Vol. A37 (1970) ACTA PHYSICA POLONICA Fasc. 2

DC ELECTRIC FIELD-INDUCED SECOND HARMONIC LIGHT GENERATION IN GASES AND LIQUIDS

By S. Kielich

Department of Molecular Physics, A. Mickiewicz University, Poznań*

(Received May 26, 1969)

A molecular-statistical theory of second-harmonic generation (SHG) by isotropic bodies immersed in an external DC or AC electric field is proposed. In particular, a microscopic interpretation of the symmetry relations of the third-order susceptibility tensor, consisting of a temperature-independent part due to the nonlinear electronic polarizability and a temperature-dependent part due to molecular reorientation, is given. The reorientation effect is discussed in detail for dense polar substances, where beside reorientation and mutual correlations of permanent dipoles yet other effects intervene due to reorientation of dipoles induced in the molecules by the electric fields of electric multipoles of neighbouring molecules, causing a strongly temperature-dependent effect in nondipolar substances too. The rôles and contributions of the various molecular mechanisms are discussed quantitatively and compared with recent measurements of DC electric field-induced SHG by fluids. Such studies are promising since, when performed in gases, they provide direct information on the second and third order nonlinear optical polarizabilities of the isolated molecules; in condensed media (liquids and solutions) they will moreover provide data on the molecular electric multipole moments and their correlations.

1. *Introduction*

The experiment of Franken *et al.* [1] shows that when a strong laser beam traverses a crystal without symmetry centre another beam of frequency equal to twice that of the incident one arises. This effect, one of the earliest in nonlinear optics and referred to as optical second harmonic generation (SHG), has since been studied in various materials and is growingly a subject of interest to experimenters and theoreticians [2]–[10].

In the paper, we shall deal essentially with second harmonic generation by centrosymmetric media immersed in a DC or AC electric field. The influence of a DC electric field is such as to polarize macroscopically isotropic media, thus depriving them of their centre of inversion and making them able to generate the second harmonic. DC electric field-induced second harmonic generation was first observed by Terhune *et al.* [11] in calcite crystal, which naturally possesses a centre of inversion. The same authors simultaneously observed SHG in the absence of a DC electric field as a result of nonlinearity related with

---

* Address: Katedra Fizyki Molekularnej, Uniwersytet im. A. Mickiewicza, Poznań, Grunwaldzka 6, Polska.

electric quadrupole polarization and electro-magnetic dipole polarization [2], [6]. Bjorkholm and Siegman [12] performed more accurate measurements of quadrupole-type SHG and electric field-induced SHG in calcite relative to the SHG obtained in crystals of ADP. In addition, some weak generation can arise by higher order multipole electric and magnetic effects in isotropic media presenting strong spatial dispersion [9, 10].

Recently, Mayer [13] investigated SHG by fluids in a DC electric field. The effect was observed in nondipolar substances such as H_2, O_2 and CCl_4 as well as in dipolar ones like CO, $CHCl_3$ and other methyl and ethyl halogenoderivatives. In nondipolar gases, in the absence of interactions, SHG is related only with the nonlinear electronic polarizability of the molecules due to the second power of the optical field strength E_ω^2 and the first power of the DC electric field E_0. On the other hand, as shown by Mayer [13], in dipolar gases this temperature-independent effect is accompanied by a temperature-dependent effect due to reorientation of the permanent molecular dipoles in the DC electric field. The temperature-dependent effect is also exhibited by nondipolar substances if condensed, where the electric fields of permanent molecular quadrupoles and octupoles induce dipoles in neighbouring molecules causing them to undergo reorientation in an externally applied DC electric field [14]. In this way, the natural symmetry of an isotropic body is destroyed so that, while acted on by a DC electric field, it is able to generate a second harmonic of light accessible to observation in experiments.

In the present paper we shall give a systematical quantitative analysis of second harmonic generation by isotropic bodies such as gases, liquids and their solutions, when polarized by immersion in a DC electric field. Particular consideration will be given to the rôle played by the various molecular mechanisms contributing to provide the conditions for SHG. Also, it will be our aim to make apparent the rôle of symmetry as well as optical and electrical properties for individual molecules, including their various correlations in condensed systems. The theoretical approach will be along classical paths permitting the derivation of expressions adapted to direct numerical evaluations and to a comparison with experimental results. For simplicity, frequency dispersion will not be considered explicitely.

2. *Phenomenological treatment*

An electromagnetic wave propagating in a medium gives rise to (in general dipolar, quadrupolar, octupolar ...) electric and magnetic polarization. The vector of electric polarization $\boldsymbol{P}(\boldsymbol{r}, t)$ at the space-time point $(\boldsymbol{r}, t)$ is [6], [9]:

$$\boldsymbol{P}(\boldsymbol{r}, t) = \boldsymbol{D}(\boldsymbol{r}, t) - \boldsymbol{\nabla} \cdot \boldsymbol{Q}(\boldsymbol{r}, t) + \ldots, \tag{1}$$

where $\boldsymbol{D}(\boldsymbol{r}, t)$ is the vector of electric dipole polarization, $\boldsymbol{Q}(\boldsymbol{r}, t)$ — the (second rank) tensor of electric quadrupolar polarization (higher rank tensors of octupolar polarization etc. can also be considered); $\boldsymbol{\nabla}$ is the spatial differential operator.

In a first approximation, the relation between $\boldsymbol{D}(\boldsymbol{r}, t)$ or $\boldsymbol{Q}(\boldsymbol{r}, t)$ and the electric field strength vector $\boldsymbol{E}(\boldsymbol{r}, t)$ is a linear one. In tensor notation, this is rendered by writing:

$$D_i^{(1)}(\boldsymbol{r}, t) = \chi_{ij}^{dd} E_j(\boldsymbol{r}, t) + \chi_{ijk}^{dq} \nabla_k E_j(\boldsymbol{r}, t) + \ldots, \tag{2}$$

$$Q_{ij}^{(1)}(\boldsymbol{r}, t) = \chi_{ijk}^{qd} E_k(\boldsymbol{r}, t) + \chi_{ijkl}^{qq} \nabla_l E_k(\boldsymbol{r}, t) + \ldots \tag{3}$$

The second tensor χ_{ij}^{dd} is the linear susceptibility tensor in the electric dipole-dipole approximation; the third rank tensors $\chi_{ijk}^{dq} = \chi_{jki}^{qd}$ are tensors of electric dipole-quadrupole susceptibility of first order; the fourth rank tensor χ_{ijkl}^{qq} is the electric quadrupole-quadrupole susceptibility tensor. In Eqs (2) and (3), the summation convention over recurring indices j, k, l is implicite.

