Molecular Electro-Optics
Part 1. Theory and Methods
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## Chapter 12

# NONLINEAR ELECTRO-OPTICS

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# I. INTRODUCTION

The classical electro-optical effects have been extensively discussed in the chapters of this book by O'Konski, Buckingham, O'Konski and Krause, Stellwagen, Yoshioka, Tinoco and Jennings. The microscopic mechanisms underlying these effects give rise to yet other, nonlinear electro-optical effects. The two principal processes are essentially these:

1. Voigt's distortional process [1]: the molecules, macromolecules, or particles undergo a nonlinear distortion of their electron shells proportional to the square of the applied electric field intensity.
2. Langevin's [2] and Born's [3] statistical-orientational process, due to anisotropy of the polarizability and permanent electric dipole moment interactions with the applied electric field.

In the classical electro-optical effects, the light wave plays the part of a measuring probe, whereas the dc or ac electric field is the agent inducing anisotropy or nonlinearity in the naturally isotropic body. With lasers [4], we have at our disposal continuous and pulsed sources of monochromatic light, coherent in time and space, conveying energy fluxes of immense density in highly parallel beams. The high intensity of these beams permits their use as an agent for modifying the properties of matter, besides their use as measuring agent. Phenomenologically speaking, a quantity $Q$, defining a physical property of the naturally isotropic body, becomes a function of the intensity $I$ of the intense incident light wave:

$$Q = Q(I) \tag{1}$$

The incident beam of intensity $I$ perturbates the initial state of the system and induces a nonlinear variation in the quantity $Q$, and in accordance with the classical perturbation method we write:

$$Q(I) = Q_0 + Q_1 I + Q_2 I^2 + \ldots = \sum_{n=0}^{\infty} Q_n I^n \tag{2}$$

where $Q_0$ is the physical quantity in the absence of the perturbating light beam and the expansion coefficients $Q_1, Q_2, \ldots$ describe the structure and thermodynamical state of the body when modified by the action of the beam.

Very intense light, when traversing an isotropic body, causes a change in its refractive index [5] and electric permittivity [6], i.e., laser light causes an isotropic medium to become optically nonlinear and, at the same time, anisotropic. This has been experimentally established by Mayer and Gires [7] following theoretical suggestions of Buckingham [5] as optical birefringence induced in liquids by a ruby laser beam. This novel effect of optically induced optical birefringence, or optical Kerr effect, has been studied thoroughly in several liquids by Paillette [8] as well as Martin and Lalanne and coworkers [9]; it provides, for example, valuable data on the nonlinear optical polarizability of atoms and molecules [10], molecular correlations [11], and very fast processes [12]. Moreover, intense laser light causes self-induced effects, such as intensity-dependent rotation of the polarization ellipse [13], self-focusing and self-trapping of laser beams [13-15], optical harmonics generation [16], stimulated light scattering [17,18], Rayleigh and Raman harmonic scattering [19,[redacted],20], light intensity-dependent optical rotation [21-23], and various other nonlinear optical effects rendering apparent the statistical properties of the electromagnetic field and matter [24-26].

A new class of nonlinear electro-optical effects is made accessible by applying simultaneously an intense laser beam and a dc or ac electric field. In the first place, laser light reveals the changes in electric permittivity predicted by Piekara and Kielich [6] and observable as optically induced electric anisotropy [27]. Centrosymmetric bodies acted on by a dc or ac electric field generate the second harmonic of laser light, as observed in cubic crystals [28-30], liquids [28-31], and gases [31-33].

By utilizing the optical electric field of laser light and, in addition, electric field in electro-optical investigations, much is to be gained with respect to technique. First, laser technique permits the electrodeless application of a strong electric field to the substance under study, enabling us to achieve complete alignment of macromolecules and particles [34]. This is particularly important in the study of suspensions of conducting particles, and in cases when we want to eliminate perturbating effects like the linear electrophoretic effect, dielectric breakdown, etc., from optical measurements. Obviously, in applying laser techniques to colloid solutions, one has to choose a wavelength of the laser beam for which the substance is transparent. Caution is needed when using very intense laser radiation, which not only causes new nonlinear processes but, upward of some critical power threshold, can destroy the substance [35].

Although nonlinear optical effects have not as yet been studied experimentally to any considerable extent in macromolecular and colloidal substances, we nevertheless intend in this chapter to deal with the essential achievements of this rapidly developing branch of science. In the next few years, it should be possible to develop investigations of the nonlinear electro-optics of molecules and macromolecules, particularly of crystal polymers and liquid crystals.

## II. PHENOMENOLOGICAL DESCRIPTION OF LINEAR AND NONLINEAR PROCESSES

### A. Strong and Weak Electric Fields

Whether the polarization of the medium shall be linear or nonlinear hinges decisively on the ratio of intensities of the externally applied electric field E and internal field F specific to the material. For instance, the average electric field intensity with which the nucleus of a hydrogen atom acts on the electron is of the order of $F_e \approx 10^9$ V/cm. In dense matter, these fields are weaker than in isolated atoms, amounting in crystals to $10^8$ V/cm and, in semiconductors, to $10^7$ V/cm. In liquids, the Onsager reaction field acting on the electric dipole of a molecule is of order $10^7$ V/cm. Hence, internal fields are generally large compared with the electric fields of order $E \approx 10^5$ V/cm which are able to cause linear electric polarization of matter in accordance with Lorentz's theory [36] in which electrons perform harmonic vibrations. Considerable nonlinear polarization can be obtained with static applied fields of $E \approx 10^6$ V/cm and more, but this is not generally feasible with regard to electric breakdown.

The light emitted by conventional sources and low power gas lasers conveys intensities in the range of $I \approx 1$ to $10^2$ W/cm$^2$ and thus electric fields of $E \approx 1$ to $10^2$ V/cm. Fields like these are weak in comparison with the strong internal fields and, if employed as analyzing agent, do not effect the properties of the body investigated. Crystal lasers of high power nowadays provide light beams of intensity $I \approx 10^8$ to $10^{12}$ W/cm$^2$ and electric fields of $E \approx 10^5$ to $10^8$ V/cm comparable to the internal fields and consequently cause nonlinear electric polarization in matter. In an electric field of such intensity, by the classical theory of Voigt [1], the harmonicity and isotropicity of vibrations of the bound electrons undergo an impairment, and we have to deal with anisotropic oscillators performing anharmonic, nonlinear vibrations.

## B. Electric Polarization, and the Electric Permittivity Tensor

For generality, we represent an electric field depending harmonically on the time $t$ and spatial coordinates $\underline{r}$ by writing it in the form of a Fourier series, as follows:

$$\underline{E}(\underline{r},t) = \sum_a \underline{E}(\omega_a,\underline{k}_a) \exp\{i(\underline{k}_a \cdot \underline{r} - \omega_a t)\} \tag{3}$$

where $\omega_a$ is the angular oscillation frequency and $\underline{k}_a$ the wave vector of the ath mode. Summation in (3) extends over all frequencies and wavevectors, both positive and negative, with $\omega_{-a} = -\omega_a$, $\underline{k}_{-a} = -\underline{k}_a$. For the field amplitude one has [redacted] $E^*(\omega_a,\underline{k}_a) = \underline{E}(-\omega_a,-\underline{k}_a) = E_A/2$.

Provided the electric field intensity (3) is not excessive, the electric polarization induced in the medium at the space-time point $(\underline{r},t)$ can be expanded in a power series:

$$\underline{P}(\underline{r},t) = \underline{P}^{(1)}(\underline{r},t) + \underline{P}^{(2)}(\underline{r},t) + \underline{P}^{(3)}(\underline{r},t) + \ldots = \sum_{n=1}^{\infty} P^{(n)}(\underline{r},t) \tag{4}$$

where the polarizations of successive orders depend linearly, quadratically, cubically, etc., on the electric field intensity (3).

A naturally isotropic body has the scalar electric permittivity $\varepsilon$, whereas that of a naturally anisotropic body is a tensor of the second rank $\varepsilon_{ij}$, where the indexes $i$ and $j$ label the permittivity components along the Cartesian axes $x$, $y$, $z$. In matrix notation we have

$$\varepsilon_{ij} = \begin{vmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xz} \\ \varepsilon_{yx} & \varepsilon_{yy} & \varepsilon_{yz} \\ \varepsilon_{zx} & \varepsilon_{zy} & \varepsilon_{zz} \end{vmatrix} \tag{5}$$

with, in general, 9 tensor elements, namely, 3 diagonal and 6 nondiagonal ones. If the tensor is symmetric, $\varepsilon_{ij} = \varepsilon_{ji}$, as is the case in the absence of absorption and optical activity, 6 of the 9 nonzero elements are mutually independent. A further reduction in number of the permittivity tensor elements (5) depends on the symmetry class of the body [37]. In the simplest case of an isotropic body, the 6 nondiagonal elements of the tensor matrix (5) will vanish, and the 3 remaining diagonal ones will be equal to one another, so that we can write:

$$\varepsilon_{ij} = \varepsilon\delta_{ij} \tag{6}$$

$\delta_{ij}$ being the unit Kronecker tensor with elements equaling 1 for $i = j$ and 0 for $i \neq j$.

In the general case, we have the following tensorial relation:

$$(\varepsilon_{ij} - \delta_{ij})E_j(\underline{r},t) = 4\pi P_i(\underline{r},t) \tag{7}$$

between the tensor of electric permittivity, the components of the electric field, and those of the electric polarization induced in the medium. This relation is valid for anisotropic bodies, as well as for isotropic ones subjected to the action of a strong electric field (3) inducing, in general, nonlinear polarization (4), so that induced electric anisotropy is quite generally described by a permittivity tensor $\varepsilon_{ij}$. In Eq. (7) we have applied (and shall henceforth apply) Einstein's summation convention, stating that an index appearing twice (here j) indicates summation over $j = x,y,z$.

## C. Linear Effects

If the electric field acting on the medium is of the form given by Eq. (3), the electric polarization of first order occurring in the expansion (4) can be written as follows:

$$\underline{P}^{(1)}(\underline{r},t) = \sum_a \underline{P}^{(1)}(\omega_a,\underline{k}_a) \exp\{i(\underline{k}_a \cdot \underline{r} - \omega_a t)\} \tag{8}$$

where the polarization $\underline{P}(\omega_a,\underline{k}_a)$ induced at frequency $\omega_a$ is a linear function of the electric field intensity. The ith polarization component on the axes $x,y,z$ is of the general form:

$$P_i^{(1)}(\omega_a,\underline{k}_a) = \chi_{ij}(\omega_a,\underline{k}_a)E_j(\omega_a,\underline{k}_a) \tag{9}$$

Above, the second-rank tensor $\chi_{ij}(\omega_a, \underline{k}_a)$ defines the linear electric susceptibility of the medium. Its dependence on the oscillation frequency $\omega_a$ is referred to as time dispersion or frequency dispersion, whereas its dependence on the wavevector $\underline{k}_a$ is termed spatial dispersion [38].

