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On the measurement of molecular anisotropies using laser techniques. I. Polarized laser fluorescence

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The tensor density matrix formalism is used to derive expressions for the circular and linear polarization of laser-induced fluorescence from molecules which have an anisotropic distribution in the spatial orientation of their ground state angular momentum components. The generalized anisotropic distribution is expressed as a series of state multipolar moments and it is shown that the excited state multipolar moments created therefrom by the absorption of laser radiation may be quite complex even in the absence of perturbations which cause cross relaxation. Under these circumstances, polarized laser fluorescence does not give an unambiguous measure of the ground state multipolar moments and in succeeding papers we discuss methods which do yield these quantities without ambiguity.

I. INTRODUCTION

If we wish to measure the alignment and orientation of an ensemble of molecules, it is clear that we require a probe that is responsive to molecular polarization, however this anisotropic distribution is created. Such a probe is polarized light and this may be used in more than one mode. Other probes exist, the electric and magnetic field effects on transport properties for example.[1] In this paper we develop theoretical expressions appropriate to the experiment in which rotationally resolved polarized laser fluorescence is used to probe the anisotropy of a molecular ensemble. Thus it is the manner in which the polarization of resolved fluorescence is altered by the ensemble anisotropy that provides the quantitative measurement. This problem has been discussed recently by Greene and Zare[2,3] with particular reference to anisotropies in molecular fragments due to photofragmentation. Our work is similar in spirit to theirs, the main difference being that we used the density matrix (or state multipolar) formalism for describing the anisotropy of both ground and excited molecular arrays. This formalism has been used by us in a series of papers on one- and two-photon processes.[4,5] The limitations of the single photon polarized fluorescence method become apparent in this description, which leads us to propose an alternative approach to the problem of determining ground state ensemble anisotropies. This latter method is described in paper II of this series[6] and in a recent Communication.[7]

A polarized array of molecules is one that possesses a nonisotropic spatial orientation of its angular momentum components. The production of such spatial anisotropy can be achieved by the application of an external field or the system can be placed in an environment whose bulk properties, such as concentration, temperature, pressure, etc. have a definite gradient in a particular direction.[1,8] In all these cases a nonisotropic interaction, whether collisional or electromagnetic (such as in the obvious example of laser excitation) produces a steady state spatial distribution of the components which possess a nonisotropic orientation.

For a diatomic molecule or any species possessing internal angular momentum, the microscopic manifestation of the polarization is a nonuniform projection of magnetic quantum state with respect to an external z axis. In most cases this z axis is well defined, the applied field direction in magnetic or electric alignment, the laser polarization or propagation vector in fluorescence experiments, and the velocity direction in a supersonic nozzle expansion are a few examples.

We will now express the excited state polarization components in terms of those present in the ground state for the case of detection by polarized fluorescence. Expressions are then derived for the experimental observables, circular and linear polarization ratios, in terms of the modified excited state.

II. THEORY

A. Excitation from a polarized array

Upon excitation from an unpolarized ground state by the transition $\alpha''J''\rightarrow\alpha J$ with light of polarization $\hat{\epsilon}$ defined with respect to a particular z axis, the excited state density matrix elements ${}^{JJ}\rho_{M_1M_2}(\hat{\epsilon},z)$ are given by

$$
{}^{JJ}\rho_{M_1M_2}(\hat{\epsilon},z)=\sum_{M''}\langle\alpha JM_1|\hat{\epsilon}\cdot d\,|\alpha''J''M''\rangle \times\langle\alpha JM_2|\hat{\epsilon}\cdot d\,|\alpha''J''M''\rangle^{*}, \tag{1}
$$

where α,α'' represent the molecular quantum numbers other than those involving molecular rotation, and d is the electric dipole moment operator. In Eq. (1) the ground state is unpolarized and thus we have equal populations in the M'' levels. A more general formulation of this equation is

$$
{}^{JJ}\rho_{M_1M_2}(\hat{\epsilon},z)=\sum_{M_1''M_2''}\langle\alpha JM_1|\hat{\epsilon}\cdot d\,|\alpha''J''M_1''\rangle \times\langle\alpha JM_2|\hat{\epsilon}\cdot d\,|\alpha''J''M_2''\rangle^{*}\,{}^{J''J''}\rho_{M_1''M_2''}(g,z), \tag{2}
$$

where ${}^{J''J''}\rho_{M_1''M_2''}(g,z)$ define the steady state density matrix elements for the *ground* state. For an unpolarized array these density matrix elements are equal and diagonal in M'',

