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## SECOND HARMONIC GENERATION OF LASER BEAM IN ELECTRICALLY POLARIZED ATOMIC AND MOLECULAR FLUID MIXTURES

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### ABSTRACT

In a semi-macroscopic approach, a general relation between the phenomenological nonlinear susceptibility tensor  $\chi_{\sigma\tau\nu\rho}(2\omega)$ , measured in DC electric field-induced second harmonic generation of laser light (DCEFISHG) and the molecular nonlinear polarizability tensors  $b_{\alpha\beta\gamma\delta}(2\omega)$  and  $c_{\alpha\beta\gamma\delta}(2\omega)$ , is derived. The relation involves the two molecular-statistical factors  $G(2\omega)$  and  $S(2\omega)$ , or one factor  $Q(2\omega)$  (at zero electronic dispersion and absorption), and the tensors  $R_{\sigma\tau}$  accounting for the geometrical setup and the difference in electric fields in and beyond the medium.  $Q(2\omega)$  is analyzed by classical statistics for multicomponent systems with unlike atoms and molecules interacting by various radial and angular forces. The many-body correlations and electric molecular field fluctuations cause that, in sufficiently dense systems, the nonlinear susceptibility of the mixture is no longer additive but is in general a nonlinear function of concentration.

### INTRODUCTION

In the course of the last 20 years much information has been obtained regarding the nonlinear electro-optical and optical polarizabilities of atoms and molecules (refs 1-6). In isotropic media, nonlinear molecular polarizabilities are apparent directly or indirectly in the electric polarisation of order 3 which, phenomenologically, is of the following form at frequency

$$\omega_4 = \omega_1 + \omega_2 + \omega_3 \quad (\text{refs } 7,8):$$

$$P_{\sigma}(\omega_4) = \chi_{\sigma\tau\nu\rho}(-\omega_4, \omega_1, \omega_2, \omega_3) E_{\tau}(\omega_1) E_{\nu}(\omega_2) E_{\rho}(\omega_3), \quad (1)$$

$\underline{E}(\omega)$  being the electric field strength conveyed by the light wave vibrating at the circular frequency  $\omega$ . The summation convention for recurring tensorial indices  $\sigma = x, y, z$  is applied throughout.

The 4-th rank tensor  $\chi_{\alpha\beta\gamma\delta}$  in Eq. (1) describing nonlinear susceptibility of order 3 can be calculated quantum-mechanically (refs 9,10) or by methods of classical statistics (refs 11,12). Its various components are accessible to determination from the electro-optical Kerr effect (refs 13,14), optical Kerr effect (refs 2 and 15-18), dielectric saturation (refs 19-22), electro-optical rectification (refs 23,24), DC electric field-induced 2-nd harmonic generation (refs 25-38), 3-rd harmonic generation (refs 8 and 39-42) and from other processes of optical frequency mixing (refs 43-47). Light scattering at doubled and tripled frequency also provides information on the nonlinear polarizabilities of atoms and molecules (refs 48-53), and techniques based on other effects have been worked out as well (refs 54-60).

Hitherto, the greatest amount of information concerning atomic and molecular nonlinear electro-optical polarizabilities has been obtained by the research group of Buckingham from Kerr effect studies (refs 2,4 and 5). The last 10 years have witnessed a rapid development of methods for the determination of nonlinear electro-optical polarizabilities by DC electric field-induced 2-nd harmonic generation, particularly due to the work of Mayer (refs 25,28), Ward and co-workers (refs 29-31, 35, 37), Levine and Bethea (refs 32-34), and others (refs 6, 36, 38, 43, 59). In the last effect, a DC electric field destroys the centre of symmetry of the isotropic body, which now becomes a source of 2-nd harmonic light generation.

If the intense laser beam propagates along the z-axis perpendicularly to the DC electric field applied along y (Fig.1), we have by Eq. (1) for an isotropic body the following two, mutually perpendicular polarisation components at the frequency  $2\omega$  :

$$P_x(2\omega) = [\chi_{xxyy}(-2\omega, \omega, \omega, 0) + \chi_{xyxy}(-2\omega, \omega, \omega, 0)] E_x(\omega) E_y(\omega) E_y(0), \quad (1a)$$

$$P_y(2\omega) = [\chi_{yxyx}(-2\omega, \omega, \omega, 0) E_x^2(\omega) + \chi_{yyyy}(-2\omega, \omega, \omega, 0) E_y^2(\omega)] E_y(0), \quad (1b)$$

with the following relation:

$$\begin{aligned} \chi_{yyyy}(-2\omega, \omega, \omega, 0) &= \chi_{xxyy}(-2\omega, \omega, \omega, 0) + \\ &+ \chi_{xyxy}(-2\omega, \omega, \omega, 0) + \chi_{yxyx}(-2\omega, \omega, \omega, 0). \end{aligned} \quad (2)$$

