

# Optical Second-Harmonic Generation by Electrically Polarized Isotropic Media

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**Abstract**—In relation to recent experiments, a quantitative discussion of the microscopic mechanisms accounting for second-harmonic generation (SHG) and harmonic mixing in isotropic media immersed in a dc electric field is given, comprising the temperature-independent effect of nonlinear electronic polarizability and the temperature-dependent effect of reorientation of permanent electric dipoles. It is shown that in the case of a very strong dc electric field, when all the microsystems undergo complete alignment in the direction of the field vector, these two mechanisms attain saturation, raising considerably the intensity of SHG in the case of prolate microsystems and lowering it in the case of oblate ones. Electric saturation effects can take place in strongly dipolar molecular substances but are especially intense in solutions of macromolecules and colloid particles.

The discussion covers, moreover, the symmetry relations between the nonzero elements of the nonlinear susceptibility tensor of the medium in weak as well as in strong electric fields, and the application of these relations in determining the values of elements of the tensors of second- and third-order polarizabilities of the individual microsystems. A preliminary interpretation of the available experimental data is proposed, and new procedures of SHG measurements are suggested.

## INTRODUCTION

**A** NATURALLY isotropic medium, when acted on by a dc electric field, undergoes polarization, thus becoming deprived of its center of inversion and gaining the ability to generate the second harmonic of light [1]. Such dc electric-field-induced second-harmonic generation (SHG) was first observed by Terhune *et al.* [2], [3] in the crystal calcite, which naturally possesses a center of inversion. In these experiments, moreover, SHG, in the absence of a dc electric field, was observed because of the nonlinearity related to electric quadrupole and magnetic dipole polarization [4]–[6]. Bjorkholm

and Siegman [7] recently performed more accurate measurements of the quadrupole-type SHG and electric-field-induced SHG in calcite relative to the SHG obtained in crystals of ADP [1].

Recently, Mayer [8] 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 the dipolar substances CO,  $CHCl_3$ , and other methyl and ethyl halogenoderivatives. In nondipolar gases, in the absence of interactions, SHG is related only to the nonlinear electronic polarizability of the molecules due to the second power of the optical field strength  $E_\omega^2$  and the first power of the dc electric field  $E^0$ . On the other hand, as shown by Mayer [8], 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 they are in condensed phase, where the fluctuating electric fields of permanent molecular quadrupoles and octupoles induce dipoles in neighboring molecules, causing them to undergo reorientation in an externally applied dc electric field [9]. 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 experimental observation.

It is our aim here to propose a simple, classical molecular theory of SHG in naturally isotropic media placed in a dc electric field. We shall give special attention to the discussion of the symmetry relations existing between the nonzero elements of the susceptibility tensor in the case of a weak dc electric field and, more particularly, to the case of a strong dc field when all the molecules of the medium become completely aligned in the field vector direction. This phenomenon, referred to as electric

saturation, strongly increases the polarization optically induced in the medium, especially in solutions of macromolecules or colloid particles, causing a very considerable and easily observable intensity of SHG. The theory provides a tentative, simple interpretation of the experimental results of Mayer [8] and encourages new and promising experiments in this domain of nonlinear optics. Considerable attention will also be given to the correspondence between the macroscopic symmetry of the electrically polarized, naturally isotropic medium, which is of the type  $C_{\infty}$ , and the various point-group symmetries of the individual microsystems.

#### WEAK DC ELECTRIC FIELD

The  $i$  component of nonlinear electric dipole polarization  $P_i$  induced in a medium by two electric fields  $E_i^{\omega_1}$  and  $E_k^{\omega_2}$  oscillating at frequencies  $\omega_1$  and  $\omega_2$ , respectively, can be expressed as [1]

$$P_i(\omega_1 + \omega_2) = \beta \chi_{ijk}^{\omega_1 + \omega_2} E_i^{\omega_1} E_k^{\omega_2}, \quad (1)$$

where the third-rank tensor  $\chi_{ijk}^{\omega_1 + \omega_2}$  defines the second-order susceptibility in the electric dipole approximation at frequency  $\omega_1 + \omega_2$ . One has  $\beta = 1$  for  $\omega_1 = \omega_2$  and  $\beta = 2$  for  $\omega_1 \neq \omega_2$  [3]. To avoid complicating the notation, we refrain in (1) and in subsequent equations from making explicit the spatial dependence by means of the wave vectors  $\mathbf{k}_1$  and  $\mathbf{k}_2$ . Einstein's summation convention over pair-wise recurring indices  $j, k, \dots$ , labeling the  $X, Y, Z$  axes of laboratory coordinates, is applied throughout.

