

SPECTRAL THEORY OF THIRD-HARMONIC LIGHT SCATTERING BY MOLECULAR LIQUIDS

BY W. ALEXIEWICZ, Z. OŹGO AND S. KIELICH

Institute of Physics, A. Mickiewicz University, Poznań*

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The spectral distribution of incoherent third-harmonic light scattering by liquids is calculated taking into account rotational self-diffusion of the molecules. In the theoretical analysis, the method of irreducible spherical tensors is applied. The spectral line broadening about the frequency 3ω due to self-diffusion is shown to be described by molecular relaxation times τ_{JM} , $J = 2$ and 4 , $|M| \leq J$, and respective molecular parameters of third-harmonic scattering C_{JM} . The C_{JM} are calculated as quadratic functions of Cartesian tensor elements of third-order nonlinear polarizability $c_{ijk}^{3\omega}$ for all molecular symmetry groups. Spectral studies of third-harmonic light scattering are seen as sources of new information on the tensor elements $c_{ijk}^{3\omega}$ and higher relaxation times τ_{JM} of molecules, and in particular on the relaxation times τ_{4M} hitherto not studied by other methods.

1. Introduction

The theoretical foundations of multi-harmonic light scattering were proposed by Kielich [1], whereas the first experimental observations are due to Terhune and co-workers [2]. The coming of laser technique made it possible to perform exact studies of the spectral line shape of Rayleigh light scattering [3] and thus to disclose the rotational motion of molecules in liquids [4]. The spectral shape of second-harmonic light scattering by liquids was investigated by Maker [5], who showed rotational diffusion to cause a broadening of the spectral line. Half-linewidth measurements of Rayleigh scattering yield information regarding molecular relaxation times related with a spherical tensor of rank 2, and second-harmonic scattering studies — regarding relaxation times related with ones of ranks 1 and 3.

The theory of third-harmonic light scattering by gases and liquids was proposed by Kielich and Kozierowski [6], who calculated the intensities, depolarisation ratios and angular dependences of the scattered light. The influence of rotational molecular motion

* Address: Zakład Optyki Niejednolitej, Instytut Fizyki, Uniwersytet A. Mickiewicza, Grunwaldzka 6, 60-780 Poznań, Poland.

on the spectrum of third-harmonic scattering by gases is discussed in Ref. [7]. Free rotation leads to a discrete spectrum, whereas rotational diffusion in viscous media leads to a spectrum continuous about the harmonic frequency.

This paper is concerned with quantitative calculations of the broadening of the spectrum of third-harmonic light scattering by liquids. We calculate the spectral distribution of scattered light, for incident light both linearly and circularly polarized, on the assumption of Debye's model of rotational self-diffusion [8, 9]. Neither translational self-diffusion nor statistical effects of radial and angular correlations are taken into account; their contribution to the intensity of third-harmonic light scattering is discussed in Refs. [6]. Although the isotropic part of the tensor of second-order molecular electric hyperpolarizability (to which, in spherical representation, corresponds a tensor of zeroth rank C^0) significantly affects the intensity of scattered light, it contributes nothing to the half-width of the spectral line. Line broadening is dependent only on spherical tensors of ranks 2 and 4, if the hyperpolarizability tensor $c_{ijkl}^{3\omega}$ is assumed to be totally symmetric in all its indices. The approximation is justified if the frequencies of the incident and scattered waves do not fall within regions of electron dispersion and absorption. Measurements of half-line-widths can be a source of data on molecular relaxation times, related with the tensors of rank 2 studied in linear Rayleigh scattering [4] and, moreover, on relaxation times inherent in the tensors of rank 4, occurring in the theory of nonlinear light scattering [10].

