

## SECOND-HARMONIC GENERATION OF LIGHT BY DIPOLAR MOLECULES TOTALLY ALIGNED IN A DC ELECTRIC FIELD

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A microscopic theory of second-harmonic generation (SHG) of light by isotropic substances whose molecular electric dipoles have undergone total alignment in an intense DC electric field is proposed. Such electric saturation strongly raises the SHG intensity; this increase can be observed in some highly dipolar molecular liquids, particularly solutions of dipolar macromolecules and colloid particles. For a weak electric field, the microscopic theory leads to Bloembergen's phenomenological symmetry relations, recently confirmed experimentally by Mayer, for the nonlinear optical susceptibility tensor elements. Investigation of SHG electric saturation is shown to provide a new method permitting direct determinations of the second-order nonlinear optical polarizability of molecules, macromolecules and colloid particles.

## 1. Introduction

A recent paper by Mayer [1] contains results of measurements of second-harmonic generation (SHG) by gases in a DC electric field. Mayer's measurements show that in non-dipolar gases ( $H_2$ ,  $O_2$ ,  $CH_4$ ,  $CCl_4$ ) as well as certain dipolar ones ( $CO$ ,  $CHCl_3$ ), the second-harmonic power  $I_{2\omega}$  measured at frequency  $2\omega$  is a quadratic function of the DC electric field strength  $E^0$ , whereas in other dipolar gases (*e. g.*  $C_2H_5I$ ,  $C_2H_5Br$ ,  $I$ ) anomalous values are obtained for field strengths  $E^0$  close to breakdown. The quadratic shape of  $I_{2\omega}(E^0)$  for dipolar gases has been explained by Mayer [1] on the basis of Langevin's dipole reorientation theory [2]. In quadrupolar ( $H_2$ ,  $O_2$ ) and octupolar ( $CH_4$ ,  $CCl_4$ ) gases, it can be explained quantitatively as being due to the reorientation, in the DC electric field, of fluctuational dipoles induced in the molecules by the electric quadrupoles and octupoles of neighbouring molecules [3]. Obviously, beside these temperature-dependent statistical effects, the temperature independent distortional effect of nonlinear electronic polarizability is also present. Hitherto, however, the most careful recent measurements [4] have failed to determine which of the two effects is predominant. Numerical evaluations for polar substances [3] point to a marked predominance of the reorientational effect. A decision can be expected

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from *e. g.* measurements of the temperature-or frequency-dependence of SHG. In the case of ethyl bromide, the most recent measurements of Mayer [4] confirm Bloembergen's [5] symmetry relations between the three principal components of the isotropic tensor of nonlinear optical susceptibility (see also Ref. [3]).

Mayer, in his communication [1], proposes no mechanism of the anomalous effect observed by him, which increases quadratically with  $E^0$  only up to some value of the field and then grows steeply exhibiting a much stronger nonlinearity. The circumstance that this anomaly appeared only in dipolar substances such as  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$  and  $\text{C}_2\text{H}_5\text{Br}$ , the molecules of which in their ground state have quite large electric dipole moments (respectively 1.62, 1.91 and 2.03 in  $10^{-18}$  e. s. u. cm [6]), suggests a rather high degree of alignment of the dipoles in the applied DC electric field as a plausible mechanism. A considerable electric saturation can arise not only owing to the high applied electric field strength able to cause total alignment of the molecules, but moreover owing to the fact that molecules in excited states gain large electric dipole moments. It is our aim here to discuss the problem quantitatively within the framework of Langevin's [2] and Debye's [7] classical theory of molecular reorientation. We shall also show by microscopic considerations that Bloembergen's [3, 5] phenomenological symmetry relations are fulfilled strictly only in a linear approximation with respect to the DC electric field strength but cease to hold in the presence of a field strong enough to cause nonlinearity of a higher order.

## 2. Phenomenological theory

The *i*-component of the second-order electric-dipole polarization  $P_i^{(2)}(\omega_1, \mathbf{k}_1)$  produced by the interaction of two electric fields  $E_j(\omega_2, \mathbf{k}_2)$  and  $E_k(\omega_3, \mathbf{k}_3)$  in a medium at frequency  $\omega_1 = \omega_2 + \omega_3$  is given by [8]:

$$P_i^{(2)}(\omega_1, \mathbf{k}_1) = \chi_{ijk}(-\omega_1, \omega_2, \omega_3) E_j(\omega_2, \mathbf{k}_2) E_k(\omega_3, \mathbf{k}_3), \quad (1)$$

where the third-rank tensor  $\chi_{ijk}$  defines second-order susceptibility in the electric dipole approximation. The spatial distribution of the polarization (1) is characterized by a wave vector  $\mathbf{k}_1 = \mathbf{k}_2 + \mathbf{k}_3$ , and the summation convention for repeated indices *j* and *k* is used.

