LASER OPTICAL SATURATION OF MOLECULAR REORIENTATION IN RAMAN LIGHT SCATTERING* **

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Abstract. Raman scattering by molecules and macromolecules, arrayed in the electric field of an intense laser beam, is analyzed. Nonlinear changes in the intensity of light scattered by linear and symmetric-top molecules are calculated and expressed in terms of even-order generalized Langevin reorientation functions for all types of Raman-active vibrations. It is shown that the Raman line intensity can undergo an abatement or an enhancement as a result of reorientation, induced by laser radiation; the analysis of these changes in intensity provides additional information on the Raman polarizability tensor, particularly on the sign and magnitude of its anisotropy.

1. Introduction

Hitherto, the process of strong electrical orientation of microsystems (molecules, macromolecules, or colloid particles) has been observed in the Kerr effect [1], in electrically induced light scattering [2], and in complete dielectric saturation [3].

Optical saturation of the Kerr effect, that is, complete alignment of the molecules by a rapidly vibrating electric field, has been invoked in order to explain small-scale trapped filaments in an intense laser beam [4]. Also, the feasibility of observing changes in the intensity of Rayleigh light scattering due to strong optical reorientation of the microsystems has been discussed [5]. Early attempts to observe such changes by the application of laser techniques to molecular liquids failed to yield quantitative results [6]. However, successful observations of a nonlinear increase in scattered light intensity with increasing laser beam intensity in suspensions containing particles of dimensions smaller than the light wavelength have been reported [7].

Quite recently, the first observations of strong birefringence due to laser-induced orientation in macromolecular suspensions have come to our knowledge [8].

In recent years, Raman scattering studies have been extended to substances the molecules of which exhibit permanent or partial orientational order. For example the Raman effect has been measured in the nematic phase [9] as well as in axially oriented polymers [10, 11]. The theory of the Raman effect for oriented polymers in the solid phase has been proposed by Snyder [12] and Bower [13].

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In the present paper, we shall be discussing Raman scattering by anisotropic molecules under the reorienting influence of the electric field of an intense laser beam. The problem, with regard to symmetric top molecules will be dealt with in a molecular-statistical treatment in terms of optical reorientation functions, used in the description of nonlinear changes in Rayleigh scattering [5, 14]. Our results, in the limiting case of complete orientational alignment of the molecules, become equivalent to those of Snyder [12].

2. Theory of Molecular Reorientation in Light Scattering

Let us consider a scattering medium, composed of N anisotropic uncorrelated microsystems, the linear dimensions of which are less than the light wavelength. The tensor of the integral intensity of ordinary Raman scattering is given, in laboratory coordinates, as follows [15]:

$$I_{ij}^{\nu} = N\left(\frac{\omega \pm \omega_{\nu}}{c}\right)^4 \langle a_{ik}^{\nu}(\omega)\, a_{jl}^{\nu}(\omega)\rangle_{\Omega}\, I_{kl}, \tag{1}$$

where

$$I_{kl} = \frac{c}{4\pi}\langle E_k E_l\rangle_t \tag{2}$$

is the intensity tensor of the incident light wave, vibrating with the angular frequency ω.

The tensor $a_{ik}^{\nu}(\omega)=(\partial a_{ik}/\partial q_{\nu})_0$ describes the linear Raman polarizability of the molecule for a normal vibration ω_{ν} of symmetry ν. We shall put $\nu=s$ for totally symmetrical vibrations, and $\nu=n$ otherwise. We shall not consider explicitly the ω-dependence of $a_{ik}^{\nu}(\omega)$ which is defined by the well known Kramers-Heisenberg formula [15].

We express the tensor a_{ik}^{ν} by its tensor elements in molecular coordinates as:

$$a_{ik}^{\nu} = R_{i\alpha}(\Omega)\, R_{k\gamma}(\Omega)\, a_{\alpha\gamma}^{\nu}, \tag{3}$$

where the $R_{i\alpha}(\Omega)$ are elements of the rotation transformation matrix $\mathbf{R}$ from laboratory axes i to molecular coordinate axes α [16]. Here, Ω denotes generally the set of three Euler angles φ, θ, ψ.

