SECOND-HARMONIC ELASTIC LIGHT SCATTERING
BY MOLECULAR LIQUID MIXTURES

S. KIELICH and M. KOZIEROWSKI

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

and J.-R. LALANNE

Centre de Recherches CNRS Paul Pascal, 33405 Talence, France

Résumé. — Nous montrons que l'étude de la diffusion bi-harmonique élastique de la lumière dans les mélanges liquides est une source de données sur les corrélations entre molécules non-centrosymétriques (par ex. dipolaires) et centrosymétriques (par ex. quadrupolaires), entre molécules dipolaires et tétraédriques, et entre les composantes des milieux polyatomiques, et qu'elle permet de déterminer les polarisabilités moléculaires d'ordres 2 et 3 quant à leur signe et leur valeur.

Abstract. — Second-harmonic light scattering (SHS) studies of liquid mixtures are shown to provide valuable information regarding correlations between non-centrosymmetric (e. g. dipolar) molecules and centrosymmetric (e. g. quadrupolar) ones, between dipolar molecules and tetrahedral ones, as well as between the components of atomic media. Such studies moreover permit determination of nonlinear second-order and third-order molecular polarizabilities as to sign and value.

1. Introduction. — Since the earliest observations of second-harmonic scattering (SHS) of laser light 10 years ago, a vast amount of work has been devoted to the study of various nonlinear processes of photon scattering in gases, liquids, and crystals [1]. Terhune *et al.* [2], Weinberg [3], and Maker [4] observed elastic incoherent SHS in liquids composed of non-centrosymmetric molecules, whereas Kielich and Lalanne [5] observed elastic cooperative SHS in liquids composed of molecules having a centre of symmetry in their ground state.

The theory of SHS was initially worked out with respect to gases [6], then for molecular liquids [7, 8, 9], and recently for atomic fluids [10, 11]. In this paper, we develop the theory of elastic SHS in liquid atomic and molecular solutions similarly as done by us with regard to usual anisotropic Rayleigh scattering [12].

2. Foundations of the theory. — We consider a medium of volume V containing $N = \sum_i N_i$ molecules. $N_i = x_i N$ is the number of molecules of species i and x_i their molar fraction. Assume as incident on V a laser light wave with electric field

$$E(r, t) = E(r, \omega) \cos \omega t ,$$

of an intensity so large that not only light of the fundamental frequency ω but moreover of the multi-ple frequencies $2\omega, 3\omega, \ldots$, is scattered. We are concerned with SHS for which the differential cross section, with analyzer polarisation given by the vector n, is expressed (in the wave zone and in an electric dipole approximation) by the formula :

$$\frac{d\sigma_n^{2\omega}}{d\Omega} = \left(\frac{2\omega}{c}\right)^4 \frac{c}{4\pi} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} (M_{pi}^{2\omega} \cdot n) \times \right.$$
$$\left. \times (M_{qj}^{2\omega} \cdot n) \exp[i(\Delta k \cdot r_{pi,qj})] \right\rangle . \quad (1)$$

Above,

$$\Delta k = k_{2\omega} - 2 k_\omega ,$$

with k_ω — the wave vector of incident light and $k_{2\omega}$ — that of the SHS wave; the absolute value of $|\Delta k|$ is defined in reference [7]; the symbol $\langle \ \rangle$ stands for statistical averaging; and

$$|r_{pi,qj}| = |r_{qj} - r_{pi}|$$

is the distance separating two scattering molecules at the positions r_{pi} and r_{qj}.

The electric dipole moment induced at the frequency 2ω in molecule p of species i is given generally by the expansion [5] :

$$M_{pi}^{2\omega} = \tfrac{1}{4} h_{2\omega} B_{pi}^{2\omega} : E^\omega E^\omega \cos 2\omega t , \quad (2)$$

where :

$$h_{2\omega} = \frac{n_{2\omega}^2 + 2 n_0^2}{3 n_0^2} \left(\frac{n_\omega^2 + 2 n_0^2}{3 n_0^2} \right)^2 , \qquad (3)$$

n_ω and $n_{2\omega}$ being the refractive indices of the scattering spherical sample V at the frequencies ω and 2ω, respectively, and n_0 that of the medium surrounding V.