In the case of an isotropic body with a center of symmetry (in the absence of optical activity and external fields) the components of the tensor  $\chi_{ijk}$  vanish, and in order to obtain wave-mixing processes or second-harmonic generation one has to proceed in (1) to higher (electric quadrupole, magnetic dipole, etc. [4]–[6]) approximations. However, we shall not consider these higher order multipole processes [10] here, as we are concerned with the interaction of two waves in a medium immersed in an external dc electric field  $E^0$ . When acted on by the field, the naturally isotropic medium polarizes anisotropically, thus becoming deprived of its center of symmetry. The situation that arises favors second-harmonic generation and harmonics mixing. The polarization, (1), and consequently the susceptibility tensor  $\chi_{ijk}$ , now become functions of the electric field strength  $E^0$ . In a classical statistical-molecular approach, we can express this by writing [11]

$$\chi_{ijk}^{\omega_1 + \omega_2}(E^0) = \frac{\rho}{4} \int \{b_{ijk}^{\omega_1 + \omega_2} + c_{ijk}^{\omega_1 + \omega_2} E_i^0 + \dots\} f(\Omega, E^0) d\Omega, \quad (2)$$

where  $\rho$  denotes the density of microsystems (atoms, molecules, macromolecules, or colloid particles) whose orientation  $\Omega$  with respect to the dc field vector  $E^0$  is given by the distribution function  $f(\Omega, E^0)$ . For simplicity, mutual correlations between the microsystems are neglected.

The third-rank tensor  $b_{ijk}^{\omega_1 + \omega_2}$  defines the nonlinear (second-order) polarizability of a microsystem at frequency  $\omega_1 + \omega_2$ . The variation of this tensor due to the dc electric field is given by the tensor  $c_{ijk}^{\omega_1 + \omega_2}$ —the third-order polarizability tensor [11]. In the case where the microsystems have permanent electric dipole moments  $\mathbf{m}$  and where the dc electric field causing their orientation is weak, the distribution function can be written in the linear approximation [12]

$$f(\Omega, E^0) = f_0 \left( 1 + \frac{1}{kT} \mathbf{m}_i E_i^0 \right), \quad (3)$$

where  $f_0$  is the distribution function in the absence of external fields, corresponding to entirely random orientation of the microsystems.

By inserting (3) into (2) and averaging over all possible orientations of microsystems with respect to the laboratory axes  $X, Y, Z$ , we obtain

$$\chi_{ijk}^{\omega_1 + \omega_2}(E^0) = \chi_{zzzz}^{\omega_1 + \omega_2} \delta_{ij} E_k^0 + \chi_{zzzy}^{\omega_1 + \omega_2} \delta_{ik} E_j^0 + \chi_{yyzz}^{\omega_1 + \omega_2} \delta_{ik} E_j^0, \quad (4)$$

where  $\delta_{ij}$  is Kronecker's unit tensor having diagonal elements equaling 1 and nondiagonal elements equaling 0. The susceptibility elements are given as follows:

$$\begin{aligned} \chi_{zzzz}^{\omega_1 + \omega_2} &= \frac{\rho}{120} \left\{ 4c_{\alpha\alpha\beta\beta}^{\omega_1 + \omega_2} - c_{\alpha\beta\alpha\beta}^{\omega_1 + \omega_2} - c_{\alpha\beta\beta\alpha}^{\omega_1 + \omega_2} \right. \\ &\quad \left. + \frac{1}{kT} (4b_{\alpha\alpha\beta}^{\omega_1 + \omega_2} m_\beta - b_{\alpha\beta\alpha}^{\omega_1 + \omega_2} m_\beta - b_{\alpha\beta\beta}^{\omega_1 + \omega_2} m_\alpha) \right\}, \\ \chi_{zzzy}^{\omega_1 + \omega_2} &= \frac{\rho}{120} \left\{ 4c_{\alpha\beta\alpha\beta}^{\omega_1 + \omega_2} - c_{\alpha\beta\beta\alpha}^{\omega_1 + \omega_2} - c_{\alpha\beta\alpha\beta}^{\omega_1 + \omega_2} \right. \\ &\quad \left. + \frac{1}{kT} (4b_{\alpha\beta\alpha}^{\omega_1 + \omega_2} m_\beta - b_{\alpha\beta\beta}^{\omega_1 + \omega_2} m_\alpha - b_{\alpha\alpha\beta}^{\omega_1 + \omega_2} m_\beta) \right\}, \quad (5) \\ \chi_{yyzz}^{\omega_1 + \omega_2} &= \frac{\rho}{120} \left\{ 4c_{\alpha\beta\beta\alpha}^{\omega_1 + \omega_2} - c_{\alpha\beta\alpha\beta}^{\omega_1 + \omega_2} - c_{\alpha\beta\alpha\beta}^{\omega_1 + \omega_2} \right. \\ &\quad \left. + \frac{1}{kT} (4b_{\alpha\beta\beta}^{\omega_1 + \omega_2} m_\alpha - b_{\alpha\alpha\beta}^{\omega_1 + \omega_2} m_\beta - b_{\alpha\beta\alpha}^{\omega_1 + \omega_2} m_\beta) \right\}. \end{aligned}$$

Obviously, (4) is a particularization of the case of an isotropic body of the general phenomenological relationship

$$\chi_{ijk}^{\omega_1 + \omega_2}(E^0) = \chi_{ijkl}^{\omega_1 + \omega_2} E_l^0, \quad (6)$$

where  $\chi_{ijkl}^{\omega_1 + \omega_2}$  is the third-order nonlinear susceptibility tensor at frequency  $\omega_1 + \omega_2$  for an arbitrary medium [4].

