

KINETIC-MOLECULAR THEORY OF NONLINEAR ROTATIONAL RELAXATION, AND ITS APPLICATION TO THE ANALYSIS OF THIRD-ORDER ELECTRIC POLARIZATION IN LIQUIDS*

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A classical theory of nonlinear relaxation phenomena, related with third-order electric polarization, is proposed taking into account polarization rise and decay processes due to the switching on and removal of external electric fields in the approximation of Debye rotational diffusion, of dipolar molecules. By statistical perturbation calculus and Racah algebra methods, it is shown that the time-variations in polarization depend on the rotational relaxation times τ_1 , τ_2 and that, during times comparable with τ_1 and τ_2 , the dispersion and absorption of polarization is described by generalized Debye relaxation factors. The results, applicable to nonlinear processes in general, are discussed in detail for the description of the dynamics of processes, related with third-order polarization in liquids, giving rise to polarization at the fundamental and third harmonic frequencies and to variations in third-order nonlinear electric susceptibility.

1. Introduction

Linear relaxation processes in liquids are a subject of interest since 1929, when Debye's well known monograph [1] appeared owing to which the dielectric methods for the study of dielectric relaxation became a source of abundant information concerning the rotational motions of molecules and macromolecules, the electric properties of these microsystems, as well as their mutual correlations in dielectric liquids [1-4].

Recently, Kasproicz-Kielich, Kielich and Lalanne [5, 6] proposed a classical theory of nonlinear relaxational processes in the approximation of Debye's rotational diffusion describing the dispersion and absorption of the third-order polarization of liquid dielectrics induced by external time-variable electric fields of high and low frequency.

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Lately, results derived from their theory have been applied to the numerical investigation, by Buchert, Kasprowicz-Kielich and Kielich [7], of the dispersion and absorption of various nonlinear effects in the case of water and fibrinogen molecules.

The electric polarization $P(E)$ of isotropic dielectrics is known to be a function of successive odd powers of the external electric field strength:

$$E(t) = \frac{1}{2} \sum_a E(\omega_a) \exp(-i\omega_a t), \quad (1)$$

where summation over a extends over positive as well as negative values of the electric field vibration frequencies ω_a , with $\omega_{-a} = -\omega_a$. Assuming the dielectric to be subject to the action of three electric fields with the frequencies $\omega_1, \omega_2, \omega_3$, its nonlinear third-order polarization $P^{(3)}(\omega_4; t)$ at the frequency $\omega_4 = \omega_1 + \omega_2 + \omega_3$ can be expressed by the relation [5]:

$$P_i^{(3)}(\omega_4; t) = \chi_{ijkl}^{(3)}(-\omega_4; \omega_1, \omega_2, \omega_3; t) E_j(\omega_1) E_k(\omega_2) E_l(\omega_3), \quad (2)$$

where $\chi_{ijkl}^{(3)}(-\omega_4; \omega_1, \omega_2, \omega_3; t)$ is the tensor of the nonlinear third-order electric susceptibility of the liquid. For an account of its rather complicated properties with respect to the entire range of electric field frequencies, we refer to Ref. [6]. When working to obtain numerical results for specific molecules, it was found convenient [7] to consider the simpler experimental configuration in which the three fields are applied along the laboratory z -axis of coordinates and the dipolar, linearly polarizable molecules possess axially-symmetrical electric properties. In conformity with Debye's assumption, the geometrical properties of the molecules can be thought to be those of the spherical top. Eq. (2) now yields the following, simple relationship:

$$P_z^{(3)}(\omega_4; t) = \chi(-\omega_4; \omega_1, \omega_2, \omega_3; t) E_z(\omega_1) E_z(\omega_2) E_z(\omega_3), \quad (3)$$

where $\chi(-\omega_4; \omega_1, \omega_2, \omega_3; t)$ is the scalar nonlinear electric susceptibility of order 3 of the medium.

