

Theory of Fluorescence Depolarization by Anisotropic Rotational Diffusion

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The general expressions for the time-dependent fluorescence depolarization caused by anisotropic rotational diffusion have been obtained. It is shown that after an instantaneous exciting light pulse, the parallel and perpendicular components of fluorescence can have a maximum of six exponential decays and the difference of these two components a maximum of five decays. The present results differ from those of previous studies and the differences are discussed.

I. INTRODUCTION

When a molecular system is excited by light, a non-uniform orientational distribution with respect to the transition dipole moments of the ground and excited state molecules can be produced. This anisotropy can decay in time due to the rotational motion of the molecules and consequently leads to a depolarization of the emitted radiation and a decay of the induced dichroism. Studies of the rotational motion of molecules in liquids by fluorescence depolarization has been limited in the past by the time response of the exciting source or the detecting system to the nanosecond time scale.¹⁻³ Thus the rotational motions in the earlier time domain could not be studied and one was restricted to systems having relatively long relaxation times. Our interest in this subject is motivated by our studies of orientational relaxation using picosecond laser techniques which yields the rotational dynamics in the subnanosecond as well as nanosecond time region. In particular, we have studied the rotational motion of Rhodamine 6G in various liquids by absorption⁴ as well as fluorescence depolarization methods.⁵

Perrin⁶ in early 1930 first formulated the relationship between fluorescence depolarization and rotational Brownian motion in considering the case of a hydrodynamically spherical molecule. However, for a molecule whose rotational diffusion about its principal axes differs considerably, the isotropic description must be replaced by an anisotropic model for rotation.^{1-3,7} Many attempts have subsequently been made to extend Perrin's treatment to that of anisotropic diffusion. In this effort, Perrin⁸ and Memming⁷ studied the rotational motion for symmetric top molecules and recently Lombardi and Dafforn,⁹ Tao,² and Weber¹⁰ obtained the formulation for the asymmetric rotor. However, there is presently disagreement as to the correct expressions for this polarization decay.

Because of the importance of the depolarization method in the study of molecular motions, we have derived the expressions for the emission depolarization due to anisotropic rotation. From our results we conclude that disagreement arises from the fact that these

prior studies either did not treat the problem in the most general fashion or for various reasons did not use the correct expressions for the transition probabilities. We will discuss certain special cases of our general formula and compare them with previous results. A few comments will also be given to Weber's novel approach to this problem.

II. THEORY AND DISCUSSION

The most convenient way, by far, for solving the anisotropic rotational diffusion is given by Favro.¹¹ He showed that the diffusion equation can be given by

$$\partial f(\mathbf{\Omega}, t) / \partial t = -Hf(\mathbf{\Omega}, t), \quad (1)$$

where $f(\mathbf{\Omega}, t)$ is the probability that the vector of a molecular dipole transition is oriented in the angle ($\mathbf{\Omega}$) at time t and the Hamiltonian is given by

$$H = \sum_{i,j} L_i D_{ij} L_j,$$

where \mathbf{L} is the quantum mechanical angular momentum operator and D_{ij} is the component of the diffusion tensor. If one is able to find a coordinate system that diagonalizes the diffusion tensor,¹² then the Hamiltonian becomes

$$H = \sum_i D_i L_i^2. \quad (2)$$

It is immediately evident that Eq. (1) is analogous to the Schrödinger equation for an asymmetric rigid rotor. It is further shown by Favro that the diffusion Eq. (1) may be solved by the Green's function method, namely

$$f(\mathbf{\Omega}, t) = \int_{\mathbf{\Omega}_0} f(\mathbf{\Omega}_0) G(\mathbf{\Omega}_0 | \mathbf{\Omega}, t) d\mathbf{\Omega}_0, \quad (3)$$

where $f(\mathbf{\Omega}_0)$ is the initial probability that the dipole vector is oriented in $\mathbf{\Omega}_0$ at $t=0$ and $G(\mathbf{\Omega}_0 | \mathbf{\Omega}, t)$ is the Green's function that describes the rotation of the dipole vector from $\mathbf{\Omega}_0$ at $t=0$ into $\mathbf{\Omega}$ at time t . The function $G(\mathbf{\Omega}_0 | \mathbf{\Omega}, t)$ can be expanded in terms of asymmetric rotor wavefunctions.