2. The spectral theory of light scattering in liquids

Consider an isotropic liquid, composed of a large number N of quite generally anisotropic molecules, on which is incident a light beam with electric field $E(t) = E \cos \omega t$ vibrating at the frequency ω . If the beam is intense enough, a component with the frequency 3ω can appear in the scattered light. The third-harmonically scattered line-shape $I_{ij}^{3\omega}(\Delta\omega)$, symmetrically distributed on both sides of the third-harmonic frequency 3ω , can be expressed by the Fourier transform of the scattered light intensity tensor $I_{ij}^{3\omega}(t)$ as follows [1, 10]:

$$I_{ij}^{3\omega}(\Delta\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} I_{ij}^{3\omega}(t) \exp(i\Delta\omega t) dt, \quad (1)$$

the incoherent scattered component being given as:

$$I_{ij}^{3\omega}(t) = \frac{N\pi^2}{9c^6} (3\omega)^4 \langle c_{ikmo}^{3\omega}(t_0) c_{jlnp}^{3\omega}(t_0+t)^* \rangle I_{kl} I_{mn} I_{op}. \quad (2)$$

Above, the $c_{ijkl}^{3\omega}$ are elements, in laboratory coordinates, of the tensor of rank 4 of the nonlinear electric third-order polarizability of the molecule, and c the light propagation velocity in the liquid. I_{kl} is the intensity tensor of incident light: $I_{kl} = c/8\pi E_k E_l^*$. We assume the tensor elements $c_{ijkl}^{3\omega}$ to depend on time not explicitly but only by way of changes in

orientation of the molecule $\Omega(t)$, as follows: $c_{ijkl}^{3\omega}(t) \equiv c_{ijkl}^{3\omega}[\Omega(t)]$. Describing the molecular orientation in terms of Euler angles, $\{\alpha, \beta, \gamma\} = \Omega'$, defined as in Ref. [11], the mean value of any function of the molecular orientation $F[\Omega(t)]$ is given by the formula:

$$\langle F[\Omega(t)] \rangle \equiv \int_{\Omega(t)} F[\Omega(t)] f(\Omega, t) d\Omega(t), \quad (3)$$

where $d\Omega = \sin \beta d\alpha d\beta d\gamma$. The auto-correlation function of the quantity $F[\Omega(t)]$ is of the form:

$$\begin{aligned} & \langle F[\Omega(t_0)] F[\Omega(t_0+t)] \rangle \\ &= \frac{1}{8\pi^2} \int_{\Omega(t_0)} \int_{\Omega(t_0+t)} F[\Omega(t_0)] F[\Omega(t_0+t)] f(\Omega, t) d\Omega(t_0) d\Omega(t_0+t) \end{aligned} \quad (4)$$

and is independent of the choice of initial moment of time t_0 . By $f(\Omega, t)$ we have denoted the statistical distribution function, describing the probability that the molecule shall have the orientation Ω at the moment of time t . The function $f(\Omega, t)$ is to be found by considering a well-defined model of the molecular dynamics. To this aim, we shall make the assumption that the orientational motion of molecules in the liquid consists in statistical changes of orientation by small angles $\Delta\Omega$ only. This, in fact, is the model of molecular motion proposed by Debye for phenomena of dielectric relaxation in liquids [8]. We now expand the distribution function in a series in Wigner functions $D_{KM}^J(\Omega)$ [11]:

$$f(\Omega, t) = \sum_{JKMM'} g_{MM'}^J(t) D_{KM}^J[\Omega(t_0)] D_{KM'}^J[\Omega(t_0+t)]^*, \quad (5)$$

where, by $g_{MM'}^J(t)$ we have denoted dynamic coefficients, dependent on time only, which we derive from the equation of Debye rotational diffusion [9]:

$$\frac{\partial f(\Omega, t)}{\partial t} = - \sum_i L_i D_i L_i f(\Omega, t). \quad (6)$$

In Eq. [6], the L_i are components (in molecular coordinates, $i = x, y, z$) of the angular momentum operator L , and the D_i are diagonal elements of the tensor of rotational diffusion of the molecule. The solution of Eq. (6) for symmetric top molecules ($D_x = D_y \neq D_z$) is of the form:

$$g_{MM'}^J(t) = \frac{2J+1}{8\pi^2} \delta_{MM'} \exp \{ -[J(J+1)D_x + M^2(D_z - D_x)]t \}; \quad (7)$$

for spherical top molecules ($D_x = D_y = D_z = D$), it reduces to:

$$g_{MM'}^J(t) = \frac{2J+1}{8\pi^2} \delta_{MM'} \exp [-J(J+1)Dt], \quad (8)$$

where $\delta_{MM'}$ is Kronecker's delta.

