

A CLASSICAL TREATMENT OF NONLINEAR PROCESSES OF MOLECULAR RELAXATION IN INTENSE ELECTRIC FIELDS OF HIGH AND LOW FREQUENCY*

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ABSTRACT

The dependence of third-order nonlinear electric polarization on low and high electric field vibration frequencies in isotropic molecular media is discussed. Nonlinear electron dispersion is described by classical Lorentz-Voigt theory and nonlinear processes of molecular rotational relaxation are solved using Debye's rotational diffusion approximation for dipolar axially symmetric molecules with linear and nonlinear anisotropy of polarizability. A strict analysis of temperature contributions to third-order nonlinear susceptibility is performed, and possibilities available for the separation of the various relaxational mechanisms by pulsed techniques are indicated. The general results are applied to the description of such nonlinear processes as third-harmonic generation of low frequencies, and second-harmonic generation in isotropic electrically polarized media, as well as optical birefringencies and dielectric saturation induced by fields of low and high frequencies. These effects constitute the basis of nonlinear relaxation spectroscopy, and their investigation will provide new data on the 3 rotational relaxation times τ_1 , τ_2 , τ_3 , related as $\tau_1 = 3 \tau_2 = 6 \tau_3$. Also, available studies on molecular relaxation processes are reviewed briefly because of their relevance to the laser technique and nonlinear optics of ultra-short processes.

I. BRIEF SURVEY OF PREVIOUS RESULTS

A. *Linear relaxation processes*

It is 45 years since Debye [1] proposed his molecular diffusional theory of

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linear processes to explain the relaxation of electric dipoles immersed in a viscous fluid. Methods of dielectric relaxation are currently applied in the study of rotational and translational molecular motions, correlations between molecular dipoles, and dynamics of liquid structure [2–7].

Debye assumed that the molecular electric dipoles have a spherical shape, of radius a , that they undergo reorientation in an a.c. electric field $E(t) = E_0 e^{-i\omega t}$ vibrating at the circular frequency ω and that they are subject to a frictional force in the fluid medium of viscosity η in accordance with Stoke's law

$$\zeta_{\text{R}} = 8\pi a^3 \eta \quad (1)$$

A spatial orientational distribution of the dipoles in the a.c. electric field is counteracted by Brownian motions, which tend to reinstate the initial randomness. With regard to (1), the rotational diffusion coefficient is

$$D_{\text{R}} = \frac{kT}{\zeta_{\text{R}}} = \frac{kT}{8\pi a^3 \eta} \quad (2)$$

leading to the Debye dipole relaxation time

$$\tau_{\text{D}} = \frac{1}{2D_{\text{R}}} = \frac{4\pi a^3 \eta}{kT} \quad (3)$$

Debye's theory [1], in a linear approximation, yields for the total dipolar polarization of a medium (with the number density $\rho = N/V$)

$$P(t) = \frac{\rho m^2}{3kT} \frac{F_0 \exp(-i\omega t)}{1 - i\omega \tau_{\text{D}}} \quad (4)$$

where F is the (Lorentz or Onsager) local electric field, acting on a molecular dipole of electric moment m .

Geometrically spherical molecules have only one relaxation time (3), whereas molecules with ellipsoidal geometry are characterized, according to Perrin [8], by at least three relaxation times along the principal axes of the molecular ellipsoid.

B. Quadratic relaxational processes

Peterlin and Stuart [9] extended Debye's linear relaxation theory to a quadratic dependence on the a.c. electric field, giving rise to an ω -dependent optical birefringence of the fluid. Quadratic theory, besides the Debye dipole relaxation time (3), involves a second rotational relaxation time, characteristic for optical birefringence,

$$\tau_{\text{B}} = \frac{1}{6D_{\text{R}}} = \frac{\tau_{\text{D}}}{3} \quad (5)$$

The following expression for the electro-optical birefringence of a fluid, acted

on by an a.c. electric field is due to Peterlin and Stuart:

$$n_{\parallel}^2 - n_{\perp}^2 = \frac{2\pi\rho}{15kT} \gamma(\omega_A) \left\{ \gamma(\omega) \left[1 + \frac{\cos(2\omega t - \delta_1)}{(1 + 4\omega^2\tau_B^2)^{\frac{1}{2}}} \right] + \frac{m^2}{kT} \left[\frac{1}{1 + \omega^2\tau_D^2} + \frac{\cos(2\omega t - \delta_2)}{(1 + \omega^2\tau_D^2)^{\frac{1}{2}}(1 + 4\omega^2\tau_B^2)^{\frac{1}{2}}} \right] \right\} F_0^2 \quad (6)$$

where

$$\gamma(\omega_A) = a_3(\omega_A) - a_1(\omega_A) \quad \text{and} \quad \gamma(\omega) = a_3(\omega) - a_1(\omega) \quad (7)$$

are the anisotropies of optical polarizability of the axially symmetric molecule with respect to the vibration frequency ω_A of the analyzing beam used for detecting the electrically induced optical birefringence and with respect to the frequency ω of the a.c. field.

If the birefringence-inducing field is static, $\omega = 0$, formula (6) gives the well-known expression of Langevin [10] and Born [11]. Optical birefringence in a.c. electric fields was studied by Benoit [12]. At very high vibration frequencies of an intense electric field, as in the case of laser light ($\omega\tau \rightarrow \infty$), formula (6) defines the optically induced optical birefringence detected experimentally in liquids by Mayer and Gires [13].

The second relaxation time (5) intervenes, moreover, in many other processes of molecular reorientation in a.c. electric fields [14–18], as well as in NMR [19], Rayleigh and Raman spectral light scattering [15, 20–22], induced Rayleigh and Raman scattering [23–25], nonlinear depolarization of scattered light [26], transient scattering by macromolecules [17, 27, 28], optical Kerr effect [29–32], nonlinear optical activity [33] and dichroism [34, 35], and magneto-optical effects [36].

Kielich [26, 29] extended the theory of Debye and Peterlin to arbitrary a.c. electric fields

$$E(t) = \sum_a E_a \exp(-i\omega_a t) \quad (8)$$

obtaining to second-order accuracy the following distribution function for dipolar axially symmetric molecules:

$$f(\Omega, t) = f(\Omega, 0) [1 + p(t) \cos \vartheta + \frac{1}{2} g(t) (3 \cos^2 \vartheta - 1) + \dots] \quad (9)$$

where

$$p(t) = \frac{1}{kT} \sum_a \frac{m(\omega_a) E_a \exp(-i\omega_a t)}{1 - i\omega_a \tau_D} \quad (10)$$

$$g(t) = \frac{1}{3kT} \sum_{ab} \frac{E_a E_b \exp[-i(\omega_a + \omega_b)t]}{1 - i(\omega_a + \omega_b)\tau_B} \left\{ \gamma(\omega_a, \omega_b) + \frac{1}{2kT} \left[\frac{m(\omega_a)m(\omega_b)}{1 - i\omega_a \tau_D} + \frac{m(\omega_b)m(\omega_a)}{1 - i\omega_b \tau_D} \right] \right\} \quad (11)$$

The sums of (8), (10) and (11) extend over all values of a and b , positive as well as negative, with $\omega_{-a} = -\omega_a$. In the expansion (9), $f(\Omega, 0)$ is the zero field distribution function (8) defining random distribution of molecules having the orientation Ω ; and ϑ is the angle between the symmetry axis of the molecule and the direction of the a.c. electric field $E(t)$.

The first approximation of (9) and (10) defines Debye's [1] linear distribution function. The second approximation of (9) with (11) leads to Peterlin and Stuart's [9] results for the quadratic distribution function. The expressions (9)–(11) allow us to calculate dielectric dispersion and absorption for optical birefringence [29], nonlinear variations in anisotropic light scattering [26], nonlinear optical activity [33], and many other quadratic effects [36, 37].

Quadratic molecular relaxational processes play an important part in numerous, recently studied processes, evolving on an ultra-short time scale, such as light self-focussing by ultra-short laser pulse [38–40], mode locking [41], self-phase modulation [42], ultra-fast light gate [43–45], ultra-short pulse measurement [46, 47], and ultra-short pulse generation [48–50], opening up a new research field of ultra-short processes [51–55] dealing with various transient phenomena, in which molecular reorientation [56–60] is apparent.

C. Cubic and higher relaxational processes

In isotropic dielectrics, the first nonlinearity of electric polarization is of the third order in the electric field strength E . This nonlinearity leads to quadratic variations in electric permittivity $\Delta\epsilon \approx E^2$, which is studied as dielectric saturation [1, 18, 61, 62]. Thus, to determine the dependence of $\Delta\epsilon(\omega)$ on the vibration frequency in an a.c. electric field, one has to calculate the distribution function (9) to an accuracy of the third power of the field strength. Cubic relaxation has been dealt with by Novikov [63] and Kasproicz-Kielich et al. [37] in relation to nonlinear electro-optical phenomena.

Cubic dispersion processes involve in general, in addition to the relaxation times (3) and (5), a third rotational relaxation time

$$\tau_3 = \frac{1}{12D_R} = \frac{\tau_B}{2} = \frac{\tau_D}{6} \quad (12)$$

which, incidentally, is obtained from the general solution of free rotational diffusion for the n th relaxation time [64]

$$\tau_n = \frac{1}{n(n+1)D_R} = \frac{2\tau_D}{n(n+1)} \quad (13)$$

Higher relaxation times occur also in the spectral theory of double-, triple- and generally multiple-photon scattering processes. Maker [65] proved that spectral broadening of double-photon elastic scattering by symmetric-top molecules

depends on the two relaxation times τ_1 and τ_3 and that their numbers increase for asymmetric-top molecules [66]. Similar times intervene in hyper-Raman light scattering spectra [67]. The spectra of triple-photon scattering [68] depend on the relaxation times τ_2 and τ_4 , whereas successive higher times (13) occur generally in multiple-photon scattering [69].

D. Nonlinear electron dispersion

Lorentz [70] is the founder of the classical theory of dispersion. Voigt [71] extended the theory to include nonlinear electron dispersion. In a modern treatment, the electron theory of matter is developed in Rosenfeld's monograph [72], as well in other books [73–77]. Voigt's ideas on nonlinear distortion of microsystems in strong electromagnetic fields have been developed by Born [11, 73], Van Vleck [74], Piekara [78, 79], Volkenshteyn [76] and others (see the review articles [18, 80–83]). Nonlinear dispersion of isotropic bodies has been described in terms of classical electron theory [82–86] as well as by quantum mechanical methods [85–96]. Modern laser techniques and nonlinear spectroscopy [98–100] provide effective methods for the extensive investigation of nonlinear dispersion and absorption in molecular substances throughout a wide range of frequencies.

E. The aim of this paper

We shall be considering electron and dielectric dispersion of third-order polarization in isotropic media. First, we shall propose the general fundamentals of the theory in the semi-macroscopic treatment initiated by Kirkwood [101] and at present applied to nonlinear phenomena [18, 102]. However, we shall refrain from entering into the details of the molecular correlation and statistical fluctuation mechanisms, discussed with regard to nonlinear effects in previous papers [9, 61, 102, 103]. Next, we shall give a discussion of nonlinear electron dispersion in the classical Lorentz–Voigt approach.

A further step will consist in the calculation of the time-dependent distribution function $f(\Omega, t)$ from the equation of rotational diffusion, perturbed by an a.c. field of the form (8), to an accuracy of the third order of approximation. Since, in the general case, the solution of the problem is not straightforward, we shall neglect molecular correlation, assuming for simplicity that the dipole molecules are axially symmetric and that, at the same time, they have anisotropic linear and nonlinear polarizabilities. The distribution function $f(\Omega, t)$ derived on these assumptions allows us to calculate the nonlinear polarization of order three, describing various molecular relaxation processes in isotropic fluid media.

The solution of the nonlinear molecular relaxation problem using the approximation of Debye rotational diffusion is dictated by simplicity, and provides insight into the kind of new information to be expected in the third approximation.

Obviously, various problems of molecular relaxation have been solved in recent years by methods of time correlation function, resulting from Kubo's [104] general theory of response to external perturbations of the system. The time correlation functions, as it were, span the gap between the relaxation nature of the dynamic quantities describing the return of the perturbed system to equilibrium on the one hand and the relaxation nature of their fluctuations in the state of thermodynamic equilibrium on the other. Kubo's formalism was first applied to processes of linear dielectric relaxation by Glarum [105] and Cole [106] in Kirkwood's semi-macroscopic treatment. Recently, Kluk et al. [107] developed a stochastic group theory of dipolar dielectric relaxation, and discussed the local field problem by Kubo's linear response theory. Ivanov [108] was the first to apply group theoretical methods to the rotational theory of Brownian motion.

Although the nonlinear response theory was formulated by Kubo [104] himself, its application to the second and third approximations of relaxation processes is by no means simple, and will be the subject of a separate paper. Obviously, proceeding by Kubo formalism in the semi-macroscopic approach, one can find appropriate relations between the macroscopic and microscopic time-correlation functions, rendering apparent the correlations between the motions of the individual molecules with regard to their mutual interactions. In the absence of interactions, the autocorrelation functions of successive (first, second, third, etc.) orders will yield results which should correspond to those we shall derive here using Debye's rotational approximation. Lately, Ben Reuven and Klein [109], applying the Kubo-Zwanzig method, performed an analysis of the nonlinear optical field response of independent molecules.

II. NONLINEAR POLARIZATION IN THE SEMI-MACROSCOPIC APPROACH

Consider a semi-macroscopic ellipsoid, with the electric permittivity tensor ϵ_{ij} , in an isotropic continuous medium of electric permittivity ϵ_0 . If an electric field E^0 is applied externally, a mean macroscopic field E , generally differing from E^0 , will exist in the dielectric ellipsoid. By electrostatics, the two fields are mutually related as follows [18]:

$$E_i^0 = L_{ij} E_j \quad (14)$$

where the summation convention applies to the recurring subscript j .