$$G(\mathbf{\Omega}_0 | \mathbf{\Omega}, t) = \sum_n \Psi_n^*(\mathbf{\Omega}_0) \Psi_n(\mathbf{\Omega}) \exp(-E_n t), \quad (4)$$

with the initial condition

$$G(\mathbf{\Omega}_0 | \mathbf{\Omega}, 0) = \delta(\mathbf{\Omega}_0, \mathbf{\Omega}) = \sum_n \Psi_n^*(\mathbf{\Omega}_0) \Psi_n(\mathbf{\Omega}),$$

where $\Psi_n(\mathbf{\Omega})$ and E_n are the stationary state eigenfunction and eigenvalue for the asymmetric rigid rotor with the substitution $\hbar^2/2I_i$ by D_i . The wavefunction $\Psi_n(\mathbf{\Omega})$ may be expanded in terms of symmetric rotor wavefunctions $\Phi_{k,m}^{(l)}(\mathbf{\Omega})$ ¹⁴

$$\Psi_n(\mathbf{\Omega}) = \Psi_{\tau,m}^{(l)}(\mathbf{\Omega}) = \sum_{k=-l}^l A_{\tau,k}^{(l)} \Phi_{k,m}^{(l)}(\mathbf{\Omega}). \quad (5)$$

The coefficients $A_{\tau,k}^{(l)}$ and eigenvalues $E_{\tau}^{(l)}$ are tabulated by Favro and Huntress¹³ for $l \leq 2$.

Let a set of Cartesian coordinates (x, y, z) be the three principal diffusion axes fixed in the molecule and (X, Y, Z) be the laboratory fixed axes. The transformation between these two sets of Cartesian coordinates may be given as

$$X = Tx, \quad (6)$$

where the transformation matrix T is expressed in terms of the Euler angles $\mathbf{\Omega} = (\theta, \psi, \phi)$ which rotate the laboratory fixed systems into the molecular fixed systems.¹⁵ Let the projections of the unit vector of absorption dipole μ_{abs} along the molecular fixed axes be $\gamma_x, \gamma_y, \gamma_z$ and the corresponding components of the emission dipole be q_x, q_y, q_z .¹⁶ For the direction of propagation of the exciting light beam along the laboratory Y axis and its electric field polarized along the Z axis, the probability that the molecule will be excited is given by

$$P_{\text{abs}} = (\gamma_x T_{zx} + \gamma_y T_{zy} + \gamma_z T_{zz})^2, \quad (7)$$

with $\gamma_x^2 + \gamma_y^2 + \gamma_z^2 = 1$, where T_{ij} is the element of the transformation matrix T . If we observe the emission along X axis, the intensities of emission polarized along the Z axis (parallel component), and along the Y axis (perpendicular component), are, respectively, proportional to

$$P_{\text{em}}^{\parallel} = (q_x T_{zx} + q_y T_{zy} + q_z T_{zz})^2 \quad (8a)$$

$$P_{\text{em}}^{\perp} = (q_x T_{yx} + q_y T_{yy} + q_z T_{yz})^2, \quad (8b)$$

with $q_x^2 + q_y^2 + q_z^2 = 1$. Now, we proceed to calculate the intensities of emission for the parallel and perpendicular components following an instantaneous light pulse of excitation. The original distribution of the absorption dipoles of the molecules at $t=0$ will be $f(\mathbf{\Omega}_0) = P_{\text{abs}}$. To obtain $f(\mathbf{\Omega}, t)$, we need the following transformation¹⁷

$$\Phi_{k,m}^{(l)}(\mathbf{\Omega}) = (-1)^{k-m} [(2l+1)/8\pi^2]^{1/2} \mathfrak{D}_{k,m}^{(l)}(\mathbf{\Omega}), \quad (9)$$

where $\mathfrak{D}_{k,m}^{(l)}(\mathbf{\Omega})$ is the element of the Wigner rotation matrix that rotates the laboratory fixed axes into the molecular axes by the angle $(\mathbf{\Omega})$. Substituting Eq. (9) into Eq. (5), Eq. (5) into (4) and finally Eqs. (4)