By Eqs. (7) to (9), we have in a linear approximation:

$$\varepsilon_{ij}(\omega_a, \underline{k}_a) = \delta_{ij} + 4\pi\chi_{ij}(\omega_a, \underline{k}_a) \tag{10}$$

a relation between the electric permittivity and susceptibility tensors.

In Eq. (10) the permittivity tensor, and consequently the refractive index, do not depend on the electric field intensity of the light wave. This obviously results from the linear polarization (9), which causes the solutions of Maxwell's equations to obey, in a first approximation, the superposition principle [cf. Eq. (8)], and states that different waves propagate simultaneously in a medium independently of one another, without distortion. Under the above-stated conditions, all optical phenomena and laws partake of the nature of a first approximation and belong to linear optics [39].

## D. Quadratic Effects

At sufficiently high intensities of the electric field (3) acting on the medium, we have to include higher-order polarizations into our considerations in the expansion (4), in particular, polarization of order 2, of the form:

$$\underline{P}^{(2)}(\underline{r},t) = \sum_{ab} \underline{P}^{(2)}(\omega_a + \omega_b) \exp \{i[(\underline{k}_a + \underline{k}_b) \cdot \underline{r} - (\omega_a + \omega_b)t]\} \tag{11}$$

The nonlinear polarization $\underline{P}^{(2)}(\omega_a + \omega_b)$ induced in the medium at frequency $\omega_a + \omega_b$ is a quadratic function of the field intensity. Its component, in the absence of spatial dispersion, is:

$$P_i^{(2)}(\omega_a + \omega_b) = \chi_{ijk}(\omega_a,\omega_b)E_j(\omega_a)E_k(\omega_b) \tag{12}$$

where the third-rank tensor $\chi_{ijk}(\omega_a,\omega_b)$ defines the nonlinear electric susceptibility of order 2.

In optically inactive media having a center of symmetry, all the tensor elements $\chi_{ijk}$ vanish. Hence, second-order polarization (12) can occur only in bodies not possessing a center of symmetry (e.g., piezoelectric and ferroelectric crystals), in regular crystals, and in isotropic optically active bodies [40]. For the case $\omega_a = \omega_b = \omega$, the nonlinear susceptibility tensor is symmetric with respect to the pair of indexes $j,k$, whence we have $\chi_{ijk} = \chi_{ikj}$, leaving but 18 of the 27 nonzero tensor elements mutually independent [41]. In optically transparent media (in regions remote from electron dispersion and absorption) one has symmetry in all the indexes, and the totally symmetric tensor $\chi_{ijk}$ then presents 10 mutually independent elements. A further reduction in number of the nonzero and independent elements of the symmetric tensor $\chi_{ijk}$ depends solely on the crystallographic symmetry class of the body [41].

On considering the shape of Eq. (11) one notes that the polarization of order 2 defines a first deviation from the superposition principle for waves. In particular, if but a single wave is propagating in the medium, we have:

$$\underline{P}^{(2)}(\underline{r},t) = \underline{2P}^{(2)}(0) + \underline{2P}^{(2)}(2\omega)\cos 2(\omega t - \underline{k}\cdot\underline{r}) \tag{11a}$$

This is a remarkable result showing that a wave of fundamental frequency $\omega$ incident on the medium produces therein, in a second approximation, a polarization which is constant in time

$$P_i^{(2)}(0) = \chi_{ijk}(\omega,-\omega)E_j(\omega)E_k(-\omega) \tag{13}$$

and, moreover, a polarization varying in time at doubled vibration frequency:

$$P_i^{(2)}(2\omega) = \chi_{ijk}(\omega,\omega)E_j(\omega)E_k(\omega) \qquad (14)$$

## 1. Second Harmonic Generation

Franken et al. [42], when observing the propagation in quartz crystal of red light of wavelength $\lambda_\omega = 6943$ Å from a ruby laser, found a new, harmonic radiation component of a frequency double that of the incident wave, in the occurrence ultraviolet light of wavelength $\lambda_{2\omega} = 3472$ Å (Fig. 1). Quartz is a crystal not having a center of symmetry, and owing to the nonlinear polarization (14), a wave of frequency $\omega$ generates therein a wave $2\omega$, referred to as the second optical harmonic. The discovery of second-harmonic generation has played an important role in the study of the nonlinear optical properties of numerous materials [16,24,43,44]. Investigation of second-harmonic generation in reflected light yields information regarding the structure of surface layers [16]. When studied in transmitted light, it permits the elucidation of volume structure in crystalline bodies [44] and of molecular structure in organic crystals [45].

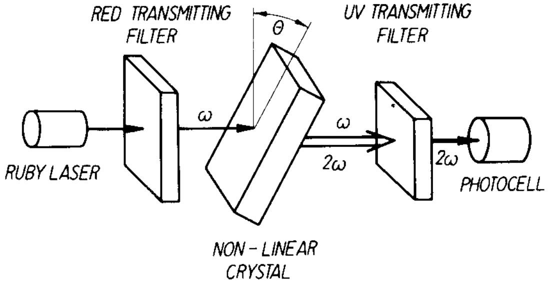

FIG. 1. Arrangement for second-harmonic generation in nonlinear crystals (e.g., quartz) [42]. The path traversed by the beam within the crystal plate is modified by varying the latter's inclination with respect to the propagation direction of the laser beam. The active thickness of the crystal is made to ensure proper phase-matching between the fundamental frequency $\omega$ and second-harmonic $2\omega$ wave. The second-harmonic beam generated in the crystal is observed on transmission through a filter, totally absorbing the fundamental (red) beam, and its intensity is recorded by means of the monochromator and photomultiplier.

Second-harmonic generation requires large single crystals of high optical quality. However, when the growing of large single crystals is difficult or not feasible, the crystal powder method can be used [46]; it is simple and handy, and permits rapid assays of the nonlinear properties of new (polycrystalline, multidomain, etc.) materials. Interesting studies have been performed on second-harmonic generation due to angular fluctuations in $NH_4Cl$ close to the critical point [47,47a] and domains in ferroelectric crystals [47b]. Of late, Bergman et al. [48] reported second-harmonic generation studies in crystalline polar polymers (polyvinylidene fluoride, mylar, etc.) and, recently, anomalously high nonlinear optical effects in m-nitroaniline [49], 5-nitrouracil [49a] and benzene derivatives [49b]. Also, first results on optical second harmonic generation in biological systems have been reported [50].

## 2. Optical Rectification

The time-independent nonlinear polarization (13) accompanying second-harmonic generation has been observed by Bass et al. [51] in ferroelectric KDP ($KH_2PO_4$) crystal. Ward and coworkers [52] made direct absolute measurements of the optical-rectification tensor elements $\chi_{ijk}(\omega,-\omega)$ in KDP, ADP ($NH_4H_2PO_4$), and quartz. The effect is termed optical rectification by analogy to the rectification of ac current and radiofrequency electromagnetic fields so highly important to electro- and radiotechniques. By using a light beam of high intensity one can polarize electrically a body without center of symmetry.

## 3. Linear Electro-Optical Effect

On putting $\omega_a = \omega$, $\underline{k}_a = \underline{k}$, and $\omega_b = \underline{k}_b = 0$ in Eqs. (11) and (12), one obtains

$$P_i^{(2)}(\omega) = \chi_{ijk}(\omega,0)E_j(\omega)E_k(0) \tag{15}$$

This polarization defines the electro-optical processes referred to as the Pockels effect [37].

On inserting into Eq. (7) the polarizations (9) and (15), one obtains the following change in electric permittivity tensor due to a dc electric field:

$$\Delta\varepsilon_{ij}^{\omega}(E) = 4\pi\chi_{ijk}(\omega,0)E_k(0) \tag{16}$$

Pockels' effect given by Eq. (16) is observable in crystals without a center of symmetry and in optically active bodies as linear electro-optical rotation. In recent years, the study of the electro-optical properties of materials has gained in significance with regard to the production of coherent light harmonics, the modulation of laser beams, parametric processes, and so forth [53]. Lately, Di Domenico and Wemple [54] developed a microscopic theory of the electro-optical properties of ferroelectrics of the oxygen octahedron type. This has also been done for molecular crystals and hexagonal semiconductors [55].

## E. Cubic Effects

In bodies possessing a center of symmetry, in the absence of natural optical and magnetic activity, no second-order polarization (11) occurs in the electric dipole approximation (12). Bodies of this kind exhibit in the expansion (4), besides the linear polarization (8), an electric polarization of order 3 which we write as follows:

$$\underline{P}^{(3)}(\underline{r},t) = \sum_{abc} \underline{P}^{(3)}(\omega_a + \omega_b + \omega_c)$$
$$\exp\{i[(\underline{k}_a + \underline{k}_b + \underline{k}_c)\cdot\underline{r} - (\omega_a + \omega_b + \omega_c)t]\} \tag{17}$$

This nonlinear polarization $P^{(3)}(\omega_a + \omega_b + \omega_c)$ induced in an isotropic medium at frequency $\omega_a + \omega_b + \omega_c$ is a cubic function of the electric field intensity, and can be written explicitly as follows in the absence of spatial dispersion:

$$P_i^{(3)}(\omega_a + \omega_b + \omega_c) = \chi_{ijkl}(\omega_a,\omega_b,\omega_c)E_j(\omega_a)E_k(\omega_b)E_l(\omega_c) \tag{18}$$

The fourth-rank tensor $\chi_{ijkl}$ defining nonlinear third-order susceptibility has nonzero elements in all bodies, including isotropic ones, thus gases and liquids. In the general case $\chi_{ijkl}$ has 81 nonzero tensor elements. Any accretion of symmetry conditions reduces their number for the various crystallographical classes [24,41]. In the regular system and in isotropic bodies, $\chi_{ijkl}$ has 21 nonzero elements, only 3 of which are mutually independent [56]:

$$\chi_{ijkl} = \chi_{xxyy}\delta_{ij}\delta_{kl} + \chi_{xyxy}\delta_{ik}\delta_{jl} + \chi_{yxxy}\delta_{il}\delta_{kj} \tag{19}$$

with the relation [41]:

$$\chi_{xxxx} = \chi_{yyyy} = \chi_{zzzz} = \chi_{xxyy} + \chi_{xyxy} + \chi_{yxxy} \tag{19a}$$

## 1. Tripling of Oscillation Frequency

Equation (17) defines a new deviation from the superposition principle, and Eq. (18) expresses the interaction of three waves in a cubic medium leading to the emergence of a fourth wave of frequency $\omega_a + \omega_b + \omega_c$. In particular, if a single wave $\omega_a = \omega_b = \omega_c = \omega$ is incident on such a medium, Eq. (18) yields:

$$P^{(3)}(\underline{r},t) = 3P^{(3)}(\omega)\cos(\omega t - \underline{k}\cdot\underline{r}) + P^{(3)}(3\omega)\cos 3(\omega t - \underline{k}\cdot\underline{r}) \tag{20}$$

We thus note that, under the influence of a wave of fundamental frequency $\omega$, two waves of nonlinear polarization arise in the cubic medium, one of them at the frequency:

$$P_i^{(3)}(\omega) = \chi_{ijkl}(\omega,\omega,-\omega)E_j(\omega)E_k(\omega)E_l(-\omega) \tag{20a}$$

and the other at the tripled frequency

$$P_i^{(3)}(3\omega) = \chi_{ijkl}(\omega,\omega,\omega)E_j(\omega)E_k(\omega)E_l(\omega) \qquad (20b)$$

Terhune and his coworkers [28,57] were the first to attempt the production of a ultraviolet third harmonic of wavelength $\lambda_{3\omega} = 2313$ Å using a ruby laser, in calcite as well as in dielectric liquids. Bey et al. [58] provided the earliest experimental evidence that phase matching can be achieved in harmonic processes by the introduction of anomalous dispersion into a normally unmatched medium; they obtained phase-matched third-harmonic generation at 3530 Å of the neodymium laser line at 10,600 Å by the addition of dye molecules to a liquid medium (fuchsin red dye in solution in hexafluoroacetone sesquihydrate). These experiments were extended by Chang and Galbraith [59] to other solvents of different index mismatch and to another dye, methylene blue.

