinations of density matrix elements,

$$^{JJ}\rho^K_Q(\hat{O}, q_A) = \sum_{M_1 M_2} (-1)^{J - M_1}$$

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

$$\times (2K + 1)^{1/2}. \qquad (3)$$

Inserting Eq. (2) into Eq. (3) and applying the Wigner–Eckart theorem in the space-fixed frame we have

$$^{JJ}\rho^K_Q(\hat{O}, q_A)$$

$$= \sum_{\substack{M_1 M_2 \\ M''}} (-1)^{J - M_1} \begin{pmatrix} J & J & K \\ M_1 & -M_2 & -Q \end{pmatrix} \begin{pmatrix} J & 1 & J \\ -M_1 & q_A & M'' \end{pmatrix}$$

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

$$\times \langle \alpha J || d^1 || \alpha'' J'' \rangle \langle \alpha J || d^1 || \alpha'' J'' \rangle (2K + 1)^{1/2}. \qquad (4)$$

Rearranging the $3j$ symbols and applying a standard sum rule to remove the summation over the magnetic quantum numbers, we have

$$^{JJ}\rho_Q^K(\hat{O},q_A) = (-1)^{J+J''+K+q_A}\begin{pmatrix} 1 & 1 & K \\ q_A & -q_A & Q \end{pmatrix}$$

$$\times \begin{Bmatrix} 1 & 1 & K \\ J & J & J'' \end{Bmatrix}(2K+1)^{1/2}|\langle \alpha J\|d^1\|\alpha''J''\rangle|^2 . \quad (5)$$

From the triangular conditions on the $3j$ and $6j$ symbols we can see that the excited state is characterized by three well-defined values of the state multipoles having rank $K = 0$, 1, and 2 which are termed the population, the orientation and the alignment, respectively. The sign and magnitude of these quantities is shown in Fig. 2 and a pictorial representation of their symmetries is given in Fig. 3.

2. Linearly polarized excitation

For absorption of light having well defined linear polarization, the quantization axis for the system is taken to be that of the polarization vector $\hat{e}$ of the laser beam (Fig. 1). The excitation operator $\hat{e}_z \cdot d_z$ becomes, in spherical coordinates

$$\hat{e}_z \cdot d_z = \epsilon_0^1 \cdot d_0^1(-1)^0 , \quad q_A = 0 .$$
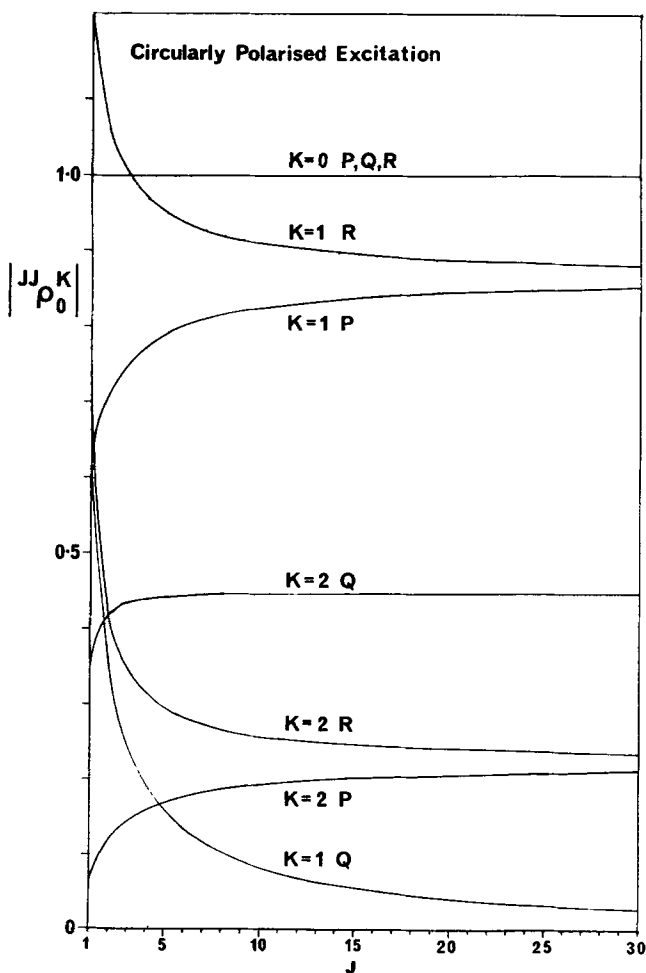
Thus,

FIG. 2. A plot of the absolute value of the state multipoles $|^{JJ}\rho_0^K|$ vs J. In this the value of $^{JJ}\rho_0^K$ has been normalized to unity for circularly polarized P, Q, and R excitation.