and (7) into (3), we obtain

$$f(\mathbf{\Omega}, t) = \frac{1}{3} + \left(\frac{8}{9}\pi^2\right)^{1/2} \sum_{\tau=-2}^2 \exp(-E_{\tau}^{(2)}t) \cdot \xi_{\tau}^{(2)} \left[\sum_{k=-2}^2 A_{\tau,k}^{(2)} \Phi_{k,0}^{(2)}(\mathbf{\Omega}) \right], \quad (10)$$

where

$$\begin{aligned} \xi_{\tau}^{(2)} = & (\gamma_z^2 - \frac{1}{3}) A_{\tau,0}^{(2)} + (6)^{-1/2} (\gamma_x - i\gamma_y)^2 A_{\tau,2}^{(2)} \\ & + (6)^{-1/2} (\gamma_x + i\gamma_y)^2 A_{\tau,-2}^{(2)} \\ & - (\sqrt{2}/\sqrt{3}) (\gamma_x - i\gamma_y) \gamma_z A_{\tau,1}^{(2)} \\ & + (\sqrt{2}/\sqrt{3}) (\gamma_x + i\gamma_y) \gamma_z A_{\tau,-1}^{(2)}. \end{aligned}$$

We recognize that the distribution $f(\mathbf{\Omega}, t)$ is independent of quantum number m which is associated with the projection of angular momentum along the laboratory fixed Z axis. This is due to the fact that the molecular system is excited symmetrically about the Z axis and remains symmetrical with respect to the Z axis as the system evolves towards an isotropic distribution.

The intensities of emission observed in the X direction are

$$I_{\parallel}(t) = \int_{\mathbf{\Omega}} P_{\text{em}}^{\parallel} P(t) f(\mathbf{\Omega}, t) d\mathbf{\Omega}, \quad (11a)$$

$$I_{\perp}(t) = \int_{\mathbf{\Omega}} P_{\text{em}}^{\perp} P(t) f(\mathbf{\Omega}, t) d\mathbf{\Omega}, \quad (11b)$$

where $P(t)$ is the probability that an initially excited molecule remains excited at time t . If the fluorescent molecule has a single exponential decay with a lifetime τ then $P(t) = \exp(-t/\tau)$. Substituting Eqs. (8) and (10) into (11), we obtain

$$\begin{aligned} I_{\parallel}(t) = & P(t) \left\{ \frac{1}{9} + (4/15) q_x q_y \gamma_x \gamma_y \exp[-3(D_z + D)t] \right. \\ & + (4/15) q_y q_z \gamma_y \gamma_z \exp[-3(D_x + D)t] \\ & + (4/15) q_z q_x \gamma_z \gamma_x \exp[-3(D_y + D)t] \\ & + (1/15) (\beta + \alpha) \exp[-(6D + 2\Delta)t] \\ & \left. + (1/15) (\beta - \alpha) \exp[-(6D - 2\Delta)t] \right\}, \quad (12a) \end{aligned}$$

and

$$I_{\perp}(t) = \frac{1}{6} P(t) - \frac{1}{2} I_{\parallel}(t), \quad (12b)$$

where

$$\begin{aligned} \beta = & q_x^2 \gamma_x^2 + q_y^2 \gamma_y^2 + q_z^2 \gamma_z^2 - (1/3), \\ \alpha = & (D_x/\Delta) (q_y^2 \gamma_y^2 + q_z^2 \gamma_z^2 - 2q_x^2 \gamma_x^2 + \gamma_x^2 + q_x^2) \\ & + (D_y/\Delta) (q_z^2 \gamma_z^2 + q_x^2 \gamma_x^2 - 2q_y^2 \gamma_y^2 + \gamma_y^2 + q_y^2) \\ & + (D_z/\Delta) (q_x^2 \gamma_x^2 + q_y^2 \gamma_y^2 - 2q_z^2 \gamma_z^2 + \gamma_z^2 + q_z^2) \\ & - (2D/\Delta), \end{aligned}$$

$$D = \frac{1}{3} (D_x + D_y + D_z),$$

$$\Delta = (D_x^2 + D_y^2 + D_z^2 - D_x D_y - D_y D_z - D_z D_x)^{1/2}.$$

The constant D is the average of the three principal diffusion constants and Δ is related to the anisotropy

of the diffusion. The fluorescence polarization anisotropy, defined as $R(t) = [I_{||}(t) - I_{\perp}(t)] / [I_{||}(t) + 2I_{\perp}(t)]$ can be obtained from Eqs. (12a) and (12b). Similarly, the steady-state fluorescence polarization, \bar{P} , given by