Hence, in a microscopic picture, the constants, (5), appear as being the result of two processes: 1) a purely distortional, temperature-independent mechanism, consisting in third-order nonlinear electronic polarizability (this mechanism is present in all molecular symmetries, since the nonlinear polarizability tensor  $c_{\alpha\beta\gamma\delta}^{\omega_1 + \omega_2}$  has non-zero elements even in the case of atoms in their fundamental state); 2) a mechanism, which in accordance with Langevin's theory [12], is of a statistical nature

related to the reorientation of electric dipoles in a dc electric field, and depends rather strongly on temperature.

The expressions, (5), hold for microsystems of arbitrary symmetry, and their further simplification can be achieved by assuming a particular type of point-group symmetry, e.g.,  $C_{2v}$ ,  $C_{3v}$ , etc. [11].

Assuming the light waves interacting in the medium as propagating in the  $Z$  direction and the dc electric field as applied perpendicularly in the  $Y$  direction, (1) and (4) lead to the following polarization components:

$$P_x(\omega_1 + \omega_2) = \beta\chi_{xx}^{\omega_1 + \omega_2}(E_y^0)L_x^{\omega_1}L_y^{\omega_2} + \beta\chi_{yy}^{\omega_1 + \omega_2}(E_y^0)L_y^{\omega_1}E_x^{\omega_2}, \quad (7)$$

$$P_y(\omega_1 + \omega_2) = \beta\chi_{yy}^{\omega_1 + \omega_2}(E_y^0)L_x^{\omega_1}E_x^{\omega_2} + \beta\chi_{yy}^{\omega_1 + \omega_2}(E_y^0)L_y^{\omega_1}E_y^{\omega_2},$$

with

$$\begin{aligned} \chi_{xx}^{\omega_1 + \omega_2}(E_y^0) &= \chi_{xyy}^{\omega_1 + \omega_2}E_y^0, & \chi_{yy}^{\omega_1 + \omega_2}(E_y^0) &= \chi_{xyy}^{\omega_1 + \omega_2}L_y^0, \\ \chi_{yy}^{\omega_1 + \omega_2}(E_y^0) &= \chi_{yzy}^{\omega_1 + \omega_2}E_y^0, & & \\ \chi_{yy}^{\omega_1 + \omega_2}(E_y^0) &= (\chi_{xyy}^{\omega_1 + \omega_2} + \chi_{yzy}^{\omega_1 + \omega_2} + \chi_{yyz}^{\omega_1 + \omega_2})E_y^0. \end{aligned} \quad (8)$$

Thus, in a linear approximation in  $E^0$ , the following relation exists between the four susceptibility components appearing in (7)

$$\chi_{xx}^{\omega_1 + \omega_2}(E_y^0) + \chi_{yy}^{\omega_1 + \omega_2}(E_y^0) + \chi_{yy}^{\omega_1 + \omega_2}(E_y^0) = \chi_{yy}^{\omega_1 + \omega_2}(E_y^0), \quad (9)$$

and the microscopic theory yields quite generally

$$\begin{aligned} \chi_{yy}^{\omega_1 + \omega_2}(E_y^0) &= \frac{\rho}{60} \left\{ c_{\alpha\alpha\beta\beta}^{\omega_1 + \omega_2} + c_{\alpha\beta\alpha\beta}^{\omega_1 + \omega_2} + c_{\alpha\beta\beta\alpha}^{\omega_1 + \omega_2} + \frac{1}{kT} \right. \\ &\quad \left. \cdot (b_{\alpha\beta}^{\omega_1 + \omega_2}m_\beta + b_{\alpha\beta\alpha}^{\omega_1 + \omega_2}m_\beta + b_{\alpha\beta\beta}^{\omega_1 + \omega_2}m_\alpha) \right\} E_y^0. \end{aligned} \quad (10)$$

In the case of second-harmonic generation,  $\omega_1 = \omega_2 = \omega$ , the tensors  $b_{\alpha\beta\gamma}^{2\omega}$  and  $c_{\alpha\beta\gamma\delta}^{2\omega}$  are symmetric in the indices  $\beta$  and  $\gamma$ , and as a consequence we have from (4)-(6)

$$\begin{aligned} \chi_{xx}^{2\omega}(E_y^0) &= \chi_{yy}^{2\omega}(E_y^0) \\ &= \frac{\rho}{120} \left\{ 3c_{\alpha\alpha\beta\beta}^{2\omega} - c_{\alpha\beta\beta\alpha}^{2\omega} + \frac{1}{kT} (3b_{\alpha\alpha\beta}^{2\omega}m_\beta \right. \\ &\quad \left. - b_{\alpha\beta\beta}^{2\omega}m_\alpha) \right\} E_y^0, \\ \chi_{yy}^{2\omega}(E_y^0) &= \frac{\rho}{60} \left\{ 2c_{\alpha\beta\beta\alpha}^{2\omega} - c_{\alpha\alpha\beta\beta}^{2\omega} + \frac{1}{kT} (2b_{\alpha\beta\beta}^{2\omega}m_\alpha \right. \\ &\quad \left. - b_{\alpha\alpha\beta}^{2\omega}m_\beta) \right\} E_y^0. \end{aligned} \quad (11)$$

