Influence of molecular reorientational processes on the circular intensity difference scattering by optically active media in dc electric field

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The influence of reorientational processes on circular intensity difference scattering (CIDS) in a static electric field E_0 is analyzed for systems of optically active dipolar molecules with the point group symmetries 3, 4, 6, and ∞ and of optically active nondipolar molecules with the symmetries 32, 422, and 622 for three experimental configurations: (i) at E_0 perpendicular to the plane of scattering; (ii) E_0 parallel to the incident light beam; and (iii) E_0 parallel to the wave scattered in the direction of observation. The effect is described in terms of molecular reorientation functions and is dependent on the experimental field configuration, the electro-optical properties of the molecules, and the field strength E_0. Numerical calculations of molecular reorientation functions are performed for arbitrary degrees of electric saturation. The effects are accessible to observation in solutions of macromolecules by advanced laser and optoelectronic techniques.

I. INTRODUCTION

Rayleigh light scattering by isotropic media has long been applied to study the optical properties of atoms and molecules as well as their interactions.[1-5] The predominant contribution to the Rayleigh intensity comes from electric-dipole scattering related with electric-dipole transitions (polarizability $^e\alpha^e$). However, other scattering processes contribute as well, due to higher-order multipole transitions (both electric and magnetic) as described in terms of the respective multipole polarizabilities.[4]

To achieve a complete description of Rayleigh and Raman optical activity, one has to take into consideration in the vibrations of the electric dipole moment induced in the molecules by the circularly polarized incident optical wave: (i) electric-dipole transitions (polarizability $^e\alpha^e$); (ii) magnetic-dipole transitions (polarizability $^e\alpha^m$); and (iii) electric-quadrupole transitions (polarizability $^e\alpha^{(2)e}$); and moreover—in the vibrations of their magnetic-dipole and electric-quadrupole moments—(iv) electric-dipole transitions with the polarizability $^m\alpha^e$ and respectively (v) with the polarizability $^{e(2)}\alpha^e$. Multipole transitions of higher order can be neglected.

Rayleigh and Raman optical activity, as closely related with molecular structure, is the object of intense theoretical and experimental investigation, both in the absence of external fields[6-17] and in the presence of a static magnetic[18-21] or electric[7,22-24] field.

The molecular theory of circular intensity difference scattering (CIDS) formulated for scattering at right angles to the propagation direction of the incident circularly polarized beam and real wave functions for the multipole transitions[6] has been extended to molecules with a degenerate electronic ground state[3,7,11] and arbitrary angles of scattering observation.[3,11,12] The entire four-by-four Mueller scatter-ing matrix has also been calculated.[17,24] In the absence of external fields, CIDS occurs only in molecular systems with natural optical activity.

The application of a static electric field perpendicularly to the scattering plane (the YZ plane in Fig. 1) causes CIDS to occur in optically inactive molecular systems too. This is due to two fundamental mechanisms: (i) the charge distribution in the molecule is modified by the external field thus affecting its multipole polarizabilities, which can be determined applying quantum-mechanical perturbation calculus;[25] and (ii) the molecules undergo a reorientation by the field, to be calculated by methods statistical mechanics.[2,26]

The present paper deals with the influence exerted on CIDS by molecular reorientations due to an external static electric field of arbitrary strength applied in threefold manner to a system of optically active molecules. The CIDS by reorientation of optically inactive molecules in an electric field has been discussed by one of us (S.W.) in full detail for arbitrarily strong molecular reorientation (from very weak up to the strongest achievable in macromolecular systems) in a separate paper.[27]

II. THE CIDS IN dc ELECTRIC FIELDS

We consider a system of N noninteracting molecules in a volume V in which a light wave, right (+) or left (−) circularly polarized, propagates in the direction of the Z axis of the laboratory coordinate system $\{XYZ\}$ (Fig. 1). The electric dipole $\mathbf{m}^e$, magnetic dipole $\mathbf{m}^m$, and electric quadrupole moment Q induced by the electric field E and magnetic field B of the incident wave in the presence of the external static electric field E_0 can be written in the form[28,29]

$$m_\alpha^e = {}^e\alpha_{\alpha\beta}^e(E_0)E_\beta + {}^e\alpha_{\alpha\beta}^m(E_0)B_\beta$$
$$+ \tfrac{1}{3}{}^e\alpha_{\alpha\beta\gamma}^{(2)e}(E_0)\nabla_\beta E_\gamma + \cdots , \tag{1}$$

$$m_\alpha^m = {}^m\alpha_{\alpha\beta}^e(E_0)E_\beta + \cdots , \tag{2}$$

$$Q_{\alpha\beta} = {}^{e(2)}\alpha_{\alpha\beta\gamma}^e(E_0)E_\gamma + \cdots . \tag{3}$$

Other higher multipole moments and higher multipolar transitions can be neglected. On denoting the CIDS by

$$^cI^D = I_z^+\left(\frac{\pi}{2}\right) - I_z^-\left(\frac{\pi}{2}\right). \tag{4}$$

where $I_z^\pm$ $(\pi/2)$ is the light intensity scattered at the angle $\theta = \pi/2$ (with respect to the propagation direction of the incident beam) linearly polarized with electric field along the Z axis, at incident light right (+) or left (−) circularly polarized, we have[7-11]