The relations (1)–(3) account for linear optics. However, such a description ceases to be adequate and requires modification when a material system is subjected to an intense electromagnetic field, such as that conveyed by the light beam of a giant laser. As long as the nonlinearity induced in the medium is not too large, this can adequately be achieved by having recourse to the second approximation [6, 9]:

$$D_i^{(2)}(\boldsymbol{r}, t) = \chi_{ijk}^{dd} E_j(\boldsymbol{r}, t) E_k(\boldsymbol{r}, t) + \chi_{ijkl}^{dq} E_j(\boldsymbol{r}, t) \nabla_l E_k(\boldsymbol{r}, t) + \ldots, \tag{4}$$

$$Q_{ij}^{(2)}(\boldsymbol{r}, t) = \chi_{ijkl}^{qd} E_k(\boldsymbol{r}, t) E_l(\boldsymbol{r}, t) + \ldots \tag{5}$$

Above, the third rank tensor χ_{ijk}^{dd} defines the electric dipole-dipole susceptibility of second order; the fourth rank tensor $\chi_{ijkl}^{dq} = \chi_{klij}^{qd}$ is that of the electric dipole-quadrupole susceptibility of second order.

In certain cases (thus, for centro-symmetric bodies), one has to consider also a nonlinearity of third order. For the electric dipolar polarization, this nonlinearity takes the form:

$$P_i^{(3)}(\boldsymbol{r}, t) = \chi_{ijkl}^{dd} E_j(\boldsymbol{r}, t) E_k(\boldsymbol{r}, t) E_l(\boldsymbol{r}, t) + \ldots, \tag{6}$$

where the fourth rank tensor χ_{ijkl}^{dd} defines the third-order susceptibility in the dipole-dipole approximation.

For the case of an isotropic body, these tensors become isotropic and, quite generally, can be written as:

$$\chi_{ij} = \chi \delta_{ij}, \quad \chi_{ijk} = 0,$$

$$\chi_{ijkl} = \chi_1 \delta_{ij} \delta_{kl} + \chi_2 \delta_{ik} \delta_{jl} + \chi_3 \delta_{il} \delta_{kj} \tag{7}$$

with δ_{ij} — the unit symmetric tensor having components equalling 1 for $i = j$ and 0 for $i \neq j$.

By Eqs (7) one sees that in isotropic bodies the second-order effects (4) and (5) are related with electric dipole-quadrupole polarization only, whereas in the third approximation (6) there appears an electric effect already in the dipolar approximation.

Considerations like these hold, too, for the magnetic polarization induced in a medium by the magnetic vector $\boldsymbol{H}(\boldsymbol{r}, t)$ of the light wave [9], though its part in nonlinear optical phenomena is small. More important, and indeed sometimes essential, are the changes in electric polarization caused by the magnetic vector $\boldsymbol{H}(\boldsymbol{r}, t)$; the relevant contribution to the second order electric polarization (4) results as:

$$D_i^{(2)}(\boldsymbol{r}, t) = \eta_{ijk}^{dd} E_j(\boldsymbol{r}, t) H_k(\boldsymbol{r}, t), \tag{8}$$

where the third rank pseudotensor η_{ijk}^{dd} defines the change induced in the electric dipole susceptibility χ_{ij}^{dd} by a magnetic field. For isotropic bodies, the pseudotensor η_{ijk} becomes [16]:

$$\eta_{ijk} = \eta \varepsilon_{ijk}, \tag{9}$$

ε_{ijk} being the third-rank antisymmetric unit tensor with components equal to 1 for (cyclically) $i = 1, j = 2, k = 3$, to -1 for (cyclically) $i = 2, j = 1, k = 3$ and to 0 if $i = j$ or $j = k$ or $k = i$.

As a contribution to third-order electric polarization (6), we adduce the following one, which is non-zero for centro-symmetric bodies also:

$$D_i^{(3)}(\boldsymbol{r}, t) = \eta_{ijkl}^{dd} E_j(\boldsymbol{r}, t) H_k(\boldsymbol{r}, t) H_l(\boldsymbol{r}, t) \tag{10}$$

the tensor η_{ijkl}^{dd} accounting for the change induced in the tensor χ_{ij}^{dd} by the square of the magnetic field strength.

In order to adapt the preceding expressions to a description of optical-harmonic generation, it is convenient to replace the vectors $\boldsymbol{P}(\boldsymbol{r}, t)$, $\boldsymbol{E}(\boldsymbol{r}, t)$ and $\boldsymbol{H}(\boldsymbol{r}, t)$ by Fourier components [8], when the space-dependent amplitudes $\boldsymbol{P}^{\omega}, \boldsymbol{P}^{2\omega}, \ldots$ have a time-dependence $e^{-i\omega t}$, $e^{-i2\omega t}$, ... Accordingly, for the case of an isotropic body, the electric polarization induced at frequency 2ω is, by (8) and (9):

$$D_i^{2\omega} = \eta^{2\omega} \varepsilon_{ijk} E_j^{\omega} H_k^{\omega} \tag{11}$$

or, in vector notation [15]:

$$\boldsymbol{D}^{2\omega} = \eta^{2\omega} \boldsymbol{E}^{\omega} \times \boldsymbol{H}^{\omega}. \tag{11a}$$

Similarly, by (4) and (5), one obtains the electric quadrupole contribution to second-harmonic generation [10, 15].

As stated at the outset, our particular interest bears on SHG in the presence of a DC electric field $\boldsymbol{E}^0$. With regard to Eqs (6) and (7) and in the case of an isotropic body, one obtains:

$$P_i^{2\omega} = (\chi_{1122}^{2\omega} + \chi_{1212}^{2\omega}) E_i^{\omega} E_j^{\omega} E_j^0 + \chi_{1221}^{2\omega} E_j^{\omega} E_j^{\omega} E_i^0, \tag{12}$$

where the notation is $\chi_{ijkl}^{2\omega} = \chi_{ijkl}^{dd}$ $(-2\omega, \omega, \omega, 0)$; for an isotropic body, this tensor has 21 non-zero components, of which only 3 are mutually independent because of the condition

$$\chi_{1111}^{2\omega} = \chi_{1122}^{2\omega} + \chi_{1212}^{2\omega} + \chi_{1221}^{2\omega} \tag{13}$$

which applies to this case.

Similarly, one readily verifies that replacement of the field $H_l(\boldsymbol{r}, t)$ in Eq. (10) by a DC magnetic field H_l^0 leads to the possibility of SHG by isotropic bodies immersed in a DC magnetic field [9].

Let us assume the light to propagate along the z-axis and the DC electric field to act along the y-axis. In this experimental setup [13] with regard to Eq. (12) the polarization components in the x- and y-directions are, respectively:

$$\begin{aligned} P_x^{2\omega} &= \chi_2^{2\omega} E_x^{\omega} E_y^{\omega} E_y^0, \\ P_y^{2\omega} &= (\chi_2^{2\omega} E_x^{\omega} E_x^{\omega} + \chi_3^{2\omega} E_y^{\omega} E_y^{\omega}) E_y^0, \end{aligned} \tag{14}$$

where we have introduced the constants:

$$\begin{aligned} \chi_1^{2\omega} &= \chi_{1221}^{2\omega}, \quad \chi_2^{2\omega} = \chi_{1122}^{2\omega} + \chi_{1212}^{2\omega}, \\ \chi_3^{2\omega} &= \chi_{1122}^{2\omega} + \chi_{1212}^{2\omega} + \chi_{1221}^{2\omega} = \chi_{1111}^{2\omega} \end{aligned} \tag{15}$$

satisfying the relation:

$$\chi_1^{2\omega}+\chi_2^{2\omega} = \chi_3^{2\omega}. \tag{16}$$

Indeed, the tensor $\chi_{ijkl}(-2\omega, \omega, \omega, 0)$ is symmetric in the indices j and k, so that the number of its mutually independent components reduces to 2, namely $\chi_{1122}^{2\omega} = \chi_{1212}^{2\omega}$ and $\chi_{1221}^{2\omega}$.