If electron dispersion is negligibly small, the tensors  $b_{\alpha\beta\gamma}^{2\omega}$  and  $c_{\alpha\beta\gamma\delta}^{2\omega}$  can be dealt with as totally symmetric, and with regard to (9) and (10) we obtain the symmetry relations [9], [13]:

$$\chi_{xx}^{2\omega}(E_y^0) = \chi_{yy}^{2\omega}(E_y^0) = \chi_{yy}^{2\omega}(E_y^0) = \frac{1}{3}\chi_{yy}^{2\omega}(E_y^0), \quad (12)$$

with

$$\chi_{yy}^{2\omega}(E_y^0) = \frac{\rho}{20} \left\{ c_{\alpha\alpha\beta\beta}^{2\omega} + \frac{1}{kT} b_{\alpha\alpha\beta}^{2\omega}m_\beta \right\} E_y^0. \quad (13)$$

## STRONG DC ELECTRIC FIELD

When there is a very strong dc electric field, the microsystems of the medium can undergo considerable alignment, and one is no longer justified in applying the linear approximation (3) for the distribution function. Generally speaking, not only the permanent electric dipoles  $\mathbf{m}$  undergo this orientation process; the dipoles induced in the microsystems, if the latter are anisotropic with different elements of their linear electric polarizability tensor  $a_{ij}$ , also become oriented in the dc electric field. The potential energy of a microsystem in the field is [11]

$$u(\Omega, \mathbf{E}^0) = -m_i E_i^0 - \frac{1}{2} a_{ij} E_i^0 E_j^0, \quad (14)$$

and for the case of axially symmetric microsystems the Boltzmann distribution function is now given as

$$f(\vartheta, E_y^0) = \frac{\exp(p \cos \vartheta \pm q \cos^2 \vartheta)}{4\pi^2 \int_0^\pi \exp(p \cos \vartheta \pm q \cos^2 \vartheta) \sin \vartheta d\vartheta}, \quad (15)$$

where  $\vartheta$  is the angle subtended by the symmetry 3 axis of the microsystem and the direction of the dc electric field, assumed parallel to the laboratory  $Y$  axis. Above,  $p$  and  $q$  are dimensionless parameters of reorientation of the dipole and the electric polarizability ellipsoid of the microsystem

$$\begin{aligned} p &= \frac{m_3 E_y^0}{kT}, \\ q &= \frac{|a_{33} - a_{11}|}{2kT} E_y^0; \end{aligned} \quad (16)$$

the plus sign in the exponents of (15) refers to microsystems having positive anisotropy  $a_{33} > a_{11}$  (e.g., the molecules HCl, CH<sub>3</sub>Cl, CH<sub>3</sub>I), whereas the minus sign applies to negative anisotropy  $a_{33} < a_{11}$  (e.g., CHCl<sub>3</sub>).

### Dipolar Microsystems

Distribution functions in the form of (15) are applicable to a great variety of dipolar molecules having symmetry of the point groups  $C_{3v}$  (e.g., NH<sub>3</sub>, CHCl<sub>3</sub>, CH<sub>3</sub>I),  $C_{4v}$  (e.g., BrF<sub>5</sub>),  $C_{6v}$ , or  $C_{\infty v}$  (e.g., HCl, CO) for which we obtain with regard to (2) and restricting ourselves to the now essential term in the tensor  $b_{\alpha\beta\gamma}^{2\omega}$

$$\begin{aligned} \chi_{xx}^{2\omega}(E_y^0) &= \chi_{yy}^{2\omega}(E_y^0) \\ &= \frac{\rho}{8} \{ (b_{333}^{2\omega} - b_{311}^{2\omega})L_1(p, \pm q) \\ &\quad + (2b_{113}^{2\omega} + b_{311}^{2\omega} - b_{333}^{2\omega})L_3(p, \pm q) \}, \\ \chi_{yy}^{2\omega}(E_y^0) &= \frac{\rho}{8} \{ (b_{333}^{2\omega} - 2b_{113}^{2\omega} + b_{311}^{2\omega})L_1(p, \pm q) \\ &\quad + (2b_{113}^{2\omega} + b_{311}^{2\omega} - b_{333}^{2\omega})L_3(p, \pm q) \}, \\ \chi_{yy}^{2\omega}(E_y^0) &= \frac{\rho}{4} \{ (2b_{113}^{2\omega} + b_{311}^{2\omega})L_1(p, \pm q) \\ &\quad + (b_{333}^{2\omega} - 2b_{113}^{2\omega} - b_{311}^{2\omega})L_3(p, \pm q) \}. \end{aligned} \quad (17)$$

The foregoing expressions involve generalized Langevin

functions which, with regard to (15), are defined as follows:

$$L_n(p, \pm q) = \frac{\int_0^\pi \cos^n \vartheta \exp(p \cos \vartheta \pm q \cos^2 \vartheta) \sin \vartheta d\vartheta}{\int_0^\pi \exp(p \cos \vartheta \pm q \cos^2 \vartheta) \sin \vartheta d\vartheta} \quad (18)$$

In particular, for strongly dipolar microsystems with very low anisotropy ( $p \gg q$ ), (18) yields the following odd Langevin functions [14]:

$$L_1(p, 0) = \coth p - \frac{1}{p}, \quad (19)$$

$$L_3(p, 0) = \left(1 + \frac{6}{p^2}\right)L_1(p, 0) - \frac{2}{p} \dots$$

Graphs of these functions are shown in Fig. 1.