Goldberg and Schnur [60] investigated harmonics generation in liquid crystals, in particular, cholesteryl nonanoate (CN), and other cholesteric and nematic systems. The solid phase of CN exhibited a high second-harmonic intensity (of the same order as in quartz crystal powder), which, on heating, fell steeply by 4 orders of magnitude near 79°C on transition from solid to cholesteric phase. In the inverse process of slow cooling from the isotropic liquid phase through the cholesteric and smectic mesophases, a clear second-harmonic signal was observed only at the point of recrystallization to the solid. Third-harmonic generation was apparent from all three phases both at heating and cooling, its intensity in the solid being 100 times stronger than in the liquid phase. Similar results have been obtained in other liquid crystals [61]; in no case did they yield a second-harmonic when in mesomorphic phases, which have to be regarded as centrosymmetric. Recently, Rentzepis and coworkers [62] reported an efficiency for third-harmonic conversion in pure organic liquids 100 times larger than in fused silica. The above-cited studies prove that some role in the process of harmonics generation is played by the molecular correlations so highly relevant to multiharmonic light scattering and optical birefringence in isotropic media [11,63].

Ward and New [64] observed third-harmonic generation at 2314 A in simple gases (He, Ne, Ar, etc.), using a focused ruby laser beam. A technique for the efficient production of ultraviolet radiation by third-harmonic generation in phase-matched metal vapors was proposed by Harris et al. [65]. Also, the conditions for frequency tripling in infrared by anharmonic molecular vibrations have been analyzed [66].

## 2. Direct-Current Field-Induced Second Optical Harmonic

With $\omega_a = \omega_b = \omega$ and $\omega_c = 0$ in Eq. (18), the third-order polarization at frequency $2\omega$,

$$P_i^{(3)}(2\omega) = \chi_{ijkl}(\omega,\omega,0)E_j(\omega)E_k(\omega)E_l(0) \tag{21}$$

describes the generation of the second harmonic of light by a centrosymmetric body immersed in a dc electric field $E(0)$.

The process of second-harmonic generation by electrically polarized bodies was first observed by Terhune et al. [28] in calcite crystal, which has a center of symmetry and belongs to the crystallographical class $3m(D_{3d})$. Their experiment, repeated by Bjorkholm and Siegman [29] with accurate CW measurements (optimally focused beams from a He-Ne laser operating at 6328 Å), revealed, moreover, some slight second-harmonic generation in the absence of a dc electric field due to induced electric-quadrupole and magnetic-dipole polarization [67]. Since the second-harmonic intensity $I(2\omega)$ is proportional to the square of the polarization (21), it should be expected to depend on the square of the laser beam intensity $I$ and the square of the dc field intensity $E(0)$.

Mayer et al. [32] studied dc electric field-induced second-harmonic generation in dipolar and quadrupolar gases, whereas Fin and Ward [33] used inert gases.

In isotropic bodies, the tensor of third-order nonlinear susceptibility is of the form (19), whence the polarization (21) takes the form:

$$P_i^{(3)}(2\omega) = \chi_1^{2\omega} E_i(\omega) E_j(\omega) E_j(0) + \chi_2^{2\omega} E_j(\omega) E_j(\omega) E_i(0) \qquad (21a)$$

where we have introduced the notation:

$$\chi_1^{2\omega} = \chi_{xxyy}(\omega,\omega,0) + \chi_{xyxy}(\omega,\omega,0)$$

$$\chi_2^{2\omega} = \chi_{yxxy}(\omega,\omega,0) \qquad (21b)$$

and

$$\chi_3^{2\omega} = \chi_{yyyy}(\omega,\omega,0) = \chi_1^{2\omega} + \chi_2^{2\omega}$$

Now let us assume the laser beam to propagate along the laboratory $z$ axis perpendicularly to the dc electric field $E(0)$, applied along the $y$ axis. Equation (21a) now yields the following two mutually perpendicular polarization components at $2\omega$:

$$\begin{aligned} P_x^{(3)}(2\omega) &= \chi_1^{2\omega} E_x(\omega) E_y(\omega) E_y(0) \\ P_y^{(3)}(2\omega) &= \{\chi_2^{2\omega} E_x^2(\omega) + \chi_3^{2\omega} E_y^2(\omega)\} E_y(0) \end{aligned} \qquad (21c)$$

The above equations enabled Mayer [32] to determine experimentally the nonlinear susceptibility coefficients (21b). Namely, if the incident light beam is linearly polarized, the coefficient $\chi_3^{2\omega}$ can be determined for its oscillations parallel to the dc field direction, $E(\omega) \parallel E_y(0)$, whereas at oscillations perpendicular to the field, $E(\omega) \perp E_y(0)$, one determines $\chi_2^{2\omega}$. When applying circularly polarized light, measurement of the component $P_x^{(3)}(2\omega)$ permits the determination of the coefficient $\chi_1^{2\omega}$, whereas measurement of $P_y^{(3)}(2\omega)$ yields the value of $\left|\chi_2^{2\omega} + \chi_3^{2\omega}\right|$.

In the absence of optical dispersion, the tensor (19) can be dealt with as being totally symmetric, and one has [68]:

$$\chi^{2\omega}_{xxyy} = \chi^{2\omega}_{xyxy} = \chi^{2\omega}_{yxxy} = \frac{1}{3}\chi^{2\omega}_{yyyy} \qquad (21d)$$

leading to Bloembergen's symmetry relations [31]:

$$\chi^{2\omega}_{1} + \chi^{2\omega}_{2} = \chi^{2\omega}_{3}$$

$$\chi^{2\omega}_{1}:\chi^{2\omega}_{2}:\chi^{2\omega}_{3} = 2:1:3 \qquad (22)$$

## 3. Light-Induced Birefringence Phenomena

We shall now consider the case when a wave of frequency $\omega_A = \omega_a$ plays the part of the analyzing agent and another wave of frequency $\omega_I = \omega_b = -\omega_c$, is the agent inducing in the medium an anisotropy of the form:

$$\Delta\varepsilon_{ij}(\omega_A) = 4\pi\chi_{ijkl}(\omega_A,\omega_I,-\omega_I)E_k(\omega_I)E_l(-\omega_I) \qquad (23)$$

resulting by Eqs. (7) and (18).

The change in electric permittivity tensor (23), induced by the strong electric field $E(\omega_I)$ and analyzed by means of the field of frequency $\omega_A$, can with regard to (19) be written as follows for the case of an isotropic body:

$$\begin{aligned}\Delta\varepsilon_{ij}(\omega_A) = 4\pi\{&\chi_{xxyy}(\omega_A,\omega_I,-\omega_I)\delta_{ij}E_k(\omega_I)E_k(-\omega_I)\\ &+ \chi_{xyxy}(\omega_A,\omega_I,-\omega_I)E_i(\omega_I)E_j(-\omega_I)\\ &+ \chi_{yxxy}(\omega_A,\omega_I,-\omega_I)E_i(-\omega_I)E_j(\omega_I)\end{aligned} \qquad (24)$$

Let the analyzing light beam propagate along z. Eq. (24) now yields for the difference of diagonal elements of the permittivity tensor:

$$\begin{aligned}\Delta\varepsilon_{xx}(\omega_A) - \Delta\varepsilon_{yy}(\omega_A) = 4\pi\{&\chi_{xyxy}(\omega_A,\omega_I,-\omega_I)\\ + \chi_{yxxy}(\omega_A,\omega_I,-\omega_I)\}\{&E_x(\omega_I)E_x(-\omega_I) - E_y(\omega_I)E_y(-\omega_I)\}\end{aligned} \qquad (24a)$$

This expression describes the birefringence induced optically in an isotropic medium, i.e., the optical Kerr effect discovered by Mayer and Gires [7] and at present studied in numerous molecular liquids [8,9,69] (Fig. 2). Obviously, putting the inducing field frequency equal to zero ($\omega_I = 0$), Eq. (24a) defines the classical Kerr effect due to a dc electric field.

For molecular substances in the gas state, in the absence of dispersion and absorption, the nonlinear optical birefringence susceptibilities (24a) are given as follows [5,6]:

$$\chi_{xyxy}(\omega_A,\omega_I,-\omega_I) = \chi_{yxxy}(\omega_A,\omega_I,-\omega_I)$$

$$= \frac{\rho}{90}\left\{3c_{ijij}^{\omega_A,\omega_I} - c_{iijj}^{\omega_A,\omega_I} + \frac{1}{kT}\left(3a_{ij}^{\omega_A}a_{ij}^{\omega_I} - a_{ii}^{\omega_A}a_{jj}^{\omega_I}\right)\right\} \qquad (24b)$$

where $\rho = N/V$ is the number density of molecules.

The first, not directly temperature-dependent term of (24b) accounts for Voigt's effect [1,39], which consists in nonlinear distortion of the atom or molecule defined by the hyperpolarizability tensor $c_{ijkl}^{\omega_A,\omega_I}$ at frequency $\omega_A$ and $\omega_I$. The other, directly temperature-dependent term, results from Langevin's [2] reorientation of molecules in the optical field [5]. The tensors $a_{ij}^{\omega_A}$ and $a_{ij}^{\omega_I}$ describe linear polarizabilities at the frequency $\omega_A$ and $\omega_I$, respectively.

In liquid systems, optically induced birefringence depends on the angular molecular correlations [11,70], spatial molecular redistribution [71,72], and other molecular-statistical processes [73,74]. Theories of optical Kerr effect dispersion exist in the quantum mechanical [75], quantum field theoretical [76], and classical [77] approaches. In recent years, the optical Kerr effect has found applications in the technique of ultrashort laser pulses [78].