$$^{JJ}\rho_{M_1M_2}(\hat{e}_z,0)$$

$$= \sum_{M''} |\epsilon_0^1|^2\langle \alpha JM_1|d_0^1|\alpha''J''M''\rangle$$

$$\times \langle \alpha JM_2|d_0^1|\alpha''J''M''\rangle^* . \quad (6)$$

Proceeding as above we obtain

$$^{JJ}\rho_Q^K(\hat{e}_z,0)$$

$$= \sum_{M_1M_2M''} (-)^{J-M_1+J-M_1+J-M_2}\begin{pmatrix} J & J & K \\ M_1 & -M_2 & -Q \end{pmatrix}$$

$$\times \begin{pmatrix} J & 1 & J'' \\ -M_1 & 0 & M'' \end{pmatrix}\begin{pmatrix} J & 1 & J'' \\ -M_2 & 0 & M'' \end{pmatrix}$$

$$\times (2K+1)^{1/2}|\langle \alpha J\|d^1\|\alpha''J''\rangle|^2 , \quad (7)$$

which, on application of the sum rule for the contraction of three 3-j symbols becomes

$$^{JJ}\rho_Q^K(\hat{e}_z,0)$$

$$= (-1)^{J+J''+K}\begin{pmatrix} 1 & 1 & K \\ 0 & 0 & Q \end{pmatrix}\begin{Bmatrix} 1 & 1 & K \\ J & J & J'' \end{Bmatrix}(2K+1)^{1/2}$$

$$\times |\langle \alpha J_1|d_1^1|\alpha''J''\rangle|^2 . \quad (8)$$

In this there is an additional restriction, namely, that K is even. Thus the excited state is characterized by the population monopole $^{JJ}\rho_0^0$ and the alignment quadrupole $^{JJ}\rho_0^2$. The sign and magnitude of these quantities depends strongly upon the nature of the excitation process as shown in Fig. 4.

3. Unpolarized excitation

An unpolarized light beam can be considered as an incoherent superposition of the two photon helicity states each with equal intensity. The total system, upon excitation, is axially symmetric about $\hat{O}$ and thus it is natural to choose this as the quantization axis. The excited state density matrix is thus diagonal in M with respect to $\hat{O}$. Therefore, we can proceed in a manner similar to above and express the excited state multipoles as

$$^{JJ}\rho_Q^K(\hat{O},u)$$

$$= \sum_{M_2M_2M''} (-1)^{J-M_1}\begin{pmatrix} J & J & K \\ M_1 & -M_2 & -Q \end{pmatrix}(2K+1)^{1/2}$$

$$\times \tfrac{1}{2}[\langle \alpha JM_1|d_1^1|\alpha''J''M''\rangle\langle \alpha JM_2|d_1^1|\alpha''J''M''\rangle^*$$
$$+ \langle \alpha JM_1|d_{-1}^1|\alpha''J''M''\rangle$$
$$\times \langle \alpha JM_2|d_{-1}^1|\alpha''J''M''\rangle^*] . \quad (9)$$

Application of the Wigner–Eckart theorem in the space fixed frame defined by the $\hat{O}$ axis gives

$$^{JJ}\rho_Q^K(\hat{O},u) = \sum_{M_1M_2M''} (-)^{J-M_1+J-M_2+J-M_1}(2K+1)^{1/2}$$

$$\times \begin{pmatrix} J & J & K \\ M_1 & -M_2 & -Q \end{pmatrix}\tfrac{1}{2}\left[\begin{pmatrix} J & 1 & J'' \\ -M_1 & 1 & M'' \end{pmatrix}\right.$$

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

$$\left.\times \begin{pmatrix} J & 1 & J'' \\ M_2 & -1 & M'' \end{pmatrix}\right]|\langle \alpha J\|d^1\|\alpha''J''\rangle|^2 . \quad (10)$$
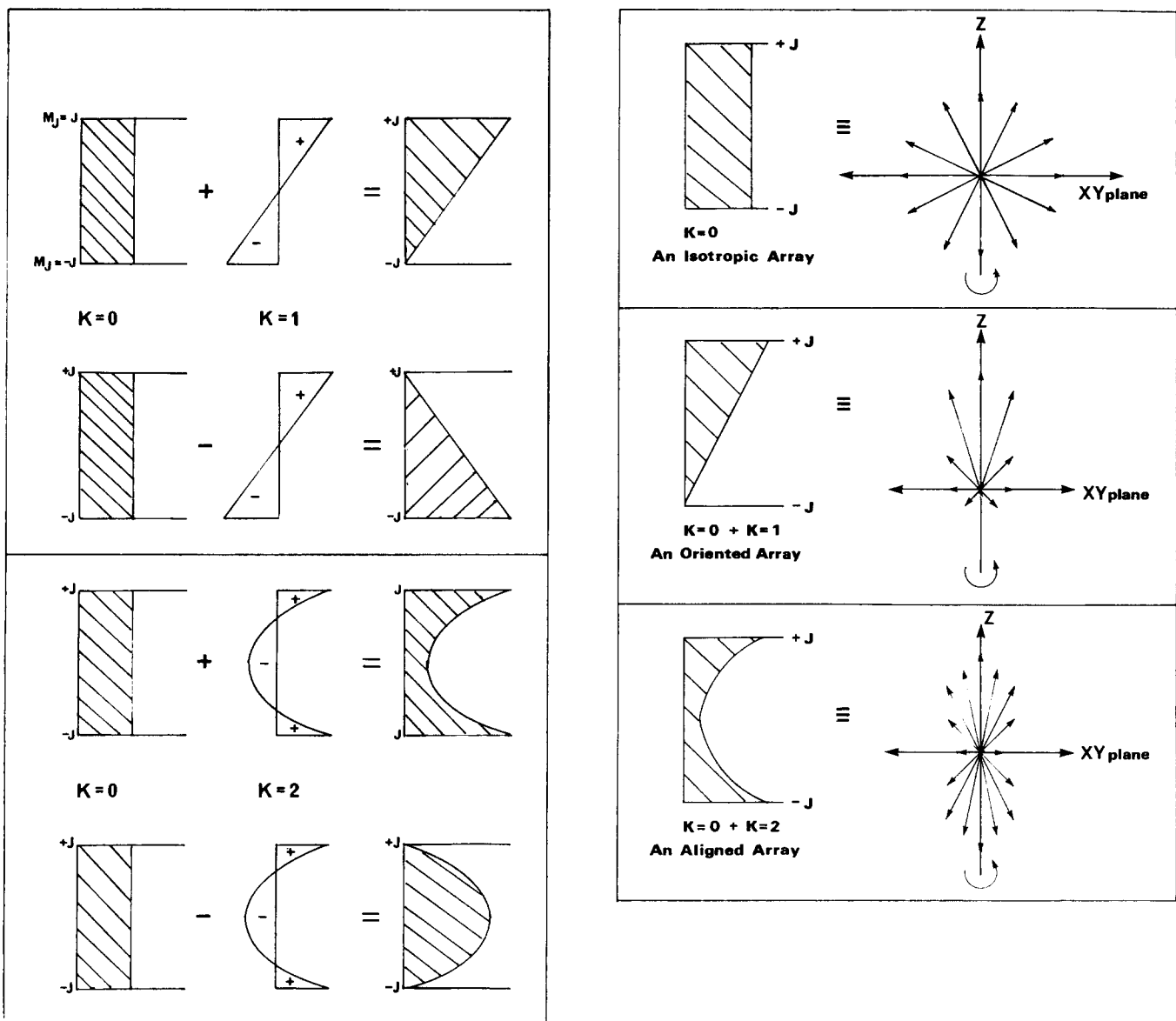
FIG. 3. (a) A representation of the manner in which oriented and aligned arrays of M_J states are created from combinations of $K = 0$ and $K \neq 0$ multipoles. (b) A pictorial description of (i) isotropic, (ii) oriented, and (iii) aligned arrays in terms of a distribution of classical angular momentum vectors. The length of the vector represents the population of the components of the ensemble in the particular orientation specified.