In the case of an isotropic body having a centre of symmetry, all tensor components  $\chi_{ijk}$  vanish and, to obtain *e. g.* second-harmonic generation, one has to proceed to the electric-quadrupole or magnetic-dipole approximation [8, 9]. However, we shall not deal with such effects in this paper since we are interested in second-harmonic generation by isotropic bodies immersed in a DC electric field  $\mathbf{E}(0) = E^0$  [10, 11]. The external field  $\mathbf{E}(0)$  polarizes the naturally isotropic body, destroying its centre of symmetry and causing it to become anisotropic with macroscopic symmetry  $C_{\infty v}$ . This absence of a centre of symmetry gives rise to a situation which favours (a necessary though not always sufficient condition) the nonlinear process of interaction (mixing) of laser light beams described in accordance with Eq. (1) by:

$$P_i^{(2)}(\omega_1, \mathbf{k}_1) = \langle \chi_{ijk}(-\omega_1, \omega_2, \omega_3) \rangle_{E^0} E_j(\omega_2, \mathbf{k}_2) E_k(\omega_3, \mathbf{k}_3), \quad (1a)$$

where the symbol  $\langle \quad \rangle_{\mathbf{E}^0}$  denotes a mean value calculated in the presence of the DC field  $\mathbf{E}^0$ .

Assuming  $\mathbf{E}^0$  to act along a given direction e.g. along the  $y$ -axis of laboratory coordinates, the macroscopic symmetry  $C_{\infty v}$  electrically induced in the medium will cause the tensor  $\langle \chi_{ijk} \rangle_{\mathbf{E}_y^0}$  of Eq. (1a) to have 7 non-zero components, 4 of them mutually independent, namely:

$$\begin{aligned} \langle \chi_{xyx} \rangle_{\mathbf{E}_y^0} &= \langle \chi_{xyz} \rangle_{\mathbf{E}_y^0}, \quad \langle \chi_{xxy} \rangle_{\mathbf{E}_y^0} = \langle \chi_{xzy} \rangle_{\mathbf{E}_y^0}, \\ \langle \chi_{yxx} \rangle_{\mathbf{E}_y^0} &= \langle \chi_{yzz} \rangle_{\mathbf{E}_y^0}, \quad \langle \chi_{yyy} \rangle_{\mathbf{E}_y^0}, \end{aligned} \quad (2)$$

With these relations, we obtain the following expressions for the components of second-order polarization (1a):

$$\begin{aligned} P_x^{(2)}(\omega_1, \mathbf{k}_1) &= \langle \chi_{yxx}(-\omega_1, \omega_2, \omega_3) \rangle_{\mathbf{E}_y^0} E_y(\omega_2, \mathbf{k}_2) E_x(\omega_3, \mathbf{k}_3) + \\ &+ \langle \chi_{xxy}(-\omega_1, \omega_2, \omega_3) \rangle_{\mathbf{E}_y^0} E_x(\omega_2, \mathbf{k}_2) E_y(\omega_3, \mathbf{k}_3), \\ P_y^{(2)}(\omega_1, \mathbf{k}_1) &= \langle \chi_{yxx}(-\omega_1, \omega_2, \omega_3) \rangle_{\mathbf{E}_y^0} \{E_x(\omega_2, \mathbf{k}_2) E_x(\omega_3, \mathbf{k}_3) + E_z(\omega_2, \mathbf{k}_2) E_z(\omega_3, \mathbf{k}_3)\} + \\ &+ \langle \chi_{yyy}(-\omega_1, \omega_2, \omega_3) \rangle_{\mathbf{E}_y^0} E_y(\omega_2, \mathbf{k}_2) E_y(\omega_3, \mathbf{k}_3), \\ P_z^{(2)}(\omega_1, \mathbf{k}_1) &= \langle \chi_{yxx}(-\omega_1, \omega_2, \omega_3) \rangle_{\mathbf{E}_y^0} E_y(\omega_2, \mathbf{k}_2) E_z(\omega_3, \mathbf{k}_3) + \\ &+ \langle \chi_{xxy}(-\omega_1, \omega_2, \omega_3) \rangle_{\mathbf{E}_y^0} E_x(\omega_2, \mathbf{k}_2) E_y(\omega_3, \mathbf{k}_3). \end{aligned} \quad (3)$$

which can now be adapted to various experimental situations.