When we proceed to calculate the auto-correlation function, it is convenient to represent the tensor $c_{ijkl}^{3\omega}(t)$ in terms of spherical tensors $C_M^J(t)$. For a Cartesian tensor of

rank 4 symmetric in all its indices, the required transformation is:

$$c_{ijkl}^{3\omega} = \sum_{JM} a_{ijkl}^{JM} C_M^J. \quad (9)$$

This is a unitary transformation; its coefficients a_{ijkl}^{JM} are calculated in Ref. [7]. Here, M denotes the M -th element of the spherical tensor of rank J . If the incident light beam propagates in the direction of the Y -axis and is linearly polarized with vibrations along the Z -axis, and assuming that observation is performed in the direction of the X -axis, then the two components: the polarized component $I_Z^{3\omega}(\Delta\omega)$, and the depolarized one $I_Y^{3\omega}(\Delta\omega)$, are described by the auto-correlation functions $\langle c_{ZZZZ}^{3\omega}(t_0) c_{ZZZZ}^{3\omega}(t_0+t)^* \rangle$ and $\langle c_{YZZZ}^{3\omega}(t_0) c_{YZZZ}^{3\omega}(t_0+t)^* \rangle$, respectively. In this particular case, we have:

$$c_{ZZZZ}^{3\omega} = \frac{4}{\sqrt{70}} C_0^4 - \frac{2}{\sqrt{7}} C_0^2 + \frac{1}{\sqrt{5}} C_0^0,$$

$$c_{YZZZ}^{3\omega} = \frac{i}{\sqrt{14}} (C_1^4 + C_{-1}^4) - \frac{i\sqrt{3}}{2\sqrt{14}} (C_1^2 + C_{-1}^2). \quad (10)$$

If the incident light wave is right-circularly polarized, the spectrum of scattered light polarized in the same sense as the incident wave $I_{+1}^{3\omega}(\Delta\omega)$ is described by the auto-correlation function $\langle c_{1-1-1-1}^{3\omega}(t_0) c_{1-1-1-1}^{3\omega}(t_0+t)^* \rangle$, whereas for scattered light circularly polarized in the opposite sense $I_{-1}^{3\omega}(\Delta\omega)$ it is described by the auto-correlation function $\langle c_{1-1-1-1}^{3\omega}(t_0) c_{-1-1-1-1}^{3\omega}(t_0+t)^* \rangle$. Here, the tensor elements of nonlinear second-order molecular polarizability are calculated with respect to a circular-cylindrical system of reference. They can be expressed in the form of spherical tensors C_M^J by having recourse to the transformation matrix given in Ref. [7]. The Cartesian tensor elements of relevance to us are given by the following formulas:

$$c_{1-1-1-1}^{3\omega} = \frac{1}{2\sqrt{7}} C_2^4 + \frac{\sqrt{3}}{\sqrt{14}} C_2^2; \quad c_{-1-1-1-1}^{3\omega} = C_{-4}^4. \quad (11)$$

The spherical tensor elements C_M^J in laboratory coordinates are related with the elements \tilde{C}_M^J in molecular coordinates (the mutual orientation of the two systems of reference being given by the Euler angles Ω) by:

$$C_M^J = \sum_{M'} D_{MM'}^J(\Omega) \tilde{C}_{M'}^J. \quad (12)$$

With regard to Eqs. (2), (5) and (10) and to the orthogonality property of Wigner functions [11]:

$$\frac{1}{8\pi^2} \int D_{KM}^J(\Omega) D_{K'M'}^J(\Omega)^* d\Omega = \frac{1}{2J+1} \delta_{JJ'} \delta_{KK'} \delta_{MM'}, \quad (13)$$

we obtain the following formulas for the spectral distribution of third-harmonic light

scattering:

$$I_{n=Y,Z}^{3\omega}(\Delta\omega) = A \sum_{JM} \frac{1}{2J+1} |a_{nZZZ}^{JM}|^2 C_{JM} G_{JM}(\Delta\omega),$$

$$I_{n=+1,-1}^{3\omega}(\Delta\omega) = A \sum_{JM} \frac{1}{2J+1} |a_{n-1-1-1}^{JM}|^2 C_{JM} G_{JM}(\Delta\omega). \quad (14)$$