Eq. (2) involves the 3-rd rank tensor $\mathbf{B}_{pi}^{2\omega}(\mathbf{r}_{pi}, \Omega_{pi})$, which describes the effective nonlinear 2-nd order polarizability of the p-th molecule of species i with the position $\mathbf{r}_{pi}$ and orientation Ω_{pi}. Insertion of (2) into (1) leads to the product $\mathbf{B}_{pi}^{2\omega} \mathbf{B}_{qj}^{2\omega}$, a 6-th rank tensor which, to start with, can be unweightedly averaged by taking recourse in general invariant formulae derived by one of us [13] (recently, these formulae have been re-written in rotation matrix form [14]). By (1), we hence obtain, for the horizontal and vertical component at vertically polarized incident light,

$$\frac{d\sigma_{hv}^{2\omega}}{d\Omega} = \frac{h_{2\omega}^2}{525} \frac{c}{128 \pi} \left(\frac{2 \omega}{c} \right)^4 E_0^4 (63 B_{2\omega} + 8 \Gamma_{2\omega}) , \quad (4)$$

$$\frac{d\sigma_{vv}^{2\omega}}{d\Omega} = \frac{h_{2\omega}^2}{175} \frac{c}{128 \pi} \left(\frac{2 \omega}{c} \right)^4 E_0^4 (189 B_{2\omega} + 4 \Gamma_{2\omega}) , \quad (5)$$

where we have introduced the following molecular quantities, characterizing SHS by many-component systems :

$$B_{2\omega} = \frac{1}{9} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} (\mathbf{B}_{pi}^{2\omega} : \mathbf{U}).(\mathbf{B}_{qj}^{2\omega} : \mathbf{U}) \times \right.$$
$$\left. \times \exp[i(\Delta\mathbf{k}.\mathbf{r}_{pi,qj})] \right\rangle , \quad (6)$$

$$\Gamma_{2\omega} = \frac{1}{2} \sum_{ij} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \{ 5 \mathbf{B}_{pi}^{2\omega} : \mathbf{B}_{qj}^{2\omega} - \right.$$
$$\left. - 3(\mathbf{B}_{pi}^{2\omega} : \mathbf{U}).(\mathbf{B}_{qj}^{2\omega} : \mathbf{U}) \} \exp[i(\Delta\mathbf{k}.\mathbf{r}_{pi,qj})] \right\rangle . \quad (7)$$

$\mathbf{U}$ denoting the symmetric unit tensor of rank 2. The parameter (6) characterizes the quasi-isotropic properties of the scattering medium, and is thus the counterpart of the isotropic scalar component in linear scattering [12], whereas (7) accounts for the anisotropic properties of SHS.

By (4) and (5), we obtain for the depolarization ratio :

$$D_v^{2\omega} = \frac{1}{3} \frac{63 B_{2\omega} + 8 \Gamma_{2\omega}}{189 B_{2\omega} + 4 \Gamma_{2\omega}} . \qquad (8)$$

Likewise, by (1) we derive, for scattering at the angle $\vartheta = 0$, the following reversal ratio of circularly polarized light [9] :

$$R^{2\omega}(0) = \frac{15 \Gamma_{2\omega}}{126 B_{2\omega} + \Gamma_{2\omega}} . \qquad (9)$$

3. Molecular-statistical analysis.

The nonlinear polarizability tensor of eq. (2) depends on the pro-

perties of the molecule pi in the ground state as well as on the orientations and electric fields $\mathbf{F}(\mathbf{r}, t)$ of its neighbours. The time- and space-fluctuations of the molecular field $\mathbf{F}(\mathbf{r}, t)$ affects the tensor $\mathbf{B}_{pi}^{2\omega}$ both directly and indirectly. It directly lowers the intrinsic symmetry of the molecule by inducing in it higher nonlinearities, in accordance with the expansion :

$$\mathbf{B}_{pi}^{2\omega} = \mathbf{b}_{pi}^{2\omega} + \mathbf{c}_{pi}^{2\omega}.\mathbf{F}_{pi}(\mathbf{r}, t) + \cdots , \qquad (10)$$

where the tensor $\mathbf{b}_{pi}^{2\omega}$ now describes its nonlinear second-order polarizability at $\mathbf{F}(\mathbf{r}, t) = 0$ and the fourth-rank tensor $\mathbf{c}_{pi}^{2\omega}$ describes linear variations in $\mathbf{b}_{pi}^{2\omega}$ due to the field $\mathbf{F}(\mathbf{r}, t)$.

The field $\mathbf{F}(\mathbf{r}, t)$, as such, is related with dispersional interactions between the molecules as well as electrostatic and inductional interaction of molecular multipoles, as given by the expression [15, 16] :

$$\mathbf{F}_{pi}(\mathbf{r}, t) = \sum_k \sum_{s \neq p}^{N_k} \mathbf{F}_{pi,sk} , \qquad (11)$$

where

$$\mathbf{F}_{pi,sk} = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2 n - 1) ! !} {}^{(1)}\mathbf{T}_{pi,sk}^{(n)}[n] \mathbf{M}_{sk}^{(n)} \qquad (11a)$$

is the field existing at the centre of molecule p of species i due to the electric multipoles of molecule s of species k. The interaction of the two molecules is described by the tensor ${}^{(1)}\mathbf{T}_{pi,sk}^{(n)}$ of rank $n + 1$.

