

## Intermolecular interaction effect on the line-shape of hyper-Rayleigh light scattering by molecular liquids

by T. BANCEWICZ and S. KIELICH

Nonlinear Optics Division, Institute of Physics of A. Mickiewicz University,  
60-780 Poznań, Grunwaldzka 6, Poland

(Received 11 June 1975)

Scattering on molecules, correlated in regions of short-range quasi-ordering, is analysed with regard to its effect on the spectrum of hyper-Rayleigh light-scattering by molecular liquids. The general form of  $S_c^{2\omega}(\mathcal{N}, \Delta\omega)$  derived using spherical tensors and expanding the orientational-positional-time pair correlation function in Wigner functions, is discussed on the assumption that Vineyard's [22] approximation can be applied to calculate  $G_c[\tau_1(t), \tau_2(0)]$ . Successive terms of the expansion are calculated assuming dipole-dipole interaction energy as predominant in the total molecular electric multipole interaction energy. In the present approximation the contribution from scattering on correlated molecules is shown to be given by the difference of two Lorentz lines, whose maxima depend on the magnitude of the interactions. The integral intensities, calculated from the formulae derived here, are in agreement with those of the literature.

### 1. INTRODUCTION

Lasers—sources of high intensity, coherent and monochromatic radiation—have led to very considerable progress in the spectral analysis of scattered light. A new laser spectroscopy has developed, with methods which have permitted one to obtain numerous, quantitative results in the study of linear scattering [1] and to observe various non-linear, qualitatively new optical effects [2]. The work carried out in these two directions is a source of abundant information regarding the structure and dynamics of the scattering medium as well as the properties of the individual molecules.

Blaton [3] first drew attention to the feasibility of observing radiation of doubled frequency in scattered light. To Kielich [4] is due the quantum-mechanical theory of many-photon light-scattering. The earliest observations of second-harmonic light-scattering (SHS) have been reported by Maker and his co-workers [5], who applied laser technique in their experiments. They succeeded in observing the integral intensity of a rather strong central hyper-Rayleigh line of frequency  $2\omega$  and the intensities of weaker hyper-Raman side lines  $2\omega \pm \omega_m$  [4], scattered from liquids composed of non-centrosymmetric molecules ( $\omega$  being the incident frequency,  $\omega_m$  that of a molecular eigen-vibration).

Subsequent theoretical work was aimed at the elaboration of a more detailed theory of non-linear light-scattering processes. The influence on integral SHS intensity of radial and angular intermolecular correlations [6-9] and molecular fields [7, 9, 10] was studied. This work led to the prediction [7],

and experimental detection by Lalanne *et al.* [10], of cooperative hyper-Rayleigh light-scattering in liquids with molecules having a centre of symmetry. Also, the possibility of hyper-Rayleigh scattering by atoms and centrosymmetric molecules was discussed in an electric quadrupole approximation [11]. The feasibility of SHS observations in atomic substances as the result of many-body distortion effects was considered [12]. Freund [13] studied SHS on fluctuations near the critical point in  $\text{NH}_4\text{Cl}$ .

Subsequent experimental work applying perfected laser techniques of measurement permitted a closer structural analysis of the spectra of non-linearly scattered light. Maker [14], experimenting with compressed methane, initiated the study of the rotational structure of the hyper-Rayleigh line. He moreover proposed a theoretical interpretation of the spectrum obtained, which is valid for spherical top molecules. The rotational structure of the hyper-Rayleigh line is discussed for linear as well as symmetric top molecules in references [15] and [16]. Maker [17], too, was the first to measure the spectral distribution of hyper-Rayleigh scattered light from liquids, and proposed a theory of the effect based on the assumption that the distribution is related with the Fourier transform of an orientational positional molecule pair distribution function  $G(\mathbf{r}, \Omega, t)$  of the Van Hove type. When interpreting his spectra, Maker assumed the molecules of the liquid to perform self-diffusional Brownian motion, i.e. he approximated the function  $G(\mathbf{r}, \Omega, t)$  by the self-diffusional single-molecule function  $G_s(\mathbf{r}, \Omega, t)$  and, neglecting the contribution of translational motion to the line width, explained the experimental line broadening in terms of free rotational motion of the molecules in the liquid. Recently, Maker's approach has been extended to the case of asymmetric top molecules [18]. Also, a theory of the spectral distribution of hyper-Raman scattered light has been proposed [19]. Quite recently, Yu and Alfano [20] have observed three and four-photon scattering in diamond and determined the spectra of these scattering phenomena.

The present paper contains a discussion of the part played in hyper-Rayleigh scattering by the correlation function  $G_c(\mathbf{r}, \Omega, t)$ , the existence of which is due to correlation, in liquids, between the motions of molecules in regions of short-range quasi-order.

Section 2 contains a discussion of the spectral line theory for SHS radiation. Applying Steele and Pecora's method [21] of expanding  $G_s(\mathbf{r}, \Omega, t)$  and  $G_c(\mathbf{r}, \Omega, t)$  in angular momentum terms describing the orientation of the molecule, we calculate the shape of the spectral component  $S_s^{2\omega}(\mathcal{H}, \Delta\omega)$ , due to self-diffusion of the molecule, and the component  $S_c^{2\omega}(\mathcal{H}, \Delta\omega)$ , due to scattering by correlated molecules. Next, for the calculation of  $G_c(\mathbf{r}, \Omega, t)$ , we follow the approximation of Vineyard [22], who assumes that the molecules are mutually correlated at the moment of time  $t=0$ , whereas at  $t>0$  they perform self-diffusional motion.

