THE JOURNAL OF CHEMICAL PHYSICS VOLUME 50, NUMBER 2 15 JANUARY 1969

Light Scattering as a Probe of Fast-Reaction Kinetics: The Depolarized Spectrum of Rayleigh Scattered Light from a Chemically Reacting Medium*

BRUCE J. BERNE*
Department of Chemistry, Columbia University, New York, New York 10027
AND
R. PECORA†
Department of Chemistry, Stanford University, Stanford, California 94305

(Received 12 August 1968)

The spectral distribution of the depolarized component of light scattered from a dilute solution of molecules in dynamic chemical equilibrium between two states differing in optical anisotropy and dynamics is calculated. It is assumed that the molecules undergo isotropic translational and anisotropic rotational diffusion. It is furthermore assumed that the duration of a molecular transformation is much less than the characteristic times for rotational and translational diffusion. It is shown that in the most general case considered, the spectrum consists of 20 superposed lines with widths dependent on the translational diffusion coefficients and components of the rotational diffusion tensors of the two species and the backward and forward chemical rate constants. The relative strengths of the lines depend on the optical anisotropies and rotational diffusion tensor components of the two species as well as on their equilibrium concentrations. When the reaction is so fast that rotational and translational diffusion contributions to the linewidth may be ignored altogether, the spectrum reduces to a single Lorentzian line with half-width independent of scattering angle and proportional to the sum of the backward and forward rate constants for the chemical transformation.

I. INTRODUCTION

Recent advances in laser spectroscopy have made possible the measurement of very small frequency shifts in the light scattered from pure fluids and solutions.[1,2] It has been shown that experiments of this type measure the spectrum of long-wavelength thermal fluctuations and therefore provide information about the low-frequency Fourier components of the molecular motion.[1]

The spectrum of the scattered light can be separated into two parts: a fully polarized part and a depolarized part. Much attention has already been given to the polarized component whose structure can be explained by microscopic hydrodynamic considerations.[3–5] The depolarized component, on the other hand, has not until recently received much attention.[6,7] Depolarization of the scattered light arises from the optical anisotropy of the scattering elements of which the fluid is composed. The spectral line shape of this component depends on the detailed way in which spontaneous fluctuations of optical anisotropy in an equilibrium fluid regress. The spontaneous fluctuations of anisotropy reflect the optical anisotropy of the individual molecules in the fluid and its detailed time dependence is associated with the translational diffusion and rotational reorientation of these molecules.

In recent papers[8–10] it was shown how the polarized component of the scattered light spectrum can be used as a probe of fast-reaction kinetics. An experiment based on these theoretical suggestions has recently been reported.[11]

In this note we explore the possibility of using the depolarized part of the spectrum as a probe of fast-reaction kinetics. We confine our discussion to unimolecular reactions in dilute solutions which are sufficiently rapid so that the reaction rates are fast compared with the translational diffusion rates. The chief advantages of using the depolarized spectrum for this purpose are fourfold. (1) If an optically isotropic solvent is used the solvent does not contribute to the depolarized spectrum and consequently does not complicate its interpretation as it may in the polarized part. (2) Only a small subset of vector and tensor transport processes such as translational and rotational diffusion contribute to the line shape, whereas in the polarized spectrum all transport properties contribute thus greatly complicating the interpretation of the spectra. (3) The reaction rate enters the line shape independently of the scattering angle and thus hopefully can be extracted by studying the width of the depolarized line as a function of this angle. This is

---

* Work supported by the National Science Foundation and the Petroleum Foundation.

† Alfred P. Sloan Foundation Fellow.

[1] I. L. Fabelinski, *Molecular Scattering of Light* (Plenum Press, Inc., New York, 1968).

[2] P. A. Fleury, "Light Scattering from Thermal Fluctuations in Fluids" (unpublished).

[3] R. Pecora, J. Chem. Phys. **40**, 1604 (1964).

[4] R. D. Mountain, Rev. Mod. Phys. **38**, 205 (1966).

[5] R. D. Mountain, J. Res. Natl. Bur. Std. **A72**, 95 (1968).

[6] R. Pecora and M. A. Steele, J. Chem. Phys. **42**, 1872 (1965).

[7] K. A. Valiev, Opt. Spectrosc. **13**, 282 (1962); R. Pecora, J. Chem. Phys. **49**, 1036 (1968).

[8] B. J. Berne and H. L. Frisch, J. Chem. Phys. **47**, 3675 (1967).

[9] L. Blum and Z. M. Salzburg, J. Chem. Phys. **48**, 2292 (1968).

[10] B. J. Berne, J. W. Deutch, J. T. Hynes, and H. L. Frisch, J. Chem. Phys. **49**, 2864 (1968).

[11] Y. Yeh and R. N. Keeler, J. Chem. Phys. (to be published).

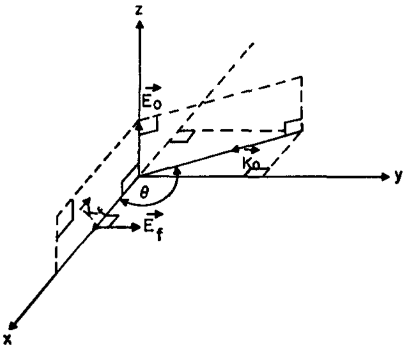

FIG. 1. The scattering geometry: $\mathbf{E}_0$, $\mathbf{E}_f$, $\mathbf{k}_0$, $\mathbf{k}_f$ are the initial and scattered electric and wave vectors, and θ is the scattering angle. This geometry corresponds to the $\perp$ component of the depolarized spectrum.

true of the polarized component as well. (4) Since we are interested in very fast reaction rates the central line of the polarized spectrum may overlap the Brilluoin doublet. This leads to great difficulty in interpreting the spectra. There exists no such difficulty with the depolarized spectrum since there are no other depolarized lines. The chief weaknesses of this method are twofold. (1) The reacting molecules must be optically anisotropic. This is not required for the polarized spectrum. On the other hand, there need be no difference in the polarizabilities of the reactant and product molecules as is required by the polarized method.[10] (2) In addition to the reaction rates, the rotational diffusion coefficients enter the linewidths independently of the scattering angle. Consequently the reaction rate cannot be separated from the rotational diffusion coefficient unless independent measurements of the latter are carried out, or the reaction rate swamps out the rotational diffusion coefficients.

II. THEORY

General equations for the spectrum of the scattered light were derived in a previous publication.[6] We present here only those formulae which are relevant to the present discussion. We restrict ourselves to the specific case in which an incident plane-polarized light wave of electric field vector $\mathbf{E}_0$, directed along the z axis of our coordinate system, propagates in the x–y plane with wave vector $\mathbf{k}_0$. The scattered wave measured at large distances, R_0, from the scattering medium generally has depolarized components. Attention will be focused on that component of the scattered wave propagating in the x direction with wave vector $\mathbf{k}_f$ and electric vector $\mathbf{E}_f$ whose polarization is parallel to the y axis, that is the perpendicular polarized component. The angle θ between $\mathbf{k}_0$ and $\mathbf{k}_f$ is called the scattering angle and the momentum transfer vector $\mathbf{k}=\mathbf{k}_f-\mathbf{k}_0$ is called the scattering vector. This geometry is illustrated in (Fig. 1). For more general scattering geometries the analysis is presented in Appendix B. With these definitions it may be shown that the scattered spectral density per unit volume at frequency shift ω, $I(\mathbf{k},\omega)$, can be related to off diagonal elements of the polarizability tensor of the scattering region located at the point $\mathbf{r}$. For the specific geometry above all that is required is the yzth component of this tensor, i.e., α_{yz}. Then