Above,

$$C_{JM} = |\tilde{C}_M^J|^2 \quad \text{and} \quad A = \frac{N\pi}{18c^6} (3\omega)^4 I^3.$$

The functions $G_{JM}(\Delta\omega)$ defining the line-shape are of the form:

$$G_{JM}(\Delta\omega) = 2\tau_{JM} [1 + (\Delta\omega \tau_{JM})^2]^{-1}; \quad (15)$$

their halfwidths $(\Delta\omega)_{1/2}$ are related with the relaxation times τ_{JM} as follows:

$$(\Delta\omega)_{1/2} = (\tau_{JM})^{-1} = J(J+1)D_x + M^2(D_z - D_x). \quad (16)$$

In the case of the spherical top ($D_x = D_y = D_z = D$) the line-shape is given by the function:

$$G_J(\Delta\omega) = 2\tau_J [1 + (\Delta\omega \tau_J)^2]^{-1} \quad (17)$$

and the half-width is:

$$(\Delta\omega)_{1/2} = (\tau_J)^{-1} = J(J+1)D = \frac{J(J+1)}{2\tau_D}, \quad (18)$$

where $\tau_D = \tau_1$ is the Debye relaxation time.

From Eqs. (14) and (15), the spectrum is found to be a superposition of lines of the Lorentz type corresponding to the values $J = 2$ and $J = 4$, ($-J \leq M \leq J$). The component with $J = 0$, corresponding to the isotropic part of third-harmonic scattering [5], contributes nothing to the line-width. Thus the linewidth depends on the anisotropic part of light scattering only, likewise to usual Rayleigh scattering [3, 4]. Investigation of the spectral distribution of third-harmonic light scattering can provide information regarding the relaxation times τ_{2M} , identical with the relaxation times of Rayleigh scattering; moreover, such investigations can yield data on the hitherto unstudied relaxation times τ_{4M} of rank 4. The assumption of Debye's model involves for them the interrelationship expressed by Eqs. (16) and (17); the experimental confirmation of the latter will provide a criterion of the correctness of the model assumed.

3. Spectral distributions of third-harmonic light scattering for some symmetry groups

We shall now give formulas for the spectral broadening of third-harmonic light scattering for some molecular symmetry groups on the basis of the preceding theory. In Table I, we give the molecular parameters C_{JM} as quadratic functions of Cartesian tensor elements $c_{ijkl}^{3\omega}$ of the nonlinear third-order molecular electric polarizability.

TABLE I

Molecular parameters $C_{JM} \equiv |\tilde{C}_M^J|^2$, as functions of Cartesian elements of the tensor $c_{ijkl}^{3\omega}$, for all molecular symmetry groups. The relation $C_{JM} = C_{J,-M}$ holds generally