We shall consider the simple case of a single light beam  $\omega_1 = 2\omega$ ,  $\omega_2 = \omega_3 = \omega$  propagating in the  $z$ -direction. The tensor  $\chi_{ijk}^{2\omega} = \chi_{ijk}(-2\omega, \omega, \omega)$  is now symmetric in the indices  $j$  and  $k$  causing the 4 mutually independent tensor elements of Eqs (2) to reduce to 3, since now we have moreover the relation:

$$\langle \chi_{xyx}^{2\omega} \rangle_{\mathbf{E}_y^0} = \langle \chi_{xxy}^{2\omega} \rangle_{\mathbf{E}_y^0}.$$

With these assumptions, Eq. (3) yields the following polarization components at frequency  $2\omega$  in the  $x$ - and  $y$ -directions:

$$\begin{aligned} P_x^{2\omega} &= 2 \langle \chi_{xxy}^{2\omega} \rangle_{\mathbf{E}_y^0} E_x^\omega E_y^\omega, \\ P_y^{2\omega} &= \langle \chi_{yxx}^{2\omega} \rangle_{\mathbf{E}_y^0} E_x^\omega E_x^\omega + \langle \chi_{yyy}^{2\omega} \rangle_{\mathbf{E}_y^0} E_y^\omega E_y^\omega, \end{aligned} \quad (4)$$

with, for simplicity, the notation  $P_i^{2\omega} = P_i^{(2)}(2\omega, 2\mathbf{k})$  and  $E_j^\omega = E_j(\omega, \mathbf{k})$ .

If the incident light is plane polarized, then for the case  $\mathbf{E}^\omega \parallel \mathbf{E}_y^0$  (oscillations along the  $y$ -axis) Eqs (4) allow to determine  $\langle \chi_{yyy}^{2\omega} \rangle_{\mathbf{E}_y^0}$ , whereas for the case  $\mathbf{E}^\omega \perp \mathbf{E}_y^0$  (oscillations along the  $x$ -axis) one determines  $\langle \chi_{yxx}^{2\omega} \rangle_{\mathbf{E}_y^0}$ . If the light wave  $\mathbf{E}^\omega$  is circularly polarized, measurement of the component  $P_x^{2\omega}$  allows to determine  $\langle \chi_{xxy}^{2\omega} \rangle_{\mathbf{E}_y^0}$ , whereas measurement of  $P_y^{2\omega}$  yields  $\langle \chi_{yxx}^{2\omega} \rangle_{\mathbf{E}_y^0} + \langle \chi_{yyy}^{2\omega} \rangle_{\mathbf{E}_y^0}$ . Thus it is seen that all 3 components can be determined separately in experiment [1].

Similar results can also be obtained along the following lines: if the DC field externally applied to the isotropic medium is not too strong, and produces only a linear change in the polarization (1), one can write, in the following third approximation:

$$P_i^{(3)}(\omega_1, \mathbf{k}_1) = \chi_{ijk}(-\omega_1, \omega_2, \omega_3, 0) E_j(\omega_2, \mathbf{k}_2) E_k(\omega_3, \mathbf{k}_3) E_l(0) \quad (5)$$

the fourth-rank tensor  $\chi_{ijkl}$  defining a dipolar susceptibility of the third order which is no longer sensitive to the presence or absence of a centre of symmetry, and has non-zero elements in the case of isotropic bodies too.

For the case of an isotropic body, the tensor  $\chi_{ijkl}$  can be subjected to an averaging procedure over all possible directions of electric fields relative to the laboratory axes, leading to:

$$\chi_{ijkl} = \chi_1 \delta_{ij} \delta_{kl} + \chi_2 \delta_{ik} \delta_{jl} + \chi_3 \delta_{il} \delta_{kj} \quad (6)$$

with  $\delta_{ij}$  — the unit tensor, and where we have introduced the constants:

$$\chi_s = \chi_{\alpha\beta\gamma\delta}(-\omega_1, \omega_2, \omega_3, 0) \sigma_{\alpha\beta\gamma\delta}^{(s)} \quad (7)$$

and the notation, for  $s = 1, 2, 3$ :

$$\begin{aligned} \sigma_{\alpha\beta\gamma\delta}^{(1)} &= \frac{1}{30} (4\delta_{\alpha\beta} \delta_{\gamma\delta} - \delta_{\alpha\gamma} \delta_{\beta\delta} - \delta_{\alpha\delta} \delta_{\beta\gamma}), \\ \sigma_{\alpha\beta\gamma\delta}^{(2)} &= \frac{1}{30} (4\delta_{\alpha\gamma} \delta_{\beta\delta} - \delta_{\alpha\delta} \delta_{\beta\gamma} - \delta_{\alpha\beta} \delta_{\gamma\delta}), \\ \sigma_{\alpha\beta\gamma\delta}^{(3)} &= \frac{1}{30} (4\delta_{\alpha\delta} \delta_{\beta\gamma} - \delta_{\alpha\beta} \delta_{\gamma\delta} - \delta_{\alpha\gamma} \delta_{\beta\delta}). \end{aligned} \quad (8)$$