In the case of nonnegligible anisotropy of the dipolar microsystems ( $p \neq 0$ ), (18) with  $q \neq 0$  leads to

$$L_1(p, \pm q) = \mp \frac{p}{2q} \pm \frac{e^p - e^{-p}}{4q^{1/2}I(p, \pm q)},$$

$$L_3(p, \pm q) = \mp \frac{p(p^2 \mp 6q)}{8q^3} - \frac{p(e^p + e^{-p})}{8q^{3/2}I(p, \pm q)} \quad (20)$$

$$\pm \frac{(p^2 \mp 4q + 4q^2)(e^p - e^{-p})}{8q^{5/2}I(p, \pm q)},$$

where we have introduced the integrals

$$I(p, \pm q) = \frac{1}{2} e^{\mp(p^2/4q) + q} \int_{-\sqrt{q \pm p/2\sqrt{q}}}^{\sqrt{q \pm p/2\sqrt{q}}} e^{\pm t^2} dt. \quad (21)$$

These integrals can be represented in tabulated form [15].

In the case of a not very strong electric field, (20) yields in a satisfactory approximation

$$L_1(p, \pm q) = \frac{p}{3} - \frac{p^3}{45} \pm \frac{4pq}{45} + \dots, \quad (22)$$

$$L_3(p, \pm q) = \frac{p}{5} - \frac{p^3}{105} \pm \frac{8pq}{105} + \dots$$

Restricting these expansions to the term linear in the electric field strength, the susceptibilities (17) reduce to

$$\chi_{zzv}^{2\omega}(E_v^0) = \frac{\rho m_3}{60kT} (b_{333}^{2\omega} + 3b_{113}^{2\omega} - b_{311}^{2\omega})E_v^0,$$

$$\chi_{vzx}^{2\omega}(E_v^0) = \frac{\rho m_3}{60kT} (b_{333}^{2\omega} - 2b_{113}^{2\omega} + 4b_{311}^{2\omega})E_v^0, \quad (23)$$

$$\chi_{vvv}^{2\omega}(E_v^0) = \frac{\rho m_3}{60kT} (3b_{333}^{2\omega} + 4b_{113}^{2\omega} + 2b_{311}^{2\omega})E_v^0.$$

One notes immediately that the preceding approximation implies the relation

$$2\chi_{zzv}^{2\omega}(E_v^0) + \chi_{vzx}^{2\omega}(E_v^0) = \chi_{vvv}^{2\omega}(E_v^0), \quad (24)$$

being a particular case of the relation (9) for  $\omega_1 = \omega_2 = \omega$  when  $\chi_{zzv}^{2\omega}(E_v^0) = \chi_{vzx}^{2\omega}(E_v^0)$ . Obviously, the expressions (23) result immediately from the general expressions (10) and (11) on the assumption that the microsystems

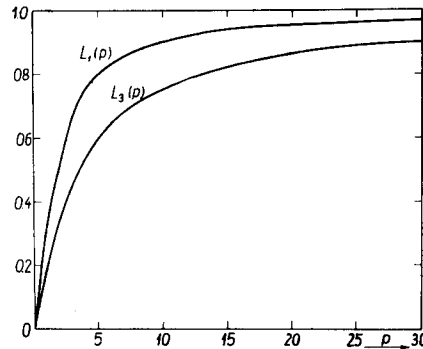


Fig. 1. Graph showing odd Langevin functions (19) versus the dipole reorientation parameter  $p = m_3 E_v^0 / kT$ .

have symmetry of the point group  $C_{3v}$ . In the absence of electronic dispersion, the symmetry relation (12) is moreover fulfilled, with

$$\chi_{vvv}^{2\omega}(E_v^0) = \frac{\rho m_3}{20kT} (b_{333}^{2\omega} + 2b_{113}^{2\omega})E_v^0. \quad (25)$$

In the case of a very strong dc electric field, the susceptibilities (17) do not in general fulfill the symmetry relations (12) and (24). In the limiting case of dipoles completely aligned in the direction of the field  $E_v^0$ , the Langevin functions (19) tend to unity with  $p$  tending to infinity, and as a consequence the expressions (17) reduce to the following simple results:

$$\chi_{zzv}^{2\omega}(E_v^0) = \frac{\rho}{4} b_{113}^{2\omega},$$

$$\chi_{vzx}^{2\omega}(E_v^0) = \frac{\rho}{4} b_{311}^{2\omega}, \quad (26)$$

$$\chi_{vvv}^{2\omega}(E_v^0) = \frac{\rho}{4} b_{333}^{2\omega}.$$

The physical meaning of (26) is that, in the state of electric saturation, the macroscopic symmetry of the susceptibility tensor (of the medium as a whole) becomes identical with the symmetry of the relevant elements of the tensor  $b_{\alpha\beta\gamma}^{2\omega}$  of the microsystem.