If the medium presents negligibly small electron dispersion, the tensor $\chi_{ijkl}^{2\omega}$ can be considered as totally symmetric, whence with satisfactory accuracy we have [17]:

$$\chi_{1122}^{2\omega} = \chi_{1212}^{2\omega} = \chi_{1221}^{2\omega} = \frac{1}{3}\chi_{1111}^{2\omega}. \tag{17}$$

The preceding condition entails the following additional relation between the constants (15):

$$\chi_1^{2\omega} : \chi_2^{2\omega} : \chi_3^{2\omega} = 1:2:3. \tag{18}$$

The symmetry relations (16) and (18) are due to Bloembergen[1] (see also Ref. [14]).

The foregoing phenomenological treatment, though quite general, is unable to provide insight into the microscopic mechanism of SHG which, if known, would guide our choice of systems with well-defined structures for experimental investigation. The relevant microscopic theory can be constructed along a twofold path: either in a quantum-mechanical approach or in a statistical-molecular approach on a classical level. Here, we shall proceed by the latter one, which is simpler and moreover permits a description not only of systems with noninteracting molecules (perfect gases) but also of systems of mutually correlating molecules, as is the case of imperfect gases and liquids. Obviously, we begin our discussion by the gaseous phase, where the mechanisms are simple, in order to go over to the condensed phase, where various molecular correlations leading to novel effects unknown in the absence of molecular interactions become of essential importance.

3. *Molecular treatment of dipolar gases*

Consider a system of N noninteracting molecules, having permanent electric dipoles μ. When in an external DC electric field, their potential energy is:

$$u(\Omega, \boldsymbol{E}^0) = u(0) - \mu_i E_i^0 \tag{19}$$

and they undergo a Langevin reorientation (when at thermodynamical equilibrium at temperature T and provided the field is not excessively strong), which is given by the Boltzmann distribution function [18]:

$$f(\Omega, \boldsymbol{E}^0) = f_0\left(1+\frac{1}{kT}\mu_i E_i^0\right) \tag{20}$$

f_0 being the distribution function in the absence of the electric field.

---

[1] Private communication, September 15, 1968.

Denoting by ϱ the density of the gas, the component of electric polarization induced therein at frequency 2ω can be written as [19]:

$$P_i^{2\omega} = \varrho \int m_i^{2\omega} f(\Omega, \boldsymbol{E}^0)\, d\Omega \tag{21}$$

the integral extending over all possible molecular orientations in the elementary body angle $d\Omega$.

A component of the total dipole moment $m_i^{2\omega}$ induced in a molecule at frequency 2ω in the presence of the DC electric field can be expressed, in accordance with the phenomenological equations (4) and (6), as follows [19]:

$$m_i^{2\omega} = \frac{1}{4}\,(b_{ijk}^{2\omega} + c_{ijkl}^{2\omega} E_l^0 + \ldots)\, E_j^{\omega} E_k^{\omega}. \tag{22}$$

Above, $b_{ijk}^{2\omega}$ is the tensor of molecular second-order polarizability, and $c_{ijkl}^{2\omega}$ that of third-order polarizability. On inspection of the expansion (22) one notes that the tensor $c_{ijkl}^{2\omega}$ defines the linear change caused in the tensor $b_{ijk}^{2\omega}$ by the direct influence of the field on the molecule, *i. e.*

$$c_{ijkl}^{2\omega} = \left(\frac{\partial b_{ijk}^{2\omega}}{\partial E_l^0}\right)_{E=0}.$$

It will be useful to note that the tensors $b_{ijk}^{2\omega}$ and $c_{ijkl}^{2\omega}$ are symmetric in the pair of indices j and k.

On inserting Eq. (22) into (21) and averageing with the distribution function (20), we obtain an equation of the form (12) where the phenomenological coefficients are now expressed as follows by way of parameters of the isolated molecule:

$$\chi_{1212}^{2\omega} = \chi_{1122}^{2\omega} = \frac{\varrho}{120}\left\{3c_{\alpha\alpha\beta\beta}^{2\omega} - c_{\alpha\beta\beta\alpha}^{2\omega} + \frac{1}{kT}\,(3b_{\alpha\alpha\beta}^{2\omega}\mu_\beta - b_{\alpha\beta\beta}^{2\omega}\mu_\alpha)\right\}, \tag{23}$$

$$\chi_{1221}^{2\omega} = \frac{\varrho}{60}\left\{2c_{\alpha\beta\beta\alpha}^{2\omega} - c_{\alpha\alpha\beta\beta}^{2\omega} + \frac{1}{kT}\,(2b_{\alpha\beta\beta}^{2\omega}\mu_\alpha - b_{\alpha\alpha\beta}^{2\omega}\mu_\beta)\right\}. \tag{24}$$

These expressions are valid for molecules of arbitrary symmetries. We shall now particularize them for some special cases. Thus, in the case of molecules belonging to the point group O_h (*e. g.* SF_6, UF_6) all the components of the tensors μ_α and $b_{\alpha\beta\gamma}^{2\omega}$ vanish whereas the tensor $c_{\alpha\beta\gamma\delta}^{2\omega}$ has 21 nonzero elements, only 3 of which are mutually independent, and the coefficients (23) and (24) become:

$$\chi_{1122}^{2\omega} = \frac{\varrho}{20}\,(c_{1111}^{2\omega} + 3c_{1122}^{2\omega} - c_{1221}^{2\omega}), \tag{25}$$

$$\chi_{1221}^{2\omega} = \frac{\varrho}{20}\,(c_{1111}^{2\omega} + 4c_{1221}^{2\omega} - 2c_{1122}^{2\omega}). \tag{26}$$

This result applies to the point group T_d also (*e. g.* CH_4, $SiCl_4$, *etc.*) where the tensor $b_{\alpha\beta\gamma}^{2\omega}$ has nonzero components (6 mutually equal components $b_{123}^{2\omega}$), but no permanent electric dipole occurs ($\mu = 0$). Hence, in the case of molecules with a centre of inversion as well as nondipolar molecules the constants $\chi^{2\omega}_{1122}$ and $\chi^{2\omega}_{1221}$ consist only of a part which does not depend directly on temperature, and results by third-order nonlinear electronic polarization of the molecules.