The general formula (24) moreover permits the calculation of differences between the nondiagonal elements of the permittivity tensor:

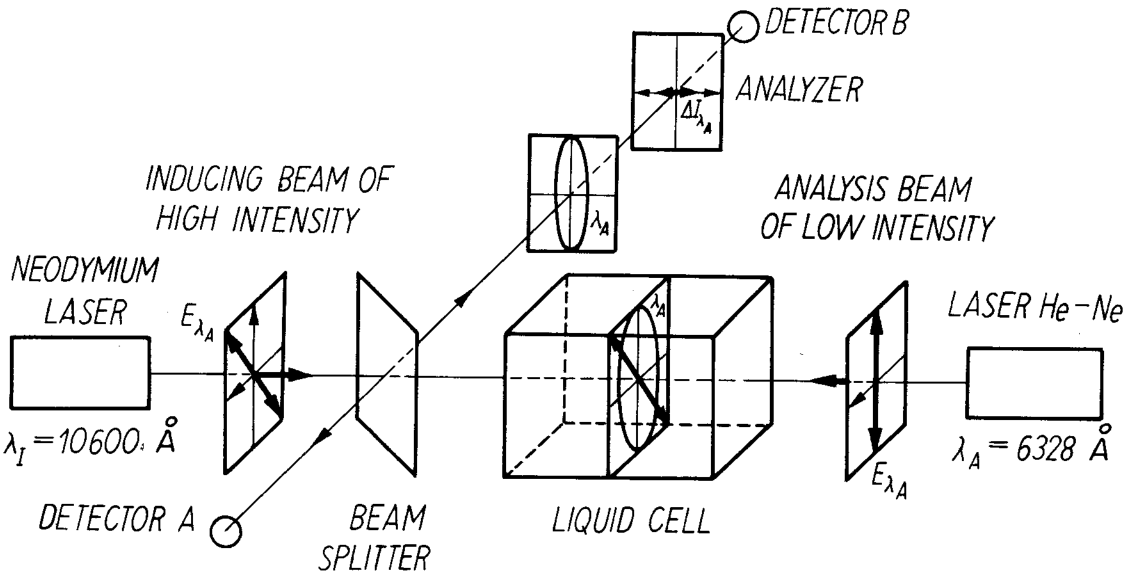

FIG. 2. Principle of optically induced birefringence experiment [8,9]. The liquid, irradiated with the intense plane-polarized wave $\lambda_I$, behaves like a uniaxial crystal with optical axis parallel to the electric vector $E(\lambda_I)$. The linearly and vertically polarized analyzing wave $\lambda_A$ of low intensity becomes elliptical. The two laser beams, i.e., the one inducing the nonlinearity and the analyzing one, are polarized at $45^0$ to one another and propagate in opposite directions. An analyzer whose plane of polarization is perpendicular to that of the initial polarizer (that is to say, horizontally), permits the measurement of this ellipticity. In the absence of an intense wave, no signal appears on the detector B because the analyzer and polarizer are at right angles. During propagation of the intense wave, the component $\Delta I(\lambda_A)$ of the analyzed wave is detected at B. The intensity of the strong inducing beam is measured with the detector A.

$$\Delta\varepsilon_{xy}(\omega_A) - \Delta\varepsilon_{yx}(\omega_A) = 4\pi\{\chi_{xyxy}(\omega_A,\omega_I,-\omega_I) - \chi_{yxxy}(\omega_A,\omega_I,-\omega_I)\}\{E_x(\omega_I)E_y(-\omega_I) - E_y(\omega_I)E_x(-\omega_I)\} \tag{24c}$$

The above circular birefringence is induced in isotropic media by circularly and elliptically polarized light [79].

For a slowly varying analyzing electric field $\omega_A << \omega_I$, Eqs. (23) and (24) define the change in electric permittivity due to intense light [6], whereas Eq. (24a) defines laser light-induced electric anisotropy in liquids [27,34].

## 4. Self-Induced Optical Birefringence

Consider the case when a single, intense laser beam $(\omega_a = \omega_b = -\omega_c = \omega)$ is incident on an isotropic medium. Equations (18) and (19) now yield the following, mutually perpendicular polarization components (perpendicular to the propagation direction z):

$$\begin{aligned} P_x^{(3)}(\omega) &= \chi_{xxxx}(\omega,\omega,-\omega)E_x(\omega)\{E_x(\omega)E_x(-\omega) + E_y(\omega)E_y(-\omega)\} \\ &\quad + \chi_{yxxy}(\omega,\omega,-\omega)E_y(\omega)\{E_y(\omega)E_x(-\omega) + E_x(\omega)E_y(-\omega)\} \\ P_y^{(3)}(\omega) &= \chi_{yyyy}(\omega,\omega,-\omega)E_y(\omega)\{E_x(\omega)E_x(-\omega) + E_y(\omega)E_y(-\omega)\} \\ &\quad + \chi_{yxxy}(\omega,\omega,-\omega)E_x(\omega)\{E_x(\omega)E_y(-\omega) - E_y(\omega)E_x(-\omega)\} \end{aligned} \tag{25}$$

whence we derive for the difference in diagonal elements of the permittivity tensor at frequency $\omega$:

$$\Delta\varepsilon_{xx}(\omega) - \Delta\varepsilon_{yy}(\omega) = 4\pi\chi_{yxxy}(\omega,\omega,-\omega)\{E_x(\omega)E_x(-\omega) - E_y(\omega)E_y(-\omega)\} \tag{25a}$$

This expression defines the optical birefringence self-induced by a linearly polarized laser beam [5,8].

Quite similarly, one obtains from (25) the following difference between nondiagonal electric permittivity tensor elements:

$$\Delta\varepsilon_{xy}(\omega) - \Delta\varepsilon_{yx}(\omega) = 8\pi\chi_{yxxy}(\omega,\omega,-\omega)\{E_y(\omega)E_x(-\omega) - E_x(\omega)E_y(-\omega)\} \tag{25b}$$

describing the self-induced rotation of the polarization ellipse detected by Maker et al. [80] when using intense elliptically polarized laser light.

## III. GENERATION OF SECOND-HARMONIC LASER LIGHT BY ELECTRICALLY POLARIZED ISOTROPIC MEDIA

When a naturally isotropic body is placed in a dc or ac electric field, its symmetry undergoes a deterioration and it becomes axially symmetric, with macroscopic symmetry of the type $C_{\infty V}$. The conditions existing in an isotropic medium with electrically destroyed center of symmetry favor second-harmonic generation of the electric dipole kind. The absence of a center of symmetry is a condition necessary, though not in all cases sufficient, for second-harmonic generation. Above, we have given a discussion of second-harmonic generation by electrically polarized bodies in a phenomenological approach. We now proceed to a detailed discussion of this new electro-optical effect in a statistical-molecular approach, with the aim of rendering apparent the microscopic mechanisms underlying it.

### A. Statistical-Molecular Theory

Consider a volume $V$, containing $N$-like dipolar molecules whose optical and electric properties remain unaffected by short-range interaction. As long as the number density $\rho = N/V$ is not excessively large, the second-order nonlinear susceptibility of the system in the presence of a dc electric field $E$ can be written in the statistical-molecular form [56]:

$$\chi_{ijk}^{2\omega}(E) = \frac{\rho}{4}\int\left(b_{ijk}^{2\omega} + c_{ijkl}^{2\omega}E_l + \dots\right)f(\Omega,E)d\Omega \tag{26}$$

where the integral extends over all possible molecular orientation $\Omega$ in the elementary body angle $d\Omega$. The third-rank tensor $b_{ijk}^{2\omega} = b_{ijk}(\omega,\omega)$ defines the molecular nonlinear polarizability of order 2 at frequency $2\omega$, whereas the fourth-rank tensor $c_{ijkl}^{2\omega} = c_{ijkl}(\omega,\omega,0)$ defines the molecular nonlinear polarizability of order 3.

The statistical distribution function $f(\Omega,E)$ describing the orientation of the dipolar molecules with respect to the direction of the field $E(0)$ is given by classical Maxwell-Boltzmann statistics, to a linear approximation in $E$, as:

$$f(\Omega,E) = f(\Omega,0)\left(1 + \frac{1}{kT}m_iE_i\right) \tag{27}$$

where $m_i$ is the ith component of the permanent dipole moment of a molecule.

By inserting (27) into (26) and averaging over all possible orientations of molecules with respect to the laboratory axes x,y,z we obtain [56]:

$$\chi_{ijk}^{2\omega}(E) = \chi_{xxyy}^{2\omega}\delta_{ij}E_k + \chi_{xyxy}^{2\omega}\delta_{ik}E_j + \chi_{yxxy}^{2\omega}\delta_{jk}E_i \tag{28}$$

with electric susceptibility coefficients $\chi_{xxyy}^{2\omega},\dots$ given, respectively, by the molecular parameters $m_i$, $b_{ijk}^{2\omega}$, and $c_{ijkl}^{2\omega}$. In the absence of optical dispersion, these tensors are totally symmetric and the relation (21d) holds, whence:

$$\chi_{yyyy}^{2\omega} = \frac{\rho}{20}\left(c_{iijj}^{2\omega} + \frac{1}{kT}b_{iij}^{2\omega}m_j\right) \tag{29}$$

Thus, in the microscopic approach, the phenomenological nonlinear susceptibilities of dipolar substances are found to consist of two terms: (a) one not directly dependent on temperature due to a purely distortional process residing in nonlinear polarization of the electron shell occurring for all molecular symmetries, since $c_{ijkl}^{2\omega}$ has nonzero elements even in the case of atoms (Voigt effect), and (b) a directly temperature-dependent term in accordance with Langevin's theory related with the statistical process of reorientation of the molecular dipoles in the dc field and Born's nonlinear distortional process [3] described by tensor $b^{2\omega}_{ijk}$. Recently, Hameka [81] developed a quantum-mechanical theory of field-induced SHG in gases.

## B. Semimacroscopic Theory

Results valid for isotropic bodies of arbitrary structure and degree of condensation are conveniently obtained by using Kirkwood's [82] semimacroscopic dielectric theory extended to nonlinear phenomena [83]. Semimacroscopically, we consider a spherical sample of macroscopic size, volume $V$, and dielectric permittivity $\varepsilon$, in a continuous isotropic medium of electric permittivity $\varepsilon_e$. In general, the mean macroscopic electric field $E_M$ existing within the sample differs from the external field $E$; if $E$ is weak, $E_M$ is given by the formula well-known from electrostatics:

$$\underline{E}_M = \frac{3\varepsilon_e}{\varepsilon + 2\varepsilon_e}\underline{E} \tag{30}$$

Similar relations hold for fields oscillating at frequency $\omega$ or $2\omega$.