$$^cI^D = 2KE^2\langle \mathrm{Im}\left[\,^c\alpha_{zy}^e(\mathbf{E}_0)\,^c\alpha_{zx}^{e*}(\mathbf{E}_0) - \,^c\alpha_{zx}^e(\mathbf{E}_0)\,^c\alpha_{zy}^{m*}(\mathbf{E}_0) + \,^c\alpha_{zy}^e(\mathbf{E}_0)\,^c\alpha_{zy}^{m*}(\mathbf{E}_0) + \,^c\alpha_{zy}^e(\mathbf{E}_0)\,^m\alpha_{xx}^{e*}(\mathbf{E}_0) \right.$$
$$- \,^c\alpha_{zx}^e(\mathbf{E}_0)\,^m\alpha_{xy}^{e*}(\mathbf{E}_0)\,] + \frac{\omega}{3}\,\mathrm{Re}\left[\,^c\alpha_{zx}^e(\mathbf{E}_0)\,^c\alpha_{zzy}^{(2)e*}(\mathbf{E}_0) - \,^c\alpha_{zy}^e(\mathbf{E}_0)\,^c\alpha_{zzx}^{(2)e*}(\mathbf{E}_0) \right.$$
$$\left.\left. - \,^c\alpha_{zx}^e(\mathbf{E}_0)\,^{e(2)}\alpha_{yyz}^{e*}(\mathbf{E}_0) + \,^c\alpha_{zy}^e(\mathbf{E}_0)\,^{e(2)}\alpha_{xyz}^{e*}(\mathbf{E}_0)\,\right]\right\rangle_{E_0}, \tag{5}$$

where E is the amplitude of the electric field of the incident light wave with frequency ω; $\langle\cdots\rangle_E$ stands for statistical averaging in the presence of the field $\mathbf{E}_0$; moreover, $K = \rho\omega^4(32\pi^2\epsilon_0 cR^2)^{-1}$ with R the distance from the scattering center; and $\rho = N/V$.

Applying quantum-mechanical stationary perturbation calculus, the multipole polarizability tensors of Eq. (5) take the form

$$T(\mathbf{E}_0) = T(0) + T_{i}\cdot\mathbf{E}_0 + \cdots, \tag{6}$$

where T stands for $^c\alpha^e$, $^c\alpha^m$, $^m\alpha^e$, $^c\alpha^{(2)e}$, or $^{e(2)}\alpha^e$.

In what follows, we shall be considering systems of molecules with a nondegenerate electronic ground state, i.e., molecules for which the wave functions can be real. The polarizabilities of interest to us describing the respective multipolar transitions can be expressed in the following form:[30]

$$^c\alpha_{\alpha\beta}^e = \,^e\beta_{\alpha\beta}^e + i^e\eta_{\alpha\beta}^e = \,^e\beta_{\beta\alpha}^e + i^e\eta_{\beta\alpha}^e. \tag{7}$$

$$^c\alpha_{\alpha\beta}^m = i(\,^e\gamma_{\alpha\beta}^m + i^e\vartheta_{\alpha\beta}^m), \tag{8}$$

$$^m\alpha_{\alpha\beta}^e = i(\,^m\gamma_{\alpha\beta}^e + i^m\vartheta_{\alpha\beta}^e) = -i(\,^c\gamma_{\beta\alpha}^m + i^e\vartheta_{\beta\alpha}^m), \tag{9}$$

$$^e\alpha_{\alpha\beta\gamma}^{(2)e} = \,^e\beta_{\alpha\beta\gamma}^e + i^e\eta_{\alpha\beta\gamma}^e = \,^e\beta_{\alpha\gamma\beta}^e + i^e\eta_{\alpha\gamma\beta}^e, \tag{10}$$

$$^{e(2)}\alpha_{\alpha\beta\gamma}^e = \,^e\beta_{\gamma\alpha\beta}^e + i^e\eta_{\gamma\alpha\beta}^e, \tag{11}$$

where all the tensor components β, γ, η, and ϑ of Eqs. (7)–(11) are real and symmetric with respect to time inversion (i tensors); the tensors η and ϑ are related with absorption. The quantum-mechanical forms of the tensors (7)–(11) are to be found in Ref. 30.

On restricting ourselves in Eq. (5) to the first term of expansion (6) (since we are interested here in the influence of reorientational processes only—the second term, related with modifications in the charge distribution of the molecule in the field $\mathbf{E}_0$ in the presence of molecular reorientation will be dealt with in a separate paper) and on neglecting absorption, we obtain

$$^cI^D = 2KE^2\left[\,\langle\,^e\beta_{zy}^e(\,^e\gamma_{xx}^m - \,^e\gamma_{zy}^m) - \,^e\beta_{zx}^e(\,^e\gamma_{zx}^m + \,^e\gamma_{yx}^m)\rangle_{E_0}\right.$$
$$+ \frac{\omega}{3}\,\langle\,^e\beta_{zx}^e(\,^e\beta_{zzy}^e - \,^e\beta_{yyz}^e)$$
$$\left. + \,^e\beta_{zy}^e(\,^e\beta_{xyz}^e - \,^e\beta_{zzx}^e)\rangle_{E_0}\right]. \tag{12}$$