For the isotropic body, the constants (7) can be written in explicit form:

$$\begin{aligned} \chi_1 &= \frac{1}{5} (\chi_{xxxx} + 4\chi_{xxyy} - \chi_{xyxy} - \chi_{xyyx}), \\ \chi_2 &= \frac{1}{5} (\chi_{xxxx} + 4\chi_{xyxy} - \chi_{xyyx} - \chi_{xxyy}), \\ \chi_3 &= \frac{1}{5} (\chi_{xxxx} + 4\chi_{xyyx} - \chi_{xxyy} - \chi_{xyxy}), \end{aligned} \quad (9)$$

or, with regard to the relation [12]

$$\chi_{xxxx} = \chi_{xxyy} + \chi_{xyxy} + \chi_{xyyx} = \chi_{yyyy} \quad (10)$$

in quite simple form:

$$\begin{aligned} \chi_1 &= \chi_{xxxx} - (\chi_{xyxy} + \chi_{xyyx}) = \chi_{xxyy}, \\ \chi_2 &= \chi_{xyxy}, \quad \chi_3 = \chi_{xyyx}. \end{aligned} \quad (11)$$

With the above-derived relations, Eq. (5) can be rewritten for the isotropic body as follows:

$$\begin{aligned} P_i^{(3)}(\omega_1, \mathbf{k}_1) &= \chi_{xxyy}(-\omega_1, \omega_2, \omega_3, 0) E_i(\omega_2, \mathbf{k}_2) E_j(\omega_3, \mathbf{k}_3) E_j(0) + \\ &+ \chi_{xyxy}(-\omega_1, \omega_2, \omega_3, 0) E_j(\omega_2, \mathbf{k}_2) E_i(\omega_3, \mathbf{k}_3) E_j(0) + \\ &+ \chi_{xyyx}(-\omega_1, \omega_2, \omega_3, 0) E_j(\omega_2, \mathbf{k}_2) E_j(\omega_3, \mathbf{k}_3) E_i(0). \end{aligned} \quad (12)$$

If the problem involves but a single light wave, the tensor  $\chi_{ijkl}^{2\omega} = \chi_{ijkl}(-2\omega, \omega, \omega, 0)$  is symmetric in the indices  $j$  and  $k$ , whence  $\chi_{xxyy}^{2\omega} = \chi_{xyxy}^{2\omega}$ . Thus, assuming as previously the DC electric field parallel to  $y$  and the light wave propagating along  $z$ , we obtain by (12) the following components of third-order polarization at frequency  $2\omega$ :

$$\begin{aligned} P_x^{2\omega} &= 2\chi_{xxyy}^{2\omega} E_x^\omega E_y^\omega E_y^0, \\ P_y^{2\omega} &= \chi_{yxyx}^{2\omega} E_x^\omega E_x^\omega E_y^0 + \chi_{yyyy}^{2\omega} E_y^\omega E_y^\omega E_y^0, \end{aligned} \quad (13)$$

where, in accordance with (10), we have:

$$\chi_{yyyy}^{2\omega} = 2\chi_{xxyy}^{2\omega} + \chi_{xyyx}^{2\omega}. \quad (14)$$

On comparing Eqs (4) and (13), one obtains in an approximation linear in the DC electric field

$$\begin{aligned} \langle \chi_{xxyy}^{2\omega} \rangle_{E_y^0} &= \chi_{xxyy}^{2\omega} E_y^0, \\ \langle \chi_{yxyx}^{2\omega} \rangle_{E_y^0} &= \chi_{yxyx}^{2\omega} E_y^0, \\ \langle \chi_{yyyy}^{2\omega} \rangle_{E_y^0} &= \chi_{yyyy}^{2\omega} E_y^0. \end{aligned} \quad (15)$$

In the absence of electronic dispersion, and in a satisfactory approximation, we are justified in considering the tensor  $\chi_{ijkl}^{2\omega}$  as totally symmetric, now leading to:

$$\chi_{yyyy}^{2\omega} = 3\chi_{xxyy}^{2\omega} = 3\chi_{xyyx}^{2\omega}. \quad (16)$$

The symmetry relations (14) and (16) for the tensor elements  $\chi_{ijkl}^{2\omega}$  of nonlinear susceptibility are similar to those discussed recently by Bloembergen [5] and Mayer [4]. Clearly, similar relations are valid by (15), in the linear approximation, for the susceptibility tensor elements  $\langle \chi_{ijkl}^{2\omega} \rangle_{E^0}$ . In the next Section, we shall prove this by a microscopic method.

### 3. Molecular theory for dipolar fluids

Let us consider a fluid consisting of noninteracting molecules of number density  $\rho$  when we have by classical statistical mechanics:

$$\langle \chi_{ijk}^{2\omega} \rangle_{E^0} = \frac{\rho}{4} \int b_{ijk}^{2\omega} f(\Omega, E^0) d\Omega. \quad (17)$$

Above,  $b_{ijk}^{2\omega}$  is the tensor of second-order polarizability of the molecule which transforms from laboratory coordinates (indices  $i, j, k$ ; axes  $x, y, z$ ) to molecular coordinates (indices  $\alpha, \beta, \gamma$ ; axes 1, 2, 3) according to the transformation formula

$$b_{ijk}^{2\omega} = c_{i\alpha} c_{j\beta} c_{k\gamma} b_{\alpha\beta\gamma}^{2\omega} \quad (18)$$

$c_{i\alpha}$  denoting the cosine of the angle between the laboratory  $i$ -axis and the molecular  $\alpha$ -axis.