We assume that the tensor elements $a_{\alpha\gamma}^{\nu}$ do not depend on the orientational variables Ω. In the absence of external forces, this enables us, after insertion of Equation (3) into Equation (1), to carry out an unweighted averaging over all molecular orientations Ω leading to results well known in the literature [17]. Here, however, we are concerned with the case when the scattering molecules are not free inasmuch as they are subject to the reorienting forces of the electric field conveyed by a light wave of sufficient intensity. Two experimental situations suggest themselves:

(a) A situation involving one incident light beam, so intense that the scattering takes place from self-oriented molecules;

(b) A situation involving two beams, when the light of a weak source (usually a

low-power gas laser) is scattered from molecules reoriented by the light wave of a very strong source vibrating at the frequency ω_L, e.g. a ruby or neodymium laser. The mutual configuration of the two beams and their polarisations are defined by the conditions of the experiment.

We shall now perform calculations of the intensity tensor (1) for three configurations of the situation (b) as shown in Figure 1. The three configurations differ as to the polarisation direction of the beam of intensity I_L which causes reorientation of the scattering molecules with respect to the probe beam of intensity I:

(A) The 'reorienting' beam is polarized perpendicularly to the plane of observation (the plane containing the propagation direction of the 'probe' beam of intensity I and the direction in which the Raman radiation is observed);

(B) The 'reorienting' beam is polarized parallel to the propagation direction of the 'probe' beam;

(C) The 'reorienting' beam is polarized parallel to the plane of observation and perpendicularly to the propagation direction of the 'probe' beam of intensity I.

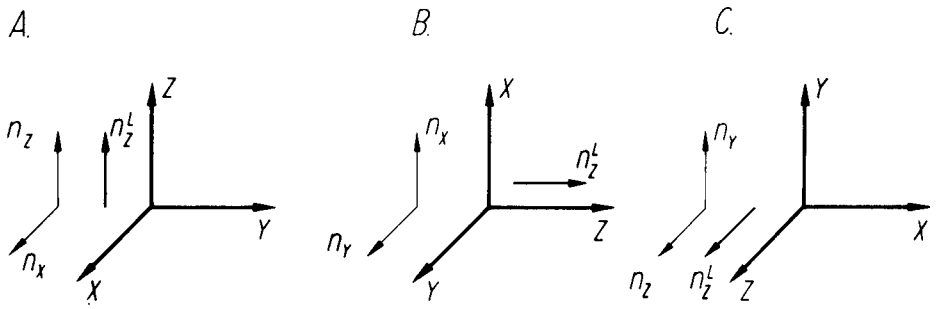

Fig. 1. Configurations of the polarization directions $\mathbf{n}^L$ and $\mathbf{n}$ of the 'reorienting' and 'probe' beams.

It should be noted that the situation (a) is a particular case of the situation (b).

Since both beams are plane polarized, we have to consider only the principal values of the intensity tensors (1) and (2):

$$I^{\nu}_{i,k} = N\left(\frac{\omega \pm \omega_{\nu}}{c}\right)^4 S^{\nu}_{i,k}(I_L)\, I_k, \tag{4}$$

where

$$S^{\nu}_{i,k}(I_L) = \int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} |a^{\nu}_{ik}|^2 f(\Omega, I_L) \sin\theta \, d\varphi \, d\theta \, d\psi \tag{5}$$

is the matrix of Raman light scattering from molecules optically reoriented in accordance with the Boltzmann-Langevin distribution function $f(\Omega, I_L)$. In the above, the subscript i refers to the polarisation of the scattered beam, and k to that of the incident beam; the subscripts i and k do not imply summation. We assume that the tensor $\mathbf{a}_{\alpha\beta}$ of linear polarizability does not depend on the intensity I_L [15].

2.1. TOTALLY SYMMETRIC VIBRATIONS

For totally symmetric vibrations, the Raman polarizability tensor $\mathbf{a}^s$ of symmetric top molecules is diagonal in form (likewise the Rayleigh polarizabilty tensor):

$$\mathbf{a}^s = \begin{vmatrix} a & \cdot & \cdot \\ \cdot & a & \cdot \\ \cdot & \cdot & b \end{vmatrix}. \tag{6}$$

Hence, the tensor (3) becomes:

$$a^s_{ik} = \alpha\{\delta_{ik} + \kappa(3R_{i3}R_{k3} - \delta_{ik})\} \tag{3a}$$

and we obtain:

$$\begin{aligned} |a^s_{ik}|^2 = \alpha^2 \{&\delta_{ik} + 2\kappa(3R_{i3}R_{k3} - \delta_{ik})\,\delta_{ik} + \\ &+ \kappa^2(9R^2_{i3}R^2_{k3} - 6\delta_{ik}R_{i3}R_{k3} + \delta_{ik})\}. \end{aligned} \tag{7}$$