Here, we shall extend the theory of nonlinear relaxation phenomena proposed by Kielich and co-workers [5-7] to dynamical rise and decay processes of the polarization $P_z^{(3)}(\omega_4; t)$ due to the application and removal of external electric fields $E_z(\omega)$. In this way, we obtain a description of the dynamics of such nonlinear processes [8] as: third-harmonic generation in liquids defined by the susceptibility $\chi(-3\omega; \omega, \omega, \omega; t)$; second-harmonic generation in liquids in the presence of a static electric field given by the susceptibility $\chi(-2\omega; \omega, \omega, 0; t)$; self-induced variations in electric susceptibility — $\chi(-\omega; \omega, \omega, -\omega; t)$; nonlinear rectification of dielectric frequencies — $\chi(0; 2\omega, -\omega, -\omega; t)$; and quadratic variations in electric permittivity $\frac{\Delta\epsilon(\omega)}{E^2(0)} \sim \chi(-\omega; \omega, 0, 0; t)$ induced by a strong static electric field.

It will be shown that the attainment of a steady state of the polarization, $P_z^{(3)}(\omega_4; t \gg \tau_1)$, is dependent on two Debye rotational relaxation times τ_1 and τ_2 and that for time intervals comparable with τ_1 and τ_2 the dispersion and absorption of nonlinear relaxation phenomena, related with the third-order electric polarization $P_z^{(3)}(\omega_4; t)$ are

described by the well known relaxation factors $R_k(\omega_{abc})$ and new relaxation factors $R_{km}(\omega_{abc})$. The present theory, when applied in experimental studies of the above named effects by usual pulse technique and ultrashort laser pulse technique, will lead to information concerning the relaxation times τ_1 and τ_2 as well as the dynamics of rotational molecular motions in liquids and solutions.

2. Rise in time of third-order electric polarization in liquids

Let us consider an isotropic dielectric of volume V containing N noninteracting axially-symmetric molecules, having a permanent dipole moment m disposed along their symmetry axis, the linear electric polarizability tensor elements $a_{xx} = a_{yy} \neq a_{zz}$, and the nonlinear electric polarizability tensor elements b_{zzz} , $b_{xxx} = b_{yzz}$. To gain insight into the influence of molecular diffusional rotation on $P_z^{(3)}(\omega_4; t)$ at a moment of time t subsequent on application of the electric fields, we have recourse to a statistical averaging procedure defined as follows [9]:

$$\langle P_z(\omega_4; t) \rangle_{\Omega, E} = \frac{1}{V} \int_{\Omega_t} M_z(\Omega_t, E) f_R(\Omega_t; t, E) d\Omega_t. \quad (4)$$

We calculate the orientational probability density function $f_R(\Omega_t; t, E)$ with the equation of Debye rotational diffusion [1]. The function $f_R(\Omega_t; t, E)$ defines the probability of the molecule having the orientation Ω_t at the moment of time t , with Ω denoting the set of Euler angles. Above, $M_z(\Omega_t, E)$ is the z -component of the total dipole moment of the dielectric in the presence of strong external electric fields; on the assumption of zero molecular interaction [10]:

$$M_z[\vartheta_t, E_z(t)] = N \{ m P_1(\cos \vartheta_t) + [a P_0(\cos \vartheta_t) + \frac{2}{3} \gamma P_2(\cos \vartheta_t)] E_z(t) + [\frac{9}{10} b P_1(\cos \vartheta_t) + \frac{1}{5} \kappa P_3(\cos \vartheta_t)] E_z^2(t) + \frac{1}{6} c P_0(\cos \vartheta_t) E_z^3(t) \} + \dots, \quad (5)$$

where $a = \frac{1}{3}(a_{zz} + 2a_{xx})$ is the mean value of the linear electric polarizability of the molecule, $\gamma = a_{zz} - a_{xx}$ its anisotropy, $b = \frac{1}{3}(b_{zzz} - 3b_{xxx})$ its mean second-order polarizability, $\kappa = b_{zzz} - 3b_{xxx}$ the anisotropy of its second-order (nonlinear) polarizability, and $c = \frac{1}{3}(c_{zzzz} + 2c_{xxxx})$ the mean value of its third-order nonlinear electric polarizability tensor; $P_l(\cos \vartheta_t)$ are the Legendre polynomials.