In the case of molecules having a permanent electric dipole, the other, directly temperature-dependent term, which is due to coupling between dipole reorientation in the DC field [18] and second-order molecular polarization, comes to play a part. Since in molecules of low symmetry the number of independent tensor components $b^{2\omega}_{\alpha\beta\gamma}$ and $c^{2\omega}_{\alpha\beta\gamma\delta}$ is quite considerable, the expressions (23) and (24) are now somewhat complicated. This leads us to restrict our present considerations to some point groups only comprising the majority of the simpler molecules.

Thus, for molecules with symmetry of the point groups C_{6v} and $C_{\infty v}$ (*e. g.* HCl, CO, HCN, *etc.*), we obtain with regard to Eqs (23) and (24):

$$\chi^{2\omega}_{1122} = \frac{\varrho}{60}\left\{c^{2\omega}_{3333}+7c^{2\omega}_{1122}+c^{2\omega}_{1221}+6c^{2\omega}_{1133}-2c^{2\omega}_{1331}+\frac{\mu_3}{kT}\left(b^{2\omega}_{333}+3b^{2\omega}_{113}-b^{2\omega}_{311}\right)\right\}, \quad (27)$$

$$\chi^{2\omega}_{1221} = \frac{\varrho}{60}\left\{c^{2\omega}_{3333}+2c^{2\omega}_{1122}+6c^{2\omega}_{1221}+8c^{2\omega}_{1331}-4c^{2\omega}_{1133}+\frac{\mu_3}{kT}\left(b^{2\omega}_{333}+4b^{2\omega}_{311}-2b^{2\omega}_{113}\right)\right\}. \quad (28)$$

For numerical evaluations, we neglect electronic dispersion; the tensors $b^{2\omega}_{\alpha\beta\gamma}$ and $c^{2\omega}_{\alpha\beta\gamma\delta}$ are then totally symmetric reducing the coefficients (27) and (28) to:

$$\chi^{2\omega}_{1122} = \chi^{2\omega}_{1221} = \frac{\varrho}{12}\left(c^{2\omega}+\frac{3\mu b^{2\omega}}{5kT}\right), \quad (29)$$

where $b^{2\omega} = (b^{2\omega}_{333}+2b^{2\omega}_{113})/3$ and $c^{2\omega} = (c^{2\omega}_{3333}+8c^{2\omega}_{1122}+4c^{2\omega}_{1133})/5$ denote mean values of nonlinear polarizabilities of the second and third order respectively [19].

Since as yet no theoretical values are known for the molecular parameters $b^{2\omega}$ and $c^{2\omega}$, we are induced to recur to an approximation which consists in taking instead the corresponding DC nonlinear polarizabilities β and γ in accordance with the relations $b^{2\omega} \simeq 2\beta$ and $c^{2\omega} \simeq 2\gamma/3$ valid in the absence of dispersion. In the first place, we note that putting $\mu = b^{2\omega} = 0$ in Eq. (29) we bring it to a form applicable to diatomic molecules of the point group $D_{\infty h}$ (*e.g.* H_2, O_2, N_2). Thus *e. g.* for H_2 theoretical calculations give [20] $\mu = \beta = 0$, $\gamma = 0.4\times10^{-36}$ e. s. u. and Eq. (29) yields coefficients $\chi^{2\omega}_3$ of Eqs (14) and (15):

$$\chi^{2\omega}_3 = 3\chi^{2\omega}_{1122} = 6.6\varrho\times10^{-38} \text{ e. s. u.}$$

However, experiments yield [13] $\chi^{2\omega}_3 = 9\varrho\times10^{-38}$ e. s. u., more than 1.4 times the theoretical value. For the dipolar molecule CO we obtain the theoretical values [21]: $\mu_3 = 0.11\times10^{-18}$ e. s. u. $\beta_{113} = -0.15\times10^{-30}$ e. s. u. $\beta_{333} = -0.98\times10^{-30}$ e. s. u. and [20] $\gamma_{3333} = 0.2\times10^{-36}$ e. s. u. With these, Eq. (29) leads to the coefficients $\chi^{2\omega}_3$ of Eqs (14) and (15) for $T = 300°K$:

$$\chi^{2\omega}_3 = 3\chi^{2\omega}_{1122} = \varrho(0.03-0.34)\times10^{-36} \text{ e. s. u.} = -0.31\varrho\times10^{-36} \text{ e. s. u.}$$

The preceding result shows that the contribution from third-order nonlinear electronic polarizability is 10 times smaller than that due to dipole reorientation, whose sign is negative.

Measurements by Mayer [13] gave $\chi_3^{2\omega} = 0.45\varrho \times 10^{-36}$ e. s. u. — a result satisfactorily coinciding in absolute value with our theoretical evaluation.

The expressions (27)–(29) apply as well to molecules of point group symmetry C_{4v} (*e. g.* BrF_5, IF_5) and C_{3v} (*e. g.* NH_3, $CHCl_3$, CH_3I). For $CHCl_3$ we have [22] $\mu = 1.01 \times 10^{-18}$ e. s. u. and from Rayleigh light scattering [19] $b_{113}^{\omega} = 12.1 \times 10^{-30}$ e. s. u., $b_{333}^{\omega} = 9.6 \times 10^{-30}$ e. s. u. whereas from optical Kerr effect [23] $c^{\omega} = 4.8 \times 10^{-36}$ e. s. u. Since here $b^{2\omega} = 2b^{\omega}$ and $c^{2\omega} \simeq c^{\omega}$, we get by Eqs (14), (15) and (29):

$$\chi_3^{2\omega} = \varrho(1.2+84) \times 10^{-36} \text{ e. s. u.}$$

Measurements in the present case yield [13] $\chi_3^{2\omega} = 1.1\varrho \times 10^{-36}$ e. s. u. which is equal to the theoretical value from the nonlinear polarizability effect alone. We ask why the dipole reorientation effect, which is 80 times larger, is not apparent experimentally? This is presumably due to the presence of mutual molecular correlations reducing strongly the effect in question, or else the value from experiments may result too low owing to insufficient absolute accuracy [13]. In any case this points to the necessity of taking intermolecular interactions into consideration, as we intend to do in the next Section.

As seen above with regard to strongly dipolar molecules, the term in nonlinear polarizability is numerically unimportant and can be dropped when applying Eqs (23) and (24) to molecules of point group symmetry C_{2v} (*e. g.* H_2O, O_3, H_2CO, CH_2Cl_2, C_6H_5Cl, $C_6H_5NO_2$ *etc.*), yielding:

$$\chi_{1122}^{2\omega} = \frac{\varrho \mu_3}{120\, kT} (2b_{333}^{2\omega} + 3b_{113}^{2\omega} + 3b_{223}^{2\omega} - b_{311}^{2\omega} - b_{322}^{2\omega}), \tag{30}$$

$$\chi_{1221}^{2\omega} = \frac{\varrho \mu_3}{60\, kT} (b_{333}^{2\omega} + 2b_{311}^{2\omega} + 2b_{322}^{2\omega} - b_{113}^{2\omega} - b_{223}^{2\omega}). \tag{31}$$

Obviously, however, molecules of lower symmetries involve too many molecular parameters, and numerical evaluations are not so easy.