The tensor relating the field strength components E_i^0 and E_j is

$$L_{ij} = \epsilon_0^{-1} [\epsilon_0 \delta_{ij} + (\epsilon_{ik} - \epsilon_0 \delta_{ik}) D_{kj}] \quad (15)$$

δ_{ij} is the Kronecker symmetric unit tensor, and D_{kj} a field depolarization tensor dependent on the shape of the ellipsoidal sample. In particular, for the sphere one

has $D_{kj} = \delta_{kj}/3$ and the tensor (15) becomes

$$L_{ij} = \frac{\epsilon_{ij} + 2\epsilon_0 \delta_{ij}}{3\epsilon_0} \quad (15a)$$

If, moreover, the electric permittivity of the spherical sample is isotropic, $\epsilon_{ij} = \epsilon \delta_{ij}$, eqn. (15a) assumes the well known form

$$L_{ij} = \frac{\epsilon + 2\epsilon_0}{3\epsilon_0} \delta_{ij} = L \delta_{ij} \quad (15b)$$

We now proceed to consider the case when the external electric field E^0 is very strong, causing the potential energy of the sample to be a nonlinear function of E . This can be expressed, to sufficient accuracy [102], as follows:

$$U(\Gamma, E) = U(\Gamma, 0) - M_i^0(\Gamma)E_i^0 - \frac{1}{2}A_{ij}(\Gamma)E_i^0E_j^0 - \frac{1}{6}B_{ijk}(\Gamma)E_i^0E_j^0E_k^0 - \frac{1}{24}C_{ijkl}(\Gamma)E_i^0E_j^0E_k^0E_l^0 - \dots \quad (16)$$

Above, $U(\Gamma, 0)$ is the potential energy of the sample at the configuration Γ in the absence of an external field. M_i^0 is the electric dipole moment component of the sample at $E^0 = 0$, and A_{ij} its linear electric polarizability tensor. The tensors B_{ijk} and C_{ijkl} of ranks three and four define, respectively, nonlinear polarizabilities of orders two and three.

By definition, the vector of dipolar polarisation of the sample of volume V is

$$P(E) = \frac{1}{V} \int M(\Gamma, E) f(\Gamma, E) d\Gamma \quad (17)$$

where, to an accuracy of the third order of approximation, the component of the total electric dipole moment in the presence of a strong external electric field is [102]

$$M_i(\Gamma, E) = M_i^0(\Gamma) + A_{ij}(\Gamma)E_j^0 + \frac{1}{2}B_{ijk}(\Gamma)E_j^0E_k^0 + \frac{1}{6}C_{ijkl}(\Gamma)E_j^0E_k^0E_l^0 + \dots \quad (18)$$

If, when acted on by the d.c. electric field E , the system is in thermodynamic equilibrium, its statistical distribution function is given by Gibb's formula

$$f(\Gamma, E) = \frac{\exp[-\beta U(\Gamma, E)]}{\int \exp[-\beta U(\Gamma, E)] d\Gamma} \quad (19)$$

where $\beta = (kT)^{-1}$.

Now we consider the situation which exists when the system is acted on by a time-variable electric field (8) and is thus no longer in thermodynamic equilibrium. Its behaviour in time can no longer be described by the Gibbs distribution function (19). The explicit determination of the time-dependent distribution function of the system for the case under consideration is in general not at all easy. Nevertheless, by analogy to the statistical perturbation expansion in powers of βU of the Gibbs function (19) with the energy (18) one can write, for a time-dependent

perturbation of the form (8), to an accuracy of the third approximation,

$$\begin{aligned}
 f[\Gamma, \mathbf{E}(t)] = & f(\Gamma, 0) + \sum_a f_i^{(1)}(\Gamma, \omega_a) E_i^0(\omega_a) \exp(-i\omega_a t) \\
 & + \sum_{ab} [f_{ij}^{(1)}(\Gamma, \omega_{ab}) + f_{ij}^{(2)}(\Gamma, \omega_{ab})] E_i^0(\omega_a) E_j^0(\omega_b) \exp(-i\omega_{ab} t) \\
 & + \sum_{abc} [f_{ijk}^{(1)}(\Gamma, \omega_{abc}) + f_{ijk}^{(2)}(\Gamma, \omega_{abc}) + f_{ijk}^{(3)}(\Gamma, \omega_{abc})] \\
 & \times E_i^0(\omega_a) E_j^0(\omega_b) E_k^0(\omega_c) \exp(-i\omega_{abc} t) + \dots
 \end{aligned} \tag{20}$$

where, for brevity,

$$\omega_{ab} = \omega_a + \omega_b, \quad \omega_{abc} = \omega_a + \omega_b + \omega_c \tag{20a}$$

In general form, the tensors of the successive perturbations of the distribution function (20) cannot be derived simply. We begin by writing them for the case when the system is in thermodynamic equilibrium obtained by (16) and (19)

$$\begin{aligned}
 f_i^{(1)}(\Gamma, 0) &= \beta f(\Gamma, 0) M_i^0(\Gamma), & f_{ij}^{(1)}(\Gamma, 0) &= \frac{\beta}{2} f(\Gamma, 0) \Delta A_{ij}(\Gamma) \\
 f_{ij}^{(2)}(\Gamma, 0) &= \frac{\beta^2}{2} f(\Gamma, 0) \Delta \{M_i^0(\Gamma) M_j^0(\Gamma)\}, & f_{ijk}^{(1)}(\Gamma, 0) &= \frac{\beta}{6} f(\Gamma, 0) B_{ijk}(\Gamma) \\
 f_{ijk}^{(2)}(\Gamma, 0) &= \frac{\beta^2}{2} f(\Gamma, 0) M_i(\Gamma) \Delta A_{jk}(\Gamma) \\
 f_{ijk}^{(3)}(\Gamma, 0) &= \frac{\beta^3}{6} f(\Gamma, 0) [M_i(\Gamma) M_j(\Gamma) M_k(\Gamma) - 3M_i(\Gamma) \langle M_j(\Gamma) M_k(\Gamma) \rangle]
 \end{aligned} \tag{21}$$

where ΔA_{ij} and $\Delta(M_i M_j)$ are, respectively, fluctuations of the polarizability tensor and the product of dipole moments

$$\Delta A_{ij} = A_{ij} - \langle A_{ij} \rangle, \quad \Delta(M_i M_j) = M_i M_j - \langle M_i M_j \rangle$$

the symbol $\langle \rangle$ denoting here a statistical average with the unperturbed distribution function $f(\Gamma, 0)$. The expansion (20) for $\omega_a = \omega_b = \omega_c = 0$, in conjunction with the tensors (21), represents the distribution function expansion for the case of a static electric field.

Later we shall show that the frequency-dependent tensors of successive perturbations $f_i^{(1)}(\omega_a), \dots, f_{ijk}^{(3)}(\omega_{abc})$ can be found in explicit form for the simple model of rotational diffusion. At the present stage, we shall assume their analytic form as known. This will enable us to write the nonlinear polarization in the third approximation, using the definition (17) and the function (20), as follows:

$$P_i^{(3)}[\mathbf{E}(t)] = \sum_{abc} \chi_{ijkl}^{\omega_{abc}}(\omega_a, \omega_b, \omega_c) E_j(\omega_a) E_k(\omega_b) E_l(\omega_c) \exp(-i\omega_{abc} t) \tag{22}$$

We have introduced above the tensor of the third-order nonlinear polarizability

of the isotropic medium

$$\chi_{ijkl}^{\omega abc}(\omega_a, \omega_b, \omega_c) = \frac{1}{6V} L_{ix}^{\omega abc} L_{j\beta}^{\omega a} L_{k\gamma}^{\omega b} L_{l\delta}^{\omega c} \langle C_{\alpha\beta\gamma\delta}^{\omega abc}(\omega_a, \omega_b, \omega_c) \rangle \quad (22a)$$

In deriving the expressions (22) and (22a) we had recourse to the tensor relation (14) between the fields, since in general an isotropic medium subject to the action of a strong electric field presents a tensorial electric permittivity. In particular, for a spherical sample, and on neglecting induced anisotropy of the electric permittivity, we can assume the isotropic relation (15b); then (22a) reduces to

$$\chi_{ijkl}^{\omega abc}(\omega_a, \omega_b, \omega_c) = \frac{1}{6V} L^{\omega abc} L^{\omega a} L^{\omega b} L^{\omega c} \langle C_{ijkl}^{\omega abc}(\omega_a, \omega_b, \omega_c) \rangle \quad (23)$$

III. THE TENSOR OF THIRD-ORDER NONLINEAR POLARIZABILITY

By the expansions (16), (18) and (20), the mean statistical value of the tensor of nonlinear polarizability of order three can be expressed in the form

$$\langle C_{ijkl}^{\omega abc} \rangle = \langle C_{ijkl}^{\omega abc} \rangle^{(0)} + \langle C_{ijkl}^{\omega abc} \rangle^{(1)} + \langle C_{ijkl}^{\omega abc} \rangle^{(2)} + \langle C_{ijkl}^{\omega abc} \rangle^{(3)} + \dots \quad (24)$$

Above, we have in explicit form for successive contributions, in accordance with increasing powers of β in (21)

$$\langle C_{ijkl}^{\omega abc} \rangle^{(0)} = \int C_{ijkl}(\Gamma, -\omega_{abc}, \omega_a, \omega_b, \omega_c) f^{(0)}(\Gamma, 0) d\Gamma \quad (25)$$

$$\begin{aligned} \langle C_{ijkl}^{\omega abc} \rangle^{(1)} = \int [& 3B_{ijk}(\Gamma, -\omega_{abc}, \omega_a, \omega_b) f_l^{(1)}(\Gamma, \omega_c) \\ & + 6A_{ij}(\Gamma, -\omega_{abc}, \omega_a) f_{kl}^{(1)}(\Gamma, \omega_b, \omega_c) \\ & + 6M_i(\Gamma, -\omega_{abc}) f_{jkl}^{(1)}(\Gamma, \omega_a, \omega_b, \omega_c)] d\Gamma \end{aligned} \quad (26)$$

$$\begin{aligned} \langle C_{ijkl}^{\omega abc} \rangle^{(2)} = 6 \int [& A_{ij}(\Gamma, -\omega_{abc}, \omega_a) f_{kl}^{(2)}(\Gamma, \omega_b, \omega_c) \\ & + M_i^0(\Gamma, -\omega_{abc}) f_{jkl}^{(2)}(\Gamma, \omega_a, \omega_b, \omega_c)] d\Gamma \end{aligned} \quad (27)$$

$$\langle C_{ijkl}^{\omega abc} \rangle^{(3)} = 6 \int M_i^0(\Gamma, -\omega_{abc}) f_{jkl}^{(3)}(\Gamma, \omega_a, \omega_b, \omega_c) d\Gamma \quad (28)$$

Recently, Bedaux and Bloembergen [110] carried out an analysis of the relationship between the macroscopic nonlinear susceptibility $\chi^{(3)}$ and microscopic polarizability $\alpha^{(3)}$ at optical frequencies, taking spatial dispersion into account. They used the method of the local Lorentz field; that is to say, they employed a procedure that is different from the semi-macroscopic method used here. In the semi-macroscopic approach, we begin by finding macroscopic corrections of the

form (15) resulting from the phenomenological relation (14), which, for time-variable fields, has to be written as

$$E_i^0(\mathbf{r}, t) = L_{ij}(\omega, \mathbf{k})E_j(\mathbf{r}, t) \quad (14a)$$

This expression is dependent, besides the frequency ω , on the wave propagation vector \mathbf{k} , describing spatial dispersion of the electric permittivity tensor [111] $\varepsilon_{ij}(\omega, \mathbf{k})$. In the second step, the macroscopic corrections are found by a molecular statistical analysis of the nonlinear polarizability tensor (24); thus, for the dipole moment of a dense medium in the absence of external fields, we write the expansion [18, 102, 112]

$$M_i^0(\Gamma) = \sum_{p=1}^N [m_i^{(p)} + a_{ij}^{(p)}F_j(\mathbf{r}_p, t) + \frac{1}{2}b_{ijk}^{(p)}F_j(\mathbf{r}_p, t)F_k(\mathbf{r}_p, t) + \frac{1}{6}c_{ijkl}^{(p)}F_j(\mathbf{r}_p, t)F_k(\mathbf{r}_p, t)F_l(\mathbf{r}_p, t) + \dots] \quad (29)$$

where $\mathbf{m}^{(p)}$ is the permanent dipole moment of the p th molecule of the medium, which is taken as consisting of N molecules. The other tensors of (29) describe linear and nonlinear electric polarizabilities of the p th molecule. The electric field existing at the point \mathbf{r}_p of the latter due to the electric charges of all the other $N-1$ molecules of the medium is, in the dipole approximation,

$$F_i(\mathbf{r}_p, t) = \sum_{q \neq p}^N T_{ij}^{(pq)} m_j^{(q)}(\mathbf{r}_q, t) \quad (30)$$

where

$$T_{ij}^{(pq)} = -(\nabla_i \nabla_j + k^2 \delta_{ij}) r_{pq}^{-1} \exp(i\mathbf{k} \cdot \mathbf{r}_{pq}) \quad (31)$$

is the dipole interaction tensor between molecules p and q , distant by \mathbf{r}_{pq} . Similarly to (29), we write expansions for the tensors A_{ij} , B_{ijk} and C_{ijkl} .

However, we are not concerned here with the calculation of corrections arising from the molecular fields (30), and so we restrict our considerations to macroscopic corrections of the form (15) and (15b). It should nevertheless be noted that Bedaux and Bloembergen [115] did not consider the temperature-dependent terms (26–28).