$$I(\mathbf{k},\omega)=\frac{k_f^4\,|E_0|^2}{16\pi^4R_0^2\mathcal{E}^2V}(2\pi)^{-1}\int_{-\infty}^{+\infty}dt\int_V d^3r$$

$$\times\exp[i(\mathbf{k}\cdot\mathbf{r}-\omega t)]\int_V d^3r'\langle\alpha_{yz}^*(\mathbf{r}+\mathbf{r}',t)\alpha_{yz}(r',0)\rangle,\quad(1)$$

where $\mathcal{E}$ is the dielectric constant of the scattering medium, V is the volume of the medium, and $\langle\ \rangle$ indicates an equilibrium ensemble average. It is assumed that the components of the polarizability tensor can be expressed in terms of individual molecular polarizabilities. Then $\alpha_{yz}(r,t)$, the polarizability density at the point $\mathbf{r}$ in the fluid at time t, is

$$\alpha_{yz}(r,t)=\sum_i\alpha_{yz}^i(t)\delta(\mathbf{r}_i(t)-\mathbf{r}),\quad(2)$$

where $\alpha_{yz}^i(t)$ is the yzth component of the polarizability of molecule i at time t and $\delta[\mathbf{r}_i(t)-r]$ indicates whether molecule i is in the neighborhood of the point $\mathbf{r}$ at time t. Substitution of Eq. (2) in Eq. (1) and subsequent use of the convolution theorem of Fourier analysis shows that

$$I(k,\omega)=(k_f^4\,|E_0|^2/16\pi^2\mathcal{E}^2)\bar{C}(k,\omega),\quad(3)$$

where

$$\bar{C}(k,\omega)=(2\pi V)^{-1}\int_{-\infty}^{+\infty}dte^{-i\omega t}$$

$$\times\langle\sum_{i=1,j=1}^{N}\alpha_{yz}^{j*}(0)\alpha_{yz}^{i}(t)\exp\{i\mathbf{k}\cdot[\mathbf{r}_i(t)-r_j(0)]\}\rangle.\quad(4)$$

The remainder of this article will be devoted in large part to a calculation of the cross correlation function.

If the solution is sufficiently dilute and the solvent is optically isotropic it is permissible to ignore the effect of one solute molecule on the polarizability of another solute molecule and thereby correlations between polarizabilities on different molecules. Under these circumstances $\bar{C}(k,\omega)$ can be written as

$$\bar{C}(\mathbf{k},\omega)=(2\pi)^{-1}\int_{-\infty}^{+\infty}dte^{-i\omega t}\bar{C}(\mathbf{k},t),\quad(5)$$

where

$$\bar{C}(k,t)=V^{-1}$$

$$\times\sum_{j=1}^{N}\langle\alpha_{yz}^{j*}(0)\alpha_{yz}^{j}(t)\exp\{i\mathbf{k}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]\}\rangle.\quad(6)$$

At this point we restrict our analysis to a reacting mixture consisting of an optically isotropic solvent and a species which unimolecularly transforms from a state labeled 1 to another state labeled 2. It is assumed that the reaction is reversible. At equilibrium there are N_1 solute molecules in state 1 and N_2 in state 2.

The precise meaning of the correlation function in Eq. (6) is most readily conveyed by explaining how a Maxwell's demon would go about calculating it. The precise motion of a particle labeled j is followed for a time t in each replica system in a Gibbsian ensemble. During the course of its motion the molecule will change its state a number of times. Furthermore it will rotate and translate. Consider first the subset of replica systems for which the particle labeled j is in the state 1 at time $t=0$. The factor

$$\alpha_{yz}^{j*}(0)\alpha_{yz}^{j}(t)\ \exp\{i\mathbf{k}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]\}$$

can be computed for each such replica system. These results can be added and averaged. The result is denoted

$$VC_1^j(\mathbf{k},t)=\langle\alpha_{yz}^{j*}(0)\alpha_{yz}^{j}(t)\ \exp\{i\mathbf{k}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]\}\rangle_1,$$

where the subscript 1 indicates that an average has been performed only for those replica systems for which particle j starts out in the state 1. Let us denote by

$$VC_{\gamma 1}^j(\mathbf{k},t)\equiv\langle\alpha_{yz}^{j*}(0)\alpha_{yz}^{j}(t)\ \exp\{i\mathbf{k}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]\}\rangle_{\gamma 1}$$

an average which is taken only over the replica systems in the subset for which j starts out in state 1 and at time t is in the state $\gamma=1$ or 2. Then it follows that

$$C_1^j(\mathbf{k},t)=\sum_{\gamma=1}^{2}C_{\gamma 1}^j(\mathbf{k},t).$$

A similar procedure can be followed if j starts out in state 2. Then

$$C_2^j(\mathbf{k},t)=\sum_{\gamma=1}^{2}C_{\gamma 2}^j(\mathbf{k},t).$$

Now the total ensemble average $C(\mathbf{k},t)$ can be found as follows. We determine the fraction of the Gibbsian ensemble for which j starts out in the state 1, and the fraction for which j starts out in the state 2 and denote these fractions f_1 and f_2, then

$$C(\mathbf{k},t)=\sum_{j=1}^{N}[f_1C_1^j(\mathbf{k},t)+f_2C_2^j(\mathbf{k},t)].$$

Now, f_1 and f_2 are merely the fractions of molecules in our equilibrium reacting mixture in the states 1 and 2, N_1/N, and N_2/N, respectively. Combining all of these results Eq. (6) can be written as

$$C(\mathbf{k},t)=\sum_{j=1}^{2}\left(\frac{N_1}{N}\sum_{\gamma=1}^{2}C_{\gamma 1}^j(\mathbf{k},t)+\frac{N_2}{N}\sum_{\gamma=1}^{2}C_{\gamma 2}^j(\mathbf{k},t)\right).$$

Noting that all of the molecules j in the sum give identical ensemble averages it is easily seen that a factor N comes out so that

$$C(\mathbf{k},t)=\sum_{\alpha,\gamma=1}^{2}c_\alpha\langle\alpha_{yz}^{j}(0)\alpha_{yz}^{j}(t)\times\exp\{i\mathbf{k}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]\}\rangle_{\gamma\alpha},\qquad(7)$$

where $c_\alpha=N_\alpha/V$ is the concentration of molecules in the state $\alpha=1$, 2 in the equilibrium system, and the subscript $\gamma\alpha$ indicates a restricted ensemble average in which the particle j starts out in the state $\alpha(=1,2)$ and finishes in the state $\gamma(=1,2)$.

The polarizability, α_{yz}^j, which appears in Eq. (7) is the yzth component of the polarizability tensor of molecule j expressed in the space-fixed coordinate system of Fig. (1). The elements of the polarizability tensor are known, however, only in the body-fixed coordinate system. It is a simple but lengthy matter to show that if molecule j is in the state γ with orientation $\mathbf{\Omega}$ with respect to the space-fixed axes

$$\alpha_{yz}^j(\Omega)=\tfrac{1}{2}i(\tfrac{8}{5}\pi^2)^{1/2}\sum_{n=-2}^{2}\alpha_n^\gamma[D_{1,n}^2(\Omega)+D_{-1,n}^2(\Omega)],\qquad(8)$$

where $D_{K,M}^J(\mathbf{\Omega})$ are the Wigner rotation matrices, and the α_n's are components of the molecular polarizability tensor in the molecule-fixed system expressed in spherical tensor form

$$\begin{aligned}
\alpha_{-2}^\gamma&=\tfrac{1}{2}(\alpha_{xx}^\gamma+\alpha_{yy}^\gamma)-i\alpha_{xy}^\gamma,\\
\alpha_{-1}^\gamma&=(\alpha_{zx}^\gamma-i\alpha_{zy}^\gamma),\\
\alpha_0^\gamma&=(2/6^{1/2})[\alpha_{zz}^\gamma-\tfrac{1}{2}(\alpha_{xx}^\gamma+\alpha_{yy}^\gamma)],\\
\alpha_1^\gamma&=-(\alpha_{-1}^\gamma)^*,\\
\alpha_2^\gamma&=(\alpha_{-2}^\gamma)^*,\\
\alpha_I^\gamma&=\tfrac{1}{3}(\alpha_{xx}^\gamma+\alpha_{yy}^\gamma\alpha_{zz}^\gamma).
\end{aligned}\qquad(9)$$

From Eq. (8) we see that α_{yz}^j varies as the orientation of the molecule varies and is thus very sensitive to the details of the molecular rotational Brownian motion. This however is not the whole story.