$$\bar{P} = (\bar{I}_{||} - \bar{I}_{\perp}) / (\bar{I}_{||} + \bar{I}_{\perp}), \tag{13}$$

can also be obtained by time averaging over the emission decay. For an exponential decay of the emission

we find

$$\bar{I}_{||} = \tau^{-1} \int_0^{\infty} I_{||}(t) dt, \tag{14a}$$

$$\bar{I}_{\perp} = \tau^{-1} \int_0^{\infty} I_{\perp}(t) dt, \tag{14b}$$

and

$$\bar{P}^{-1} - \frac{1}{3} = \frac{20}{9} \left/ \left(\frac{4q_x q_y \gamma_x \gamma_y}{1+3(D_x+D)\tau} + \frac{4q_y q_z \gamma_y \gamma_z}{1+3(D_x+D)\tau} + \frac{4q_x q_z \gamma_x \gamma_z}{1+3(D_y+D)\tau} + \frac{\beta+\alpha}{1+(6D+2\Delta)\tau} + \frac{\beta-\alpha}{1+(6D-2\Delta)\tau} \right) \right. \tag{15}$$

From Eqs. (12a) and (12b), we see that in general, aside from $P(t)$, the polarized components of the fluorescence and its anisotropy $R(t)$ have five exponentials in their decay. This is expected since both the probability functions of excitation and emission transform as the second rank of the rotation matrices which have $2l+1=5$ dimensionality. Only eigenfunctions and eigenvalues for the rigid rotor with $l=2$ are therefore involved in the evaluation of $I_{||}(t)$ and $I_{\perp}(t)$. Hence for a given molecular system, one can see clearly how many exponentials and what type of exponents one would expect to obtain by examining the transformation properties of the asymmetric rotor wavefunctions. Let us consider, for example, the case that the vector

of absorption dipole is parallel to one of the molecular axes. In this case the absorption probability is proportional to $\cos^2\theta_0$ which transforms as $\mathfrak{D}_{0,0}^{(2)}(\mathfrak{Q}_0)$ and $\mathfrak{D}_{0,0}^{(2)}(\mathfrak{Q}_0)$. The component $\mathfrak{D}_{0,0}^{(2)}(\mathfrak{Q}_0)$ leads only to a constant. From the orthogonality property of the rotation matrices, one would expect to obtain only two exponentials with exponents $(6D+2\Delta)$ and $(6D-2\Delta)$ which are the eigenvalues associated with $\Psi_{2,0}^{(2)}(\mathfrak{Q}_0)$ and $\Psi_{0,0}^{(2)}(\mathfrak{Q}_0)$, respectively. This is due to the fact that only these two asymmetric rotor eigenfunctions contain the symmetric rotor wavefunction $\Phi_{0,0}^{(2)}(\mathfrak{Q}_0)$ which transforms as $\mathfrak{D}_{0,0}^{(2)}(\mathfrak{Q}_0)$. This consideration is verified when we reduce Eq. (12a) by setting, say $\gamma_x=1, \gamma_y=\gamma_z=0$ and obtain

$$I_{||}(t) = \left\{ \frac{1}{9} + (1/15) \left[(q_z^2 - \frac{1}{3}) - \Delta^{-1} (D_x q_y^2 + D_y q_x^2 + D_z q_z^2 - D) \right] \exp[-(6D+2\Delta)t] \right. \\ \left. + (1/15) \left[(q_z^2 - \frac{1}{3}) + \Delta^{-1} (D_x q_y^2 + D_y q_x^2 + D_z q_z^2 - D) \right] \exp[-(6D-2\Delta)t] \right\} P(t). \tag{16}$$