In the above, we have introduced the mean Raman polarizability α and the mean anisotropy of Raman polarizability κ defined as follows:

$$\alpha = \tfrac{1}{3}(2a + b), \qquad \kappa = \frac{b - a}{2a + b}.$$

Here, the rotation matrix elements are:

$$R_{x3} = \sin\varphi \sin\theta, \qquad R_{y3} = -\cos\varphi \sin\theta, \qquad R_{z3} = \cos\theta. \tag{7a}$$

On insertion of (7) into (5) we obtain, for the change in the scattering matrix under the influence of intense light:

$$\begin{aligned} \Delta S^s_{i,k}(I_L) &= S^s_{i,k}(I_L) - S^s_{i,k}(0) = \\ &= \alpha^2\{2\kappa[3\langle R_{i3}R_{k3}\rangle_{\Omega, I_L} - \delta_{ik}]\,\delta_{ik} + \\ &\quad + \tfrac{1}{5}\kappa^2[45\langle R^2_{i3}R^2_{k3}\rangle_{\Omega, I_L} - 30\delta_{ik}\langle R_{i3}R_{k3}\rangle_{\Omega, I_L} + \\ &\quad + 4\delta_{ik} - 3]\}, \end{aligned} \tag{8}$$

where

$$S^s_{i,k}(0) = \alpha^2\{\delta_{ik} + \tfrac{1}{5}\kappa^2(3 + \delta_{ik})\} \tag{9}$$

is the scattering matrix in the absence of the intense light beam ($I_L = 0$).

For axially symmetric molecules the Boltzmann-Langevin distribution function takes the form [14]:

$$f(\Omega, I_L) = \frac{\exp(\pm q\cos^2\theta)}{\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} \exp(\pm q\cos^2\theta)\sin\theta\,\mathrm{d}\varphi\,\mathrm{d}\theta\,\mathrm{d}\psi}, \tag{10}$$

where the dimensionless, positive parameter

$$q = \frac{2\pi I_L}{ckT}\,|a^{\omega_L}_{33} - a^{\omega_L}_{11}|, \tag{11}$$

provides a measure of the reorientation of the molecule by the electric field of the laser beam of intensity I_L. The positive sign in Equation (10) refers to molecules with positive anisotropy of their linear optical polarisability ($a_{33}^{\omega L} - a_{11}^{\omega L} > 0$, i.e. general cigar-like molecules), whereas the negative sign refers to molecules with negative optical anisotropies ($a_{33}^{\omega L} - a_{11}^{\omega L} < 0$, i.e. disc-like molecules).

For the sake of convenience, we now introduce the following notation for the scattering matrix elements:

$$S_1^s(\pm q) = S_{x,x}^s(I_L) = S_{y,y}^s(I_L),$$
$$S_2^s(\pm q) = S_{z,z}^s(I_L), \qquad S_3^s(\pm q) = S_{x,y}^s(I_L),$$
$$S_4^s(\pm q) = S_{x,z}^s(I_L) = S_{y,z}^s(I_L).$$

Tables I and II show which of them are accessible to measurement when applying the configurations *A*, *B*, or *C* of reorienting, probe, and scattered light.

TABLE I

Scattering matrix elements, accessible to measurement in three experimental configurations *A*, *B*, *C* involving two light beams[a]

	Polarisation direction of the probe beam	Polarisation direction of the reorienting beam					
		Polarisation direction of the Raman radiation					
		A		*B*		*C*	
		V	H	V	H	V	H
Right angle observation	V	S_2	S_4	S_1	S_4	S_1	S_3
	H	S_4	S_3	S_3	S_4	S_4	S_4
Backwards observation	V	S_2	S_4	S_1	S_3	S_1	S_4
	H	S_4	S_1	S_3	S_1	S_4	S_2

[a] See footnote (a) in Table II.

TABLE II

Scattering matrix elements at self-induced reorientation[a]

Polarisation of the laser beam	Right angle observation		Backwards observation	
	Polarisation of the Raman radiation			
	V	H	V	H
V	S_2	S_4	S_2	S_4
H	S_4	S_4	S_4	S_2

[a] In Tables I and II, 'V' and 'H' stand for polarisation vertical, or horizontal, to the plane of observation.

