

Frequency Doubling of Laser Light in an Isotropic Medium with Electrically Destroyed Centre of Inversion

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The non-zero non-linear susceptibility tensor components $\chi_{\sigma\tau\nu}^{2\omega}(E^0)$ which account for frequency doubling of laser light in a naturally isotropic medium immersed in a DC electric field E^0 are discussed. The conditions for extremal second harmonic generation (SHG) are derived, which depend on E^0 and on the incident laser intensity but primarily on the microstructure of the medium. With growing E^0 , the susceptibilities $\chi_{\sigma\tau\nu}^{2\omega}(E^0)$ increase for cigar-like microsystems but decrease for disc-shaped ones, according to whether the induced dipole helps or hinders the permanent dipole in reorienting the microsystem along E^0 . Non-linear electronic distortion alone is insufficient for explaining the anomalous experimental results.

Generally, upon the electrically induced anisotropy, an anisotropy self-induced by the laser beam is superimposed, with optical axis along the propagation direction if the beam is circularly polarised or unpolarised, or along the oscillation direction of the light vector if it is linearly polarised.

Extremal anisotropy of the medium occurs at saturation of electric or optical reorientation. This is experimentally inachievable in molecular substances even with very strong fields but is easy to obtain in solutions of macromolecules or colloid particles, where yet other opto-electronic processes intervene significantly.

1. Introduction

An externally applied DC electric field acts on an isotropic body in a manner to destroy its natural symmetry. The body, thus deprived of its centre of inversion, gives rise to a doubling of the oscillation frequency of a laser beam incident upon it [1, 2]. This capability is maintained as long as the DC field is applied. The effect, known as DC Electric Field-Induced Second Harmonic Generation (ESHG), was first observed by Terhune *et al* [3] in calcite crystal and studied in detail by Bjorkholm and Siegman [4]. The experiments revealed, moreover, a slight amount of second harmonic generation in the absence of a DC electric field due to induced electric quadrupolar polarisation and induced magnetic dipolar polarisation [2, 4]. Recently, Mayer [5] observed radiation of a light wave with doubled frequency from dilute molecular dipolar and non-dipolar substances placed in a DC electric field.

In this paper, we shall consider only frequency doubling of laser light in isotropic bodies subjected to the action of a weak or strong DC electric field E^0 . In a not very strong field E^0 , essentially two processes occur in a molecular, sufficiently dilute medium. One consists in a non-linear distortion of the electron shells of the atoms or molecules. This is equivalent to inducing in them an anisotropy which, then, causes an anisotropy of the medium as a whole like that considered by Voigt [6] in his theory of the Kerr effect. This distortional effect, obviously, is present to a larger or smaller degree in all matter. The other process takes place in substances where the molecules possess permanent dipoles, and consists in a reorientation of

these dipoles under the influence of the applied DC electric field. In this case, the partially electrically-oriented molecules present an ordering, causing the medium to become anisotropic, in accordance with Langevin's theory [7]. Contrary to the non-linear distortional process, this process of dipole reorientation in the DC electric field depends rather strongly on temperature because of the deorienting thermal motion, which tends to re-establish the random distribution of molecular orientation as it existed in the absence of the DC field. Temperature-dependent processes take place also in non-dipolar substances if the degree of condensation is so considerable as to provide for the existence of strong fluctuating electric fields of molecular quadrupoles or octupoles; these fields act on the neighbouring molecules, inducing dipoles in them and thus causing them to undergo a reorientation by the DC electric field applied to the dense medium [8]. The numerical evaluations of an earlier paper [8] show that, in polar substances, the effect of molecular reorientation markedly predominates over that of non-linear distortion of the electron shells.

If the applied DC electric field is very intense, all the electric dipoles of the medium tend to align completely in the direction of the field. This leads to an ordered structure resembling a quasi-crystalline structure. Such "saturation" of electric dipole reorientation [9] can give rise to a considerable increase in second harmonic generation by strongly dipolar substances, like solutions of macromolecules or of colloid particles [10].

In this paper, we shall show that the intensity of second harmonic generation depends not only on saturation of reorientation of the permanent electric dipoles but also on saturation of reorientation of the electric dipoles induced in electrically anisotropic molecules or particles. In such systems, superposition of the two saturations can lead to a steep increase in SHG intensity, as is the case for cigar-shaped molecules, or to a considerable decrease in SHG as in systems with disc-like ones. We shall moreover show that intense laser light induces additionally an optical birefringence in the medium and that this birefringence influences the SHG in the presence of a weak electric field.

2. Theoretical Considerations

Beside the usual linear dipolar polarisation at frequency ω , a sufficiently intense light wave with electric vector \mathbf{E}^ω oscillating at frequency ω will induce non-linear polarisations at double frequency 2ω , triple frequency 3ω and, in general, at higher multiples of the fundamental frequency ω [1, 2]. Since here our interest bears essentially on the dipole polarisation \mathbf{P} induced at frequency 2ω (omitting higher multiples of ω), we write its σ -component in the form [1]:

$$P_\sigma(2\omega) = \chi_{\sigma\tau\nu}^{2\omega} E_\tau^\omega E_\nu^\omega, \quad (1)$$

where the quantities $\chi_{\sigma\tau\nu}^{2\omega} = \chi_{\sigma\tau\nu}(-2\omega, \omega, \omega)$ are components of the tensor of rank 3 of non-linear susceptibility.

In the absence of external fields, the tensor $\chi_{\sigma\tau\nu}^{2\omega}$ possesses non-zero components only in the case of media which do not present a centre of inversion [2]. Now, when a naturally isotropic medium is placed in a DC electric field (say, of field strength \mathbf{E}^0), it becomes deprived of its centre of symmetry, so that its symmetry undergoes a degrading. This field-induced change in symmetry leads to the non-vanishing of certain of the tensor components $\chi_{\sigma\tau\nu}^{2\omega}$, which now become functions of the field strength \mathbf{E}^0 , consequently $\chi_{\sigma\tau\nu}^{2\omega}(\mathbf{E}^0)$ [10]. Assuming the laser beam to propagate along the z -axis of laboratory co-ordinates, and the DC electric field as applied along the y -axis, equation 1 leads to the following expressions for mutually perpendicular polarisation components at 2ω [5, 10]:

$$\begin{aligned} P_x(2\omega, E_y^0) &= \chi_{xxy}^{2\omega}(E_y^0) E_x^\omega E_y^\omega + \chi_{xyx}^{2\omega}(E_y^0) E_y^\omega E_x^\omega, \\ P_y(2\omega, E_y^0) &= \chi_{yxx}^{2\omega}(E_y^0) E_x^\omega E_x^\omega + \chi_{yyy}^{2\omega}(E_y^0) E_y^\omega E_y^\omega. \end{aligned} \quad (2)$$

The explicit form of the susceptibility tensor components $\chi_{\sigma\tau\nu}^{2\omega}(E_y^0)$ depends in general on the microstructure of the medium as well as on the field strength \mathbf{E}^0 . For weak fields \mathbf{E}^0 , they are linear in E_y^0 in all media. For strong fields \mathbf{E}^0 , they are rather involved; with the aim of

simplifying these expressions we shall henceforth neglect the non-linear electronic dispersion, as a result of which the tensor $\chi_{\sigma\tau\nu}^{2\omega}(\mathbf{E}^0)$ can be dealt with as symmetric in all its indices and our problem reduces to a discussion of only two independent components [10]:

$$\chi_{xxy}^{2\omega}(E_y^0) = \chi_{xyx}^{2\omega}(E_y^0) = \chi_{yxx}^{2\omega}(E_y^0) \text{ and } \chi_{yyy}^{2\omega}(E_y^0) . \quad (2a)$$

We moreover assume for simplicity that the medium is so dilute that the microsystems (molecules, macromolecules or particles having axially symmetric electric and geometrical structures with respect to the molecular 3-axis) do not interact appreciably. The reorientation of permanent electric dipoles μ in the DC electric field component direction E_y^0 is thus given by the dimensionless parameter

$$p = \mu_3 E_y^0 / kT \quad (3)$$

whereas the reorientation of induced dipoles is given by the parameter

$$q = |\alpha_{33} - \alpha_{11}| E_y^0 / 2kT , \quad (4)$$

α_{33} and α_{11} being respectively the tensor components of linear polarisability parallel and perpendicular to the symmetry axis of the microsystem.