If the incident light is linearly polarized with electric vibrations parallel to the DC field, Eq. (1b) permits the determination of the susceptibility  $\chi_{yyyy}$ ; whereas if its vibrations are perpendicular to  $E_y(0)$ , we determine  $\chi_{yxyx}$ . When applying circularly polarized light, measurement of the polarisation

component (1a) yields the susceptibilities  $\chi_{xxyy}$  and  $\chi_{xyxy}$ , whereas by measuring the component (1b) we obtain  $\chi_{yxyx}$  and  $\chi_{yyyy}$ . This method of determining the components of the nonlinear susceptibility tensor  $\chi_{\sigma\tau\mu\nu}^{2\omega}$  is due to Mayer (refs 25,28).

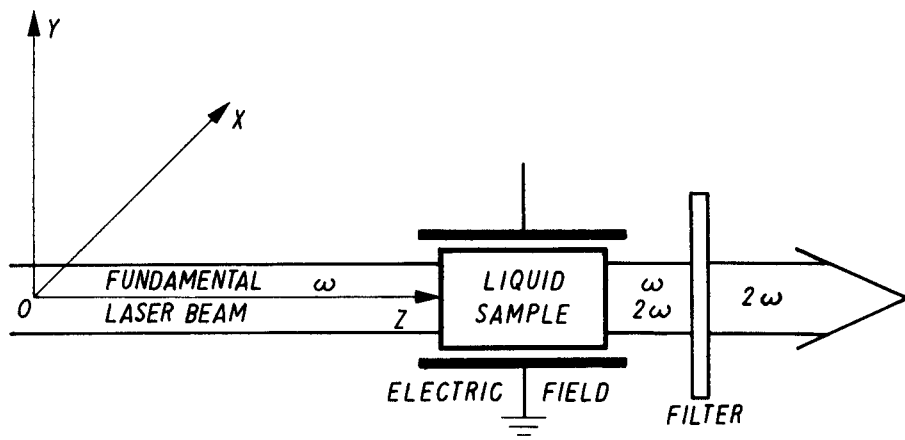


Fig.1. Diagram of setup for the observation of SHG by liquids in a DC electric field.

The present paper is concerned with classical SHG theory in naturally isotropic, electrically polarized media. Our formulation will be sufficiently general to permit the inclusion of various correlations, not only between atoms and molecules of the same species but moreover between unlike ones such as exist in gas mixtures and liquid solutions.

#### GENERAL THEORY

To derive the general relation between the macroscopic phenomenological nonlinear susceptibility tensor  $\chi_{\sigma\tau\mu\nu}^{2\omega}$  and the appropriate microscopic nonlinear polarizabilities of the atoms or molecules, we have recourse to the semi-macroscopic theory of Kirkwood (refs 20, 22). In the semi-macroscopic approach, we consider a macroscopic ellipsoidal, spherical or otherwise shaped sample of volume  $V$  and electric permittivity  $\epsilon$  within an isotropic, continuous medium of permittivity  $\epsilon_0$ . When an external, sufficiently strong electric field  $\underline{E}^0$  acts on the medium, the sample becomes anisotropic, with the electric permittivity tensor  $\epsilon_{\sigma\tau}$ . In general, the macroscopic electric field  $\underline{E}$ , existing in the sample, differs from the external field  $\underline{E}^0$  in the

absence of the sample, and the following relation, resulting from electrostatics, holds ( ref. 61 ) :

$$\underline{E}^{\circ} = R_{\sigma\tau} \underline{E}_{\tau} . \quad (3)$$

The tensor relating  $\underline{E}^{\circ}$  to  $\underline{E}$  is, here, of the form:

$$R_{\sigma\tau} = \epsilon_0^{-1} \left[ \epsilon_0 \delta_{\sigma\tau} + (\epsilon_{\sigma\nu} - \epsilon_e \delta_{\sigma\nu}) L_{\nu\tau} \right] , \quad (4)$$

where  $\delta_{\sigma\tau}$  is Kronecker's symmetric unit tensor and  $L_{\sigma\tau}$  is a symmetric field depolarisation tensor, dependent on the shape of the electric sample and defined so that its trace shall equal unity:  $L_{\sigma\sigma} = L_{xx} + L_{yy} + L_{zz} = 1$ . In particular, for a spherical sample  $L_{\sigma\tau} = \frac{1}{3} \delta_{\sigma\tau}$ , and the tensor (4) becomes:

$$R_{\sigma\tau} = (\epsilon_{\sigma\tau} + 2 \epsilon_0 \delta_{\sigma\tau}) / 3 \epsilon_0 , \quad (4a)$$

or

$$R_{\sigma\tau} = \delta_{\sigma\tau} (\epsilon + 2 \epsilon_0) / 3 \epsilon_0 = R \delta_{\sigma\tau} , \quad (4b)$$

if the electric permittivity of the sample is isotropic,  $\epsilon_{\sigma\tau} = \epsilon \delta_{\sigma\tau}$ .

