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

A. J. Bain and A. J. McCaffery

Citation: The Journal of Chemical Physics 83, 2641 (1985); doi: 10.1063/1.449265

View online: http://dx.doi.org/10.1063/1.449265

View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/83/6?ver=pdfcov

Published by the AIP Publishing

Articles you may be interested in

Measuring polarizability anisotropies of rare gas diatomic molecules by laser-induced molecular alignment technique

Generation and Detection of Higher Harmonics in Rayleigh Waves Using Laser Ultrasound

Method and system for measuring and azimuthal anisotropy effects using acoustic multipole transducers
J. Acoust. Soc. Am. 86, 2474 (1989); 10.1121/1.398380

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

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

A. J. Bain and A. J. McCaffery

School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, United Kingdom

(Received 5 September 1984; accepted 4 April 1985)

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

I. INTRODUCTION

In previous papers in this series,\(^1\,^2\) we have considered the problems associated with the characterization of an anisotropic array of molecules in their electronic ground states but with single quantum level resolution. This anisotropy may arise in more than one way; through chemical reaction, via photofragmentation\(^3\) or as a result of flow in a concentration gradient\(^4\) to name some commonly occurring instances. In part I\(^1\) we demonstrated that resonance fluorescence polarization ratios are not an unequivocal guide to ground state molecular polarizations since the experimental observables have contributions from more than one multipole component of the ground state. Perturbations during the excited state lifetime further reduce the value of the technique by introducing the possibility of cross relaxation between multipole components. Part II develops an alternative method, namely circular and linear differential absorption and we showed that unambiguous determination of ground state multipole moments of rank up to \( K^* = 2 \) was possible via these experiments by choosing the proper experimental geometry and probe polarization.

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

Here however we consider an alternative method, namely, two photon linear and circular dichroism. Developments in laser technology have made high resolution two-photon spectroscopy a readily accessible spectroscopic technique\(^2\) and in this work we describe how the method may be used to obtain directly the higher moments of the ground state anisotropy.

In the first part of this series\(^1\) we derived a relationship between the state multipolar moments of an excited state and those of an anisotropic ground state array:
sented by Nairn et al. Their approach uses one- and two- vector, density-of-states functions to describe the polarization of an arbitrarily ordered ensemble and does not extend to a full multipolar treatment nor to direct rotational resolution. In the following section we consider the nonresonant TPA for both circularly and linearly polarized photons and proceed to derive expressions for rotationally resolved two photon circular and linear absorption ratios. For simplicity we will restrict the discussion to rotational transitions in which \( \Delta J = \pm 2 \). The selection rules in this case permit the contribution of only one intermediate (virtual) rotational level \( J' \) to the transition moment thus:

\[
\alpha^*J^* \rightarrow \alpha \alpha J.
\]

Here \( \alpha \) represents all quantum numbers other than rotational and \( \omega_1 \) and \( \omega_2 \) are the frequencies of the two photons.

II. CIRCULARLY POLARIZED TWO PHOTON ABSORPTION

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

\[
I(2q_A, \hat{O}) = g(\omega) \sum_{M_1=M'_1}^{M_1+M'_1}(aJ'M'_{aJ'M'})
\]

\[
\times \langle \alpha'J'M'_{aJ'M'} | d_{aJ'M'}^{\frac{1}{2}} | \alpha^*J^*M^* \rangle
\]

\[
\times \langle \alpha J'M'd_{aJ'M'}^{\frac{1}{2}} | \alpha^*J^*M^* \rangle^*.
\]

The corresponding expression for two photons each having polarization \(- q_A\) is given by

\[
I(-2q_A, \hat{O}) = g(\omega) \sum_{aJ'M'}(2a_1 + 1)(2a_2 + 1)(-1)^{J' + J' + q_A} D(aJ'M'_{aJ'M'}) (\alpha J'M'd_{aJ'M'}^{\frac{1}{2}} | aJ'M'd_{aJ'M'}^{\frac{1}{2}} | \alpha^*J^*M^*)^2
\]

\[
\times \langle a_1 a_2 | J J' J J' J J' \rangle (a_1 a_2 | q_a q_a - q_a - q_a - q_a)
\]

\[
\times \langle q_a q_a - q_a - q_a - q_a | (2q_a + 1) \rangle (2q_a + 1)^{1/2} J^* \rho_{0g}^K (g, \hat{O}) (-1)^K.
\]