In the isotropic case we can perform an unweighted averaging on (25). To this aim, we carry out a transformation of the nonlinear polarizability tensor

$$C_{ijkl} = c_{i\alpha} c_{j\beta} c_{k\gamma} c_{l\delta} C_{\alpha\beta\gamma\delta}$$

where the $c_{i\alpha}$ are cosines of the angles between the axes $i = X, Y, Z$ of the laboratory coordinate system and the axes $\alpha = 1, 2, 3$ of mobile coordinates, rigidly attached to the body. On performing the unweighted averaging we obtain [114]

$$\langle c_{i\alpha} c_{j\beta} c_{k\gamma} c_{l\delta} \rangle_{\Omega} = \frac{1}{30} \begin{pmatrix} \delta_{ij} & \delta_{kl} \\ \delta_{ik} & \delta_{jl} \\ \delta_{il} & \delta_{jk} \end{pmatrix}^T \begin{pmatrix} 4 & -1 & -1 \\ -1 & 4 & -1 \\ -1 & -1 & 4 \end{pmatrix} \begin{pmatrix} \delta_{\alpha\beta} & \delta_{\gamma\delta} \\ \delta_{\alpha\gamma} & \delta_{\beta\delta} \\ \delta_{\alpha\delta} & \delta_{\beta\gamma} \end{pmatrix} \quad (32)$$

hence, using (25) and (32), we have

$$\langle C_{ijkl}^{\omega abc} \rangle^{(0)} = C_{xxyy}^{\omega abc} \delta_{ij} \delta_{kl} + C_{xyxy}^{\omega abc} \delta_{ik} \delta_{jl} + C_{xyyx}^{\omega abc} \delta_{il} \delta_{jk} \quad (25a)$$

with the notation

$$C_{xxyy}^{\omega abc} = \frac{1}{30} \langle 4C_{\alpha\alpha\beta\beta}^{\omega abc} - C_{\alpha\beta\alpha\beta}^{\omega abc} - C_{\alpha\beta\beta\alpha}^{\omega abc} \rangle \quad (33)$$

The other two components of (25a) are obtained by an appropriate interchange of the indices $x\alpha$ and $y\beta$ in (33).

One notes that, in the zeroth approximation, the tensor of third-order non-linear polarizability is dependent on high frequencies and also, but very weakly, on molecular redistribution [18, 29].

In particular, if $C_{\alpha\beta\gamma\delta}$ is a completely symmetric tensor, as is the case in the absence of electron dispersion and absorption, one has

$$C_{xxyy} = C_{xyxy} = C_{xyyx} = \frac{1}{15} \langle C_{\alpha\alpha\beta\beta} \rangle = \frac{1}{3} C_{xxxx} \quad (33a)$$

To carry out the averaging of the temperature contributions (26)–(28), we need to know how the tensors (21) of the distribution function (20) depend on frequency. The problem will be solved using the Debye rotational diffusion model in Sect. V of this paper. But here we shall calculate the tensors (26)–(28) for the static field case, when use can be made of expressions (21). On the assumption of complete symmetricity of all polarizability tensors ($\omega_a = \omega_b = \omega_c = 0$), we obtain

$$\begin{aligned} \langle C_{ijkl} \rangle^{(1)} = & \frac{\beta}{30} [90 \langle (\Delta A)^2 \rangle \delta_{ij} \delta_{kl} + 2 \langle 3B_{\alpha\alpha\beta} M_\beta + M_\alpha B_{\alpha\beta\beta} \rangle \sigma_{ijkl} \\ & + \langle 3A_{\alpha\beta} A_{\alpha\beta} - A_{\alpha\alpha} A_{\beta\beta} \rangle \mathcal{H}_{ijkl}] \end{aligned} \quad (26a)$$

$$\begin{aligned} \langle C_{ijkl} \rangle^{(2)} = & \frac{2\beta^2}{15} [15 \langle \Delta A \Delta M^2 \rangle \delta_{ij} \delta_{kl} \\ & + \langle 3A_{\alpha\beta} M_\alpha M_\beta - A_{\alpha\alpha} M_\beta M_\beta \rangle \mathcal{H}_{ijkl}] \end{aligned} \quad (27a)$$

$$\langle C_{ijkl} \rangle^{(3)} = \frac{\beta^3}{15} [5 \langle (\Delta M^2)^2 \rangle \delta_{ij} \delta_{kl} - \langle M^4 \rangle \eta_{ijkl}] \quad (28a)$$

where we have introduced the following unit tensor operators:

$$\begin{aligned} \sigma_{ijkl} &= \delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} \\ \mathcal{H}_{ijkl} &= 3\delta_{ik} \delta_{jl} + 3\delta_{il} \delta_{jk} - 2\delta_{ij} \delta_{kl} \\ \eta_{ijkl} &= 4\delta_{ij} \delta_{kl} - \delta_{ik} \delta_{jl} - \delta_{il} \delta_{jk} \end{aligned} \quad (34)$$

and

$$A = A_{\alpha\alpha}/3, \quad M^2 = M_\alpha M_\alpha$$

Thus, in the semi-macroscopic approach, each of the temperature contributions (26a)–(28a) consists of an isotropic part, which is related to fluctuations of

the polarizability or the dipole moment of the medium, and several anisotropic parts, which are strongly dependent on various angular molecular correlations [18].

IV. NONLINEAR ELECTRON DISPERSION

Consider a molecular system, composed of n electrons, the s th electron having the mass m_s , electric charge e_s and radius vector \mathbf{r}_s . In the classical theory of Lorentz, the equation of motion of the electron is of the form

$$m_s \frac{d^2 \mathbf{r}_s(t)}{dt^2} + m_s \Gamma_s \frac{d\mathbf{r}_s(t)}{dt} = \mathbf{f}_s^L + \mathbf{f}_s^B \quad (35)$$

Quite generally, the electron is acted on by a Lorentz force

$$\mathbf{f}_s^L(\mathbf{r}, t) = e_s \left[\mathbf{E}(\mathbf{r}, t) + \frac{1}{c} \frac{d\mathbf{r}_s(t)}{dt} \times \mathbf{H}(\mathbf{r}, t) \right] \quad (36)$$

$\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{H}(\mathbf{r}, t)$ denoting the electric and magnetic electromagnetic field vectors in the space-time point (\mathbf{r}, t) .

In accordance with Voigt's hypothesis [71], the electron is bound to the centre of the microsystem by the anharmonic force

$$\mathbf{f}_{si}^B(\mathbf{r}, t) = \alpha_{ij}^{(s)} r_{si}(t) + \frac{1}{2} \beta_{ijk}^{(s)} r_{si}(t) r_{sk}(t) + \frac{1}{6} \gamma_{ijkl}^{(s)} r_{si}(t) r_{sk}(t) r_{sl}(t) + \dots \quad (37)$$

where $\alpha_{ij}^{(s)}$ are harmonic and $\beta_{ijk}^{(s)}$, $\gamma_{ijkl}^{(s)}$ anharmonic vibrations of the s th electron.

In the absence of damping forces ($\Gamma_s = 0$) and of the Lorentz force (36), the electronic oscillator performs harmonic vibrations

$$\alpha_{ij}^{(s)} = -m_s \omega_s^2 \delta_{ij} \quad (38)$$

at the circular vibration frequency ω_s .

In the presence of a Lorentz force with a time dependence of the form (8), the electron performs forced vibrations with the fundamental frequency ω_a and sum frequencies (20a), i.e.

$$\begin{aligned} r_{si}(t) = & \sum_a r_{si}(\omega_a) \exp(-i\omega_a t) + \sum_{ab} r_{si}(\omega_{ab}) \exp(-i\omega_{ab} t) \\ & + \sum_{abc} r_{si}(\omega_{abc}) \exp(-i\omega_{abc} t) + \dots \end{aligned} \quad (39)$$

Our solution will be restricted to the electric part of the Lorentz force (36) (the magnetic field has been considered in Refs. 85, 86); hence, by (35)–(39) and (8), we obtain

$$\begin{aligned} r_{si}(\omega_a) &= e_s D_s(\omega_a) E_i(\omega_a) \\ r_{si}(\omega_{ab}) &= \frac{1}{2} \beta_{ijk}^{(s)} D_s(\omega_{ab}) r_{sj}(\omega_a) r_{sk}(\omega_b) \\ r_{si}(\omega_{abc}) &= \frac{1}{6} \{ 3\beta_{ijk}^{(s)} [r_{sj}(\omega_a) r_{sk}(\omega_{bc}) + r_{sj}(\omega_{ab}) r_{sk}(\omega_c)] \\ & \quad + \gamma_{ijkl}^{(s)} r_{sj}(\omega_a) r_{sk}(\omega_b) r_{sl}(\omega_c) \} D_s(\omega_{abc}) \end{aligned} \quad (40)$$

where we have introduced the complex electron dispersion functions

$$\begin{aligned} D_s^{-1}(\omega_a) &= m_s(\omega_s^2 - \omega_a^2 - i\omega_a\Gamma_s) \\ D_s^{-1}(\omega_{ab}) &= m_s[\omega_s^2 - (\omega_a + \omega_b)^2 - i(\omega_a + \omega_b)\Gamma_s] \\ D_s^{-1}(\omega_{abc}) &= m_s\{\omega_s^2 - (\omega_a + \omega_b + \omega_c)^2 - i(\omega_a + \omega_b + \omega_c)\Gamma_s\} \end{aligned} \quad (41)$$

Since, by definition, the total induced electric dipole moment of the molecule is

$$\mathbf{p}(t) = \sum_{s=1}^n e_s \mathbf{r}_s(t) \quad (42)$$

we obtain, by (39),

$$\begin{aligned} \mathbf{p}(t) &= \sum_a \mathbf{p}^{(1)}(\omega_a) \exp(-i\omega_a t) + \sum_{ab} \mathbf{p}^{(2)}(\omega_{ab}) \exp(-\omega_{ab} t) \\ &\quad + \sum_{abc} \mathbf{p}^{(3)}(\omega_{abc}) \exp(-i\omega_{abc} t) + \dots \end{aligned} \quad (43)$$

where the dipole moment components of successive orders are

$$\begin{aligned} p_i^{(1)}(\omega_a) &= a_{ij}^{\omega_a}(\omega_a) E_j^0(\omega_a) \\ p_i^{(2)}(\omega_{ab}) &= \frac{1}{2} b_{ijk}^{\omega_{ab}}(\omega_a, \omega_b) E_j^0(\omega_a) E_k^0(\omega_b) \\ p_i^{(3)}(\omega_{abc}) &= \frac{1}{6} c_{ijkl}^{\omega_{abc}}(\omega_a, \omega_b, \omega_c) E_j^0(\omega_a) E_k^0(\omega_b) E_l^0(\omega_c) \end{aligned} \quad (44)$$

The tensors of the linear electron polarizability and nonlinear electron polarizabilities of the molecule are expressed as follows:

$$a_{ij}^{\omega_a}(\omega_a) = \sum_{s=1}^n e_s^2 D_s(\omega_a) \delta_{ij} \quad (45)$$

$$b_{ijk}^{\omega_{ab}}(\omega_a, \omega_b) = \sum_{s=1}^n e_s^3 D_s(\omega_a) D_s(\omega_b) D_s(\omega_{ab}) \beta_{ijk}^{(s)} \quad (46)$$

$$\begin{aligned} c_{ijkl}^{\omega_{abc}}(\omega_a, \omega_b, \omega_c) &= \frac{1}{2} \sum_{s=1}^n e_s^4 [3\beta_{iml}^{(s)} \beta_{mjk}^{(s)} D_s(\omega_{ab}) + 3\beta_{ijm}^{(s)} \beta_{mkl}^{(s)} D_s(\omega_{bc}) \\ &\quad + 2\gamma_{ijkl}^{(s)}] D_s(\omega_a) D_s(\omega_b) D_s(\omega_c) D_s(\omega_{abc}) \end{aligned} \quad (47)$$

Once it is known how these molecular polarizability tensors depend on high (optical) frequencies, we are in a position to determine the electron dispersion and absorption of the macroscopic polarizability tensors of eqns. (25)–(27). In fact, high-frequency dispersion, which is due to electron processes being practically independent of molecular correlations, can be written, to a very good approximation, for a medium of N molecules

$$\begin{aligned} A_{ij}^{\omega_a}(\Gamma, \omega_a) &= \sum_{p=1}^N a_{ij}^{\omega_a}(\Gamma_p, \omega_a) \\ B_{ijk}^{\omega_{ab}}(\Gamma, \omega_a, \omega_b) &= \sum_{p=1}^N b_{ijk}^{\omega_{ab}}(\Gamma_p, \omega_a, \omega_b) \\ C_{ijkl}^{\omega_{abc}}(\Gamma, \omega_a, \omega_b, \omega_c) &= \sum_{p=1}^N c_{ijkl}^{\omega_{abc}}(\Gamma_p, \omega_a, \omega_b, \omega_c) \end{aligned} \quad (48)$$

On the assumption that all N molecules in V are of one species, the sum of eqn. (48) can simply be replaced by N . Thus, formulae (45)–(48) describe linear and non-linear electron dispersion and absorption by resolution of the complex functions (41) and their products into real and imaginary parts.

V. TIME-DEPENDENT DISTRIBUTION FUNCTION IN THE ROTATIONAL DIFFUSION MODEL

On Debye's model [1], the time-dependent distribution function can be determined from the kinetic equation of diffusion

$$\frac{\partial f(\Gamma, t)}{\partial t} = D_{ij} \{ \nabla_i \nabla_j f(\Gamma, t) + \beta [\nabla_i f(\Gamma, t) \nabla_j U(\Gamma, t) + f(\Gamma, t) \nabla_i \nabla_j U(\Gamma, t)] \} \quad (49)$$

with D_{ij} the second rank symmetric diffusion tensor and ∇_i the operator of spatial differentiation.