Indirectly, the molecular field $\mathbf{F}(\mathbf{r}, t)$ affects the expansion (10) by way of translational fluctuations, which cause spatial redistribution of the molecules in regions of short-range order [9, 12]. The latter effect, as well as many-body distortion effects, play an essential role in atomic substances [10, 11].

With regard to (10) and (11), the molecular parameters (6) and (7) can be written for a many-component system as follows :

$$B_{2\omega} = \sum_i x_i B_{2\omega}^{(i)} + \sum_{ij} x_i x_j B_{2\omega}^{(ij)} +$$
$$+ \sum_{ijk} x_i x_j x_k B_{2\omega}^{(ijk)} + \cdots , \qquad (12)$$

$$\Gamma_{2\omega} = \sum_i x_i \Gamma_{2\omega}^{(i)} + \sum_{ij} x_i x_j \Gamma_{2\omega}^{(ij)} +$$
$$+ \sum_{ijk} x_i x_j x_k \Gamma_{2\omega}^{(ijk)} + \cdots . \qquad (13)$$

We shall now discuss the various terms for several models and approximations.

3.1 NO MOLECULAR FIELD. — The first two terms of (12) and (13) describe additive, incoherent SHS by individual molecules with the parameters :

$$B_{2\omega}^{(i)} = \frac{N}{9} (\mathbf{b}_i^{2\omega} : \mathbf{U}).(\mathbf{b}_i^{2\omega} : \mathbf{U}) , \qquad (14)$$

$$\Gamma_{2\omega}^{(i)} = \frac{N}{2} [5 \mathbf{b}_i^{2\omega} : \mathbf{b}_i^{2\omega} - 3(\mathbf{b}_i^{2\omega} : \mathbf{U}).(\mathbf{b}_i^{2\omega} : \mathbf{U})] .$$
$$(15)$$

The parameters (14) and (15) differ from zero for non-centrosymmetric molecules only [6]. Their application to molecular symmetry groups proceeds as in the single-component case.

The second and higher terms of the expansions (12) and (13) account for coherent light scattering on molecules statistically correlated as to their positions and mutual spatial orientation [7, 8], and express the non-additivity of scattering by the components of the mixture. In a first approximation, neglecting the molecular fields, we obtain for the two-molecule correlation parameters :

$$B_{2\omega}^{(ij)} = \frac{N}{9\,x_j} \left\langle \sum_{\substack{q \neq p}}^{N_j} (\mathbf{b}_{pi}^{2\omega} : \mathbf{U}).(\mathbf{b}_{qj}^{2\omega} : \mathbf{U}) \times \right.$$

$$\left. \times \cos(\Delta\mathbf{k}.\mathbf{r}_{pi,qj}) \right\rangle, \quad (16)$$

$$\Gamma_{2\omega}^{(ij)} = \frac{N}{2\,x_j} \left\langle \sum_{\substack{q \neq p}}^{N_j} \{ 5\,\mathbf{b}_{pi}^{2\omega} : \mathbf{b}_{qj}^{2\omega} - \right.$$

$$\left. - 3(\mathbf{b}_{pi}^{2\omega} : \mathbf{U}).(\mathbf{b}_{qj}^{2\omega} : \mathbf{U}) \} \cos(\Delta\mathbf{k}.\mathbf{r}_{pi,qj}) \right\rangle. \quad (17)$$

In this approximation, the parameters (16) and (17) differ from zero for non-centrosymmetric molecules only if the statistical averaging $\langle\ \rangle$ is performed with a correlation function dependent on molecular orientation.

3.2 INFLUENCE OF THE MOLECULAR FIELD IN THE ABSENCE OF ANGULAR CORRELATIONS.

— Averaging, performed with the (angular correlation-independent) radial correlation function, causes the two-molecule parameters (16) and (17) to vanish. The contributions from the molecular field (11), inherent in the expansion (10), have now to be taken into account. The non-zero result thus obtained is, obviously, proportional to the square $\mathbf{F}^2$ (in the linear approximation, it vanishes on isotropic averaging). On assuming moreover for simplicity the nonlinear polarizability tensor

$$c_{pi}^{2\omega} = \tfrac{1}{5}\,\mathbf{U} : c_{pi}^{2\omega} : \mathbf{U}$$

as isotropic, we obtain :