Changes in the state of molecule j can (1) change the body-fixed polarizability tensor, (2) change the rotational diffusion tensor, and (3) change the translational diffusion coefficient. Unimolecular reactions will effect the time dependence of α_{yz}^j, through (1) and (2), and will effect the time dependence of

$$\exp\{i\mathbf{k}\cdot[\mathbf{r}_j(t)-\mathbf{r}_j(0)]\}$$

through (3). Consequently the time dependence of $\alpha_{yz}^j\exp(i\mathbf{k}\cdot\mathbf{r}_j)$ will reflect the details of translational, rotational, and unimolecular rate processes.

III. ROTATIONAL AND TRANSLATIONAL BROWNIAN MOTION IN THE PRESENCE OF UNIMOLECULAR REACTIONS

In order to calculate the rate of change of the correlation function

$$VC_{\gamma\alpha}^{j}(\mathbf{k},t) = \langle \alpha_{yz}^{j}(0)^{*}\alpha_{yz}^{j}(t)\exp\{i\mathbf{k}\cdot[\mathbf{r}_{j}\cdot(t)-\mathbf{r}_{j}\cdot(0)]\}\rangle_{\gamma\alpha}$$

we must first determine the equation of motion for the probability distribution function, $P_{\gamma\alpha}(\mathbf{r},\boldsymbol{\Omega},t)$. Let $P_{\gamma\alpha}(\mathbf{r},\boldsymbol{\Omega},t)d^3r d^3\Omega$ be the joint probability of finding a molecule in the state γ, located in the neighborhood d^3r of the point $\mathbf{r}$ and oriented within the solid angle $d^3\Omega$ at time t, given that it was in the state α located in the neighborhood d^3r_0 of the origin, and oriented within the solid angle $d^3\Omega_0$ at time zero. We assume that $P_{\gamma\alpha}(\mathbf{r},\boldsymbol{\Omega},t)$ changes by (1) rearrangement of the molecule to form a new "species" (or state) (2) rotational diffusion, and (3) translational diffusion.

The computation of $P_{\gamma\alpha}(\mathbf{r},\boldsymbol{\Omega},t)$ poses a few difficulties which are not encountered in the nonreactive case (where it is usually assumed that the translational and rotational motions are independent so that $P(\mathbf{r},\boldsymbol{\Omega},t)$ can be factorized). In Appendix A the following equation of motion is derived for $P_{\gamma\alpha}(\mathbf{r},\boldsymbol{\Omega},t)$,

$$(\partial/\partial t)P_{\gamma\alpha}(\mathbf{r},\boldsymbol{\Omega},t) = +[D_\gamma\nabla^2 - L_i^\gamma D_{ij}^\gamma L_j^\gamma]P_{\gamma\alpha}(\mathbf{r},\boldsymbol{\Omega},t) + \sum_{\beta}[\lambda_{\gamma\beta}P_{\beta\alpha}(\mathbf{r},\boldsymbol{\Omega},t) - \lambda_{\beta\gamma}P_{\gamma\alpha}(\mathbf{r},\boldsymbol{\Omega},t)], \quad (10)$$

where D_γ is the translational self-diffusion coefficient for the molecule in the state γ, $\lambda_{\beta\gamma}$ is the rate constant for the unimolecular reaction $\gamma\rightarrow\beta$, ∇^2 is the Laplacian operator in $\mathbf{r}$ space, D_{ij}^γ is the rotational diffusion tensor for a molecule in the state γ with specified body-fixed axis, and L_i^γ is the angular momentum operator of the molecule in the state γ along the body-fixed axis i. It should be noted that the diffusion tensors can change symmetry when the molecule goes from one state into another, and that the Einstein summation convention is implied. On the right-hand side of Eq. (10) the first term represents the rate of change of $P_{\gamma\alpha}(\mathbf{r},\boldsymbol{\Omega},t)$ due to diffusion and the second term represents the change due to the chemical reactions. The equation can be rewritten as

$$\partial P_{\gamma\alpha}/\partial t = [D_\gamma\nabla^2 - L_i^\gamma D_{ij}^\gamma L_j^\gamma - \lambda_\gamma]P_{\gamma\alpha} + \sum_{\beta\neq\gamma}\lambda_{\gamma\beta}P_{\beta\alpha}, \quad (11)$$

where

$$\lambda_\gamma = \sum_{\beta\neq\gamma}\lambda_{\beta\gamma}$$

is the rate at which the molecules leave the state γ.

It should be emphasized that these equations are derived under the assumption that the molecule remains in a state for a given time and then jumps to a new state with a jump time very short compared with characteristic molecular reorientation and translational diffusion times.

The correlation function $C_{\gamma\alpha}^{j}(\mathbf{k},t)$ is then given by

$$VC_{\gamma\alpha}^{j}(\mathbf{k},t) = \int d^3\boldsymbol{\Omega} \times \int d^3\boldsymbol{\Omega}_0 \alpha_{yz}^{j}([\boldsymbol{\Omega}],\gamma)\alpha_{yz}^{j}([\boldsymbol{\Omega}_0],\alpha)F_{\gamma\alpha}(\mathbf{k},\Omega,t)P(\boldsymbol{\Omega}_0), \quad (12)$$

where $\alpha_{yz}^{j}([\boldsymbol{\Omega}],\gamma)$ is the polarizability of molecule j in the space fixed system when its orientation is $\boldsymbol{\Omega}$ and when it is in the state γ, or from Eq. (8)

$$\alpha_{yz}^{j}([\boldsymbol{\Omega}],\gamma) = \tfrac{1}{2}i(\tfrac{8}{5}\pi^2)^{1/2}\sum_{n=-2}^{2}\alpha_n^\gamma[D_{1,n}^2(\Omega)+D_{-1,n}^2(\Omega)]. \quad (13)$$

$P(\Omega_0)d^3\Omega_0$ is the probability that j's initial orientation is in $d^3\Omega_0$ (assumed uniform here $P(\Omega_0)=1/8\pi^2$) and

$$F_{\gamma\alpha}(\mathbf{k},\Omega,t) = \int d^3r\exp(i\mathbf{k}\cdot\mathbf{r})P_{\gamma\alpha}(\mathbf{r},\boldsymbol{\Omega},t). \quad (14)$$

The equation for $F_{\gamma\alpha}(\mathbf{k},t)$, found from Eq. (11), is

$$\partial F_{\gamma\alpha}(\mathbf{k},\boldsymbol{\Omega},t)/\partial t = -[k^2D_\gamma + L_i^\gamma D_{ij}L_j^\gamma + \lambda_\gamma]F_{\gamma\alpha}(\mathbf{k},\boldsymbol{\Omega},t) + \sum_{\beta\neq\gamma}\lambda_{\gamma\beta}F_{\beta}\alpha(\mathbf{k},\boldsymbol{\Omega},t). \quad (15)$$

To find $F_{11}(\mathbf{k},\boldsymbol{\Omega},t)$ and $F_{21}(\mathbf{k},\boldsymbol{\Omega},t)$ Eq. (12) is solved subject to the boundary conditions

$$F_{\gamma\beta}(\mathbf{k},\boldsymbol{\Omega},0) = \delta_{\gamma1}\delta_{\beta1}\delta(\boldsymbol{\Omega}-\boldsymbol{\Omega}_0). \quad (16a)$$

Likewise to find F_{22} and F_{12} the boundary conditions

$$F_{\gamma\beta}(\mathbf{k},\boldsymbol{\Omega},0) = \delta_{\gamma2}\delta_{\beta2}\delta(\boldsymbol{\Omega}-\boldsymbol{\Omega}_0) \quad (16b)$$

are used.