With regard to the distribution function (10), we obtain from (8) for the change in each of the scattering matrix elements,

$$\Delta S_1^s(\pm q) = \alpha^2\{-2\kappa\Phi(\pm q) + \tfrac{1}{5}\kappa^2 R_1(\pm q)\}, \tag{12}$$

$$\Delta S_2^s(\pm q) = \alpha^2\{4\kappa\Phi(\pm q) + \tfrac{1}{5}\tfrac{6}{}\kappa^2 R_2(\pm q)\}, \tag{13}$$

$$\Delta S_3^s(\pm q) = -\tfrac{3}{5}\alpha^2\kappa^2 R_3(\pm q), \tag{14}$$

$$\Delta S_4^s(\pm q) = -\tfrac{3}{5}\alpha^2\kappa^2 R_4(\pm q), \tag{15}$$

where we make use of the optical molecular reorientation functions:

$$\Phi(\pm q) = \tfrac{1}{2}\{3L_2(\pm q - 1\}, \tag{16}$$

$$R_1(\pm q) = \tfrac{1}{8}\{135L_4(\pm q) - 150L_2(\pm q) + 23\}, \tag{17}$$

$$R_2(\pm q) = \tfrac{1}{16}\{45L_4(\pm q) - 30L_2(\pm q) + 1\}, \tag{18}$$

$$R_3(\pm q) = \tfrac{1}{8}\{30L_2(\pm q) - 15L_4(\pm q) - 7\}, \tag{19}$$

$$R_4(\pm q) = \tfrac{1}{2}\{15L_4(\pm q) - 15L_2(\pm q) + 2\}. \tag{20}$$

Above, the L's are Langevin functions of even order:

$$L_{2n}(\pm q) = \frac{\int_0^\pi \cos^{2n}\theta \exp(\pm q\cos^2\theta)\sin\theta\,\mathrm{d}\theta}{\int_0^\pi \exp(\pm q\cos^2\theta)\sin\theta\,\mathrm{d}\theta} \tag{21}$$

calculated analytically and given in the form of graphs for $n=1, 2$ and $0\leqslant q\leqslant 25$ in an earlier paper by one of us [14].

The reorientation functions (16)–(20) are defined in such a way that they vanish for $q=0$ and tend to 1 for $q\to+\infty$. The function (16) occurs in Optical Kerr saturation [1, 4, 5]. The functions (18)–(20) occur in Optical Rayleigh Scattering saturation and exhibit highly interesting shapes [14].

2.2. Nontotally symmetric vibrations

In cases of nontotally symmetric vibrations, the Raman polarizability tensor $\mathbf{a}^n$ of symmetric top molecules can in general be written (Table III) in the form:

$$\mathbf{a}^n = \begin{vmatrix} c & d & e \\ d & -c & f \\ e & f & \cdot \end{vmatrix}. \tag{22}$$

The particular form for each symmetry class and various Raman active vibrations is specified in Refs [18].

For an isotropic distribution of molecular orientation, we get

$$S_{i,k}^n(0) = \tfrac{1}{15}\gamma^2(3+\delta_{ik}), \tag{9a}$$

TABLE III

Raman polarizability tensors for nontotally symmetric vibrations of symmetric top molecules