For molecules presenting permanent dipoles  $\mu$ , the potential energy of a molecule in the DC electric field  $E^0$  is [7]:

$$u(E^0) = -\mu_i E_i^0 = -c_{i\alpha} \mu_\alpha E_i^0 \quad (19)$$

and Boltzmann's statistical distribution function at thermodynamical equilibrium at temperature  $T$  takes the form:

$$f(\Omega, \mathbf{E}^0) = \frac{\exp\left(\frac{\mu_\alpha}{kT} c_{i\alpha} E_i^0\right)}{\int \exp\left(\frac{\mu_\alpha}{kT} c_{i\alpha} E_i^0\right) d\Omega}. \quad (20)$$

Integration in the expressions (17) and (20) is over all possible dipole orientations in the elementary body angle  $d\Omega = \sin \vartheta d\vartheta d\varphi d\psi$ .

Since we are interested in the elements  $\chi_{xxy}^{2\omega}$ ,  $\chi_{yxx}^{2\omega}$  and  $\chi_{yyy}^{2\omega}$ , with regard to the transformation formula (18) we require the directional cosines  $c_{x\alpha}$  and  $c_{y\alpha}$  in explicit form. Expressed by way of Euler's angles  $\vartheta$ ,  $\varphi$ ,  $\psi$ , they are:

$$\begin{aligned} c_{x1} &= \cos \vartheta \sin \varphi \cos \psi + \cos \varphi \sin \psi, \\ c_{x2} &= \cos \vartheta \cos \varphi \cos \psi - \sin \varphi \sin \psi, \\ c_{x3} &= -\sin \vartheta \cos \psi, \\ c_{y1} &= \sin \vartheta \sin \varphi, \\ c_{y2} &= \sin \vartheta \cos \varphi, \\ c_{y3} &= \cos \vartheta. \end{aligned} \quad (21)$$

One notes the advantage of assuming the electric dipoles as directed along the molecular 3-axis, the latter subtending the angle  $\vartheta$  with the DC electric field  $E_y^0$  acting along the laboratory y-axis. In this situation, the distribution function (20) becomes simply [2]:

$$f(\vartheta, E_y^0) = \frac{\exp(a \cos \vartheta)}{4\pi^2 \int_0^\pi \exp(a \cos \vartheta) \sin \vartheta d\vartheta} \quad (22)$$

with the dimensionless parameter of orientation of the dipole in the electric field:

$$a = \frac{\mu_3 E_y^0}{kT}. \quad (23)$$

Since the statistical distribution function (22) does not depend on  $\varphi$  and  $\psi$ , we can begin the calculation of the mean values (17) by carrying out integrations over all values of  $\varphi$  and  $\psi$ , thus considerably simplifying the final results. In this way, and applying the procedure to the case of dipolar molecules having symmetry of the point group  $C_{2v}$  (e. g.  $\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_5\text{NO}_2$ ), we derive by Eqs (17)–(22):

$$\begin{aligned} \langle \chi_{xxy}^{2\omega} \rangle_{E_y^0} &= \frac{\rho}{16} \{2(b_{113}^{2\omega} + b_{223}^{2\omega})L_3(a) + (2b_{333}^{2\omega} - b_{311}^{2\omega} - b_{322}^{2\omega})[L_1(a) - L_3(a)]\}, \\ \langle \chi_{yxx}^{2\omega} \rangle_{E_y^0} &= \frac{\rho}{16} \{(b_{311}^{2\omega} + b_{322}^{2\omega})[L_1(a) + L_3(a)] + 2(b_{333}^{2\omega} - b_{113}^{2\omega} - b_{223}^{2\omega})[L_1(a) - L_3(a)]\}, \\ \langle \chi_{yyy}^{2\omega} \rangle_{E_y^0} &= \frac{\rho}{8} \{2b_{333}^{2\omega}L_3(a) + (2b_{113}^{2\omega} + 2b_{223}^{2\omega} + b_{311}^{2\omega} + b_{322}^{2\omega})[L_1(a) - L_3(a)]\}, \end{aligned} \quad (24)$$

where we have introduced a Langevin function of the  $n$ -th order:

$$L_n(a) = \frac{\int_0^\pi \cos^n \vartheta \exp(a \cos \vartheta) \sin \vartheta d\vartheta}{\int_0^\pi \exp(a \cos \vartheta) \sin \vartheta d\vartheta} \quad (25)$$

Integration *per partes* yields [13]:

$$L_n(a) = \sum_{k=0}^n \frac{n!(-1)^k}{(n-k)!} \left[ \frac{e^a - (-1)^{n-k} e^{-a}}{a^{k+1}(e^a - e^{-a})} \right], \quad (26)$$

whence we have in turn for  $n = 0, 1, 2, 3, \dots$ :

$$L_0(a) = 1, L_1(a) = L(a) = \coth a - \frac{1}{a},$$

$$L_2(a) = 1 - 2 \frac{L(a)}{a}, \quad L_3(a) = L(a) - \frac{2}{a} + 6 \frac{L(a)}{a^2}, \dots \quad (27)$$

$L(a)$  standing for the well-known Langevin function [2] (Fig. 1).