With regard to (17) and (26) we note that the macroscopic symmetry relations (12) and (24) can also be fulfilled, in a strong dc electric field, if the following microscopic symmetry relation holds:

$$3b_{113}^{2\omega} = 3b_{311}^{2\omega} = b_{333}^{2\omega}. \quad (27)$$

Equations (17) with (23)–(27) provide a direct method of determining the values of elements of the tensor  $b_{\alpha\beta\gamma}^{2\omega}$  for dipolar molecules presenting various symmetries.

### Centrosymmetric Microsystems

In microsystems having a center of symmetry when in their ground state, all elements of the tensor  $b_{\alpha\beta\gamma}^{2\omega}$  vanish. In dealing with the expansion (2), one has now to take the second, distortional term which, under the influence of a strong dc electric field is subject to new variations due to the effect of reorientation of the polarizability ellipsoid. Considering only microsystems of point-

group symmetry  $D_{6h}$  (e.g.,  $C_6H_6$ ) and  $D_{\infty h}$  (e.g.,  $H_2$ ,  $O_2$ ,  $CO_2$ ,  $CS_2$ ,  $C_2H_2$ ), where the distribution function of (15) at  $p = 0$  is valid, we obtain, in the absence of electronic dispersion,

$$\begin{aligned} \chi_{xxv}^{2\omega}(E_v^0) &= \chi_{xvv}^{2\omega}(E_v^0) = \chi_{yzz}^{2\omega}(E_v^0) \\ &= \frac{\rho}{24} \{c_{1111}^{2\omega} + 3c_{1133}^{2\omega} \\ &\quad + (2c_{1111}^{2\omega} - 15c_{1133}^{2\omega} + 3c_{3333}^{2\omega})L_2(\pm q) \\ &\quad - 3(c_{1111}^{2\omega} - 6c_{1133}^{2\omega} + c_{3333}^{2\omega})L_4(\pm q)\}E_v^0, \end{aligned} \quad (28)$$

$$\begin{aligned} \chi_{yvv}^{2\omega}(E_v^0) &= \frac{\rho}{4} \{c_{11}^{2\omega} + 2(3c_{1133}^{2\omega} - c_{1111}^{2\omega})L_2(\pm q) \\ &\quad + (c_{1111}^{2\omega} - 6c_{1133}^{2\omega} + c_{3333}^{2\omega})L_4(\pm q)\}E_v^0. \end{aligned}$$

Above, by the general definition (18), the even Langevin functions for  $p = 0$  are expressed as follows [16]:

$$\begin{aligned} L_2(\pm q) &= \pm \frac{1}{2q^{1/2}I(\pm q)} \mp \frac{1}{2q}, \\ L_4(\pm q) &= \pm \frac{2q \mp 3}{4q^{3/2}I(\pm q)} + \frac{3}{4q^2}. \end{aligned} \quad (29)$$

These functions are plotted in Fig. 2.

In the case of not very considerable reorientation ( $q < 1$ ), the functions (29) can be expanded as follows:

$$\begin{aligned} L_2(\pm q) &= \frac{1}{3} \pm \frac{4q}{45} + \frac{8q^2}{945} \mp \frac{16q^3}{14\,175} + \dots, \\ L_4(\pm q) &= \frac{1}{5} \pm \frac{8q}{105} + \frac{16q^2}{1575} \mp \frac{32q^3}{51\,975} + \dots \end{aligned} \quad (30)$$

and the susceptibilities of (28) can be expressed to within the third power of the field strength as

$$\begin{aligned} \chi_{xxv}^{2\omega}(E_v^0) &= \frac{\rho}{12} c^{2\omega} (1 \pm \frac{1}{15} \kappa^{2\omega} q) E_v^0, \\ \chi_{yvv}^{2\omega}(E_v^0) &= \frac{\rho}{4} c^{2\omega} (1 \pm \frac{4}{15} \kappa^{2\omega} q) E_v^0, \end{aligned} \quad (31)$$

where the parameters

$$\begin{aligned} c^{2\omega} &= (3c_{3333}^{2\omega} + 8c_{1111}^{2\omega} + 12c_{1133}^{2\omega})/15, \\ \kappa^{2\omega} &= 2(3c_{3333}^{2\omega} - 4c_{1111}^{2\omega} + 3c_{1133}^{2\omega})/21c^{2\omega} \end{aligned} \quad (32)$$

denote, respectively, the mean value and the anisotropy of the nonlinear polarizability of the microsystem [11].