The sums over 3-j symbols are removed in the standard way to yield

$$^{JJ}\rho_Q^K(\hat{O},u) = \sum_{M_1 M_2 M''} (-1)^{J + J'' + K + 1}\tfrac{1}{2}[1 + (-1)^K]$$

$$\times \begin{pmatrix} 1 & 1K \\ 1 & -1Q \end{pmatrix}\begin{Bmatrix} 11K \\ JJJ'' \end{Bmatrix}(2K + 1)^{1/2}$$

$$\times |\langle \alpha J ||d^1|| \alpha'' J'' \rangle|^2 . \tag{11}$$

The excited state ensemble is thus characterized by the population monopole and the alignment quadrupole $^{JJ}\rho_0^0(\hat{O})$ and $^{JJ}\rho_0^2(\hat{O})$. The sign and magnitude of the population and alignment are identical to those for circularly polarized excitation. However, as both photon helicity states are involved, the $K = 1$ orientation multipole is not prepared (Fig. 5).

B. Transformation properties of the excited state

The state multipoles contain all the population and polarization information stored in the excited state as a result of the interaction with the laser beam. The monopole or population $^{JJ}\rho_0^0$ is a scalar quantity. It is invariant to all rotations and is directly related to the occupation number of the ensemble. It makes no direct contribution to the fluorescence *polarization*.

The orientation dipole on the other hand is a vector quantity and expresses the orientation of the array with respect to the particular axis. Reversal of this axis causes a change in sign, a characteristic property of odd rank tensors. The degree of orientation is directly related to the net circular polarization component of the fluorescence intensity.

The alignment quadrupole transforms as a second rank

Linearly Polarised Excitation

$|^{JJ}\rho_0^K|$

K=0 P,Q,R

K=2 Q

K=2 R

K=2 P

FIG. 4. A plot of $|^{JJ}\rho_0^K|$ as a function of rotational quantum number J for linearly polarized P, Q or R excitation. As before $^{JJ}\rho_0^0$ is normalized to unity.

"Unpolarised" Excitation

$|^{JJ}\rho_0^K|$

K=0 P,Q,R

K=2 Q

K=2 R

K=2 P

FIG. 5. A plot of $|^{JJ}\rho_0^K|$ as a function of J for *unpolarized* P, Q or R excitation.

tensor and has even parity to inversion of the z axis. The magnitude of the alignment is related to the net linear polarization of emission from the excited state.

We now consider the symmetry properties of the polarized ensemble created by the absorption of light in the manner outlined in the previous section. The excitation process in all three cases is referred to a particular z axis about which there is axial symmetry. These z axes may be the propagation direction of the laser beam $\hat{O}$ for circularly polarized and unpolarized excitation or alternatively may be the polarization vector of the radiation in the case of linearly polarized excitation.