In § 3 we discuss in detail the SHS component  $S_c^{2\omega}(\mathcal{H}, \Delta\omega)$  on the assumption of a well-specified intermolecular interaction. The dipole-dipole interaction energy is assumed as predominant with respect to all multipole interaction energies and the  $S_c^{2\omega}(\mathcal{H}, \Delta\omega)$  spectrum is shown to be given by the difference of two lorentzians, with relaxation times  $\tau_0^1$  and  $\tau_0^3$  defined by the self-diffusing molecule and height dependent on a parameter  $\gamma'(\mathcal{H})$ , defined by the intermolecular interactions. It is also shown that, on integration with respect to

frequency, the formulae derived in this paper for the SHS spectral distribution go over into the well-known expressions for integral intensity [4, 7].

## 2. THEORY OF THE SPECTRAL LINE OF HYPER-RAYLEIGH SCATTERED LIGHT

We consider scattering of linearly polarized laser light

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0 \exp [i(\mathbf{k}_0 \cdot \mathbf{r} - \omega t)]$$

by a molecular medium consisting of a large number  $N$  of non-centrosymmetric molecules. A system of laboratory coordinates  $xyz$  is rigidly attached to the scattering medium; the incident light propagates in the direction of the  $y$ -axis and is polarized along  $z$ . Observation is assumed to be performed perpendicularly, along the  $x$ -axis. Let  $\theta$  denote the angle between the principal plane of the analyser and the laboratory  $xz$ -plane. The spectrum of light scattered at frequency  $2\omega$  is expressed by the formula [17]

$$I^{2\omega}(\mathcal{H}, \Delta\omega) = \frac{c}{4\pi} \mathcal{F}_t \langle E_R^{2\omega}(t'+t) * E_R^{2\omega}(t') \rangle, \quad (1)$$

with scattering phases  $\mathcal{H} = \mathbf{k}_s - 2\mathbf{k}_0$ ;  $\Delta\omega$  is the line broadening, measured with respect to the central line  $2\omega$ ;  $\mathcal{F}_t$  is the Fourier time transform; the symbol  $\langle \rangle$  denotes time and ensemble averaging.  $E_R^{2\omega}(t)$ , the electric field of the SHS light wave is given by the expression

$$E_R^{2\omega}(t) = -2\pi \left( \frac{n_{2\omega}^2 + 2}{3} \right) \left( \frac{n_\omega^2 + 2}{3} \right)^2 \frac{(2\omega)^2}{c^3 R} I_0 \times \sum_{j=1}^N p_0^{2\omega}[\Omega_j(t)] \exp \{i[2\mathbf{k}_0 \cdot \mathbf{r}_j(t) - 2\omega(t - R_j/c)]\}, \quad (2)$$

with  $I_0$  the incident light intensity, and

$$p_0^{2\omega}[\Omega_j(t)] = b_{zzz}^{2\omega}[\Omega_j(t)] \cos \theta + b_{yzz}^{2\omega}[\Omega_j(t)] \sin \theta, \quad (3)$$

where  $b_{rst}^{2\omega}$  is the molecular hyperpolarizability tensor at  $2\omega$  in the laboratory reference system,  $\Omega_j(t)$  stands for the set of Euler angles, defining the orientation of the  $j$ th molecule, and  $n_\omega, n_{2\omega}$  are the refractive indices at  $\omega$  and  $2\omega$ , respectively.

On insertion of (2) into (1) and introducing the notation

$$I^{2\omega}(\mathcal{H}, \Delta\omega) = A^{2\omega} S^{2\omega}(\mathcal{H}, \Delta\omega), \quad (4)$$

we obtain :

$$S^{2\omega}(\mathcal{H}, \Delta\omega) = \mathcal{F}_t \left\langle \sum_{j,k=1}^N p_0^{2\omega}[\Omega_j(t+t')] * p_0^{2\omega}[\Omega_k(t')] \times \exp \{i \mathcal{H} \cdot [\mathbf{r}_j(t+t') - \mathbf{r}_k(t')]\} \right\rangle, \quad (5)$$

$$A^{2\omega} = \frac{\pi(2\omega)^4}{2R^2 c^5} \left( \frac{n_{2\omega}^2 + 2}{3} \right)^2 \left( \frac{n_\omega^2 + 2}{3} \right)^4 I_0^2. \quad (6)$$

We shall be assuming that the origin of the time axis is fixed in a manner to have  $t' = 0$ , and proceed to calculate in detail the average over the statistical

ensemble in equation (5). The sum over the  $N$  molecules in (5) decomposes into the two sums  $i = j$  and  $i \neq j$ . For averaging, we introduce generalized Van Hove [23] space-time functions: self  $G_s[\tau_1(t), \tau_1(0)]$ , and correlation  $G_c[\tau_1(t), \tau_2(0)]$  [17, 24], where  $\tau$  stands for the set of positional variables  $\mathbf{r}$  and orientational variables  $\Omega$  of the molecule†. The expression for  $S^{2\omega}(\mathcal{H}, \Delta\omega)$  now takes the form of the sum:

$$S^{2\omega}(\mathcal{H}, \Delta\omega) = S_s^{2\omega}(\mathcal{H}, \Delta\omega) + S_c^{2\omega}(\mathcal{H}, \Delta\omega), \quad (7)$$

where

$$S_s^{2\omega}(\mathcal{H}, \Delta\omega) = \mathcal{F}_l \frac{\rho}{8\pi^2} \iint p_0^{2\omega}[\Omega_1(t)]^* p_0^{2\omega}[\Omega_1(0)] \\ \times \exp\{i\mathcal{H} \cdot [\mathbf{r}_1(t) - \mathbf{r}_1(0)]\} G_s[\tau_1(t), \tau_1(0)] d\tau_1(t) d\tau_1(0), \quad (8a)$$

$$S_c^{2\omega}(\mathcal{H}, \Delta\omega) = \mathcal{F}_l \frac{\rho^2}{8\pi^2} \iint p_0^{2\omega}[\Omega_1(t)]^* p_0^{2\omega}[\Omega_2(0)] \\ \times \exp\{i\mathcal{H} \cdot [\mathbf{r}_1(t) - \mathbf{r}_2(0)]\} G_c[\tau_1(t), \tau_2(0)] d\tau_1(t) d\tau_2(0). \quad (8b)$$