Its solution with a potential energy of the form (16) with field (9), and successive perturbations of the distribution function in the form (21), is highly complex. We accordingly simplify it to the case when no molecular correlations or statistical fluctuations are present in the system and the dipolar molecules are symmetric about their s -axis. For axially symmetric molecules, the dipole moment and polarizability tensors can be expressed as follows:

$$\begin{aligned} m_i &= m s_i, & a_{ij} &= a \delta_{ij} + \frac{1}{3} \gamma (3 s_i s_j - \delta_{ij}) \\ b_{ijk} &= \frac{1}{5} \{ 3 b (s_i \delta_{jk} + s_j \delta_{ki} + s_k \delta_{ij}) + \kappa (5 s_i s_j s_k - s_i \delta_{jk} - s_j \delta_{ki} - s_k \delta_{ij}) \} \end{aligned} \quad (50)$$

where we have denoted the mean polarizabilities and anisotropies of linear and nonlinear polarizability as

$$\begin{aligned} a &= (a_{33} + 2 a_{11})/3, & \gamma &= a_{33} - a_{11} \\ b &= (b_{333} + 2 b_{113})/3, & \kappa &= b_{333} - 3 b_{113} \end{aligned} \quad (51)$$

With regard to eqn. (50), the distribution functions of the successive approximations (21) are dependent on the polar angle ϑ ; when solving eqn. (49), this enables us to restrict ourselves to the part describing rotational motion of axially symmetric molecules, in accordance with the Debye model

$$\begin{aligned} \frac{\partial f(\vartheta, t)}{\partial t} &= D_R \left\{ \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial f}{\partial t} \right) \right. \\ &\quad \left. + \beta \left[\frac{\partial U}{\partial \vartheta} \frac{\partial f}{\partial \vartheta} + \frac{f}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left(\sin \vartheta \frac{\partial U}{\partial \vartheta} \right) \right] \right\} \end{aligned} \quad (52)$$

On taking into account (16) and (21) for the case (50) and the field (8), we

derive a solution of eqn. (52) in the form (20), with

$$\begin{aligned}
 f_i^{(1)}(\Gamma, \omega_a) &= \beta f(\Gamma, 0) m(\omega_a) \tilde{R}_1(\omega_a) s_i \\
 f_{ij}^{(1)}(\Gamma, \omega_{ab}) &= \frac{\beta}{6} f(\Gamma, 0) \gamma(\omega_a, \omega_b) \tilde{R}_2(\omega_{ab}) (3s_i s_j - \delta_{ij}) \\
 f_{ij}^{(2)}(\Gamma, \omega_{ab}) &= \frac{\beta^2}{6} f(\Gamma, 0) m(\omega_a) m(\omega_b) \tilde{R}_1(\omega_a) \tilde{R}_2(\omega_{ab}) (3s_i s_j - \delta_{ij}) \\
 f_{ijk}^{(1)}(\Gamma, \omega_{abc}) &= \frac{\beta}{30} f(\Gamma, 0) \{3b(\omega_a, \omega_b, \omega_c) \tilde{R}_1(\omega_{abc}) (s_i \delta_{jk} + s_j \delta_{ki} + s_k \delta_{ij}) \\
 &\quad + \kappa(\omega_a, \omega_b, \omega_c) \tilde{R}_3(\omega_{abc}) [5s_i s_j s_k - (s_i \delta_{jk} + s_j \delta_{ki} + s_k \delta_{ij})]\} \\
 f_{ijk}^{(2)}(\Gamma, \omega_{abc}) &= \frac{\beta^2}{6} f(\Gamma, 0) m(\omega_a) \gamma(\omega_b, \omega_c) [3\tilde{R}_3(\omega_{abc}) s_i s_j s_k - \tilde{R}_1(\omega_{abc}) s_i \delta_{jk}] \\
 f_{ijk}^{(3)}(\Gamma, \omega_{abc}) &= \frac{\beta^3}{6} f(\Gamma, 0) m(\omega_a) m(\omega_b) m(\omega_c) \{\tilde{S}_3(\omega_{abc}) s_i s_j s_k - \tilde{S}_1(\omega_{abc}) s_i \delta_{jk}\}
 \end{aligned} \tag{53}$$

Above, the following complex relaxation functions have been introduced:

$$\begin{aligned}
 \tilde{R}_1(\omega_a) &= (1 - i\omega_a \tau_1)^{-1} \\
 \tilde{R}_2(\omega_{ab}) &= \{1 - i(\omega_a + \omega_b) \tau_2\}^{-1} \\
 \tilde{R}_3(\omega_{abc}) &= \{1 - i(\omega_a + \omega_b + \omega_c) \tau_3\}^{-1} \\
 \tilde{R}_1(\omega_{abc}) &= \{1 - i(\omega_a + \omega_b + \omega_c) \tau_1\}^{-1}
 \end{aligned} \tag{54}$$

involving successively higher and higher rotational relaxation times, defined by eqn. (13) with $n = 1, 2, 3, \dots$

The tensors of the distribution function (53) contain the following relaxation functions:

$$\begin{aligned}
 \tilde{K}_1(\omega_{abc}) &= \{6\tilde{R}_1(\omega_a)[1 - \tilde{R}_3(\omega_{abc})] + \tilde{R}_2(\omega_{bc})[4 - 3\tilde{R}_3(\omega_{abc})]\} \tilde{R}_1(\omega_{abc}) \\
 \tilde{K}_3(\omega_{abc}) &= \frac{1}{3}[2\tilde{R}_1(\omega_a) + \tilde{R}_2(\omega_{bc})] \tilde{R}_3(\omega_{abc})
 \end{aligned} \tag{55}$$

$$\begin{aligned}
 \tilde{S}_1(\omega_{abc}) &= \tilde{R}_1(\omega_a) \tilde{R}_2(\omega_{ab}) [4 - 3\tilde{R}_3(\omega_{abc})] \tilde{R}_1(\omega_{abc}) \\
 \tilde{S}_3(\omega_{abc}) &= \tilde{R}_1(\omega_a) \tilde{R}_2(\omega_{ab}) \tilde{R}_3(\omega_{abc})
 \end{aligned} \tag{56}$$

VI. RELAXATIONAL CONTRIBUTIONS TO NONLINEAR POLARIZABILITY

Knowing explicitly the frequency dependence of the distribution function tensors in (53), we can proceed to calculate the relaxation temperature contributions (26)–(28) for a fluid with N axially symmetric molecules immersed in it. On taking the unweighted averages of the unit vectors [19]

$$\langle s_i s_j \rangle_\Omega = \frac{1}{3} \delta_{ij}, \quad \langle s_i s_j s_k s_l \rangle_\Omega = \frac{1}{15} \sigma_{ijkl} \tag{57}$$

and on insertion of (53) into the tensors (26)–(28), we get in the absence of angular correlations

$$\begin{aligned} \langle C_{ijkl}^{\omega abc} \rangle^{(1)} = & \frac{\beta N}{15} \{ 3[3b(-\omega_{abc}, \omega_a, \omega_b)m(\omega_c)\tilde{R}_1(\omega_c) \\ & + m(-\omega_{abc})b(\omega_a, \omega_b, \omega_c)\tilde{R}_1(\omega_{abc})]\sigma_{ijkl} \\ & + \gamma(-\omega_{abc}, \omega_a)\gamma(\omega_b, \omega_c)\tilde{R}_2(\omega_{bc})\mathcal{H}_{ijkl} \} \end{aligned} \quad (58)$$

$$\begin{aligned} \langle C_{ijkl}^{\omega abc} \rangle^{(2)} = & \frac{\beta^2 N}{15} \{ \gamma(-\omega_{abc}, \omega_a)m(\omega_b)m(\omega_c)\tilde{R}_1(\omega_a)\tilde{R}_2(\omega_{bc})\mathcal{H}_{ijkl} \\ & + m(-\omega_{abc})m(\omega_a)\gamma(\omega_b, \omega_c)[3\tilde{K}_3(\omega_{abc})\sigma_{ijkl} \\ & - 5\tilde{K}_1(\omega_{abc})\delta_{ij}\delta_{kl}] \} \end{aligned} \quad (59)$$

$$\begin{aligned} \langle C_{ijkl}^{\omega abc} \rangle^{(3)} = & \frac{\beta^3 N}{15} m(-\omega_{abc})m(\omega_a)m(\omega_b)m(\omega_c) \\ & \times [\tilde{S}_3(\omega_{abc})\sigma_{ijkl} - 5\tilde{S}_1(\omega_{abc})\delta_{ij}\delta_{kl}] \end{aligned} \quad (60)$$

with the tensors σ_{ijkl} and \mathcal{H}_{ijkl} defined by (34).

For $\omega_a = \omega_b = \omega_c = 0$, all relaxation functions (54), (55) and (56) become equal to unity and the contributions (58)–(60) are particularizations of the expressions (26a)–(28a) for the case of axially symmetric molecules in the absence of statistical fluctuations and molecular correlations.

For the isotropic body, the well-known relation for the third-order nonlinear susceptibility tensor holds [88]

$$\chi_{xxxx}^{(3)} = \chi_{xxyy}^{(3)} + \chi_{xyxy}^{(3)} + \chi_{xyyx}^{(3)} \quad (61)$$

thus with regard to (23) an identical relation is valid for the tensor of nonlinear polarizability

$$\langle C_{xxxx}^{\omega abc} \rangle = \langle C_{xxyy}^{\omega abc} \rangle + \langle C_{xyxy}^{\omega abc} \rangle + \langle C_{xyyx}^{\omega abc} \rangle \quad (62)$$

In the zeroth approximation, we obtain by (25a), (33) and (48), in the absence of molecular correlations,

$$\langle C_{xxxx}^{\omega abc} \rangle^{(0)} = \frac{N}{15} (c_{\alpha\alpha\beta\beta}^{\omega abc} + c_{\alpha\beta\alpha\beta}^{\omega abc} + c_{\alpha\beta\beta\alpha}^{\omega abc}) \quad (63)$$

In this approximation, the tensor of nonlinear polarizability is not directly affected by processes of rotational molecular relaxation. The expressions (63) can be written out explicitly for specific molecular symmetries, for which the nonzero and mutually independent tensor elements $c_{\alpha\beta\gamma\delta}$ are known in full [18, 115].

The relaxation contributions (58)–(60) derived above for axially symmetric molecules also satisfy the relation (62). With regard to (58), we have

$$\begin{aligned}
\langle C_{xxyy}^{\omega_{abc}} \rangle^{(1)} &= \frac{\beta N}{15} \{ 3[3b(-\omega_{abc}, \omega_a, \omega_b)m(\omega_c)\tilde{R}_1(\omega_c) \\
&\quad + m(-\omega_{abc})b(\omega_a, \omega_b, \omega_c)\tilde{R}_1(\omega_{abc})] \\
&\quad - 2\gamma(-\omega_{abc}, \omega_a)\gamma(\omega_b, \omega_c)\tilde{R}_2(\omega_{bc}) \} \\
\langle C_{xyxy}^{\omega_{abc}} \rangle^{(1)} &= \langle C_{xyyx}^{\omega_{abc}} \rangle^{(1)} \\
&= \frac{\beta N}{5} [3b(-\omega_{abc}, \omega_a, \omega_b)m(\omega_c)\tilde{R}_1(\omega_c) \\
&\quad + m(-\omega_{abc})b(\omega_a, \omega_b, \omega_c)\tilde{R}_1(\omega_{abc}) \\
&\quad + \gamma(-\omega_{abc}, \omega_a)\gamma(\omega_b, \omega_c)\tilde{R}_2(\omega_{bc})] \tag{58a}
\end{aligned}$$

hence

$$\begin{aligned}
\langle C_{xxxx}^{\omega_{abc}} \rangle^{(1)} &= \frac{\beta N}{15} \{ 9[3b(-\omega_{abc}, \omega_a, \omega_b)m(\omega_c)\tilde{R}_1(\omega_c) \\
&\quad + m(-\omega_{abc})b(\omega_a, \omega_b, \omega_c)\tilde{R}_1(\omega_{abc})] \\
&\quad + 4\gamma(-\omega_{abc}, \omega_a)\gamma(\omega_b, \omega_c)\tilde{R}_2(\omega_{bc}) \} \tag{64}
\end{aligned}$$

Similarly, in the second approximation, we have by (59)

$$\begin{aligned}
\langle C_{xxyy}^{\omega_{abc}} \rangle^{(2)} &= -\frac{\beta^2 N}{15} \{ 2\gamma(-\omega_{abc}, \omega_a)m(\omega_b)m(\omega_c)R_1(\omega_b)R_2(\omega_{bc}) \\
&\quad + m(-\omega_{abc})m(\omega_a)\gamma(\omega_b, \omega_c)[5\tilde{K}_1(\omega_{abc}) - 3\tilde{K}_3(\omega_{abc})] \} \\
\langle C_{xyxy}^{\omega_{abc}} \rangle^{(2)} &= \langle C_{xyyx}^{\omega_{abc}} \rangle^{(2)} \\
&= \frac{\beta^2 N}{5} [\gamma(-\omega_{abc}, \omega_a)m(\omega_b)m(\omega_c)\tilde{R}_1(\omega_b)\tilde{R}_2(\omega_{bc}) \\
&\quad + m(-\omega_{abc})m(\omega_a)\gamma(\omega_b, \omega_c)\tilde{K}_3(\omega_{abc})] \tag{59a}
\end{aligned}$$

yielding, on insertion into (62),

$$\begin{aligned}
\langle C_{xxxx}^{\omega_{abc}} \rangle^{(2)} &= \frac{4\beta^2 N}{15} [\gamma(-\omega_{abc}, \omega_a)m(\omega_b)m(\omega_c)\tilde{R}_1(\omega_b)\tilde{R}_1(\omega_{bc}) \\
&\quad + m(-\omega_{abc})m(\omega_a)\gamma(\omega_b, \omega_c)\tilde{K}(\omega_{abc})] \tag{65}
\end{aligned}$$

where we have introduced the relaxation function

$$\begin{aligned}
\tilde{K}(\omega_{abc}) &= \frac{1}{4}[9\tilde{K}_3(\omega_{abc}) - 5\tilde{K}_1(\omega_{abc})] \\
&= \frac{1}{2}[3R_1(\omega_a) - R_2(\omega_{bc})]R_1(\omega_{abc}) \tag{66}
\end{aligned}$$