This result is the same as Weber's general expression.¹⁰ For symmetric-top molecules, one would generally expect three exponential decay terms, aside from $P(t)$, because there is a twofold degeneracy of eigenvalues in the components of the angular momentum along the symmetric axis for this type of system. The eigenfunctions $\Psi_{1,m}^{(2)}(\mathfrak{Q})$ and $\Psi_{-1,m}^{(2)}(\mathfrak{Q})$, and $\Psi_{2,m}^{(2)}(\mathfrak{Q})$ and $\Psi_{-2,m}^{(2)}(\mathfrak{Q})$ are degenerate when $D_x = D_y \neq D_z$. In this case Eq. (12a) is reduced to

$$I_{||}(t) = \left\{ \frac{1}{9} + (1/15) \left[2(q_x \gamma_x + q_y \gamma_y)^2 - (1 - q_z^2)(1 - \gamma_z^2) \right] \right. \\ \times \exp[-(2D_x + 4D_z)t] + (4/15) q_x \gamma_x (q_x \gamma_x + q_y \gamma_y) \\ \times \exp[-(5D_x + D_z)t] + (1/15) (3q_z^2 - 1) (\gamma_z^2 - \frac{1}{3}) \\ \left. \times \exp(-6D_z t) \right\} P(t). \tag{17}$$

This corresponds to the rotation of an ellipsoid, prolate or oblate in shape. As for the case of isotropic diffusion, only one constant, namely $6D$, can characterize the decay in polarization since rotation along any axis has the same diffusion constant. From Eqs. (12a) and

(12b) we have

$$I_{||}(t) = \left\{ (1/9) + (2/45) \exp(-6Dt) (3 \cos^2\lambda - 1) \right\} P(t), \tag{18a}$$

$$I_{\perp}(t) = \left\{ (1/9) - (1/45) \exp(-6Dt) (3 \cos^2\lambda - 1) \right\} P(t), \tag{18b}$$

and

$$R(t) = \frac{1}{3} (3 \cos^2\lambda - 1) \exp(-6Dt), \tag{19}$$

$$\bar{P}^{-1} - \frac{1}{3} = (\bar{P}_0^{-1} - \frac{1}{3}) (1 + 6D\tau), \tag{20}$$

where

$$\bar{P}_0^{-1} - \frac{1}{3} = (10/3) (3 \cos^2\lambda - 1)^{-1}, \tag{21}$$

and λ is the angle between the absorption and emission dipoles. We recognize that Eq. (20) is just the expression for steady-state polarization given by Perrin for spherical molecules.¹⁸ Finally, if we have a system with its vector of emission dipole parallel to the vector of absorption dipole, i.e., $\gamma_i = q_i (i=x, y, z)$, then Eq. (12a) is reduced to

$$I_{||}(t) = \left\{ \frac{1}{9} + (4/15) \gamma_x^2 \gamma_y^2 \exp[-3(D_x + D)t] + (4/15) \gamma_y^2 \gamma_z^2 \exp[-3(D_x + D)t] + (4/15) \gamma_z^2 \gamma_x^2 \exp[-3(D_y + D)t] \right. \\ \left. + (1/15) (\beta + \alpha) \exp[-(6D + 2\Delta)t] + (1/15) (\beta - \alpha) \exp[-(6D - 2\Delta)t] \right\} P(t), \tag{22}$$

where

$$\beta = \gamma_x^4 + \gamma_y^4 + \gamma_z^4 - \frac{1}{3}$$

$$\alpha = (D/\Delta) - (D_x/\Delta)(\gamma_x^4 + 2\gamma_y^2\gamma_z^2)$$

$$- (D_y/\Delta)(\gamma_y^4 + 2\gamma_z^2\gamma_x^2) - (D_z/\Delta)(\gamma_z^4 + 2\gamma_x^2\gamma_y^2)$$

Again we have generally five exponentials besides $P(t)$.

In conclusion, we have obtained the general expressions for the time-dependent and steady-state fluorescent depolarization. We have shown that after an instantaneous exciting light pulse, the polarized components of fluorescence can have a maximum of six experimental decays, instead of three exponentials as Weber argued. The reason that Weber obtained only three exponentials is that he assumed the absorption vector is along one of the molecular axes. This is clearly not the most general case, since the absorption dipole can have an arbitrary direction in the molecular frame. It is also seen that Tao incorrectly projected the absorption vector along the molecular axes, thus leading to errors in the expressions for the polarized emission. Lombardi and Dafforn used expressions for the transition probabilities for the special case which corresponds to the excitation of orthogonal and noninterfering transitions and thus does not contain the cross terms present in the most general case for which an individual electronic transition has components along the different diffusion axes of the molecule.¹⁹ The importance of obtaining correct expressions for these polarized components lies in the fact that the primary physical quantities of interest, i.e., D_x , D_y , D_z , are deduced from the experimentally observed $I_{||}(t)$ and $I_{\perp}(t)$. These expressions are also essential for obtaining additional information about the projections of the absorption and emission dipoles along the principal diffusion axes. Knowing the directions of the dipoles, one is able to locate the axes of rotation and vice versa.