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$$^{J''J''}\rho_{M_1''M_2''}(g,z) = \text{const} \times \delta_{M_1''M_2''}. \tag{3}$$

For a polarized ensemble however this is not the case, the density matrix elements are not equal and are only diagonal in M'' if the array is cylindrically symmetric about the chosen z axis. The most convenient way to treat the problem is to carry out a multipolar expansion of the ground state density matrix elements in terms of the state multipoles $^{J''J''}\rho_{Q''}^{K''}(g,z)$ as follows:

$$^{J''J''}\rho_{M_1''M_2''}(g,z) = \sum_{K''Q''} (-1)^{J''-M_1''} \times \begin{pmatrix} J'' & J'' & K'' \\ M_1'' & -M_2'' & -Q'' \end{pmatrix} \times (2K''+1)^{1/2}\, {}^{J''J''}\rho_{Q''}^{K''}(g,z). \tag{4}$$

Substituting this into Eq. (2) the *excited* state density matrix elements become

$$^{JJ}\rho_{M_1M_2}(\hat{\epsilon},z) = \sum_{\substack{K''Q''\\ M_1''M_2''}} (-1)^{J''-M''} \times \begin{pmatrix} J'' & J'' & K'' \\ M_1'' & -M_2'' & -Q'' \end{pmatrix} \times (2K''+1)^{1/2} \langle \alpha J M_1 | \hat{\epsilon}\cdot d | \alpha'' J'' M_1'' \rangle \times \langle \alpha J M_2 | \hat{\epsilon}\cdot d | \alpha'' J'' M_2'' \rangle^{*}\, {}^{J''J''}\rho_{Q''}^{K''}(g,z). \tag{5}$$

The excited state multipoles are given by a linear combination of excited state density matrix elements:

$$^{JJ}\rho_Q^K(\hat{\epsilon},z) = \sum_{M_1M_2} {}^{JJ}\rho_{M_1M_2}(\hat{\epsilon},z)(-1)^{J-M_1} \times (2K+1)^{1/2} \begin{pmatrix} J & J & K \\ M_1 & -M_2 & -Q \end{pmatrix} \tag{6}$$

substituting for $^{JJ}\rho_{M_1M_2}(\hat{\epsilon},z)$ we have

$$^{JJ}\rho_Q^K(\hat{\epsilon},z) = \sum_{\substack{K''Q''\\ M_1M_2\\ M_1''M_2''}} (-1)^{J-M_1+J''-M_1''} \begin{pmatrix} J & J & K \\ M_1 & -M_2 & -Q \end{pmatrix} \begin{pmatrix} J'' & J'' & K'' \\ M_1'' & -M_2'' & -Q'' \end{pmatrix}$$

$$\times (2K+1)^{1/2}(2K''+1)^{1/2} \langle \alpha J M_1 | \hat{\epsilon}\cdot d | \alpha'' J'' M_1'' \rangle \langle J M_2 | \hat{\epsilon}\cdot d | \alpha'' J'' M_2'' \rangle^{*}\, {}^{J''J''}\rho_{Q''}^{K''}(g,z). \tag{7}$$

This expression gives the relationship between ground and excited state multipoles for a general laser polarization $\hat{\epsilon}$ referred to a particular space-fixed z axis.

We will now consider excitation using both circularly and linearly polarized radiation and the way each of these probes the multipolar array presented by the ground state, i.e., we describe the nature of the multipoles produced in the excited state by different forms of polarized radiation.

B. Circularly polarized excitation

The quantization axis for the excitation process is the propagation vector $\hat{O}$ of the laser beam and we write $\hat{\epsilon}$ and d in terms of their spherical components for electric dipole absorption,

$$\hat{\epsilon}\cdot d = (-1)^{q_A} d^1_{q_A} \epsilon^1_{-q_A} \quad (q_A = \pm 1), \tag{8}$$

$$^{JJ}\rho_Q^K(q_A,\hat{O}) = \sum_{\substack{K''Q''\\ M_1''M_2''\\ M_1M_2}} (-1)^{J-M_1+J''-M_1''+J-M_1+J-M_2}(2K''+1)^{1/2}(2K+1)^{1/2} \begin{pmatrix} J & J & K \\ M_1 & -M_2 & -Q \end{pmatrix}$$

$$\times \begin{pmatrix} J'' & J'' & K'' \\ M_1'' & -M_2'' & -Q'' \end{pmatrix} \begin{pmatrix} J & 1 & J'' \\ M_1 & q_A & M_1'' \end{pmatrix} \begin{pmatrix} J & 1 & J'' \\ -M_2 & q_A & M_2'' \end{pmatrix} |\langle \alpha J \| d^1 \| \alpha'' J'' \rangle|^2 \; {}^{J''J''}\rho_{Q''}^{K''}(g,\hat{O}). \tag{9}$$