If the sample is a cylinder, with axis directed along the  $x$ -axis, one has  $L_{xx} = 0$ ,  $L_{yy} = L_{zz} = 1/2$ . For a circular oblate disc,  $L_{xx} = L_{yy} = 0$  and  $L_{zz} = 1$ .

Similar relations hold for AC electric fields, provided the electric permittivity tensor is introduced as dependent on frequency,  $\omega$  .

Semi-macroscopically, the electric polarisation induced in the sample at the frequency  $2\omega$  is defined as:

$$P_{\sigma}(2\omega) = \frac{1}{V} \int M_{\sigma}^{2\omega}(\underline{E}) f(\Gamma, \underline{E}) d\Gamma , \quad (5)$$

where the statistical distribution function  $f(\Gamma, \underline{E})$  refers in general to the whole medium acted on by the external field  $\underline{E}$  when the microsystems ( atoms, molecules, macromolecules, ions ) are at the configuration  $\Gamma$  .

On the assumption that reorientation of microsystems is caused by the DC field alone, we have in the linear approximation of Gibbs' statistical perturbation calculus:

$$f(\Gamma, \underline{E}) = f(\Gamma, 0) \left[ 1 + \frac{1}{kT} M_{\sigma}^0 E_{\sigma}^{\circ}(0) \right] , \quad (6)$$

where  $M_p^0$  is the total electric dipole moment of the sample in the absence of external fields.

In the same approximation, the momentary electric dipole moment induced in the sample at the frequency  $2\omega$  is:

$$M_p^{2\omega}(\underline{E}) = \frac{1}{4} \left[ B_{\sigma\tau\nu}^{2\omega} + C_{\sigma\tau\nu\rho}^{2\omega} E_p(0) \right] E_\tau^e(\omega) E_\nu^e(\omega), \quad (7)$$

$B_{\sigma\tau\nu}^{2\omega}$  and  $C_{\sigma\tau\nu\rho}^{2\omega}$  being tensors of 2-nd and 3-rd order nonlinear polarizability referring to the sample of volume  $V$  as a whole.

By Eqs (6) and (7), we write the polarisation (5) in explicit form:

$$P_p^{2\omega} = \frac{1}{4V} \left\langle C_{\sigma\tau\nu\rho}^{2\omega} + \frac{1}{kT} B_{\sigma\tau\nu}^{2\omega} M_p^0 \right\rangle E_\tau^e(\omega) E_\nu^e(\omega) E_p^e(0), \quad (5a)$$

where the symbol  $\langle \dots \rangle$  denotes statistical averaging with the unperturbed Gibbs distribution function  $f(\Gamma, 0)$ .

On averaging the right-hand term of Eq. (5a) and comparing the result thus obtained with the phenomenological equation (1) we get, on taking into account the relation (3), the following expression for the nonlinear susceptibility tensor of an arbitrary isotropic body:

$$\chi_{\sigma\tau\nu\rho}^{2\omega} = \left[ G^{2\omega} (\delta_{\eta\lambda} \delta_{\mu\varepsilon} + \delta_{\eta\mu} \delta_{\lambda\varepsilon}) + S^{2\omega} \delta_{\eta\varepsilon} \delta_{\lambda\mu} \right] R_{\eta\sigma}^{2\omega} R_{\lambda\tau}^{\omega} R_{\mu\nu}^{\omega} R_{\varepsilon\rho}^0, \quad (8)$$

where we have introduced the following factors, characterizing the microscopic structure of the medium:

$$G^{2\omega} = \frac{1}{120V} \left\langle 3 C_{\alpha\alpha\beta\beta}^{2\omega} - C_{\alpha\beta\beta\alpha}^{2\omega} + \frac{1}{kT} (3 B_{\alpha\alpha\beta}^{2\omega} M_p^0 - B_{\alpha\beta\beta}^{2\omega} M_p^0) \right\rangle, \\ S^{2\omega} = \frac{1}{60V} \left\langle 2 C_{\alpha\beta\beta\alpha}^{2\omega} - C_{\alpha\alpha\beta\beta}^{2\omega} + \frac{1}{kT} (2 B_{\alpha\beta\beta}^{2\omega} M_p^0 - B_{\alpha\alpha\beta}^{2\omega} M_p^0) \right\rangle. \quad (9)$$

