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# INFLUENCE OF ELECTRIC REORIENTATION OF MOLECULES ON THE ROTATIONAL BROADENING OF THE SPECTRA OF RAYLEIGH LIGHT SCATTERING BY SMALL MACROMOLECULES IN SOLUTION\*

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## SYNOPSIS

Spectral line broadening of Rayleigh scattered light in the presence of weak molecular reorientation is calculated by Racah algebra using the Debye rotational diffusion approximation. It is shown that if the incident beam is linearly polarized, the polarized and depolarized scattered components are superpositions of the well known Lorentzian, typical for free rotational diffusion, and non-Lorentzian lines with intensities dependent on the reorientation parameters of the permanent and induced electric dipoles of the macromolecules. The measurement of electrically induced changes in peak intensity is proposed as a method for determining the sign of the optical polarizability anisotropy.

## INTRODUCTION

Electric field induced reorientation of molecules in liquids leads to a variety of interesting electro-optical effects [1, 2], in particular, to changes in the intensity of Rayleigh light scattering (RLS) [3], whereas the RLS spectra of infinitely dilute macromolecular solutions provide information on translational and rotational diffusion coefficients [4, 5]. In the simple case of symmetric top macromolecules, measurements of the depolarized component, which is connected only with the anisotropic part of the scattered light, permit the determination of the rotational diffusion coefficient and respective relaxation time  $\tau_2$  of orientational birefringence [6]. We consider RLS in dilute, monodisperse solutions of small, rigid macromolecules (about 100 Å in diameter) having a permanent electric dipole moment  $\mu$  in the direction of their symmetry axis and polarizability tensor elements  $\alpha_{xx} = \alpha_{yy} = \alpha_{\perp}$  and  $\alpha_{zz} = \alpha_{\parallel}$  not equal to zero.

By Racah algebra and in Debye's rotational diffusion approximation for spherical top molecules [7], we calculate the spectral line broadening of linearly

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polarized RLS in infinitely dilute monodisperse macromolecular solutions having weak reorientation, induced by the electric field  $E$  of an intense laser beam [3].

We show that molecular reorientation modifies the RLS line shape causing non-Lorentzian deformation. A numerical analysis of these changes in line shape is performed by us for the case of weak reorientation, for some selected values of the molecular reorientation parameters  $p$  and  $q$ .

### APPROXIMATION OF DEBYE'S ROTATIONAL DIFFUSION

We assume the validity of the approximation of Debye's rotational diffusion of spherical top macromolecules. Then  $f(\Omega_t | \Omega_0; t, E)$ , the conditional probability distribution function for the orientation of an individual macromolecule to be given by the Euler angles  $\Omega_t$  in the moment of time  $t$  under the initial condition  $\Omega_0$  at  $t = 0$ , is given by the well known Debye equation [7, 8]:

$$\frac{1}{D_R} \frac{\partial f}{\partial t} = \nabla_{\Omega}^2 f + \frac{1}{kT} \nabla_{\Omega} (f \nabla_{\Omega} u) \quad (1)$$

where  $\nabla_{\Omega}$  is the angular part of the spatial derivation operator and  $D_R$  is the rotational diffusion coefficient. The potential energy  $u$  of a dipolar macromolecule in an external field  $E_z$ , which causes reorientation, is equal (and accurate up to the square of the electric field strength) to

$$u(\vartheta_t, E) = -\mu P_1(\vartheta_t) E_z(t) - \left[ \frac{1}{2} \alpha P_0(\vartheta_t) + \frac{1}{3} \gamma P_2(\vartheta_t) \right] E_z^2(t) \quad (2)$$

Here,  $\mu$  is the electric dipole moment,  $\alpha = 1/3(2\alpha_{\perp} + \alpha_{\parallel})$  is the mean linear polarizability of the macromolecule,  $\gamma = \alpha_{\parallel} - \alpha_{\perp}$  is the anisotropy of its linear polarizability,  $kT$  is the energy of its thermal motion, and  $P_j(\vartheta_t)$  are Legendre polynomials. The energy now depends on the angle  $\vartheta_t$  only.