As for Weber's discontinuous distribution approach, he claims that his method is applicable not only to the small angular rotation case, but also to the finite angular jump case. It has been shown, however, that the rotational dipole correlation function, which is the function obtained from fluorescence measurements, does not yield an exponential decay for the early time behavior,²⁰ nor for the case where the molecular rotation is described as that of a nearly free rotor.²¹ Based on these

considerations, it is not clear what the limits are in Weber's very interesting approach to the problem of molecular rotations of a finite jump size.

¹ P. Wahl, *Compt. Rend.* **263D**, 1525 (1966).

² T. Tao, *Biopolymers* **8**, 609 (1969).

³ J. Yguerabide, H. F. Epstein, and L. Stryer, *J. Mol. Biol.* **51**, 573 (1970).

⁴ T. J. Chuang and K. B. Eisenthal, *Chem. Phys. Letters* **11**, 368 (1971).

⁵ T. J. Chuang and K. B. Eisenthal (unpublished).

⁶ F. Perrin, *J. Phys. Radium* **5**, 497 (1934).

⁷ R. Memming, *Z. Physik. Chem. (Frankfurt)* **28**, 168 (1961).

⁸ F. Perrin, *J. Phys. Radium* **7**, 1 (1936).

⁹ J. R. Lombardi and G. A. Dafforn, *J. Chem. Phys.* **44**, 3882 (1966).

¹⁰ G. Weber, *J. Chem. Phys.* **55**, 2399 (1971).

¹¹ L. D. Favro, *Phys. Rev.* **119**, 53 (1960).

¹² In practice, it may be rather difficult to find the coordinate system that diagonalizes the diffusion tensor, especially for asymmetric rotors that have such low symmetry that the diffusion axes may be rotationally shifted from the principal inertial axes by intermolecular interactions. This point has been discussed by Huntress in Ref. 13.

¹³ W. T. Huntress, Jr., *Advances in Magnetic Resonance*, edited by J. S. Waugh (Academic, New York, 1970), Vol. 4, p. 1.

¹⁴ See, e.g., C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy*, (McGraw-Hill, New York, 1955), p. 95.

¹⁵ Here we use the Euler angles defined by H. Goldstein [*Classical Mechanics* (Addison-Wesley, Cambridge, Mass., 1950), p. 107]. His (x, y, z) and (x', y', z') are our (Y, X, Z) and (y, x, z) , respectively.

¹⁶ We assume in this treatment that the symmetry of the molecule is sufficiently low such that the transition dipole has a component along each of the molecular axes and furthermore that there is only one excited electronic state at the transition frequency. In the event that there are two different electronic states at the transition frequency, the transition probability is generally given by the sum of the individual transition probabilities. However, in the absence of perturbations which randomize the phases of the wavefunctions there can be interference effects between the two transitions. In this treatment we do not consider any of the effects due to the presence of more than one electronic state at the transition frequency.

¹⁷ E. P. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra* (Academic, New York, 1959), p. 215.

¹⁸ F. Perrin, *J. Phys.* **7**, 390 (1926).

¹⁹ This point can be seen clearly by comparing Eq. (7) of the present treatment with Eq. (6) of Lombardi and Dafforn's paper. By setting $\rho = 1$, namely, the exciting light is polarized along the A axis (our Z axis), the Lombardi and Dafforn Eq. (6) is given by

$$\rho_{\text{obs}} = \gamma_z T_{Zz}^2 + \gamma_y T_{Zy}^2 + \gamma_x T_{Zx}^2.$$

Thus we note that the cross terms which appear in the general case, Eq. (7), are absent in the Lombardi and Dafforn treatment.

²⁰ R. G. Gordon, *J. Chem. Phys.* **44**, 1830 (1966); see also the paper on the time dependence for relaxation of a symmetric top by M. Fixman and K. Rider, *J. Chem. Phys.* **51**, 2425 (1969).

²¹ W. A. Steele, *J. Chem. Phys.* **38**, 2411 (1963).