Now consider two right-handed Cartesian axes xyz and $x'y'z$ as shown in Fig. 6. xyz is transformed onto $x'y'z$ by the Euler rotation $\mathscr{D}$ (00γ). The state multipoles defined in the frame xyz are related to those in $x'y'z$ by

$$^{JJ}\rho_Q^K(xyz) = \sum_{Q'} \mathscr{D}_{Q'Q}^K(00\gamma)^{JJ}\rho_{Q'}^K(x'y'z) . \tag{12}$$

It is known that,[12]

$$\mathscr{D}_{Q'Q}^K(00\gamma) = \exp(-iQ\gamma)\delta_{QQ'}. \tag{13}$$

and thus

$D(0,0,\gamma) (X,Y,Z) \rightarrow (X',Y',Z)$

$^{JJ}\rho_0^0 + {}^{JJ}\rho_0^2$

FIG. 6. The top part of this figure demonstrates the way in which the two Cartesian coordinate systems (xyz) and $(x'y'z)$, that possess a common z axis, are connected by the Euler rotation D (00γ) about this axis. The lower part is a pictorial representation of an aligned array demonstrating the rotational symmetry about the z axis.

$$^{JJ}\rho_Q^K(xyz) = \exp(-iQ\gamma)^{JJ}\rho_Q^K(x'y'z) \,. \tag{14}$$

In fact for linearly polarized excitation $Q = 0$ by definition and thus the multipole $^{JJ}\rho_Q^K$ is unchanged by a rotation in the xy plane. The physical basis of this can be seen pictorially in Fig. 6. Observation of the multipoles created by linearly polarized light is not confined to the 90° geometry conventionally used and is isotropic in the horizontal plane. The same is true for circularly polarized excitation except now the z axis is the propagation direction and the xy plane is perpendicular to this. Circular polarization observations are therefore constrained to the 180° or 360° geometries.

C. Detection of fluorescence

We now consider the emission process for the circular and linear polarization cases. The intensity of light of a particular polarization emitted from an array populated by absorption of light of polarization $\hat{e}$, is given by the scalar product of the excitation and detection matrix elements summed over all excited state magnetic quantum numbers

$$I(\hat{e}_E) = \sum_{M_1, M_2} {}^{JJ}\rho_{M_1 M_2}(\hat{e}_A) \mathbb{D}_{M_2 M_2}(\hat{e}_E) \,, \tag{15}$$

where $\mathbb{D}_{M_2 M_1}$ is a detection matrix element and reflects the fact that detection of the polarized array is by means of a radiative transition, i.e., spontaneous emission. Thus for rotationally resolved emission $\alpha J \rightarrow \alpha''' J'''$

$$\mathbb{D}_{M_2 M_1} = \sum_{M'''} \langle JM_2 | \hat{e}_E \cdot d_E | \alpha''' J''' M''' \rangle^*$$

$$\times \langle \alpha''' J''' M''' | \hat{e}_E \cdot d_E | JM_1 \rangle \,. \tag{16}$$

This form of expression has been widely used in atomic spectroscopy[13] and was introduced in the treatment of molecular fluorescence by Broyer et al.[4] Rearranging the above expressions

$$I(\hat{e}_e) = \sum_{\substack{M_1, M_2, M''' \\ K, Q}} {}^{JJ}\rho_Q^K(\hat{e}_A)(-)^{J - M_1}(2K + 1)^{1/2}$$

$$\times \begin{pmatrix} J & J & K \\ M_1 & -M_2 & -Q \end{pmatrix} \langle \alpha''' J''' M''' | \hat{e}_E \cdot d_E | JM_1 \rangle$$

$$\times \langle \alpha''' J''' M''' | \hat{e}_E \cdot d_E | JM_2 \rangle^* \,. \tag{17}$$

We finally consider the emission process from the optically prepared excited state and show the explicit dependence of experimental observables on the state multipoles. Of particular interest are circular and linear polarization ratios in fully rotationally resolved experiments.

1. Circularly polarized excitation and detection

For circularly polarized emission from $\alpha J \rightarrow \alpha''' J'''$,

$$I_{q_E}(q_A) = \sum_{\substack{K, Q, M_1 \\ M_2, M'''}} {}^{JJ}\rho_Q^K(q_A, \hat{O})(-1)^{J - M_1}(2K + 1)^{1/2}$$

$$\times \begin{pmatrix} J & J & K \\ M_1 & -M_2 & -Q \end{pmatrix} \langle \alpha''' J''' M''' | d_{q_E}^1 | \alpha J M_1 \rangle$$

$$\times \langle \alpha''' J''' M''' | d_{q_e}^1 | \alpha J M_2 \rangle^*$$

$$\times (\epsilon_{-q_E}^1)(\epsilon_{-q_E}^1)^*(-1)^{q_E + q_E} \,. \tag{18}$$

For σ^+, $q_E = -q_A$ and for σ^-, $q_E = q_A$.

Applying the Wigner–Eckart theorem in the space-fixed frame and proceeding as before to remove summations over magnetic quantum numbers we have

$$I_{q_E}(q_A) = \sum_{K, Q} {}^{JJ}\rho_Q^K(q_A, \hat{O}) \begin{pmatrix} 1 & 1 & K \\ -q_E & q_E & Q \end{pmatrix}(2K + 1)^{1/2}$$

$$\times \begin{Bmatrix} 1 & 1 & K \\ J & J & J''' \end{Bmatrix}(-1)^{J + J''' + K + q_E} |\langle \alpha''' J''' ||d^1||\alpha J \rangle|^2 \,. \tag{19}$$