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

\[
\frac{I_{2q_A} - I_{-2q_A}}{I_{2q_A} + I_{-2q_A}} = \sum_{aJ'M'}(2a_1 + 1)(2a_2 + 1)(-1)^{J' + J' + q_A} \langle a_1 a_2 | a_1 a_2 | q_a q_a - q_a - q_a - q_a \rangle (2q_a + 1)^{1/2}
\]

\[
\times \langle J J' J J' J J' | q_a q_a - q_a - q_a - q_a \rangle (2q_a + 1)^{1/2} \rho_{0g}^K (g, \hat{O})
\]

\[
\times \sum_{K, q_a} \sum_{aJ'M'}(2a_1 + 1)(2a_2 + 1)(-1)^{J' + J' + q_A} \langle a_1 a_2 | a_1 a_2 | q_a q_a - q_a - q_a - q_a \rangle (2q_a + 1)^{1/2} \rho_{0g}^K (g, \hat{O})
\]

\[
\times \left[ \frac{q_a q_a - q_a - q_a - q_a}{2q_a + 1} \right] (2q_a + 1)^{1/2} \rho_{0g}^K (g, \hat{O})^{-1}.
\]
all other quantities cancelling in the ratio.

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

\[
\frac{I_{2q_A} - I_{-2q_A}}{I_{2q_A} + I_{-2q_A}} = \sum_{a_j K'''} (2a_2 + 1)(-1)^{i'' + j'' + q_a} \left[ \begin{array}{ccc}
2 & 1 & a_2 \\
J' & J'' & J''
\end{array} \right] \left[ \begin{array}{ccc}
a_2 & 1 & K'' \\
J'' & J'' & J''
\end{array} \right] q_A
\]

\[
\times \left( 2q_A - q_A - q_A \right) \left( \frac{q_A}{q_A} - q_A \right) \left( 2K'' + 1 \right) \left( 1 + ( -1 )^{K'' + 1} \right) \left( -1 \right)^{i'' + j'' + q_a} \left[ \begin{array}{ccc}
2 & 1 & a_2 \\
J' & J'' & J''
\end{array} \right] \left[ \begin{array}{ccc}
a_2 & 1 & K'' \\
J'' & J'' & J''
\end{array} \right]
\]

\[
\times \left( 2q_A + 1 \right) \left( -1 \right)^{i'' + j'' + q_a} \left[ \begin{array}{ccc}
2 & 1 & a_2 \\
J' & J'' & J''
\end{array} \right] \left[ \begin{array}{ccc}
a_2 & 1 & K'' \\
J'' & J'' & J''
\end{array} \right] q_A
\]

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

\[
\frac{I_{2q_A} - I_{-2q_A}}{I_{2q_A} + I_{-2q_A}} = \frac{\left[ B_1 \right]^{i'' + j''} \rho_0^1(g, \hat{O}) + \left[ B_3 \right]^{i'' + j''} \rho_0^3(g, \hat{O})}{\left[ B_0 \right]^{i'' + j''} \rho_0^0(g, \hat{O}) + \left[ B_2 \right]^{i'' + j''} \rho_0^2(g, \hat{O}) + \left[ B_4 \right]^{i'' + j''} \rho_0^4(g, \hat{O})},
\]

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

### III. LINEARLY POLARIZED TWO PHOTON ABSORPTION

In calculating the two photon linear absorption ratio the most straightforward route is to calculate the absorption intensities in the two orthogonal axis systems \( Z_1 \) and \( Z_2 \) defined by \( I_1 \) and \( I_{2q_A} \), respectively. The measurement in \( Z_2 \) is then related to that in \( Z_1 \) by the appropriate rotational transformation, as in paper II on single photon linear dichroism. For linearly polarized light the polarization vector \( E_z \) is \( E_0^j \) in a spherical basis and we simply need to put \( q_A = 0 \) in Eq. (3).