It is apparent from (28) and (31) that the symmetry relations (12) and (24) are fulfilled only in the absence of reorientation ( $q = 0$ ), i.e., when one deals with a purely distortional effect of nonlinear electronic polarizability

$$3\chi_{xxv}^{2\omega}(E_v^0) = \chi_{yvv}^{2\omega}(E_v^0) = \frac{\rho}{4} c^{2\omega} E_v^0. \quad (33)$$

At electric saturation ( $q \rightarrow \infty$ ), one has in the case of prolate microsystems (positive anisotropy, such as  $CS_2$ )  $L_2(+q) = L_4(+q) = 1$ , and the formulas, (28),

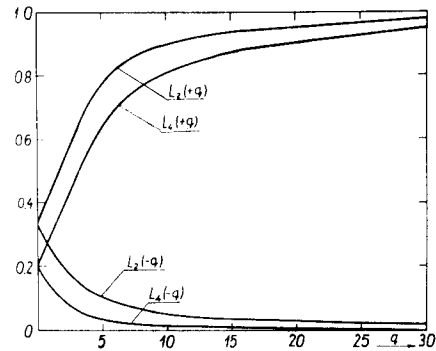


Fig. 2. Graph showing even Langevin functions (29) versus the parameter of reorientation of the electric polarizability ellipsoid,  $q = (a_{33} - a_{11})E_v^0/2kT$ , for prolate molecules (positive anisotropy) as well as oblate molecules (negative anisotropy).

lead to

$$\chi_{xxv}^{2\omega}(E_v^0) = \frac{\rho}{4} c_{1133}^{2\omega} E_v^0, \quad (34)$$

$$\chi_{yvv}^{2\omega}(E_v^0) = \frac{\rho}{4} c_{3333}^{2\omega} E_v^0,$$

whereas in the case of oblate microsystems (negative anisotropy, such as  $C_6H_6$ )  $L_2(-q) = L_4(-q) = 0$ , and formulas (28) yield

$$\chi_{xxv}^{2\omega}(E_v^0) = \frac{\rho}{24} (c_{1111}^{2\omega} + 3c_{1133}^{2\omega}) E_v^0, \quad (35)$$

$$\chi_{yvv}^{2\omega}(E_v^0) = \frac{\rho}{4} c_{1111}^{2\omega} E_v^0.$$

If, at electric saturation, one postulates that the macroscopic symmetry relations (12) and (24) shall be fulfilled, (34) and (35) lead to the following obvious relations for the microscopic symmetry in the absence of electronic dispersion:

$$3c_{1133}^{2\omega} = c_{1111}^{2\omega} = c_{3333}^{2\omega}. \quad (36)$$

Similar relations hold quite strictly for atoms in a very strong dc electric field [11].

#### DISCUSSION AND CONCLUSIONS

Mayer's measurements [8] prove that in nondipolar gases ( $H_2$ ,  $O_2$ ,  $CH_4$ ,  $CCl_4$ ) and certain dipolar gases ( $CO$ ,  $CHCl_3$ ) the second-harmonic generation power measured at frequency  $2\omega$  and fixed values of  $E^\omega$  is a quadratic function of the dc electric field strength  $E^0$  in agreement with the formulas (7), (23), and (31). However, in the case of dipolar gases, these measurements failed to decide which microscopic mechanism, nonlinear distortion (31) or molecular reorientation (23), played the predominant part. Numerical evaluations [9] point to a predominant role of reorientation of the dipoles over the distortional effect at usual temperatures. A final decision can be hoped for from new measurements of SHG as a function of temperature or of the oscillation frequency of the laser light or applied ac electric field [9]. In nondipolar gases in the absence of molecular cor-

relations where, by (31), only the electronic distortion effect can occur, the theoretical calculations [9] are in satisfactory agreement with the experimental data [8].

Mayer found anomalous effects in certain dipolar substances such as  $\text{CH}_3\text{I}$ ,  $\text{C}_2\text{H}_5\text{I}$ , and  $\text{C}_2\text{H}_5\text{Br}$  [8]. Namely, in not excessively strong dc electric fields, the SHG power  $\Pi_{2\omega}$  increased, as in other gases, with the square of the field strength  $E^0$ , whereas at field strengths near the breakdown threshold a steep increase in  $\Pi_{2\omega}$  occurred. Significantly, these anomalies were by no means restricted to the three above-mentioned gases, whose molecules in the ground state have quite large dipole moments (1.62, 1.91, and 2.03 in  $10^{-18}$  ESU·cm, respectively) and positive anisotropy of polarizability (thus, in  $\text{CH}_3\text{I}$ ,  $a_{33} - a_{11} = 2.15 \times 10^{-24}$  cm<sup>3</sup>). One is inclined to attribute this anomaly to a mechanism consisting in a high degree of alignment of the dipoles in the direction of the dc electric field. Moreover, as is obvious from (20)–(22), in the case of dipolar molecules with positive anisotropy, dipole alignment is enhanced by reorientation of the polarizability ellipsoids. This latter type of reorientation takes place not only under the influence of the dc electric field, but essentially in the field of an intense laser beam able to cause even optical saturation [16]–[18]. Conditions favoring the superposition of these two cooperating processes can lead to the steep increase in  $\Pi_{2\omega}$  observed experimentally by Mayer [8].