In particular, on neglecting electronic dispersion and absorption and the anisotropy of the tensor (4), the phenomenological nonlinear susceptibility tensor (8) becomes completely isotropic:

$$\chi_{\sigma\tau\nu\rho}^{2\omega} = \frac{1}{3} Q^{2\omega} (\delta_{\sigma\tau} \delta_{\nu\rho} + \delta_{\sigma\nu} \delta_{\tau\rho} + \delta_{\sigma\rho} \delta_{\tau\nu}) R^{2\omega} (R^\omega)^2 R^0, \quad (8a)$$

with the single molecular factor:

$$Q^{2\omega} = 3 G^{2\omega} = 3 S^{2\omega} = \frac{1}{20V} \left\langle C_{\alpha\alpha\beta\beta}^{2\omega} + \frac{1}{kT} B_{\alpha\alpha\beta}^{2\omega} M_p^0 \right\rangle, \quad (10)$$

and, by Eq. (4b),  $R^\omega = (\varepsilon^\omega + 2 \varepsilon_e) / 3 \varepsilon_e$  etc.

For this particular case we have, by Eq. (8a) :

$$\chi_{yyyy}^{2\omega} = Q^{2\omega} R^{2\omega} (R^{\omega})^2 R^0 \quad (8b)$$

Thus, in the semi-macroscopic treatment, the microscopic calculation of the nonlinear susceptibility tensor reduces to the molecular-statistical analysis of the factor (10). A different approach to the relation between the molecular polarizabilities and the macroscopic nonlinear susceptibility has been proposed by Bedeaux and Bloembergen (ref. 62).

Otherwise than theirs, our approach automatically separates the geometrical-macroscopic factors (4) from the molecular-statistical factors (9) and (10).

#### APPLICATION TO FLUID MIXTURES

We shall now analyze the molecular constant (10) for the case of a sample of volume  $V$  containing  $N = \sum_i N_i$  unlike microsystems,  $N_i = N x_i$  being the number of microsystems of the  $i$ -th species and  $x_i$  the molar fraction of the  $i$ -th component of the mixture; obviously,  $\sum_i x_i = 1$ .

#### The role of angular correlations

To begin with, we assume the dipole moment and macroscopic nonlinear polarizabilities occurring in the factor (10) to be, simply, sums of the respective quantities, referred to the microsystems:

$$M_{\alpha}^0 = \sum_i \sum_{p=1}^{N_i} \mu_{\alpha}^{(p,i)}, \quad B_{\alpha\beta\gamma}^{2\omega} = \sum_i \sum_{p=1}^{N_i} b_{\alpha\beta\gamma}^{2\omega(p,i)}, \quad c_{\alpha\beta\gamma\delta}^{2\omega} = \sum_i \sum_{p=1}^{N_i} c_{\alpha\beta\gamma\delta}^{2\omega(p,i)}, \quad (11)$$

$\mu_{\alpha}^{(p,i)}$  denoting the permanent dipole moment component of the  $p$ -th isolated microsystem of species  $i$ , and  $b_{\alpha\beta\gamma}^{2\omega(p,i)}$  and  $c_{\alpha\beta\gamma\delta}^{2\omega(p,i)}$  — the tensors of its 2-nd and 3-rd order nonlinear polarizabilities, respectively.

On insertion of (11) into Eq. (10), we obtain the equation for the mixture:

$$Q_m^{2\omega} = \sum_i x_i Q_i^{2\omega} + \sum_{ij} x_i x_j Q_{ij}^{2\omega}, \quad (12)$$

where

$$Q_i^{2\omega} = \frac{1}{20} \rho \left( c_{\alpha\alpha\beta\beta}^{2\omega(i)} + \frac{1}{kT} b_{\alpha\alpha\beta\beta}^{2\omega(i)} \mu_{\beta}^{(i)} \right) \quad (13)$$

is a factor referring to the  $i$ -th component of the perfect mixture, with  $\rho = N/V$  — the number density of the microsystems. Accordingly, in the absence of correlations between the microsystems, the factor  $Q_m^{2\omega}$  and hence the nonlinear susceptibility is additive.

From Eq. (13) we see that, in the microscopic interpretation, the phenomenological nonlinear susceptibility of a dilute dipolar substance consists of two parts (refs 25, 63): a part not dependent directly on temperature, resulting from the purely distortional process of nonlinear electronic polarizability of order 3 (Voigt effect), which occurs for all molecular symmetries since  $c_{\alpha\beta\gamma\delta}^{2\omega(i)}$  has non-zero tensor components even for atoms in their ground state; and a part directly dependent on temperature in accordance with the Langevin-Debye theory related with the statistical process of reorientation of the permanent electric dipoles  $\mu_{\alpha}^{(i)}$  in the DC electric field and with the process of 2-nd order nonlinear distortion, described by the tensor  $b_{\alpha\beta\gamma}^{2\omega(i)}$ . The last effect occurs only in gases of molecules dipolar in groundstate. The temperature effect occurs moreover if dipole reorientation is caused by an AC electric field with a frequency below Debye dispersion (refs 27, 11).