When solving eq. (1) we had recourse to the following expansion of the function  $f(\Omega_t | \Omega_0; t, E)$  in a series in the Wigner rotation functions  $D_{mm'}^j(\Omega)$ ,  $|m|, |m'| \leq j$ , [9, 10] and in successive powers  $n$  of the coefficients  $(1/kT)^n$  of statistical perturbation calculus:

$$f(\Omega_t | \Omega_0; t, E) = \sum_{n=0}^{\infty} \sum_{j,m,m'} \frac{1}{(kT)^n} {}^{(n)}f_{mm'}^j(\Omega_0, t, E) D_{mm'}^j(\Omega_t) \quad (3)$$

where the  ${}^{(n)}f_{mm'}^j(\Omega_0, t, E)$  are dynamic coefficients of rotational diffusion, and  $\Omega$  denotes the set of Euler angles. The preceding expansion makes it possible to apply statistical perturbation calculus to the case of weak reorientation of the macromolecules.

### SPECTRA OF RAYLEIGH LIGHT SCATTERING

The spectral line shapes of the polarized and depolarized RLS component, respectively,  $I_{VV}(\Delta\omega)$  and  $I_{VH}(\Delta\omega)$ , are defined by the Fourier transforms of the autocorrelation functions of the linear polarizability tensor elements, expressed in laboratory coordinates, in the following way:

$$I_{VV}(\Delta\omega) \sim F_t \langle a_{zz}(0) a_{zz}^*(t) \rangle$$

$$I_{VH}(\Delta\omega) \sim F_t \langle a_{yz}(0) a_{yz}^*(t) \rangle \quad (4)$$

where  $a_{yz}$  and  $a_{zz}$  are optical polarizability tensor elements.

The averaging procedure to be adopted is defined as follows:

$$\langle \dots \rangle = \int_{\Omega_0} \int_{\Omega_t} d\Omega_0 d\Omega_t \dots f(\Omega_0, E) f(\Omega_t | \Omega_0; t, E) \quad (5)$$

The probability distribution function  $f(\Omega_0, E)$  is to be obtained from the following well known condition [11]:

$$f(\Omega_0, E) = \lim_{t \rightarrow \infty} f(\Omega_t | \Omega_0; t, E) \quad (6)$$

In order to proceed further, we have to rewrite the polarizability tensor components  $a_{zz}$ ,  $a_{yz}$  in the form of irreducible spherical tensors  $a_{mm}^2$ ,  $a_0^0$  and have recourse to the elegant methods of Racah algebra [9, 10]. By inserting the series expansion (3) into eq. (1) and using the orthogonality properties of the Wigner functions, we obtain explicitly the coefficients  ${}^{(n)}f_{mm}^j(\Omega_0, t, E)$  and, in the next step, calculate the autocorrelation functions (4) which describe the RLS spectra. We intend to publish the details of our calculations in a separate paper [12]; here, we shall give directly the final formulas for the general case when the macromolecules undergo reorientation by an electric field which varies in time with the frequency  $\omega_a$ :

$$E_z(t) = \frac{1}{2} \sum_a E_z(\omega_a) \exp(-i\omega_a t) \quad (7)$$

At weak molecular reorientation, we obtain the components of the RLS spectrum with accuracy up to the square of the reorienting field strength in the following form:

$$I_{VV}(\Delta\omega) \sim a^2 \left[ \delta(\Delta\omega) + \frac{4}{5} \kappa^2 L_2(\Delta\omega) \right]$$

$$+ a^2 q \left[ \frac{4}{15} \kappa A(\Delta\omega) + \frac{16}{105} \kappa^2 B(\Delta\omega) \right]$$

$$+ a^2 p^2 \left[ \frac{2}{15} \kappa C(\Delta\omega) + \frac{8}{105} \kappa^2 D(\Delta\omega) \right] + O(E^4) \quad (8)$$

$$I_{VH}(\Delta\omega) \sim \frac{3a^2}{5} \kappa^2 \left[ L_2(\Delta\omega) + \frac{2}{21} q B(\Delta\omega) + \frac{1}{21} p^2 D(\Delta\omega) \right] + O(E^4) \quad (9)$$