For molecules of very low symmetry for which the tensor of linear electric polarizability ($\omega = 0$) possesses three different components $^e\beta_{11}^e(0) \neq \,^e\beta_{22}^e(0) \neq \,^e\beta_{33}^e(0)$ (symmetries of the point groups 1, $\bar{1}$, 2, m, $2/m$, 222, $mm2$, and mmm), the averaging procedure (12) leads to results of a high degree of complication. Accordingly here, we shall consider molecules for which the tensor components $^e\beta_{\alpha\beta}^e(0)$ fulfill the relation $^e\beta_{11}^e(0) = \,^e\beta_{22}^e(0) \neq \,^e\beta_{33}^e(0)$ (the subscripts 1, 2, and 3 refer to the molecular system of coordinates). This is the case for optically inactive molecules with the point group symmetries $\bar{3}$, $3m$, $\bar{3}m$, $\bar{4}$, $4/m$, $4mm$, $\bar{4}2m$, $4/mmm$, $\bar{6}$, $6/m$, $6mm$, $\bar{6}m2$, $6/mmm$, ∞m, ∞/m, and ∞/mmm for which the influence of reorientation in a static electric field on CIDS has been analyzed by one of us (S.W.) in detail;[27] this too is the case for the optically active molecules of interest to us here (point group symmetries 3, 4, 6, ∞, 32, 422, and 622) among which those belonging to the point groups 3, 4, 6, and ∞ possess a nonzero permanent electric dipole moment μ (directed along the 3 axis of molecular coordinates), whereas the others (point groups 32, 422, and 622) are nondipolar.
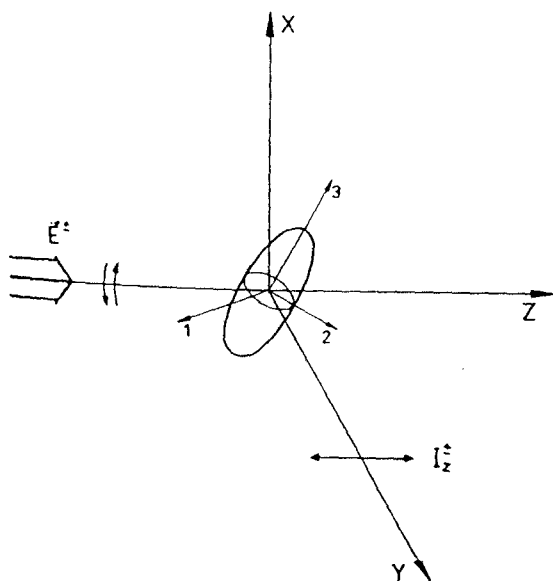

FIG. 1. Scattering configuration discussed in the present paper.

In the case of dipolar molecules of the point groups 3, 4, 6, and ∞, the distribution function to be applied in the averaging procedure (12) is of the form[2,31]

$$f(\vartheta, E_0) = \frac{\exp(p\cos\vartheta \pm q\cos^2\vartheta)}{4\pi\int_0^\pi \exp(p\cos\vartheta \pm q\cos^2\vartheta)\sin\vartheta\,d\vartheta}, \quad (13)$$

where we have introduced the dimensionless parameter of reorientation of the electric dipole and the dimensionless parameter of reorientation of the polarizability ellipsoid

$$p = \frac{\mu E_0}{kT}, \quad (14)$$

$$q = \frac{|\delta(0)|}{2kT}E_0^2, \quad (15)$$

with $\delta(0) = {}^e\beta_{33}^e(0) - {}^e\beta_{11}^e(0)$— the anisotropy of polarizability of ${}^e\beta^e(0)$. The signs " + " and " − " correspond, respectively, to molecules with positive and negative anisotropy $\delta(0)$, whereas ϑ is the angle subtended by the field $\mathbf{E}_0$ and the 3 axis of molecular coordinates (the symmetry axis of the molecule). The distribution function (13) being independent of the other two Euler angles φ and ψ ($0\leqslant\varphi\leqslant2\pi$, $0\leqslant\psi\leqslant2\pi$, $0\leqslant\vartheta\leqslant\pi$), when going over with the multipole polarizability tensor components (12) to molecular coordinates, the averaging over these two angles reduces to isotropic averaging[2,26]

$$\langle\cos^n\varphi\rangle = \langle\cos^n\psi\rangle$$
$$= \langle\sin^n\varphi\rangle = \langle\sin^n\psi\rangle$$
$$= \begin{cases} \dfrac{(2t-1)!!}{2^t t!}, & \text{for } n = 2t \\ 0, & \text{for } n = 2t+1. \end{cases}$$

For nondipolar molecules (point group 32, 422, and 622), averaging Eq. (12) is carried out with a distribution function of the form (13) with $p = 0$.

III. THE CIDS FOR SPECIFIC CONFIGURATIONS OF dc ELECTRIC FIELDS

A. The CIDS in dc electric field $\mathbf{E}_0$ perpendicular to the scattering plane

We assume the system of anisotropic molecules to be acted by a dc, electric field $\mathbf{E}_0 = \mathbf{e}_x E_0$ parallel to the X axis of the laboratory coordinates $\{XYZ\}$ (Fig. 1). The orientation of the molecular coordinates $\{1,2,3\}$ with respect to the coordinates $\{XYZ\}$ is given by the Euler angles φ, ψ, ϑ, where ϑ is the angle between $\mathbf{E}_0$ and the symmetry 3 axis of the molecule. We now transform the multipole polarizability tensor components of Eq. (12) from the laboratory set of coordinates into molecular coordinates and then perform the averaging with the distribution function (13).

1. Optically active dipolar molecules

As a result of these calculations, we obtain for dipolar molecules exhibiting symmetry of the point groups 3, 4, 6, or ∞

$$^cI^D = {}^cI_0^D[1 - R_1(p, \pm q)] + I_1 S_1(p, \pm q), \quad (16)$$

where

$$^cI_0^D = -\frac{4}{15}KE^2({}^e\beta_{33}^e - {}^e\beta_{11}^e)$$
$$\times\left({}^e\gamma_{33}^m - {}^e\gamma_{11}^m + \frac{\omega}{3}{}^e\beta_{123}^e\right) \quad (17)$$

gives the CIDS at zero external field

$$I_1 = -KE^2({}^e\beta_{33}^e - {}^e\beta_{11}^e)\left({}^e\gamma_{21}^m + \frac{\omega}{e}{}^e\beta_{113}^e\right), \quad (18)$$

whereas the molecular reorientational functions[32]

$$R_1(p, \pm q) = \frac{1}{16}[45L_4(p, \pm q) - 30L_2(p, \pm q) + 1] \quad (19)$$

and[33]

$$S_1(p, \pm q) = L_1(p, \pm q) - L_3(p, \pm q) \quad (20)$$

are given, respectively, by the even and odd generalized Langevin functions[31]

$$L_n(p, \pm q) = \frac{\int_0^\pi \cos^n\vartheta\,\exp(p\cos\vartheta \pm q\cos^2\vartheta)\sin\vartheta\,d\vartheta}{\int_0^\pi \exp(p\cos\vartheta \pm q\cos^2\vartheta)\sin\vartheta\,d\vartheta}. \quad (21)$$