$$_F B_{2\omega}^{(ij)} = \frac{25\,N}{162\,x_j} \sum_{n=0}^{\infty} \frac{(n+1)!}{(2n-1)!!} \{(c_i^{2\omega})^2\,(\mathbf{M}_j^{(n)}[n]\,\mathbf{M}_j^{(n)}) + (c_j^{2\omega})^2\,(\mathbf{M}_i^{(n)}[n]\,\mathbf{M}_i^{(n)})\} \left\langle \sum_{q \neq p}^{N_j} r_{pi,qj}^{-2(n+2)} \right\rangle, \quad (18)$$

and $_F\Gamma_{2\omega}^{(ij)} = 0$. This approximation, consequently, yields no contribution to the anisotropic parameter (7). In the same way, we derive for the quasi-isotropic parameter of three-molecule correlations :

$$_F B_{2\omega}^{(ijk)} = \frac{25\,N}{81\,x_j\,x_k}\,c_i^{2\omega}\,c_j^{2\omega} \sum_{n=0}^{\infty} \frac{(n+1)!}{(2n-1)!!}\,\mathbf{M}_k^{(n)}[n]\,\mathbf{M}_k^{(n)} \times \left\langle \sum_{\substack{q \neq p}}^{N_j} \sum_{\substack{s \neq q \\ s \neq p}}^{N_k} r_{pi,sk}^{-(n+2)}\,r_{sk,qj}^{-(n+2)} \times \right.$$

$$\left. \times P_{n+1}\left(\frac{\mathbf{r}_{pi,sk}\cdot\mathbf{r}_{sk,qj}}{r_{pi,sk}\cdot r_{sk,qj}}\right) \cos(\Delta\mathbf{k}.\mathbf{r}_{pi,qj}) \right\rangle, \quad (19)$$

where P_{n+1} is a Legendre polynomial of order $n+1$. Here, too, $_F\Gamma_{2\omega}^{(ijk)} = 0$. Clearly, the anisotropic parameters $_F\Gamma_{2\omega}^{(ij)}$, $_F\Gamma_{2\omega}^{(ijk)}$ will differ from zero in the absence of angular correlations only if anisotropy in the tensor $c_{pi}^{2\omega}$ is taken into account [5] or if, in the expansion (10), higher nonlinearities are taken, thus the quadratic nonlinearity $\mathbf{d}_{pi}^{2\omega} : \mathbf{F}(\mathbf{r}, t)\,\mathbf{F}(\mathbf{r}, t)$ etc., or other components, due to the action of the field gradient etc. [16, 17].

3.3 INFLUENCE OF THE MOLECULAR FIELD IN THE PRESENCE OF ANGULAR CORRELATIONS.

— In the presence of orientational molecular correlations the non-vanishing contributions are those linear in the molecular field $\mathbf{F}$. However, for the sake of simplicity, we shall assume the molecular species i as dipolar (albeit without higher multipoles) and the species j as centrosymmetric, $\mathbf{b}_j^{2\omega} = 0$. We now get, for the two-molecule angular correlations :

$$_F B_{2\omega}^{(ij)} = \frac{N}{3\,x_j}\,b_i^{2\omega}\,\mu_i \left\{ (\gamma_j^{2\omega} + \varepsilon_j^{2\omega}) \left\langle \sum_{q \neq p}^{N_j} (3\cos^2\theta_{pi} - 1)\,r_{pi,qj}^{-3} \times \cos(\Delta\mathbf{k}.\mathbf{r}_{pi,qj}) \right\rangle + (\delta_j^{2\omega} + 7\,\gamma_j^{2\omega}) \times \right.$$

$$\left. \times \left\langle \sum_{q \neq p}^{N} (3\cos\theta_{pi,qj}\cos\theta_{pi}\cos\theta_{qj} - \cos^2\theta_{pi,qj})\,r_{pi,qj}^{-3}\cos(\Delta\mathbf{k}.\mathbf{r}_{pi,qj}) \right\rangle \right\}, \quad (20)$$

$$_F\Gamma_{2\omega}^{(ij)} = \frac{N}{2\,x_j}\,\kappa_i^{2\omega}\,\mu_i \left\{ \delta_j^{2\omega} \left\langle \sum_{q \neq p}^{N_j} (5\cos^2\theta_{pi,qj} - 3)(3\cos\theta_{pi,qj} \times \cos\theta_{pi}\cos\theta_{qj} - \cos^2\theta_{pi,qj})\,r_{pi,qj}^{-3} \times \right. \right.$$

$$\left. \times \cos(\Delta\mathbf{k}.\mathbf{r}_{pi,qj}) \right\rangle + 3\,\gamma_j^{2\omega} \left\langle \sum_{q \neq p}^{N} [(5\cos^2\theta_{pi,qj} - 1)(3\cos^2\theta_{pi} - 1) \right.$$