These boundary conditions follow from the fact that the molecule must be located at the origin in $\mathbf{r}$ space with orientation $\boldsymbol{\Omega}_0$ and in addition must be in the state 1 [Eq. (16a)], or in the state 2 [Eq. (16b)] at the initial instant $t=0$.

To simplify the analysis we restrict this study to the case where the symmetry of the diffusion tensor does not change when the molecule changes state. In actual calculations it is convenient to use that set of body axes in which D_{jk}^{γ} is diagonal so that the operator $L_i^{\gamma}D_{ij}^{\gamma}L_j^{\gamma}$ is $L_i^{\gamma}D_{ii}^{\gamma}L_i^{\gamma}$. If the symmetry of $\mathbf{D}$ were not assumed to be the same in all states then there would exist no set of body axis which would in general diagonalize all the $\mathbf{D}^{\gamma}$'s, although in special cases this could be achieved. In these principle axes Eq. (12) can be rewritten as

$$\partial F_{\gamma\alpha}(\mathbf{k},\,\mathbf{\Omega},\,t)/\partial t$$
$$=-[k^2D_{\gamma}+\sum_i D_i^{\gamma}[L_i^{\gamma}]^2+\lambda_{\gamma}]F_{\gamma\alpha}(\mathbf{k},\,\mathbf{\Omega},\,t)$$
$$+\sum_{\beta\neq\gamma}\lambda_{\gamma\beta}F_{\beta\alpha}(\mathbf{k},\,\mathbf{\Omega},\,t). \quad (17)$$

Note that $\sum_i D_i^{\gamma}L_i^{\gamma 2}$ has the form of the Hamiltonian of a rigid rotor with $\hbar^2/2I_i^{\gamma}$ replaced by D_i^{γ}. In order to solve Eq. (16) the eigenvalues and eigenstates of this operator are needed. Here we study the case of the asymmetric-top molecule and then successively specialize to the spherical-top and symmetric-rotor molecules.

To solve Eq. (17) subject to Eq. (16) it is convenient to expand $F^{\gamma\alpha}(\mathbf{k},\,\mathbf{\Omega},\,t)$ in terms of the eigenfunctions $\psi_{\tau,M}^{J}$ of the operators $D_i^{\gamma}(L_i^{\gamma})^2$. (Implicit in this statement is the assumption that when $\alpha\rightarrow\beta$ the symmetry and the orientation of the principal axes of the diffusion tensor are unchanged.) Then

$$F^{\gamma\alpha}(\mathbf{k},\,\mathbf{\Omega},\,t)=\sum_{J,\tau,M}R_{\tau,M}^{\gamma\alpha J}(\mathbf{k},\,t)\psi_{\tau,M}^{J*}(\mathbf{\Omega}_0)\psi_{\tau,M}^{J}(\mathbf{\Omega}), \quad (18)$$

where

$$\Big(\sum_{i=1}^{3}D_i^{\gamma}L_i^{\gamma 2}\Big)\psi_{\tau,M}^{J}(\mathbf{\Omega})=\Lambda_{\tau}^{\gamma J}\psi_{\tau,M}^{J}(\mathbf{\Omega}). \quad (19)$$

From this notation it is obvious that $\Lambda_{\tau}^{\gamma J}$ are the eigenvalues of the operator in Eq. (19). For the general case of the asymmetric top, $\Lambda_{\tau}^{\gamma J}$ and $\psi_{\tau,M}^{J}$ can be found for $J=0$, 1, 2. Fortunately we will only need the result for $J=2$.

Combining Eqs. (17)-(19), multiplying by

$$\psi_{\tau,k'}^{J}(\mathbf{\Omega}_0)\psi_{\tau,k}^{J*}(\mathbf{\Omega}),$$

and integrating over $\mathbf{\Omega}_0$ and $\mathbf{\Omega}$ (taking into account the orthogonality of the eigenstates $\psi_{\tau,k}^{J}$) yields an equation for the coefficients $R_{\tau,M}^{\gamma\alpha J}(\mathbf{k},\,t)$:

$$\partial R_{\tau,M}^{\gamma\alpha J}(\mathbf{k},\,t)/\partial t=-[k^2D_{\gamma}+\Lambda_{\tau}^{\gamma\alpha J}+\lambda_{\gamma}]R_{\tau,M}^{\gamma\alpha J}(\mathbf{k},\,t)$$
$$+\sum_{\beta\neq\gamma}\lambda_{\gamma\beta}R_{\tau,M}^{\gamma\alpha J}(\mathbf{k},\,t). \quad (20)$$

It should be noted that R does not depend on M. These equations must be solved serially subject to the boundary conditions

$$R_{\tau}^{\gamma\alpha J}(\mathbf{k},\,0)=\delta_{\gamma 1}\delta_{\alpha 1}$$

and

$$R_{\tau}^{\gamma\alpha J}(\mathbf{k},\,0)=\delta_{\gamma 2}\delta_{\alpha 2}. \quad (21)$$

TABLE I. The coefficients $A_K^J(\tau)$ for the asymmetric rotor $J=2$.

$K \backslash \tau$	2	1	0	-1	-2
2	$b_1/\sqrt{2}N_1$	$1/\sqrt{2}$	0	0	$-a_1/\sqrt{2}N$
1	0	0	$1/\sqrt{2}$	$1/\sqrt{2}$	0
0	a_1/N_1	0	0	0	b_1/N_1
-1	0	0	$-1/\sqrt{2}$	$1/\sqrt{2}$	0
-2	$b_1/\sqrt{2}N_1$	$-1/\sqrt{2}$	0	0	$-a_1/\sqrt{2}N_1$

where

$$a_{\gamma}=\sqrt{3}(D_x^{\gamma}-D_y^{\gamma})$$
$$b_{\gamma}=[2D_z^{\gamma}-D_x^{\gamma}-D_y^{\gamma}+2\Delta_{\gamma}]$$
$$N_{\gamma}=2\Delta_{\gamma}^{1/2}b_{\gamma}^{1/2}$$
$$\Delta_{\gamma}=[(D_x^{\gamma}-D_y^{\gamma})^2+(D_z^{\gamma}-D_x^{\gamma})(D_z^{\gamma}-D_y^{\gamma})]^{1/2}$$
$$D_S^{\gamma}=\tfrac{1}{3}(D_x^{\gamma}+D_y^{\gamma}+D_z^{\gamma})$$

Substitution of Eqs. (21) into Eq. (18) and use of the closure relation yields Eqs. (16a) and (16b) as is required.