The self-function  $G_s[\tau_1(t), \tau_1(0)]$  has the meaning of the probability of finding molecule 1 at the moment of time  $t$  with the coordinates  $\tau_1(t)$  if its coordinates at  $t=0$  were  $\tau_1(0)$ . The correlation function  $G_c[\tau_1(t), \tau_2(0)]$  defines the probability of finding molecule 1 with the coordinates  $\tau_1(t)$  at the moment of time  $t$  if, at  $t=0$ , molecule 2 had the coordinates  $\tau_2(0)$ .

Further, so as not to complicate our formulae, we shall be considering the spectral distribution of the polarized component  $I_z^{2\omega}$  of scattered light, i.e. we shall put  $\theta=0^\circ$ . Also, we shall consider scattering by a unit volume of the medium. Hence, and on the assumption of translation-invariant molecular functions  $G_s$  and  $G_c$ , we obtain by (8a) and (8b):

$$S_s^{2\omega}(\mathcal{H}, \Delta\omega) = \frac{\rho}{8\pi^2} \mathcal{F}_l \iiint b_{zzz}^{2\omega}[\Omega_1(t)]^* b_{zzz}^{2\omega}[\Omega_1(0)] \\ \times G_s[\Omega_1(t), \Omega_1(0), \mathbf{r}_l] \exp(i\mathcal{H} \cdot \mathbf{r}_l) d\Omega_1(t) d\Omega_1(0) d\mathbf{r}_l, \quad (9)$$

where  $\mathbf{r}_l = \mathbf{r}_1(t) - \mathbf{r}_1(0)$ , and

$$S_c^{2\omega}(\mathcal{H}, \Delta\omega) = \frac{\rho^2}{16\pi^3} \mathcal{F}_l \iiint b_{zzz}^{2\omega}[\Omega_1(t)]^* b_{zzz}^{2\omega}[\Omega_2(0)] \\ \times G_c[\Omega_1^{12}(t), \Omega_2^{12}(0), \mathbf{r}_{12}] \exp(i\mathcal{H} \cdot \mathbf{r}_{12}) d\Omega_1^{12}(t) d\Omega_2^{12}(0) d\Omega_{12} r_{12}^2 dr_{12}, \quad (10)$$

where  $\mathbf{r}_{12} = \mathbf{r}_1(t) - \mathbf{r}_2(0)$ .

In the above,  $\rho$  is the number of molecules per unit volume; whereas  $\Omega_1^{12}$ ,  $\Omega_2^{12}$  stands for the orientation of the molecules 1 and 2 with respect to a system of coordinates, the  $z$ -axis of which is directed along the vector  $\mathbf{r}_{12}$ ;

† Van Hove [23] introduces the positional time pair distribution function  $G(\mathbf{r}, t)$ , which he decomposes into a self-function  $G_s[\mathbf{r}_1(t), \mathbf{r}_1(0)]$  and a distinct function  $G_d[\mathbf{r}_1(t), \mathbf{r}_2(0)]$ . Ours is an orientational-positional-time pair distribution function  $G(\tau, t)$ , with  $\tau = \Omega, \mathbf{r}$ , which we decompose into a self-function  $G_s[\tau_1(t), \tau_1(0)]$ , or autocorrelation function, and a function analogous to Van Hove's  $G_d$  which, however, we prefer to denote as the correlation function  $G_c[\tau_1(t), \tau_2(0)]$ , accounting essentially for correlation between molecules.

$\Omega_{12}$  denotes the orientation of the vector  $\mathbf{r}_{12}$  in the system of laboratory coordinates  $xyz$  [24].

The explicit form of  $G_s$  and  $G_c$  is, in general, not known. Especially, we know very little about the function  $G_c$ . Nonetheless, following the procedure of Steele and Pecora [21], we can expand the two functions in the set of orthonormal functions  $D'^J_{KM}[\Omega] = \sqrt{(2J+1/8\pi^2)}D^J_{KM}[\Omega]$  (where the  $D^J_{KM}[\Omega]$  are Wigner matrices) :

$$G_s[\Omega_1(t), \Omega_1(0), \mathbf{r}_i] = \sum_{JKMM'} f'_{MM'}(\mathbf{r}_i, t) D'^J_{KM}[\Omega_1(t)] D'^J_{KM}[\Omega_1(0)]^*, \quad (11)$$

$$G_c[\Omega_1^{12}(t), \Omega_2^{12}(0), \mathbf{r}_{12}] = \sum_{\substack{J(1), K(1), M(1) \\ J(2), K(2), M(2)}} g^{J(1), J(2)}_{K(1), M(1), K(2), M(2)}(\mathbf{r}_{12}, t) \\ \times D'^{J(1)}_{K(1), M(1)}[\Omega_1^{12}(t)] D'^{J(2)}_{K(2), M(2)}[\Omega_2^{12}(0)], \quad (12)$$