Symmetry groups	Nonzero parameters C_{JM}
K, K_h, Y, Y_h	$C_{00} = 25(c_{xxxx}^{3\omega})^2$
T, T_h, T_d, O, O_h	$C_{44} = \frac{5}{14} C_{40} = \frac{1}{4} (c_{xxxx}^{3\omega} - 3c_{xxyy}^{3\omega})^2$ $C_{00} = \frac{9}{5} (c_{xxxx}^{3\omega} + 2c_{xxyy}^{3\omega})^2$
$C_6, C_{3h}, C_{6h}, D_6,$ $C_{6v}, D_{3h}, D_{6h},$ $C_{\infty}, C_{\infty v}, C_{\infty h}$ $D_{\infty h}, C_5, C_{5v}$	$C_{40} = \frac{8}{35} (c_{xxxx}^{3\omega} + c_{zzzz}^{3\omega} - 6c_{xzzz}^{3\omega})^2$ $C_{20} = \frac{4}{63} (4c_{xxxx}^{3\omega} - 3c_{zzzz}^{3\omega} - 3c_{xzzz}^{3\omega})^2$ $C_{00} = \frac{1}{45} (8c_{xxxx}^{3\omega} + 3c_{zzzz}^{3\omega} + 12c_{xzzz}^{3\omega})^2$
$D_4, C_{4v}, D_{2d}, D_{4h}$	$C_{44} = \frac{1}{4} (c_{xxxx}^{3\omega} - 3c_{xxyy}^{3\omega})^2$ $C_{40} = \frac{1}{70} (3c_{xxxx}^{3\omega} + 4c_{zzzz}^{3\omega} + 3c_{xxyy}^{3\omega} - 24c_{yyzz}^{3\omega})^2$ $C_{20} = \frac{4}{49} (c_{xxxx}^{3\omega} - c_{zzzz}^{3\omega} + c_{xxyy}^{3\omega} - c_{yyzz}^{3\omega})^2$ $C_{00} = \frac{1}{5} (2c_{xxxx}^{3\omega} + c_{zzzz}^{3\omega} + 2c_{xxyy}^{3\omega} + 4c_{xzzz}^{3\omega})^2$
D_2, C_{2v}, D_{2h}	$C_{44} = \frac{1}{6} (c_{xxxx}^{3\omega} + c_{yyyy}^{3\omega} - 6c_{xxyy}^{3\omega})^2$ $C_{42} = \frac{1}{28} (c_{yyyy}^{3\omega} - c_{xxxx}^{3\omega} + 6c_{xzzz}^{3\omega} - 6c_{yyzz}^{3\omega})^2$ $C_{40} = \frac{1}{70} [\frac{3}{2} (c_{xxxx}^{3\omega} + c_{yyyy}^{3\omega}) + 4c_{zzzz}^{3\omega} + 3c_{xxyy}^{3\omega} - 12(c_{xzzz}^{3\omega} + c_{yyzz}^{3\omega})]^2$ $C_{22} = \frac{3}{14} (c_{yyyy}^{3\omega} - c_{xxxx}^{3\omega} - c_{xzzz}^{3\omega} + c_{yyzz}^{3\omega})^2$ $C_{20} = \frac{1}{7} (c_{xxxx}^{3\omega} + c_{yyyy}^{3\omega} - 2c_{zzzz}^{3\omega} + 2c_{xxyy}^{3\omega} - c_{xzzz}^{3\omega} - c_{yyzz}^{3\omega})^2$ $C_{00} = \frac{1}{5} (c_{xxxx}^{3\omega} - c_{yyyy}^{3\omega} + c_{zzzz}^{3\omega} + 2c_{xxyy}^{3\omega} + 2c_{xzzz}^{3\omega} + 2c_{yyzz}^{3\omega})^2$
C_4, S_4, C_{4h}	$C_{44} = \frac{1}{4} [(c_{xxxx}^{3\omega} - 3c_{xxyy}^{3\omega})^2 + (c_{xzzz}^{3\omega})^2]$ $C_{40} = \frac{1}{70} (3c_{xxxx}^{3\omega} + 4c_{zzzz}^{3\omega} + 3c_{xxyy}^{3\omega} - 24c_{yyzz}^{3\omega})^2$ $C_{20} = \frac{4}{7} (c_{xxxx}^{3\omega} - c_{zzzz}^{3\omega} + c_{xxyy}^{3\omega} - c_{yyzz}^{3\omega})^2$ $C_{00} = \frac{1}{5} (2c_{xxxx}^{3\omega} + c_{zzzz}^{3\omega} + 2c_{xxyy}^{3\omega} + 4c_{xzzz}^{3\omega})^2$
$C_{3v}, D_{3d}, D_3, C_3, C_{3i}$	$C_{43} = 2(c_{yyyz}^{3\omega})^2$ $C_{40} = \frac{8}{35} (c_{xxxx}^{3\omega} - c_{zzzz}^{3\omega} - 6c_{xzzz}^{3\omega})^2$ $C_{20} = \frac{4}{63} (4c_{xxxx}^{3\omega} - 3c_{zzzz}^{3\omega} - 3c_{xzzz}^{3\omega})^2$ $C_{00} = \frac{1}{45} (8c_{xxxx}^{3\omega} - 3c_{zzzz}^{3\omega} + 12c_{xzzz}^{3\omega})^2$
C_2, C_s, C_{2h}	$C_{44} = \frac{1}{6} (c_{xxxx}^{3\omega} + c_{yyyy}^{3\omega} - 6c_{xxyy}^{3\omega})^2$ $C_{42} = \frac{1}{8} [(c_{xxxx}^{3\omega} - c_{yyyy}^{3\omega} + 6c_{xzzz}^{3\omega} - 6c_{yyzz}^{3\omega})^2 + 144(c_{xyzz}^{3\omega})^2]$ $C_{40} = \frac{1}{70} [\frac{3}{2} (c_{xxxx}^{3\omega} + c_{yyyy}^{3\omega}) + 4c_{zzzz}^{3\omega} + 3c_{xxyy}^{3\omega} - 12(c_{xzzz}^{3\omega} + c_{yyzz}^{3\omega})]^2$ $C_{22} = \frac{3}{14} [(c_{yyyy}^{3\omega} - c_{xxxx}^{3\omega} - c_{xzzz}^{3\omega} + c_{yyzz}^{3\omega})^2 - 4(c_{xyyy}^{3\omega} + c_{xxyy}^{3\omega} + c_{xyzz}^{3\omega})^2]$ $C_{20} = \frac{1}{7} (c_{xxxx}^{3\omega} + c_{yyyy}^{3\omega} - 2c_{zzzz}^{3\omega} + 2c_{xxyy}^{3\omega} - c_{xzzz}^{3\omega} - c_{yyzz}^{3\omega})^2$ $C_{00} = \frac{1}{5} (c_{xxxx}^{3\omega} + c_{yyyy}^{3\omega} + c_{zzzz}^{3\omega} + 2c_{xxyy}^{3\omega} + 2c_{xzzz}^{3\omega} + 2c_{yyzz}^{3\omega})^2$