The solutions of Eq. (20) consistent with Eq. (21\` are

$$\tilde{R}_{\tau}^{11J}(\mathbf{k},\,s)=(s+k^2D_2+\Lambda_{\tau}^{2J}+\lambda_2)/\Delta_{\tau}(s),$$
$$\tilde{R}_{\tau}^{21J}(\mathbf{k},\,s)=\lambda_{21}/\Delta_{\tau}(s),$$
$$\tilde{R}_{\tau}^{12J}(\mathbf{k},\,s)=\lambda_{12}/\Delta_{\tau}(s),$$
$$\tilde{R}_{\tau}^{22J}(\mathbf{k},\,s)=(s+k^2D_1+\Lambda_{\tau}^{1J}+\lambda_1)/\Delta_{\tau}(s), \quad (22)$$

where

$$R_{\tau}^{\gamma\alpha J}(\mathbf{k},\,s)=\int_0^{\alpha}dte^{-st}R_{\tau}^{\gamma\alpha J}(\mathbf{k},\,t)$$

is the Laplace transform of $R_{\tau}^{\gamma\alpha J}(\mathbf{k},\,t)$ and

$$\Delta_{\tau}(s)=[s+k^2D_1+\Lambda_{\tau}^{1J}+\lambda_1][s+k^2D_2+\Lambda_{\tau}^{2J}+\lambda_2]-\lambda_1\lambda_2.$$

The solutions $R_{\tau}^{\gamma\alpha}(\mathbf{k},\,t)$ can be found by Laplace inversion of Eq. (22). Actually $\tilde{R}_{\tau}^{\gamma\alpha J}(\mathbf{k},\,s)$ can be used directly to compute the Fourier transform $\bar{R}_{\tau}^{\gamma\alpha J}(\mathbf{k},\,\omega)$ of $R_{\tau}^{\gamma\alpha J}(\mathbf{k},\,t)$ and consequently to compute $\bar{C}(\mathbf{k},\,\omega)$.

The asymmetric rotor functions $\psi_{\tau,M}^{J}(\mathbf{\Omega})$ can be expressed in terms of the symmetric rotor functions

TABLE II. The components $\beta_{n',n}^{\gamma\alpha 2}(\mathbf{k}, s)$ of the rotational correlation function for $J=0, 2$.

$$B_{00}^{\gamma\alpha 2}(\mathbf{k}, s)=[(a^2/N^2)R_2^{\gamma\alpha 2}(\mathbf{k}, s)+(b^2/N^2)R_{-2}^{\gamma\alpha 2}(\mathbf{k}, s)]$$

$$B_{1,\pm 1}^{\gamma\alpha}(\mathbf{k}, s)=\tfrac{1}{2}[R_{-1}^{\gamma\alpha 2}(\mathbf{k}, s)\pm R_0^{\gamma\alpha 2}(\mathbf{k}, s)]$$

$$B_{2,\pm 2}^{\gamma\alpha 2}(\mathbf{k}, s)=[(b^2/2N^2)R_2^{\gamma\alpha 2}(\mathbf{k}, s)\pm\tfrac{1}{2}R_1^{\gamma\alpha 2}(\mathbf{k}, s)+(a^2/2N^2)R_{-2}^{\gamma\alpha 2}(\mathbf{k}, s)]$$

$$B_{2,0}^{\gamma\alpha 2}(\mathbf{k}, s)=(ab/2N^2)[R_2^{\gamma\alpha 2}(\mathbf{k}, s)-R_{-2}^{\gamma\alpha 2}(\mathbf{k}, s)]$$

where $R_\tau^{\gamma\alpha 2}(\mathbf{k}, s)$ appears in Eq. (22) with

$$\Lambda_2^{\gamma 2}=6D_s^\gamma+2\Delta_\gamma \qquad \Lambda_{-2}^{\gamma 2}=6D_s^\gamma-2\Delta_\gamma$$

$$\Lambda_1^{\gamma 2}=3(D_z^\gamma+D_s^\gamma) \qquad \Lambda_{-1}^{\gamma 2}=3(D_y^\gamma+D_s^\gamma)$$

$$\Lambda_0^{\gamma 2}=3(D_y^\gamma+D_s^\gamma).$$

$\varphi_{k,M}^J(\mathbf{\Omega})$ as

$$\psi_{\tau,M}^J(\mathbf{\Omega})=\sum_k A_k^J(\tau)\varphi_{k,M}^J(\mathbf{\Omega}), \tag{23}$$

where the coefficients $A_k^J(\tau)$ are listed in Table I for $J=2$. The symmetric rotor functions $\varphi_{k,M}^J(\mathbf{\Omega})$ can be expressed in terms of the Wigner rotation matrices $D_{M,k}^J(\mathbf{\Omega})$ so that

$$\psi_{\tau,M}^J(\mathbf{\Omega})=\sum_k(-1)^{M-k}A_k^J(\tau)D_{-M,-k}^J(\mathbf{\Omega}). \tag{24}$$

Substitution of Eq. (24) into the Laplace transform of Eq. (18) yields

$$\tilde{F}^{\gamma\alpha}(\mathbf{k}, s)=\sum_{J,M,K,K'}(-1)^{K,K'}B_{K,K'}^{\gamma\alpha J}(\mathbf{k}, s)\times D_{-M,-K'}^{F*}(\mathbf{\Omega}_0)D_{-M-K}^J(\mathbf{\Omega}), \tag{25}$$

where

$$B_{K,K'}^{\gamma\alpha J}(\mathbf{k}, s)=\sum_\tau A_{K'}^J(\tau)A_K^J(\tau)R_\tau^{\gamma\alpha J}(\mathbf{k}, s). \tag{26}$$

Combining Eqs. (12), (13), and (25) and taking into account the orthornormality condition

$$\int d\mathbf{\Omega}D_{K_1,M_1}^{J_1*}(\mathbf{\Omega})D_{K_2,M_2}^{J_2}(\mathbf{\Omega})=\delta_{K_1,K_2}\delta_{M_1,M_2}\delta_{J_1,J_2}, \tag{27}$$

it is a simple but tedious matter to show that

$$\tilde{C}_{\gamma\alpha}(\mathbf{k}, s)=\tfrac{1}{5}\sum_{n,n'=-2}^{+2}(-1)^{n+n'}\alpha_n^\gamma\alpha_{n'}^{\alpha*}B_{n',n}^{\gamma\alpha 2}(\mathbf{k}, s), \tag{28}$$

where the quantities $B_{n',n}^{\gamma\alpha 2}(\mathbf{k}, s)$ are listed in Table II, and the components of the spherical polarizability tensor are listed in Eq. (9). Equation (28) can be rearranged to read

$$\tilde{C}_{\gamma\alpha}(\mathbf{k}, s)=\tfrac{1}{5}\sum_{\tau=-2}^{2}S_\tau^{\gamma\alpha}R_\tau^{\gamma\alpha 2}(\mathbf{k}, s). \tag{29}$$

The coefficients $S_\tau^{\gamma\alpha}$ are the strengths with which the functions $R_\tau^{\gamma\alpha}$ contribute to the spectrum of the depolarized light:

$$S_\tau^{\gamma\alpha}=\sum_{n,n=-2}^{2}(-1)^{n+n'}\alpha_n^\alpha\alpha_{n'}^\gamma A_n^2(\tau)A_{n'}^2(\tau). \tag{30}$$

These values are listed in Table III.