The two parameters (equations 3, 4) enter the Maxwell-Boltzmann distribution function:

$$f(\vartheta, E_y^0) = \frac{\exp(p \cos\vartheta \pm q \cos^2\vartheta)}{\int \exp(p \cos\vartheta \pm q \cos^2\vartheta) d\Omega} \quad (5)$$

which describes the degree of reorientation of the microsystems caused in the elementary body angle $d\Omega$ by the DC electric field E_y^0 . The angle ϑ is subtended by the symmetry axis (principal 3-axis) of the microsystem and the direction of E_y^0 .

The sign "plus" in equation 5 has to be taken if the microsystems are cigar-like in shape thus presenting positive electric anisotropy ($\alpha_{33} - \alpha_{11} > 0$), whereas the sign "minus" refers to disc-shaped microsystems (negative electric anisotropy, $\alpha_{33} - \alpha_{11} < 0$).

With regard to an average number density ρ of microsystems in the medium, and in the absence of molecular interactions, one can express the phenomenological non-linear susceptibility tensor $\chi_{\sigma\tau\nu}^{2\omega}(E_y^0)$ in terms of molecular properties as follows [10]:

$$\chi_{\sigma\tau\nu}^{2\omega}(E_y^0) = \frac{\rho}{4} \int (b_{\sigma\tau\nu}^{2\omega} + c_{\sigma\tau\nu}^{2\omega} E_y^0 + \dots) f(\vartheta, E_y^0) d\Omega \quad (6)$$

where $b_{\sigma\tau\nu}^{2\omega}$ is the tensor of second-order non-linear polarisability of the microsystem induced by the square of the optical field \mathbf{E}^ω , whereas the tensor $c_{\sigma\tau\nu}^{2\omega}$ defines the variation in $b_{\sigma\tau\nu}^{2\omega}$ caused by the distortional effect of the first power of E_y^0 . Obviously, the tensor $b_{\sigma\tau\nu}^{2\omega}$ of rank 3 has non-zero components in the case of microsystems which lack a centre of symmetry in their ground state. Here, for instance, belong microsystems having symmetry of the point groups C_{2v} or C_{3v} . The tensor $c_{\sigma\tau\nu}^{2\omega}$ of rank 4 has non-zero components for all molecular symmetries, including atoms which are spherically symmetrical in their ground state. Since, for low molecular symmetries, the number of mutually independent components of the tensors $b_{\sigma\tau\nu}^{2\omega}$ and $c_{\sigma\tau\nu}^{2\omega}$ is quite considerable, we shall restrict our considerations to axially symmetric microsystems having symmetry of the point groups C_{3v} (e.g. NH_3 , CHCl_3 , CH_3Cl , CH_3I), C_{4v} (e.g. BrF_5) and $C_{\infty v}$ (e.g. CO , HCl , CN , N_2O).

2.1. Process of Electrical Pure Reorientation

To begin with, we shall assume that the DC electric field applied to the medium produces a pure reorientation defined by the distribution function (equation 5). By this we mean a reorientation of the microsystems unaccompanied by the distortional effect described by the second term of equation 6, $c_{\sigma\tau\nu}^{2\omega} E_y^0$. With this restriction and on the preceding assumptions, equations 5 and 6 yield (see Appendix):

$$\chi_{xxy}^{2\omega}(E_y^0)_R = \frac{\rho}{8} \{ (b_{333}^{2\omega} - b_{113}^{2\omega})L_1(p, \pm q) - (b_{333}^{2\omega} - 3b_{113}^{2\omega})L_3(p, \pm q) \} ,$$

$$\chi_{yyy}^{2\omega}(E_y^0)_R = \frac{\rho}{4} \{ 3b_{113}^{2\omega}L_1(p, \pm q) + (b_{333}^{2\omega} - 3b_{113}^{2\omega})L_3(p, \pm q) \} , \quad (7)$$

where $L_1(p, \pm q)$ and $L_3(p, \pm q)$ are generalised Langevin functions [7] of odd order, of the form [11]:

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

$$L_3(p, \pm q) = \mp \frac{p(p^2 \mp 6q)}{8q^3} - \frac{p(e^p + e^{-p})}{8q^{3/2}I(p, \pm q)} \pm \frac{(p^2 \mp 4q + 4q^2)(e^p - e^{-p})}{16q^{5/2}I(p, \pm q)} . \quad (8)$$

The integrals:

$$I(p, \pm q) = \frac{1}{2} \exp \left\{ \mp \left(\frac{p^2}{4q} + q \right) \right\} \int_{l_1}^{l_2} \exp(\pm t^2) dt \quad (9)$$

are well adapted for numerical tabulation [12, 13]. The limits of integration are:

$$l_1 = -\sqrt{q} \pm \frac{p}{2\sqrt{q}}$$

and

$$l_2 = \sqrt{q} \pm \frac{p}{2\sqrt{q}} .$$

The graphs of figs. 1 and 2 show the odd Langevin functions (equation 8) as functions of p at values of $q = p^2/n$ for $n = 1, 4, 9, 16, 25, 36, \dots$.

In cigar-shaped microsystems (positive anisotropy), the permanent electric dipoles and induced electric dipoles tend to orient themselves in a concordant manner in the direction of the DC field. As a result of this, with increasing DC field strength and parameter q , the values of $L_1(p, +q)$ and $L_3(p, +q)$ tend very steeply from 0 to the limiting value 1, which defines a state of complete alignment of the microsystems in the direction of the DC electric field (electric saturation of orientation). This is illustrated in the dashed curves of figs. 1 and 2.

In the case of disc-like microsystems (negative anisotropy) the situation is entirely different. Here with the permanent dipole moment μ_3 directed along the symmetry axis of the microsystem, the polarisability α_{33} along this axis will be less than the polarisability α_{11} perpendicularly to it. Hence the torque acting on the permanent dipole will tend to orient the microsystem into alignment with the DC electric field E^0 , while the torque on the induced dipole will act in a manner to orient the microsystem perpendicularly to E^0 . In this way, a disc-like microsystem is subject to two mutually orthogonal torques. With increasing field strengths E^0 , the induced dipole parameter (equation 4) increases thus causing the microsystem to go over from parallel orientation to perpendicular orientation with respect to the field E^0 , and the Langevin functions $L_1(p, -q)$ and $L_3(p, -q)$ decrease in value correspondingly, tending rapidly to zero as the parameter q of induced dipole reorientation grows (figs. 1 and 2, continuous curves lying below the curve for $q = 0$).

2.2. Electric Distortional-Reorientational Cross-Process

In addition to reorientation of the microsystems, a DC electric field if sufficiently intense will cause a distortion of their electron shells, which in our case will become apparent as a linear variation of the tensor $b_{\sigma\tau\nu}^{2\omega}$ given by the second term of the right hand side of the expansion (equation 6). Since this distortional effect is in general coupled to the reorientation effect by way of the distribution function of equation 5, we obtain finally in the absence of electronic dispersion:

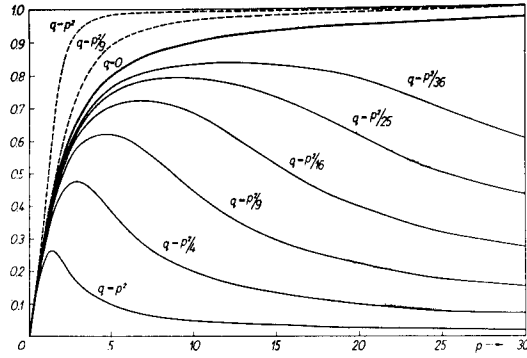


Figure 1 Generalised Langevin functions plotted vs. the parameter p . Dashed lines ---- $L_1(p, +q)$. Continuous bold face type line — $L_1(p, 0)$. Continuous lines — $L_1(p, -q)$.