On the molecular model assumed, the potential energy $u[\vartheta_t, E_z(t)]$ and dipole moment component $M_z[\vartheta_t, E_z(t)]$ in the AC external electric field $E_z(t)$ are functions of but one angle — the polar angle ϑ_t , corresponding to the Euler angle β . The energy can be expressed with sufficient accuracy in the form of the following expansion in the set of Legendre polynomials:

$$u[\vartheta_t, E_z(t)] = - \sum_{s=0} u_s[E_z(t)] P_s(\cos \vartheta_t) = -m E_z(t) P_1(\cos \vartheta_t) - [\frac{1}{2} a P_0(\cos \vartheta_t) + \frac{1}{3} \gamma P_2(\cos \vartheta_t)] E_z^2(t) - [\frac{3}{10} b P_1(\cos \vartheta_t) + \frac{1}{15} \kappa P_3(\cos \vartheta_t)] E_z^3(t) - \dots \quad (6)$$

In the present case, the equation of Debye rotational diffusion reduces to:

$$\frac{1}{D_R} \frac{\partial f_R(\vartheta_t; t, E)}{\partial t} = \frac{1}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left[\sin \vartheta \frac{\partial f_R(\vartheta_t; t, E)}{\partial \vartheta} \right] + \frac{1}{kT} \left\{ \frac{\partial u(\vartheta_t, E)}{\partial \vartheta} \frac{\partial f_R(\vartheta_t; t, E)}{\partial \vartheta} + \frac{f_R(\vartheta_t; t, E)}{\sin \vartheta} \frac{\partial}{\partial \vartheta} \left[\sin \vartheta \frac{\partial u(\vartheta_t, E)}{\partial \vartheta} \right] \right\}, \quad (7)$$

D_R denoting the scalar coefficient of rotational diffusion of the molecule.

If the potential energy $u[\vartheta_t, E_z(t)]$ of the molecule is small compared with its thermal energy kT , Eq. (7) is accessible to solution by statistical perturbation calculus; to this aim, we have recourse to the following expansion of the probability density function $f_R(\vartheta_t; t, E)$ in a series in the set of Legendre polynomials:

$$f_R(\vartheta_t; t, E) = \sum_{n=0}^{\infty} \sum_{k=0}^{\infty} (kT)^{-n} f_k^{(n)}(t, E) P_k(\cos \vartheta_t). \quad (8)$$

Inserting the preceding expansion into (7), equating the terms with the same powers of kT , and applying the well known orthogonality properties of Legendre polynomials [11, 12], we obtain the following simple linear differential equation for the successive dynamical coefficients $f_k^{(n)}(t, E)$

$$\frac{1}{D_R} \frac{\partial f_k^{(n)}(t, E)}{\partial t} = -k(k+1) f_k^{(n)}(t, E) - \frac{1}{2} \sum_{k', s} u_s[E(t)] \times f_k^{(n-1)}(t, E) \left[k'(k'+1) - k(k+1) - s(s+1) \right] \begin{bmatrix} s & k' & k \\ 0 & 0 & 0 \end{bmatrix}^2, \quad (9)$$

where the $\begin{bmatrix} s & k' & k \\ 0 & 0 & 0 \end{bmatrix}$ are the Clebsch-Gordan coefficients, well known from angular momentum theory, and summation over k' and s is defined by the "triangle inequality" [11, 12].