The summations over magnetic quantum numbers are removed by rearranging the four 3-*j* symbols and their phase factors and then upon using a standard angular momentum sum rule[9] we have

$$^{JJ}\rho_Q^K(q_A,\hat{O}) = \sum_{\substack{K''Q''\\ a}} (-1)^{K+K''+Q''}(2a+1)(2K''+1)^{1/2}(2K+1)^{1/2}$$

$$\times \begin{pmatrix} K & 1 & a \\ Q & q_A & -\mu \end{pmatrix} \begin{pmatrix} a & K'' & 1 \\ \mu & -Q'' & -q_A \end{pmatrix} \begin{Bmatrix} a & 1 & K'' \\ J'' & J'' & J \end{Bmatrix} \begin{Bmatrix} a & 1 & K \\ J & J & J'' \end{Bmatrix} {}^{J''J''}\rho_{Q''}^{K''}(g,\hat{O}) |\langle \alpha J \| d^1 \| \alpha'' J'' \rangle|^2 \delta_{Q''Q}. \tag{10}$$

For an unpolarized ground state we have only $^{J''J''}\rho_0^0(g,\hat{O})$ and Eq. (10) becomes

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

$$\times \begin{pmatrix} a & 0 & 1 \\ q_A & 0 & -q_A \end{pmatrix} \begin{Bmatrix} a & 1 & 0 \\ J'' & J'' & J \end{Bmatrix} \begin{Bmatrix} a & 1 & K \\ J & J & J'' \end{Bmatrix} {}^{J''J''}\rho_0^0(g,\hat{O}) |\langle \alpha J \| d^1 \| \alpha'' J'' \rangle|^2 \delta_{Q''Q}. \tag{11}$$

Now

$$\begin{Bmatrix} a & 1 & 0 \\ J'' & J'' & J \end{Bmatrix} = (-1)^{J+J''+1}\delta_{a1}\delta_{JJ''} \times \frac{1}{(2J''+1)^{1/2}} \times \frac{1}{\sqrt{3}}, \begin{Bmatrix} a & 0 & 1 \\ q_A & 0 & -q_A \end{Bmatrix} = (-1)^{1+q_A}\frac{1}{\sqrt{3}}\delta_{a1}. \tag{12}$$

Thus

$$^{JJ}\rho_Q^K(q_A,\hat{O}) = (-1)^{J+J''+K+q_A}(2K+1)^{1/2} \times \begin{pmatrix} 1 & 1 & K \\ q_A & -q_A & Q \end{pmatrix} \begin{Bmatrix} 1 & 1 & K \\ J & J & J'' \end{Bmatrix} \times \frac{^{J''J''}\rho_0^0(g,\hat{O})}{(2J''+1)^{1/2}} |\langle \alpha J \| d \| \alpha'' J''\rangle|^2. \tag{13}$$

Apart from a factor of $^{J''J''}\rho_0^0(g,\hat{O})/(2J''+1)^{1/2}$, this is exactly the same as the standard expression for the state multipoles produced by circularly polarized excitation as derived by Rowe and McCaffery.[10]

Inspection of the triangle rules governing the various $3j$ and $6j$ symbols contained in Eq. (10) shows that the inclusion of multipoles of rank $K''>0$ in the ground state leads to multipoles of higher rank than $K=2$ in the excited state.

For the $6j$ and $3j$ symbols we have

$$\begin{aligned} &\Delta(K'',a,1) \quad \therefore \quad a = K''+1, \ldots, |K''-1|, \\ &\Delta(a,1,K) \quad \therefore \quad K = |a+1|, \ldots, |a-1|. \end{aligned} \tag{14}$$

Thus $K_{\max} = K''+2$.

From the $3j$ symbols it can be seen that both even and odd values of K are allowed for the excited state. In an experiment in which excitation occurs from an *aligned* ground state (characterized by $K''=0,2$) we will have an excited state in which $K=0,1,2,3,4$. Here $K''=2$ contributes to each excited state multipole, whereas $K''=0$ gives rise only to $K=0,1,2$ in the usual manner.