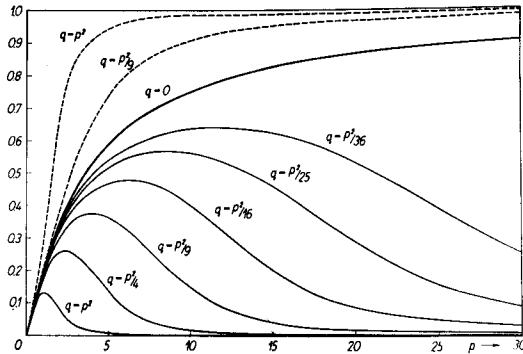


Figure 2 Generalised Langevin functions plotted vs. the parameter p . Dashed lines ---- $L_3(p, +q)$. Continuous bold face type line — $L_3(p, 0)$. Continuous lines — $L_3(p, -q)$.

$$\begin{aligned} \chi_{xxy}^{2\omega}(E_y^0)_D &= \frac{\rho}{24} \{c_{1111}^{2\omega} + 3c_{1133}^{2\omega} + (2c_{1111}^{2\omega} - 15c_{1133}^{2\omega} + 3c_{3333}^{2\omega})L_2(p, \pm q) \\ &\quad - 3(c_{1111}^{2\omega} - 6c_{1133}^{2\omega} + c_{3333}^{2\omega})L_4(p, \pm q)\} E_y^0, \\ \chi_{yyy}^{2\omega}(E_y^0)_D &= \frac{\rho}{4} \{c_{1111}^{2\omega} + 2(3c_{1133}^{2\omega} - c_{1111}^{2\omega})L_2(p, \pm q) \\ &\quad + (c_{1111}^{2\omega} - 6c_{1133}^{2\omega} + c_{3333}^{2\omega})L_4(p, \pm q)\} E_y^0 \end{aligned} \quad (10)$$

where the generalised Langevin functions are now of even order [11]:

$$\begin{aligned} L_2(p, \pm q) &= \frac{p^2 \mp 2q}{4q^2} \pm \frac{e^p + e^{-p}}{4q^{1/2}I(p, \pm q)} - \frac{p(e^p - e^{-p})}{8q^{3/2}I(p, \pm q)}, \\ L_4(p, \pm q) &= \frac{p^4 + 12q(q \mp p^2)}{16q^4} \pm \frac{(p^2 \mp 6q + 4q^2)(e^p + e^{-p})}{16q^{5/2}I(p, \pm q)} - \frac{p(p^2 + 4q^2 \mp 10q)(e^p - e^{-p})}{32q^{7/2}I(p, \pm q)}. \end{aligned} \quad (11)$$

These functions are plotted against the reorientation parameters p and q in figs. 3 and 4.

In the absence of electric reorientation ($p = q = 0$), the even Langevin functions of equation 11 differ from zero and take the values $L_2(0, 0) = 1/3$ and $L_4(0, 0) = 1/5$; accordingly, the expressions of equation 10 reduce to:

$$\begin{aligned} \chi_{xxy}^{2\omega}(E_y^0)_D &= \frac{\rho}{180} (3c_{3333}^{2\omega} + 8c_{1111}^{2\omega} + 12c_{1133}^{2\omega}) E_y^0, \\ \chi_{yyy}^{2\omega}(E_y^0)_D &= \frac{\rho}{60} (3c_{3333}^{2\omega} + 8c_{1111}^{2\omega} + 12c_{1133}^{2\omega}) E_y^0. \end{aligned} \quad (12)$$

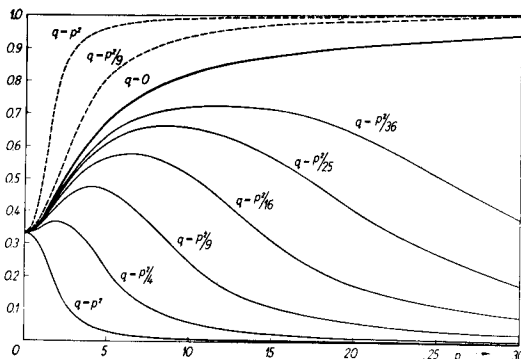


Figure 3 Generalised Langevin functions plotted vs. the parameter p . Dashed lines ---- $L_2(p, +q)$. Continuous bold face type line — $L_2(p, 0)$. Continuous lines — $L_2(p, -q)$.

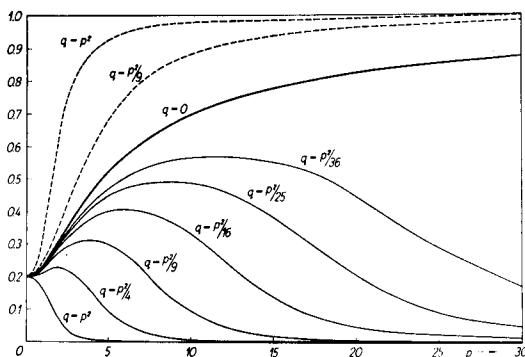


Figure 4 Generalised Langevin functions plotted vs. the parameter p . Dashed lines ---- $L_4(p, +q)$. Continuous bold face type line — $L_4(p, 0)$. Continuous lines — $L_4(p, -q)$.

The results expressed by equation 12 describe the already mentioned non-linear purely distortional effect, which does not depend directly on temperature and is present in all matter, including atomic gases.

The purely distortional effect depends linearly (within the present approximation) on the field component E_y^0 . With regard to equation 2a, the susceptibility tensor components in equation 12 fulfil the following symmetry relations [8, 10]:

$$\chi_{xxy}^{2\omega}(E_y^0) + \chi_{xyx}^{2\omega}(E_y^0) + \chi_{yxx}^{2\omega}(E_y^0) = \chi_{yyy}^{2\omega}(E_y^0) ,$$

$$\chi_{xxy}^{2\omega}(E_y^0) = \chi_{xyx}^{2\omega}(E_y^0) = \chi_{yxx}^{2\omega}(E_y^0) = \frac{1}{3}\chi_{yyy}^{2\omega}(E_y^0) . \quad (13)$$

Returning to equations 7 and 10 we note that the symmetry relations of equation 13 are fulfilled strictly only in an approximation linear in E^0 , but fail to hold generally in very strong electric fields unless simplifying assumptions are made with respect to the molecular symmetry of the tensors $b_{\sigma\tau\nu}^{2\omega}$ and $c_{\sigma\tau\nu\rho}^{2\omega}$. We shall proceed to do so further on.

In very strong electric fields, the distortional effect is modified by the effect of reorientation of microsystems in accordance with formulae of equation 10. From graphs 3 and 4, the Langevin functions are seen to grow steeply to saturation with growing E^0 for cigar-like microsystems (dashed curves) and to decrease just as steeply to zero for disc-like ones (continuous curves lying below the curves $q = 0$). In contradiction of the previous case of section 2.1, we have now to keep in mind that the reorientational process in accordance with the expressions of equation 10 superimposes itself as a perturbation on the (in this case essential) distortional process which, as seen from equation 12, takes place also in weak fields E^0 independently of molecular reorientation.

At $p = 0$, the expressions in equation 10 are applicable to non-dipolar, axially symmetric microsystems of the point group symmetries D_{6h} (e.g. C_6H_6) and $D_{\infty h}$ (H_2 , O_2 , CO_2 , CS_2 and the like). Obviously, for such microsystems, which possess a centre of symmetry, the susceptibility components of equation 7 vanish.