In the zeroth approximation of perturbation calculus, we obtain from (9) the equation of free rotational diffusion of spherical top molecules [13, 14]

$$\frac{\partial f_k^{(0)}(t)}{\partial t} = -k(k+1) D_R f_k^{(0)}(t), \quad (10)$$

with the well known solution

$$f_k^{(0)}(t) = \text{const} \exp\left(-\frac{t}{\tau_k}\right). \quad (11)$$

Above, the τ_k are rotational relaxation times, related simply with the rotational diffusion coefficient as follows:

$$\tau_k = [k(k+1)D_R]^{-1} = 2\tau_1[k(k+1)]^{-1}. \quad (12)$$

The solution of Eq. (9) for $n \geq 1$ is of the form:

$$f_k^{(n)}(t, E) = -D_R \exp\left(-\frac{t}{\tau_k}\right) \sum_{s, k'} \frac{k'(k'+1) - k(k+1) - s(s+1)}{2} \\ \times \begin{bmatrix} s & k' & k \\ 0 & 0 & 0 \end{bmatrix}^2 \int_0^t f_k^{(n-1)}(t', E) u_s[E(t')] \exp\left(+\frac{t'}{\tau_k}\right) dt'. \quad (13)$$

If integration in (13) is made to extend from 0 to ∞ , the distribution function corresponds to the case when only the steady state of nonlinear third-order polarization is considered i.e. the state attained by the dielectric after a sufficiently long time since the moment of application or removal of the electric fields (for a complete discussion of this case, see Refs [5-7]). On applying in (4) the probability density function $f_R(\vartheta_i; E, t)$ given by Eqs (8) and (13), on integrating from 0 to ∞ , and on having recourse to the orthogonality properties of Legendre polynomials, one arrives at the following result, analyzed in detail in Ref. [7]:

$$\chi(-\omega_4; \omega_1, \omega_2, \omega_3; t \gg \tau_1) = \frac{N}{90V} \left\{ 15c + \frac{1}{kT} [36mbA(\omega_1 + \omega_2 + \omega_3; t \gg \tau_1) \right. \\ \left. + 4\gamma^2 B(\omega_1 + \omega_2 + \omega_3; t \gg \tau_1)] + \frac{1}{(kT)^2} 8m^2\gamma C(\omega_1 + \omega_2 + \omega_3; t \gg \tau_1) \right. \\ \left. - \frac{2}{(kT)^3} m^4 D(\omega_1 + \omega_2 + \omega_3; t \gg \tau_1) \right\} \exp[-i(\omega_1 + \omega_2 + \omega_3)t]. \quad (14)$$

This expression describes the dispersion and absorption of the third-order electric polarization of the liquid on attainment of equilibrium (neglecting the dependence of the molecular parameters m , γ , b , c on high-frequency electron dispersion). The nonlinear relaxation functions $A(\omega_1 + \omega_2 + \omega_3; t \gg \tau_1)$, $B(\omega_1 + \omega_2 + \omega_3; t \gg \tau_1)$, $C(\omega_1 + \omega_2 + \omega_3; t \gg \tau_1)$ and $D(\omega_1 + \omega_2 + \omega_3; t \gg \tau_1)$ of Eq. (14) have the form:

$$A(\omega_1 + \omega_2 + \omega_3; t \gg \tau_1) = \frac{1}{24} \sum_{abc=1,2,3} [R_1(\omega_{abc}) + 3R_1(\omega_c)], \quad (15)$$

$$B(\omega_1 + \omega_2 + \omega_3; t \gg \tau_1) = \frac{1}{6} \sum_{ab=1,2,3} R_2(\omega_{ab}), \quad (16)$$

$$C(\omega_1 + \omega_2 + \omega_3; t \gg \tau_1) = \frac{1}{12} \sum_{abc=1,2,3} \{R_1(\omega_a)R_2(\omega_{ab}) \\ + \frac{1}{2} [3R_1(\omega_a) - R_2(\omega_{bc})]R_1(\omega_{abc})\}, \quad (17)$$

$$D(\omega_1 + \omega_2 + \omega_3; t \gg \tau_1) = \frac{1}{6} \sum_{abc=1,2,3} R_1(\omega_a)R_2(\omega_{ab})R_1(\omega_{abc}), \quad (18)$$

are dependent on the Debye relaxation factors [5, 6]:

$$R_k(\omega_{abc\dots}) = (1 - i\omega_{abc\dots}\tau_k)^{-1}, \quad (19)$$

$$\omega_{abc\dots} = \omega_a + \omega_b + \omega_c + \dots$$

In Eqs (15)—(18), summation has to extend over all distinct frequencies of the electric fields, $a \neq b \neq c$.