As the result of correlations between microsystems of the same or different components of the system, the factor  $Q_m^{2\omega}$  ceases to be additive. In a first approximation, with regard to the expansion (12), a measure of the deviation from additivity is provided by the binary factor:

$$Q_{ij}^{2\omega} = \frac{\rho}{40kT} \left( b_{\gamma\delta\alpha}^{2\omega(i)} \mu_{\beta}^{(j)} + \mu_{\alpha}^{(i)} b_{\gamma\delta\beta}^{2\omega(j)} \right) J_{\alpha\beta}^{(ij)}, \quad (14)$$

where we have introduced the tensor of angular binary correlations between dipolar microsystems of the species  $i$  and  $j$ :

$$J_{\alpha\beta}^{(ij)} = \frac{\rho}{V} \iint c_{\alpha\beta}^{(pi,qj)} g_{ij}^{(2)}(\Gamma_{pi}, \Gamma_{qj}) d\Gamma_{pi} d\Gamma_{qj}. \quad (15)$$

Above,  $g_{ij}^{(2)}(\Gamma_{pi}, \Gamma_{qj})$  is the binary correlation function for two microsystems at  $\Gamma_{pi}$  and  $\Gamma_{qj}$ , whereas  $c_{\alpha\beta}^{(pi,qj)}$  is the cosine of the angle subtended by the axis  $\alpha$  of the microsystem at  $\Gamma_{pi}$  and the axis  $\beta$  of the one at  $\Gamma_{qj}$ .

If, in particular, the molecules are axially symmetric, Eq. (14) reduces to the simple form:

$$Q_{ij}^{2\omega} = \frac{3\rho}{40kT} \left( b_i^{2\omega} \mu_j + \mu_i b_j^{2\omega} \right) J_{ij}, \quad b_i^{2\omega} = b_{\alpha\alpha\alpha}^{2\omega(i)}/3, \quad (14a)$$

where the angular binary correlation parameter

$$J_{ij} = \frac{\rho}{V} \iint \cos \theta_{pi,qj} g_{ij}^{(2)}(\Gamma_{pi}, \Gamma_{qj}) d\Gamma_{pi} d\Gamma_{qj} \quad (15a)$$

is analogical to that intervening in the theory of linear dipole polarisation and Kerr effect in mixtures (ref. 64). For a one-component system, (15a)

reduces directly to the well known Kirkwood parameter.

The role of electric molecular fields in polar fluids.

In strongly condensed media, electric molecular fields  $\underline{F}$  are present even if the medium is not acted on by external fields. Owing to fluctuations of the molecular fields in regions of short-range order, the molecular symmetry is impaired e.g. a molecular centre of symmetry can be destroyed. In this way, electric moments of higher orders are induced in nondipolar centrosymmetric molecules in accordance with the expansion:

$$M_{\alpha}^0 = \sum_i \sum_{p=1}^{N_i} \alpha_{\alpha\beta}^{(pi)} F_{\beta}^{(pi)} + \dots ,$$

$$B_{\alpha\beta\gamma\delta}^{2\omega} = \sum_i \sum_{p=1}^{N_i} c_{\alpha\beta\gamma\delta}^{2\omega(pi)} F_{\delta}^{(pi)} + \dots , \tag{16}$$

where  $\alpha_{\alpha\beta}^{(pi)}$  is the tensor of linear electric polarizability, induced in molecule  $p$  of species  $i$  by the electric field originating in the  $N-1$  molecules of the medium:

$$\underline{F}^{(pi)} = \sum_j \sum_{\substack{q=1 \\ q \neq p}}^{N_j} \underline{F}^{(pi,qj)} , \tag{17}$$

with  $\underline{F}^{(pi,qj)}$  — the field at the centre of molecule  $pi$  due to the electric charges of a neighbouring molecule  $qj$ . We neglect here the influence of the molecular field on the tensor  $c_{\alpha\beta\gamma\delta}^{2\omega}$  as well as the effect of Yvon-Kirkwood molecular redistribution (refs 4, 58).