The absorption intensity in \( Z_1 \) is thus

\[
I_{Z_1} = g(\omega) \sum_{a_j K''} (2a_2 + 1)(2a_2 + 1)(-1)^{i'' + j'' + q_a} \left[ \begin{array}{ccc}
1 & 1 & a_1 \\
J & J'' & J''
\end{array} \right] \left[ \begin{array}{ccc}
a_1 & 1 & a_2 \\
J'' & J'' & J''
\end{array} \right] \left[ \begin{array}{ccc}
a_2 & 1 & K'' \\
J'' & J'' & J''
\end{array} \right]
\]

\[
\times \left( 2K'' + 1 \right)^{1/2} \left[ j'' + j' \rho_0^0(g, \hat{O}) \right] \left[ D(\alpha J'', \omega, \theta) \right] \left[ \langle \alpha J'' || d || \alpha' J' \rangle \langle \alpha' J' || d' || \alpha'' J'' \rangle \right]^2.
\]

We have an identical expression for \( I_{Z_2} \) though of course it refers to a different coordinate frame. From the restrictions imposed by the \( 3j \) and \( 6j \) symbols, only \( j'' + j' \rho_0^0 \) and \( i'' + j'' \rho_0^0 \) can contribute to the absorption intensity with respect to each frame. The multipoles in \( Z_2 \) are related to those in \( Z_1 \) by the standard Euler rotation of \( \beta = \Pi/2 \) about their common \( y \) axis in the usual way:

\[
I_{Z_2} = \sum_{a_2 K''} d_{K''}^{J''} \rho_0^0(g, \hat{O}) \frac{\Pi}{2} \rho_0^0(g, \hat{O}).
\]

\[
\frac{I_{2q_A} - I_{-2q_A}}{I_{2q_A} + I_{-2q_A}} = \frac{\left[ B_1 \right]^{i'' + j''} \rho_0^1(g, \hat{O}) + \left[ B_3 \right]^{i'' + j''} \rho_0^3(g, \hat{O})}{\left[ B_0 \right]^{i'' + j''} \rho_0^0(g, \hat{O}) + \left[ B_2 \right]^{i'' + j''} \rho_0^2(g, \hat{O}) + \left[ B_4 \right]^{i'' + j''} \rho_0^4(g, \hat{O})},
\]

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

### FIG. 1. Angular plots of \( d_{K''}^{J''} \) where \( K'' = 1, 2, 3, 4 \). The angles for which \( d_{K''}^{J''} \) is 0 correspond to geometries between the ground state symmetry axis and the probe quantization axis for which the particular multipole \( K \) does not contribute to the absorption strength.
extensive tables are given by Buckmaster and Chiu.\textsuperscript{12} The relevant numerical values of \(d^\ast_{\infty}(\Pi/2)\) are

\[
d^\ast_{\infty}(\Pi/2) = 3/8, \quad d^\ast_{0 \pm 1}(\Pi/2) = d^\ast_{0 \pm 2}(\Pi/2) = 0, \\
d^\ast_{0 \pm 2}(\Pi/2) = \mp \sqrt{10}/8, \\
d^\ast_{0 \pm 2}(\Pi/2) = \mp \sqrt{20}/8.
\]

Thus if the ground state multipole distribution is not axially symmetric about \(z_1\), there will be contributions to the absorption measured in \(z_2\) from \(J''J'\rho_{J_2}^\ast(g,z_1)\), \(J''J'\rho_{J_2}^\ast(g,z_1)\) as well as the axially symmetric components \(J''J'\rho_{J_2}^\ast(g,z_1)\).

The linear absorption ratio under these circumstances is given by

\[
\left( \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \right)_{\text{TPA}} = \sum_{\sigma,\sigma',K} (-1)^{J' + J'}(2a_1 + 1)(2a_2 + 1)\left[ \begin{array}{ccc} 1 & 1 & a_1 \\ J'' & J'' & J' \\ J' & J' & J \\ \end{array} \right] \left[ \begin{array}{ccc} 1 & 1 & a_2 \\ J'' & J'' & J' \\ J' & J' & J \\ \end{array} \right] \\
\times \left[ J''J'\rho_{K}^\ast(g,z_1) - \sum d^\ast_{\infty}(\Pi/2)J''J'\rho_{K}^\ast(g,z_1) \right] \\
\left[ \sum_{\sigma,\sigma',K} (-1)^{J' + J'}(2a_1 + 1)(2a_2 + 1)\left[ \begin{array}{ccc} 1 & 1 & a_1 \\ J'' & J'' & J' \\ J' & J' & J \\ \end{array} \right] \left[ \begin{array}{ccc} 1 & 1 & a_2 \\ J'' & J'' & J' \\ J' & J' & J \\ \end{array} \right] \\
\times (2K'' + 1)^{1/2}J''J'\rho_{K}^\ast(g,z_1) \right]^{-1}.
\]