and insert the expansions into equations (9) and (10), thus considerably simplifying the problem of integration over the orientations. The task becomes quite simple on transforming the cartesian tensors  $b^{2\omega}_{zzz}$ , occurring in equations (9) and (10), to spherical coordinates, [17] :

$$b^{2\omega}_{rst}[\Omega] = \sum_{klm} c^{klm}_{rst} B^l_m{}^k[\Omega], \quad (13)$$

as now the transformation from the laboratory to the molecular coordinate system is of the form [25] :

$$B^l_m[\Omega] = \sum_{m'} D^l_{mm'}[\Omega] \tilde{B}^l_{m'} \quad (14)$$

and the two formulae (9) and (10) become orientation-dependent by way of Wigner matrices  $D^l_{KM}[\Omega]$  only. On carrying out the integration, we obtain

$$S_s^{2\omega}(\mathcal{H}, \Delta\omega) = \mathcal{F} \rho^2 \int \left\{ \frac{1}{5} \sum_{m_1, m_2} f^1_{m_1, m_2}(\mathbf{r}_i, t) \tilde{B}^{1*}_{m_1} \tilde{B}^1_{m_2} \right. \\ \left. + \frac{2}{3^5} \sum_{m_3, m_4} f^3_{m_3, m_4}(\mathbf{r}_i, t) \tilde{B}^{3*}_{m_3} \tilde{B}^3_{m_4} \right\} \exp(i\mathcal{H} \cdot \mathbf{r}_i) d\mathbf{r}_i, \quad (15 a)$$

$$S_c^{2\omega}(\mathcal{H}, \Delta\omega) = \mathcal{F} \rho^2 \int \left\{ \frac{1}{15} \sum_{R, m_1, m_2} (-1)^{R-m_2} g^1_{R, m_1, -R, -m_2}(\mathbf{r}_{12}, t) \right. \\ \times \tilde{B}^{1*}_{m_1} \tilde{B}^1_{m_2} + \frac{2}{2 \cdot 4^5} \sum_{R, m_3, m_4} (-1)^{R-m_4} g^3_{R, m_3, -R, -m_4}(\mathbf{r}_{12}, t) \\ \left. \times \tilde{B}^{3*}_{m_3} \tilde{B}^3_{m_4} \right\} \frac{\sin \mathcal{H} r_{12}}{\mathcal{H} r_{12}} 4\pi r_{12}^2 dr_{12}. \quad (15 b)$$

The formulae derived above are of a general nature. However, when it comes to determining the explicit form of the expansion coefficients  $f'_{M, M'}(\mathbf{r}_i, t)$  and  $g^{J(1), J(2)}_{K(1), M(1), K(2), M(2)}(\mathbf{r}_{12}, t)$ , one has to make assumptions specifying the model of molecular motion in the liquid. We shall now discuss the shape of equations (15 a) and (15 b) for the following conditions.

(i) When calculating  $G_s[\Omega_1(t), \Omega_1(0), \mathbf{r}_i]$ , we assume [26, 27] :

(1) translation and orientational motion as mutually independent :

$$G_s[\Omega_1(t), \Omega_1(0), \mathbf{r}_i] = G_R[\Omega_1(t), \Omega_1(0)] G_T(\mathbf{r}_i). \quad (16)$$

(2) translation and orientational motion as free, i.e.  $G_T$  and  $G_R$  as solutions of the following equations :

$$\frac{\partial G_T}{\partial t} = D_T \Delta G_T, \quad (17 a)$$

$$\frac{\partial G_R}{\partial t} = \hat{L}_j D_{jk}^R \hat{L}_k G_R, \quad (17 b)$$

in (17 a),  $D_T$  is the coefficient of translational diffusion ; in (17 b),  $D_{jk}^R$  is the tensor of rotational diffusion ; and  $\hat{L}_j$ ,  $\hat{L}_k$  are operator components of molecular angular momentum.

(ii) When calculating  $G_c[\tau_1(t), \tau_2(0)]$ , we assume that the approximation proposed by Vineyard [22] :

$$G_c[\tau_1(t), \tau_2(0)] = \int g^{(2)}[\tau_1(0), \tau_2(0)] G_s[\tau_1(t) - \tau_2(0), t] d\tau_1(0), \quad (18)$$

is applicable ( $g^{(2)}[\tau_1(0), \tau_2(0)]$  is the equilibrium pairwise correlation function). Vineyard assumes that the molecules are correlated at the moment of time  $t=0$  and that, at  $t>0$ , they move in conformity with the laws of self-diffusion.

The solution of (17 a) is given by a Smoluchowski function of the form

$$\mathcal{G}_T(r, t) = \frac{1}{(4\pi D_T t)^{3/2}} \exp\left(-\frac{r^2}{4D_T t}\right), \quad (19)$$

whereas that of (17 b), on the assumption that the molecules are of the symmetric top, i.e. that the tensor  $D_{ij}^R$  is diagonal and  $D_1^R = D_2^R \neq D_3^R$ , is given by coefficients  $f_{MM}^J(t)$  of the expansion of  $G_R$  in Wigner functions  $D_{KM}^{J*}[\Omega_1(0)]$ ,  $D_{KM}^J[\Omega_1(t)]$  [26] :

$$f_{MM}^J(t) = \delta_{MM'} \exp\left(-\frac{t}{\tau_M^J}\right), \quad (20)$$

where

$$\tau_M^J = [J(J+1)D_1^R + M^2(D_3^R - D_1^R)]^{-1}.$$

On insertion of (19) and (20) into (15 a) and on calculation of the complete Fourier transform, we finally obtain, with regard to the explicit form of the non-zero parameters  $|\tilde{B}_M^J|^2$  for non-centrosymmetric molecules [15] :

$$S_s^{2\omega}(\mathcal{H}, \Delta\omega) = \rho \left\{ \frac{1}{5} g_{00}^1(\mathcal{H}, \Delta\omega) |\tilde{B}_0^1|^2 + \frac{2}{35} \sum_M g_{MM}^3(\mathcal{H}, \Delta\omega) |\tilde{B}_M^3|^2 \right\}, \quad (21)$$