2.3. Optical Reorientation Process

The polarisability ellipsoids of microsystems also undergo reorientation in the electric field of laser light. Even optical saturation can be achieved, if the laser beam is sufficiently intense [14, 15]. From our previous considerations, it is obvious that optical reorientation can influence the susceptibility tensor components $\chi_{\sigma\tau\nu}^{2\omega}$ in isotropic bodies only in the presence of a DC electric field. At optical frequencies there is no reorientation of permanent dipoles, and only reorientation of induced dipoles given by a parameter analogous to equation 4 takes place:

$$q_y^{\omega} = |\alpha_{33}^{\omega} - \alpha_{11}^{\omega}| I_y / 2kT . \quad (4a)$$

Above, $I_y = E_y^{\omega} E_y^{-\omega} / 2$ is the intensity of laser light linearly polarised with electric oscillations along the direction of the DC electric field component E_y^0 . However, in this case, considering equation 2, we shall be measuring only the second part of the polarisation y -component:

$$P_y(2\omega, E_y^0) = \chi_{yyy}^{2\omega}(E_y^0) E_y^{\omega} E_y^{\omega} . \quad (14)$$

In the Langevin functions of equations 7 and 10 for the component $\chi_{yyy}^{2\omega}(E_y^0)$, the parameter q_y^{ω} of equation 4a, accounting for optical orientation in light of intensity I_y , has now to be added to the parameter q of induced dipole reorientation. One sees that this superposition of optical orientation upon electric orientation still further raises the polarisation values of equation 14 for cigar-like microsystems and lowers them for disc-like ones.

When carrying out experimental work, one is usually concerned with avoiding electric breakdown, so that too strong DC electric fields cannot be applied. This sets a limit to the degree of electric reorientation achievable in molecular liquids, which has necessarily to remain at a low level, and one is justified in restricting accuracy to a linear dependence of $\chi_{\sigma\tau\nu}^{2\omega}$ on E_y^0 . This limitation need not in general apply to experiments with the electric field of laser light, where a high degree of molecular alignment, or even optical saturation [14], can be achieved before breakdown occurs. Obviously, in this case when calculating the distribution function of equation 5, one has to take into account the state of polarisation of the laser beam. Thus, if the beam propagating along the z -axis is circularly polarised, the susceptibility components fulfil the relations in equation 13, the two contributions now being of the form:

$$\chi_{xxy}^{2\omega}(E_y^0)_R = \frac{\rho\mu_3}{32kT} \{ b_{113}^{2\omega} + b_{333}^{2\omega} + 2(b_{113}^{2\omega} - b_{333}^{2\omega})L_2(\mp q_c^{\omega}) + (b_{333}^{2\omega} - 3b_{113}^{2\omega})L_4(\mp q_c^{\omega}) \} E_y^0 , \quad (15)$$

$$\chi_{xxy}^{2\omega}(E_y^0)_D = \frac{\rho}{288} \{ 25c_{1111}^{2\omega} - 30c_{1313}^{2\omega} + 9c_{3333}^{2\omega} + 2(42c_{1313}^{2\omega} - 5c_{1111}^{2\omega} - 9c_{3333}^{2\omega})L_2(\mp q_c^{\omega}) + 9(c_{1111}^{2\omega} - 6c_{1313}^{2\omega} + c_{3333}^{2\omega})L_4(\mp q_c^{\omega}) \} E_y^0 , \quad (16)$$

where the even Langevin functions are given by [15]:

$$L_2(\mp q_c^{\omega}) = \pm \frac{1}{2q_c^{\omega}} \mp \frac{1}{2\sqrt{q_c^{\omega}} I(\mp q_c^{\omega})} ,$$

$$L_4(\mp q_c^{\omega}) = \frac{1}{4q_c^{\omega}} \left\{ \frac{3}{q_c^{\omega}} \mp \frac{2q_c^{\omega} \pm 3}{\sqrt{q_c^{\omega}} I(\pm q_c^{\omega})} \right\} \quad (17)$$

with

$$I(\mp q_c^{\omega}) = \exp(\pm q_c^{\omega}) \int_0^{\sqrt{q_c^{\omega}}} \exp(\mp t^2) dt . \quad (18)$$

It is readily seen that the functions in equation 17 and integrals in equation 18 result respectively from equations 11 and 9, on putting $p = 0$ and $q = -q_c^\omega$; this last parameter has now to be replaced by

$$q_c^\omega = |\alpha_{33}^\omega - \alpha_{11}^\omega| (I_+ + I_-) / 4kT \quad (4b)$$

where I_+ and I_- are intensities of laser light for the two senses of circular polarisation.

In equations 15 to 18, in the situation now under consideration, the upper sign "minus" is relevant for cigar-like microsystems and the lower sign "plus" for disc-like ones. This inversion of the signs is due to the fact that in the case of circularly polarised light the microsystems tend to orient themselves with their symmetry axis in the direction of propagation of the light beam, which is identical with the direction of the induced optical axis of the medium. Cigar-shaped microsystems tend to align themselves with their long axis, which is the symmetry axis, perpendicular to the plane of oscillations of the light wave; in this way, the short axes of the microsystems come to lie in the plane of oscillations; as a result, the reorientation functions $L_2(-q_c^\omega)$ and $L_4(-q_c^\omega)$ decrease to zero at saturation (complete orientation). With disc-like microsystems the situation is the inverse: the long axes lie in the oscillation plane, whereas the short symmetry axis tends to be parallel to the propagation direction; the reorientation functions $L_2(+q_c^\omega)$ and $L_4(+q_c^\omega)$ increase and tend to unity at saturation.

The preceding considerations together with formulae of equations 15 to 18 remain valid in the case of natural (unpolarised) light incident on the medium along the z -axis. Obviously, in equation 4b, $I_+ + I_-$ has to be replaced by $I_n = I_x + I_y$.

If the light beam incident on the medium is linearly polarised with oscillations parallel to the direction of the DC electric field component E_y^0 , then with regard to equation 2 we measure only the susceptibility component $\chi_{yyy}^{2\omega}(E_y^0)$ which is of the form:

$$\chi_{yyy}^{2\omega}(E_y^0) = \frac{\rho\mu_3}{4kT} \{3b_{113}^{2\omega} L_2(\pm q_y^\omega) + (b_{333}^{2\omega} - 3b_{113}^{2\omega}) L_4(\pm q_y^\omega)\} E_y^0 \quad (19)$$

with q_y^ω given by equation 4a.

Conversely, if the linearly polarised light oscillations are perpendicular to the DC field component E_y^0 (i.e. are parallel to the laboratory x -axis), we measure, with regard to equation 2, solely the component:

$$\chi_{yxx}^{2\omega}(E_y^0) = \frac{\rho\mu_3}{8kT} \{b_{113}^{2\omega} + (b_{333}^{2\omega} - 4b_{113}^{2\omega}) L_2(\pm q_x^\omega) - (b_{333}^{2\omega} - 3b_{113}^{2\omega}) L_4(\pm q_x^\omega)\} E_y^0 \quad (20)$$

with q_x defined by equation 4a on replacing I_y by I_x .