4. *General theory for dense isotropic bodies*

Molecular correlations can be expected to affect SHG in liquids just as they affect other nonlinear phenomena (*e. g.* nonlinear refractive index, nonlinear light scattering, *etc.* [24]). The problem is most conveniently approached by way of the semimacroscopic method first used by Kirkwood [25] in linear dielectric theory and extended [23], [26] to nonlinear optical phenomena. This consists in taking a macroscopic isotropic spherical specimen of volume V and electric permittivity ε immersed in a different, external medium of permittivity ε_e or in vacuum ($\varepsilon_e = 1$). When an external electric field of sufficient strength $\boldsymbol{E}_e^0$ is applied, the specimen becomes electrically anisotropic with electric permittivity tensor ε_{ij}, and the macroscopic field $\boldsymbol{E}^0$ existing in the specimen is related to the externally applied field $\boldsymbol{E}_e^0$ as follows [27]:

$$3\varepsilon_e E_{ei}^0 = (\varepsilon_{ij} + 2\varepsilon_e \delta_{ij}) E_j^0. \tag{32}$$

A similar relationship holds for an electric field $\boldsymbol{E}_e^\omega$ oscillating at frequency ω; the quantities ε_{ij} and ε_e have now to be replaced appropriately by ε_{ij}^ω and ε_e^ω. In particular, for a weak field, when the medium has isotropic permittivity $\varepsilon_{ij} = \varepsilon\,\delta_{ij}$, the relation (32) reduces to the much simpler form [16]:

$$\boldsymbol{E}^0 = \frac{3\varepsilon_e}{\varepsilon+2\varepsilon_e}\,\boldsymbol{E}_e^0. \tag{33}$$

We now define a dipolar electric polarization at frequency 2ω as follows [23]:

$$P_i^{2\omega} = \frac{1}{V}\int M_i^{2\omega} f(\tau, \boldsymbol{E}^0)\,d\tau. \tag{34}$$

The statistical distribution function $f(\tau, \boldsymbol{E}^0)$, when the microsystems (atoms, molecules, macromolecules) of the system immersed in the external field $\boldsymbol{E}^0$ are at configuration τ, is in a first approximation:

$$f(\tau, \boldsymbol{E}^0) = f(\tau, 0)\left(1+\frac{1}{kT}\,M_i^0 E_{ei}^0\right), \tag{35}$$

where $\boldsymbol{M}^0$ is the total electric dipole moment of the medium in the absence of external fields.

The dipole moment $\boldsymbol{M}^{2\omega}$ induced in the medium (volume V) at frequency 2ω in the presence of a DC electric field can be written thus [26]:

$$M_i^{2\omega} = \frac{1}{4}\,(B_{ijk}^{2\omega}+C_{ijkl}^{2\omega}E_{el}^0)\,E_{ej}^\omega E_{ek}^\omega, \tag{36}$$

$B_{ijk}^{2\omega}$ and $C_{ijkl}^{2\omega}$ being tensors describing respectively the nonlinear polarizabilities of the second and third order, per unit volume of the medium.

With regard to Eqs (33)–(36), we find that, for a dense medium, the phenomenological coefficients of Eq. (12) are of the form:

$$\chi_{1122}^{2\omega} = \frac{L^{2\omega}}{120\,V}\,\langle 3C_{\alpha\alpha\beta\beta}^{2\omega} - C_{\alpha\beta\beta\alpha}^{2\omega} + \frac{1}{kT}\,(3B_{\alpha\alpha\beta}^{2\omega}M_\beta^0 - B_{\alpha\beta\beta}^{2\omega}M_\alpha^0)\rangle, \tag{37}$$

$$\chi_{1221}^{2\omega} = \frac{L^{2\omega}}{60\,V}\,\langle 2C_{\alpha\beta\beta\alpha}^{2\omega} - C_{\alpha\alpha\beta\beta}^{2\omega} + \frac{1}{kT}\,(2B_{\alpha\beta\beta}^{2\omega}M_\alpha^0 - B_{\alpha\alpha\beta}^{2\omega}M_\beta^0)\rangle, \tag{38}$$

where the smybol $\langle\ \ \rangle$ stands for statistical averageing at zero external fields, whereas the macroscopic factor $L^{2\omega}$ resulting by the isotropic relation (33) on assuming $\varepsilon_e = 1$ is [2]:

$$L^{2\omega} = \left(\frac{\varepsilon_{2\omega}+2}{3}\right)\left(\frac{\varepsilon_\omega+2}{3}\right)^2\left(\frac{\varepsilon_0+2}{3}\right). \tag{39}$$

The expressions (37) and (38) hold irrespective of the structure and symmetry of the microsystems of which the dense isotropic medium consists. We shall now apply them to some special cases.

4.1 Dipolar substances

We consider substances having dipolar molecules which (we assume) do not change their optical and electrical properties as a result of short-range mutual correlations. If now the volume V contains N like molecules, we can express the macroscopic parameters of Eqs (37) and (38) in terms of molecular parameters as follows:

$$M_\alpha^0 = \sum_{p=1}^{N} \mu_\alpha^{(p)},\ B_{\alpha\beta\gamma}^{2\omega} = \sum_{p=1}^{N} b_{\alpha\beta\gamma}^{2\omega(p)},$$

$$C_{\alpha\beta\gamma\delta}^{2\omega} = \sum_{p=1}^{N} c_{\alpha\beta\gamma\delta}^{2\omega(p)} \tag{40}$$

so that Eqs (37) and (38) now become:

$$\chi_{1122}^{2\omega} = \frac{L^{2\omega}}{120\,V}\left\{\left\langle\sum_{p=1}^{N}\left(3c_{\alpha\alpha\beta\beta}^{2\omega(p)} - c_{\alpha\beta\beta\alpha}^{2\omega(p)}\right)\right\rangle + \frac{1}{kT}\left\langle\sum_{p=1}^{N}\sum_{q=1}^{N}\left(3b_{\alpha\alpha\beta}^{2\omega(p)}\mu_\beta^{(q)} - b_{\alpha\beta\beta}^{2\omega(p)}\mu_\alpha^{(q)}\right)\right\rangle\right\}, \tag{41}$$

$$\chi_{1221}^{2\omega} = \frac{L^{2\omega}}{60\,V}\left\{\left\langle\sum_{p=1}^{N}\left(2c_{\alpha\beta\beta\alpha}^{2\omega(p)} - c_{\alpha\alpha\beta\beta}^{2\omega(p)}\right)\right\rangle + \frac{1}{kT}\left\langle\sum_{p=1}^{N}\sum_{q=1}^{N}\left(2b_{\alpha\beta\beta}^{2\omega(p)}\mu_\alpha^{(q)} - b_{\alpha\alpha\beta}^{2\omega(p)}\mu_\beta^{(q)}\right)\right\rangle\right\}. \tag{42}$$