Our formulas involve the well known parameters [6] of permanent dipole reorientation  $p = \mu E / kT$  and induced dipole reorientation  $q = (|\gamma| / 2kT) E^2$ , and the dimensionless parameter of optical polarizability anisotropy  $\kappa = (a_{\parallel} - a_{\perp}) / (a_{\parallel} + 2a_{\perp})$ , as well as the following spectral line shape functions:

$$A(\Delta\omega) = \sum_{a,b} R_{20}(\omega_{ab}) [\delta(\Delta\omega) + \delta(\Delta\omega + \omega_{ab})] \quad (10)$$

$$B(\Delta\omega) = \sum_{a,b} \left( R_{20}(\omega_{ab})L_2(\Delta\omega) + \frac{1}{2} R_{22}(\omega_{ab})[L_2(\Delta\omega + \omega_{ab}) - L_2(\Delta\omega)] \right) \quad (11)$$

$$C(\Delta\omega) = \sum_{a,b} R_{10}(\omega_a)R_{20}(\omega_{ab})[\delta(\Delta\omega) + \delta(\Delta\omega + \omega_{ab})] \quad (12)$$

$$D(\Delta\omega) = \sum_{a,b} \left( R_{10}(\omega_a)R_{20}(\omega_{ab})L_2(\Delta\omega) + \frac{7}{5} R_{10}(\omega_a)R_{21}(\omega_b)[L_1(\Delta\omega + \omega_b) - L_2(\Delta\omega)] - \frac{9}{10} R_{10}(\omega_a)R_{23}(\omega_b)[L_3(\Delta\omega + \omega_b) - L_2(\Delta\omega)] - \frac{7}{10} R_{12}(\omega_a)\{R_{22}(\omega_{ab})[L_2(\Delta\omega + \omega_{ab}) - L_2(\Delta\omega)] - R_{21}(\omega_b)[L_1(\Delta\omega + \omega_b) - L_2(\Delta\omega)]\} - \frac{3}{10} R_{32}(\omega_a)\{R_{22}(\omega_{ab})[L_2(\Delta\omega + \omega_{ab}) - L_2(\Delta\omega)] - R_{23}(\omega_b)[L_3(\Delta\omega + \omega_b) - L_2(\Delta\omega)]\} \right) \quad (13)$$

The sums extend over all values of  $a$  and  $b$ , positive as well as negative, with  $\omega_{-a} = -\omega_a$ .

Formulas (10)–(13) contain the following dispersion factors:

$$R_{mm'}(\omega_{ab}) = \left( 1 - \frac{\tau_m}{\tau_{m'}} - i\omega_{ab}\tau_m \right)^{-1} \quad (14)$$

which, for  $m' = 0$ , go over into the well known Debye dispersion factors [1];  $\delta(\Delta\omega)$  is Dirac's delta. On inspection of formulas (10)–(13) one sees that the RLS spectra (eqs. (8) and (9)) additionally exhibit side lines related to the effect of the modulating electric field. The frequencies of the side lines are shifted with respect to the center of the RLS line ( $\Delta\omega = 0$ ) by amounts equal to the frequencies  $\omega_a$ ,  $\omega_b$  of the reorientating field:  $\omega_{ab} = \omega_a \pm \omega_b$ . The intensities of the side lines are dependent on the dispersion factors  $R_{mm}(\omega_{ab})$  and reorientation parameters  $p$ ,  $q$ .

For the case of a reorienting field constant in time,  $\omega_a = \omega_b = 0$  and formulas (8) and (9) reduce to the following simple form:

$$I_{VV}(\Delta\omega) \sim a^2 \left[ \delta(\Delta\omega) + \frac{4}{5} \kappa^2 L_2(\Delta\omega) \right] + a^2 q \left\{ \frac{8}{15} \kappa \delta(\Delta\omega) + \frac{16}{105} \kappa^2 \left[ L_2(\Delta\omega) + \frac{1}{2} L_2'(\Delta\omega) \right] \right\} + a^2 p^2 \left\{ \frac{4}{15} \kappa \delta(\Delta\omega) + \frac{8}{105} \kappa^2 \left[ \frac{63}{40} L_1(\Delta\omega) - \frac{7}{8} L_2(\Delta\omega) + \frac{3}{10} L_3(\Delta\omega) - \frac{1}{4} L_2'(\Delta\omega) \right] \right\} \quad (15)$$