3. Applications and Discussion

3.1. Macroscopic and Microscopic Symmetry Relations

As long as reorientation of the microsystems in the DC electric field is not excessive ($p \ll 1$, $q \ll 1$), the Langevin functions of equations 8 and 11 can be expressed with sufficient accuracy as follows:

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

$$L_2(p, \pm q) = \frac{1}{3} + \frac{2p^2}{45} \pm \frac{4q}{45} + \dots$$

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

$$L_4(p, \pm q) = \frac{1}{5} + \frac{4p^2}{105} \pm \frac{8q}{105} + \dots$$

On inserting the above expansions into equations 7 and 10, the symmetry relations of equation 13 are fulfilled in an approximation linear in E_y^0 , the contribution due to the distortional effect alone being given by equation 12 and the contribution due to the process of dipole reorientation by:

$$\chi_{xxy}^{2\omega}(E_y^0)_R = \frac{1}{3}\chi_{yyy}^{2\omega}(E_y^0)_R = \frac{\rho\mu_3}{60kT}(b_{333}^{2\omega} + 2b_{113}^{2\omega})E_y^0 . \quad (21)$$

In the case of complete alignment of all microsystems along the field direction ($p \rightarrow \infty$, $q \rightarrow \infty$, if the field is intense or the dipole moments and polarisabilities of the microsystems are considerable), the Langevin functions (equations 8 and 11) tend rapidly to unity for positive anisotropy, and equations 7 and 10 reduce to:

$$\begin{aligned} \chi_{xxy}^{2\omega}(E_y^0) &= \frac{\rho}{4}(b_{113}^{2\omega} + c_{1133}^{2\omega}E_y^0) , \\ \chi_{yyy}^{2\omega}(E_y^0) &= \frac{\rho}{4}(b_{333}^{2\omega} + c_{3333}^{2\omega}E_y^0) . \end{aligned} \quad (22a)$$

For disc-shaped microsystems at complete alignment, the Langevin functions of equations 8 and 11 tend to zero, as a result of which the components of equation 7 vanish and the components of equation 10 reduce to:

$$\begin{aligned} \chi_{xxy}^{2\omega}(E_y^0)_D &= \frac{\rho}{24}(c_{1111}^{2\omega} + 3c_{1133}^{2\omega})E_y^0 , \\ \chi_{yyy}^{2\omega}(E_y^0)_D &= \frac{\rho}{4}c_{1111}^{2\omega}E_y^0 . \end{aligned} \quad (22b)$$

Were we to postulate the fulfilment of the macroscopic symmetry relations (equation 13) in the two cases of equations 22a and 22b, the following microscopic relations would have to hold for the individual microsystems:

$$b_{333}^{2\omega} = 3b_{113}^{2\omega} , \quad (23)$$

$$c_{3333}^{2\omega} = c_{1111}^{2\omega} = 3c_{1133}^{2\omega} . \quad (24)$$

It may be worth mentioning that the symmetry relations of equation 24 are strictly fulfilled only with regard to the spherical symmetry, for example, atoms in their ground state in the absence of electron dispersion and absorption.

As we have seen, Bloembergen's symmetry relations [8, 10] which we have adduced here for the non-linear susceptibility tensor components $\chi_{\sigma\tau\nu}^{2\omega}(E_y^0)$ in the form of equation 13, are fulfilled strictly in an approximation linear in E^0 only if electron dispersion is neglected. These relations have been confirmed experimentally by Mayer* in ethyl bromide. For very strong DC fields, the symmetry relations of equation 13 are in general not fulfilled.

For the case of electric saturation, the expressions of equation 22 suggest that the symmetry of the electro-optical properties of the individual microsystem becomes identical with the macroscopic symmetry of the isotropic medium as a whole which, in the presence of the DC field, is endowed with symmetry of the type $C_{\infty v}$. This is a rather obvious conclusion, as indeed with all the microsystems in alignment along the field direction the properties of the body as a whole have to coincide with those of the microsystems. In accordance with equations 7 and 10 as well as 15 and 16 any deviations from the state of ordering (equation 22) are of a statistical nature and can be a source of information relating to the non-linear electro-optical properties of individual microsystems.

3.2. The Rôle of Induced Electric and Optical Birefringence

If, for asymmetrical microsystems, one assumes the relation of equation 23 but replaces the relation of equation 24 by

*Private communications of 3 September and 15 October, 1968.

$$c_{1133}^{2\omega} = \frac{1}{6}(c_{1111}^{2\omega} + c_{3333}^{2\omega}) \quad (25)$$

equations 7 and 10 reduce to the form:

$$\chi_{yyy}^{2\omega}(E_y)_R = 3\chi_{xxy}^{2\omega}(E_y)_R = \frac{\rho}{4} b_{333}^{2\omega} L_1(p, \pm q) , \quad (26)$$

$$\chi_{yyy}^{2\omega}(E_y)_D = 3\chi_{xxy}^{2\omega}(E_y)_D = \frac{\rho}{12} \{c_{3333}^{2\omega} + 2c_{1111}^{2\omega} + 2(c_{3333}^{2\omega} - c_{1111}^{2\omega})\Phi(p, \pm q)\} E_y^0 . \quad (27)$$

Equation 27 involves the reorientation function [12, 13]

$$\Phi(p, \pm q) = \frac{3}{2} L_2(p, \pm q) - \frac{1}{2} \quad (28)$$

which defines the well-known Kerr effect in a strong DC electric field:

$$n_{\parallel} - n_{\perp} = \frac{2\pi}{n} \rho (\alpha_{33}^{\omega} - \alpha_{11}^{\omega}) \Phi(p, \pm q) \quad (29)$$

where n is the refractive index of the medium in the absence of an electric field and $n_{\parallel} = n_y$, $n_{\perp} = n_x$ the indices for light vector oscillations parallel and perpendicular to the DC field vector E_y^0 .

One sees that, with the symmetry relation of equation 23, the reorientational contribution (equation 26) to the non-linear optical susceptibility is isotropic and its dependence on the DC electric field strength is defined by the Langevin function $L_1(p, \mp q)$ i.e. in analogy with electric saturation of the static polarisation of dipolar gases in Debye's well-known theory of dielectrics [9]. The assumption of the symmetry relation of equation 25 causes the distortional contribution (equation 27) to split into an isotropic part $c_{3333}^{2\omega} + 2c_{1111}^{2\omega}$ independent of the reorientation process, and an anisotropic part related to the process of molecular reorientation, in the same way as the optical birefringence of the medium (equation 29) induced by a DC electric field. The shape of the reorientation function (equation 28) is shown in fig. 5; one notes that in the case of cigar-like microsystems (positive anisotropy) the function $\Phi(p, +q)$ tends upward to the limiting value 1 with growing field strength and growing q , whereas in the case of disc-like microsystems (negative anisotropy) the function $\Phi(p, -q)$ decreases with growing field strength, exhibiting a reversal of sign at a well-defined value of the parameter q and tending to the value $-\frac{1}{2}$ at saturation.

Let us moreover consider the case when the DC electric field is not very strong whereas the electric field of the laser beam is very intense and, causing optical reorientation of the micro-

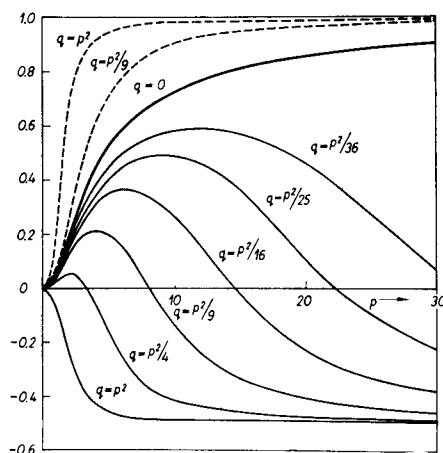


Figure 5 Birefringence functions $\Phi(p, \pm q)$. Above the continuous bold face type curve $\Phi(p, 0)$ lie the dashed type curves $\Phi(p, +q)$ for cigar-shaped microsystems; and below lie the continuous line curves $\Phi(p, -q)$ for disc-like microsystems.