Symmetry class	Tensor			
	$\begin{vmatrix} c & d & e \\ d & -c & f \\ e & f & \cdot \end{vmatrix}$	$\begin{vmatrix} d & -c & -f \\ -c & -d & e \\ -f & e & \cdot \end{vmatrix}$		
C_3	$E(x)$	$E(y)$		
C_{3i}	$E_g(1)$	$E_g(2)$		
	$\begin{vmatrix} c & \cdot & \cdot \\ \cdot & -c & f \\ \cdot & f & \cdot \end{vmatrix}$	$\begin{vmatrix} \cdot & c & -f \\ -c & \cdot & \cdot \\ -f & \cdot & \cdot \end{vmatrix}$		
D_3	$E(x)$	$E(y)$		
D_{3d}	$E_g(1)$	$E_g(2)$		
	$\begin{vmatrix} c & \cdot & e \\ \cdot & -c & \cdot \\ e & \cdot & \cdot \end{vmatrix}$	$\begin{vmatrix} \cdot & -c & \cdot \\ -c & \cdot & e \\ \cdot & e & \cdot \end{vmatrix}$		
C_{3v}	$E(x)$	$E(y)$		
	$\begin{vmatrix} c & d & \cdot \\ d & -c & \cdot \\ \cdot & \cdot & \cdot \end{vmatrix}$	$\begin{vmatrix} \cdot & \cdot & e \\ \cdot & \cdot & f \\ e & f & \cdot \end{vmatrix}$	$\begin{vmatrix} \cdot & \cdot & -f \\ \cdot & \cdot & e \\ -f & e & \cdot \end{vmatrix}$	
C_4	B	$E(x)$	$E(y)$	
S_4	$B(z)$	$E(x)$	$-E(y)$	
C_{4h}	B_g	$E_g(1)$	$E_g(2)$	
	$\begin{vmatrix} c & \cdot & \cdot \\ \cdot & -c & \cdot \\ \cdot & \cdot & \cdot \end{vmatrix}$	$\begin{vmatrix} \cdot & d & \cdot \\ d & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{vmatrix}$	$\begin{vmatrix} \cdot & \cdot & e \\ \cdot & \cdot & \cdot \\ e & \cdot & \cdot \end{vmatrix}$	$\begin{vmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & e \\ \cdot & e & \cdot \end{vmatrix}$
C_{4v}	B_1	B_2	$E(x)$	$E(y)$
D_4	B_1	B_2	$-E(y)$	$E(x)$
D_{4h}	B_{1g}	B_{2g}	$-E_g(2)$	$E_g(1)$
D_{2d}	B_1	$B_2(z)$	$E(y)$	$E(x)$
	$\begin{vmatrix} \cdot & \cdot & e \\ \cdot & \cdot & f \\ e & f & \cdot \end{vmatrix}$	$\begin{vmatrix} \cdot & \cdot & -f \\ \cdot & \cdot & e \\ -f & e & \cdot \end{vmatrix}$	$\begin{vmatrix} c & d & \cdot \\ d & -c & \cdot \\ \cdot & \cdot & \cdot \end{vmatrix}$	$\begin{vmatrix} d & -c & \cdot \\ -c & -d & \cdot \\ \cdot & \cdot & \cdot \end{vmatrix}$
C_6	$E_1(x)$	$E_1(y)$	$E_2(1)$	$E_2(2)$
C_{3h}	$E''(1)$	$E''(2)$	$E'(x)$	$E'(y)$
C_{6h}	$E_{1g}(1)$	$E_{1g}(2)$	$E_{2g}(1)$	$E_{2g}(2)$
	$\begin{vmatrix} \cdot & \cdot & \cdot \\ \cdot & \cdot & f \\ \cdot & f & \cdot \end{vmatrix}$	$\begin{vmatrix} \cdot & \cdot & -f \\ \cdot & \cdot & \cdot \\ -f & \cdot & \cdot \end{vmatrix}$	$\begin{vmatrix} c & \cdot & \cdot \\ \cdot & -c & \cdot \\ \cdot & \cdot & \cdot \end{vmatrix}$	$\begin{vmatrix} \cdot & -c & \cdot \\ -c & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{vmatrix}$
D_6	$E_1(x)$	$E_1(y)$	$E_2(1)$	$E_2(2)$
D_{6h}	$E_{1g}(1)$	$E_{1g}(2)$	$E_{2g}(1)$	$E_{2g}(2)$
D_{3h}	$E''(1)$	$E''(2)$	$E'(x)$	$E'(y)$
C_{6v}	$E_1(y)$	$-E_1(x)$	$E_2(1)$	$E_2(2)$
$D_{\infty h}$	$\pi_g(1)$	$\pi_g(2)$	$A_g(2)$	$A_g(2)$
$C_{\infty v}$	$\pi(y)$	$\pi(x)$	$A(1)$	$A(2)$

where:

$$\gamma^2 = c^2 + d^2 + e^2 + f^2 .$$

An averaging procedure, similar to that of the previous Section, leads from (22) to the following changes in scattering tensor elements under the influence of optical reorientation:

$$\Delta S_1^n(\pm q) = \tfrac{1}{30}\{7\gamma_1^2 R_5(\pm q) - 8\gamma_2^2 R_2(\pm q)\}, \tag{23}$$

$$\Delta S_2^n(\pm q) = -\tfrac{4}{15}\{\gamma_1^2 R_3(\pm q) + \gamma_2^2 R_4(\pm q)\}, \tag{24}$$

$$\Delta S_3^n(\pm q) = \tfrac{1}{10}\{3\gamma_1^2 R_6(+q) - 2\gamma_2^2 R_7(\pm q)\}, \tag{26}$$

$$\Delta S_4^n(\pm q) = -\tfrac{1}{10}\{2\gamma_1^2 R_7(\pm q) - 3\gamma_2^2 R_8(\pm q)\}. \tag{25}$$