By Eqs (16) and (17), we obtain the factor (10) for systems of nondipolar molecules ( we write out the temperature-dependent part only):

$$Q_m^{2\omega} = \frac{1}{20V kT} \sum_{ijkl} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \sum_{s=1}^{N_l} c_{\alpha\beta\gamma\delta}^{2\omega(pi)} \alpha_{\beta\delta}^{(qj)} F_{\gamma}^{(pi,rk)} F_{\delta}^{(qj,sl)} \right\rangle . \tag{18}$$

This expression shows that nondipolar fluids too exhibit a temperature-dependent part of their nonlinear susceptibility, due to space and time fluctuations of the molecular electric fields lowering the symmetry of the molecules as such as well as of the region of short-range order (refs 27,51). In general, the field existing at the centre of molecule  $p$  of species  $i$  due to the electric multipoles of molecule  $q$  of species  $j$  is (ref. 64):

$$\underline{F}_{pi,qj} = \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n-1)!!} {}^{(1)}\underline{T}_{pi,qj}^{(n)} [n] \underline{M}_{qj}^{(n)} , \tag{19}$$



where  $\underline{M}_{qj}^{(n)}$  is the electric  $2^n$ -pole moment of molecule  $q$  of species  $j$  and  ${}^{(1)}\underline{T}_{pi,qj}^{(n)} = -\nabla^{n+1}(r_{pi,qj}^{-1})$  is the interaction tensor of rank  $n+1$  describing interactions between molecules  $pi$  and  $qj$ , mutually distant by  $r_{pi,qj}$ . The symbol  $[n]$  denotes  $n$ -fold contraction of the product of two tensors of rank  $n$ .

Binary radial correlations. In our analysis of the rather complex expression (18) we shall at first restrict ourself to binary correlations of the radial type, neglecting polarizability tensor anisotropy. We thus write:

$$Q_{ij}^{2\omega} = \frac{\rho}{24kT} \sum_{n=1}^{\infty} \frac{(n+1)!}{(2n-1)!!} \left[ c_i^{2\omega} \alpha_i \underline{M}_j^{(n)} [n] \underline{M}_j^{(n)} + c_j^{2\omega} \alpha_j \underline{M}_i^{(n)} [n] \underline{M}_i^{(n)} \right] \langle r_{ij}^{-2(n+2)} \rangle, \quad (20)$$

where we have introduced the radial binary correlation parameters:

$$\langle r_{ij}^{-m} \rangle = 4\pi\rho \int r_{pi,qj}^{-m+2} \varepsilon_{ij}^{(2)}(r_{pi,qj}) dr_{pi,qj}. \quad (21)$$

From Eq. (20) we derive in particular for axially-symmetric quadrupolar molecules with the quadrupole moment  $\mathbb{H}$  (e.g.  $\text{CO}_2$ ):

$$Q_{ij}^{2\omega} = \frac{\rho}{8kT} (c_i^{2\omega} \alpha_i \mathbb{H}_j^2 + \mathbb{H}_i^2 c_j^{2\omega} \alpha_j) \langle r_{ij}^{-8} \rangle, \quad (20a)$$

and for tetrahedrally symmetric molecules (e.g.  $\text{CH}_4$ ):

$$Q_{ij}^{2\omega} = \frac{\rho}{5kT} \left[ (c_i^{2\omega} \alpha_i \Omega_j^2 + \Omega_i^2 c_j^{2\omega} \alpha_j) \langle r_{ij}^{-10} \rangle + \frac{25}{7} (c_i^{2\omega} \alpha_i \Phi_j^2 + \Phi_i^2 c_j^{2\omega} \alpha_j) \langle r_{ij}^{-12} \rangle \right], \quad (20b)$$

with  $\Omega_i$  and  $\Phi_i$  denoting, respectively, the octupole and hexadecapole moment of the tetrahedral molecule (refs 1,4).

Putting  $\Omega = 0$ , Eq. (20b) holds for octahedral molecules (e.g.  $\text{SF}_6$ ) the lowest nonzero electric moment of which is a hexadecapole  $\Phi$ .

Ternary radial correlations. From (18) we obtain, in higher approximations, components related with ternary and quaternary (four-molecule) etc. correlations, permitting the replacement of (12) by the more general expansion:

$$Q_m^{2\omega} = \sum_i x_i Q_i^{2\omega} + \sum_{ij} x_i x_j Q_{ij}^{2\omega} + \sum_{ijk} x_i x_j x_k Q_{ijk}^{2\omega} + \dots \quad (22)$$

Here, by (18) and (19), we get for the ternary molecular correlation factor:

$$Q_{ijk}^{2\omega} = \frac{\rho}{24kT} (c_i^{2\omega} \alpha_j + \alpha_i c_j^{2\omega}) \sum_{n=1}^{\infty} \frac{(n+1)!}{(2n-1)!} \frac{M_k^{(n)}[n]}{M_k} \langle (r_{ik} r_{jk})^{-(n+2)} \rangle \quad (23)$$

with the following ternary radial correlation parameters:

$$\langle (r_{ik} r_{jk})^{-(n+2)} \rangle = \frac{\rho^2}{V} \iiint (r_{pi,sk} r_{qj,sk})^{-(n+2)} P_{n+1} \left( \frac{r_{pi,sk} \cdot r_{qj,sk}}{r_{pi,sk} r_{qj,sk}} \right) \varepsilon_{ijk}^{(3)}(r_{pi}, r_{qj}, r_{sk}) dr_{pi} dr_{qj} dr_{sk}, \quad (24)$$