These two expressions are immediately seen to go over into the ones (23), (24) derived previously for the gaseous state by neglecting statistical molecular correlations and putting $L^{2\omega} = 1$. As in the above-considered approximation, the terms in third-order nonlinear polarizability are practically correlation-independent and thus can be omitted in the present considerations, so that Eqs (41) and (42) become:

$$\chi_{1122}^{2\omega} = \frac{\varrho L^{2\omega}}{120\,kT}\left(3b_{\gamma\gamma\alpha}^{2\omega} - b_{\alpha\gamma\gamma}^{2\omega}\right)\mu_\beta K_{\alpha\beta}, \tag{43}$$

$$\chi_{1221}^{2\omega} = \frac{\varrho L^{2\omega}}{60\,kT}\left(2b_{\alpha\gamma\gamma}^{2\omega} - b_{\gamma\gamma\alpha}^{2\omega}\right)\mu_\beta K_{\alpha\beta}. \tag{44}$$

Here, we have introduced a tensor of angular molecular correlations:

$$K_{\alpha\beta} = \delta_{\alpha\beta} + \varrho\int c_{\alpha\beta}^{(pq)}\, g(\tau_{pq})\, d\,\tau_{pq} \tag{45}$$

with $c_{\alpha\beta}^{(pq)}$ — the cosine of the angle between the axis α of molecule p and the axis β of q, and $g(\tau_{pq})$ — the function of binary correlation between molecules p and q when at mutual configuration τ_{pq} [28].

In the absence of angular correlations, the correlation tensor (45) reduces to the unit tensor $\delta_{\alpha\beta}$, and Eqs (43), (44) at $L^{2\omega} = 1$ take the form valid for gases. We also note that if the dipole moment of the molecule has the direction of the molecule's symmetry axis, *e. g.* the 3-axis, then $c_{33}^{(pq)} = \cos\theta_{pq}$, and the correlation tensor (45) reduces to the well-known angular correlation parameter $K_{33} = K$ of Kirkwood's linear theory of dielectrics [25]:

$$K = 1 + \varrho\int\cos\theta_{pq}\, g(\tau_{pq})\, d\,\tau_{pq} \tag{46}$$

θ_{pq} denoting the angle subtended by the dipoles of molecules p and q.

In addition to the short-range statistical correlations (46), Kirkwood considered a long-range contribution in accordance with Onsager's model [29] involving the replacement of the dipole moments in Eqs (41)–(44) by the following one:

$$\mu^* = \left(\frac{3\varepsilon_0}{2\varepsilon_0+\varepsilon_\infty}\right)\left(\frac{\varepsilon_\infty+2}{3}\right)\mu, \tag{47}$$

where ε_0 is the static and ε_∞ the high-frequency dielectric constant.

By (47), $\mu^* > \mu$ in all cases, whereas the angular correlation parameter (46) can exceed unity (in general, for molecules whose dipole moment has the direction of the short axis, as in $CHCl_3$) or can be less than 1 (if the dipole moment is parallel to the longer axis, as in C_6H_5Cl).

Specifically, for the $CHCl_3$ molecule, $K = 1.2$ and $\mu^* = 1.47\,\mu = 1.48\times10^{-18}$ cm e. s. u., whereas for C_6H_5Cl $K = 0.6$ and $\mu^* = 1.86\,\mu = 3.14\times10^{-18}$ cm e. s. u. since [22] $\mu = 1.69\times10^{-18}$ cm e. s. u.

Moreover, it may be of interest to note that on the assumption that a molecule interacts with but one of its neighbours Kirkwood's parameter (46) takes the following values according to the angle between the two molecular dipoles:

$$K = \begin{cases} 0 \text{ for } \theta_{pq} = 180^\circ \\ 1 \text{ for } \theta_{pq} = 90^\circ \\ 2 \text{ for } \theta_{pq} = 0^\circ. \end{cases}$$

These values are thus found to vary from 0 at antiparallel orientation to 2 at parallel orientation of the dipoles, and the contribution of dipole reorientation to SHG in dense media will depend largely on what kind of angular dipole correlation is relevant.

4.2 Nondipolar substances

With the aim of simplifying this discussion of the temperature effect for nondipolar molecules, we shall neglect electron dispersion of the tensor $B^{2\omega}_{\alpha\beta\gamma}$ justifying us by Eqs (37) and (38) in writing simply:

$$\chi^{2\omega}_{1122} = \chi^{2\omega}_{1221} = \frac{L^{2\omega}}{60\,VkT}\langle B^{2\omega}_{\alpha\alpha\beta} M^0_\beta\rangle. \tag{48}$$

In dense media, electric molecular fields $\boldsymbol{F}$ exist even if no field is applied externally. Owing to fluctuations of these molecular fields, electric moments of higher order arise in centrosymmetric molecules. The latters' symmetry is destroyed in accordance with the following relations:

$$M^0_\alpha = \sum_{p=1}^{N} \alpha^{(p)}_{\alpha\beta} F^{(p)}_\beta + \ldots,$$

$$B^{2\omega}_{\alpha\beta\gamma} = \sum_{p=1}^{N} c^{2\omega(p)}_{\alpha\beta\gamma\delta} F_\delta + \ldots, \tag{49}$$

$\boldsymbol{F}^{(p)}$ is the field at the centre of the p-th molecule due to the electric multipoles of the remaining molecules of the medium.

Omitting anisotropy of the polarizability tensors $\alpha_{\alpha\beta}$ and $c^{2\omega}_{\alpha\beta\gamma\delta}$, we can write with regard to (48) and (49):

$$\chi^{2\omega}_{1122} = \frac{\varrho L^{2\omega}}{12\,kT}\alpha c^{2\omega}\langle F^2\rangle = {}_{NL}\chi^{2\omega}_{1122}\,\frac{\alpha}{kT}\,\langle F^2\rangle, \tag{50}$$

where $\alpha = \alpha_{\alpha\alpha}/3$ is the mean electric polarizability of the molecule, and ${}_{NL}\chi^{2\omega}_{1122}$ is the term resulting by the effect of third-order nonlinear polarizability given in Eqs (29) and (41) by the temperature-independent term.

In particular for axially-symmetric molecules possessing a quadrupole moment Θ only (for a definition of molecular multipole moments, see *e. g.* Refs [30] and [31]), the mean statistical value of the square electric quadrupole-type field is [26]:

$$\langle F^2\rangle = \Theta^2\,\langle r^{-8}\rangle, \qquad (51$$

where $\langle r^{-8}\rangle$ is defined as:

$$\langle r^{-n}\rangle = 4\pi\varrho \int r^{2-n}g(r)dr, \tag{52}$$

$g(r)$ defining a radial distribution function [28].

Applying Kirkwood's [32] model of hard sphere of diameter d and volume $v = \pi d^3/6$ to the calculation of (52), one gets with $n \geqslant 4$ [24], [33]:

$$\langle r^{-n}\rangle = \frac{4\pi\varrho}{n-3}\left(\frac{\pi}{6v}\right)^{(n-3)/3}. \tag{53}$$

Mean values of (52) can also be calculated for imperfect gases by applying the Lennard-Jones potential [30].