A discussion of nonlinear relaxational processes based on Eqs (14)—(18) for a variety of nonlinear effects, as well as numerical calculations of the dispersion and absorption curves of these effects for the molecules of water and fibrinogen, are to be found in Ref. [7].

We now shall consider the dynamical process whereby a steady state of the polarization $P_z^{(3)}(\omega_4; t \gg \tau_k)$ is attained on switching on the AC electric fields $E_z(\omega_i)$ at the moment of time $t = 0$. We shall use the orientational statistical distribution function $f_R(\theta; E, t)$, given by Eqs (8), (13). The result thus derived states that the polarization rise is described, with accuracy up to $E_z^3(t)$, by the following time-dependent contributions to the third-order polarization tensor:

$$\begin{aligned} \chi(-\omega_4; \omega_1, \omega_2, \omega_3; t) &= \chi^{(0)}(-\omega_4; \omega_1, \omega_2, \omega_3; t) + \frac{1}{kT} \chi^{(1)}(-\omega_4; \omega_1, \omega_2, \omega_3; t) \\ &+ \left(\frac{1}{kT}\right)^2 \chi^{(2)}(-\omega_4; \omega_1, \omega_2, \omega_3; t) + \left(\frac{1}{kT}\right)^3 \chi^{(3)}(-\omega_4; \omega_1, \omega_2, \omega_3; t) + \dots \quad (20) \end{aligned}$$

In the zeroth approximation of statistical perturbation calculus we have:

$$\chi^{(0)}(-\omega_4, \omega_1, \omega_2, \omega_3; t) = \frac{1}{6} \frac{N}{V} c \exp[-i(\omega_1 + \omega_2 + \omega_3)t], \quad (21)$$

showing that the third-order electric polarizability c does not take part, within the $E_z^3(t)$ -approximation, in the rise process of the polarization $P_z^{(3)}(\omega_4; t)$; nor does it contribute, as is seen from Eq. (14) also, to the dispersion or absorption of $P_z^{(3)}(\omega_4; t)$ due to rotational reorientation of the molecules.

In the higher approximation of statistical perturbation calculus we obtain the results:

$$\begin{aligned} \chi^{(1)}(-\omega_4; \omega_1, \omega_2, \omega_3; t) &= \frac{N}{V} \sum_{abc} \left[\frac{1}{10} m(-\omega_{abc}) b(\omega_a, \omega_b, \omega_c) Q_{10}(\omega_{abc}; t) \right. \\ &+ \frac{3}{10} b(-\omega_{abc}, \omega_a, \omega_b) m(\omega_c) \exp(-i\omega_{ab}t) Q_{10}(\omega_c; t) + \frac{2}{45} \gamma(-\omega_{abc}, \omega_a) \gamma(\omega_b, \omega_c) \\ &\quad \times \exp(-i\omega_a t) Q_{20}(\omega_{bc}; t), \quad (22) \\ \chi^{(2)}(-\omega_4; \omega_1, \omega_2, \omega_3; t) &= \frac{2}{45} \frac{N}{V} \sum_{abc} (m(-\omega_{abc}) m(\omega_a) \\ &\quad \times \gamma(\omega_b, \omega_c) \frac{1}{2} \{3R_{10}(\omega_a) [Q_{10}(\omega_{abc}; t) - Q_{11}(\omega_{bc}; t)] \\ &\quad - R_{20}(\omega_{bc}) [Q_{10}(\omega_{abc}; t) - Q_{12}(\omega_a; t)]\} \\ &\quad + \gamma(-\omega_{abc}, \omega_a) m(\omega_b) m(\omega_c) R_{10}(\omega_c) [Q_{20}(\omega_{bc}; t) - Q_{21}(\omega_b; t)] \exp(-i\omega_a t), \end{aligned}$$