Eqs (24) with

$$b_{113}^{2\omega} = b_{223}^{2\omega} \neq b_{311}^{2\omega} = b_{322}^{2\omega} \neq b_{333}^{2\omega}, \quad (28)$$

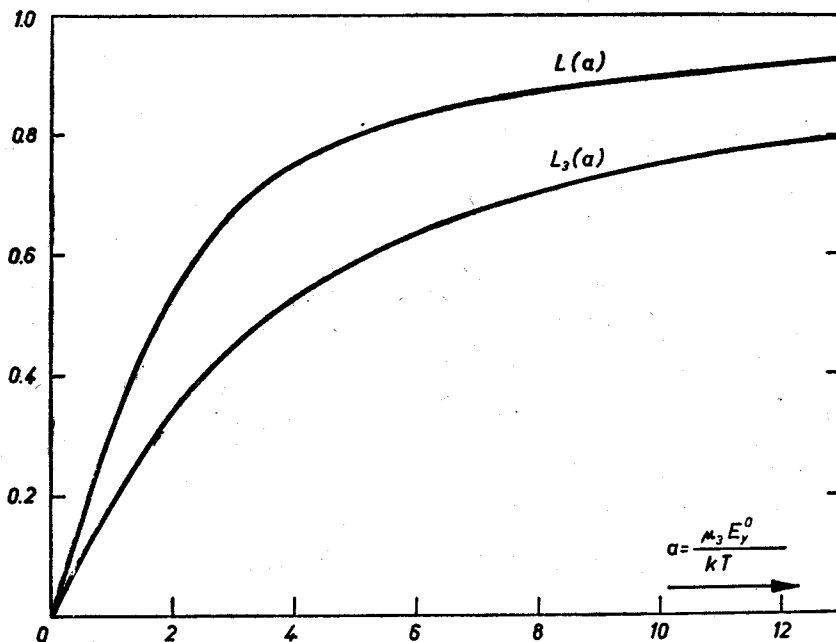


Fig. 1. Graphs of the Langevin functions  $L(a)$  and  $L_3(a)$  defined by Eq. (27)

reduce to:

$$\begin{aligned}\langle \chi_{xxy}^{2\omega} \rangle_{E_y^0} &= \frac{\rho}{8} \{2b_{113}^{2\omega} L_3(a) + (b_{333}^{2\omega} - b_{311}^{2\omega}) [L_1(a) - L_3(a)]\}, \\ \langle \chi_{yxx}^{2\omega} \rangle_{E_y^0} &= \frac{\rho}{8} \{b_{311}^{2\omega} [L_1(a) + L_3(a)] + (b_{333}^{2\omega} - 2b_{113}^{2\omega}) [L_1(a) - L_3(a)]\}, \\ \langle \chi_{yyx}^{2\omega} \rangle_{E_y^0} &= \frac{\rho}{4} \{b_{333}^{2\omega} L_3(a) + (2b_{113}^{2\omega} + b_{311}^{2\omega}) [L_1(a) - L_3(a)]\}\end{aligned}\quad (29)$$

(expressions valid for molecules of point group symmetries  $C_{3v}$  (e. g.  $\text{NH}_3$ ,  $\text{CHCl}_3$ ,  $\text{CH}_3\text{F}$ , and so forth),  $C_{4v}$  (e. g.  $\text{BrF}_5$ ),  $C_{6v}$  and  $C_{\infty v}$  (e. g.  $\text{HCl}$ ,  $\text{CO}$ ).

At small values of the reorientation parameter (23) *i. e.* if the DC electric field strength is low or if the molecules are but weakly dipolar, the Langevin functions (27) can be expanded:

$$\begin{aligned}L_1(a) &= \frac{a}{3} - \frac{a^3}{45} + \frac{2a^5}{945} - \dots, \\ L_3(a) &= \frac{a}{5} - \frac{a^3}{105} + \frac{4a^5}{4725} - \dots\end{aligned}\quad (30)$$

Taking only terms linear in the field strength, we reduce (24) to the form:

$$\begin{aligned}\langle \chi_{xxy}^{2\omega} \rangle_{E_y^0} &= \frac{\rho\mu_3}{120kT} (2l_{333}^{2\omega} + 3l_{113}^{2\omega} + 3l_{223}^{2\omega} - b_{311}^{2\omega} - b_{322}^{2\omega}) E_y^0, \\ \langle \chi_{yxx}^{2\omega} \rangle_{E_y^0} &= \frac{\rho\mu_3}{60kT} (b_{333}^{2\omega} - b_{113}^{2\omega} - b_{223}^{2\omega} + 2b_{311}^{2\omega} + 2b_{322}^{2\omega}) E_y^0, \\ \langle \chi_{yyx}^{2\omega} \rangle_{E_y^0} &= \frac{\rho\mu_3}{60kT} (3b_{333}^{2\omega} + 2b_{113}^{2\omega} + 2b_{223}^{2\omega} + b_{311}^{2\omega} + b_{322}^{2\omega}) E_y^0.\end{aligned}\quad (31)$$