Semimacroscopic theory [31] in linear approximation leads back to Eq. (28); however, in the absence of optical dispersion, we have instead of (29):

$$\chi^{2\omega}_{yyyy} = \frac{L^{2\omega}}{20V} \langle C^{2\omega}_{iijj} + \frac{1}{kT} B^{2\omega}_{iij} M_j \rangle \tag{31}$$

the symbol $\langle\ \rangle$ denoting appropriate statistical averaging with molecular correlations. The tensors of (31) written in capital roman letters now refer to the whole volume $V$ of the sample; $\underline{M}$ is its total electric dipole moment, and $B^{2\omega}_{ijk}$, $C^{2\omega}_{ijkl}$ are tensors of its nonlinear polarizabilities at $2\omega$. The macroscopic parameter $L^{2\omega}$ is of the form:

$$L^{2\omega} = \left(\frac{\varepsilon_{2\omega} + 2\varepsilon_e}{3\varepsilon_e}\right)\left(\frac{\varepsilon_\omega + 2\varepsilon_e}{3\varepsilon_e}\right)^2\left(\frac{\varepsilon_0 + 2\varepsilon_e}{3\varepsilon_e}\right) \tag{32}$$

## 1. Dipolar Liquids

With $N$ dipolar molecules per volume $V$ of the liquid, one has:

$$M_i = \sum_{s=1}^{N} m_i^{(s)}, \quad B_{ijk}^{2\omega} = \sum_{s=1}^{N} b_{ijk}^{2\omega(s)}, \quad C_{ijkl}^{2\omega} = \sum_{s=1}^{N} c_{ijkl}^{2\omega(s)} \tag{33}$$

the tensors $m_i^{(s)}$, $b_{ijk}^{2\omega(s)}$, and $c_{ijkl}^{2\omega(s)}$ referring to the sth molecule, immersed in the medium.

By (32), the nonlinear susceptibility (31) can be written in molecular-statistical form as:

$$\chi_{yyyy}^{2\omega} = \frac{L^{2\omega}}{20V} \left< \sum_{s=1}^{N} c_{iijj}^{2\omega(s)} + \frac{1}{kT} \sum_{s=1}^{N} \sum_{t=1}^{N} b_{iij}^{2\omega(s)} m_j^{(t)} \right> \tag{34}$$

In particular, for molecules symmetric about their dipole moment, we thus obtain, as a satisfactory approximation:

$$\chi_{yyyy}^{2\omega} = \frac{\rho}{4} L^{2\omega} \left(c^{2\omega} + \frac{3mb^{2\omega}}{5kT} K\right) \tag{34a}$$

where by

$$c^{2\omega} = \frac{c_{iijj}^{2\omega}}{5} = \frac{c_{3333}^{2\omega} + 2c_{1122}^{2\omega} + 4c_{1133}^{2\omega} + 2c_{1111}^{2\omega}}{5} \tag{35}$$

we have denoted the mean nonlinear polarizability of order 3, and by

$$b^{2\omega} = \frac{b_{ii3}^{2\omega}}{3} = \frac{b_{333}^{2\omega} + 2b_{113}^{2\omega}}{3} \tag{36}$$

the mean nonlinear polarizability of order 2, whereas

$$K = 1 + \rho \int \cos \theta_{st} g(\tau_{st}) d\tau_{st} \tag{37}$$

defines Kirkwood's angular correlation parameter [82], $\theta_{st}$ being the angle between the electric dipoles of molecules s and t at mutual configuration $\tau_{st}$ statistically interdependent by way of the pair correlation function $g(\tau_{st})$.

Comparing Eqs. (34) and (34a), on the one hand, and (29), on the other, we note that in dipolar liquids the temperature-dependent term undergoes a modification by the Kirkwood correlation parameter (37), which is larger or less than 1 according to the mutual configuration of the dipoles (e.g., nearly parallel, nearly antiparallel, of perpendicular configuration).

## 2. Nondipolar Liquids

Here, the temperature-dependent term of Eqs. (29) and (34) vanishes. A result like this, however, can hold only as long as one neglects the existence, in liquids, of intense molecular fields $\underline{F}$, which are in fact very strong in comparison with the currently applied external fields. In regions of short-range ordering, the molecular field $\underline{F}$ fluctuates in time and space, inducing dipole and higher moments in neighboring molecules, thus impairing the symmetry of the molecules themselves and of their neighborhood. Hence we can write, for centrosymmetric molecules, in place of (33):

$$M_i = \sum_{s=1}^{N} \left\{ a_{ij}^{(s)} F_j^{(s)} + \frac{1}{2} b_{ijk}^{(s)} F_j^{(s)} F_k^{(s)} + \cdots \right\}$$

$$B_{ijk}^{2\omega} = \sum_{s=1}^{N} \left\{ c_{ijkl}^{2\omega(s)} F_l^{(s)} + \cdots \right\} \tag{38}$$

where $a_{ij}^{(s)}$ is the linear electric polarizability tensor of the molecule.

On inserting the expansion (38) into the general equation (31) and neglecting, for simplicity, the anisotropies in tensors

$a_{ij}$ and $c_{ijkl}$, we have:

$$\chi^{2\omega}_{yyyy} = \frac{\rho}{4} c^{2\omega} L^{2\omega} \left( 1 + \frac{a}{kT} \langle F^2 \rangle \right) \tag{39}$$

where

$$a = \frac{a_{ii}}{3} = \frac{a_{11} + a_{22} + a_{33}}{3}$$

stands for the mean linear polarizability and $\langle F^2 \rangle$ for the mean statistical value of the square of the electric molecular field which, generally, is nonzero for nondipolar liquids.

In the case of axially symmetric molecules having a permanent electric quadrupole moment $\Theta$ (e.g., the molecules $CO_2$ and $C_6H_6$) we have [63]:

$$\langle F^2 \rangle = \Theta^2 \langle r^{-8} \rangle \tag{40}$$

where the mean statistical value $\langle r^{-8} \rangle$ is given at $n = 8$ by the definition [84]:

$$\langle r^{-n} \rangle = 4\pi\rho \int r_{st}^{-n+2} g(r_{st}) dr_{st} \tag{41}$$

with $g(r_{st})$ denoting the radial distribution function of a pair of molecules $s,t$ mutually distant by $r_{st}$.

Since the molecular fields produced by various electric multipoles are well known [85], formula (39) can be applied to other molecular symmetries, too. In particular, for tetrahedrally symmetric molecules ($CH_4$, $CCl_4$, etc.) whose lowest nonzero moment is the octupole $\Omega_{123}$, one has [63]:

$$\langle F^2 \rangle = \frac{16}{5} \Omega^2_{123} \langle r^{-10} \rangle \tag{40a}$$

Mean statistical values (41) can be computed numerically for real gases using the Lennard-Jones potential, as well as for liquids resorting to the simple Kirkwood model [86] of rigid spheres of diameter $d$ and volume $V = \pi d^3/6$, leading to the simple result [84]

$$\langle r^{-n} \rangle = \frac{4\pi\rho}{n - 3} \left(\frac{\pi}{6V}\right)^{(n-3)/3} \quad ; \quad n \geq 4 \tag{41a}$$

One thus finds that in conformity with Eq. (39), nondipolar liquids too present a temperature-dependent term of the nonlinear electric susceptibility as a result of reorientation of the electric dipoles which are induced in molecules by the fluctuating electric fields of their nearest neighbors in the liquid.

### C. Strong Electric Reorientation of Macromolecules

The theories presented in Secs. IIIA, B hold for molecular substances, where the reorientation due to a dc electric field is relatively weak, as given by the distribution function (27). In substances consisting of macromolecules and colloid particles strong reorientation is achieved quite easily. On the assumption of axial symmetry, the distribution function takes the form [87, 88]:

$$f(\theta, E_y) = \frac{\exp\,(p \cos\theta \pm q \cos^2\theta)}{\int \exp\,(p \cos\theta \pm q \cos^2\theta)\,d\Omega} \tag{42}$$

where $\theta$ is the angle subtended by the symmetry axis of a macromolecule and the field direction $E_y$, and $d\Omega = \sin\theta\, d\,\theta\, d\phi$. In the Boltzmann factor,

$$p = \frac{mE_y}{kT} \tag{42a}$$

is the dimensionless Langevin-Debye reorientation parameter for permanent electric dipoles, and

$$q = \frac{|a_{33} - a_{11}|}{2kT} E_y^2 \tag{42b}$$

the Langevin parameter of electric dipoles induced in macromolecules having the polarizabilities $a_{33}$ and $a_{11}$, respectively, along and perpendicular to their symmetry axis (see Chap. 3).

In the function (42), the sign "+" is for prolate macromolecules having positive anisotropy, $a_{33} - a_{11} < 0$, e.g., $CS_2$, whereas the lower sign "-" refers to disk-shaped ones, of negative anisotropy $a_{33} - a_{11} < 0$, e.g., $C_6H_6$.

Once the distribution function (42) is known explicitly, we are in a position to calculate the nonlinear susceptibility (26) for strong reorientation of macromolecules or of axially symmetric molecules of the point groups $C_{3V}$; e.g., $NH_3$, $CH_3Cl$, $CH_3I$, and $C_{4V}$; $BrF_5$ and $C_{\infty V}$; HCN, $N_2O$.

If the isotropic medium is placed in a strong electric field, the polarization induced by laser light at frequency $2\omega$ is no longer a linear function of the field $E(0)$, as stated by Eq. (21), but takes the form of some nonlinear function; we express this generally by writing:

$$P_i^{2\omega}(E) = \chi_{ijk}^{2\omega}(E)E_j(\omega)E_k(\omega) \tag{43}$$

or, for light propagation along $z$ and a dc field applied along $y$:

$$\begin{aligned} P_x^{2\omega}(E_y) &= 2\chi_{xxy}^{2\omega}(E_y)E_x(\omega)E_y(\omega) \\ P_y^{2\omega}(E_y) &= \chi_{yxx}^{2\omega}(E_y)E_x^2(\omega) + \chi_{yyy}^{2\omega}(E_y)E_y^2(\omega) \end{aligned} \tag{44}$$

with, in the absence of dispersion, $\chi_{xxy}^{2\omega}(E_y) = \chi_{yxx}^{2\omega}(E_y)$.

Let us assume the dc field to cause only a reorientation of the microsystems given by the distribution function (42), with no contribution from the distortional effect defined by the second term $c_{ijkl}^{2\omega}E_l$ of the expansion (26); on the same assumptions as before, we get:

$$\begin{aligned} \chi_{xxy}^{2\omega}(E_y) &= \frac{\rho}{8}\left\{\left(b_{333}^{2\omega} - b_{113}^{2\omega}\right)L_1\left(p,\pm q\right) - \left(b_{333}^{2\omega} - 3b_{113}^{2\omega}\right)L_3\left(p,\pm q\right)\right\} \\ \chi_{yyy}^{2\omega}(E_y) &= \frac{\rho}{4}\left\{3b_{113}^{2\omega}L_1\left(p,\pm q\right) + \left(b_{333}^{2\omega} - 3b_{113}^{2\omega}\right)L_3\left(p,\pm q\right)\right\} \end{aligned} \tag{45}$$

involving the generalized Langevin functions of odd order $L_1(p,\pm q)$ and $L_3(p,\pm q)$, defined analytically in Ref. [88] and plotted in Figs. 3 and 4 vs. $p$ for some values of $q = p^2/n$, for $n = 1, 4, 9, 16, 25, 36, \ldots$ .

In the case of prolate (positively-anisotropic) microsystems the permanent dipoles as well as the induced ones tend concordantly to orient themselves into the electric field direction $\underline{E}$, so that with growing field intensity and parameter $q$ the functions $L_1(p,+q)$ and $L_3(p,+q)$ tend very steeply from 0 to the limiting value 1, which defines the state of complete electric saturation of orientation of the mocrosystems (dashed curves in Figs. 3 and 4).