As we have seen in Eq. (3), the scattered-light spectrum is determined by $\tilde{C}(\mathbf{k}, \omega)$, which is related to the Laplace transform $\tilde{C}(\mathbf{k}, s)$ of $C(\mathbf{k}, t)$ through

$$\tilde{C}(\mathbf{k}, \omega)=\mathrm{Re}\tilde{C}(k, s=i\omega); \tag{31}$$

TABLE III. The line strengths $S_\tau^{\gamma\alpha}$.[a]

$$S_2^{\gamma\alpha}=[\alpha_0^\gamma\alpha_0^{\alpha*}(a_1^2/N_1^2)+(\alpha_2^\gamma\alpha_2^{\alpha*}+\alpha_{-2}^\gamma\alpha_{-2}^{\alpha*}-\alpha_2^\gamma\alpha_{-2}^{\alpha*}-\alpha_2^\gamma\alpha_{-2}^{\alpha*}-\alpha_{-2}^\gamma\alpha_2^{\alpha*})(b_1^2/2N_1^2)]$$

$$S_1^{\gamma\alpha}=\tfrac{1}{2}[\alpha_2^\gamma\alpha_2^{\alpha*}+\alpha_{-2}^\gamma\alpha_{-2}^{\alpha*}-\alpha_2^\gamma\alpha_{-2}^{\alpha*}-\alpha_{-2}^\gamma\alpha_2^{\alpha*}]$$

$$S_0^{\gamma\alpha}=\tfrac{1}{2}[\alpha_1^\gamma\alpha_1^{\alpha*}+\alpha_{-1}^\gamma\alpha_{-1}^{\alpha*}-\alpha_1^\gamma\alpha_{-1}^{\alpha*}-\alpha_{-1}^\gamma\alpha_1^{\alpha*}]$$

$$S_{-1}^{\gamma\alpha}=\tfrac{1}{2}[\alpha_1^\gamma\alpha_1^{\alpha*}+\alpha_{-1}^\gamma\alpha_{-1}^{\alpha*}+\alpha_1^\gamma\alpha_{-1}^{\alpha*}+\alpha^\gamma{}_{-1}\alpha_1^{\alpha*}]$$

$$S_{-2}^{\gamma\alpha}=[\alpha_0^\gamma\alpha_0^{\alpha*}(b_1^2/N_1^2)+(\alpha_2^\gamma\alpha_2^\alpha+\alpha_{-2}^\gamma\alpha_{-2}^{\alpha*}-\alpha_2^\gamma\alpha_{-2}^{\alpha*}-\alpha_{-2}^\gamma\alpha_2^{\alpha*})(a_1^2/2N_1^2)]$$

---

[a] α_n^* defined by Eq. (9).

combining Eq. (30), (29), and (6) yields

$$\bar{C}(\mathbf{k},\omega)=\tfrac{1}{5}\sum_{\tau=-2}^{2}\sum_{\alpha,\gamma=1}^{2}c_\alpha S_\tau^{\gamma\alpha}\bar{R}_\tau^{\gamma\alpha2}(\mathbf{k},\omega),\qquad(32)$$

where

$$R_\tau^{\gamma\alpha2}(\mathbf{k},\omega)=\mathrm{Re}\tilde{R}_\tau^{\gamma\alpha2}(\mathbf{k},s).\qquad(33)$$

Thus the line shape is the sum of 20 individual contributions corresponding to the four values $(\gamma\alpha)$ and the five values of τ.

The case where the reaction rates are extremely rapid compared with the translational and rotational diffusion times is especially simple to treat. In this case $\bar{R}_\tau^{\gamma\alpha}(k,\omega)$ has the simple form

$$\bar{R}_\tau^{\gamma\alpha}(k,\omega)=\frac{1}{C}\sum_{\beta=1}^{2}(-1)^{\alpha+\gamma}C_\alpha C_\beta(1-\delta_{\beta\alpha})\,\frac{\lambda}{\omega^2+\lambda^2},\qquad(34)$$

where $C=C_1+C_2$ and $\lambda=\lambda_{12}+\lambda_{21}$. Substitution of Eq. (34) into Eq. (32) leads to

$$\bar{C}(k,\omega)=C^{-1}S[\lambda/(\lambda^2+\omega^2)],\qquad(35)$$

where

$$S=\sum_{\alpha,\beta,\gamma}(-1)^{\alpha+\gamma}C_\alpha C_\beta(1-\delta_{\beta\alpha})\sum_{\tau=-2}^{2}S_\tau^{\gamma\alpha}$$

or

$$S=\sum_{\tau=-2}^{+2}C_1C_2(S_\tau^{11}-S_\tau^{21}+S_\tau^{22}-S_\tau^{12}).$$

A quick look at Table III shows that if the polarizabilities of states 1 and 2 are identical $S=0$ and no scattering is observable.

When the principal axes of the diffusion tensor coincide with the principal axes of the polarizability tensor, we see from Eq. (9) that since $\alpha_{xy}=\alpha_{yz}=\alpha_{xz}=0$ $\alpha_{\pm2}=\frac{1}{2}(\alpha_x-\alpha_y)$, $\alpha_{\pm1}=0$, and $\alpha_0=(2/6^{1/2})[\alpha_z-\frac{1}{2}(\alpha_x+{}_{\alpha z})]$. Substituting these results into Table III yields

$$S_\pm^{\gamma\alpha}=S_0^{\gamma\alpha}=0,$$

$$S_2^{\gamma\alpha}=\alpha_0^\gamma\alpha_0^{\alpha*}(a_1/N_1^2),$$

$$S_{-2}^{\gamma\alpha}=\alpha_0^\gamma\alpha_0^{\alpha*}(b_1/N_1^2).$$

Therefore it follows from Eq. (32) that

$$\bar{C}(\mathbf{k},\omega)=\sum_{\alpha,\gamma}c_\alpha\alpha_0^\gamma\alpha_0^{\alpha*}[(a_1^2/N_1^2)\bar{R}_2^{\gamma\alpha}(\mathbf{k},\omega)+(b_1^2/N_1^2)\bar{R}_{-2}^{\gamma\alpha}(\mathbf{k},\omega)]\qquad(36)$$

with eight contributions to the sum [2 for each of the four possible values of (γ,α)].

The case of molecules with cylindrical symmetry is especially simple. For this system $D_x^\gamma=D_y^\gamma=D^\gamma$, and $\alpha_x=\alpha_y=\alpha$. A quick glance at Table I shows that $a_1/N_1=0$, $b_1/N_1=1$, and consequently

$$\bar{C}(\mathbf{k},\omega)=\sum_{\alpha,\gamma}C_\alpha\alpha_0^\gamma\alpha_0^{\alpha*}R_{-2}^{\gamma\alpha}(\mathbf{k},\omega),\qquad(37)$$

where $\bar{R}_{-2}^{\gamma\alpha}(\mathbf{k},\omega)$ can be found from Eqs. (22), (31), and Table II. This formula gives the correct answer in the limit of no reaction.

IV. DISCUSSION

A theory for the depolarized spectrum of light scattered from dilute solutions of optically anisotropic molecules undergoing unimolecular transitions between two states has been presented. The total depolarized scattering spectrum is given by the weighted sum of 20 non-Lorentzian line shapes. The strengths with which these lines contribute to the spectrum are proportional to the squares of the anisotropic polarizability components. In addition to the translational diffusion coefficients and the components of the diffusion tensors of the molecules in the two different states, the widths of these lines depend on the rate constants $\lambda_{\beta\alpha}$ for the unimolecular rearrangement. When the molecular symmetry is such that the rotational diffusion tensor and the molecular polarizability tensor is simultaneously diagonalized, the depolarized spectrum is given by the weighted sum of eight non-Lorentzian lines. When the molecule is cylindrically symmetric, only four lines remain.