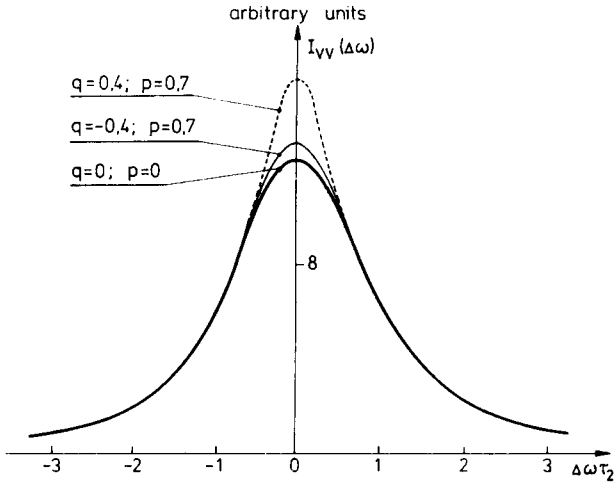


FIG. 1. Spectral line broadening of the polarized RLS component  $I_{VV}(\Delta\omega)$  due to rotational diffusion in the presence of an electrical orienting field, for the parameter values  $q = -0.4$ ,  $p = 0.4$  and  $q = 0.4$ ,  $p = 0.7$ .

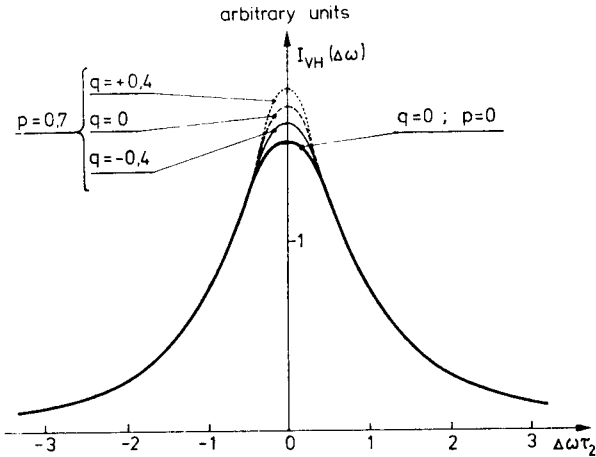


FIG. 2. Spectral line broadening of the depolarized RLS component  $I_{VH}(\Delta\omega)$  due to rotational diffusion in the presence of an electrical orienting field, for the parameter values  $p = 0.7$  and  $q = -0.4, 0, 0.4$ .

$$\begin{aligned}
 I_{VH}(\Delta\omega) \sim & \frac{3a^2}{5} \kappa^2 \left\{ L_2(\Delta\omega) + \frac{2}{21} q \left[ L_2(\Delta\omega) + \frac{1}{2} L_2'(\Delta\omega) \right] \right. \\
 & + \frac{1}{21} p^2 \left[ \frac{63}{40} L_1(\Delta\omega) - \frac{7}{8} L_2(\Delta\omega) \right. \\
 & \left. \left. + \frac{3}{10} L_3(\Delta\omega) - \frac{1}{4} L_2'(\Delta\omega) \right] \right\}
 \end{aligned} \tag{16}$$

One notes that electric molecular reorientation modifies the RLS line shape, which is given by a superposition of well known Lorentzians:

$$L_j(\Delta\omega) = \frac{2\tau_j}{1 + (\Delta\omega\tau_j)^2} \quad (j = 1, 2, 3) \quad (17)$$

and an additional non-Lorentzian factor:

$$L'_j(\Delta\omega) = 2\tau_j \frac{1 - (\Delta\omega\tau_j)^2}{[1 + (\Delta\omega\tau_j)^2]^2} \quad (18)$$

where the  $\tau_j$ 's are molecular relaxation times,

$$\tau_j = \frac{1}{j(j+1)D_R} = \frac{2\tau_D}{j(j+1)} \quad (19)$$

where  $\tau_D = \tau_1$  is the Debye relaxation time. It is worth mentioning that the Dirac deltas  $\delta(\Delta\omega)$  and  $\delta(\Delta\omega + \omega_{ab})$  do not contribute to RLS line broadening.

### CONCLUSIONS

Formulas (15) and (16) make it possible to predict that, for weak reorientation, the RLS spectra will deviate from the Lorentz shape of eq. (17) which was characteristic for "free" rotational diffusion having parameters  $p = q = 0$ . This circumstance can give rise to some experimental difficulties when determining the rotational diffusion contribution from measurements of RLS spectra.