For negatively anisotropic microsystems, the picture is entirely different. If the permanent dipole $\underline{m}$ lies along the symmetry axis, the polarizability $a_{33}$ parallel to the latter is less than the polarizability $a_{11}$ perpendicular thereto.

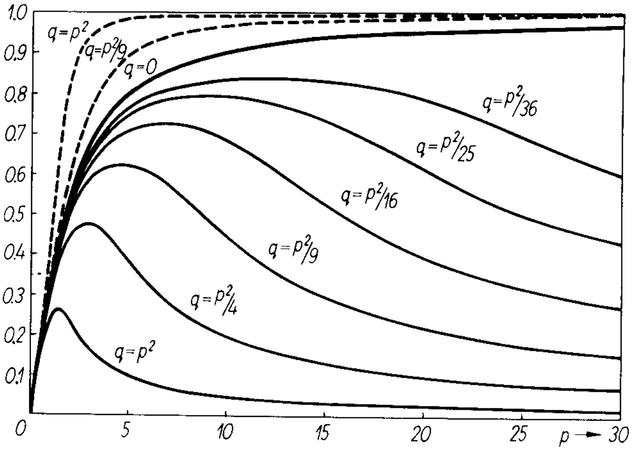

FIG. 3. Langevin function $L_1(p,\pm q)$ vs. the reorientation parameters $p$ and $q$. Above the $L_1(p,0)$ curve for dipolar unpolarizable $(q = 0)$ molecules lie the (dashed-line) curves $L_1(p,+q)$ for molecules having positive anisotropy. Below it lie the curves of $L_1(p,-q)$ pertaining to molecules with negative anisotropy.

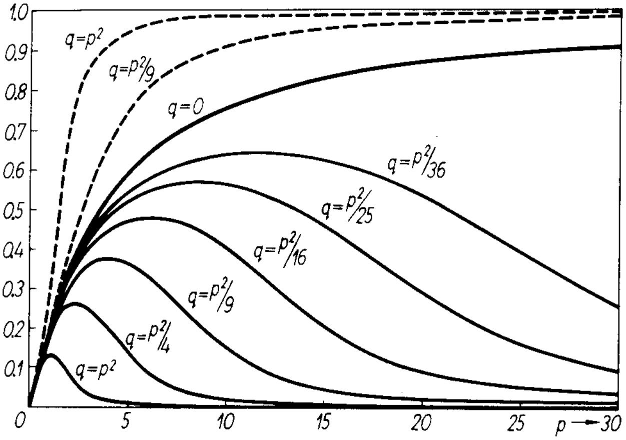

FIG. 4. Langevin functions $L_3(p, q)$ vs. the reorientation parameters p and q. Above the curve $L_3(p,0)$ for dipolar unpolarizable ($q = 0$) microsystems lie the (dashed-line) curves $L_3(p,+q)$ for microsystems having positive anisotropy; below $L_3(p,0)$ lie curves of the function $L_3(p,-q)$ relating to ones having negative anisotropy.

Consequently, whereas the torque of the permanent electric dipole tends to align the microsystem parallel to the applied field direction, the torque due to the induced dipole tends to orient it perpendicular to the field $\underline{E}$ (see Ref. [89]). With growing field intensity E, increasing the induced dipole parameter (42b), the microsystem goes over from parallel to perpendicular orientation with respect to $\underline{E}$. As a result of this reorientation, the Langevin functions $L_1(p,-q)$ and $L_3(p,-q)$ decrease with growing E tending rapidly to 0 as q, the parameter of induced dipole reorientation, grows (continuous-line curves in Figs. 3 and 4 below the curve for $q = 0$).

## D. Macroscopic and Microscopic Symmetry Relations

At moderate reorientation by the electric field E (at $p < 1$, $q < 1$), the Langevin functions can be written to a satisfactory approximation in the form of the expansions [88]:

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

$$L_3(p,\pm q) = \frac{p}{5} - \frac{p^3}{105} \pm \frac{8pq}{105} + \dots \tag{46}$$

which, inserted into (45), lead to the fulfillment of the symmetry relations (22) in an approximation linear in the field $E_y$:

$$\chi^{2\omega}_{xxy}(E_y) = \frac{1}{3}\chi^{2\omega}_{yyy}(E_y) = \frac{\rho m}{60kT}\left(b^{2\omega}_{333} + 2b^{2\omega}_{113}\right)E_y \tag{45a}$$

In the case of complete alignment of all the microsystems into the field direction ($p \to \infty$, $q \to \infty$, when the field is strong or the dipole moments and polarizabilities of the microsystems are large) the Langevin functions tend rapidly to 1 for positive anisotropy, and Eqs. (45) reduce to:

$$\chi^{2\omega}_{xxy}(E_y \to \infty) = \frac{\rho}{4}\, b^{2\omega}_{113}$$

$$\chi^{2\omega}_{yyy}(E_y \to \infty) = \frac{\rho}{4}\, b^{2\omega}_{333} \tag{45b}$$

In that of complete alignment of negatively anisotropic microsystems, the Langevin functions tend to 0; in consequence, the components (45) vanish.

The fulfillment of the macroscopic symmetry relations (22) would necessarily have entailed that of the following microscopic relation for the individual microsystems:

$$b^{2\omega}_{333} = 3b^{2\omega}_{113} \tag{47}$$

The Bloembergen symmetry relations in the form (22) are strictly fulfilled in the approximation linear in the field $E$, on neglecting electron dispersion. In very strong fields $E$ the relations (22) are, in general, not fulfilled. For electric saturation, the expression (45b) suggests that the symmetry of the electro-optical properties of the individual microsystems become identical to the macroscopic symmetry of the isotropic body as a whole which, in the presence of an electric field, is endowed with symmetry of the type $C_{\infty v}$. The preceding conclusion seems obvious, since at concordant alignment of all the microsystems in the direction of the external field, the properties of the body as a whole have to coincide with those of the microsystem.

## E. Rarefied Molecular Substances

As yet, experimental data are too scarce to permit a full comparative analysis of the above theory. Obviously, one cannot hope to achieve complete electric or optical saturation [90] in gases and molecular liquids for fear that the effect will be preceded by electric (optical) breakdown. In the dipolar substances studied by Mayer, where the electric reorientation parameters were at the best of order $p = 10^{-3}E_y$ and $q = 10^{-9}E_y^2$, it would be necessary to apply a very strong electric field upward of $10^6$ V/cm to approach saturation (see the graphs of Figs. 3 and 4). In this situation, considerable optical ordering of the molecules, or even some degree of optical saturation, appear much more feasible (in Mayer's measurements, the laser field $E_\omega$ amounted to $1.5 \times 10^6$ V/cm). In fact, it should be taken into consideration that some increase in the numerical value of $p$ and $q$ can be due to the circumstance that, generally, molecules in states excited by a strong electric field have dipole moments and polarizabilities much in excess of those in their ground state.

Available measurements of $I^{2\omega}$ as yet do not permit a quantitative decision as to which of the microscopic processes discussed here, namely, nonlinear electron distortion or molecular reorientation, plays the predominant role. The fact that an anomalous increase in intensity $I^{2\omega}$ with growing field $E_y$ was observed by Mayer [32] (Fig. 5) to occur exclusively in the substances $CH_3I$, $C_2H_5I$ and $C_2H_5Br$ whose molecules have considerable dipole moments of order $2 \times 10^{-18}$ esu cm and a positive anisotropy of electric and optical polarizability speaks in favor of reorientation. On the other hand, in chloroform and other

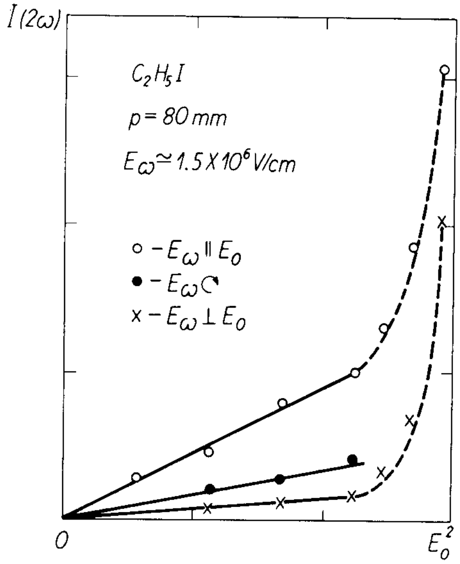

FIG. 5. Mayer's results [32] for the intensity $I^{2\omega}$, measured at frequency $2\omega$ in ethyl iodide vs. the square $E_0^2$ of the applied dc electric field. Unit on abscissas axis: $2.7 \times 10$ (V/cm) ; unit of ordinate: 25 photoelectrons in the detector equivalent to $6.2 \times 10$ photons emitted into the body angle of observation. Stimulating peak power: 7 MW; breakdown threshold $E_0^2$ lies at $E_0^2 = 8.1 \times 10$ (V/cm) ; field intensity of the collimated ruby laser beam $E_\omega = 1.5 \times 10$ V/cm. Linearity (continuous straight lines in the graph), expressing quadratic dependence on $E_0$, maintains itself by nigh up to breakdown $E_0^b$; upward of $E_0 > 0.8\ E_0^b$ anomalous effects are observed (dashed-line curves).

weakly dipolar and nondipolar substances, he failed to observe an anomalous increase in $I^{2\omega}$; in the light of our theory this can plausibly be explained by the fact that $CHCl_3$ molecules have a much smaller dipole moment as well as negative anisotropy of polarizability causing, in conformity with the graphs of Figs. 3 and 4, a decrease in value of the nonlinear susceptibilities and hence of $I^{2\omega}$. Numerical evaluations show that in dipolar substances the molecular reorientation process decidedly predominates over that of nonlinear electron distortion. The final decision can be expected from studies of second-harmonic generation as a function of temperature, concentration and light frequency or the frequency of a slowly varying electric field $E(\omega_0) = E(0)e^{i\omega_0 t}$ oscillating at $\omega_0$ much below optical frequencies $\omega$. With the isotropic medium polarized by means of an ac field $E$, one has to replace the constant moment $\underline{m}$ in Eq. (29) by a time-oscillating dipole moment $\underline{m}(t)$. Relaxation theory [91,92] leads to:

$$m_j(t) = \frac{m_j e^{i\omega_0 t}}{1 + i\omega_0 \tau_j} \tag{48}$$

where $\tau_j$ is the relaxation time corresponding to the inertia moment for the principal axis $j$ of the molecule. By appropriately raising the applied field frequency one can reduce, or entirely eliminate, the process of reorientation in various substances.

### F. The Role of Molecular Correlations

In condensed substances, nonlinear optical susceptibility is affected by various molecular correlations, such as molecular redistribution [71,72] and angular correlations between anisotropic molecules [83] as well as the local field and its anisotropy [71]. These correlations can act in a manner to enhance or lower electric reorientation according to the structure of the individual molecules and the degree of their condensation. Molecular redistribution is highly important to nonlinear processes, since it leads to anisotropy even in the case of interacting nearly spherical molecules, like $CCl_4$ [71,72]. In the latter case, only correlations of the radial kind intervene, causing a spatial regrouping of the molecules giving rise to pairwise, three-molecule, etc. aggregates, apt to undergo a reorientation by the external electric field. The process of nonlinear molecular distortion as such is but insignificantly affected by spatial redistribution.