$$\left. \left. - 2(3\cos\theta_{pi,qj}\cos\theta_{pi}\cos\theta_{qj} - \cos^2\theta_{pi,qj})]\,r_{pi,qj}^{-3} \times \cos(\Delta\mathbf{k}.\mathbf{r}_{pi,qj}) \right\rangle \right\}, \quad (21)$$

with the notation :

$$\kappa^{2\omega} = \mathbf{b}^{2\omega}_{333} - 3\,\mathbf{b}^{2\omega}_{113}\,,$$
$$\mathbf{b}^{2\omega} = \tfrac{1}{3}(\mathbf{b}^{2\omega}_{333} + 2\,\mathbf{b}^{2\omega}_{113}) \tag{22}$$

$$\varepsilon^{2\omega} = \tfrac{5}{3}\,\mathbf{c}^{2\omega}_{1111}\,, \quad \gamma^{2\omega} = \tfrac{1}{3}(3\,\mathbf{c}^{2\omega}_{1133} - \mathbf{c}^{2\omega}_{1111})\,,$$
$$\delta^{2\omega} = \mathbf{c}^{2\omega}_{1111} - 6\,\mathbf{c}^{2\omega}_{1133} + \mathbf{c}^{2\omega}_{3333}\,. \tag{23}$$

These formulae describe a curious situation in which the fields of electric dipoles μ_{pi} of a non-centrosymmetric molecular species induce nonlinear electric moments $\mathbf{c}^{2\omega}_{qj}.\mathbf{F}_{qj,pi}$ in the molecules of a centrosymmetric species thus destroying their centre of symmetry and rendering SHS of a cooperative kind possible [5]. We are dealing here with a mixed SHS due to the intrinsic absence of a centre of symmetry and to the removal of one by a molecular electric field.

The contributions (20) and (21) are easily seen to vanish on isotropic averaging. However, averaged with a two-molecule angular function correlating a dipolar molecule μ_i and a quadrupolar one Θ_j :

$$g^{(2)}_{ij}(r_{pq}, \Omega_{pi}, \Omega_{qj}) = g_{ij}(r_{pq}) \times$$
$$\times \exp\left\{\frac{3\,\mu_i\,\Theta_j}{2\,kT}(\cos\theta_{pi} + 2\cos\theta_{pi,qj}\cos\theta_{qj} - 5\cos\theta_{pi}\cos^2\theta_{qj})\,r^{-4}_{pi,qj} + \cdots\right\}\,, \tag{24}$$

they become, in a satisfactory approximation :

$$_F B^{(ij)}_{2\omega} = \frac{4\,N\mu_i^3\,\Theta_j^2}{525\,x_j\,k^2\,T^2}\,\mathbf{b}_i^{2\omega}(42\,\gamma_j^{2\omega} + 7\,\varepsilon_j^{2\omega} + 5\,\delta_j^{2\omega}) \times \left\langle \sum_{q\neq p}^{N_j} r^{-11}_{pi,qj} \cos(\Delta\mathbf{k}.\mathbf{r}_{pi,qj}) \right\rangle\,, \tag{20a}$$

$$_F \Gamma^{(ij)}_{2\omega} = -\frac{24\,N\mu_i^3\,\Theta_j}{1\,225\,x_j\,k^2\,T^2}\,\kappa_i^{2\omega}\,\gamma_j^{2\omega} \left\langle \sum_{q\neq p}^{N_j} r^{-11}_{pi,qj} \cos(\Delta\mathbf{k}.\mathbf{r}_{pi,qj}) \right\rangle\,. \tag{21a}$$

Now let us see what happens when the species i is dipolar but the species j tetrahedral. By (16) and (17), we now get :

$$B^{(ij)}_{2\omega} = 0\,,$$
$$\Gamma^{(ij)}_{2\omega} = 15\,N\kappa_i^{2\omega}\,\mathbf{b}^{2\omega}_{123j}\,x_j^{-1} \left\langle \sum_{q\neq p}^{N_j} \cos\theta^{(31)}_{pi,qj} \cos\theta^{(32)}_{pi,qj} \cos\theta^{(33)}_{pi,qj} \cos(\Delta\mathbf{k}.\mathbf{r}_{pi,qj}) \right\rangle\,, \tag{25}$$

$\theta^{(3k)}_{pi,qj}$ ($k = 1, 2, 3$) denoting the angle between the permanent dipole and the k-axis of molecular coordinates, attached to the tetrahedral molecule.