$\varepsilon_{ijk}^{(3)}(r_{pi}, r_{qj}, r_{sk})$  being the function of ternary radial correlation between three molecules at the positions  $r_{pi}$ ,  $r_{qj}$  and  $r_{sk}$ , whereas  $P_{n+1}$  is a Legendre polynomial of degree  $n+1$ .

The ternary parameters (24), according to the model adopted, can take positive as well as negative values in contradistinction to the binary parameters (21), which are always positive.

In particular, for quadrupolar molecules, Eq. (23) yields:

$$Q_{ijk}^{2\omega} = \frac{\rho}{8kT} (c_i^{2\omega} \alpha_j + \alpha_i c_j^{2\omega}) \left( \frac{H}{k} \right)^2 \langle (r_{ik} r_{jk})^{-4} \rangle. \quad (23a)$$

Similarly, other particular cases can be derived from Eq. (23). It is worth stressing that both Eqs (20) and (23) are applicable to mixtures where one of the components is atomic and the others molecular.

#### General tensorial correlations.

Eqs (20) and (23) hold moreover for molecules with (beside higher multipoles) a dipole moment. In this case, however, when calculating (10), one has to apply the following correlation function:

$$f(\Gamma, 0) = \exp[-U(\Gamma)/kT] / \int \exp[-U(\Gamma)/kT] d\Gamma, \quad (25)$$

where the total potential energy  $U(\Gamma)$  contains, beside the radial interaction energy  $U(\underline{r})$ , the energy of tensorial molecular interaction  $V(\underline{r}, \underline{\Omega})$  consisting of multipolar interactions of the electrostatic, inductive and dispersive types (refs 1,4). For polar molecules, the chief role generally belongs to electrostatic interactions, described by the multipole expansion (ref. 64):

$$V(\underline{r}, \underline{\Omega}) = -\frac{1}{2} \sum_{ij} \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{(-1)^m}{(2n-1)!! (2m-1)!!} \underline{M}_{pi}^{(n)} [n] \underline{T}_{pi,qj}^{(n)} [m] \underline{M}_{qj}^{(m)} \quad (26)$$

In this case, however, one has moreover to insert into Eq. (10) the sum of (11) and (16), so that (in addition to the term (18) containing contributions from the square of the molecular fields) we now obtain additionally a term containing contributions linear in the molecular field:

$$Q_m^{2\omega} = \frac{1}{20V kT} \sum_{ijk} \left\langle \sum_{p=1}^{N_i} \sum_{q=1}^{N_j} \sum_{r=1}^{N_k} \left[ b_{\alpha\alpha\beta\gamma}^{2\omega(pi)} \alpha_{\beta\gamma}^{(qj)} F_{\delta}^{(qj,rk)} + c_{\alpha\alpha\beta\gamma}^{2\omega(pi)} \mu_{\beta}^{(qj)} F_{\delta}^{(pi,rk)} \right] \right\rangle \quad (27)$$

With (19) and (26) taken into account, we hence obtain new contributions to  $Q_{ij}^{2\omega}$ ,  $Q_{ijk}^{2\omega}$ , etc. Obviously, the contributions from higher-order molecular fields (the gradient, or gradient of the gradient, etc.) can in some cases turn out to be very essential. However, we refrain from considering them here [see, (refs 1,4,65,66)].

#### DISCUSSION AND CONCLUSIONS

The DC-EFISHGL theory formulated by us leads to the following conclusions:

- (i) In the general case of a dense isotropic body, the relation between the tensor of phenomenological nonlinear 3-rd order susceptibility and the tensors of nonlinear molecular polarizabilities is not isotropic. This relation is resolved into a geometrical-macroscopic factor, related with the difference between the electric fields within and beyond the sample, and a molecular-statistical factor defining the microstructure of the medium.
- (ii) In mixtures of dense fluids, the nonlinear susceptibility is not additive but, in general, is nonlinearly dependent on the molar fractions of the components of the mixture.

These two facts have to be kept in mind when determining nonlinear polarizabilities from DC-EFISHGL studies in fluids, in which various radial and angular correlations can exist between molecules of the same and different species. Even in dilute solutions an important role is played by the solvent effect (refs 67-70), with ternary and higher correlations contributing importantly beside binary radial molecular correlations (ref. 69).