In the absence of an external field, correlations between anisotropic molecules lead to a time-fluctuating short-range ordering, i.e., a cybotactic structure [93]. An externally applied electric field can cause a transition from a phase with partly ordered to one with with more highly ordered molecules similar to the nematic mesophase of liquid crystals [73]. Transition processes involving macromolecules are mentioned in Chap. 3. In the field-induced mesophase of nearly nematic substances, SHG can become enhanced as is the case in liquid crystals [60]. A rise in $I^{2\omega}$ can moreover be caused by strong fluctuations of molecular angular orientation close to the critical point [47].

In nondipolar substances, with regard to Eqs. (31) and (39), the presence of multipole interactions can cause a temperature-statistical process, consisting in a dc field-orientation of dipoles induced in the molecules by fields of the electric quadrupoles and octupoles of neighboring molecules. We have to deal with a similar mechanism in the cooperative second harmonic scattering in liquids with centrosymmetric molecules recently detected by Lalanne, Martin, and this author [94].

Studies of SHG in molecular solutions versus the concentration can also be expected to permit the quantitative determination of contributions from the various above-discussed processes. Namely, the process of third-order nonlinear molecular distortion depends but insignificantly on statistical correlations and should thus be nearly additive, meaning that the nonlinear susceptibilities of the components of the solutions will not depend on concentration. Inversely, molecular reorientation depends strongly on radial and angular correlation, whence the nonlinear susceptibility tensor will depend on higher powers of the concentrations thus not fulfilling the law of additivity similarly to the electric polarization and Kerr constant of liquid solutions [74].

## G. Macromolecular Solutions

The theory expounded here is directly applicable to solutions of macromolecules and colloid particles. The latter have to be considered as being rigid, and the solution has to be so dilute as to exclude solute-solvent or solute-solute interactions.

In the class of synthetic polypeptides, the most often studied are the macromolecules of the helical poly-γ-benzyl-L-glutamate, roughly of the shape of long cylinders, presenting large dipole moments (of order $10^3$ D) and high anisotropy of their electric polarizability (of order $10^{-18}$ cm$^3$) [87]. In this case, the reorientation parameters amount to $p = 0.1\ E$ and $q = 10^{-5}\ E^2$, which means that reorientation of permanent dipoles predominates over that of induced ones; electric saturation can set in at an external field intensity of as little as $E > 10^4$ V/cm. In bentonite suspensions, we deal with plate-shaped microsystems; here [89], $p = 0.5E$ and $q = 0.7E^2$, whence $q/p^2 > 1$ and, with growing $E$, orientation of induced dipoles becomes rapidly predominant leading to electric saturation already at $E > 10^3$ V/cm and a reorientation of the microsystems with their short axis in the $E$-direction and consequently a steep decrease to 0 of the nonlinear susceptibilities.

If the laser pulse duration is more than $10^{-4}$ sec, thus sufficiently long to permit optical reorientation of the macromolecules, some optical anisotropy will additionally arise in the medium contributing to an increase or decrease of the nonlinear susceptibilities. One is easily convinced that continuously operating intermediate power gas lasers are quite sufficient for the study of substances of the kind under consideration. From what has been said, it is obvious that we are able to induce, both electrically and optically, considerable nonlinearities in solutions of rod- or thread-shaped macromolecules and colloid particles. These cause a strong rise in $I^{2\omega}$ with growing dc electric field or growing intensity of the light wave itself; this capacity of the substances under consideration of increasing their optical nonlineaties and exhibiting saturation predestines them to play an important role in problems of optoelectronics. Experimental work in this direction should, moreover, prove of the highest value in providing us with new data concerning the nonlinear properties of biomacromolecules, viruses, and colloid particles in general [74].

## IV. NONLINEAR ELECTRO-OPTICAL POLARIZABILITIES

Processes of second-harmonic generation are strongly sensitive to the structure exhibited by crystals, gases, liquids, and macromolecular solutions. In the wake of the new electro-optical phenomena discussed above, a search is continuing for new materials, having the ability to produce these phenomena to a high degree.

Much information concerning nonlinear electric and optical properties has been gleaned from the study of other effects, not considered by us above. We shall, however, adduce the most important results thus obtained with regard to the values of the nonlinear tensors $b_{ijk}$ and $c_{ijkl}$.

### A. Second-Order Nonlinear Polarizabilities

The dipole moment of order 2, induced in a microsystem at frequency $\omega_a + \omega_b$, is:

$$m_i^{(2)}(\omega_a + \omega_b) = \beta b_{ijk}(\omega_a, \omega_b) E_j(\omega_a) E_k(\omega_b) \tag{49}$$

where the ordering factor $\beta$ is equal to 1/4 for $\omega_a = \omega_b$ and to 1/2 if the two frequencies are different. In the static case ($\omega_a = \omega_b = 0$), $\beta$ amounts to 1/2.

In the absence of electron absorption and dispersion, the second-order nonlinear polarizability tensor $b_{ijk}(\omega_a,\omega_b)$ can be dealt with as totally symmetric and the numbers of its nonzero and independent elements for the various point groups are listed in Table 1. Static values of the nonlinear polarizability $b^0_{ijk} = b_{ijk}(0,0)$ have been computed theoretically for some molecules [95,96]. Tensor elements $b^{\omega}_{ijk} = b_{ijk}(\omega,0)$ are determined from dc Kerr effect measurements [74,96] and molecular light scattering in liquids [83]. Values of $b^{2\omega}_{ijk} = b_{ijk}(\omega,\omega)$ can be determined from nonlinear light scattering at doubled frequency by gases and liquids [97,98] or from SHG by a gas or liquid in the presence of a dc electric field [32].

## B. Third-Order Nonlinear Polarizabilities

The dipole moment of order 3 induced in a microsystem at frequency $\omega_a + \omega_b + \omega_c$ is:

$$m_i^{(3)}(\omega_a + \omega_b + \omega_c) = \gamma c_{ijkl}(\omega_a,\omega_b,\omega_c)E_j(\omega_a)E_k(\omega_b)E_l(\omega_c) \qquad (50)$$

where the ordering factor $\gamma$ is 1/4 if all the frequencies are different, 1/8 if two differ, 1/24 for $\omega_a = \omega_b = \omega_c$, and 1/6 in the single-field static case.

On assuming total symmetry for the tensor of third-order nonlinear polarizability $c_{ijkl}(\omega_a,\omega_b,\omega_c)$ we obtain its nonzero and independent elements as listed in Table 2 (see also Ref. [99]). Direct theoretical calculations of $c^0_{ijkl} = c_{ijkl}(0,0,0)$ have been effected for the atoms of inert gases and simple molecules [100]. Tensor elements $c^{\omega}_{ijkl} = c_{ijkl}(\omega,0,0)$ have been determined as to their value for numerous molecules from static Kerr effect studies [96,101,102] and values $c^{\omega}_{ijkl} = c_{ijkl}(\omega,\omega_I,-\omega_I)$ from laser light-induced optical birefringence [10]. Measurements of dc field-induced SHG by gases [32] yield the tensor elements $c^{2\omega}_{ijkl} = c_{ijkl}(\omega,\omega,0)$, which can also be obtained from cooperative second harmonic scattering by liquids

## TABLE 1

Nonzero and Independent Tensor Elements
$b_{\alpha\beta\gamma}$ of the Second-Order Nonlinear Elements
on the Assumption of Total Symmetry in the Indexes $\alpha$, $\beta$, $\gamma$

| Point group | Number of nonzero elements | Number of independent elements | Elements of $b_{\alpha\beta\gamma}$ are denoted only by their subscripts $\alpha, \beta, \gamma = 1,2,3$ |
|---|---|---|---|
| $C_1$ | 27 | 10 | 111; 222; 333;<br>112 = 121 = 211; 113 = 131 = 311;<br>223 = 232 = 322; 122 = 212 = 221;<br>133 = 313 = 331; 233 = 323 = 233;<br>123 = 132 = 213 = 231 = 312 = 321 |
| $C_3$ | 15 | 4 | 333; 111 = -122 = -212 = -211;<br>222 = -211 = -121 = -112;<br>311 = 131 = 113 = 322 = 232 = 233 |
| $C_s$ | 14 | 6 | 111; 222; 122 = 212 = 221;<br>211 = 121 = 112; 133 = 313 = 331;<br>233 = 323 = 332 |
| $C_2$ | 13 | 4 | 333; 311 = 131 = 113; 322 = 232 = 223;<br>123 = 132 = 213 = 231 = 312 = 321 |
| $S_4$ | 12 | 2 | 311 = 131 = 113 = -322 = 232 = -223;<br>123 = 132 = 213 = 231 = 312 = 321 |
| $C_{3v}$ | 11 | 3 | 333; 222 = -211 = -121 = -112<br>311 = 131 = 113 = 322 = 232 = 223 |
| $C_{3h}$ | 8 | 2 | 111 = -122 = -212 = -221;<br>222 = -211 = -121 = -112 |
| $C_{2v}$ | 7 | 3 | 333; 311 = 131 = 113; 322 = 232 = 223 |
| $C_4$, $C_{4v}$<br>$C_6$, $C_{6v}$<br>$C_{\infty v}$ | 7 | 2 | 333;<br>311 = 131 = 113 = 322 = 232 = 223 |
| $D_2$, $D_{2d}$<br>$T$, $T_d$ | 6 | 1 | 123 = 132 = 213 = 231 = 312 = 321 |
| $D_3$ | 4 | 1 | 111 = -122 = -212 = -221 |
| $D_{3h}$ | 4 | 1 | 222 = -211 = -121 = -112 |