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

\[
\left( \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \right)_{\text{TPA}} = \sum_{\sigma,\sigma',K} (-1)^{J' + J'}(2a_1 + 1)(2a_2 + 1)\left[ \begin{array}{ccc} 1 & 1 & a_1 \\ J'' & J'' & J' \\ J' & J' & J \\ \end{array} \right] \left[ \begin{array}{ccc} 1 & 1 & a_2 \\ J'' & J'' & J' \\ J' & J' & J \\ \end{array} \right] \\
\times (2K'' + 1)^{1/2}J''J'\rho_{K}^\ast(g,z_1) \right]^{-1}.
\]

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

\[
\left( \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \right)_{\text{TPA}} = \sum_{\sigma,\sigma',K} (-1)^{J' + J'}(2a_1 + 1)(2a_2 + 1)\left[ \begin{array}{ccc} 1 & 1 & a_1 \\ J'' & J'' & J' \\ J' & J' & J \\ \end{array} \right] \left[ \begin{array}{ccc} 1 & 1 & a_2 \\ J'' & J'' & J' \\ J' & J' & J \\ \end{array} \right] \\
\times (2K'' + 1)^{1/2}J''J'\rho_{K}^\ast(g,z_1) \right]^{-1}.
\]

where

\[
d^\ast_{\infty}(\beta) = 1, \\
d^\ast_{\infty}(\beta) = 3(3 \cos^2 \beta - 1), \\
d^\ast_{\infty}(\beta) = 3(3 \cos^2 \beta - 10 \cos^2 \beta + 3).
\]

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

\[
\left( \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} \right)_{\text{TPA}} = \sum_{\sigma,\sigma',K} (-1)^{J' + J'}(2a_1 + 1)(2a_2 + 1)\left[ \begin{array}{ccc} 1 & 1 & a_1 \\ J'' & J'' & J' \\ J' & J' & J \\ \end{array} \right] \left[ \begin{array}{ccc} 1 & 1 & a_2 \\ J'' & J'' & J' \\ J' & J' & J \\ \end{array} \right] \\
\times (2K'' + 1)^{1/2}J''J'\rho_{K}^\ast(g,z_1) \right]^{-1}.
\]

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

**IV. "MAGIC ANGLE" CONSIDERATIONS**

An examination of Eq. (13) shows that in addition to the well known settings of \(\beta = 54.7^\circ\) to remove the alignment contribution,\textsuperscript{3} there are analogous geometries for which the absorption will contain no hexadecapole term. These are the values of \(\beta\) for which \(d^\ast_{\infty}(\beta)\) is zero; these being,

\[
\beta_4 = 30.556^\circ, 70.124^\circ, 109.875^\circ, 149.444^\circ.
\]

Thus if we perform a two photon linearly polarized absorption measurement at a polarization setting of \(\beta_4\) to the
ground state symmetry axis it will contain solely $^{J^*J^*}\rho_0^0(g,z)$ and $^{J^*J^*}\rho_0^0(g,z)$ terms:

$$
I_{\alpha} = C \left[ [B_0]^{J^*J^*}\rho_0^0(g,z) + d_\alpha^{J^*J^*}[B_4]^{J^*J^*}\rho_0^0(g,z) \right],
$$

$$
I_\parallel = C \left[ [B_0]^{J^*J^*}\rho_0^0(g,z) + [B_4]^{J^*J^*}\rho_0^0(g,z) \right]
$$

(16)

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

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

$$
d_{\alpha\beta}(\beta) = \cos \beta, \quad \beta_1 = 90^\circ,
$$

$$
d_{\infty\beta}(\beta) = \frac{1}{2} (5 \cos^3 \beta - 3 \cos \beta),
$$

$$
\beta_3 = 39.231^\circ, 90^\circ, 140.768^\circ.
$$

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

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

V. CONCLUSIONS

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

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

ACKNOWLEDGMENT

We thank the Science and Engineering Research Council for financial support.