Hence, a field $\mathbf{E}_0$ applied perpendicularly to the scattering YZ plane, in addition to modifying the value of the CIDS [the first term of Eq. (16)], leads to a dependence on the components ${}^e\gamma_{21}^m$ and ${}^e\beta_{113}^e$ of the magnetic-dipole and electric-quadrupole polarizability tensors by comparison with the effect in the absence of $\mathbf{E}_0$.

The function $R_1(p, \pm q)$ has the following properties: $R_1(0,0) = 0$; $R_1(\infty, \infty) = 1$; and $R_1(\infty, -\infty) = 1/16$.

For weak molecular reorientation ($p\ll1$, $q\ll1$), the functions $L_2(p, \pm q)$ and $L_4(p, \pm q)$ can be written as follows:[31]

$$L_2(p, \pm q) = \frac{1}{3} + \frac{2p^2}{45} \pm \frac{4q}{45} + \cdots, \quad (22)$$

$$L_4(p, \pm q) = \frac{1}{5} + \frac{4p^2}{105} \pm \frac{8q}{105} + \cdots, \quad (23)$$

so that

$$R_1(p, \pm q) = \frac{1}{42}\left[\left(\frac{\mu}{kT}\right)^2 + \frac{\delta(0)}{kT}\right]E_0^2. \quad (24)$$

Thus, for weak reorientation of molecules with positive anisotropy $\delta(0)$, we have $R_1(p, +q) > 0$, whereas for $\delta(0) < 0$, we may have $R_1(p, -q) > 0$ or $R_1(p, -q) < 0$ depending on the mutual relation between the value of the reorientation parameters p and q, i.e., depending on the parameter $a = q/p^2$. If $a < 1/2$, we have $R_1(p, -q) > 0$, whereas if $a > 1/2$, we have $R_1(p, -q) < 0$ (see the portions of the curves for small value of p, thus for $a = 1/9$ and $a = 1$ in Fig. 3). This permits the statement that at weak reorientation of optically active dipolar molecules, the reorienting action of the field $\mathbf{E}_0$ described by the function $R_1(p, \pm q)$ can enhance the CIDS [if the molecules possess anisotropy $\delta(0) < 0$ fulfilling the condition $|\delta(0)| > \mu^2/kT$] or can cause a diminishing of the CIDS [for molecules with $\delta(0) < 0$ at $|\delta(0)| < \mu^2/kT$ and for molecules with $\delta(0) \geqslant 0$], the variation being directly proportional to E_0^2 in either case.

Calculations for arbitrarily strong reorientation in a field $\mathbf{E}_0$ show that for dipolar molecules with $\delta(0) \geqslant 0$, the

FIG. 2. The molecular reorientation function $R_1(p, +q)$ for molecules with positive anisotropy $\delta(0)$; $a = q/p^2 = \delta(0)kT/2\mu^2$.
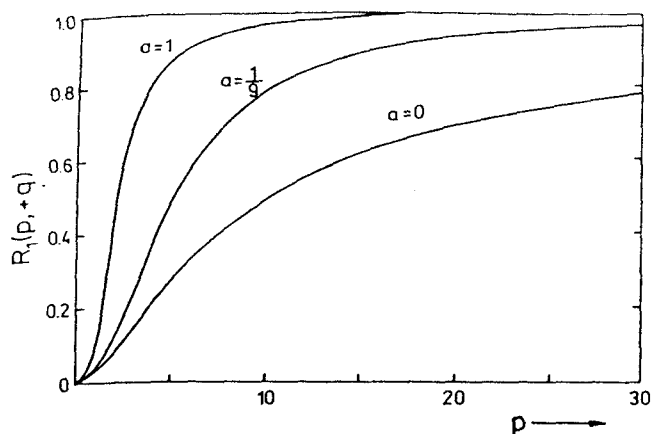

FIG. 4. The molecular reorientation fucntion $S_1(p, +q)$ for molecules with positive anisotropy $\delta(0)$; $a = q/p^2 = \delta(0)kT/2\mu^2$.

reorientation described by the function $R_1(p, +q)$ always diminishes the CIDS [$R_1(p, +q) > 0$] down to zero at electric saturation, at which $R_1(\infty, \infty) = 1$ (Fig. 2). In the case of molecules with $\delta(0) < 0$, the effect of the field can be positive or negative according to the parameters p and a (i.e., p and q) and moreover can undergo a change in sign (at a fixed value of the parameter a) with increasing field strength E_0 (Fig. 3) [in Figs. 2, 3, and 5–8, an increase in p—for a given molecular system at constant temperature—corresponds to an increase in the field strength E_0; $a = q/p^2 = |\delta(0)|kT/2\mu^2$]. At electric saturation of a system of molecules with $\delta(0) < 0$, we have $R_1(\infty, -\infty) = \frac{1}{16}$; thus, the term of Eq. (16) does not vanish at complete reorientational ordering of the system.