One sees immediately that this approximation linear in  $E_y^0$  implies the symmetry relation:

$$2\langle \chi_{xxy}^{2\omega} \rangle_{E_y^0} + \langle \chi_{yxx}^{2\omega} \rangle_{E_y^0} = \langle \chi_{yyx}^{2\omega} \rangle_{E_y^0} \quad (32)$$

which results also by way of the macroscopic expressions (14) and (15).

Putting

$$b_{113}^{2\omega} = l_{223}^{2\omega} = l_{311}^{2\omega} = b_{322}^{2\omega} \neq b_{333}^{2\omega}, \quad (33)$$

in Eqs (31), which is true for the point groups  $C_{3v}$ ,  $C_{4v}$ ,  $C_{6v}$  and  $C_{\infty v}$  in the absence of electronic dispersion, we obtain:

$$\langle \chi_{yyx}^{2\omega} \rangle_{E_y^0} = 3 \langle \chi_{xxy}^{2\omega} \rangle_{E_y^0} = 3 \langle \chi_{yxx}^{2\omega} \rangle_{E_y^0} \quad (34)$$

with

$$\langle \chi_{yyx}^{2\omega} \rangle_{E_y^0} = \frac{\rho\mu_3}{20kT} (b_{333}^{2\omega} + 2b_{113}^{2\omega}) E_y^0. \quad (35)$$



Thus, the symmetry relations (32) and (34) derived microscopically in a linear approximation are proved to be equivalent to the phenomenologically derived relations (14) and (16).

By insertion of (33) into (24) or (29), we obtain:

$$\begin{aligned}\langle \chi_{xxy}^{2\omega} \rangle_{E_y^0} &= \langle \chi_{yxx}^{2\omega} \rangle_{E_y^0} = \frac{\rho}{8} \{ (b_{333}^{2\omega} - b_{113}^{2\omega}) L_1(a) + (3b_{113}^{2\omega} - b_{333}^{2\omega}) L_3(a) \}, \\ \langle \chi_{yyy}^{2\omega} \rangle_{E_y^0} &= \frac{\rho}{4} \{ 3b_{113}^{2\omega} L_1(a) + (b_{333}^{2\omega} - 3b_{113}^{2\omega}) L_3(a) \}\end{aligned}\quad (36)$$

showing that in the case of a strong DC electric field the symmetry relations (32) and (34) do not hold generally.

In the limit, when the DC field is very strong causing total alignment of the electric dipoles, the Langevin functions (27) tend to 1 at  $a \rightarrow \infty$  and the expressions (24) reduce to the quite simple form:

$$\begin{aligned}\langle \chi_{xxy}^{2\omega} \rangle_{\infty} &= \frac{\rho}{8} (b_{113}^{2\omega} + b_{223}^{2\omega}), \\ \langle \chi_{yxx}^{2\omega} \rangle_{\infty} &= \frac{\rho}{8} (b_{311}^{2\omega} + b_{322}^{2\omega}), \\ \langle \chi_{yyy}^{2\omega} \rangle_{\infty} &= \frac{3}{4} b_{333}^{2\omega}.\end{aligned}\quad (37)$$

Hence, in the case of total electric alignment either, the macroscopic symmetry relations (32) and (34) are not fulfilled. One finds that, in order that these relations shall be maintained, the following molecular relations have to be fulfilled:

$$b_{113}^{2\omega} + b_{223}^{2\omega} = b_{311}^{2\omega} + b_{322}^{2\omega} = \frac{2}{3} b_{333}^{2\omega}\quad (38)$$

or, in the absence of electronic dispersion:

$$b_{113}^{2\omega} = b_{223}^{2\omega} = b_{311}^{2\omega} = b_{322}^{2\omega} = \frac{1}{3} b_{333}^{2\omega}.\quad (39)$$

The relations (38) and (39) appear to be justified in juxtaposition with the relations [14]

$$\chi_{1133}^{2\omega} = \chi_{1313}^{2\omega} = \chi_{3311}^{2\omega} = \dots = \frac{1}{3} \chi_{3333}^{2\omega}\quad (40)$$

which are valid in the absence of electronic dispersion for the elements of the third-order susceptibility tensor.