Finally, the third and last contribution (60) leads, for the various components, to

$$\begin{aligned}
\langle C_{xxyy}^{\omega_{abc}} \rangle^{(3)} &= -\frac{\beta^3 N}{15} m(-\omega_{abc})m(\omega_a)m(\omega_b)m(\omega_c)[5\tilde{S}_1(\omega_{abc}) - \tilde{S}_3(\omega_{abc})] \\
\langle C_{xyxy}^{\omega_{abc}} \rangle^{(3)} &= \langle C_{xyyx}^{\omega_{abc}} \rangle^{(3)} \\
&= \frac{\beta^3 N}{15} m(-\omega_{abc})m(\omega_a)m(\omega_b)m(\omega_c)\tilde{S}_3(\omega_{abc}) \tag{60a}
\end{aligned}$$

their sum yielding

$$\langle C_{xxxx}^{\omega_{abc}} \rangle^{(3)} = -\frac{2\beta^3 N}{15} m(-\omega_{abc})m(\omega_a)m(\omega_b)m(\omega_c)\tilde{S}(\omega_{abc}) \quad (67)$$

with the relaxation function:

$$\tilde{S}(\omega_{abc}) = \frac{1}{2}[5\tilde{S}_1(\omega_{abc}) - 3\tilde{S}_3(\omega_{abc})] = \tilde{R}_1(\omega_a)\tilde{R}_2(\omega_{ab})\tilde{R}_1(\omega_{abc}) \quad (68)$$

The above expressions can also be written in a form completely symmetric in $\omega_a, \omega_b, \omega_c$. Strictly, each of the polarizability tensors $a_{\alpha\beta}, b_{\alpha\beta\gamma}, c_{\alpha\beta\gamma\delta}$ is to be multiplied by an appropriate factor $K(-\omega_{ab}, \omega_a, \omega_b), K(-\omega_{abc}, \omega_a, \omega_b, \omega_c)$, whose numerical value depends on the appropriate power of $\frac{1}{2}$ and the frequency degeneracy factors [90] D resulting from the relationship between the field frequencies $\omega_a, \omega_b, \omega_c$ and their methods of combination (whether they are different, equal to one another, or zero). The factor should enter the Fourier field representation (8). However, in order not to complicate our formulae excessively, we refrain from adding these numerical factors. They can be added eventually by the well-known method [81, 83]; as yet there is no convention on the matter.

VII. NONLINEAR EFFECTS OF ELECTRON RELAXATION; NONLINEAR ELECTRON-RELAXATION PHENOMENA

The third-order nonlinear polarization (22), using eqns. (23) and (25a), becomes for an isotropic body in the shape of a spherical sample

$$\begin{aligned} P_i^{(3)}(t) = \sum_{abc} [& \chi_{xxx}^{\omega_{abc}}(\omega_a, \omega_b, \omega_c)E_i(\omega_a)E_j(\omega_b)E_j(\omega_c) \\ & + \chi_{xyxy}^{\omega_{abc}}(\omega_a, \omega_b, \omega_c)E_j(\omega_a)E_i(\omega_b)E_j(\omega_c) \\ & + \chi_{xyyx}^{\omega_{abc}}(\omega_a, \omega_b, \omega_c)E_j(\omega_a)E_j(\omega_b)E_i(\omega_c)] \exp(-i\omega_{abc}t) \end{aligned} \quad (69)$$

We shall now use this polarization for the description of nonlinear relaxation in a variety of phenomena.

A. Vibration frequency tripling

We begin by considering the case when a single, intense electromagnetic wave is incident on the medium. The real part of (69) now is

$$\begin{aligned} P_i^{(3)}(t) = 2[& 3\chi_{xxx}^{\omega}(\omega, \omega, -\omega) \cos \omega t \\ & + \chi_{xxx}^{3\omega}(\omega, \omega, \omega) \cos 3\omega t] E_i(\omega)E_j(\omega)E_j(\omega) \end{aligned} \quad (70)$$

involving, by (23) and (63)–(68), the following nonlinear susceptibilities at the frequencies ω and 3ω , respectively:

$$\begin{aligned}
\chi_{xxxx}^{\omega}(\omega, \omega, -\omega) &= \frac{\rho}{270} (L^{\omega})^4 \{9c_{\alpha\alpha\beta\beta}(-\omega, \omega, \omega, -\omega) \\
&\quad + 54\beta[b(-\omega, \omega, \omega)m(-\omega)R_1(\omega) \\
&\quad + b(-\omega, \omega, -\omega)m(\omega)R_1(\omega)] \\
&\quad + 4\beta[2\gamma(-\omega, \omega)\gamma(\omega, -\omega) + \gamma(-\omega, -\omega)\gamma(\omega, \omega)R_2(2\omega)] \\
&\quad + 8\beta^2\gamma(-\omega, \omega)|m(\omega)|^2[R_1^2(\omega) + K(\omega)] \\
&\quad + 4\beta^2\gamma(-\omega, -\omega)m(\omega)^2[R_1(\omega)R_2(2\omega) \\
&\quad + K'(\omega)] - 6\beta^3|m(\omega)|^4S(\omega)\} \quad (71)
\end{aligned}$$

$$\begin{aligned}
\chi_{xxxx}^{3\omega}(\omega, \omega, \omega) &= \frac{\rho}{90} L^{3\omega}(L^{\omega})^3 \{3c_{\alpha\alpha\beta\beta}(-3\omega, \omega, \omega, \omega) \\
&\quad + 9\beta[3b(-3\omega, \omega, \omega)m(\omega)R_1(\omega) \\
&\quad + m(-3\omega)b(\omega, \omega, \omega)R_1(3\omega)] \\
&\quad + 4\beta\gamma(-3\omega, \omega)\gamma(\omega, \omega)R_2(2\omega) \\
&\quad + 4\beta^2[\gamma(-3\omega, \omega)m(\omega)^2R_1(\omega)R_2(2\omega) \\
&\quad + m(-3\omega)m(\omega)\gamma(\omega, \omega)K(3\omega)] \\
&\quad - 2\beta^3m(-3\omega)m(\omega)^3S(3\omega)\} \quad (72)
\end{aligned}$$

Eqns. (71) and (72) contain the real parts of the relaxation functions (54)

$$\begin{aligned}
R_1(\omega_a) &= (1 + \omega_a^2\tau_1^2)^{-\frac{1}{2}} \\
R_2(\omega_{ab}) &= [1 + (\omega_a + \omega_b)^2\tau_2^2]^{-\frac{1}{2}} \\
R_3(\omega_{abc}) &= [1 + (\omega_a + \omega_b + \omega_c)^2\tau_3^2]^{-\frac{1}{2}} \\
R_1(\omega_{abc}) &= [1 + (\omega_a + \omega_b + \omega_c)^2\tau_1^2]^{-\frac{1}{2}} \quad (54a)
\end{aligned}$$

With the preceding functions and eqns. (66) and (68), we determine the functions $K(3\omega)$ and $S(3\omega)$, for $\omega_a = \omega_b = \omega_c = \omega$, obtaining moreover

$$K(\omega) = \frac{1}{2}[3R_1(\omega) - 1]R_1(\omega), \quad K'(\omega) = \frac{1}{2}[3R_1(\omega) - R_2(2\omega)]R_1(\omega) \quad (66a)$$

$$S(\omega) = \frac{1}{3}R_1^2(\omega)[2 + R_2(2\omega)] \quad (68a)$$

Eqn. (70) shows that, in the case of a single intense electric field vibrating with the frequency ω , the nonlinear polarization of order three consists of a part which vibrates with the frequency ω of the incident electric field and a part which vibrates with the tripled frequency 3ω . If the vibration frequency of the field is very high, as it is in laser light, then (at $\omega\tau \rightarrow \infty$) all relaxation functions (54a) tend to 0, and the nonlinear susceptibilities (71) and (72) are related to electron dispersion only thus

$$\begin{aligned}
\chi_{xxxx}^{\omega}(\omega, \omega, -\omega) &= \frac{\rho}{270} (L^{\omega})^4 \{9c_{\alpha\alpha\beta\beta}(-\omega, \omega, \omega, -\omega) \\
&\quad + 8\beta\gamma(-\omega, \omega)\gamma(\omega, -\omega)\} \quad (71a)
\end{aligned}$$

$$\chi_{xxxx}^{3\omega}(\omega, \omega, \omega) = \frac{\rho}{30} L^{3\omega} (L^\omega)^3 c_{\alpha\alpha\beta\beta}(-3\omega, \omega, \omega, \omega) \quad (72a)$$

Third-harmonic generation (THG) of laser light has been studied in gases [117], liquids [90, 116], liquid crystals [118] and solutions of large macromolecules [119]. Hitherto, no reports are available on low-frequency THG by the rotational relaxation mechanisms of eqn. (72). However, Sussmann [120] showed the feasibility of the observation of low-frequency THG by nonlocalized electric dipoles in paraelectric media.

B. Frequency doubling in a d.c. electric field

On assuming $\omega_c = 0$, i.e. that one of the fields is constant in time, we obtain, by (69)

$$\begin{aligned} P_i^{(3)}(t) = & 2\{[\chi_{xxxx}^0(0, \omega, -\omega) - 2\chi_{xyxy}^0(0, \omega, -\omega)]E_j(\omega)E_j(-\omega)E_i(0) \\ & + 2\chi_{xyxy}^0(0, \omega, -\omega)E_i(\omega)E_j(-\omega)E_j(0)\} \\ & + 2\{[\chi_{xxxx}^{2\omega}(0, \omega, \omega) - 2\chi_{xyxy}^{2\omega}(0, \omega, \omega)]E_j(\omega)E_j(\omega)E_i(0) \\ & + 2\chi_{xyxy}^{2\omega}(0, \omega, \omega)E_i(\omega)E_j(\omega)E_j(0)\} \cos 2\omega t \end{aligned} \quad (73)$$

where, using (23) and (63)–(68), we have for the nonlinear susceptibilities at 2ω

$$\begin{aligned} \chi_{xxxx}^{2\omega}(0, \omega, \omega) = & \frac{\rho}{270} L^{2\omega} L^0 (L^\omega)^2 \{3[c_{\alpha\alpha\beta\beta}(-2\omega, 0, \omega, \omega) \\ & + 2c_{\alpha\beta\alpha\beta}(-2\omega, 0, \omega, \omega)] + 27\beta[b(-2\omega, \omega, \omega)m(0) \\ & + 2b(-2\omega, 0, \omega)m(\omega)R_1(\omega) + m(-2\omega)b(0, \omega, \omega)R_1(2\omega)] \\ & + 4\beta[2\gamma(-2\omega, \omega)\gamma(0, \omega)R_2(\omega) + \gamma(-2\omega, 0)\gamma(\omega, \omega)R_2(2\omega)] \\ & + 4\beta^2\gamma(-2\omega, \omega)m(0)m(\omega)[1 + R_1(\omega)]R_2(\omega) \\ & + 4\beta^2\gamma(-2\omega, 0)m(\omega)^2R_1(\omega)R_2(2\omega) \\ & + 4\beta^2m(-2\omega)[2m(\omega)\gamma(0, \omega)K(2\omega) + m(0)\gamma(\omega, \omega)K'(2\omega)] \\ & - 6\beta^3m(-2\omega)m(0)m(\omega)^2S(2\omega)\} \end{aligned} \quad (74)$$

$$\begin{aligned} \chi_{xyxy}^{2\omega}(0, \omega, \omega) = & \chi_{xyyx}^{2\omega}(0, \omega, \omega) \\ = & \frac{\rho}{180} L^{2\omega} L^0 (L^\omega)^2 \{3c_{\alpha\beta\alpha\beta}(-2\omega, 0, \omega, \omega) - c_{\alpha\alpha\beta\beta}(-2\omega, 0, \omega, \omega) \\ & + 6\beta[b(-2\omega, \omega, \omega)m(0) + 2b(-2\omega, 0, \omega)m(\omega)R_1(\omega) \\ & + m(-2\omega)b(0, \omega, \omega)R_1(2\omega)] \\ & + 2\beta[2\gamma(-2\omega, \omega)\gamma(0, \omega)R_2(\omega) + \gamma(-2\omega, 0)\gamma(\omega, \omega)R_2(2\omega)] \\ & + 2\beta^2\gamma(-2\omega, \omega)m(0)m(\omega)[1 + R_1(\omega)]R_2(\omega) \\ & + 2\beta^2\gamma(-2\omega, 0)m(\omega)R_1(\omega)R_2(2\omega) \\ & + 2\beta^2m(-2\omega)[2m(\omega)\gamma(0, \omega)K_3(2\omega) + m(0)\gamma(\omega, \omega)K'_3(2\omega)] \\ & - 2\beta^3m(-2\omega)m(0)m(\omega)^2S_3(2\omega)\} \end{aligned} \quad (75)$$

Above, we have the following relaxation functions:

$$K(2\omega) = \frac{1}{2}[3R_1(\omega) - R_2(\omega)]R_1(2\omega)$$

$$K'(2\omega) = \frac{1}{2}[3 - R_2(2\omega)]R_1(2\omega) \quad (66b)$$

$$S(2\omega) = \frac{1}{3}[R_1(\omega)R_2(\omega) + R_2(\omega) + R_1(\omega)R_2(2\omega)]R_1(2\omega) \quad (68b)$$

The other functions are defined similarly on the basis of (55), (56) and (54a).