For optically active dipolar molecules, the reorienting effect of the field E_0 on the CIDS is described [in addition to the function $R_1(p, \pm q)$ considered above] by the function $S_1(p, \pm q)$ [the second term of Eq. (16)]. The properties of

the function $S_1(p, \pm q)$ are these: $S_1(0,0) = S_1(\infty,0) = S_1(\infty, \pm\infty) = 0$ and $S_1(\pm q) \equiv S_1(0, \pm q) = 0$. For strongly dipolar molecules with low anisotropy $\delta(0)$ $(p \gg q)$ we have[34]

$$L_n(p) = \sum_{k=0}^{n} \frac{n!}{(n-k)!}$$
$$\times \frac{(-1)^k \exp(p) - (-1)^n \exp(-p)}{p^k[\exp(p) - \exp(-p)]}. \quad (25)$$

At weak reorientation ($p < 1$), this gives

$$S_1(p) \simeq \frac{2}{15} p = \frac{2}{15} \frac{\mu E_0}{kT}. \quad (26)$$

Since at small values of p the function $S_1(p, \pm q)$ is practically independent of q [in fact $S_1(p, \pm q) \simeq S_1(p,0)$ for $p \ll 1$ (see Figs. 4 and 5)], we get by Eqs. (16), (24), and (26) for weak reorientation of optically active dipolar molecules

$$^cI^D = {}^cI_0^D + \frac{2\mu}{15kT} I_1 E_0$$
$$- \frac{1}{42}\left[\left(\frac{\mu}{kT}\right)^2 + \frac{\delta(0)}{kT}\right] {}^cI_0^D E_0^2 + \cdots. \quad (27)$$

With growing E_0 (with growing p, Figs. 4 and 5), $S_1(p, \pm q)$ diverges from linearity in E_0. Depending on the sign of $\delta(0)$ and the relation between the magnitudes of p and q (as expressed by the parameter a in Figs. 4 and 5), the function $S_1(p, \pm q)$ tends to zero more steeply (for greater a) or less steeply (for smaller a) with increasing field strength E_0.

Taking into consideration the molecular reorientations described by the functions $R_1(p, \pm q)$ and $S_1(p, \pm q)$, we have under condition of electric saturation ($p \to \infty$, $q \to \infty$): for the molecules with anisotropy $\delta(0) > 0$

$$^cI^D \underset{\substack{p \to \infty \\ q \to \infty}}{\longrightarrow} 0, \quad (28)$$

whereas for ones with $\delta(0) < 0$

$$^cI^D \underset{\substack{p \to \infty \\ q \to \infty}}{\longrightarrow} \frac{15}{16} {}^cI_0^D. \quad (29)$$
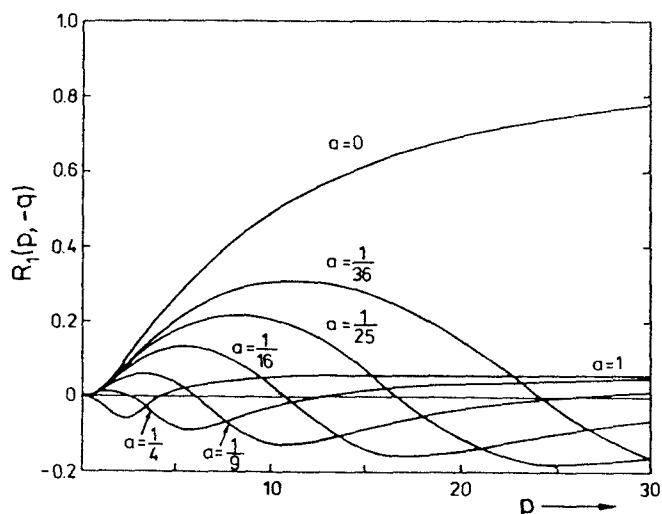

FIG. 3. The molecular reorientation function $R_1(p, -q)$ for molecules with negative anisotropy $\delta(0)$; $a = q/p^2 = |\delta(0)|kT/2\mu^2$.
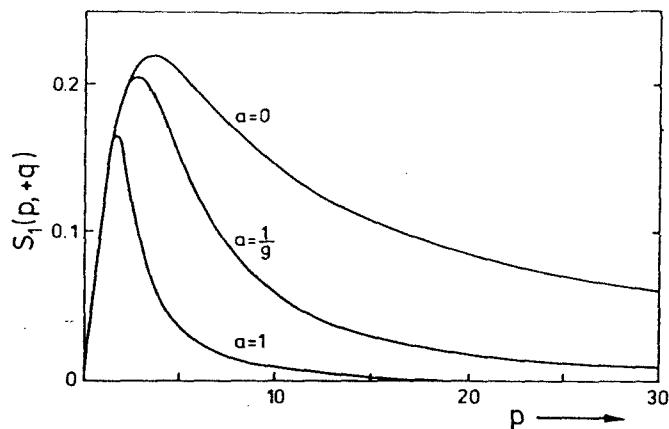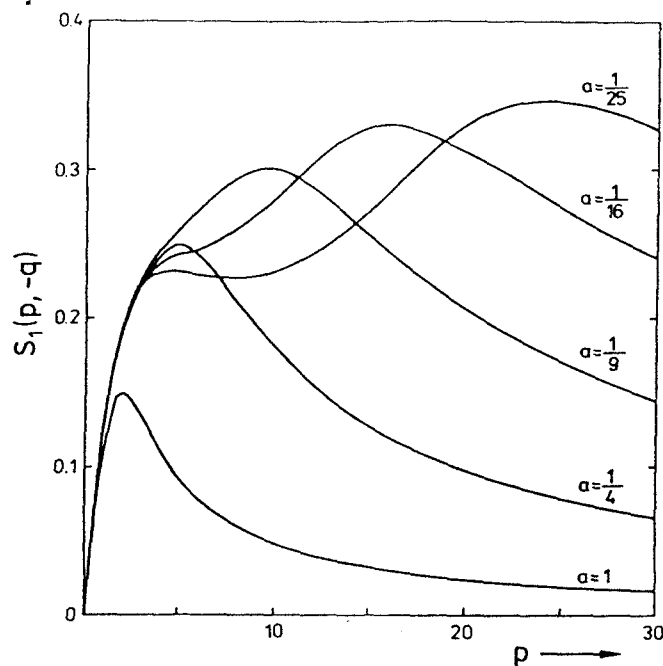
FIG. 5. The molecular reorientation function $S_1(p, -q)$ for molecules with negative anisotropy $\delta(0)$; $a = q/p^2 = |\delta(0)|kT/2\mu^2$.