In the case of benzene at 295°K we have [14]:

$$\varrho = 6.74\times10^{21}\ \mathrm{cm^{-3}},\ \alpha = 10.32\times10^{-24}\ \mathrm{cm^3},\ \langle r^{-8}\rangle = 5\times10^{58}\ \mathrm{cm^{-8}},$$

so recurring to the calculated quadrupole [34] $\Theta = (12 \div 26.3)\ 10^{-26}$ e. s. u. cm^2 and with regard to (50) and (51) we find that the temperature-dependent quadrupole-induced dipole effect amounts to $(20 \div 80)$ per cent of the effect due to third-order nonlinear polarizability. In CS_2 this quadrupole contribution is twice larger [14], but nevertheless failed to produce signals in Mayer's measurements [13].

For the H_2 molecule one has: $\alpha = 0.79\times10^{-24}$ cm^3, $\Theta = 0.66\times10^{-26}$ e. s. u. cm^2 [31], $\langle r^{-8}\rangle = 2\times10^{63}$ cm^{-8}, whence by (59) and (51) $\chi^{2\omega}_{1122} = 1.7\,{}_{NL}\chi^{2\omega}_{1122}$. Similarly, for CO: $\alpha = 1.95\times10^{-24}$ cm^3, $\Theta = -2.5\times10^{-26}$ e. s. u. cm^2 [31], [35], $\langle r^{-8}\rangle = 6\times10^{60}$ cm^{-8}, yielding $\chi^{2\omega}_{1122} = 0.2\,{}_{NL}\chi^{2\omega}_{1122}$. Consequently, in these cases also, reorientation of dipoles which are induced by molecular quadrupoles leads to contributions which, when added to the values calculated in Section 3 enhance accordance with the experimental data [13].

The expression (50) applies also to tetrahedral molecules, which have neither a dipole nor a quadrupole moment [30], but possess an octupole moment Ω and a hexadecapole moment Φ giving rise to an electric field [26]:

$$\langle F^2\rangle = \frac{16}{5}\,\Omega^2\langle r^{-10}\rangle + \frac{80}{7}\,\Phi^2\langle r^{-12}\rangle. \tag{54}$$

Specifically, for CCl_4 one has: $\varrho = 6.22\times10^{21}$ cm^{-3}, $\alpha = 10.5\times10^{-24}$ cm^3, $\langle r^{-10}\rangle = 6\times10^{72}$ cm^{-10} [14]; the hexadecapole moment is as yet not available, but $\Omega = 5.5\times10^{-34}$ [42] or 15×10^{-34} e. s. u. cm^3 [37], whence with regard to (50) and (54) we conclude that the contribution from reorientation of dipoles which are induced in the molecules by the octupole moments of other molecules amounts to only 2 per cent of the third-order nonlinear polarizability effect. It is yet to be hoped that in other substances this octupolar effect may prove more considerable, although in molecules such as CH_4 or CF_4 the octupole moment is known to be three times smaller than in CCl_4 [30], [31], [36]—[38].

Eq. (54) with $\Omega = 0$ describes octahedral molecules like SF_6, where the first non-zero moment is hexadecapolar Φ. Predictably, however, its contribution here is very small.

5. *Final remarks and conclusions*

As shown above, the third-order susceptibility (in the absence of molecular correlations, as is the case in dipolar gases) consists of a temperature-independent part due to nonlinear electric polarizability and a temperature-dependent part resulting from the reorientation of permanent dipoles in a DC electric field. As yet, experiments on SHG [13] have not led to separation of the two effects. Nevertheless the present numerical evaluations permit the statement that in dipolar gases at room temperature the dipole reorientation effect is the predominant one. It also seems worth while to attempt a resolution of the two effects in experiment by measuring the temperature-dependence of SHG. Information as to the order of magnitude of nonlinear electronic polarization can be obtained from work on second-harmonic scattering [19], [39], third-harmonic generation by gases [40], optical Kerr effect [23], and DC Kerr effect [41].

There is yet another way of resolving the two effects in question, namely by studies of electronic or dipolar dispersion in an AC electric field. In the latter case, in accordance with Debye's dipole relaxation theory [18], one has to replace the permanent dipole moment μ in the distribution function (20) and Eqs (23) and (24) by a dipole moment μ^{ω_0} oscillating at frequency ω_0 much smaller than the optical frequency ω:

$$\mu_\alpha^{\omega_0} = \frac{\mu_\alpha e^{i\omega_0 t}}{1+i\omega_0\tau_\alpha}, \tag{55}$$

where τ_α is Debye's relaxation time for the principal molecular axis α. Eq. (55) suggests to investigate to what amount SHG is affected by Debye dipole dispersion, at the same time extending the scope of studies on molecular relaxation processes [42] and providing a means of making directly apparent the rôle of dipole reorientation in SHG.

In dense media, the two effects are more or less dependent on the molecular correlations within the system. The nonlinear polarizability effect is but slightly affected by the so-called translational fluctuation effect [32] (not discussed in this text, see Refs [24], [26]). On the other hand the molecular reorientation effect, which is of a statistical nature, is strongly dependent on the various molecular correlations. Particularly in dipolar liquids the effect of reorientation of the dipoles can undergo an enhancement or a decrease according to the kind of angular short range dipole correlations, and SHG investigations can be expected to provide highly valuable data on the structure of such liquids and their dielectric properties [25], [30].

The temperature-dependent effect can be said to occur not only in dipolar substances but also in quadrupolar and octupolar ones owing to the strong molecular electric fields existing in the condensed state and inducing dipole moments, which then undergo a reorientation in an applied DC electric field. The preceding statement results from Eq. (49), which shows that even in the case of molecules that are centrosymmetrical in their ground state ($\mu_\alpha = b^{2\omega}_{\alpha\beta\gamma} = 0$), the effective values of M^0_α and $B^{2\omega}_{\alpha\beta\gamma}$ are in general non-zero in regions with fluctuations of the electric fields of molecular multipoles causing a destruction of the initial symmetry of the isotropic medium as long as the DC electric field is kept applied. A naturally centro-symmetrical medium when acted on by a DC electric field becomes macroscopically anisotropic, with symmetry $C_{\infty v}$. As we have for the case of quadrupolar substances, this effect is strongly temperature-dependent and, at not too high temperatures, plays an important part in comparison to the distortional electronic effect.

A qualitative resolution of the two effects can also be hoped for from SHG investigations in solutions as a function of concentration. Indeed, from the shape of Eqs (37) and (38) or (41) and (42), it is readily seen that the distortional electronic effect has to be practically additive (neglecting translational fluctuations), whereas the molecular reorientation effect can deviate considerably from additivity as a result of angular correlations. The situation is similar with regard to dielectric polarization [30] and optical Kerr effect [23], [24].