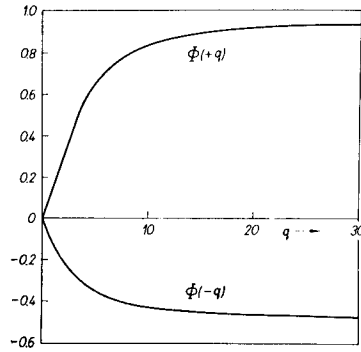


Figure 6 Birefringence functions from induced dipole reorientation alone: $\Phi(+q)$ for cigar-like microsystems, $\Phi(-q)$ for disc-like ones.

systems, modifies their non-linear susceptibilities as seen, e.g. from equations 15 and 16. Let us furthermore restrict our considerations to the reorientational contribution (equation 15) which, with regard to equation 23, reduces to the form:

$$\chi_{xxy}^{2\omega}(E_y^0)_R = \frac{\rho b_{113}^{2\omega} \mu_3}{12kT} \{1 - \Phi(\mp q_c^\omega)\} E_y^0 \quad (30)$$

where $\Phi(\mp q_c^\omega)$ is the reorientation function of microsystems in the electric field of circularly polarised laser light defined by equation 28 for $p = 0$ and $q = -q_c^\omega$.

The function $\Phi(\pm q_c^\omega)$ defines the non-linear change in angle of optical rotation Θ in optically active substances due to intense circularly polarised laser light [16]:

$$\frac{\Theta - \Theta_0}{\Theta_0} = \frac{(2g_{33}^\omega - g_{11}^\omega - g_{22}^\omega)}{2(g_{11}^\omega + g_{22}^\omega + g_{33}^\omega)} \Phi(\mp q_c^\omega) \quad (31)$$

where Θ_0 is the angle of rotation of the polarisation plane in the absence of the intense laser beam, and $g_{11}^\omega, g_{22}^\omega, g_{33}^\omega$ are principal values of the tensor $g_{\sigma\tau}^\omega$ of natural gyration.

With regard to the properties of the function $\Phi(\pm q)$ plotted in fig. 6, we see that optical reorientation entails a rise in the non-linear susceptibility (equation 30) in the case of cigar-like microsystems but causes it to fall to zero in the case of disc-like ones.

Similarly, for the cases of linearly polarised light with oscillations parallel to the DC field (y -axis)

$$\chi_{yyy}^{2\omega}(E_y^0)_R = \frac{\rho b_{113}^{2\omega} \mu_3}{4kT} \{1 + 2\Phi(\pm q_y^\omega)\} E_y^0 \quad (32)$$

and oscillations perpendicular to E_y^0 (x -axis), equations 19 and 20 yield

$$\chi_{yxx}^{2\omega}(E_y^0)_R = \frac{\rho b_{113}^{2\omega} \mu_3}{12kT} \{1 - \Phi(\pm q_x^\omega)\} E_y^0 \quad (33)$$

The reorientation functions $\Phi(\pm q_y^\omega)$ and $\Phi(\pm q_x^\omega)$ of equations 32 and 33, which are plotted in fig. 6, describe the optical birefringence induced in the medium by intense linearly polarised laser light. Optically induced birefringence is defined by equation 29 with $p = 0$ and $q = q_y^\omega$; as hitherto, it has been observed in molecular liquids [17] in an approximation linear in q_y^ω as the optical Kerr effect.

We thus see that in the case of molecules with positive anisotropy, when optical reorientation increases the susceptibility (equation 32) grows most steeply, the susceptibility (equation 30) less steeply, whereas the susceptibility (equation 33) decreases to zero. This relationship is apparent (except for the component in equation 33) in Mayer's [5] measurements on the dipolar substances CH_3I , $\text{C}_2\text{H}_5\text{I}$ and $\text{C}_2\text{H}_5\text{Br}$. However, at field strengths E_y^0 close to breakdown, the same substances exhibited a very steep rise in SHG power not observed by Mayer in other dipolar (CO , CHCl_3) and non-dipolar (H_2 , O_2 , CH_4 , CCl_4) substances. So we ask: to what extent is one justified in attributing this anomalous increase in SHG to the increase in reorientation of the microsystems, and to what extent may it rather be due to other mechanisms, not considered here?

3.3. Application to Molecular Substances

Available data are as yet too scanty for making an extensive comparative analysis of the theoretical results against the background of experiment. Clearly, one can hardly hope to achieve electric or optical saturation (complete molecular alignment) in molecular gases or liquids without incurring dielectric or optical breakdown. In the dipolar substances studied by Mayer, the electric reorientation parameters were, at the best, of the order $p = 10^{-3} E_y^{02}$ and $q = 10^{-9} E_y^{02}$; accordingly, as seen from the curves of figs. 1-5, one would have to resort to a very strong DC electric field upward of 10^3 e.s.u. (3×10^7 v/m) in order to achieve an onset of saturation. In this situation, optical alignment of the molecules or even some degree of optical saturation seems a more feasible proposition (in Mayer's work [5], the laser field strength E^ω amounted to 5×10^3 e.s.u.). Indeed, one should take into consideration that the values of p and q can moreover be subject to an enhancement owing to the fact that molecules in their excited states (into which state they go as a result of applying a strong field) generally possess much larger dipole moments and polarisabilities than when in their ground state.

Existing experimental results on ESHG do not as yet permit a quantitative decision as to which of the microscopic processes under consideration by us, namely non-linear electronic distortion or molecular reorientation, plays the chief part. But it may well be reorientation, considering that Mayer [5] observed the anomalous increase in ESHG with growing DC electric field in CH_3I , $\text{C}_2\text{H}_5\text{I}$ and $\text{C}_2\text{H}_5\text{Br}$, the molecules of which have large dipole moments of about 2 Debyes and positive anisotropy of their electric and optical polarisabilities. But he failed to observe a rise in SHG signal in chloroform and other weakly dipolar and non-dipolar substances. This, in the light of the present theory, was most probably due to the circumstance that CHCl_3 has a smaller dipole moment, about 1 D, and a negative anisotropy of polarisability leading, with regard to the curves of figs. 1-5, to a decrease of the non-linear susceptibilities and thus of ESHG. Numerical evaluations [8] show that in dipolar substances the process of molecular reorientation predominates markedly compared to non-linear electronic distortion. A final decision can be expected from ESHG investigations as a function of temperature, of concentration or of an applied AC electric field frequency.

In condensed substances, the non-linear optical susceptibility is modified by various molecular correlations such as molecular redistribution [18-20], angular correlations between anisotropic molecules [18, 21], as well as the local field and its anisotropy [18]. These factors can either enhance or hinder the process of electric reorientation according to the structure of the molecules and the degree of condensation of the substance. Molecular redistribution is of considerable importance to non-linear processes, since it gives rise to molecular anisotropy even if the interacting molecules are nearly spherical, like CCl_4 [18, 19]; in this case (in dense phases) only correlations of the radial type occur, causing the molecules to re-group giving rise temporarily to pairwise, triple and larger assemblages, which then undergo reorientation in the externally applied electric field. When this process is taken into account in the calculations, the reorientation parameter (equation 4) is found to be non-zero even if the molecules are isotropic in their ground state. This is most readily demonstrable on the basis of Silberstein's polarisability theory [22], according to which the effective anisotropy of a pair of mutually interacting isotropic molecules, having the same polarisability α in their ground state, at mean mutual distance d is:

$$\alpha_{33} - \alpha_{11} = \frac{2\alpha}{1 - \frac{2\alpha}{d^3}} - \frac{2\alpha}{1 + \frac{\alpha}{d^3}} \approx \frac{6\alpha^2}{d^3}. \quad (34)$$

Assuming this approximation is sufficiently good for liquids of nearly symmetric molecules, and with regard to equation 29, we obtain:

$$n_{\parallel} - n_{\perp} = \frac{12\pi\rho\alpha^2}{nd^3} \left(\frac{n^2 + 2}{3} \right)^2 \Phi(q_s) \quad (35)$$

a result which shows that these media are apt to exhibit induced birefringence, like that observed in CCl_4 when using either a DC or laser electric field [17]. From equations 4 and 34, the electric reorientation parameter for symmetric molecules, assuming a Lorentz local field in the medium of dielectric constant ϵ , is:

$$q_s = \alpha^2(\epsilon + 2)^2(E_y^0)^2/3d^3kT \quad (4c)$$

whereas in considering optical reorientation one has to put $\epsilon = n^2$ and to replace $(E_y^0)^2$ by I_y or $I_c/2$ (the intensity of linearly or circularly polarised light, respectively, cf. equations 4a and 4b). Thus, for liquid CCl_4 , equation 4c immediately yields $q_s = 2 \times 10^{-10} E_y^0{}^2$, which is a reorientation parameter of nearly the same order as for isolated anisotropic molecules.