FIG. 6. The molecular reorientation function $R_1(\pm q)$ and $R_2(\pm q)$ for molecules with positive (+) and negative (−) anisotropy $\delta(0)$.

The functions $R_1(p, \pm q)$ and $S_1(p, \pm q)$ intervene (among others) in the effect of magnetochiral birefringence in a static electric field applied perpendicularly to the magnetic field.[35,36] Moreover, $S_1(p) \equiv S_1(p,0)$ describes generation of the second harmonic of light in systems of dipolar molecules in a static electric field.[33]

2. Optically active nondipolar molecules

In the case of the optically active nondipolar molecules considered in this paper (point groups 32, 422, and 622), the reorientating effect of $\mathbf{E}_0$ on the CIDS obtained on averaging Eq. (12) with the distribution function (13) at $p = 0$ has the form

$$^C I^D = {}^C I_0^D [1 - R_1(\pm q)],\qquad(30)$$

where $R_1(\pm q) \equiv R_1(p = 0, \pm q)$ is the reorientation function (19) with $p = 0$. Thus, a field $\mathbf{E}_0$ applied perpendicularly to the scattering plane causes a change in magnitude of the CIDS by molecules of the point group symmetries 32, 422, and 622, though the effect is still dependent on the same magnetic-dipole and electric-quadrupole polarizability components as in the absence of $\mathbf{E}_0$. The influence of $\mathbf{E}_0$ reorienting the molecules as described by the function $R_1(\pm q)$ leads to the following effects:

(i) it lowers the CIDS—at arbitrary values of q in the case of molecules with $\delta(0) > 0$ and at $q > 12,5$ in that of ones with $\delta(0) < 0$, albeit in the latter case the variations are rather small (see Fig. 6), and

(ii) it enhances the CIDS at $q < 12,5$ in the case of molecules with anisotropy $\delta(0) < 0$.

In particular, at $q \ll 1$, the variations are proportional to the square of E_0 both for molecules with positive and negative anisotropy $\delta(0)$,
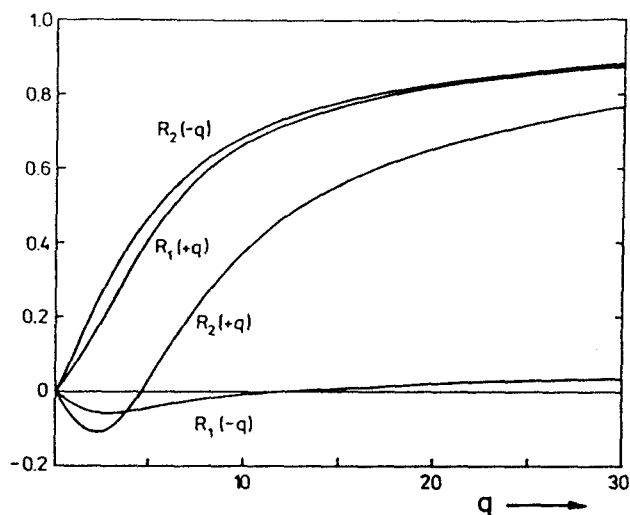
$$\Delta^C I^D = {}^C I^D - {}^C I_0^D = -\frac{\delta(0)}{42kT} {}^C I_0^D E_0^2 + \cdots,\qquad(31)$$

whereas for $q \to \infty$, we get relations similar to Eqs. (28) and (29):

$$^C I^D \underset{q \to \infty}{\to} 0, \quad \text{for } \delta(0) > 0,\qquad(32)$$

$$^C I^D \underset{q \to \infty}{\to} \frac{15}{16} {}^C I_0^D, \quad \text{for } \delta(0) < 0.\qquad(33)$$

Figure 6 shows graphs of $R_1(\pm q)$ in a wide range of the parameter q (i.e., in a wide range of E_0). $R_1(\pm q)$ is moreover one of the several functions governing the changes in Rayleigh[32] and Raman[37] light scattering and magneto-chiral birefringence[36,38] due to the reorientation of molecules under the influence of laser light.

The CIDS by systems of optically inactive molecules at the configuration analyzed in Sec. III A has been discussed in full detail in Ref. 27.

B. The CIDS in dc electric field E_0 parallel to the incident light beam

We now proceed to consider the situation when a system of optically active anisotropic molecules is acted on by a static electric field $\mathbf{E}_0 = \mathbf{e}_z E_0$ directed along the Z axis of laboratory coordinates $\{XYZ\}$ (see Fig. 1). As previously, the orientation of the molecular coordinate system $\{1,2,3\}$ with respect to the laboratory coordinate system is described in terms of Euler angles on the assumption that ϑ is the angle between $\mathbf{E}_0$ and the 3 axis (the symmetry axis of the molecule).