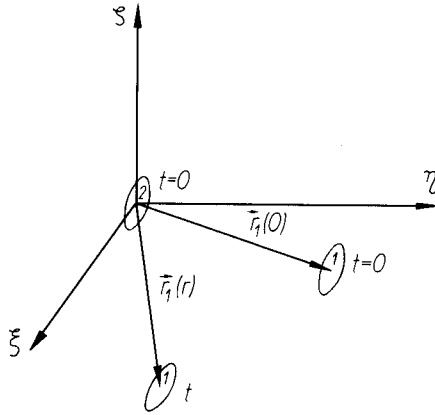
where

$$g_{MM}^J(\mathcal{H}, \Delta\omega) = \frac{2 \left( \frac{1}{\tau_M^J} + \mathcal{H}^2 D_T \right)}{\left( \frac{1}{\tau_M^J} + \mathcal{H}^2 D_T \right)^2 + (\Delta\omega)^2}. \quad (22)$$

This result is in agreement with that of Maker [17].

In order to achieve a higher degree of clarity in the presentation of our calculations leading to  $S_c^{2\omega}(\mathcal{H}, \Delta\omega)$ , we introduce the following system of

co-ordinates for the analysis of the function  $G_c[\tau_1(t), \tau_2(0)]$  :



By (18), we now have

$$G_c[\tau_1(t), \tau_2(0)] = \frac{1}{3k^2} \int \int g^{(2)}[\tau_1(0), \tau_2(0)] \mathcal{G}_T[\mathbf{r}_1(t) - \mathbf{r}_1(0), t] \times \mathcal{G}_R[\Omega_1(t) - \Omega_1(0), t] d\mathbf{r}_1(0) d\Omega_1(0), \quad (23)$$

where

$$g^{(2)}[\tau_1(0), \tau_2(0)] = 8\pi^2 \sum_{N(1), N(2)} g_{K(1), M(1), K(2), M(2)}^{J(1), J(2)}[\mathbf{r}_1(0)] \times D'^{J(1)}_{K(1), M(1)}[\Omega_1^{12}(0)] D'^{J(2)}_{K(2), M(2)}[\Omega_1^{12}(0)], \quad (24)$$

$$\mathcal{G}_R[\Omega_1(t) - \Omega_1(0), t] = \sum_{JKMM'} f_{MM'}^J(t) D'^J_{KM}[\Omega_1(t)] D'^{J*}_{KM}[\Omega_1(0)]. \quad (25)$$

On insertion of the expansions (24), (25) into (23) and of (23) into (10), and on integrating over orientations, we obtain

$$S_c^{2\omega}(\mathcal{H}, \Delta\omega) = \rho^2 \mathcal{F}_t \int \left\{ \frac{1}{15} \sum_{R, m_1, m_2} (-1)^{R-m_2} \times \tilde{g}_{R, m_1, -R, -m_2}^1[r_1(t), t] \tilde{B}_{m_1}^{1*} \tilde{B}_{m_2}^1 + \frac{2}{245} \sum_{R, m_3, m_4} (-1)^{R-m_4} \times \tilde{g}_{R, m_3, -R, -m_4}^3[r_1(t), t] \tilde{B}_{m_3}^{3*} \tilde{B}_{m_4}^3 \right\} \exp[i\mathcal{H} \cdot \mathbf{r}_1(t)] d\mathbf{r}_1(t), \quad (26)$$

where  $\tilde{g}_{N(1), N(2)}[\mathbf{r}_1(t), t]$  is of the following form [21, 27] :

$$\tilde{g}_{K(1), M(1), K(2), M(2)}^{J(1), J(2)}[\mathbf{r}_1(t), t] = 8\pi^{\frac{1}{2}} \sum_{M'} f_{M', M(1)}^{(1)}(t) \times \int g_{K(1), M', K(2), M(2)}^{J(1), J(2)}[\mathbf{r}_1(0)] \mathcal{G}_T[\mathbf{r}_1(t) - \mathbf{r}_1(0), t] d\mathbf{r}_1(0). \quad (27)$$

We occasionally write  $N(1)$  ;  $N(2)$  to denote the set of numbers  $J(1), K(1), M(1)$  ;  $J(2), K(2), M(2)$ .