The consequences of such an array on the polarization of resonance fluorescence will be discussed later. We next consider the nature of the excited state produced by linearly polarized excitation from an anisotropic ensemble.

C. Linearly polarized excitation

For linearly polarized excitation the quantization axis is taken to be that of the polarization vector of the light beam. Thus for electric dipole radiation, $\hat{\epsilon} = \hat{\epsilon}_z = \epsilon_0^1$ in spherical coordinates.

Following the same procedure as in the case of circularly polarized excitation but remembering that now the z axis is perpendicular to $\hat{O}$ and we have $q_A = 0$. The angular momentum manipulations are the same as above, the final result being

$$^{JJ}\rho_Q^K(q_A=0,z) = \sum_{\substack{K''Q'' \\ a\,\mu}} (-1)^{K+K''+Q''+1} \times (2K''+1)^{1/2}(2K+1)^{1/2}(2a+1) \times \begin{pmatrix} K & 1 & a \\ Q & 0 & \mu \end{pmatrix} \begin{pmatrix} a & K'' & 1 \\ -\mu & -Q'' & 0 \end{pmatrix} \begin{Bmatrix} a & 1 & K'' \\ J'' & J'' & J \end{Bmatrix} \times \begin{Bmatrix} a & 1 & K \\ J & J & J'' \end{Bmatrix} {}^{J''J''}\rho_{Q''}^{K''}(g,z) |\langle \alpha J \| d^1 \| \alpha'' J''\rangle|^2 \delta_{Q''Q}. \tag{15}$$

If the ground state polarization is axially symmetric about $z(\hat{\epsilon})$, $Q''=0$ and we have $3j$ symbols of the form $\left(\begin{smallmatrix} a & 1 & k \\ 0 & 0 & 0 \end{smallmatrix}\right)$ $\left(\begin{smallmatrix} a & 1 & K'' \\ 0 & 0 & 0 \end{smallmatrix}\right)$. Thus in addition to the usual triangular conditions we have that the sum of the coupled angular momenta, i.e., $a, 1, K$ and $a, 1, K''$ must be even, or, alternatively $a+K$ and $a+K''$ must be odd.

Thus $2a+K+K''$ = even and since a is always a positive integer we have $K+K''$ = even. For an axially symmetric ensemble we have the constraint that even rank multipoles in the ground state are coupled by the radiation field to give solely even rank multipoles in the excited state; multipoles of odd rank in the ground state similarly can only give rise to odd rank multipoles in the excited state.

This restriction is relaxed when the ground state is not totally symmetric to rotations about the z axis. For such components $Q''\neq 0$ and these "coherences" are transformed directly to the excited state ensemble and we have $3j$ symbols,

$$\begin{pmatrix} K & 1 & a \\ Q & 0 & -Q \end{pmatrix} \begin{pmatrix} a & K'' & 1 \\ Q & -Q'' & 0 \end{pmatrix} \delta_{QQ''}$$

in the expression for the excited multipoles. This yields a much more complex set of excited state multipoles as can be seen in the following example. Consider a ground state characterized by $^{J''J''}\rho_0^0, {}^{J''J''}\rho_0^2, {}^{J''J''}\rho_{\pm 1}^2, {}^{J''J''}\rho_{\pm 2}^2$. The following multipoles will be created in the excited state upon excitation with linearly polarized light:

$$\begin{aligned} &^{JJ}\rho_0^0 \;\; ^{JJ}\rho_0^2 \;\; ^{JJ}\rho_0^4, \quad \text{from } ^{J''J''}\rho_0^0 \;\; ^{J''J''}\rho_0^2, \\ &^{JJ}\rho_{\pm 1}^1 \;\; ^{JJ}\rho_{\pm 1}^2 \;\; ^{JJ}\rho_{\pm 1}^3 \;\; ^{JJ}\rho_{\pm 1}^4 \;\; \text{from } ^{J''J''}\rho_{\pm 1}^2, \\ &^{JJ}\rho_{\pm 2}^2 \;\; ^{JJ}\rho_{\pm 2}^3 \;\; ^{JJ}\rho_{\pm 2}^4 \;\; \text{from } ^{J''J''}\rho_{\pm 2}^2. \end{aligned}$$