The circular polarization ratio

$$C = [(I_{\sigma^+} - I_{\sigma^-})(I_{\sigma^+} + I_{\sigma^-})^{-1}]$$

is obtained by substituting for these quantities using Eq. (19) to yield, on insertion of the numerical values of the $3j$ symbols,

$$C = \frac{{}^{JJ}\rho_0^1(q_A, \hat{O}) \begin{Bmatrix} 1 & 1 & 1 \\ J & J & J''' \end{Bmatrix}}{\left(\dfrac{2}{3}\right)^{1/2} \begin{Bmatrix} 1 & 1 & 0 \\ J & J & J''' \end{Bmatrix} {}^{JJ}\rho_0^0(q_A, \hat{O}) + \left(\dfrac{1}{3}\right)^{1/2} \begin{Bmatrix} 1 & 1 & 2 \\ J & J & J''' \end{Bmatrix} {}^{JJ}\rho_0^2(q_A, \hat{O})} \,. \tag{20}$$

In terms of the relative multipole magnitudes of the excited states

$$C = \frac{\left(\begin{Bmatrix} 1 & 1 & 1 \\ J & J & J''' \end{Bmatrix} \middle/ \begin{Bmatrix} 1 & 1 & 0 \\ J & J & J''' \end{Bmatrix}\right)[\alpha_1]}{\left(\dfrac{2}{3}\right)^{1/2} + \left(\dfrac{1}{3}\right)^{1/2}\left(\begin{Bmatrix} 1 & 1 & 2 \\ J & J & J''' \end{Bmatrix} \middle/ \begin{Bmatrix} 1 & 1 & 0 \\ J & J & J''' \end{Bmatrix}\right)[\alpha_2]} \,, \tag{21}$$

where

$$[\alpha_1] = \frac{{}^{JJ}\rho_0^1(q_A, \hat{O})}{{}^{JJ}\rho_0^0(q_A, \hat{O})} \,,$$

$$[\alpha_2] = \frac{{}^{JJ}\rho_0^2(q_A, \hat{O})}{{}^{JJ}\rho_0^0(q_A, \hat{O})} \,. \tag{22}$$

On substituting the values of the excited state multipoles from Eq. (11) into Eq. (21) we obtain the expression

$$C = \frac{\begin{Bmatrix} 1 & 1 & 1 \\ J & J & J'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 1 \\ J & J & J''' \end{Bmatrix}}{\dfrac{2}{3} \begin{Bmatrix} 1 & 1 & 0 \\ J & J & J'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 0 \\ J & J & J''' \end{Bmatrix} + \dfrac{1}{3} \begin{Bmatrix} 1 & 1 & 2 \\ J & J & J'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 2 \\ J & J & J''' \end{Bmatrix}} \,, \tag{23}$$

which, on substitution of the algebraic forms of the $6j$ symbols, leads to the familiar closed expressions for C as given in Feofilov[14] or by Jeyes et al.[5]

2. Linearly polarized excitation and detection

In the case of linearly polarized excitation and emission, the two experimental parameters are $(I_\parallel - I_\perp)$ and $(I_\parallel + I_\perp)$ and we may proceed in a manner similar to that just outlined to obtain

$$I_\parallel = \sum_{M_1 M_2} {}^{JJ}\rho_{M_1 M_2}(\hat{e}_z A) \mathbb{D}_{M_2 M_1}(\epsilon_z E) \tag{24}$$

and

$$I_\perp = \sum_{M_1 M_2} {}^{JJ}\rho_{M_1 M_2}(\hat{e}_z A) \mathbb{D}_{M_2 M_1}(\epsilon_y^x E) \,. \tag{25}$$

Expanding Eq. (24) in terms of the tensor components we have

$$I_{\parallel} = \sum_{\substack{M_1 M_2 \\ M'''}} {}^{JJ}\rho_Q^K(\hat{\epsilon}_z A)(-1)^{J-M_1'}(2K+1)^{1/2}$$

$$\times \begin{pmatrix} J & J & K \\ M_1 & -M_2 & -Q \end{pmatrix} |\epsilon_0^1|^2$$

$$\times \langle JM_1|d_0^1(E)|J'''M'''\rangle \langle JM_2|d_0^1(\epsilon)|J'''M'''\rangle^* . \quad (26)$$

Applying the Wigner–Eckart theorem in the space-fixed frame and with some angular momentum manipulations we have

$$I_{\parallel} = \sum_{KQ} (-1)^{J+J'''+K} \begin{pmatrix} 11K \\ 00Q \end{pmatrix} (2K+1)^{1/2} \begin{Bmatrix} 11K \\ JJJ''' \end{Bmatrix} {}^{JJ}\rho_Q^K(\hat{\epsilon}_z A) ,$$

$$(27a)$$

$$I_{\perp} = \sum_{KQ} (-1)^{J+J'''+K} \left[\frac{1}{2} \begin{pmatrix} 1 & 1K \\ -1 & -1Q \end{pmatrix} \right.$$

$$+ \frac{1}{2} \begin{pmatrix} 11K \\ 11Q \end{pmatrix} + \frac{1}{2}[1+(-1)^K] \begin{pmatrix} 1 & 1K \\ 1 & -1Q \end{pmatrix} \right]$$

$$\times \begin{Bmatrix} 11K \\ JJJ''' \end{Bmatrix} (2K+1)^{1/2} {}^{JJ}\rho_Q^K(\hat{\epsilon}_z A) . \quad (27b)$$

The tensor moments of the emission matrix do possess $\mathbb{D}_{\pm 2}^K$ terms but since only $Q = 0$ terms are prepared in absorption only the $K = 0$, 2, and $Q = 0$ components of $\mathbb{D}_Q^K$ contribute to the fluorescence signal.