Integration over  $\mathbf{r}_1(t)$  and the calculation of the Fourier time transform in (26) is equivalent to calculating the complete Fourier transform. On applying the theorem concerning the transform of a convolution of functions, we have

$$S_c^{2\omega}(\mathcal{H}, \Delta\omega) = \rho^2 \int \frac{1}{15} \sum_{R, m_1, m_2, M'} (-1)^{R-m_2} \Gamma_{M', m_1}^{v1}(\mathcal{H}, \Delta\omega)$$

$$\begin{aligned} & \times \gamma_{R, M', -R, -m_2}^{1,1}(\mathcal{H}) \tilde{B}_{m_1}^{1*} \tilde{B}_{m_2}^1 + \frac{2}{\sqrt{45}} \sum_{m_3, m_4, R, M'} (-1)^{R-m_4} \\ & \times \Gamma_{M', m_3}^{\prime 3}(\mathcal{H}, \Delta\omega) \gamma_{R, M', -R, -m_4}^{3,3}(\mathcal{H}) \tilde{B}_{m_3}^{3*} \tilde{B}_{m_4}^3 \}, \quad (28) \end{aligned}$$

where, assuming the molecules to be of the symmetric top :

$$\Gamma_{M, M'}^{\prime J}(\mathcal{H}, \Delta\omega) = \frac{2 \left( \frac{1}{\tau_M^J} + \mathcal{H}^2 D_T \right)}{\left( \frac{1}{\tau_M^J} + \mathcal{H}^2 D_T \right)^2 + (\Delta\omega)^2} \delta_{MM'}, \quad (29)$$

whereas the radial correlation parameters

$$\gamma_{N(1), N(2)}(\mathcal{H}) = 4\pi \int_0^\infty g_{N(1), N(2)}(r) \frac{\sin \mathcal{H}r}{\mathcal{H}r} r^2 dr, \quad (30)$$

are of a form similar to that derived by Berson *et al.* [6].

Single-molecule hyper-Rayleigh light-scattering can take place only for molecules without a centre of symmetry [4]. With regard to the shape taken by the non-zero parameters  $\tilde{B}_M^J$  for such molecules, equation (28) reduces to

$$\begin{aligned} S_c^{2\omega}(\mathcal{H}, \Delta\omega) &= \rho^2 \left\{ \frac{1}{15} \Gamma_{0,0}^{\prime 1}(\mathcal{H}, \Delta\omega) \gamma_{0,0}^{\prime 1,1}(\mathcal{H}) |\tilde{B}_0^1|^2 \right. \\ & \left. + \frac{2}{\sqrt{45}} \sum_M \Gamma_{MM}^{\prime 3}(\mathcal{H}, \Delta\omega) \sum_m (-1)^m \gamma_{M,-m}^{\prime 3,3}(\mathcal{H}) \tilde{B}_M^{3*} \tilde{B}_m^3 \right\}, \quad (31) \end{aligned}$$

where

$$\gamma_{M,-m}^{\prime J,J}(\mathcal{H}) = \sum_R (-1)^R \gamma_{R,M,-R,-m}^{\prime J,J}(\mathcal{H}). \quad (31 a)$$

Equation (31) states that, in the approximation made here when calculating  $G_c$ , the contribution to the light-scattering spectrum from scattering by correlated molecules is a sum of Lorentz lines, the characteristic relaxation times of which are identical to those of self-diffusion scattering. This statement results on comparison of equations (22) and (29). The intermolecular correlations, described by the factors  $\gamma_{N(1), N(2)}(\mathcal{H})$  (30), modify the heights of the individual Lorentz lines. The lines height related with the relaxation time  $\tau_0$  has to be multiplied by  $\frac{1}{3} \gamma_{0,0}^{\prime 1,1}(\mathcal{H})$ , whereas those related with relaxation times  $\tau_M^3$  by  $\frac{1}{7} \sum_m (-1)^m \gamma_{M,-m}^{\prime 3,3}(\mathcal{H})$ .

On frequency integration of (31), we obtain for the integral intensity of radiation, scattered by correlated molecules :

$$S_c^{\text{integ}}(\mathcal{H}) = \rho^2 \left\{ \frac{1}{15} \gamma_{0,0}^{\prime 1,1}(\mathcal{H}) |\tilde{B}_0^1|^2 + \frac{2}{\sqrt{45}} \sum_{M,m} (-1)^m \gamma_{M,-m}^{\prime 3,3}(\mathcal{H}) \tilde{B}_M^{3*} \tilde{B}_m^3 \right\}. \quad (32)$$

It will be shown in § 3 that, for a specified model of intermolecular interaction [28], equation (32) coincides with the formulae previously derived by Kielich [7].

### 3. ANALYSIS OF THE CONTRIBUTION $S_c^{2\omega}(\mathcal{H}, \Delta\omega)$ FOR A SELECTED MODEL OF INTERMOLECULAR INTERACTION

We shall now analyse in detail the contribution to the light-scattering spectrum from correlated molecules on the assumption that dipole-dipole



energy predominates in the total interaction energy of electric multipoles in the liquid. The assumption seems justified since, in order to cause hyper-Rayleigh light-scattering, the molecules of the liquid cannot possess a centre of symmetry, and thus fulfil the pre-condition for possessing a permanent electric dipole moment. The expansion coefficients  $g_{K(1), M(1), K(2), M(2)}^{J(1), J(2)}(\mathbf{r})$  of equation (30) required for our analysis are accessible to calculations once we know the form of the equilibrium two-molecule distribution function  $g^{(2)}(\tau_1, \tau_2)$ , since then

$$g_{K(1), M(1), K(2), M(2)}^{J(1), J(2)}(\mathbf{r}_{12}) = \frac{1}{8\pi^2} \iint g^{(2)}(\tau_1, \tau_2) D_{K(1), M(1)}^{J(1)*}[\Omega_1^{12}] \times D_{K(2), M(2)}^{J(2)*}[\Omega_2^{12}] d\Omega_1^{12} d\Omega_2^{12}. \quad (33)$$

On calculating  $g^{(2)}(\tau_1, \tau_2)$  with the Yvon-Born-Green-Kirkwood equation (e.g. [29]) and rejecting all but the two-molecule correlation, we obtain [7]

$$g^{(2)}(\tau_1, \tau_2) = \exp \left[ -\frac{U(\tau_1, \tau_2)}{kT} \right], \quad (34)$$

where  $U(\tau_1, \tau_2)$  is the potential energy of interaction between two molecules and can be written in the form of the sum

$$U(\tau_1, \tau_2) = U_A(\Omega_1, \Omega_2, \mathbf{r}_{12}) + U_R(\mathbf{r}_{12}). \quad (35)$$

$U_A(\Omega_1, \Omega_2, \mathbf{r}_{12})$  is the energy of angular interaction of electric multipoles [28], whereas  $U_R(\mathbf{r}_{12})$  is that of radial interaction of the molecules.