III. POLARIZATION OF EMISSION

Our earlier work,[4-6] demonstrated that for single photon electric dipole emission only the population, orientation, and alignment multipoles can contribute to the fluorescence intensity. The degree of polarization of resonance fluorescence can be expressed for the transition $\alpha J \rightarrow \alpha''' J'''$ in the standard way.[4,10]

(a) Circularly polarized fluorescence. Both I^+ and I^- are measured along a common z axis and thus sample solely $Q=0$ multipoles

$$C = \frac{\dfrac{^{JJ}\rho_0^1(q_A,\hat{O})\begin{Bmatrix} 1 & 1 & 1 \\ J & J & J''' \end{Bmatrix}}{^{JJ}\rho_0^0(q_A,\hat{O})\begin{Bmatrix} 1 & 1 & 0 \\ J & J & J''' \end{Bmatrix}}}{\left(\dfrac{2}{3}\right)^{1/2} + \left(\dfrac{1}{3}\right)^{1/2} \dfrac{^{JJ}\rho_0^2(q_A,\hat{O})\begin{Bmatrix} 1 & 1 & 2 \\ J & J & J''' \end{Bmatrix}}{^{JJ}\rho_0^0(q_A,\hat{O})\begin{Bmatrix} 1 & 1 & 0 \\ J & J & J''' \end{Bmatrix}}}. \tag{16}$$

(b) Linearly polarized fluorescence. Linear polarization observables do not impose a unique z axis upon the system. The measurement of $I_\perp$ is sensitive to both $Q=0$ and $Q=\pm 2$ multipoles.[4] Thus for axially symmetric systems ($Q=0$):

$$P=\frac{{}^{JJ}\rho_0^2(q_A=O,z)\begin{Bmatrix}1&1&2\\J&J&J'''\end{Bmatrix}}{{}^{JJ}\rho_0^0(q_A=O,z)\begin{Bmatrix}1&1&O\\J&J&J'''\end{Bmatrix}}\left[\left(\frac{8}{9}\right)^{1/2}-\left(\frac{1}{9}\right)^{1/2}\frac{{}^{JJ}\rho_0^2(q_A=O,z)\begin{Bmatrix}1&1&2\\J&J&J'''\end{Bmatrix}}{{}^{JJ}\rho_0^0(q_A=O,z)\begin{Bmatrix}1&1&0\\J&J&J'''\end{Bmatrix}}\right]^{-1}. \tag{17a}$$

When $Q=\pm 2$ terms are prepared by the excitation process

$$P=-\frac{\begin{Bmatrix}1&1&2\\J&J&J'''\end{Bmatrix}}{\begin{Bmatrix}1&1&0\\J&J&J'''\end{Bmatrix}}\frac{\{{}^{JJ}\rho_0^2\mp(\tfrac{1}{6})^{1/2}[{}^{JJ}\rho_2^2+{}^{JJ}\rho_{-2}^2]\}}{{}^{JJ}\rho_0^0}\left[\left(\frac{8}{9}\right)^{1/2}+\frac{\begin{Bmatrix}1&1&2\\J&J&J'''\end{Bmatrix}}{\begin{Bmatrix}1&1&0\\J&J&J'''\end{Bmatrix}}\frac{\{-\tfrac{1}{3}{}^{JJ}\rho_0^2\mp(\tfrac{1}{6})^{1/2}[{}^{JJ}\rho_2^2+{}^{JJ}\rho_{-2}^2]\}}{{}^{JJ}\rho_0^0}\right]^{-1}. \tag{17b}$$

The $+/-$ signs for the ${}^{JJ}\rho^2_{\pm 2}$ contributions to P are when $I_\perp$ is measured collinearly with excitation (I_x) and in the right angled geometry (I_y), respectively.[11]

For a given transition (i.e., P, Q, or R) simple relationships exist between the products of the $6\hat{j}$ symbols in Eqs. (10) and (15). In the case of axially symmetric observables, for instances those involved in circularly polarized excitation and fluorescence detection, we can expand the excited state density matrix as follows:

$$\begin{aligned}{}^{JJ}\rho_0^K(q_A,\hat{O})&={}^{JJ}\rho_Q^K(q_A,\hat{O},K''=0)\Bigg[1+\sum_{\substack{K''\neq 0\\a}}(-1)^{K+K''}(2a+1)(2K+1)^{1/2}\\&\quad\times\begin{pmatrix}K&1&a\\0&q_A&-q_A\end{pmatrix}\begin{pmatrix}a&K''&1\\q_A&0&-q_A\end{pmatrix}\begin{Bmatrix}a&1&K''\\J''&J''&J\end{Bmatrix}\begin{Bmatrix}a&1&K''\\J&J&J''\end{Bmatrix}{}^{J''J''}\rho_{Q''}^{K''}(g,\hat{O})\Bigg]\\&={}^{JJ}\rho_Q^K(q_A,\hat{O},K''=0)[1+[\alpha_{10}]P_J(K,K''=1,Q''=0)+[\alpha_{20}]P_J(K,K''=2,Q''=0)+\cdots],\end{aligned} \tag{18}$$

where ${}^{JJ}\rho_0^K(q_A,O,K''=0)$ is the contribution to ${}^{JJ}\rho_Q^K(q_A,\hat{O})$ from the isotropic (population) component of the ground state, $[\alpha_{10}]$ is the degree of orientation in the ground state and so on

$$\begin{aligned}[][\alpha_{10}]&={}^{J''J''}\rho_0^1(g,\hat{O})({}^{J''J''}\rho_0^0(g,\hat{O}))^{-1},\\ [\alpha_{20}]&={}^{J''J''}\rho_0^2(g,\hat{O})({}^{J''J''}\rho_0^0(g,\hat{O}))^{-1}.\end{aligned} \tag{19}$$

$P_J(K,K'',Q'')$ is a simple polynominal in J depending upon the type of excitation and the rank of the ground and excited state multipoles concerned. In the high J limit this expression will tend to a constant value. Similar considerations can be applied to linearly polarized excitation and analagous expressions obtained.

The measurement of laser-induced fluorescence polarization ratios, however, is not an unequivocal guide to ground state polarization as we now demonstrate. The experimentally determined quantities C and P are given by a ratio of the population orientation and alignment multipoles of the excited state as shown in Eqs. (16), (17a), and (17b). All of these excited state multipoles have, in general, contributions from more than one multipole component of the ground state. The situation can be shown more precisely in the following examples.

Case 1, circularly polarized excitation and detection

(i) population ${}^{JJ}\rho_0^0(q_A,\hat{O})={}^{JJ}\rho_0^0(q_A,\hat{O},K''=0)$

$\times[1+P_J(0,1,0)[\alpha_{10}]+P_J(0,2,0)[\alpha_{20}]]$,

(ii) orientation ${}^{JJ}\rho_0^1(q_A,\hat{O})={}^{JJ}\rho_0^1(q_A,\hat{O},K''=0)$

$\times[1+P_J(1,1,0)[\alpha_{10}]+P_J(1,2,0)[\alpha_{20}]+P_J(1,3,0)[\alpha_{30}]]$,

(iii) alignment ${}^{JJ}\rho_0^2(q_A,\hat{O})={}^{JJ}\rho_0^2(q_A,\hat{O},K''=0)$

$\times[1+P_J(2,1,0)[\alpha_{10}]+P_J(2,2,0)[\alpha_{20}]+P_J(2,3,0)[\alpha_{30}]$

$+P_J(2,4,0)[\alpha_{40}]]$. (20)

Case 2, linearly polarized excitation

(i) population ${}^{JJ}\rho_0^0(q_A=O,z)={}^{JJ}\rho_0^0(q_A=O,z,K''=0)$

$\times[1+P_J(0,2,0)[\alpha_{20}]]$,

(ii) alignment ${}^{JJ}\rho_0^2(q_A=0,2)={}^{JJ}\rho_0^2(q_A=0,K''=0)$

$\times[1+P_J(2,2,0)[\alpha_{20}]+P_J(2,4,0)[\alpha_{40}]],{}^{JJ}\rho^2_{\pm 2}(q_A=0,2)$

$=[P_J(2,2,\pm 2){}^{JJ}\rho^2_{\pm 2}]+[P_J(2,4,\pm 2)[\alpha_4]]$. (21)

When these expressions are substituted into the appropriate equations for the polarization observables [Eqs. (16), (17a), and (17b)] it can be seen immediately that very complex forms will exist in which ground state alignment, orientation, and higher multipoles will, in general, contribute. Thus the effect of the interaction of the polarized probing beam with the polarized array of molecules is to add to the information carried ultimately by the fluorescent radiation when the excited state spontaneously emits. Since only a limited number of experimental parameters is available, namely I_+, I_-; $I_\parallel$, $I_\perp$ and their sums and differences it is clear that the unambiguous determination of the complete ground state multipole distribution will be difficult unless for some reason only a small set of multipoles exists in the ground state. Greene and Zare,[2,3] for example, obtain expressions for the $K=0$, 2, and 4 multipoles but their treatment requires an axially symmetry in the system and hence the odd rank multipoles vanish. This is not, of course, a physically unreasonable condition in many experimental circumstances.