TABLE I (continued)

Symmetry groups	Nonzero parameters C_{JM}
C_1, C_i	$C_{44} = \frac{1}{16} [(c_{xxxx}^{3\omega} + c_{yyyy}^{3\omega} - 6c_{xyxy}^{3\omega})^2 + 16(c_{xxyy}^{3\omega} - c_{yyyz}^{3\omega})^2]$ $C_{43} = \frac{1}{2} [(3c_{xyyz}^{3\omega} - c_{xxxx}^{3\omega})^2 + (3c_{xxyz}^{3\omega} - c_{yyyyz}^{3\omega})^2]$ $C_{42} = \frac{1}{28} [(c_{yyyy}^{3\omega} - c_{xxxx}^{3\omega} + 6c_{xzzz}^{3\omega} - 6c_{yyzz}^{3\omega})^2 + 4(c_{xyyy}^{3\omega} + c_{xxyy}^{3\omega} - 6c_{xyzz}^{3\omega})^2]$ $C_{41} = \frac{1}{14} [(3c_{xzzz}^{3\omega} + 3c_{xyyz}^{3\omega} - 4c_{zzzz}^{3\omega})^2 + 3(c_{xyyz}^{3\omega} + 3c_{xxyy}^{3\omega} - 4c_{yyzz}^{3\omega})^2]$ $C_{40} = \frac{1}{70} [\frac{3}{2}(c_{xxxx}^{3\omega} + c_{yyyy}^{3\omega}) + 4c_{zzzz}^{3\omega} + 3c_{xxyy}^{3\omega} - 12(c_{xzzz}^{3\omega} + c_{yyzz}^{3\omega})]^2]$ $C_{22} = \frac{3}{14} [(c_{yyyy}^{3\omega} - c_{xxxx}^{3\omega} - c_{xzzz}^{3\omega} + c_{yyzz}^{3\omega})^2 + 4(c_{xyyy}^{3\omega} + c_{xxyy}^{3\omega} + c_{xyzz}^{3\omega})^2]$ $C_{21} = \frac{6}{7} [(c_{xzzz}^{3\omega} + c_{zzzz}^{3\omega} + c_{xyyz}^{3\omega})^2 + (c_{xyyz}^{3\omega} + c_{yyzz}^{3\omega} + c_{xxyy}^{3\omega})^2]$ $C_{20} = \frac{1}{7} (c_{xxxx}^{3\omega} + c_{yyyy}^{3\omega} - 2c_{zzzz}^{3\omega} + 2c_{xxyy}^{3\omega} - c_{xzzz}^{3\omega} - c_{yyzz}^{3\omega})^2]$ $C_{00} = \frac{1}{5} (c_{xxxx}^{3\omega} + c_{yyyy}^{3\omega} + c_{zzzz}^{3\omega} + 2c_{xxyy}^{3\omega} + 2c_{xzzz}^{3\omega} + 2c_{yyzz}^{3\omega})^2]$