Since usually  $U_A \ll kT$ , one is justified in expanding  $\exp(-U_A/kT)$  in  $U_A/kT$ , whence

$$g^{(2)}(\tau_1, \tau_2) = g(\mathbf{r}_{12}) \sum_{n=0}^{\infty} \frac{1}{n!} \left( -\frac{U_A}{kT} \right)^n. \quad (36)$$

Assuming dipole-dipole energy, one has [30]

$$U_A(\Omega_1, \Omega_2, \mathbf{r}_{12}) = -r_{12}^{-3} \mu^2 \frac{8\pi^2}{3} (2D'_{00}{}^1[\Omega_1^{12}]D'_{00}{}^1[\Omega_2^{12}] + D'_{10}{}^1[\Omega_1^{12}]D'_{-10}{}^1[\Omega_2^{12}] + D'_{-10}{}^1[\Omega_1^{12}]D'_{10}{}^1[\Omega_2^{12}]), \quad (37)$$

with  $\mu$  the permanent electric dipole moment of the molecule.

We shall calculate the coefficients  $g_{N(1), N(2)}(\mathbf{r}_{12})$  with accuracy to the fourth term of the expansion (36) inclusively.

By (30) and (31), SHS is described by those coefficients  $g_{N(1), N(2)}(\mathbf{r}_{12})$  for which  $J=1$  and 3. Such terms are obtained in the first and third approximations. The terms obtained in the second approximation are related to linear light-scattering [31, 32]. On calculating higher and higher powers of the energy  $U_A$  of equation (37) and performing integration in conformity with (33), we obtain :

(i) In the first approximation

$$\left. \begin{aligned} g_{0,0,0,0}^1(\mathbf{r}_{12}) &= \frac{2}{3} J_1(\mathbf{r}_{12}), \\ g_{-1,0,1,0}^1(\mathbf{r}_{12}) &= g_{1,0,-1,0}^1(\mathbf{r}_{12}) = \frac{1}{3} J_1(\mathbf{r}_{12}). \end{aligned} \right\} \quad (38)$$

(ii) In the third approximation

$$\left. \begin{aligned} g_{0,0,0,0}^{1,1,0,0}(r_{12}) &= \frac{1}{75} J_3(r_{12}), \\ g_{-1,0,1,0}^{1,1,0,0}(r_{12}) &= g_{1,0,-1,0}^{1,1,0,0}(r_{12}) = \frac{4}{75} J_3(r_{12}), \\ g_{0,0,0,0}^{3,3,0,0}(r_{12}) &= \frac{2}{525} J_3(r_{12}), \\ g_{-1,0,1,0}^{3,3,0,0}(r_{12}) &= g_{1,0,-1,0}^{3,3,0,0}(r_{12}) = \frac{17}{525} J_3(r_{12}), \\ g_{-2,0,2,0}^{3,3,0,0}(r_{12}) &= g_{2,0,-2,0}^{3,3,0,0}(r_{12}) = \frac{2}{105} J_3(r_{12}), \\ g_{-3,0,3,0}^{3,3,0,0}(r_{12}) &= g_{3,0,-3,0}^{3,3,0,0}(r_{12}) = \frac{1}{105} J_3(r_{12}), \end{aligned} \right\} \quad (39)$$

where we have introduced the notation  $J_n(r_{12}) = \beta^n \mu^{2n} r_{12}^{-3n} g(r_{12})$ . The remaining values of  $g_{N(1), N(2)}(r_{12})$  vanish in the approximation applied here.

Analysis of the above results shows that the only non-zero components of  $g_{N(1), N(2)}(r_{12})$  are of the type  $g_{R,0,-R,0}^{1,1,0,0}(r_{12})$  and  $g_{R,0,-R,0}^{3,3,0,0}(r_{12})$ , whence, in the approximation under consideration,  $S_c$  depends solely on the hyperpolarizability components  $\tilde{B}_0^1$  and  $\tilde{B}_0^3$  of the molecule and the sole relaxation times to be related to light-scattering by mutually correlated molecules are  $\tau_0^1$  and  $\tau_0^3$ . Moreover, analysis of the values (38) reveals that the contribution to SHS from the first approximation is but apparent, since with regard to (31 a) and (38) we have

$$\gamma'_{0,0}^{1,1}(\mathcal{H}) = \sum_R (-1)^R \gamma_{R,0,-R,0}^{1,1}(\mathcal{H}) = 0. \quad (40)$$

Consequently, the lowest contribution to SHS comes from the third approximation [7].