In cw fluorescence experiments, the polarization ratios are given by the steady state (time evolved) values of the state multipoles (Fig. 1). If significant perturbation of the excited state occurs during this evolution the relationship between fluorescence polarization and that of the ground state becomes less well defined. For instance, the collisional mecha-

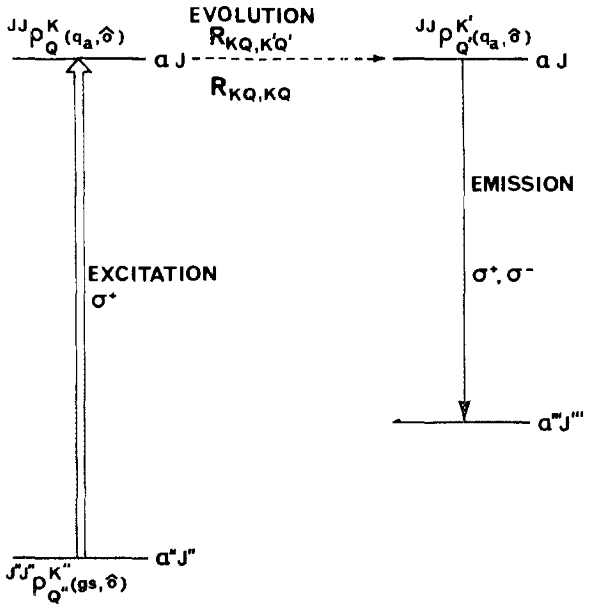

FIG. 1. Following laser excitation, the excited state is prepared at time $t = 0$ with well-defined values of the state multipolar moments which are related to those of the ground state by angular momentum factors alone. In a cw experiment, relaxation of the excited state will occur prior to emission. The nature of this relaxation depends upon the environment of the ensemble—isotropic processes R_{KQKQ} allow the separate evolution of individual multipole components while anisotropic mechanisms $R_{KQK'Q'}$ cause cross relaxation and consequent scrambling of the excited state polarization. If such perturbations are significant, it is not possible to relate the emission polarization to that of the ground state without a detailed knowledge of the dynamics of the excited state.

nisms responsible for ground state alignment in gaseous and fluid transport can cause cross relaxation of the excited state multipoles. In such cases, not only population, orientation, and alignment may scramble but contributions to and from octupole and hexadecapole tensors (hitherto unobserved) cannot be ruled out.

It is clear then that although polarized laser fluorescence provides a convenient method of detecting anisotropic ground state molecular distributions, there are problems when quantitative data on a generalized anisotropic ensemble is required. This will be more fully illustrated in a forthcoming article in which we analyze the polarized fluorescence from diatomic molecules aligned by flow.[12] However, there are ways in which the problems referred to above may be overcome using sensitive absorption techniques and we develop this latter point further in a second paper in this series which amplifies a Note recently published.[7]

IV. CONCLUSIONS

We have developed general expressions for the polarization of laser induced fluorescence from molecules which have been polarized by some process and consequently have anisotropic distributions of M states. Such a situation may arise in photofragmentation experiments or in molecules in a directed flow. The treatment considers the way in which ground state polarization is transferred to the excited state and is therefore related to a recent treatment by Greene and Zare.[2] However, we use the density matrix approach throughout to emphasize the unity with previous studies by us.[4–6] In addition, our approach is somewhat more general in that odd order multipolar moments of the ground state are considered as well as even. Expressions are derived for laser fluorescence polarizations following excitation using linear and circularly polarized light. It is seen that in the general case the expressions for the excited state multipoles (and hence those for the polarization observables) are a complex function of the ground state multipolar moments. Perturbations in the excited state are capable of altering the relationship between ground and excited state multipoles and in these circumstances the measurement may not be reliable due to cross relaxation. Although polarized laser fluorescence is a useful probe of the presence of ground state anisotropy, it is of less value as a quantitative measure of the individual ground state multipolar moments. In a second paper on this topic, we propose an alternative experimental technique which overcomes many of these problems.

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