The experimental polarization ratio P, given by $P = (I_{\parallel} - I_{\perp})(I_{\parallel} + I_{\perp})^{-1}$ may then be obtained in terms of the state multipoles by substituting the equations above to yield

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} = \frac{\sum_K (-1)^{J+J'''+K}(2K+1)^{1/2}\left[\begin{pmatrix} 11K \\ 00Q \end{pmatrix} - \frac{1}{2}[1+(-1)^K]\begin{pmatrix} 1 & 1K \\ 1 & -10 \end{pmatrix}\right]\begin{Bmatrix} 11K \\ JJJ''' \end{Bmatrix}{}^{JJ}\rho_0^K(\hat{\epsilon}_z A)}{\sum_K (-1)^{J+J'''+K}(2K+1)^{1/2}\left[\begin{pmatrix} 11K \\ 00Q \end{pmatrix} + \frac{1}{2}[1+(-1)^K]\begin{pmatrix} 1 & 1K \\ 1 & -10 \end{pmatrix}\right]\begin{Bmatrix} 11K \\ JJJ''' \end{Bmatrix}{}^{JJ}\rho_0^K(\hat{\epsilon}_z A)} \quad (28)$$

in which the reduced matrix elements cancel.

Expanding Eq. (28) and inserting the numerical values of the $3j$ symbols we have

$$P = \frac{\left(\frac{3}{2}\right)^{1/2}\begin{Bmatrix} 112 \\ JJJ''' \end{Bmatrix}{}^{JJ}\rho_0^2(\epsilon_z A)}{-\frac{2}{\sqrt{3}}\begin{Bmatrix} 110 \\ JJJ''' \end{Bmatrix}{}^{JJ}\rho_0^0(\epsilon_z A) + \frac{1}{\sqrt{6}}\begin{Bmatrix} 112 \\ JJJ''' \end{Bmatrix}{}^{JJ}\rho_0^2(\hat{\epsilon}_z A)}$$

$$= \frac{-\left(\begin{Bmatrix} 112 \\ JJJ''' \end{Bmatrix} \Big/ \begin{Bmatrix} 110 \\ JJJ''' \end{Bmatrix}\right)[\alpha_2]}{\left(\frac{8}{9}\right)^{1/2} - \frac{1}{3}\left(\begin{Bmatrix} 112 \\ JJJ''' \end{Bmatrix} \Big/ \begin{Bmatrix} 110 \\ JJJ''' \end{Bmatrix}\right)[\alpha_2]} , \quad (29)$$

where

$$[\alpha_2] = \frac{{}^{JJ}\rho_0^2(\epsilon_z A)}{{}^{JJ}\rho_0^0(\epsilon_z A)} . \quad (30)$$

Substituting for the excited state multipoles using Eq. (11) we obtain

$$P = \frac{\begin{Bmatrix} 112 \\ JJJ'' \end{Bmatrix}\begin{Bmatrix} 112 \\ JJJ''' \end{Bmatrix}}{\frac{2}{3}\begin{Bmatrix} 110 \\ JJJ'' \end{Bmatrix}\begin{Bmatrix} 110 \\ JJJ''' \end{Bmatrix} + \frac{1}{3}\begin{Bmatrix} 112 \\ JJJ'' \end{Bmatrix}\begin{Bmatrix} 112 \\ JJJ''' \end{Bmatrix}} . \quad (31)$$

This gives the well known closed forms for P[8] when the algebraic forms of the $6j$ symbols are substituted.

III. DISCUSSION

Four main experimental detection methods are used in polarization experiments and it is useful to describe these briefly.

A. Circularly polarized resolution

Here the 180° (or 360°) configuration is employed in which fluorescence is measured along $\hat{O}$. The experimental observable is the circular polarization ratio C defined as

$$C = (I_+ - I_-)/(I_+ + I_-),$$

where $I_{\pm}$ are the intensities of ($\pm$) circularly polarized light.

B. Linearly polarized resolution

In this case fluorescence is generally observed at right angles to $\hat{O}$ and two parameters recorded which define P, the degree of linear polarization of emission as $P = (I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$. Here, of course, $I_{\parallel}$ and $I_{\parallel}$ are the intensities of emitted light polarized parallel and perpendicular to the initial quantization axis.

C. "Unpolarized" detection

Consider a measurement perpendicular to $\hat{O}$. Unpolarized detection is equivalent to the integration of linearly polarized signals over all angles θ as shown in Fig. 7. I_θ can be decomposed into parallel and perpendicular components and the signal is given by

$$I_\theta = (\cos^2 \theta)I_{\parallel} + (\sin^2 \theta)I_{\perp} . \quad (32)$$

The total intensity recorded by the detector is thus

$$I_{\text{tot}} = \int_0^{2\pi} [(\cos^2 \theta)I_{\parallel} + (\sin^2 \theta)I_{\perp}]d\theta = \pi[I_{\parallel} + I_{\perp}] . \quad (33)$$