With regard to equation (31) and the values of coefficients (39), the intensity of the SHS radiation scattered on correlated molecules amounts to

$$S_c^{2\omega}(\mathcal{H}, \Delta\omega) = \rho^2 \left\{ \left( \frac{1}{15} \right) \left( \frac{2}{25} \right) \Gamma'_{0,0}{}^1(\mathcal{H}, \Delta\omega) \gamma'(\mathcal{H}) |\tilde{B}_0^1|^2 - \left( \frac{2}{45} \right) \left( \frac{2}{525} \right) \Gamma'_{0,0}{}^3(\mathcal{H}, \Delta\omega) \gamma'(\mathcal{H}) |\tilde{B}_0^3|^2 \right\}, \quad (41)$$

where

$$\gamma'(\mathcal{H}) = 4\pi\beta^3\mu^6 \int_0^\infty r_{12}^{-9} g(r_{12}) \frac{\sin \mathcal{H} r_{12}}{\mathcal{H} r_{12}} r_{12}^2 dr_{12}. \quad (41 a)$$

On performing in (41) an integration over  $\Delta\omega$ , the integral intensity of scattered radiation is found to be

$$S_c^{\text{integ}}(\mathcal{H}) = \rho^2 \left\{ \left( \frac{1}{15} \right) \left( \frac{2}{25} \right) \gamma'(\mathcal{H}) |\tilde{B}_0^1|^2 - \left( \frac{2}{45} \right) \left( \frac{2}{525} \right) \gamma'(\mathcal{H}) |\tilde{B}_0^3|^2 \right\}. \quad (42)$$

On going over to  $\mathcal{H} \rightarrow 0$  in (42), one obtains the result previously derived by Kielich [7]. Similar analyses can be performed for electric multipole correlations [28] as well as dispersive London interactions [31].

#### 4. DISCUSSION AND CONCLUSIONS

As seen from equation (41) in the present approximation the contribution to the spectrum from scattering by mutually correlated molecules is equal to the difference of two Lorentzians with half-widths  $2[(1/\tau_0^{1,3}) + \mathcal{H}^2 D_T]$  and heights

proportional to their correlation parameters  $\gamma'(\mathcal{H})\dagger$ . Hence, with regard to our results, if Vineyard's approximation is applied in calculating  $G_c[\tau_1(t), \tau_2(0)]$ , scattering on correlated molecules is defined by relaxation times with values determined by self-diffusional scattering. The molecular correlations define the statistical weights of the respective lines, composing the total scattered spectrum. Our result, stating that the only relaxation times active in  $S_c^{2\omega}(\mathcal{H}, \Delta\omega)$  are the times  $\tau_0^1$  and  $\tau_0^3$ , is a consequence of the dipole-dipole intermolecular interaction approximation assumed. The inclusion of higher multipolar interactions in the expression for the energy  $U_A[\Omega_1, \Omega_2, r_{12}]$  will lead to the occurrence in equation (41) of terms with relaxation times  $\tau_M^3$ , for which  $M \neq 0$ . However, from Steele's work [30], if a molecule possesses a symmetry  $z$ -axis of order  $n$ , the values permitted for  $M$  are  $0, \pm n, \pm 2n, \dots$  only. Hence, for molecules with a three-fold symmetry axis, only the relaxation times  $\tau_0^1, \tau_0^3$  and  $\tau_{\pm 3}^3$  are permitted, whereas in the case of molecules of higher symmetry only times  $\tau_0^1, \tau_0^3$  can occur in the correlation-scattering spectrum. Moreover, since dipole-dipole interaction predominates, the statistical weight for lines with  $\tau_M^3, M \neq 0$  yields but a small contribution to the total spectrum. We hence deduce tentatively that scattering by correlated molecules is defined essentially by the relaxation times  $\tau_0^1$  and  $\tau_0^3$ .

Besides, equation (41) leads to the following interesting conclusions :

(i) Molecules for which the hyperpolarizability tensor elements  $\tilde{B}_0^1$  and  $\tilde{B}_0^3$  vanish, cause no correlation scattering (in the present approximation); (ii)  $S_c^{2\omega}(\mathcal{H}, \Delta\omega)$  from arbitrarily symmetric molecules, active in single-molecule hyper-Rayleigh scattering, has to be identical to correlation scattering by linear molecules having hyperpolarizability tensor elements equal to the tensor elements  $\tilde{B}_0^1$  and  $\tilde{B}_0^3$  of the former; (iii) the intensity of the spectral line of correlation hyper-Rayleigh scattering depends on temperature decreasing with the third power of the latter,  $T^{-3}$ . Our conclusion regarding the equality of the relaxation times for the spectral distribution of light intensity scattered by correlated molecules and that of self-diffusional scattering differs from the conclusion drawn by the authors of references [33] and [34], who calculate the spectrum of linearly scattered light applying Mori's theory. Albeit, the Vineyard approximation, to which we have recourse, permits one to analyse the influence of intermolecular interaction on the spectrum. This would be beset with considerable difficulties if proceeding by Mori's approach.

By integrating equation (41) over  $\Delta\omega$  we obtained an expression for the integral intensity in agreement with the one previously derived in the literature [7]. This proves that the curve of (41) determines a spectral distribution of scattered light under which the area is defined correctly.

Any further development of the method proposed here will have to apply a corrected Vineyard approximation [35]. Moreover, the role of the molecular fields existing in liquids [28] will have to be analysed in fuller detail. There can be no doubt but that these fields affect the scattered light spectrum and molecular relaxation times [36]. The present theory can be extended to comprise various polarization states of the incident and scattered light as well as the angular dependence of the latter [37], with various molecular correlations

$\dagger$  Numerical values of  $\gamma'(\mathcal{H})$  for various radial interaction potentials are to be found in reference [44].

taken into account [38]. Work on an extension of the present analysis to other types of many-photon cooperative processes [39–43] is under way.

The authors wish to thank the Institute of Physical Chemistry of the Polish Academy of Sciences for sponsoring in part this investigation.

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