One notes that the third-order polarization (73) in the presence of a d.c. electric field contains a part that varies in time at the doubled frequency 2ω . At laser light frequencies, the nonlinear susceptibilities (74) and (75) at 2ω reduce to

$$\chi_{xxxx}^{2\omega}(0, \omega, \omega) = \frac{\rho}{90} L^{2\omega} L^0 (L^\omega)^2 [c_{\alpha\beta\beta}(-2\omega, 0, \omega, \omega) + 2c_{\alpha\beta\alpha\beta}(-2\omega, 0, \omega, \omega) + 9\beta b(-2\omega, \omega, \omega)m(0)] \quad (74a)$$

$$\chi_{xyxy}^{2\omega}(0, \omega, \omega) = \frac{\rho}{180} L^{2\omega} L^0 (L^\omega)^2 [3c_{\alpha\beta\alpha\beta}(-2\omega, 0, \omega, \omega) - c_{\alpha\alpha\beta\beta}(-2\omega, 0, \omega, \omega) + 6\beta b(-2\omega, \omega, \omega)m(0)] \quad (75a)$$

A d.c. electric field-induced SHG of laser light has been observed in nondipolar and dipolar gases [122]. It would be of interest to investigate SHG for low frequencies, at which the electric dipoles still keep pace with the field variation, in accordance with eqns. (74) and (75). Besides, as shown earlier [123], this effect is subject to considerable enhancement in the case of complete electric reorientation of molecules and macromolecules.

C. Induced optical birefringence

In a strong electric field, isotropic media become anisotropic, with a tensor of electric permittivity

$$(\varepsilon_{ij} - \delta_{ij})E_j(t) = 4\pi[P_i^{(1)}(t) + P_i^{(3)}(t) + \dots] \quad (76)$$

Since, in the absence of the intense electric field, the electric permittivity of the isotropic medium is scalar

$$[\varepsilon(0) - 1]E_i(t) = 4\pi P_i^{(1)}(t) \quad (77)$$

the anisotropic variation in permittivity tensor induced by the intense field is, using (76),

$$\Delta\varepsilon_{ij}E_j(t) = 4\pi P_i^{(3)}(t) + \dots \quad (78)$$

We now assume that the isotropic medium is acted on by two electromagnetic fields: the one, of frequency ω_A , serves to analyze the variations induced in the electric permittivity tensor by the other, strong field of frequency ω_1 . Eqns. (69)

and (78) yield

$$\begin{aligned} \Delta \varepsilon_{ij}(\omega_A) &= 4\pi \sum_{bc} [\chi_{xxyy}^{\omega_Abc}(\omega_A, \omega_b, \omega_c) \delta_{ij} E_k(\omega_a) E_k(\omega_c) \\ &\quad + \chi_{xyxy}^{\omega_Abc}(\omega_A, \omega_b, \omega_c) E_i(\omega_b) E_j(\omega_c) \\ &\quad + \chi_{xyyx}^{\omega_Abc}(\omega_A, \omega_b, \omega_c) E_j(\omega_b) E_i(\omega_c)] \exp(-i\omega_{Abc} t) \end{aligned} \quad (79)$$

If the analyzing electromagnetic wave propagates in the direction of the Z-axis, the optical birefringence induced in the medium at ω_1 is defined as the difference between the diagonal and orthogonal elements of the tensor (79) (we omit the part dependent on $2\omega_1$).

$$\begin{aligned} \Delta \varepsilon_{xx}(\omega_A) - \Delta \varepsilon_{yy}(\omega_A) &= 8\pi [\chi_{xyxy}^{\omega_A}(\omega_A, \omega_1, -\omega_1) \\ &\quad + \chi_{xyyx}^{\omega_A}(\omega_A, \omega_1, -\omega_1)] \\ &\quad \times [E_x(\omega_1) E_x(-\omega_1) - E_y(\omega_1) E_y(-\omega_1)] \end{aligned} \quad (80)$$

In the case now under consideration, we obtain by eqns. (23) and (58a)–(60a)

$$\begin{aligned} \chi_{xyxy}^{\omega_A}(\omega_A, \omega_1, -\omega_1) &= \chi_{xyyx}^{\omega_A}(\omega_A, \omega_1, -\omega_1) \\ &= \frac{\rho}{180} (L^{\omega_A} L^{\omega_1})^2 \{ 3c_{\alpha\beta\alpha\beta}(-\omega_A, \omega_A, \omega_1, -\omega_1) \\ &\quad - c_{\alpha\beta\alpha\beta}(-\omega_A, \omega_A, \omega_1, -\omega_1) + 12\beta [b(-\omega_A, \omega_A, \omega_1) \\ &\quad \times m(-\omega_1) R_1(\omega_1) \\ &\quad + m(-\omega_A) b(\omega_A, \omega_1, -\omega_1) R_1(\omega_A)] \\ &\quad + 2\beta [\gamma(-\omega_A, \omega_A) \gamma(\omega_1, -\omega_1) \\ &\quad + \gamma(-\omega_A, \omega_1) \gamma(\omega_A, -\omega_1) R_2(\omega_A - \omega_1) \\ &\quad + \gamma(-\omega_A, -\omega_1) \gamma(\omega_A, +\omega_1) R_2(\omega_A + \omega_1) \\ &\quad + 2\beta^2 \gamma(-\omega_A, \omega_A) m(\omega_1)^2 R_1^2(\omega_1) \\ &\quad + \beta^2 m(\omega_A) m(-\omega_1) \gamma(-\omega_A, \omega_1) \\ &\quad \times [R_1(\omega_A) + R_1(-\omega_1)] R_2(\omega_A - \omega_1) \\ &\quad + \beta^2 m(\omega_A) m(\omega_1) \gamma(-\omega_A, -\omega_1) \\ &\quad \times [R_1(\omega_A) + R_1(\omega_1)] R_2(\omega_A + \omega_1) \\ &\quad + 2\beta^2 m(-\omega_A) [m(\omega_A) \gamma(\omega_1, -\omega_1) K_3(\omega_A) \\ &\quad + \gamma(\omega_A, -\omega_1) m(\omega_1) K_3(\omega_A - \omega_1) \\ &\quad + \gamma(\omega_A, \omega_1) m(-\omega_1) K_3(\omega_A + \omega_1) \\ &\quad + 2\beta^3 |m(\omega_A)|^2 |m(\omega_1)|^2 S_3(\omega_1 + \omega_A - \omega_1)] \} \end{aligned} \quad (81)$$

where, by eqns. (55) and (56)

$$\begin{aligned} K_3(\omega_A) &= \frac{1}{3} [1 + 2R_1(\omega_A)] R_3(\omega_A) \\ K_3(\omega_A \pm \omega_1) &= \frac{1}{3} [2R_1(\mp \omega_1) + R_2(\omega_A \pm \omega_1)] R_3(\omega_A) \end{aligned} \quad (55a)$$

$$\begin{aligned}
S_3(\omega_1 + \omega_A - \omega_1) &= \frac{1}{6} \{ R_1(\omega_A) [R_2(\omega_A + \omega_1) + R_2(\omega_A - \omega_1)] \\
&\quad + R_1(\omega_1) [1 + R_2(\omega_A + \omega_1)] \\
&\quad + R_1(-\omega_1) [1 + R_2(\omega_A - \omega_1)] \} R_3(\omega_A)
\end{aligned} \tag{56a}$$

If the analyzing wave is a light beam ($\omega_A, \tau_n \rightarrow \infty$), the nonlinear susceptibilities (81) define the a.c. electric field-induced Kerr effect:

$$\begin{aligned}
\chi_{xyxy}^{\omega_A}(\omega_A, \omega_1, -\omega_1) &= \frac{\rho}{180} (L^{\omega_A} L^{\omega_1})^2 \{ 3c_{\alpha\beta\alpha\beta}(-\omega_A, \omega_A, \omega_1, -\omega_1) \\
&\quad - c_{\alpha\beta\beta\alpha}(-\omega_A, \omega_A, \omega_1, -\omega_1) \\
&\quad + 12\beta b(-\omega_A, \omega_A, \omega_1) m(-\omega_1) R_1(\omega_1) \\
&\quad + 2\beta\gamma(-\omega_A, \omega_A) [\gamma(\omega_1, -\omega_1) + |m(\omega_1)|^2 R_1^2(\omega_1)] \}
\end{aligned} \tag{81a}$$

But for the terms in nonlinear molecular polarizabilities, the preceding expression coincides with the result (6), derived by Peterlin and Stuart [9]. On putting $\omega_1 = 0$ in eqns. (80) and (81a), we obtain the case of the d.c. Kerr effect.

If the field inducing optical birefringence in the medium is that of an intense laser beam, eqn. (81a) reduces to

$$\begin{aligned}
\chi_{xyxy}^{\omega_A}(\omega_A, \omega_1, -\omega_1) &= \frac{\rho}{180} (L^{\omega_A} L^{\omega_1})^2 [3c_{\alpha\beta\alpha\beta}(-\omega_A, \omega_A, \omega_1, -\omega_1) \\
&\quad - c_{\alpha\beta\beta\alpha}(-\omega_A, \omega_A, \omega_1, -\omega_1) \\
&\quad + 2\beta\gamma(-\omega_A, \omega_A) \gamma(\omega_1, -\omega_1)]
\end{aligned} \tag{81b}$$

This formula describes the optical birefringence [13, 29] induced in an isotropic medium by intense laser light of frequency ω_1 .

Eqns. (69) and (78) allow us to write the second part of the dynamical optical birefringence, induced by intense laser light and modulated at the frequency $2\omega_1$, as follows:

$$\begin{aligned}
\Delta\varepsilon_{xx}(\omega_A) - \Delta\varepsilon_{yy}(\omega_A) &= 8\pi [\chi_{xyxy}^{\omega_A + 2\omega_1}(\omega_A, \omega_1, \omega_1) \\
&\quad + \chi_{xyyx}^{\omega_A + 2\omega_1}(\omega_A, \omega_1, \omega_1)] [E_x(\omega_1) E_x(\omega_1) \\
&\quad - E_y(\omega_1) E_y(\omega_1)] \cos 2\omega_1 t
\end{aligned} \tag{82}$$

The nonlinear susceptibilities occurring above are easily derived in explicit form from eqns. (58a)–(60a).

Along similar lines, by using eqns. (69) and (78), one calculates the difference between nondiagonal permittivity tensor elements, i.e. circular birefringence. On applying a single, intense elliptically polarized laser beam, one obtains the well-studied intensity-dependent rotation of the light polarization plane [90, 124].

The individual terms of (81) are able to be resolved by pulsed technique, down to picosecond laser pulses inclusively [38], or by a judicious choice of the substance, e.g. a polymer solution [60] or liquid crystal [125].

D. Dielectric saturation

Assume now that the analyzing electric field $E(\omega_A)$ and inducing field $E(\omega_1)$ act in the same direction, e.g. along the X -axis. Eqns. (69) and (78) now yield for the time-independent part at ω_A

$$\Delta\varepsilon_{xx}(\omega_A) = 8\pi\chi_{xxxx}^{\omega_A}(\omega_A, \omega_1, -\omega_1)E_x(\omega_1)E_x(-\omega_1) \quad (83)$$

where, using (63)–(68), we have

$$\begin{aligned} \chi_{xxxx}^{\omega_A}(\omega_A, \omega_1, -\omega_1) = & \frac{\rho}{270} (L^{\omega_A} L^{\omega_1}) \{ 3 [c_{\alpha\beta\beta}(-\omega_A, \omega_A, \omega_1, -\omega_1) \\ & + 2c_{\alpha\beta\alpha\beta}(-\omega_A, \omega_A, \omega_1, -\omega_1)] \\ & + 54\beta [b(-\omega_A, \omega_A, \omega_1)m(\omega_1)R_1^2(\omega_1) \\ & + m(-\omega_A)b(\omega_A, \omega_1, -\omega_1)R_1(\omega_A)] \\ & + 4\beta [\gamma(-\omega_A, \omega_A)\gamma(\omega_1, -\omega_1) \\ & + \gamma(-\omega_A, -\omega_1)\gamma(\omega_A, +\omega_1)R_2(\omega_A + \omega_1) \\ & + \gamma(-\omega_A, \omega_1)\gamma(\omega_A, -\omega_1)R_2(\omega_A - \omega_1)] \\ & + 4\beta^2\gamma(-\omega_A, \omega_A)|m(\omega_1)|^2R_1^2(\omega_1) \\ & + 2\beta^2m(\omega_A)m(-\omega_1)\gamma(-\omega_A, \omega_1) \\ & \quad \times [R_1(\omega_A) + R_1(-\omega_1)]R_2(\omega_A - \omega_1) \\ & + 2\beta^2m(\omega_A)m(\omega_1)\gamma(-\omega_A, -\omega_1) \\ & \quad \times [R_1(\omega_A) + R_1(\omega_1)]R_2(\omega_A + \omega_1) \\ & + 4\beta^2m(-\omega_A)[m(\omega_A)\gamma(\omega_1, -\omega_1)K(\omega_A) \\ & + \gamma(\omega_A, -\omega_1)m(\omega_1)K(\omega_A - \omega_1) \\ & + \gamma(\omega_A, \omega_1)m(-\omega_1)K(\omega_A + \omega_1)] \\ & - 6\beta^3|m(\omega_A)|^2|m(\omega_1)|^2S(\omega_1 + \omega_A - \omega_1) \} \end{aligned} \quad (84)$$

and, using (66) and (68),

$$\begin{aligned} K(\omega_A) &= \frac{1}{2}[3R_1(\omega_A) - 1]R_1(\omega_A) \\ K(\omega_A \pm \omega_1) &= \frac{1}{2}[3R_1(\mp \omega_1) - R_2(\omega_A \pm \omega_1)]R_1(\omega_A) \end{aligned} \quad (66c)$$

$$\begin{aligned} S(\omega_1 + \omega_A - \omega_1) = & \frac{1}{6} \{ R_1(\omega_A)[R_2(\omega_A + \omega_1) + R_2(\omega_A - \omega_1)] \\ & + R_1(\omega_1)[1 + R_2(\omega_A + \omega_1)] \\ & + R_1(-\omega_1)[1 + R_2(\omega_A - \omega_1)] \} R_1(\omega_A) \end{aligned} \quad (68c)$$

Eqn. (83) describes the variations in electric permittivity of an isotropic medium induced by the square of the strong electric field intensity.