TABLE 2

Tensor Elements $c_{\alpha\beta\gamma\delta}$ of Third-Order Nonlinear Polarizability on the Assumption of Total Symmetricity in the Indexes $\alpha, \beta, \gamma, \delta$

| Point group | Number of nonzero elements | Number of independent elements | Elements of $c_{\alpha\beta\gamma\delta}$ are denoted only by their subscripts $\alpha, \beta, \gamma, \delta = 1,2,3$ |
|---|---|---|---|
| $C_i$ | 81 | 15 | 1111; 2222; 3333<br>1122 = 1212 = 1221 = 2211 = 2121 = 2112;<br>1133 = 1313 = 1331 = 3311 = 3131 = 3113;<br>2233 = 2323 = 2332 = 3322 = 3232 = 3223;<br>1112 = 1121 = 1211 = 2111;<br>2221 = 2212 = 2122 = 1222;<br>1333 = 3133 = 3313 = 3331;<br>2333 = 3233 = 3323 = 3332;<br>1113 = 1131 = 1311 = 3111;<br>2223 = 2232 = 2322 = 3222;<br>1123 = 1213 = 1231 = 1132 = 1312 = 1321 = 2113 = 2131 = 2311 = 3112 = 3121 = 3211;<br>2213 = 2123 = 2132 = 2231 = 2321 = 2312 = 1223 = 1232 = 1322 = 3221 = 3212 = 3122;<br>1332 = 1323 = 1233 = 2133 = 2313 = 2331 = 3123 = 3213 = 3231 = 3132 = 3321 = 3312 |
| $C_3$<br>$C_{3i}$ | 53 | 5 | 3333; 1111 = 2222 = 1122 + 1212 + 1221;<br>1122 = 1212 = 1221 = 2211 = 2121 = 2112;<br>1133 = 1313 = 1331 = 3311 = 3131 = 3113 = 2233 = 2323 = 2332 = 3322 = 3232 = 3223;<br>1113 = 1131 = 1311 = 3111 = -2123 = -2312 = -2231 = -2321 = -2213 = -2132 = -1223 = -1232 = -1322 = -3122 = -3212 = -3221;<br>2223 = 2232 = 2322 = 3222 = -1213 = -1132 = -1312 = -1123 = -1231 = -1321 = -2113 = -2131 = -2311 = -3211 = -3121 = -3112 |
| $C_2$<br>$C_5$<br>$C_{2h}$ | 41 | 9 | 1111; 2222; 3333;<br>1122 = 1212 = 1221 = 2211 = 2121 = 2112;<br>1133 = 1313 = 1331 = 3311 = 3131 = 3113;<br>2233 = 2323 = 2332 = 3322 = 3232 = 3223;<br>1112 = 1121 = 1211 = 2111;<br>2221 = 2212 = 2122 = 1222;<br>1332 = 1323 = 1233 = 2133 = 2313 = 2331 = 3123 = 3213 = 3231 = 3132 = 3321 = 3312 |

TABLE 2 (Continued)

| Point group | Number of nonzero elements | Number of independent elements | Elements of $c_{\alpha\beta\gamma\delta}$ are denoted only by their subscripts $\alpha, \beta, \gamma, \delta = 1,2,3$ |
|---|---|---|---|
| $C_{3v}$<br>$D_{3d}$<br>$D_3$ | 37 | 4 | 3333; 1111 = 2222 = 1122 + 1212 + 1221;<br>1122 = 1212 = 1221 = 2211 = 2121 = 2112;<br>1133 = 1313 = 1331 = 3311 = 3131 = 3113 = 2233 = 2323 = 2332 = 3322 = 3232 = 3223;<br>2223 = 2232 = 2322 = 3222 = -1213 = -1132 = -1312 = -1123 = -1231 = -1321 = -2113 = -2131 = -2311 = -3211 = -3121 = -3112 |
| $C_4$<br>$S_4$<br>$C_{4h}$ | 29 | 5 | 3333; 1111 = 2222;<br>1122 = 1212 = 1221 = 2211 = 2121 = 2112;<br>1133 = 1313 = 1331 = 3311 = 3131 = 3113 = 2233 = 2323 = 2332 = 3322 = 3232 = 3223;<br>1112 = 1121 = 1211 = 2111 = -2221 = -2212 = -2122 = -1222 |
| $D_2$<br>$C_{2v}$<br>$D_{2h}$ | 21 | 6 | 1111; 2222; 3333;<br>1122 = 1212 = 1221 = 2211 = 2121 = 2112;<br>1133 = 1313 = 1331 = 3311 = 3131 = 3113;<br>2233 = 2323 = 2332 = 3322 = 3232 = 3223 |
| $D_4$<br>$C_{4v}$<br>$D_{2d}$<br>$D_{4h}$ | 21 | 4 | 3333; 1111 = 2222;<br>1122 = 1212 = 1221 = 2211 = 2121 = 2112;<br>1133 = 1313 = 1331 = 3311 = 3131 = 3113 = 2233 = 2323 = 2332 = 3322 = 3232 = 3223 |
| $C_6$<br>$C_{3h}$ $C_\infty$<br>$C_{6h}$ $C_{\infty v}$<br>$D_6$ $C_{\infty h}$<br>$C_{6v}$ $D_{\infty h}$<br>$D_{3h}$<br>$D_{6h}$ | 19 | 3 | 3333; 1111 = 2222 = 1122 + 1212 + 1221;<br>1122 = 1212 = 1221 = 2211 = 2121 = 2112;<br>1133 = 1313 = 1331 = 3311 = 3131 = 3113 = 2233 = 2323 = 2332 = 3322 = 3232 = 3223 |

TABLE 2 (Continued)

| Point group | Number of nonzero elements | Number of independent elements | Elements of $c_{\alpha\beta\gamma\delta}$ are denoted only by their subscripts $\alpha$, $\beta$, $\gamma$, $\delta$ = 1,2,3 |
|---|---|---|---|
| T | 21 | 2 | 1111 = 2222 = 3333;<br>1122 = 1212 = 1221 = 2211 = 2121 =<br>2112 = 3311 = 3131 = 3113 = 1133 =<br>1313 = 1331 = 2233 = 2323 = 3223 =<br>3322 = 3232 = 3223 |
| $T_h$ | | | |
| O | | | |
| $T_d$ | | | |
| $O_h$ | | | |
| K $K_h$ | 21 | 1 | Nonzero elements as in the tetrahedral groups with the relation<br>1111 = 1122 + 1212 + 1221 |
| Y $Y_h$ | | | |

with centrosymmetric molecules [94]. Finally, tensor elements $c^{3\omega}_{ijkl} = c_{ijkl}(\omega,\omega,\omega)$ are determined by measuring third-harmonic generation in gases and liquids [57,64], and have recently been calculated theoretically for perfect gases [103].

Numerical values of the nonlinear polarizabilities of atoms and molecules determined by experiment or calculated from the theory are listed in Table 3. None are as yet available for macromolecules, with regard to which, however, the theory points to highly interesting and promising possibilities both in the experimental and theoretical domains [19a,104].

## V. CONCLUDING REMARKS AND PROSPECTS

The study of optical harmonics in transmitted light provides information on the microscopic structure, phase transitions (e.g., in ferroelectrics), and crystallographical symmetry of the medium. That of harmonics in reflected light provides data on the electro-optical properties of surfaces, double electric layers, and surface phenomena at the boundary of two media [16]. The new optical and electro-optical phenomena concisely discussed by us here constitute

TABLE 3

Numerical Values of Linear and Nonlinear Optical Polarizabilities of Atoms and Molecules Calculated Theoretically and Determined from Experimental Data

| Units | $10^{-24}$ $cm^3$ | $10^{-30}$ $cm^5$ $esu^{-1}$ | | $10^{-36}$ $cm^7$ $esu^{-2}$ | | |
|---|---|---|---|---|---|---|
| Atom or molecule | $a^{\omega}$ | $b^{\omega}$ | $b^{2\omega}$ | $c^{\omega}$ | $c^{2\omega}$ | $c^{3\omega}$ |
| He | 0.205 | | | 0.027 [101]<br>0.022 [100] | 0.023 [100] | 0.024 [100]<br>0.021 [103] |
| Ne | 0.394 | | | 0.051 [24]<br>0.055 [96] | 0.24 [33] | 0.041 [103]<br>0.214 [64] |
| Ar | 1.66 | | | 0.59 [24]<br>0.73 [96] | 2.74 [33] | 3.024 [64]<br>0.672 [103] |
| Kr | 2.52 | | | 1.4 [24]<br>1.6 [96] | 6.69 [33] | 9.264 [64]<br>1.704 [103] |
| Xe | 4.11 | | | 3.9 [24]<br>4.0 [96] | 18.52 [33] | 23.496 [64]<br>5.328 [103] |
| $H_2$ | 0.79 | | | 0.28 [101] | 0.36 [32] | 1.920 [64] |
| $N_2$ | 1.76 | | | 0.7 [101] | | 2.568 [64] |
| $O_2$ | 1.60 | | | | 0.64 [32] | |
| CO | 1.95 | | | | 1.81 [32] | |
| $CO_2$ | 2.65 | | | 4.5 [101] | | 2.744 [64] |
| $CH_4$ | 2.6 | | 0.01 [98] | 1.45 [96] | 1.48 [32] | |
| $CCl_4$ | 10.5 | | 0.03 [98] | 3.5 [10]<br>6.51 [83] | 3.6 [32]<br>2.1 | |

TABLE 3 (continued)

| Units | $10^{-24}$ cm$^3$ | $10^{-30}$ cm$^5$ esu$^{-1}$ | | $10^{-36}$ cm$^7$ esu$^{-2}$ | | |
|---|---|---|---|---|---|---|
| Atom or molecule | $a^{\omega}$ | $b^{\omega}$ | $b^{2\omega}$ | $c^{\omega}$ | $c^{2\omega}$ | $c^{3\omega}$ |
| $CH_3F$ | 3.55 | -0.28 [96] | | 1.28 [96] | | |
| $CHF_3$ | 2.81 | +0.41 [96] | -0.06 [32] | 0.92 [96] | 0.27 [32] | |
| $CHCl_3$ | 8.23 | 14.4 [96] | 0.33 [32] | 4.8 [10] | 4.4 [32] | |
| $CS_2$ | 8.74 | | | 56.5 [83]<br>50.1 [10]<br>54.4 [96]<br>57.4 [101] | | |
| $C_2H_6$ | 4.47 | | | 1.9 [101] | 4.8 [32] | |
| $C_6H_6$ | 10.32 | | | 6.5 [101] | | |
| $C_6H_{12}$ | 10.87 | | | 1.2 [10] | | |
| $C_6H_5CH_3$ | 12.29 | | | 27.2 [10] | | |
| $C_6H_5NO_2$ | 12.17 | | | 85.0 [10] | | |
| $CH_3I$ | 7.28 | | 0.84 [32] | | 8.0 [32] | |
| $SF_6$ | 4.47 | | | 1.2 [101] | 0.26 [32] | |
| $C_2H_5I$ | | | 1.1 [32] | | 13.6 [32] | |

[a] Only mean values are given: $a = a_{11}/3$, $b = b_{113}/3 = b_{333}$ (for the axial symmetry), $b = b_{123}$ (for tetrahedral symmetry), and $c = c_{iijj}/5 = c_{3333}$.

a highly effective method for the elucidation of the electronic, atomic, molecular and macromolecular structures of matter in a wide range of the electromagnetic spectrum.

Especially promising is the new technique of producing ultrashort light pulses [12], of duration $10^{-8}$ to $10^{-12}$ s and consequently comparable to the relaxation times of molecules [92], making it possible for us to "seize," as it were, the momentary structure of molecular and macromolecular bodies and to perform a separation between the various nonlinear processes, differing as to the times necessary for attaining the steady state. Thus, in certain conditions, one can separate the processes of nonlinear electron polarizability from those of molecular reorientation and redistribution. This will, moreover, depend on the electro-optical structure of the constituent molecules or macromolecules, on their size and interactions, and on whether they are more highly susceptible to nonlinear electron distortion or to orientation by an external electric field. The future of these studies lies with the now rapidly developing nonlinear molecular spectroscopy [20,105].

Quite recently, numerous papers have appeared reporting determinations of various nonlinear optical and electro-optical properties of atomic and molecular systems [106-145].

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