Generally, the spectral distribution of third-harmonic light scattering is described by the formulas:

$$I_Y^{3\omega}(\Delta\omega) = \frac{A}{63} \sum_M C_{4M} G_{4M}(\Delta\omega) + \frac{3A}{140} \sum_M C_{2M} G_{2M}(\Delta\omega),$$

$$I_Z^{3\omega}(\Delta\omega) = \frac{8A}{315} \sum_M C_{4M} G_{4M}(\Delta\omega) + \frac{4A}{35} \sum_M C_{2M} G_{2M}(\Delta\omega),$$

$$I_{+1}^{3\omega}(\Delta\omega) = \frac{A}{252} \sum_M C_{4M} G_{4M}(\Delta\omega) + \frac{3A}{70} \sum_M C_{2M} G_{2M}(\Delta\omega),$$

$$I_{-1}^{3\omega}(\Delta\omega) = \frac{A}{9} \sum_M C_{4M} G_{4M}(\Delta\omega). \quad (19)$$

In the case of molecules having the symmetries T , T_h , T_d , O and O_h , they reduce to the form:

$$I_Y^{3\omega}(\Delta\omega) = \frac{5}{8} I_Z^{3\omega}(\Delta\omega) = \frac{A}{63} (C_{40} + 2C_{44}) G_4(\Delta\omega),$$

$$I_{+1}^{3\omega}(\Delta\omega) = \frac{1}{28} I_{-1}^{3\omega}(\Delta\omega) = \frac{A}{9} (C_{40} + 2C_{44}) G_4(\Delta\omega), \quad (20)$$

showing that the spectral distribution depends on a single relaxation time τ_4 , which is related with the Debye time τ_D as follows: $\tau_D = 10\tau_4$, and on the molecular parameter $C_{40} + 2C_{44} = \frac{6}{5} (c_{xxxx}^{3\omega} - 3c_{xxyy}^{3\omega})^2$.

In that of molecules with a threefold axis having the symmetries C_3 , C_{3v} , C_{3i} , D_3

and D_{3d} , the line broadening of third-harmonic light scattering:

$$I_Y^{3\omega}(\Delta\omega) = \frac{A}{63} [2C_{43}G_{43}(\Delta\omega) + C_{40}G_{40}(\Delta\omega)] + \frac{3A}{140} C_{20}G_{20}(\Delta\omega),$$

$$I_Z^{3\omega}(\Delta\omega) = \frac{8A}{315} [2C_{43}G_{43}(\Delta\omega) + C_{40}G_{40}(\Delta\omega)] + \frac{4A}{35} C_{20}G_{20}(\Delta\omega),$$

$$I_{+1}^{3\omega}(\Delta\omega) = \frac{A}{252} [2C_{43}G_{43}(\Delta\omega) + C_{40}G_{40}(\Delta\omega)] + \frac{3A}{70} C_{20}G_{20}(\Delta\omega),$$

$$I_{-1}^{3\omega}(\Delta\omega) = \frac{A}{9} [2C_{43}G_{43}(\Delta\omega) + C_{40}G_{40}(\Delta\omega)] \quad (21)$$

depends on two relaxation times τ_{40} and τ_{43} of rank 4 and on one relaxation time τ_{20} of rank 2.

For molecules of the symmetries D_4 , D_{4h} , C_{4v} and D_{2d} , the broadening of the spectral line is given by Eqs. (21) where $C_{43}G_{43}(\Delta\omega)$ has to be replaced by $C_{44}G_{44}(\Delta\omega)$; instead of τ_{43} , the relaxation time τ_{44} appears. The difference in line broadening for third-harmonic scattering by these molecules and by molecules having a threefold symmetry axis is due solely, by Eq. (16), to the anisotropy $\Delta = D_z - D_x$ of the rotational diffusion tensor.