In the case of a two-component mixture it is convenient to expand  $q_m^{2\omega}$  in powers of concentration  $x$  (with  $x = x_2 = 1 - x_1$  — the molar fraction of the solute):

$$q_m^{2\omega} = \sum_{n=0}^{\infty} A_n^{2\omega} x^n = A_0^{2\omega} + A_1^{2\omega} x + A_2^{2\omega} x^2 + A_3^{2\omega} x^3 + \dots \quad (28)$$

The expansion coefficients  $A_n^{2\omega}$  are accessible to determination, on the one hand, directly from experiment and, on the other, from the theory formulated above. Thus,  $A_0^{2\omega}$  depends on the molecular properties of the pure solvent only:

$$A_0^{2\omega} = q_1^{2\omega} + q_{11}^{2\omega} + q_{111}^{2\omega} + \dots, \quad (29)$$

whereas the other coefficients  $A_1^{2\omega}$ ,  $A_2^{2\omega}$ ,  $A_3^{2\omega}$ , ... depend on the properties of the solute and mixture:

$$\begin{aligned} A_1^{2\omega} &= q_2^{2\omega} - q_1^{2\omega} + 2(q_{12}^{2\omega} - q_{11}^{2\omega}) + 3(q_{112}^{2\omega} - q_{111}^{2\omega}) + \dots, \\ A_2^{2\omega} &= q_{11}^{2\omega} - 2q_{12}^{2\omega} + q_{22}^{2\omega} + 3(q_{111}^{2\omega} - 2q_{112}^{2\omega} + q_{122}^{2\omega}) + \dots, \\ A_3^{2\omega} &= -q_{111}^{2\omega} + 3q_{112}^{2\omega} - 3q_{122}^{2\omega} + q_{222}^{2\omega} + \dots \end{aligned} \quad (30)$$

The molecular factors occurring in (29) and (30) can be found from Eqs (13), (14), (20) and (24). Their numerical calculation requires that well defined assumptions be made concerning the binary and ternary radial correlation functions (e.g. the hard sphere model of Kirkwood, the Lennard-Jones potential, etc). Our calculations show that, for quadrupole molecules such as  $H_2$ ,  $CO_2$  and  $C_6H_6$  the temperature contribution from quadrupole reorientation amounts to 20 - 80 % of the contribution resulting from 3-rd order nonlinear polarizability, depending on the model assumed. Whereas in the case of dipole molecules like CO or HCl the quadrupole effect contributes up to 20 %. These evaluations prove that agreement with experiment can be achieved only when taking into account the contributions to nonlinear susceptibility resulting from radial and angular molecular correlations.

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DISCUSSIONS. KIELICH

Buckingham - Professor KIELICH has mentioned the role of intermolecular electric fields in liquids in changing effective molecular susceptibilities. Intermolecular forces may change properties by other means. For example, the electronic interactions leading to the long-range dispersion forces and the short-range repulsive forces change the polarizability of a pair of helium atoms (Molec. Phys., 26, 7 (1973)). The importance of the short-range overlap effects presumably increases with the density of the system and with increasing temperature; at very high pressures there is a reduction in the polarizability of inert gas atoms that presumably relates to a "cage" effect. Do you have a feeling for the relative importance of the "field" and "overlap" effects ?

Kielich - I agree with Professor Buckingham that short-range overlap effects play an important part in the changes in linear polarizability of pairs of interacting atoms/Mol. Phys. 30/1975.535/. Collisional pair polarizabilities are directly apparent in depolarisation of scattered light and in temperature electro-optical birefringence of atomic gases under pressure.

However, in phenomena of light harmonics generation, we deal with an entirely different situation since they are due directly to nonlinear electro-  
nic polarizabilities of isolated atoms and molecules. Here, interactions of atoms/molecules/ play but an indirect role modifying the nonlinear polarizabilities, which now become effective polarizabilities. The present paper is concerned essentially with effects of molecular electric fields fluctuating in time and space and inducing directly, in the molecules, linear and nonlinear polarizabilities which are the source of temperature-dependent second-harmonic generation, even in nondipolar systems. In systems composed of dipolar molecules, in addition to molecular field fluctuations an important part is played by direct angular correlations, strongly dependent on the temperature, density and concentration. It is my opinion that in DC electric field-induced second-harmonic generation at not excessively high temperatures, the influence of overlap effects can be omitted by comparison with the effect of molecular field fluctuations, which causes a stronger dependence on the concentration of the mixture. The situation in the case of spontaneous second-harmonic scattering by atomic systems which is caused by three-atom overlapping effects (Chem. Phys. Letters 23/1973/53; 25/1974/405) is somewhat different.