Finally, let us note that quite recent, very careful and accurate measurements by Mayer[2] for bromoethane have resulted in full agreement with the symmetry relations (16) and (18); though as yet, it has not been possible to decide unequivocally as to which of the relevant mechanisms: nonlinear distortion alone, or in combination with molecular reorientation, is essential in SHG. Predictably, considerable intensities of SHG are to be expected in macromolecular substances and colloid solutions, where the reorientation of particles and the optical nonlinearity are strong [43].

The author wishes to express his sincere indebtedness to Professors N. Bloembergen and C. Mayer for their interesting letters, in particular regarding the symmetry relations for nonlinear susceptibility.

The author wishes to thank Dr G. Birnbaum for his fruitful discussions of certain spectral and molecular aspects of the subject when at the Warsaw Laser Measurements Conference.

I also wish to thank K. Flatau, M. Sci., for his cooperation in the English translation.

REFERENCES

[1] P. A. Franken, A. E. Hill, C. W. Peters, G. Weinreich, *Phys. Rev. Letters*, **7,** 118 (1961).
[2] J. A. Armstrong, N. Bloembergen, J. Ducuing, P. S. Pershan, *Phys. Rev.*, **127,** 1918 (1962).
[3] N. Bloembergen, P. S. Pershan, *Phys. Rev.*, **128,** 606 (1962).
[4] D. A. Kleinman, *Phys. Rev.*, **128,** 1761 (1962).
[5] P. A. Franken, J. F. Ward, *Rev. Mod. Phys.*, **35,** 23 (1963).

---

[2] Private communications of September 3 and October 15, 1968.

[6] P. S. Pershan, *Phys. Rev.*, **130**, 919 (1963); E. Adler, *Phys. Rev.*, **134**, A 728 (1964).

[7] S. A. Akhmanov, R. V. Khokhlov, *Problemy Nyelineynoy Optiki*, Moscow: WINJTJ, Akad. Nauk, USSR, 1964.

[8] P. D. Maker, R. W. Terhune, *Phys. Rev.*, **137**, A801 (1965); R. W. Minck, R. W. Terhune, C. C. Wang, *Appl. Optics*, **5**, 1595 (1966) and references therein.

[9] S. Kielich, *Proc. Phys. Soc.*, **86**, 709 (1965); *Acta Phys. Polon.*, **29**, 875 (1966) and references therein.

[10] N. Bloembergen, R. K. Chang, S. S. Jha, C. H. Lee, *Phys. Rev.*, **174**, 813 (1968).

[11] R. W. Terhune, P. D. Maker, C. M. Savage, *Phys. Rev. Letters*, **8**, 404 (1962).

[12] J. E. Bjorkholm and A. E. Siegman, *Phys. Rev.*, **154**, 851 (1967).

[13] G. Mayer, *C.R. Acad. Sci.* (France), **267*B***, 54 (1968).

[14] S. Kielich, *Chem. Phys. Letters*, **2**, 569 (1968).

[15] S. S. Jha, *Phys. Rev.*, **140**, A2020 (1965).

[16] L. D. Landau, E. M. Lifshitz, *Electrodynamics of Continuous Media*, New York: Pergamon Press Inc., 1960.

[17] S. S. Jha, N. Bloembergen, *Phys. Rev.*, **171**, 891 (1968).

[18] P. Debye, *Polar Molecules*, Dover Publications: Inc. New York 1945.

[19] S. Kielich, *J. Phys.*, **28**, 519 (1967).

[20] A. D. McLean M. Yoshimine, *J. Chem. Phys.*, **46**, 3682 (1967).

[21] J. M. O'Hare, R. P. Hurst, *J. Chem. Phys.*, **46**, 2356 (1967).

[22] R. D. Nelson, Jr., D. R. Lide, Jr., A. A. Maryott, *Selected Values of Electric Dipole Moments for Molecules in the Gas Phase*, U.S. Department of Commerce, National Bureau of Standards, Washington, September 1967.

[23] S. Kielich, *Proc. Phys. Soc.*, **90**, 847 (1967).

[24] S. Kielich, *IEEE J. Quantum Electronics*, QE-**4**, 744 (1968).

[25] J. G. Kirkwood, *J. Chem. Phys.*, **7**, 911 (1939).

[26] S. Kielich, *Acta Phys. Polon.*, **33**, 89 (1968).

[27] S. Kielich, *J. Colloid Interface Sci.*, **30**, 159 (1969).

[28] G. H. A. Cole, *The Statistical Theory of Classical Simple Dense Fluids*, Oxford: Pergamon Press 1967.

[29] H. Fröhlich, *Theory of Dielectrics*, Oxford, Oxford University Press, 2nd ed., 1958.

[30] S. Kielich, *Physica*, **31**, 444 (1965); *Molecular Phys.*, **9**, 549 (1965).

[31] D. E. Stogryn, A. P. Stogryn, *Molecular Phys.*, **11**, 371 (1966).

[32] J. G. Kirkwood, *J. Chem. Phys.*, **4**, 592 (1936).

[33] J. H. Van Vleck, *J. Chem. Phys.*, **5**, 556 (1937).

[34] P. Sen, S. Basu, *J. Chem. Phys.*, **48**, 4075 (1968); T. H. Spurling, A. G. De Rocco, *J. Chem. Phys.*, **49**, 2867 (1968).

[35] Krishnaji, V. Prakash, *Rev. Mod. Phys.*, **38**, 690 (1966); T. H. Spurling, E. A. Mason, *J. Chem. Phys.*, **46**, 322 (1967).

[36] T. H. Spurling, A. G. De Rocco, T. S. Storvick, *J. Chem. Phys.* **48**, 1006 (1968).

[37] S. Kielich, *Phys. Letters*, **27*A***, 307 (1968).

[38] A. Rosenberg, G. Birnbaum, *J. Chem. Phys.* **48**, 1396 (1968); G. Birnbaum, A. Rosenberg, *Phys. Letters*, **27*A***, 272 (1968); I. Ozier, K. Fox, *Phys. Letters*, **27*A***, 274 (1968).

[39] R. W. Terhune, P. D. Maker, C. M. Savage, *Phys. Rev. Letters*, **14**, 681 (1965); D. L. Weinberg, *J. Chem. Phys.*, **47**, 1307 (1967).

[40] W. G. Rado, *Appl. Phys. Letters*, **11**, 123 (1967); G. H. C. New, J. F. Ward, *Phys. Rev. Letters*, **19**, 556 (1967).

[41] A. D. Buckingham, B. J. Orr, *Quart. Rev.*, **21**, 195 (1967); A. D. Buckingham, D. A. Dunmur, *Trans. Faraday Soc.*, **64**, 1776 (1968); G. H. Meeten, *Trans. Faraday Soc.*, **64**, 2267 (1968).

[42] C. P. Smyth, *Ann. Rev. Phys. Chem.*, **17**, 433 (1966); S. K. Garg, J. E. Betric, H. Kilp, C. P. Smyth, *J. Chem. Phys.*, **49**, 2551 (1968).

[43] S. Kielich, *Chem. Phys. Letters*, **1**, 675 (1968); *J. Colloid Interface Sci.*, **28**, 214 (1968).