Finally, for molecules having a symmetry axis higher than fourfold, the spectral distributions are:

$$I_Y^{3\omega}(\Delta\omega) = \frac{A}{63} C_{40}G_{40}(\Delta\omega) + \frac{3A}{140} C_{20}G_{20}(\Delta\omega),$$

$$I_Z^{3\omega}(\Delta\omega) = \frac{8A}{315} C_{40}G_{40}(\Delta\omega) + \frac{4A}{35} C_{20}G_{20}(\Delta\omega),$$

$$I_{+1}^{3\omega}(\Delta\omega) = \frac{A}{252} C_{40}G_{40}(\Delta\omega) + \frac{3A}{70} C_{20}G_{20}(\Delta\omega),$$

$$I_{-1}^{3\omega}(\Delta\omega) = \frac{A}{9} C_{40}G_{40}(\Delta\omega) \quad (22)$$

and depend on one relaxation time τ_{40} of rank 4 and one, τ_{20} , of rank 2.

On having recourse to the approximate relationship, valid for axial molecules in the absence of electron dispersion and absorption:

$$c_{xxxx}^{3\omega} + c_{zzzz}^{3\omega} = 6c_{xxxx}^{3\omega}, \quad (23)$$

we see from Table I that the parameter C_{40} vanishes, and the spectral distribution depends on a single relaxation time τ_{20} , related with the molecular parameter:

$$C_{20} = \frac{7}{9} (c_{xxxx}^{3\omega} - c_{zzzz}^{3\omega})^2. \quad (24)$$

In the present case Eqs. (21) reduce to the relation:

$$I_Y^{3\omega}(\Delta\omega) = \frac{3}{16} I_z^{3\omega}(\Delta\omega) = \frac{1}{2} I_{+1}^{3\omega}(\Delta\omega) = \frac{A}{60} (c_{zzzz}^{3\omega} - c_{xxxx}^{3\omega})^2 G_{20}(\Delta\omega),$$

$$I_{-1}^{3\omega}(\Delta\omega) = 0. \quad (25)$$

Thus, the intensities of the components depend directly on the anisotropy $c_{zzzz}^{3\omega} - c_{xxxx}^{3\omega}$ of the molecule's nonlinear polarizability.

It is worth noting that circularly polarized light, scattered third-harmonically, yields in general two components, the one polarized in the opposite sense $I_{-1}^{3\omega}(\Delta\omega)$ depending on relaxation times τ_{4M} of rank 4 only, and neither of them depending on the isotropic part C_0^0 of the hyperpolarizability tensor.

Neither atomic liquids nor ones composed of icosahedral molecules can exhibit a line broadening related with rotational diffusion of their molecules, since here only the isotropic part C_0^0 differs from zero.

4. Discussion and conclusions

The dependence on temperature of the above derived intensity formulas is determined essentially by the temperature-dependent behaviour of the diffusion constants of Eqs. (15–18). Were we to take into account molecular-statistical fluctuations [12, 13], a coherent component $I^{3\omega}(\Delta\omega)$, dependent on temperature, would appear.

It is moreover worth stressing that most of the nonlinear invariants listed in Table I intervene also in the theory of the cooperative second-harmonic scattering effect, recently observed by Lalanne [13] in his experiments. This is a fact of great impact, since the two kinds of light scattering — the third-harmonic incoherent scattering considered in the present paper, and the effect of cooperative second-harmonic (coherent) scattering — are approximately of the same order of magnitude, pointing to the feasibility of observing spectra of third-harmonic light scattering in appropriately chosen experimental conditions of laser technique.

In the absence of electron dispersion and absorption, we have the direct relationship: $c_{ijkl}^{3\omega} = 6 c_{ijkl}^{2\omega}$. This permits to make comparisons between the values of tensor elements $c_{ijkl}^{2\omega}$, determined by the measurements of cooperative second-harmonic scattering now performed [13], and the values of $c_{ijkl}^{3\omega}$ measured in third-harmonic scattering. On the other hand, we now have at our disposal a method for determining $c_{ijkl}^{\omega, \omega_I} \cong c_{ijkl}^{2\omega}$ from measurements of optical Kerr effect, induced in molecular liquids by intense laser light of frequency ω_I [10, 14]. We thus can adopt the following procedure: knowing the nonlinear polarizability tensor elements c_{ijkl} from measurements of optical Kerr effect and of cooperative second-harmonic light scattering, we can apply spectral observations of third-harmonic scattering to gain information on the higher molecular relaxation times τ_{4M} , inaccessible to study by other methods.

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