1. Optically active dipolar molecules

Averaging in Eq. (12) with the distribution function (13) for a system of the optically active molecules of interest here (ones with the point group symmetries 3, 4, 6, and ∞) leads to

$$^{C}I^{D} = {^{C}I_0^{D}}[1 - R_2(p, \pm q)], \tag{34}$$

where $^{C}I_0^{D}$ is given by Eq. (17), whereas the molecular reorientation function $R_2(p, \pm q)$ is of the form[32]

$$R_2(p, \pm q) = \tfrac{1}{2}\{15L_4(p, \pm q) - 15L_2(p, \pm q) + 2\}. \tag{35}$$

At weak reorientation due to E_0 ($p \ll 1$, $q \ll 1$), we have

$$R_2(p, \pm q) = -\frac{1}{25}\left[\left(\frac{\mu}{kT}\right)^2 + \frac{\delta(0)}{kT}\right]E_0^2 + \cdots, \tag{36}$$

signifying that here for molecules with $\delta(0) > 0$, we get

$$\frac{\Delta^{C}I^{D}}{^{C}I_0^{D}} = \frac{^{C}I^{D} - {^{C}I_0^{D}}}{^{C}I_0^{D}} > 0, \tag{37a}$$

whereas for ones with anisotropy $\delta(0) < 0$, we have

$$\frac{\Delta^{C}I^{D}}{^{C}I_0^{D}} > 0, \quad \text{if } |\delta(0)| < \frac{\mu^2}{kT}, \tag{37b}$$

$$\frac{\Delta^{C}I^{D}}{^{C}I_0^{D}} < 0, \quad \text{if } |\delta(0)| > \frac{\mu^2}{kT}. \tag{37c}$$

Figures 7 and 8 show the reorientation function $R_2(p, \pm q)$ vs p for different values of $a = q/p^2$. For molecules with positive anisotropy $\delta(0)$, an increase in CIDS occurs for $0 < p < p_0$, where p_0 is the value for p for which $R_2(p, +q) = 0$, whereas for $p > p_0$ we have $R_2(p > p_0, + q) > 0$ and the CIDS decreases with growing p and tends to zero as $p \to \infty$. At some value $p = p_m$ from the interval $(0, p_0)$ the CIDS attains its maximal value $^{C}I_m^{D}$. For molecules with $\delta(0) > 0$, we have $(^{C}I_m^{D} - {^{C}I_0^{D}})/^{C}I_0^{D} < 0.2$. The value of p_0, that of maximum $^{C}I_m^{D}$, as well as the rate at which $^{C}I^{D}$ tends to zero with growing p for $p > p_0$ are dependent on the value of the parameter $a = \delta(0)kT/2\mu^2$. The greater the parameter a, the smaller are p_0 and $^{C}I_m^{D}$ and the effect tends more steeply to zero at $p > p_0$. Similar behavior is observed for molecules with $\delta(0) < 0$ at $a < 1/2$; here the
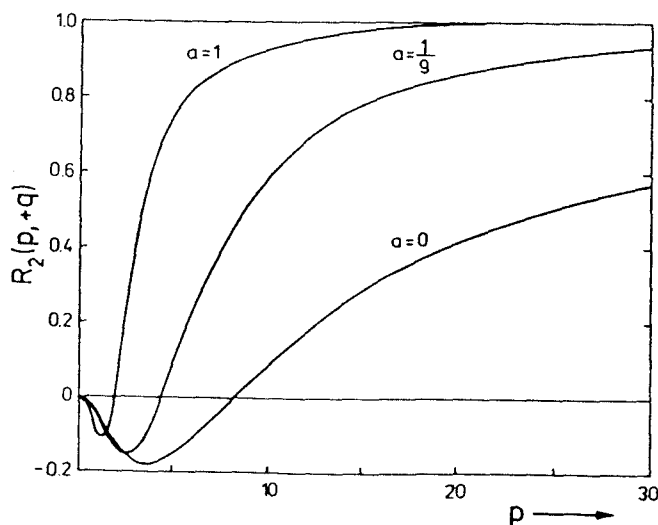
effect due to molecular reorientation in the field E_0 can be enhanced by as much as 50% (for small values of the parameter a, see Fig. 8), whereas for $a > 1/2$ the CIDS decreases monotonically with growing p. For the case of reorientation saturation ($p \to \infty$, $q \to \infty$),

$$\underset{\substack{p \to \infty \\ q \to \infty}}{^{C}I^{D}} \to 0 \tag{38}$$

for molecules with positive as well as negative anisotropy $\delta(0)$.

It is worth mentioning that $R_2(p, \pm q)$ is among the reorientational functions describing the changes in magnetochiral birefringence and magnetochiral dichroism in a field E_0 parallel to the static magnetic field[36,39] as well as the changes in Rayleigh scattered light intensity from macromolecular systems in a static electric field.[32]

2. Optically active nondipolar molecules

In this (the molecules are assumed to be of the point group 32, 422, or 622) the reorienting effect of E_0 on the CIDS is given by the expression

$$^{C}I^{D} = {^{C}I_0^{D}}[1 - R_2(\pm q)], \tag{39}$$

where $^{C}I_0^{D}$ is given by Eq. (17) and $R_2(\pm q) \equiv R_2(p = 0, \pm q)$. At weak molecular reorientation ($q \ll 1$)

$$R_2(\pm q) = -\frac{\delta(0)}{25kT}E_0^2 + \cdots, \tag{40}$$

and at $\delta(0) > 0$, we have $\Delta^{C}I^{D}/^{C}I_0^{D} > 0$, whereas at $\delta(0) < 0$, $\Delta^{C}I^{D}/^{C}I_0^{D} < 0$.