In order to gain an explicit idea of the influence of reorientation on the RLS spectra, we plotted the spectral lines numerically for the following values of the reorientation parameters of dipolar macromolecules:  $p = 0.7$ ,  $q = \pm 0.4$  (Figs. 1 and 2) and those of nondipolar macromolecules:  $p = 0$ ,  $q = \pm 0.4$  (Figs. 3 and 4), for the case of an external d.c. electric field. If the reorienting field is that of a light wave of high frequency, that is, at "optical reorientation," both dipolar

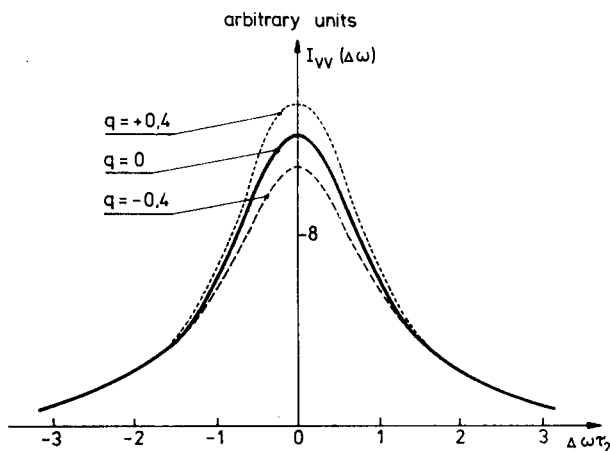


FIG. 3. Spectral line broadening of the polarized RLS component  $I_{VV}(\Delta\omega)$  due to rotational diffusion in the presence of an optical orienting field, for the parameter values  $q = -0.4, 0, 0.4$ .

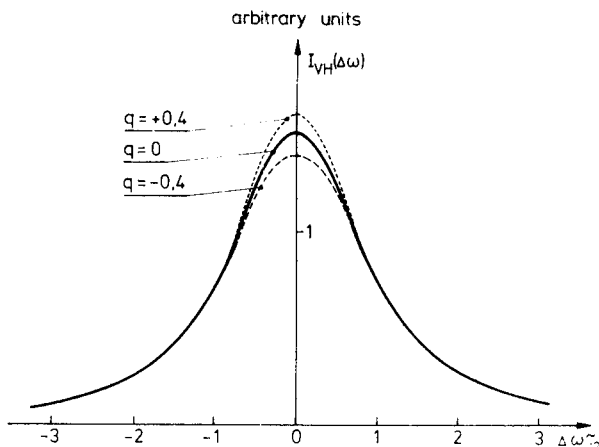


FIG. 4. Spectral line broadening of the depolarized RLS component  $I_{VH}(\Delta\omega)$  due to rotational diffusion in the presence of an optical orienting field, for the parameter values  $q = -0.4, 0, 0.4$ .

and nondipolar macromolecules will yield the spectra depicted in Figures 3 and 4, since the permanent dipoles (owing to the large inertia of the macromolecule) cannot keep pace with the vibration frequency of the light wave.

These curves, plotted from eqs. (15) and (16), show that the influence of reorientation of permanent dipole moments causes a slight increase in intensity of the spectral lines of RLS by macromolecules and that the line intensity at the center ( $\Delta\omega = 0$ ) depends on the sign of the parameter  $q$  of optical reorientation of the electric dipoles induced in the macromolecules; increasing at  $q > 0$  and decreasing at  $q < 0$ . Herein one has a new method for determining the sign of the anisotropy of optical polarizability  $\alpha_{\parallel} - \alpha_{\perp}$  using comparative intensity measurements at the center of the RLS spectrum obtained in the presence and absence of an external d.c. electric field.

It is also worth noting that molecular reorientation, although modifying the shape and intensity at the center of the RLS line, causes only very insignificant modifications of the half-width at half-intensity of the line and thus does not essentially affect the corresponding rotational relaxation times  $\tau_j$ .

One sees from Eqs. (10)–(13) that the case of a.c. field reorientation is much more complicated because the RLS spectra of macromolecules now exhibit additional Lorentzian lines  $L_j(\Delta\omega \pm \omega_{ab})$ ,  $j = 1, 2, 3$ , related to the functions  $A, B, C$ , and  $D$ . Their frequencies are shifted by well defined amounts  $\pm\omega_{ab}$  with respect to the line center  $\Delta\omega = 0$ . Hence, studies of line broadening in the presence of weak reorientation in an a.c. electric field can lead to the discovery of numerous new lines in the so-called RLS wings.

Similar results are obtained in the case of RLS of circularly polarized light as well as multiharmonic light scattering by monodisperse solutions of small macromolecules [12].

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