Molecular redistribution, of course, also plays an essential rôle in liquids consisting of anisotropic molecules. The calculations are, however, quite involved and can be performed to the end in an approximation linear in q (cf. references 18-20).

These various collective processes can lead to phase transitions from a system of partially aligned molecules to a quasi-crystalline phase with a higher degree of ordering [21]. As a result, all internal and external factors co-operating, the naturally isotropic medium can produce enough optical non-linearity and anisotropy for a considerable enhancement of SHG.

3.4. Application to Macromolecular Substances

The theory proposed in section 3 can be applied to macromolecules in solution or colloid particles in suspension. The microsystems have to be assumed as rigid, and the solutions as sufficiently dilute to exclude interactions between the macromolecules or particles and between them and the solvent, which is assumed to be isotropic, of electric permittivity ϵ_0 . For electrically anisotropic microsystems with electric permittivity ϵ_3 parallel to the symmetry axis and $\epsilon_1 = \epsilon_2$ perpendicular to it, the difference between principal electric polarisabilities of the microsystem is [23]:

$$\alpha_{33} - \alpha_{11} = \frac{V(\epsilon_3 - \epsilon_1)\epsilon_0 + (\epsilon_1 - \epsilon_0)(\epsilon_3 - \epsilon_0)(A_1 - A_3)}{4\pi[\epsilon_0 + (\epsilon_1 - \epsilon_0)A_1][\epsilon_0 + (\epsilon_3 - \epsilon_0)A_3]}, \quad (36)$$

where V is its volume, whereas its geometrical shape is defined by the parameters A_1 and A_3 , with $2A_1 + A_3 = 1$. The first term of equation 36, namely $(\epsilon_3 - \epsilon_1)\epsilon_0$, accounts for the anisotropy of the electric properties of the microsystem. The second term, which is proportional to $A_1 - A_3$, describes the anisotropy of its shape. Putting $\epsilon_0 = n_0^2$, $\epsilon_1 = n_1^2$ and $\epsilon_3 = n_3^2$ in equation 36, one obtains an expression for the anisotropy of optical polarisability of the macromolecule or particle.

In the class of synthetic polypeptides, the most often studied are macromolecules of poly- γ -benzyl-L-glutamate [12] in the shape of long cylinders presenting large dipole moments of the order of 10^3 Debyes and a large positive anisotropy of electric polarisability $\approx 10^{-18} \text{ cm}^3$. For such macromolecules, the reorientation parameters (equations 3 and 4) amount respectively to $p = 0.1 E$ and $q = 10^{-5} E^2$, which means that reorientation of the permanent dipoles predominates over reorientation of induced dipoles, and electric saturation can set in already at $E \geq 100$ e.s.u. As an example of disc-shaped particles, we mention bentonite suspensions, where $p = 0.5 E$ and $q = 0.7 E^2$ [13]. Here, $q/p^2 > 1$ and with growing field strength the reorientation of induced dipoles rapidly becomes predominant. At electric saturation, which sets in already at a field of $E \geq 10$ e.s.u., this reorientation brings the particles into alignment

with their short axis parallel to \mathbf{E} , causing the Langevin curves to fall steeply to zero. Similarly high saturation of electric orientation can be caused in solutions of collagen or Tobacco Mosaic Virus [12] as well as other biomacromolecules or colloid particles.

When working with laser light, it is essential that the pulse duration shall exceed 10^{-4} sec in order that the macromolecule or colloid particle can undergo an optical reorientation. This gives rise additionally to an optical anisotropy of the medium which, with regard to equations 30, 32 and 33, can contribute to raise or reduce the non-linear susceptibilities. One is readily convinced of the adequacy of intermediate power continuously operating gas lasers for the study of systems like these.

The preceding considerations prove that media in which the microsystems are cigar-like macromolecules or colloid particles permit the electric and optical induction of considerable non-linearities, entailing a strong increase in SHG intensity with growing DC electric field strength or, if a gas laser is used, with growing intensity of the light beam. The high optical non-linearity, including saturation* of such systems promises to be useful in various branches of opto-electronics. Also, experimental work in this direction will surely provide us with much new information concerning the non-linear properties of biomolecules, viruses and colloid particles.

When discussing the laser beam variant in a quantum-mechanical approach, the magnetic vector of the wave may well prove worth considering, inasmuch as the magnetic field of a laser beam easily attains intensities which are by no means irrelevant to the states of microsystems like those dealt with here. This, however, would exceed the space of our paper.

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Appendix

A system of weakly interacting microsystems at thermodynamical equilibrium at temperature T in the presence of an external field E is described by a Maxwell-Boltzmann distribution function of the form:

$$f(\Omega, \mathbf{E}) = \frac{\exp\{-\beta u(\Omega, \mathbf{E})\}}{\int \exp\{-\beta u(\Omega, \mathbf{E})\} d\Omega} \quad (\text{A1})$$

where $\beta = 1/kT$ and the potential energy of any individual microsystem is, with an accuracy to the square of the field \mathbf{E} , of the form:

$$u(\Omega, \mathbf{E}) = u(0) - \mu_\sigma E_\sigma - \frac{1}{2} \alpha_{\sigma\tau} E_\sigma E_\tau - \dots \quad (\text{A2})$$

The transformation of dipole moment components and polarisability tensor components from macroscopic laboratory co-ordinates x, y, z (indices σ, τ) to microsystem co-ordinates 1, 2, 3 (indices α, β) is of the form:

$$\mu_\sigma = c_{\sigma\alpha} \mu_\alpha, \quad \alpha_{\sigma\tau} = c_{\sigma\alpha} c_{\tau\beta} \alpha_{\alpha\beta} \quad (\text{A3})$$

In the case when the two co-ordinate systems are Cartesian (rectangular), the transformation coefficients $c_{\sigma\alpha}$ have the meaning of cosines of the angles between axes σ and α . These coefficients fulfil the orthonormality conditions $c_{\sigma\alpha} c_{\tau\alpha} = \delta_{\sigma\tau}$ and $c_{\sigma\alpha} c_{\sigma\beta} = \delta_{\alpha\beta}$, where $\delta_{\alpha\beta}$ is the Kronecker unit tensor.

For microsystems which are symmetrical with respect to their 3-axis, the energy equation A2 with regard to equation A3 can be written in the form:

$$u(\Omega, \mathbf{E}) = u(0) - \mu_3 c_{\sigma 3} E_\sigma - \frac{1}{2} (\alpha_{33} - \alpha_{11}) (c_{\sigma 3} c_{\tau 3} - \frac{1}{3} \delta_{\sigma\tau}) E_\sigma E_\tau \quad (\text{A4})$$

where μ_3 is the dipole moment component along the symmetry 3-axis and α_{33}, α_{11} are the polarisability tensor components respectively parallel and perpendicular to the 3-axis.

*Complete electric saturation in solutions of poly- γ -benzyl-L-glutamate has been observed in Kerr effect [12] and, recently, in measurements of non-linear variations in dielectric permittivity [25].