Thus $I_{\text{tot}} \propto (I_{\parallel} + I_{\perp})$ which as was shown in the previous section, contains contributions from both the population and the alignment.
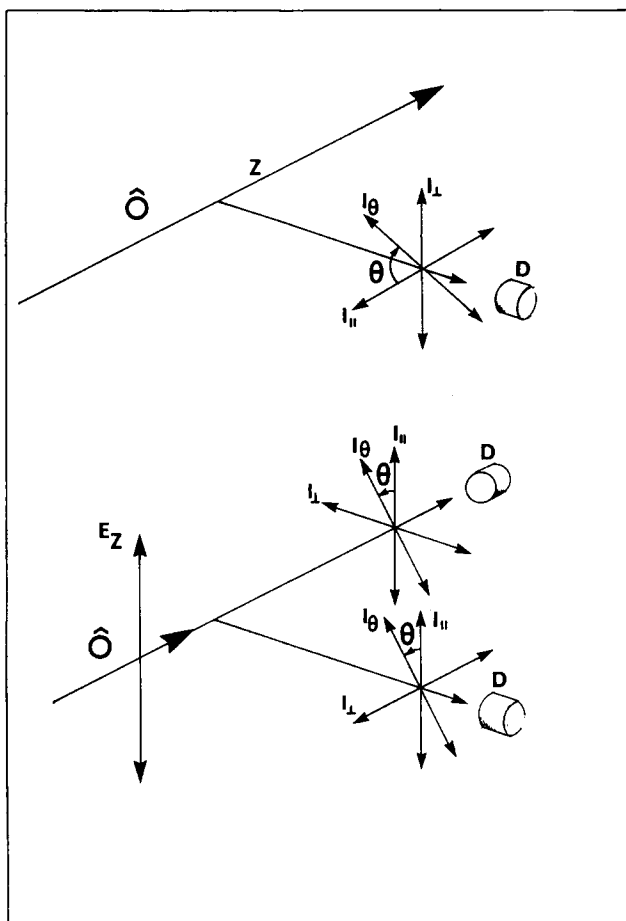
FIG. 7. Unpolarized detection with quantization axis along $\hat{O}$ (upper figure) and perpendicular to $\hat{O}$ (lower figure).

D. Monopole detection

It is clear from the foregoing that in all cases considered so far, some contribution from the polarization of the array enters into the measurement of intensity. However, the combination $I_{\parallel} + 2I_{\perp}$ contains only the population ($K = 0$) monopole and this may be achieved experimentally by a linear polarizer placed before the detector at an angle of $54.7°$ to the quantization axis.[14]

Thus we see that only if proper linear or circular detection is performed can we hope to measure quantitatively the contribution from the various multipoles created in the excited state. The use of the "magic angle" of $54.7°$ is of course to be preferred over "unpolarized" or inadvertent polarization detection since at least in the former case we can be certain that a pure multipole is being measured. However, since this method represents a deliberate rejection of valuable information concerning the excited molecular array, its use except in conjunction with direct measurements of $K = 1$ and/or $K = 2$ appears to be wasteful.

In describing the transformation properties of the state multipoles we showed that there is in general an axial symmetry about the quantization axis and that the excited state multipoles are invariant to rotations about this axis. The implication of this is that linear polarization experiments may be performed in the 180° geometry with no loss of information. Thus linear and circular polarization experiments may be carried out using the same experimental configuration. Since the measurement of linearly polarized fluorescence following linearly polarized excitation represents a trivial manipulation of two optical elements in an apparatus set up to measure circularly polarized emission following circularly polarized excitation, it should be straightforward to obtain all three tensor density matrix elements of the excited array in a single experiment. This would involve making two spectral runs of the region of interest, one with linear excitation and detection the other with circular; both with the straight-through geometry (Fig. 8). We note at this point that the symmetry of the excited multipoles preclude a rotation of the circular polarization experiment into the 90° geometry conventionally used in linear polarization experiments.

It is straightforward to treat the linear polarization observables in the same way as was done for circular polarization quantities[6,7] to obtain cross sections for disalignment by elastic collisions the transfer of population and alignment by inelastic collisions. Thus the linear polarization ratio for a fully resolved rotational transfer feature can be written as

$$P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} = \frac{\begin{Bmatrix} 112 \\ JJJ'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 2 \\ J'J'J''' \end{Bmatrix} \sigma^2_{J \to J'}}{\frac{2}{3} \begin{Bmatrix} 110 \\ JJJ'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 0 \\ J'J'J''' \end{Bmatrix} \sigma^0_{J \to J'} + \frac{1}{3} \begin{Bmatrix} 112 \\ JJJ'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 2 \\ J'J'J''' \end{Bmatrix} \sigma^2_{J \to J'}}, \tag{34}$$

where $\sigma^K_{J \to J'}$ represents the cross section for the transfer of multipole K in the rotationally inelastic transition $J \to J'$. The analogous expression for circularly polarized emission is

$$C = \frac{I_+ - I_-}{I_+ + I_-} = \frac{\begin{Bmatrix} 111 \\ JJJ'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 1 \\ J'J'J''' \end{Bmatrix} \sigma^1_{J \to J}}{\frac{2}{3} \begin{Bmatrix} 110 \\ JJJ'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 0 \\ J'J'J''' \end{Bmatrix} \sigma^0_{J \to J'} + \frac{1}{3} \begin{Bmatrix} 112 \\ JJJ'' \end{Bmatrix} \begin{Bmatrix} 1 & 1 & 2 \\ J'J'J''' \end{Bmatrix} \sigma^2_{J \to J'}}. \tag{35}$$