On averaging, performed isotropically or with the function (27), the anisotropic factor $\Gamma^{(ij)}_{2\omega}$ vanishes; for dipole-tetrahedral octupole interaction, it will differ from zero only in the fourth approximation of the distribution function expansion ($\sim \mu_i^3\,\Omega_j^3/k^3\,T^3$) and will thus be practically negligible.

Furthermore, taking into account the molecular field of the dipoles and a nearly isotropic tensor $\mathbf{c}_j^{2\omega}$, we get :

$$_F B^{(ij)}_{2\omega} = \frac{5\,N}{9\,x_j}\,\mu_i\,\mathbf{b}_i^{2\omega}\,\mathbf{c}_j^{2\omega} \left\langle \sum_{q\neq p}^{N} (3\cos^2\theta_{pi} - 1) \times r^{-3}_{pi,qj} \cos(\Delta\mathbf{k}.\mathbf{r}_{pi,qj}) \right\rangle\,, \tag{26}$$

$$_F \Gamma^{(ij)}_{2\omega} = 0\,.$$

On averaging the preceding expression with the angular correlation function for interaction between the permanent dipole and the dipole induced in the tetrahedral molecule :

$$g^{(2)}_{ij}(r_{pq}, \Omega_{pi}, \Omega_{qj}) = g_{ij}(r_{pq}) \times$$
$$\times \exp\left\{\frac{a_j^\omega\,\mu_i^2}{2\,kT}(3\cos^2\theta_{pi} + 1)\,r^{-6}_{pi,qj}\right\} \tag{27}$$

(with a_j-linear optical polarizability), we obtain in the first, nonvanishing approximation :

$$_F B^{(ij)}_{2\omega} = \frac{2\,N\mu_i^3\,a_j^\omega}{9\,x_j\,kT}\,\mathbf{b}_i^{2\omega}\,\mathbf{c}_j^{2\omega} \left\langle \sum_{q\neq p}^{N} r^{-9}_{pi,qj} \times \cos(\Delta\mathbf{k}.\mathbf{r}_{pi,qj}) \right\rangle\,. \tag{26a}$$

The preceding formulae for specific molecular symmetries prove that temperature-dependent studies of SHS in liquid mixtures are a source of information not only concerning the two- and three-molecule distribution function (19) but, primarily, permit one

to determine the signs of the tensor elements of nonlinear second-order and third-order polarizabilities. This information is essential to our knowledge of molecular structure.

3.4 ATOMIC DISPERSIONAL INTERACTIONS. — In the case of SHS in atomic media, we have by (6) and (7) :

$$\Gamma_{2\omega} = 0 ,$$

$$B_{2\omega} = \frac{25}{81} \sum_{ijkl} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} \mathbf{c}_{pi}^{2\omega} \mathbf{c}_{qj}^{2\omega} \times \right.$$

$$\left. \times (\mathbf{F}_{pi,rk} \cdot \mathbf{F}_{qj,sl}) \cos (\Delta \mathbf{k} \cdot \mathbf{r}_{pi,qj}) \right\rangle , \quad (28)$$

with $\mathbf{F}$ now denoting the field of London dispersional interactions. The tensor $\mathbf{c}_i^{2\omega}$ is defined as in eq. (18). By (8) and (9) we find that $D_v^{2\omega} = \frac{1}{9}$ and $R^{2\omega}(0) = 0$ for all orders of atomic interaction.

We see moreover, from (28), that even in the limit $\Delta \mathbf{k} \cdot \mathbf{r}_{pi,qj} \to 0$ the molecular factor of quasi-isotropic scattering already differs from zero for two-body interaction of different atoms. For $i = j$ the factor (28) vanishes in such cases [10], since a pair of identical atoms is still a centrosymmetric element.

The molecular quantities (6) and (7) are accessible to discussion by the method of statistical perturbation calculus [17] for polar molecules with arbitrary symmetries and interaction energies, as done previously for the molecular polarisation of many-component systems [18].

4. Discussion and conclusions. — For a binary system, the expansions (12) and (13) are conveniently written as a series in powers of x ($= x_2$ — the molar fraction of the solute; $x_1 = 1 - x$ — that of the solvent) [19] :

$$Q(x) = Q_0 + Q_1 x + Q_2 x^2 + \cdots = \sum_{n=0}^{\infty} Q_n x^n , \quad (29)$$

where the expansion coefficients :

$$Q_n = \frac{1}{n!} \left(\frac{\partial^n B_{2\omega}}{\partial x^n} \right)_{x=0} \quad \text{or} \quad Q_n = \frac{1}{n!} \left(\frac{\partial^n \Gamma_{2\omega}}{\partial x^n} \right)_{x=0} \quad (30)$$

are accessible to direct determination by measurements of $B_{2\omega}$ or $\Gamma_{2\omega}$.