In the case of a strong inducing field constant in time ($\omega_1 = 0$), we obtain with respect to (83) and (84)

$$\Delta\varepsilon_{xx}(\omega_A) = 4\pi\chi_{xxxx}^{\omega_A}(\omega_A, 0)E_x^2(0) \quad (83a)$$

where

$$\begin{aligned} \chi_{xxxx}^{\omega_A}(\omega_A, 0) = & \frac{\rho}{270} (L^{\omega_A}L^0)^2 \{3[c_{\alpha\alpha\beta\beta}(-\omega_A, \omega_A, 0, 0) \\ & + 2c_{\alpha\beta\alpha\beta}(-\omega_A, \omega_A, 0, 0) + 54\beta[b(-\omega_A, \omega_A, 0)m(0) \\ & + m(-\omega_A)b(\omega_A, 0, 0)R_1(\omega_A)] + 4\beta[\gamma(-\omega_A, \omega_A)\gamma(0, 0) \\ & + 2\gamma(-\omega_A, 0)^2R_2(\omega_A)] + 4\beta^2\gamma(-\omega_A, \omega_A)m(0)^2 \\ & + 4\beta^2\gamma(-\omega_A, 0)m(\omega_A)m(0)[1 + R_1(\omega_A)]R_2(\omega_A) \\ & + 4\beta^2m(-\omega_A)[m(\omega_A)\gamma(0, 0)K(\omega_A) + 2\gamma(\omega_A, 0)m(0)K'(\omega_A)] \\ & - 6\beta^3|m(\omega_A)|^2m(0)^2S(\omega_A)\} \end{aligned} \quad (84a)$$

If, in particular, the analyzing field is constant or very slowly variable in time, the relaxation functions $R_1(\omega_A)$, $R_2(\omega_A)$ and $K(\omega_A)$ tend to unity, and the preceding expressions describe dielectric saturation, studied by Piekara [103] and co-workers [18] in dipolar liquids,

$$\begin{aligned} \chi_{xxxx}^0(0) = & \frac{\rho}{90} (L^0)^4 \{c_{\alpha\alpha\beta\beta}(0) + 2c_{\alpha\beta\alpha\beta}(0) + 36\beta b(0)m(0) \\ & + 4\beta\gamma(0)[\gamma(0) + 2\beta m(0)^2] - 2\beta^3m(0)^4\} \end{aligned} \quad (84b)$$

If the vibration frequency ω_A of the analyzing field lies above the region of dipole dispersion ($\omega_A > \omega_d$), we obtain from eqn. (84a)

$$\begin{aligned} \chi_{xxxx}^{\omega_A}(\omega_A > \omega_d, 0) = & \frac{\rho}{270} (L^{\omega_A}L^0)^2 \{3[c_{\alpha\alpha\beta\beta}(-\omega_A, \omega_A, 0, 0) \\ & + 2c_{\alpha\beta\alpha\beta}(-\omega_A, \omega_A, 0, 0) + 54\beta b(-\omega_A, \omega_A, 0)m(0) \\ & + 4\beta\gamma(-\omega_A, \omega_A)[\gamma(0, 0) + \beta m(0)^2]\} \end{aligned} \quad (84c)$$

corresponding to the dielectric saturation studied by Gregson et al. [62] in solutions of polymers.

Before laser technique was used, Piekara and Kielich [61, 79] proposed as a subject for study the absolute variation in electric permittivity induced by intense light as defined by eqn. (83) with nonlinear susceptibility of the form

$$\begin{aligned} \chi_{xxxx}^{\omega_A}(\omega_A, \omega_1, -\omega_1) = & \frac{\rho}{270} (L^{\omega_A}L^{\omega_1})^2 \{3[c_{\alpha\alpha\beta\beta}(-\omega_A, \omega_A, \omega_1, -\omega_1) \\ & + 2c_{\alpha\beta\alpha\beta}(-\omega_A, \omega_A, \omega_1, -\omega_1)] \\ & + 54\beta m(-\omega_A)b(\omega_A, \omega_1, -\omega_1)R_1(\omega_A) \\ & + 4\beta[\gamma(-\omega_A, \omega_A) \\ & + \beta m(-\omega_A)m(\omega_A)K(\omega_A)]\gamma(\omega_1, -\omega_1)\} \end{aligned} \quad (85)$$

or for $\omega_A \rightarrow 0$

$$\begin{aligned} \chi_{xxxx}^0(0, \omega_1, -\omega_1) = & \frac{\rho}{270} (L^0 L^{\omega_1})^2 \{ 3 [c_{\alpha\alpha\beta\beta}(0, 0, \omega_1, -\omega_1) \\ & + 2c_{\alpha\beta\alpha\beta}(0, 0, \omega_1, -\omega_1)] + 54\beta m(0)b(0, \omega_1, -\omega_1) \\ & + 4\beta [\gamma(0, 0) + \beta m(0)^2] \gamma(\omega_1, -\omega_1) \} \end{aligned} \quad (85a)$$

Using the general equation (69) of third-order polarization and eqns. (63)–(68) for nonlinear polarizations, we can extend the present discussion to other processes of nonlinear relaxation, e.g. frequency mixing, especially at difference frequencies $\omega_a - \omega_b$, $\omega_a - \omega_b - \omega_c$; their investigation would require the application of two, or three laser beams, with frequencies adjusted so that their differences lie in the regions of the reciprocals of the relevant relaxation times (13). Also, besides the relaxation dispersions already considered with regard to nonlinear effects, processes of nonlinear relaxational absorption can profitably be considered.

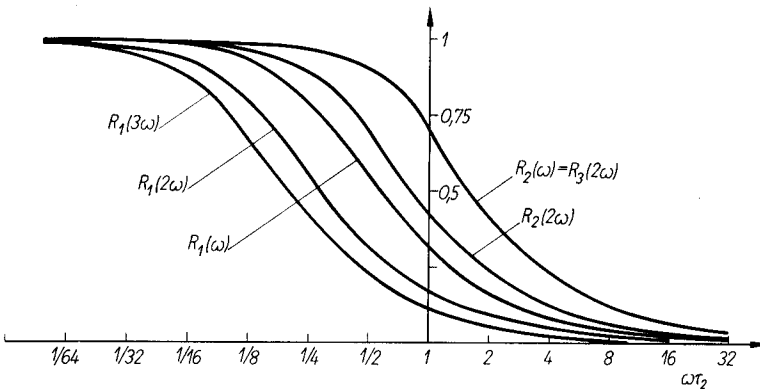


Fig. 1. Graphs of the relaxation functions (54a) vs. $\omega\tau_2$.

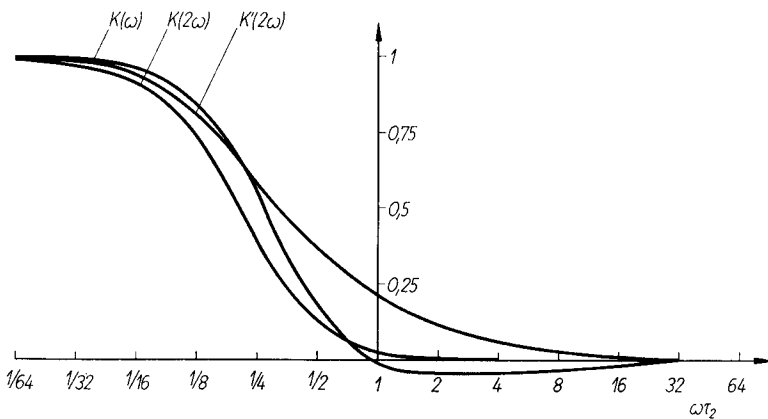


Fig. 2. Relaxation functions defined by (66a) and (66b) characteristic for the Kerr effect, plotted vs. $\omega\tau_2$.

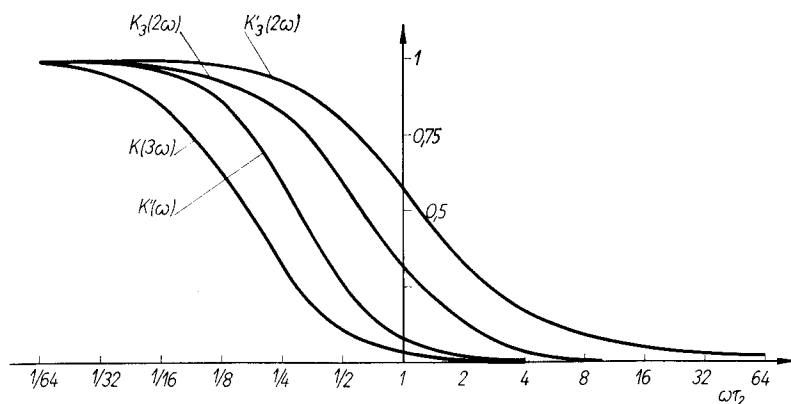


Fig. 3. Kerr-type relaxation functions, given by (55) and (66), plotted vs. $\omega\tau_2$.

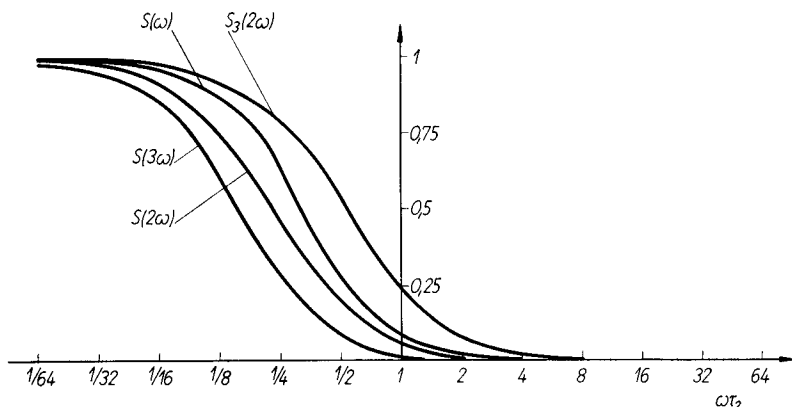


Fig. 4. Relaxation functions characteristic for dielectric saturation phenomena defined in general by (68) and in particular by (68a), (68b), plotted as functions of $\omega\tau_2$.

The molecular rotational relaxation functions occurring in the various temperature-dependent contributions to the nonlinear susceptibility of the medium are plotted in Figs. 1-4.

VIII. GENERAL CONCLUSIONS AND OUTLOOK

We have shown that relaxational processes, related to the three (respectively shorter and shorter) relaxation times $\tau_1 = 3\tau_2 = 6\tau_3$ are apparent in many nonlinear effects of order three, e.g. in SHG and THG, induced birefringences and dielectric saturation. Hitherto, however, only a few cases have been studied in experimental conditions chosen in a manner to render directly apparent the various rotational relaxation mechanisms inherent in third-order nonlinear susceptibility.

Because of the formulae derived in this paper, new and wider fields are open to the experimenter in nonlinear rotational relaxation spectroscopy, including processes of absorption [126].

The present results are, as yet, derived in the approximation of diffusional rotation; doubtless, however, the treatment of nonlinear relaxation processes can be developed by the methods of time correlation functions, extensively presented by Berne [127] for linear responses, and by others [128] for nonlinear responses. But obviously relaxation processes should be dealt with from a more general standpoint, by the theory of stochastic processes in its modern form [129]. These general stochastic methods let us describe relaxation processes involving statistically correlated molecules and take into account translational, translational-reorientational, and molecular field fluctuations [130] in the regions of short-range order.

The simple theory of nonlinear relaxation processes at low and high frequencies presented above shows the wide variety of information that can be gained concerning the higher molecular relaxation times and the dynamical structure of statistically inhomogeneous isotropic media.