At the present time it would be most interesting to perform experiments on systems in which the rate constants for the unimolecular reactions are very fast compared to the translational and rotational diffusion times. In this case Eq. (34) applies, and the width of the depolarized spectrum should be independent of the scattering angle and equal to the kinetic rate constant, $\lambda(=\lambda_{12}+\lambda_{21})$. It should be emphasized that the optical anisotropy of the molecules in the two different states should be quite different and large for the effect to be experimentally detected, since the reaction rates will spread the intensity over a large frequency range, leaving very low intensity at any given frequency. Furthermore the line strength will be zero if the two states have identical polarizabilities.

In the more general case when the diffusion coefficients are sufficiently large that they must be retained the spectrum becomes extremely complicated because of many contributions. Some of these contributions may be small because their strengths are weak due to the smallness of certain components of the anisotropic polarizability tensor. The most practical case to consider here is that of the cylindrically symmetric molecules. It is interesting to note that even in the event that the polarizabilities and diffusion coefficients are equal for different states of the molecule, the kinetic rate constant contributes to the depolarized spectrum [see Eq. (36)].

It should be noted that in the limit of zero reaction rate all of the formulas in this paper reduce correctly to those reported in Ref. 7.

Finally, we must again note the approximations in the treatment of the depolarized line shapes:

(a) The molecule remains in a state for a certain time and then jumps rapidly to another state. The jump time is assumed rapid compared to diffusion rates (k^2D_i, $D_{ij}{}^{\gamma}$).

(b) Polarizabilities on one molecule are uncorrelated with polarizabilities on other molecules.

(c) The translation and rotational diffusion approximation is valid.

(d) The coupling between translations and rotations can be neglected.

In the event that all of these approximations are valid a study of the depolarized component of Rayleigh scattered light offers in principle a novel method for the study of rapid intramolecular conformation changes in molecules. This method has many advantages, some of which are discussed in the introduction.

APPENDIX A

Let $P_{\gamma\alpha}(\mathbf{r}, \Omega, t)d^3rd^3\Omega$ be the probability of finding a particle in the state γ, in the neighborhood d^3r of the point $\mathbf{r}$ with orientation in the neighborhood $d^3\Omega$ of $\mathbf{\Omega}$ at time t given that it was in the state α, at the point $\mathbf{r}_0$ with orientation $\mathbf{\Omega}_0$ at the initial time $t=0$. The state, orientation, and position of the molecule are assumed to be stationary Markov processes. The probability $P_{\gamma\alpha}(\mathbf{r}, \Omega, t+\Delta t)d^3rd^3\Omega$ can be related to its value at time t through a modification of the Chapman–Kolmogorov equation

$$P_{\gamma\alpha}(\mathbf{r}, \mathbf{\Omega}, t+\Delta t) = \int_v d^3\Delta r \int d^3\theta K_{\gamma\gamma}(\mathbf{\Delta r}, \theta, \Delta t) P_{\gamma\alpha}(\mathbf{r}', \mathbf{\Omega}', t) + \sum_{\beta\neq\gamma} \int_v d^3\Delta r \int d^3\theta K_{\gamma\beta}(\mathbf{\Delta r}, \boldsymbol{\theta}, \Delta t) P_{\beta\alpha}(\mathbf{r}', \mathbf{\Omega}', t). \quad \text{(A1)}$$

The function $K_{\gamma\beta}(\mathbf{\Delta r}, \boldsymbol{\theta}, \Delta t)$ is the probability that a molecule in the state β will make a transition to the state γ and suffer a displacement $\mathbf{\Delta r}$ and a change in orientation $\boldsymbol{\theta}$ in the time interval Δt. The point $\mathbf{r}'$ is such that if a particle suffers a displacement $\mathbf{\Delta r}$ from this point it will be at the point $\mathbf{r}$, i.e., $\mathbf{r}=\mathbf{r}'+\mathbf{\Delta r}$. Likewise for the orientation $\mathbf{\Omega}'$.

The transition probability $K_{\gamma\gamma}(\mathbf{\Delta r}, \boldsymbol{\theta}, \Delta t)$ is assumed to be

$$K_{\gamma\gamma}(\mathbf{\Delta r}, \boldsymbol{\theta}, \Delta t) = [1-\lambda_\gamma\Delta t]K_\gamma(\mathbf{\Delta r}, \theta, \Delta t), \quad \text{(A2)}$$

where λ_γ is the rate at which a molecule leaves the state γ, i.e., $\lambda_\gamma = \sum_{\alpha\neq\gamma}\lambda_{\alpha\gamma}$. Here $(1-\lambda_\gamma\Delta t)$ is the probability that the molecule doesn't make a transition out of the state γ in the time Δt, and $K_\gamma(\mathbf{\Delta r}, \boldsymbol{\theta}, \Delta t)$ is the probability density that a molecule in state γ will suffer a displacement $\mathbf{\Delta r}$, and a change in orientation, θ, in the time Δt. Now assume that

$$K_{\gamma\beta}(\mathbf{\Delta r}, \boldsymbol{\theta}, \Delta t) = \int_0^{\Delta t} d\Delta t_1' \int_V d^3\Delta r' \int d^3\theta' K_{\gamma\gamma}(\mathbf{\Delta r}-\mathbf{\Delta r}', \boldsymbol{\theta}-\boldsymbol{\theta}', \Delta t-\Delta t')\lambda_{\gamma\beta}K_{\beta\beta}(\mathbf{\Delta r}', \boldsymbol{\theta}', \Delta t'), \quad \text{(A3)}$$

where $\lambda_{\gamma\beta}$ is the transition rate from β to γ.

A rotation through the angle $\boldsymbol{\theta}$ can be generated with the finite rotation operator $R(\boldsymbol{\theta}) = \exp(-i\boldsymbol{\theta}\cdot\mathbf{L})$, where $\mathbf{L}$ is the angular momentum operator. Likewise the finite displacement of the center of mass $\mathbf{\Delta r}$ can be generated by the finite displacement operator $\exp(-\mathbf{\Delta r}\cdot\nabla)$. Thus

$$P_{\gamma\alpha}(\mathbf{r}', \mathbf{\Omega}', t) = P_{\gamma\alpha}(\mathbf{r}-\mathbf{\Delta r}, \mathbf{\Omega}-\boldsymbol{\theta}, t) = \exp(-i\boldsymbol{\theta}\cdot\mathbf{L}-\mathbf{\Delta r}\cdot\nabla)P_{\gamma\alpha}(\mathbf{r}, \mathbf{\Omega}, t). \quad \text{(A4)}$$

Substituting Eqs. (A2)–(A4) into Eq. (A1) yields

$$P_{\gamma\alpha}(\mathbf{r}, \mathbf{\Omega}, t+\Delta t) = \int_v d^3\Delta r \int d^3\theta [1-\lambda_\gamma\Delta t]K_\gamma(\mathbf{\Delta r}, \boldsymbol{\theta}, \Delta t) \exp(-i\boldsymbol{\theta}\cdot\mathbf{L}-\mathbf{\Delta r}\cdot\nabla)P_{\gamma\alpha}(\mathbf{r}, \Omega, t)$$
$$+\sum_{\beta\neq\gamma}\int_0^{\Delta t} d\Delta t_1' \int_v d^3\Delta r \int d^3\theta \int_v d^3\Delta r' \int d^3\theta' K_{\gamma\gamma}(\mathbf{\Delta r}-\mathbf{\Delta r}', \boldsymbol{\theta}-\boldsymbol{\theta}', \Delta t-\Delta t')$$
$$\times\lambda_{\gamma\beta}K_{\beta\beta}(\Delta r', \theta', \Delta t') \exp(-i\boldsymbol{\theta}\cdot\mathbf{L}-\mathbf{\Delta r}\cdot\nabla\mathbf{r})P_{\beta\alpha}(\mathbf{r}; \mathbf{\Omega}; t). \quad \text{(A5)}$$