The coefficient Q_0 of (29) describes the properties of the solvent alone and, with regard to (12), is given by :

$$Q_0 = (B_{2\omega}^{(1)} + B_{2\omega}^{(11)} + B_{2\omega}^{(111)} + \cdots)_{x=0} . \quad (30a)$$

The other coefficients of (29) describe the solution ; by (12), they can be approximately expressed as :

$$Q_1 = (B_{2\omega}^{(2)} - B_{2\omega}^{(1)} + B_{2\omega}^{(12)} + B_{2\omega}^{(21)} - 2 B_{2\omega}^{(11)} - $$
$$- 3 B_{2\omega}^{(111)} + \cdots)_{x=0} , \quad (30b)$$

$$Q_2 = (B_{2\omega}^{(11)} + B_{2\omega}^{(22)} - B_{2\omega}^{(12)} - B_{2\omega}^{(21)} + $$
$$+ 3 B_{2\omega}^{(111)} - \cdots)_{x=0} . \quad (30c)$$

Similar expressions can be written for the $\Gamma_{2\omega}$'s.

Knowing the properties of the pure solvent, eq. (29) can be re-written in the form of the variation :

$$\Delta Q(x) = \frac{Q(x) - Q_0}{x} = Q_1 + Q_2 x + Q_3 x^2 + \cdots = $$
$$= \sum_{n=1}^{\infty} Q_n x^{n-1} . \quad (31)$$

For an infinitely dilute solution, (31) becomes :

$$\lim_{x \to 0} \Delta Q(x) = Q_1 . \quad (31a)$$

Thus, the infinitely dilute solution is characterized by the quantity Q_1, defined by (30b). Concentrated solutions markedly diverge from additivity i.e. from linearity in x, so that higher terms of (31), like Q_2, Q_3, ..., have to be taken into account.

Let us consider the case when the solvent molecules are centrosymmetric and those of the solute noncentrosymmetric. We now have in the absence of correlations for the solvent, by (14) and (15) :

$$B_{2\omega}^{(1)} = 0 , \qquad \Gamma_{2\omega}^{(1)} = 0 . \quad (32)$$

In the dilute solution, the predominant role belongs to molecules which, by interacting with one another, cause cooperative light scattering as given by eq. (18), unless one takes anisotropy of nonlinear polarizability into account. In particular, for quadrupole molecules one has by (18) and (19) :

$$B_{2\omega}^{(11)} = \frac{25}{27} N(\mathbf{c}_1^{2\omega} \Theta_1)^2 \left\langle \sum_{q \neq p}^{N} r_{p1,q1}^{-8} \right\rangle , \quad (33)$$

$$B_{2\omega}^{(111)} = \frac{25}{27} N(\mathbf{c}_1^{2\omega} \Theta_1)^2 \left\langle \sum_{q \neq p}^{N} \sum_{s \neq q}^{N} r_{p1,s1}^{-4} r_{s1,q1}^{-4} \times \right.$$

$$\left. \times P_3 \left(\frac{r_{p1,s1} \cdot r_{s1,q1}}{r_{p1,s1} r_{s1,q1}} \right) \cos (\Delta \mathbf{k} \cdot r_{p1,q1}) \right\rangle , \quad (34)$$

where Θ_1 is the electric quadrupole moment of the solvent molecule.

For highly symmetric e.g. octahedral solvent molecules the first non-zero electric moment is the hexadecapole Φ_1, and one has by (18) :

$$B_{2\omega}^{(11)} = \frac{2\,000}{189} N(\mathbf{c}_1^{2\omega} \Phi_1)^2 \left\langle \sum_{q \neq p}^{N} r_{p1,q1}^{-12} \right\rangle . \quad (35)$$

Likewise, by (19), a contribution is derived for triple radial correlations.

In the infinitely dilute case, with regard to (30b), (14) and (15), it suffices to consider for the solute the quantities

$$B_{2\omega}^{(2)} = \frac{N}{9} (\mathbf{b}_{113}^{2\omega} + \mathbf{b}_{223}^{2\omega} + \mathbf{b}_{333}^{2\omega})^2 , \quad (36)$$

$$\Gamma_{2\omega}^{(2)} = \frac{N}{4} (2 \mathbf{b}_{333}^{2\omega} - 3 \mathbf{b}_{113}^{2\omega} - 3 \mathbf{b}_{223}^{2\omega})^2 \quad (37)$$