From the point of view of the simple theory proposed here, the experimental absence of an anomalous rise in  $\Pi_{2\omega}$  in the case of chloroform is easily explained. The dipole moment of the chloroform molecule is one-half that of  $\text{C}_2\text{H}_5\text{I}$  and, moreover, its anisotropy of polarizability is negative,  $a_{33} - a_{11} = -2.33 \times 10^{-24}$  cm<sup>3</sup>. The expressions (20)–(22) and Fig. 2 show that for molecules with negative anisotropy the Langevin functions decrease rapidly to zero, and the nonlinear susceptibility cannot increase with the applied electric field strength.

In general, the achievement of complete dipole alignment in molecular substances by external electrical means alone, is not feasible unless other mechanisms are concomitant. On the other hand, in certain liquids an increase in SHG power can be favored already below saturation by factors such as the various molecular correlations [9], [19] and electric-field-induced phase transitions [20]. In many cases, the molecule in condensed phase presents an effective dipole moment and polarizability anisotropy larger than in the gaseous phase. These factors can act to raise or sometimes reduce the values of the reorientation parameters (16), thus favoring a tendency to electric saturation at an earlier stage. As an example, taking into consideration, for simplicity, the effect of a local field according to the model of Lorentz,  $(\epsilon + 2)E^0/3$ , one obtains for nitrobenzene ( $\epsilon = 35$  and  $\mu = 4.24 \times 10^{-18}$  ESU·cm) a reorientation parameter amounting to  $p = 1.2 \times 10^{-3} E_v^0$  for the molecule when immersed in the liquid, which is  $(\epsilon + 2)/3 \simeq 12$  times more than for the gaseous molecule. For the limiting

field strength  $10^3$  ESU below which the liquid, if thoroughly purified, does not exhibit dielectric breakdown, Fig. 1 yields values of  $L_1(1.2) = 0.366$  and  $L_3(1.2) = 0.225$  lying below the region of saturation. Notwithstanding the fact that these conditions do not correspond to complete saturation (alignment), they nevertheless suffice for inducing a nonlinear increase in SHG intensity under the influence of a strong dc electric field.

Considerable electric saturation is easily achievable in solutions of macromolecules such as rigid polypeptides and flexible polyelectrolytes having very large dipole moments,  $\mu = 3 \times 10^{-15}$  ESU·cm [15]. Here, at  $T = 300^\circ\text{K}$ , one has  $p = 0.1 E_v^0$ ; consequently, electric saturation sets in at field strengths of about 100 ESU. Indeed, Fig. 1 yields  $L_1(10) = 0.90$  and  $L_3(10) = 0.754$ . Solutions of dipolar colloid particles, too, can present considerable saturation phenomena. Thus the vanadium pentoxide particle  $\text{V}_2\text{O}_5$  has a dipole moment 100 times larger than that of the nitrobenzene molecule  $\text{C}_6\text{H}_5\text{NO}_2$ .

Measurements in this domain are highly promising if performed on solutions of strongly anisotropic macromolecules, like tobacco mosaic virus in water, where [15]  $a_{33} - a_{11} = 3 \times 10^{-14}$  cm<sup>3</sup>, and from (16) the reorientation parameter of the polarizability ellipsoid amounts to  $q = 0.4 E_v^0$ . Accordingly, Fig. 2 yields  $L_2(+10) = 0.89$  and  $L_4(+10) = 0.80$  for an electric field strength of as little as 5 ESU so that saturation of the nonlinear distortional effect defined by (28) sets in. A similar effect can be expected to occur in solutions of colloid gold particles in water (positive anisotropy  $a_{33} - a_{11} = 5 \times 10^{-18}$  cm<sup>3</sup> in gold particles of diameter 300 Å [21]) where strong optical orientation of the particles has been observed when using a laser beam [22].

In conclusion, it may be worth noting that recent careful measurements by Mayer<sup>1</sup> in ethyl bromide confirmed Bloembergen's symmetry relations in the form [9]

$$\chi_1^{2\omega} : \chi_2^{2\omega} : \chi_3^{2\omega} = 2 : 1 : 3 \quad (37)$$

which result immediately from (12) and (24) on introducing the notation

$$\begin{aligned} \chi_1^{2\omega} &= 2\chi_{xxz}^{2\omega}(E_v^0), \\ \chi_2^{2\omega} &= \chi_{yzz}^{2\omega}(E_v^0), \\ \chi_3^{2\omega} &= \chi_{yvv}^{2\omega}(E_v^0) = \chi_1^{2\omega} + \chi_2^{2\omega}. \end{aligned} \quad (38)$$

It would be very useful to continue SHG measurements in both weak and strong dc electric fields, since this would help to check the symmetry relations (12), (24), and (37). Work in this direction, simultaneously recurring in the microscopic expressions derived above for experimentally measured elements of the tensor of macroscopic susceptibility  $\chi_{ijk}^{2\omega}$ , will provide direct numerical data on the various elements of the nonlinear polarizability tensors  $b_{\alpha\beta\gamma}^{2\omega}$  and  $c_{\alpha\beta\gamma\delta}^{2\omega}$  of the individual microsystems.

<sup>1</sup> Private communications of September 3, 1968 and October 15, 1968.

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