Above, we use the notation:

$$\gamma_1^2 = c^2 + d^2 \quad \text{and} \quad \gamma_2^2 = e^2 + f^2$$

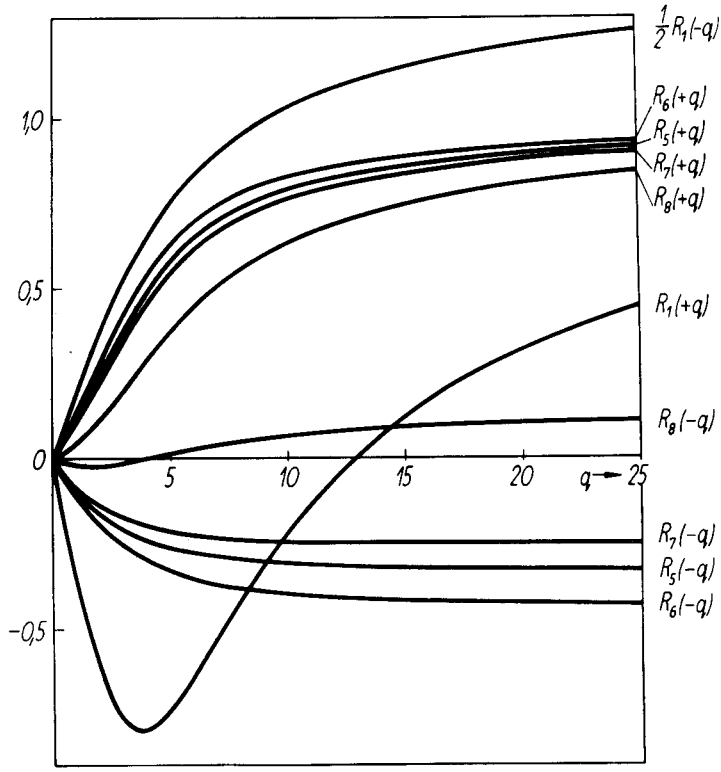

Fig. 2. Graphs of the new reorientation functions $R_n(\pm q)$ for positive and negative anisotropy.

and introduce the new optical molecular reorientation functions:

$$R_5(\pm q) = \tfrac{1}{56}\{45L_4(\pm q) + 30L_2(\pm q) - 19\}, \tag{27}$$

$$R_6(\pm q) = \tfrac{1}{24}\{5L_4(\pm q) + 30L_2(\pm q) - 11\}, \tag{28}$$

$$R_7(\pm q) = \tfrac{1}{4}\{5L_4(\pm q) - 1\}, \tag{29}$$

$$R_8(\pm q) = \tfrac{1}{6}\{20L_4(\pm q) - 15L_2(\pm q) + 1\}. \tag{30}$$

Like the functions (16)–(20), they are defined to vanish for $q=0$ and tend to 1 at $q \to +\infty$. Graphs of the functions R_n are shown in Figure 2, for $n=1$ and 5–8.

3. Discussion

Formulae (12)–(20) and (23)–(30) hold for any degree of ordering, including optical saturation (i.e. complete alignment). In the latter, limiting case, the Langevin functions $L_{2n}(\pm q)$ for cigar-like molecules tend to 1, but tend to 0 in the case of disc-like ones. Hence, for cigar-like microsystems (molecules, macromolecules, colloid particles) we have:

$$\Delta S_1^s(+\infty) = -2\alpha^2\kappa(1 - \tfrac{1}{10}\kappa), \tag{12a}$$

$$\Delta S_2^s(+\infty) = 4\alpha^2\kappa(1 + \tfrac{4}{5}\kappa), \tag{13a}$$

$$\Delta S_3^s(+\infty) = -\tfrac{3}{5}\alpha^2\kappa^2, \tag{14a}$$

$$\Delta S_4^s(+\infty) = -\tfrac{3}{5}\alpha^2\kappa^2, \tag{15a}$$

and:

$$\Delta S_1^n(+\infty) = \tfrac{1}{30}(7\gamma_1^2 - 8\gamma_2^2), \tag{23a}$$

$$\Delta S_2^n(+\infty) = -\tfrac{4}{15}(\gamma_1^2 + \gamma_2^2), \tag{24a}$$

$$\Delta S_3^n(+\infty) = \tfrac{1}{10}(3\gamma_1^2 - 2\gamma_2^2), \tag{25a}$$

$$\Delta S_4^n(+\infty) = -\tfrac{1}{10}(2\gamma_1^2 - 3\gamma_2^2), \tag{26a}$$

whereas for disc-like microsystems:

$$\Delta S_1^s(-\infty) = \alpha^2\kappa(1 + \tfrac{23}{40}\kappa), \tag{12b}$$

$$\Delta S_2^s(-\infty) = -2\alpha^2\kappa(1 - \tfrac{1}{10}\kappa), \tag{13b}$$

$$\Delta S_3^s(-\infty) = \tfrac{21}{40}\alpha^2\kappa^2, \tag{14b}$$

$$\Delta S_4^s(-\infty) = -\tfrac{3}{5}\alpha^2\kappa^2, \tag{15b}$$

and:

$$\Delta S_1^n(-\infty) = -\tfrac{1}{240}(19\gamma_1^2 + 4\gamma_2^2), \tag{23b}$$

$$\Delta S_2^n(-\infty) = \tfrac{1}{30}(7\gamma_1^2 - 8\gamma_2^2), \tag{24b}$$

$$\Delta S_3^n(-\infty) = -\tfrac{1}{80}(11\gamma_1^2 - 4\gamma_2^2), \tag{25b}$$

$$\Delta S_4^n(-\infty) = \tfrac{1}{20}(\gamma_1^2 + \gamma_2^2). \tag{26b}$$

As we see, optical molecular reorientation can act either way, causing an either increase or a decrease in the values of the scattering matrix elements. In Equations (14a), (15a), and (24a) $\Delta S_k^{\nu}(\pm\infty) = -S_k^{\nu}(0)$, meaning that in these cases the tensor elements $S_k^{\nu}(\pm\infty)$ vanish totally at saturation. The preceding results, derived for saturation, are equivalent to the expressions of Snyder [12], who analyzed the Raman intensities scattered by polymer molecules aligned in the solid state assuming ideal ordering of the latter into one direction or plane.

Our considerations hold for the orientation of nondipolar molecules by a DC electric field, in which case one has but to replace the optical linear polarizabilities $a_{ij}^{\omega_L}$ in the reorientation parameter q of Equation (11) by the electric polarizabilities a_{ij}^{e}. Recently, a large increase in the intensity and depolarisation ratio of Raman lines from liquid benzene and carbon disulphide under the effect of a DC electric field have been reported [19]. Such large variations cannot be attributed to reorientation alone, even were we to invoke electric saturation. Maybe, some increase in intensity can be derived from a coupling between reorientation and nonlinear molecular distortion [20]. In order to achieve strong optical orientation of normal molecules, it would be necessary to have recourse to extremely intense laser beams of intensity $I_L \simeq 10^{10}$ esu in the focal point [14] which is hardly feasible because of possible optical breakdown and destruction of liquids at these high light intensities. Recently reported observations of laser-induced orientation in macromolecular suspensions [8] by the use of the unfocussed beam of a Nd^{3+}–YAG laser with a pulse duration of 200 μs corroborate earlier predictions [5] that optical saturation can be achieved in solutions of strongly anisotropic macromolecules and colloid particles. Our present results also apply to the optical orientation of macromolecules having Raman-active groups, the symmetry axes of which are parallel or perpendicular to the symmetry axis of the macromolecule.

Optically induced reorientation will permit a more complete determination of the values of Raman tensor elements. For totally symmetric vibrations of symmetric top molecules, normal Raman scattering permits the determination of the squares of the mean Raman polarizability α^2 and polarizability anisotropy κ^2 only. The phenomenon of induced reorientation yields the product $\alpha^2\kappa$ as well, whence one can determine the sign of the anisotropy κ. For nontotally symmetric vibrations, Raman scattering by freely reorienting molecules yields but the single quadratic invariant

$$\gamma^2 = \gamma_1^2 + \gamma_2^2 .$$

Scattering measurements involving an external reorienting agent permit the determination of γ_1^2 and γ_2^2 separately.

The study of the changes in shape of the spectrum caused by an intense laser beam can moreover prove helpful in the identification of Raman lines.

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