If a modulation technique[15] (Fig. 8) is used, and this is by far the most sensitive method of obtaining reliable polarization results when light levels are low as in the fully rotationally resolved case, Eqs. (34) and (35) show that two spectral runs suffice to measure all three $\sigma^K_{J \to J'}$'s unambiguously. The two observables $I_{\parallel} - I_{\perp}$ and $I_+ - I_{\perp}$ are proportional to $\sigma^2_{J \to J'}$ and $\sigma^1_{J + J'}$, respectively, while the total intensity in both experiments
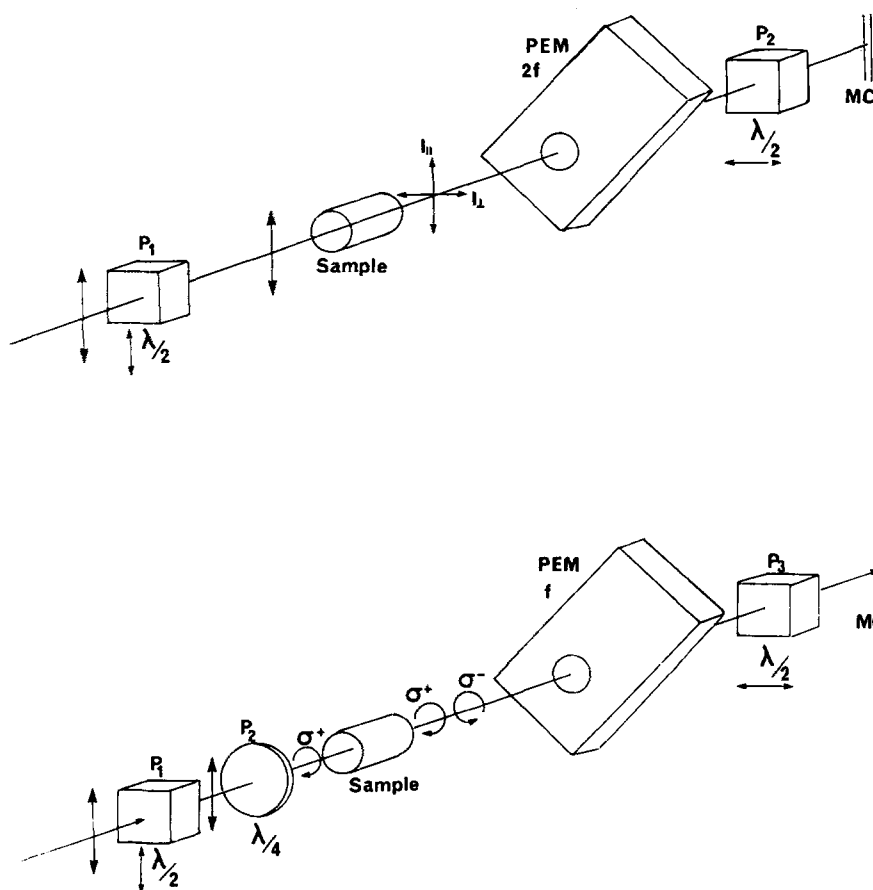
FIG. 8. Experimental arrangements for linear (upper figure) and circular polarization (lower figure) determinations using the straight-through geometry.

$$[(I_+ + I_-) = (I_\parallel + I_\perp)]$$

contains definite proportions of $\sigma^0_{J\to J'}$ and $\sigma^2_{J\to J'}$. Absolute values of these cross-sections may be obtained from the pressure dependence of the experimental observables in cw laser experiments.[6,7]

An additional point of note is that a combination of the observables in a linear polarization experiment may be made to yield the multipoles $K = 2,0$ directly without the use of the "magic angle" polarizer setting referred to earlier. The combination

$$\tfrac{2}{3}[(I_\parallel + I_\perp) - \tfrac{1}{3}(I_\parallel - I_\perp)]$$

is proportional to $I_\parallel + 2I_\perp$ which gives the $K = 0$ multipole uncontaminated by $K = 2$. As noted previously, the quantity $I_\parallel - I_\perp$ is directly related to the $K = 2$ multipole. Extraction of the $K = 0,2$ parameters in a linear polarization experiment would thus involve only a simple electronic manipulation of the data without recourse to rotation of the final polarizer.

IV. CONCLUSIONS

We have shown that the resonant absorption of radiation which possesses a definite propagation direction with respect to the ensemble with which it interacts leads to the creation of an excited state which *invariably* is polarized. In this paper the polarization of the molecular arrays formed on excitation of a single rotational level is treated in terms of the tensor density matrix with particular emphasis placed on the commonly encountered linear and circular polarization cases. The symmetry properties of the excited arrays have been displayed and it is apparent that these possess an axial symmetry about the quantization axis, this latter varying with the nature of the experiment. One consequence of this axial symmetry is that the multipoles created by the absorption of linearly polarized radiation may be rotated in the horizontal plane about the quantization axis without loss of information and without introduction of coherence terms and therefore linear polarization may be observed using the 180° experimental configuration characteristic of a circular polarization experiment. Thus with a single experimental geometry, all three tensor density matrix elements, the population, the orientation, and the alignment may be determined in routine experiments. This is of particular value in rotational energy transfer experiments or in any rotationally resolved spectroscopic study of collision or reaction dynamics since cross sections for transfer of population, orientation, and alignment may be readily obtained. Expressions relating these cross sections to experimental observables are given explicitly and methods of obtaining each separately are discussed.

Finally we note, and have demonstrated herein that so called "unpolarized" excitation leads to the creation of polarized excited arrays and that this is a consequence of the unique direction of propagation of a well collimated light beam such as laser radiation. We also have shown that most forms of detection are affected by the polarization of the excited array unless special care is taken to exclude all but the population monopole.

ACKNOWLEDGMENT

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