REFERENCES

- 1 P. Debye, *Polare Molekeln*, Hirzel, Leipzig, 1929.
- 2 N. E. Hill, W. E. Vaughan, A. H. Price and M. Davies, *Dielectric Properties and Molecular Behaviour*, Van Nostrand-Reinhold, London, 1969.
- 3 B. K. P. Scaife, in *Complex Permittivity*, English Universities Press, London, 1971, pp. 2-51.
- 4 G. Wyllie, in M. Davies, (Ed.) *Dielectric and Related Molecular Processes*, Chemical Society London, 1972, pp. 21-64.
- 5 W. J. Orville-Thomas and R. Kosfeld (Eds.) *Molecular Relaxation Studies*, Elsevier, Amsterdam, 1972. J. Lascombe, (Ed.) *Molecular Motions in Liquids*, D. Reidel, Dordrecht, Holland, 1974.
- 6 G. Boudouris, *Riv. Nuovo Cimento, Ser. I*, 1 (1969) 1-56.
- 7 B. Keller and F. Kneubühl, *Helv. Phys. Acta*, 45 (1972) 1127-1164.
- 8 P. Bordewijk, *Advan. Mol. Relaxation Processes*, 5 (1973) 285-300.
- 9 F. Perrin, *J. Phys. Radium*, 5 (1934) 497; 7 (1936) 1.
- 10 A. Peterlin and H. Stuart, *Doppelbrechung Insbesondere Künstliche Doppelbrechung*, Akademische Verlagsgesellschaft, Leipzig, 1943.
- 11 P. Langevin, *Le Radium*, (1910) 249.
- 12 M. Born, *Optik*, J. Springer, Berlin, 1933.
- 13 H. Benoit, *Ann. Phys.*, 6 (1951) 561; *J. Chim. Phys.* 49 (1952) 517.
- 14 G. Mayer and F. Gires, *C. R. Acad. Sci Paris, Ser B*, 258 (1964) 2039. M. Paillette, *Ann. Phys.* 4 (1969) 671.
- 15 J. Frenkel, *Kinetic Theory of Liquids*, Oxford University Press, Oxford, 1946.
- 16 I. M. Fabielinskii, *Molecular Scattering of Light*, Plenum Press, New York, 1968.
- 17 C. T. O'. Kanski, *Encyclopedia of Polymer Science and Technology*, Vol. 9, Wiley, New York, 1968, pp. 551-590.
- 18 S. P. Stoylov, *Advan. Colloid Interface Sci.*, 3 (1971) 45-110.
- 19 S. Kielich, in M. Davies, (Ed.) *Dielectric and Related Molecular Processes* Chemical Society, London, 1972, Vol. 1, pp. 192-387.
- 20 N. Bloembergen, E. M. Purcell and R. V. Pound, *Phys. Rev.*, 73 1948 679.

- 20 A. Ben-Reuven and N. D. Gershon, *J. Chem. Phys.* 51 (1969) 893; T. Keys and D. Kivelson, *J. Chem. Phys.*, 54 (1971) 1786; 56 (1972) 1057.
- 21 F. J. Bartoli and T. A. Litowitz, *J. Chem. Phys.*, 56 (1972) 413.
- 22 P. A. Fleury and J. P. Boon, *Advan. Chem. Phys.*, 24 (1973) 1-93; V. S. Vikhre'ntko, *Usp. Fiz. Nauk*, 113 (1974) 627-664.
- 23 N. Bloembergen and P. Lallemand, *Phys. Rev. Lett.*, 16 (1966) 81; N. Bloembergen, *Amer. J. Phys.*, 35 (1967) 989-1023; P. Lallemand, in A. Anderson, (Ed.) *The Raman Effect*, Vol. I Dekker, New York, 1971, pp. 287-342.
- 24 R. M. Herman, *Phys. Rev.*, 164 (1967) 200.
- 25 V. S. Starunov and I. L. Fabelinskii, *Usp. Fiz. Nauk*, 98 (1969) 441-491; B. Ya. Zeldovich and I. I. Sobelman, *Usp. Fiz. Nauk*, 101 (1970) 3-20.
- 26 S. Kielich, *J. Phys.* 28 (1967) 519; *Phys. Lett.* 25A (1967) 153; *Acta Phys. Pol.* 37A (1970) 447; 37A (1970) 719.
- 27 H. Plummer and B. J. Jennings, *J. Chem. Phys.*, 50 (1969) 1033; J. Schweitzer and B. R. Jennings, *Biopolymers*, 11 (1972) 1077; *J. Phys.*, D. 5 (1972) 297. A. R. Foweraker and B. R. Jennings, *Advan. Mol. Relaxation Processes*, 6 (1974) 241.
- 28 J. C. Ravey, *J. Chem. Phys.*, 59 (1973) 5221.
- 29 S. Kielich, *Acta Phys. Pol.* 30 (1966) 393; 31 (1967) 689.
- 30 R. Pecora, *J. Chem. Phys.*, 50 (1969) 2650.
- 31 R. Y. Chiao and A. Godine, *Phys. Rev.*, 185 (1969) 430.
- 32 C. Flytzanis and Y. R. Shen, *Phys. Rev. Lett.* 33 (1974) 14.
- 33 S. Kielich, *Opt. Commun.*, 1 (1969) 129.
- 34 K. Yoshioka and H. Watanabe, *Physical Principles and Techniques of Protein Chemistry*, Academic Press, New York, 1969, pp. 335-367.
- 35 E. Fredericq and C. Houssier, *Electric Dichroism and Electric Birefringence*, Clarendon Press, Oxford, 1973.
- 36 S. Kielich, *Phys. Lett.*, 24A (1967) 435; *Acta Phys. Pol.*, 31 (1967) 929.
- 37 B. Kasprowicz-Kielich, S. Kielich and J. R. Lalanne, in J. Lascombe, (Ed.) *Molecular Motions in Liquids*, D. Reidel, Dordrecht, Holland, 1974, pp. 563-573.
- 38 R. G. Brewer and C. H. Lee, *Phys. Rev. Lett.* 21 (1968) 267.
- 39 R. Cubeddu, R. Polloni, C. A. Sacchi and O. Svelto, *Phys. Rev.*, A, 2 (1970) 1955.
- 40 J. A. Fleck, Jr., and R. L. Carman, *Appl. Phys. Lett.*, 20 (1972) 290.
- 41 J. P. Laussade and A. Yariv, *Appl. Phys. Lett.*, 13 (1968) 65; *IEEE J. Quantum Electron.*, QE-5 (1969) 435.
- 42 A. C. Cheung, D. M. Rank, R. Y. Chiao and C. H. Townes, *Phys. Rev. Lett.*, 20 (1968) 786. R. R. Alfano, L. L. Hope and S. L. Shapiro, *Phys. Rev.*, A, 6 (1972) 433.
- 43 M. A. Duguay and J. W. Hansen, *Appl. Phys. Lett.*, 15 (1969) 192.
- 44 T. C. Owen, L. W. Coleman and T. J. Burgess, *Appl. Phys. Lett.*, 22 (1973) 272.
- 45 R. R. Alfano and S. L. Shapiro, *Scientific American*, 228 (1973) 43; W. Yu, and R. R. Alfano, *Opto-Electronics*, 6 (1974) 243.
- 46 L. Dahlström, *Opt. Commun.*, 3 (1971) 399; H. Baumhacker, E. Fill and W. Schmid, *Phys. Lett.*, 44A (1973) 3.
- 47 D. J. Bradley and G. H. C. New, *Proc. IEEE*, 62 (1974) 313; A. Labreau and W. Kaiser, *Opto-Electronics*, 6 (1974) 1-24.
- 48 R. A. Fisher, P. L. Kelley and T. K. Gustafson, *Appl. Phys. Lett.*, 14 (1969) 140. J. C. Comly, A. Yariv and E. M. Garmire, *Appl. Phys. Lett.*, 15 (1969) 148.
- 49 A. Piekara, *Jap. J. Appl. Phys.*, Suppl., 14 (1975) 7.
- 50 B. Ya. Zeldovich and T. I. Kuznietzova, *Usp. Fiz. Nauk*, 106 (1972) 47-84.
- 51 I. L. Fabelinskii, *Usp. Fiz. Nauk*, 104 (1971) 77-94.
- 52 S. A. Akhmanov, R. V. Khoklov and A. P. Sukhorukov, in Arecchi and Schultz-Dubois (Eds.) *Laser Handbook*, Vol. 2, North-Holland, Amsterdam, 1972 pp. 1151-1228.
- 53 O. Svelto, *Progress in Optics*, Vol. 12, North-Holland, Amsterdam, 1974, pp. 1-51.
- 54 P. M. Rentzepis, *Advan. Chem. Phys.*, 23 (1973) 189-225.
- 55 A. M. Prokhorov, F. V. Bunkin, K. S. Gochelashvili and V. I. Shishov, *Usp. Fiz. Nauk*, 114 (1974) 415-456.
- 56 A. Piekara, *IEEE J. Quantum Electron.*, OE-2 (1966) 249; *Appl. Phys. Lett.*, 13 (1968) 225;

- T. K. Gustafson and C. H. Townes, *Phys. Rev.*, *A*, 6 (1972) 1659; A. Piekara, J. S. Moore and M. S. Feld, *Phys. Rev.*, *A*, 9 (1974) 1403.
- 57 Y. R. Shen and Y. J. Shaham, *Phys. Rev.*, 163 (1967) 224; H. A. Haus and T. K. Gustafson, *IEEE J. Quantum Electron.*, QE-4 (1968) 519; E. L. Kerr, *IEEE J. Quantum Electron.*, QE-6 (1970) 616.
- 58 J. Prost and J. R. Lalanne, *Phys. Rev.*, *A*, 8 (1973) 2090; G. K. L. Wong and J. R. Shen, *Phys. Rev.*, *A*, 10 (1974) 1277; L. N. Rao and S. Jayaraman, *Phys. Rev.*, *A*, 10 (1974) 2457.
- 59 T. Bischofberger and E. Courtens, *Phys. Rev. Lett.*, 32 (1974) 163; E. Courtens, *Phys. Rev.*, *A*, 10 (1974) 967.
- 60 B. R. Jennings and H. J. Coles, *Nature*, 252 (1974) 33.
- 61 A. Piekara and S. Kielich, *J. Chem. Phys.*, 29 (1958) 1297; A. Piekara, *J. Chem. Phys.*, 36 (1962) 2145.
- 62 M. Gregson, G. P. Jones and M. Davies, *Trans. Faraday Soc.*, 67 (1971) 1630; G. P. Jones and T. Krupkowski, *J. Chem. Soc. Faraday Soc.*, 70 (1974) 862.
- 63 M. A. Novikov, in *Nelineynaya Optika*, Izd. Nauka, Novosibirsk, 1968, pp. 52-59.
- 64 P. S. Hubbard, *Phys. Rev.*, 131 (1963) 1155; W. A. Steele, *J. Chem. Phys.*, 38 (1963) 2404, 2411.
- 65 P. D. Maker, *Phys. Rev. A*, 1 (1970) 923.
- 66 W. Alexiewicz, *Acta Phys. Pol.*, A47 (1975) 657; J. C. Leicknam and Y. Guissau, in J. Lascombe (Ed.), *Molecular Motions in Liquids*, Dordrecht, 1974, p. 257.
- 67 W. Alexiewicz, T. Bancewicz, S. Kielich and Z. Ożgo, *J. Raman Spectrosc.*, 2 (1974) 529.
- 68 W. Alexiewicz, Z. Ożgo and S. Kielich, *Acta Phys. Pol.*, A48 (1975) 243.
- 69 S. Kielich, Spectral theory of multiple-photon scattering, in *European Study Conference on Light Scattering Studies of Motion Molecular Systems*, Verbier, Switzerland, December 16-20, 1974.
- 70 H. A. Lorentz, *The Theory of Electrons*, Teubner, Leipzig, 1909.
- 71 W. Voigt, *Ann. Phys. Chem.*, 69 (1899) 297; *Ann. Phys.*, 4 (1901) 197; *Lehrb. Magnet-u. Electro-Optik*, Teubner, Leipzig 1908.
- 72 L. Rosenfeld, *Theory of Electrons*, North-Holland, Amsterdam, 1951.
- 73 M. Born and P. Jordan, *Elementare Quantenmechanik*, Springer, Berlin, 1930.
- 74 J. H. Van Vleck, *Theory of Electric and Magnetic Susceptibilities*, Oxford University Press, Oxford, 1932.
- 75 H. A. Stuart, *Molekülstruktur*, Springer, Berlin, 1967.
- 76 M. Volkenshteyn, *Molekularnaya Optika*, Moskva, 1951.
- 77 J. Leite-Lopez, *Fondements de la Physique Atomique*, Hermann, Paris, 1967; P. W. Atkins, *Molecular Quantum Mechanics*, Clarendon Press, Oxford, 1970.
- 78 A. Piekara, *Acta Phys. Pol.*, 4 (1935) 53; 6 (1937) 150.
- 79 S. Kielich and A. Piekara, *Acta Phys. Pol.*, 18 (1959) 439.
- 80 R. J. W. Le Fèvre, in V. Gold (Ed.) *Advances in Physical Organic Chemistry*, Vol. 3, Academic Press, London, 1965, pp. 1-90.
- 81 S. Kielich, *Opto-electronics*, 2 (1970) 125-151; *Ferroelectrics*, 4 (1972) 257-28.
- 82 P. Görlich and C. Hofmann, *Feingerätetechnik*, 19 (1970) 49, 101; C. Hofmann, *Feingerätetechnik*, 20 (1971) 544; 21 (1972) 35.
- 83 A. D. Buckingham and B. J. Orr, *Quart. Rev.*, 21 (1967) 195-212; M. P. Bogaard and B. J. Orr, *M. T. P. Review of Molecular Structure and Properties*, Butterworth, London, 1974.
- 84 S. Kielich, *Bull. Acad. Pol. Sci. Sér. Sci. Math. Astr. Phys.*, 11 (1963) 193; 12 (1964) 53; *Acta Phys. Pol.*, 27 (1965) 913.
- 85 S. A. Akhmanov and R. V. Khokhlov, *Problemy Nelineynoy Optiki*, Akademiya Nauk USSR, Moskva, 1964.
- 86 B. Kasprowicz, *M. Sc. Thesis*. Poznań, 1966.
- 87 N. Bloembergen, *Nonlinear Optics*, Benjamin, New York, 1965.
- 88 P. N. Butcher, *Nonlinear Optical Phenomena*, Ohio State University 1965.
- 89 S. Kielich *Proc. Phys. Soc.*, 86 (1965) 709.
- 90 R. W. Minck, R. W. Terhune and C. C. Wang, *Appl. Opt.*, 5 (1966) 1595-1612; P. D. Maker and R. W. Terhune, *Phys. Rev.*, *A*, 137 (1965) 801.