Performing a transformation similar to equation A3 on the symmetric tensors of non-linear polarisability $b_{\sigma\tau\nu}^{2\omega}$ and $c_{\sigma\tau\nu\rho}^{2\omega}$ of equation 6, we obtain for axially-symmetric molecules [24]:

$$b_{\sigma\tau\nu}^{2\omega} = (b_{333}^{2\omega} - 3b_{113}^{2\omega})c_{\sigma 3}c_{\tau 3}c_{\nu 3} + b_{113}^{2\omega}(c_{\sigma 3}\delta_{\tau\nu} + c_{\tau 3}\delta_{\nu\sigma} + c_{\nu 3}\delta_{\sigma\tau}) \quad (\text{A5})$$

$$c_{\sigma\tau\nu\rho}^{2\omega} = (c_{1111}^{2\omega} - 6c_{1133}^{2\omega} + c_{3333}^{2\omega})c_{\sigma 3}c_{\tau 3}c_{\nu 3}c_{\rho 3} + \frac{1}{3}(3c_{1133}^{2\omega} - c_{1111}^{2\omega})(c_{\sigma 3}c_{\tau 3}\delta_{\nu\rho} + c_{\tau 3}c_{\nu 3}\delta_{\rho\sigma} + c_{\nu 3}c_{\rho 3}\delta_{\sigma\tau} + c_{\tau 3}c_{\rho 3}\delta_{\sigma\nu} + c_{\rho 3}c_{\sigma 3}\delta_{\tau\nu} + c_{\sigma 3}c_{\nu 3}\delta_{\rho\tau}) + \frac{1}{3}c_{1111}^{2\omega}(\delta_{\sigma\tau}\delta_{\nu\rho} + \delta_{\sigma\nu}\delta_{\tau\rho} + \delta_{\sigma\rho}\delta_{\tau\nu}) . \quad (\text{A6})$$

Let the DC electric field be applied along the y -axis and let it subtend the angle ϑ with the symmetry 3-axis of the microsystem. We have $c_{x3} = \sin\vartheta \sin\phi$ and $c_{y3} = \cos\vartheta$ and by equations 6 and A5 the non-linear susceptibility components become:

$$\chi_{xxy}^{2\omega}(E_y^0) = \chi_{xyx}^{2\omega}(E_y^0) = \chi_{yyx}^{2\omega}(E_y^0) = \frac{\rho}{4} \int \{b_{113}^{2\omega} \cos\vartheta + (b_{333}^{2\omega} - 3b_{113}^{2\omega}) \cos\vartheta \sin^2\vartheta \sin^2\phi\} f(\vartheta, E_y^0) d\Omega ,$$

$$\chi_{yyy}^{2\omega}(E_y^0) = \frac{\rho}{4} \int \{3b_{113}^{2\omega} \cos\vartheta + (b_{333}^{2\omega} - 3b_{113}^{2\omega}) \cos^3\vartheta\} f(\vartheta, E_y^0) d\Omega . \quad (\text{A7})$$

Since in the present case, with regard to equations A1 and A4, the distribution function is of the form of equation 5 independent of the azimuth ϕ , we are directly justified in performing an averaging in equation A7 over all values of the angle ϕ ; this yields the result of equation 7, since the Langevin functions of order n are defined as follows:

$$L_n(p, \pm q) = \frac{\int_0^\pi \cos^n\vartheta \exp(p \cos\vartheta \pm q \cos^2\vartheta) \sin\vartheta d\vartheta}{\int_0^\pi \exp(p \cos\vartheta \pm q \cos^2\vartheta) \sin\vartheta d\vartheta} \quad (\text{A8})$$

and can quite generally be expressed as [11]:

$$L_n(p, \pm q) = \frac{\exp\left\{\mp\left(\frac{p^2}{4q} + q\right)\right\}}{2q^{n/2}I(p, \pm q)} \int_{l_1}^{l_2} \left(t \mp \frac{p}{2q^{1/2}}\right)^n \exp(\pm t^2) dt \quad (\text{A9})$$

where $l_1 = -\sqrt{q} \pm p/2\sqrt{q}$, and

$$l_2 = \sqrt{q} \pm p/2\sqrt{q}$$

Similarly, resorting to equations 5, 6 and A6, we come to equation 10.

In cases when the DC electric field \mathbf{E}^0 is weak and the oscillating field \mathbf{E}^ω of the light wave intense, the distribution function with regard to equations A1 and A4 can be represented in an approximation linear in E_y^0 as:

$$f(\vartheta, \mathbf{E}) = \frac{(1 + pc_{y3}) \exp\left\{\frac{\beta}{2}(\alpha_{33} - \alpha_{11})c_{\sigma 3}c_{\tau 3}\langle E_\sigma^\omega E_\tau^\omega \rangle_t\right\}}{\int \exp\left\{\frac{\beta}{2}(\alpha_{33} - \alpha_{11})c_{\sigma 3}c_{\tau 3}\langle E_\sigma^\omega E_\tau^\omega \rangle_t\right\} d\Omega} \quad (\text{A10})$$

where the brackets $\langle \rangle_t$ symbolise time-averaging over the oscillation period of the light wave vector.

In the case of light circularly polarised with electric vector amplitudes

$$E_\pm^\omega = (E_x^\omega \pm iE_y^\omega)/\sqrt{2} \quad (\text{A11})$$

for the two senses of circular polarisation, it is convenient to assume the symmetry 3-axis of the microsystem as forming an angle ϑ with the laboratory z -axis (propagation direction). This yields, as usual

$$c_{x3} = \sin\vartheta \cos\phi, \quad c_{y3} = \sin\vartheta \sin\phi, \quad c_{z3} = \cos\vartheta \quad (\text{A12})$$

so that the distribution function in equation A10 can be written in the form:

$$f(\vartheta, \phi, \mathbf{E}) = \frac{(1 + p \sin\vartheta \sin\phi) \exp(\mp q_c^\omega \cos^2\vartheta)}{\int_0^\pi \int_0^{2\pi} \exp(\mp q_c^\omega \cos^2\vartheta) \sin\vartheta \, d\vartheta \, d\phi} \quad (\text{A13})$$

since by equation A11 we have $\langle E_x^\omega E_x^\omega \rangle_t = \langle E_y^\omega E_y^\omega \rangle_t = (I_+ + I_-)/2$ and $\langle E_x^\omega E_y^\omega \rangle_t = 0$.

With the transformation (equation A12) and the distribution function in the form of equation A13, we get by equations 6, A5 and A6 the equations 15 and 16.

Similarly, in the case of linearly polarised light we adopt a procedure which ensures that the exponential factors in the distribution function (equation A10) shall not depend on the azimuth angles but solely on the angle ϑ . As a result, we obtain with regard to equations 6 and A5, for oscillations respectively parallel and perpendicular to the DC field component E_y^0 equations 19 and 20, and as expressions for the distortional effect:

$$\chi_{yyy}^{2\omega}(E_y^0) = \frac{\rho}{4} \{c_{1111}^{2\omega} + 2(3c_{1133}^{2\omega} - c_{1111}^{2\omega})L_2(\pm q_y^\omega) + (c_{1111}^{2\omega} - 6c_{1133}^{2\omega} + c_{3333}^{2\omega})L_4(\pm q_y^\omega)\} E_y^0, \quad (\text{A14})$$

$$\chi_{yxx}^{2\omega}(E_y^0) = \frac{\rho}{24} \{c_{1111}^{2\omega} + 3c_{1133}^{2\omega} + (2c_{1111}^{2\omega} - 15c_{1133}^{2\omega} + 3c_{3333}^{2\omega})L_2(\pm q) - 3(c_{1111}^{2\omega} - 6c_{1133}^{2\omega} + c_{3333}^{2\omega})L_4(\pm q_x^\omega)\} E_y^0. \quad (\text{A15})$$

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