only, since the probability of correlation between the scarce solute molecules, separated by very numerous molecules of the solvent, is small. In this situation, however, one has to consider correlation between a non-centrosymmetric solute molecule and its centrosymmetric neighbours. Neglecting angular correlations in a first approximation, one has by (18) :

$$B_{2\omega}^{(12)} = \frac{25\,N}{162} \left\{ 2(c_1^{2\omega}\,\mu_2)^2 \left\langle \sum_{q \neq p}^{N} r_{p1,q2}^{-6} \right\rangle + \right.$$

$$\left. + 3(c_2^{2\omega}\,\Theta_1)^2 \left\langle \sum_{q \neq p}^{N} r_{p1,q2}^{-8} \right\rangle \right\}, \quad (38)$$

where μ_2 is the dipole moment of the solute molecule. The quantity $B_{2\omega}^{(21)}$ is defined similarly.

If correlations between the solute and solvent molecules are anisotropic, one has instead of (38), by eq. (20a) and (21a) :

$$B_{2\omega}^{(21)} = \frac{4\,N}{525}\,b_2^{2\omega}\,\mu_2^3\,\Theta_1^2(7\,\varepsilon_1^{2\omega} + 42\,\gamma_1^{2\omega} + 5\,\delta_1^{2\omega}) \times$$

$$\times\,(kT)^{-2} \left\langle \sum_{q \neq p}^{N} r_{p2,q1}^{-11} \cos(\Delta k.r_{p2,q1}) \right\rangle, \quad (39)$$

$$\Gamma_{2\omega}^{(21)} = -\frac{24\,N}{1\,225}\,\frac{\mu_2^3\,\Theta_1^2}{(kT)^2}\,\kappa_2^{2\omega}\,\gamma_1^{2\omega} \times$$

$$\times \left\langle \sum_{q \neq p}^{N} r_{p2,q1}^{-11} \cos(\Delta k.r_{p2,q1}) \right\rangle. \quad (40)$$

Hence, the variation $\Delta B_{2\omega}(x)$ in an infinitely dilute solution is described by the quantities in (30b) with the terms (33), (34), (36) as well as (38) and (39). On the other hand, the variation of the anisotropic parameter is, in this approximation :

$$\lim_{x \to 0} \Delta\Gamma_{2\omega}(x) = \Gamma_{2\omega}^{(2)} + \Gamma_{2\omega}^{(21)} + \cdots, \quad (41)$$

where the non-zero contributions are given by (37) and (40).

One can likewise discuss the inverse case of a solute consisting of quadrupolar centrosymmetric molecules

and a solvent with tetrahedral ones e.g. CCl_4, for which by (14) and (15) one has in the absence of correlations :

$$B_{2\omega}^{(1)} = 0, \qquad \Gamma_{2\omega}^{(1)} = 15\,N(b_{123(1)}^{2\omega})^2. \quad (42)$$

In the presence of radial correlations only, $\Gamma_{2\omega}^{(11)} = 0$, and by eq. (18) one has :

$$B_{2\omega}^{(11)} = \frac{80}{27}\,N(c_1^{2\omega}\,\Omega_{123(1)})^2 \left\langle \sum_{q \neq p}^{N} r_{p1,q1}^{-10} \right\rangle, \quad (43)$$

where Ω_{123} is the octupole moment component of the tetrahedral molecule [17]. On taking into account interaction between molecules of the solute and solvent, one has :

$$B_{2\omega}^{(12)} = \frac{5\,N}{54} \left\{ 5(c_1^{2\omega}\,\Theta_2)^2 \left\langle \sum_{q \neq p}^{N} r_{p1,q2}^{-8} \right\rangle + \right.$$

$$\left. + 16(c_2^{2\omega}\,\Omega_{123(1)})^2 \left\langle \sum_{q \neq p}^{N} r_{p1,q2}^{-10} \right\rangle \right\}. \quad (44)$$

Since the octupolar contributions are generally much smaller than the quadrupolar ones, the infinite dilution method suggests itself for the determination of the quadrupole moments of molecules from eq. (44). The values thus obtained will surely be more accurate than those previously determined from SHS studies of pure liquids [20].

For concentrated solutions, higher terms of (31) have to be taken. By eq. (30c) etc., they now involve also parameters related with correlations between molecules of the solute.

The preceding example proves that the investigation of the quantities $B_{2\omega}(x)$ and $\Gamma_{2\omega}(x)$ vs. concentration permits to study the correlations existing not only between molecules of the same species, but, in the first place, between molecules of different species. If the dependence of $B_{2\omega}(x)$ and $\Gamma_{2\omega}(x)$ on the concentration x is linear, one deals exclusively with an influence of the solvent on the molecules of the solute amounting to at least 10 %.

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