Accordingly, assuming the relations (39), we obtain with regard to (36) the following relation:

$$\langle \chi_{yyy}^{2\omega} \rangle_{E_y^0} = 3 \langle \chi_{xxy}^{2\omega} \rangle_{E_y^0} = 3 \langle \chi_{yxx}^{2\omega} \rangle_{E_y^0} = \frac{1}{4} \rho b_{333}^{2\omega} L(a)\quad (41)$$

showing that (in the absence of dispersion) the nonlinear optical susceptibilities depend on the DC electric field in the same way as the dielectric polarization in Langevin's [2] and Debye's [7] theory of dipolar dielectrics:

$$\mathbf{P}^0 = \rho \mu L(a).\quad (42)$$

#### 4. Discussion and conclusions

We thus see that in a strong DC electric field the macroscopic symmetry relations (32) and (34) are fulfilled only if the molecular symmetry satisfies the relations (38) and (39). For the case of electric saturation, the relations (38) and (39) were easily predictable, since at total alignment of dipoles the macroscopic symmetry of a body as a whole has in general to coincide with the symmetry of its individual molecules. Consequently, by (37), measurements of the various elements of the nonlinear optical susceptibility tensor  $\langle \chi_{ijk}^{2\omega} \rangle_{E_0}$  can be concluded to constitute a novel, direct method of determining numerically the respective elements of the tensor  $b_{ijk}^{2\omega}$  of nonlinear optical polarizability of the isolated molecule. Also, the expressions (24)–(36) permit determinations of the tensor elements  $b_{ijk}^{2\omega}$  for dipolar molecules of certain symmetries and pave the way for comparisons with the results of other methods [15].

Another conclusion is that the occurrence of the anomalous effects observed by Mayer [1] in dipolar substances is attributable to the effect of molecular reorientation rather than to that of nonlinear distortion. But the shape of the Langevin curves of Fig. 1 is such as to render difficult the achievement of electric saturation in molecular gases without risking the intervention of yet other mechanisms. In this context, photoionization of molecules in the intense laser field is presumably by no means unimportant as a factor precipitating optical breakdown as well as dielectric breakdown in the DC electric field.

It seems highly probable that the achievement of electric saturation is aided by a very effective mechanism, one known to participate *e. g.* in electric dichroism [16] and electric fluorescence polarization: we have in mind the induction of very considerable electric dipoles in excited molecular states under the influence of external or internal electric fields [17, 18]. The local electric field in a dense medium affects the molecular dipole moment giving rise to an effective value defined in the Lorentz model by [7]:

$$\mu^* = \frac{\epsilon + 2}{3} \mu, \quad (43)$$

and in the Onsager model by [19]:

$$\mu^* = \left( \frac{3\epsilon}{2\epsilon + \epsilon_\infty} \right) \left( \frac{\epsilon_\infty + 2}{3} \right) \mu \quad (44)$$

with  $\epsilon$  the static and  $\epsilon_\infty$  the high-frequency dielectric constant.

Effective dipole values are especially strongly raised in the Lorentz model in dipolar substances with large dielectric constant. *E. g.* for nitrobenzene at  $T = 300^\circ\text{K}$  one has  $\epsilon = 35$  and [6]  $\mu = 4.24 \times 10^{-18}$  e. s. u. cm, leading to a reorientation parameter (23)  $a = 1.2 \times 10^{-3} E_0^0$ . Assuming a field  $E^0 \simeq 10^3$  e. s. u., which is not strong enough for producing breakdown in nitrobenzene of high purity, one obtains  $a = 1$  and the graphs of Fig. 1 yield  $L(1.2) = 0.366$  and  $L_3(1.2) = 0.225$ . Thus, in the case of nitrobenzene, a considerable increase in second-harmonic intensity can be expected to take place.

In water  $\epsilon = 79$  and [6]  $\mu = 1.85 \times 10^{-18}$  e. s. u. cm; one finds that, with the Lorentz model (43), the electric saturation effect attains the same level as in nitrobenzene. However,

considerations of conductance impose the use of the pulse method [20] if applying a strong electric field to water.

A considerable degree of electric saturation can easily be achieved in solutions of macromolecules such as a rigid polypeptide (poly- $\gamma$ -benzyl-L-glutamate) or a flexible polyelectrolyte (sodium polyethylene sulfonate), which present very large electric dipole moments  $\mu = 3 \times 10^{-16}$  e. s. u. cm [21, 22]. Here, at  $T = 300^\circ\text{K}$ , the reorientation parameter (23)  $a = 0.1 E_y^0$ , and high saturation results even at a field of  $E^0 = 100$  e. s. u., since the graphs of Fig. 1 now yield  $L(10) = 0.9$  and  $L_3(10) = 0.754$ .

Also, solutions of dipolar colloid particles are well worth taking into consideration. Colloidal  $\text{V}_2\text{O}_5$  (vanadium pentoxide) has a moment  $\mu = 4 \times 10^{-16}$  e. s. u. cm leading to  $a = 10^{-2} E_y^0$ , so that a field strength of as little as 100 e. s. u. will produce an effect equal to that produced in nitrobenzene by a field of  $10^3$  e. u. s.

From the preceding calculations and examples, we draw the conclusion that intense second-harmonic generation due to electric saturation should be easily observable in solutions of dipolar macromolecules or colloid particles.

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