It is now assumed that

(a) $$\int d^3\Delta r \int d^3\theta K_\gamma(\mathbf{\Delta r}, \boldsymbol{\theta}, \Delta t)\mathbf{\Delta r}\mathbf{\Delta r} = \langle\mathbf{\Delta r}\mathbf{\Delta r}\rangle\Delta t = O(\Delta t),$$

(b) $$\int d^3\Delta r \int d^3\theta K_\gamma(\mathbf{\Delta r}, \boldsymbol{\theta}, \Delta t)\boldsymbol{\theta}\boldsymbol{\theta} = \langle\boldsymbol{\theta}\boldsymbol{\theta}\rangle\Delta t = O(\Delta t),$$

(c) All higher moments are $O(\Delta t^2)$,

(d) the coupling between rotations and translations can be ignored,

(e) $$\int d^3\Delta r \int d^3\theta K_\gamma(\mathbf{\Delta r}, \theta, \Delta t)\{\mathbf{\Delta r} \text{ or } \boldsymbol{\theta}\} = 0.$$

Both sides of Eq. (A5) are expanded to order Δt. This is accomplished by expanding the displacement operator to orders $O\{[\mathbf{\Delta r}\cdot(\partial/\partial\mathbf{r})]^2\}$ and $O[(\boldsymbol{\theta}\cdot\mathbf{L})^2]$ taking into account Eqs. (a)–(e). Note that the second term on the right-hand side contributes only $\lambda_{\gamma\beta}P_{\beta\alpha}(\mathbf{r}, \mathbf{\Omega}, t)$, since $K(\mathbf{\Delta r}, \boldsymbol{\theta}, 0) = \delta(\mathbf{\Delta r})\delta(\boldsymbol{\theta})$. Collecting these terms yields

$$\partial P_{\gamma\alpha}(\mathbf{r}, \mathbf{\Omega}, t)/\partial t = \{D_\gamma \nabla_r^2 - L_i D_{ij}^\gamma L_j - \lambda_\gamma\} P_{\gamma\alpha}(\mathbf{r}, \mathbf{\Omega}, t) + \sum_{\beta\neq\gamma} \lambda_{\gamma\beta} P_{\beta\alpha}(\mathbf{r}, \mathbf{\Omega}, t), \tag{A6}$$

where the translational diffusion coefficient of species γ is

$$D_\gamma = \lim_{\Delta t \gg \tau_p} [\langle \Delta r^2(\Delta t)\rangle / 6\Delta t],$$

where τ_p is the momentum correlation time, and the *ij*th element of the rotational diffusion tensor of species γ is

$$D_{ij}^\gamma = \lim_{\Delta t \gg \tau_\Omega} [\langle \theta_i(\Delta t)\theta_j(\Delta t)\rangle / 2\Delta t],$$

where τ_Ω is the angular-momentum correlation time. Equation (A6) can be cast in the form

$$\partial P_{\gamma\alpha}(\mathbf{r}, \mathbf{\Omega}, t)/\partial t = \{D_\gamma \nabla_r^2 - L_i D_{ij}^\gamma L_j\} P_{\gamma\alpha}(\mathbf{r}, \mathbf{\Omega}, t) + \sum_\beta [\lambda_{\gamma\beta} P_{\beta\alpha}(\mathbf{r}, \mathbf{\Omega}, t) - \lambda_{\beta\gamma} P_{\gamma\alpha}(\mathbf{r}, \mathbf{\Omega}, t). \tag{A7}$$

APPENDIX B: THEORY FOR GENERAL SCATTERING ANGLES AND POLARIZATIONS

In the text, the theory was presented only for the most widely used experimental geometry. We present here the general formula to be used in place of Eq. (1) when the wave vector of the scattered light k_f and component of the scattered field whose intensity is to be observed are no longer necessarily in the x–y plane.

The incident wave is propagating in the x–y plane with wave vector $\mathbf{k}_0$ and electric field vector $\mathbf{E}_0$ polarized is parallel to the z axis, and k_f lies in the x–z plane. φ_0 is the angle between the $(\mathbf{k}_f, \mathbf{E}_0)$ plane and $\mathbf{E}_f$. It may then be shown that

$$I(k, \omega) = \frac{k_f^4 |E_0|^2}{16\pi^4 R_0^2 \epsilon^2 V} (2\pi)^{-1} \int_{-\infty}^{+\infty} dt \int_V d^3r \exp[i(\mathbf{k}\cdot\mathbf{r} - \omega t)] \times \int_V d^3r \langle \{\cos\phi_0[\cos\theta_0 \alpha_{xz}^*(\mathbf{r}+\mathbf{r}', t)$$
$$- \sin\theta_0 \alpha_{zz}^*(\mathbf{r}+\mathbf{r}', t)] + \sin\phi_0 \alpha_{yz}^*(\mathbf{r}+\mathbf{r}' t)\} \times \{\cos\phi_0[\cos\theta_0 \alpha_{xz}(\mathbf{r}', 0') - \sin\theta_0 \alpha_{zz}(\mathbf{r}', 0)] + \sin\phi_0 \alpha_{yz}(r', 0)\}\rangle. \tag{B1}$$

Expressions for the $\alpha_{lm}(\mathbf{r}, t)$ occurring in Eq. (B1) may be found by the methods used in the text for $\alpha_{yz}(r, \Omega, t)$. We first write $\alpha_{lm}(r, \Omega, t)$ in terms of molecular polarizabilities,

$$\alpha_{lm}(r, t) = \sum_i \alpha_{lm}^i(t)\delta[\mathbf{r}_i(t) - \mathbf{r}] \tag{B2}$$

and then express these laboratory system molecular polarizability components in terms of the molecule-fixed components and the orientation Ω of the molecule-fixed axes relative to the laboratory axes. By use of the relation

$$\alpha_n^i(\Omega) = (8\pi^2/5)^{1/2} \sum_{n'} \alpha_{n'}^i D_{nn'}^2(\Omega) \tag{B3}$$

and the definition of α_n given in Eq. (9), expressions for all of α_{lm} appearing in Eq. (B1) may be found in terms of the $D_{nn'}^2$ functions and the molecule-fixed polarizabilities.

Equation (B1) reduces to Eq. (1) when θ_0 and φ_0 are set equal to $\pi/2$. If we allow θ_0 to remain $\pi/2$ and set $\varphi_0 = 0$, we obtain the intensity of the component of the scattered field that is parallel to $\mathbf{E}_0$,

$$I(k, \omega) = \frac{k_f^4 |E_0|^2}{16\pi^4 R_0^2 \epsilon^2 V} (2\pi)^{-1} \int_{-\infty}^{+\infty} dt \int_V d^3r \exp[i(\mathbf{k}\cdot\mathbf{r} - \omega t)] \times \int d^3r' \langle \alpha_{zz}^*(r+r' t)\alpha_{zz}(r', 0)\rangle. \tag{B4}$$

It should be noted by inspection of Eqs. (9) and (B3) that $\langle \alpha_{zz}^*(r+r', t)\alpha_{zz}(r', 0)\rangle$ depends on the isotropic polarizability components, α_I, as well as on the anisotropies. This term then contains both the effects considered in previous articles on chemical kinetics and light scattering as well as the effects discussed here. We have used the term "polarized spectrum" (or "polarized component") in the text to mean the part of the spectrum of Eq. (B4) which depends on α_I and not on the optical anisotropies.[4]