As q increases, the function $R_2(\pm q)$ ceases to be linear in q (Fig. 6). As a result, $^{C}I^{D}$ decreases with growing q for molecules with $\delta(0) < 0$, whereas for ones with $\delta(0) > 0$, the

FIG. 7. The molecular reorientation function $R_2(p, +q)$ for molecules with positive anisotropy $\delta(0)$; $a = q/p^2 = \delta(0)kT/2\mu^2$.
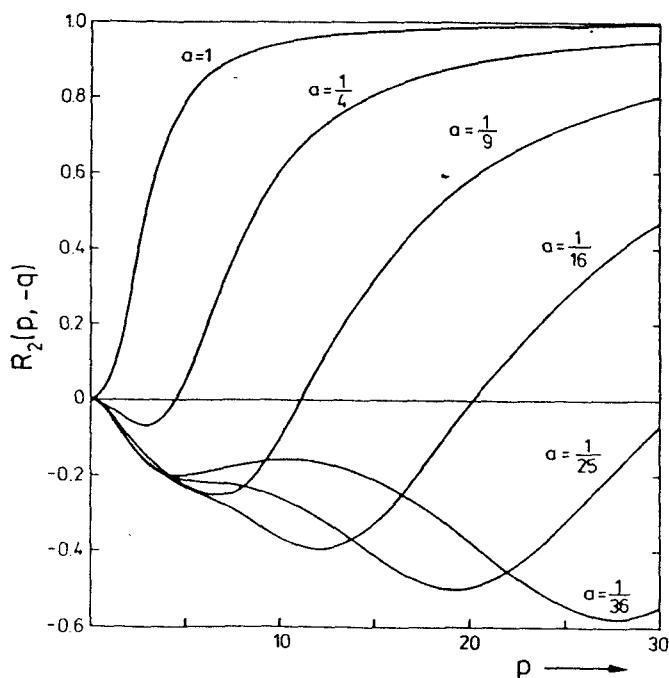

FIG. 8. The molecular reorientation function $R_2(p, -q)$ for molecules with negative anisotropy $\delta(0)$; $a = q/p^2 = |\delta(0)|kT/2\mu^2$.

*effect at first becomes greater, then exhibits a maximum, and finally decreases monotonically. At complete saturation of molecular reorientation,

$$^CI^D \xrightarrow[q\to\infty]{} 0$$

both for molecules with positive and negative anisotropy $\delta(0)$. The shape of $R_2(+q)$ is such that for a given molecular system with $\delta(0) > 0$ there exists a field E_{0m} for which the effect becomes maximal.

In the case of optically inactive molecules, no CIDS take place in the experimental configuration considered in Sec. III B.

The function $R_2(\pm q)$ intervenes as well in the description of Rayleigh[40] and Raman[37] light scattering in strong optical fields, Rayleigh light scattering by nondipolar macromolecules in a static electric field,[32] and magnetochiral birefringence and dichroism in systems of optically active nondipolar molecules in an external electric field parallel to the magnetic field.[36,39]

C. The CIDS in dc electric field E_0 parallel to the observation direction of scattered light

Consider a system of optically active anisotropic molecules in a static field E_0 applied along the laboratory Y axis of coordinates $\{XYZ\}$ (Fig. 1). Averaging in Eq. (12) is performed with the distribution function (13), with ϑ—the angle between the Y axis (the field E_0) and the 3 axis of molecular coordinates $\{1,2,3\}$.

1. Optically active dipolar molecules

At this experimental configuration, the influence of the field-induced molecular reorientation on CIDS is given by the expressions

$$^CI^D = {}^CI_0^D[1 - R_1(p, \pm q)], \tag{41}$$

where $^CI_0^D$ and $R_1(p, \pm q)$ are given by Eqs. (17) and (19). Expression (41) is thus identical with the first right-hand term of Eq. (16). It has been discussed in detail in Sec. III A. Hence, in the present case, similarly as for the configuration of Sec. III B, the effect is dependent on the same multipole polarizability components as in the absence a field E_0.

2. Optically active nondipolar molecules

In the case of optically active nondipolar molecules, the effect of field-induced reorientation on $^CI^D$ is given by the expression

$$^CI^D = {}^CI_0^D[1 - R_1(\pm q)]. \tag{42}$$

which is identical with Eq. (30). It has been discussed fully in Sec. III A.

IV. CONCLUSION

We have shown that, quite generally, processes of reorientation of optically active molecules induced by a static electric field modify the magnitude of CIDS in a way dependent on the experimental configuration (the direction of E_0 with respect to the direction of light incidence and scattering) and the electro-optical properites of the molecules (the

presence of permanent electric dipole moments and anisotropy of their electric polarizability). The effects are described in terms of appropriate molecular reorientation functions of the dimensionless reorientation parameters p and q.

It should be feasible to observe the influence of the reorientation processes in solutions of optically active macromolecules with an electric dipole moment $\mu \approx 10^{-28} \div 10^{-27}$ Cm in a field $E_0 \approx 10^6 \div 10^7$ V m^{-1}, for which $p > 1$. A readily apparent degree of saturation of molecular reorientation can be achieved, e.g., in solutions of rigid polypeptides which present a very great electric dipole moment, as is the case for poly-γ-benzyl-L-glutamate, the molecules of which possess an electric dipole moment of $\mu = 9 \times 10^{-27}$ Cm and anisotropy $\delta(0) = 0.89 \times 10^{-34}$ Fm^2;[41] here, the parameter p at room temperature in a field $E_0 = 5 \times 10^6$ V m^{-1} amounts to $p = 12$ and the achievement of electric saturation is experimentally feasible.[42]

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