$$\chi^{(3)}(-\omega_4; \omega_1, \omega_2, \omega_3; t) = -\frac{1}{4^{\frac{1}{2}}} \frac{N}{V} \sum_{abc} m(-\omega_{abc})m(\omega_a)m(\omega_b)m(\omega_c)R_{10}(\omega_c) \\ \times \{R_{20}(\omega_{bc}) [Q_{10}(\omega_{abc}; t) - Q_{12}(\omega_a; t)] - R_{21}(\omega_b) [Q_{11}(\omega_{ab}; t) - Q_{12}(\omega_a; t)]\}. \quad (24)$$

In Eqs (22)–(24), we have introduced the time-dependent relaxational functions

$$Q_{km}(\omega_{abc}; t) = R_{km}(\omega_{abc}) \left[\exp\left(-i\omega_{abc}t - \frac{t}{\tau_m}\right) - \exp\left(-\frac{t}{\tau_k}\right) \right] \quad (25)$$

\sum_{abc} being the operator of symmetrization over the frequencies $\omega_a, \omega_b, \omega_c$.

Eqs (22)–(24) are written in a way to stress the dependence of the electric properties of the molecule (its dipole moment m , anisotropy of polarizability γ , and mean electric hyperpolarizability b) on the frequencies of the external electric fields [5, 6]. The dependence in question is related with the well known Voigt–Lorentz electron dispersion [15, 16] which is apparent chiefly in the range of optical frequencies [6], and is of essential importance in electro-optical effects involving Debye molecular reorientation in addition to electron dispersion due to the electric field of a laser light wave. The Debye reorientation can be due to difference frequencies between modes of laser light (the inverse difference frequencies being comparable with the rotational relaxation times τ_k) or to modulation of the medium by an external slowly variable electric field.

Eqs (20)–(25) represent the chief result of this investigation. They describe the evolution in time of the process leading, in liquids, to a steady state of third-order polarization under the action of three, in general time-variable electric fields. Each of the temperature contributions to the susceptibility $\chi(-\omega_4; \omega_1, \omega_2, \omega_3; t)$ (20) given by Eqs (22)–(24) can be resolved into a steady state part and a dynamical part, the former describing the steady state of the polarization of the medium and the latter its rise in time immediately after switching on the fields. The dynamical part consists, in addition to terms oscillating with the frequencies of the externally applied electric fields, of non-oscillating terms with exponential time growths, their dispersive properties determined by the factors [17]:

$$R_{km}(\omega_{abc}) = \left(1 - \frac{\tau_k}{\tau_m} - i\omega_{abc}\tau_k\right)^{-1}. \quad (26)$$

For $m = 0$, these generalized dispersive factors go over into the well known Debye factors (19), defining dispersion and absorption of third-order polarization in the steady state, as already discussed in Refs [5–7]. Eqs (20)–(25) are of a form which makes it possible to analyze directly the time-evolution of the individual nonlinear electro-optical phenomena enumerated in the Introduction simply by specifying the frequencies of the electric fields applied. The decay in time of the polarization $P_z^{(3)}(\omega_4; t)$ after the fields are switched off is described similarly.

The above results provide a consistent description of the time-dependent variations in nonlinear relaxational phenomena in the approximation of Debye rotational diffusion taking into account the processes of time-variable polarization which set in when the

externally applied fields are switched on, or off. This, obviously, is essentially important with regard to measurements of the dielectric and optical properties of the molecules by pulse techniques, when the switch-on time of the fields can be of the same order as the Debye rotational relaxation times.

The above applied method of determining the orientational probability density function from the equation of Debye rotational diffusion can be extended by taking into consideration the molecular interactions in the liquid [18, 19], and is well adapted to application within the more general method of nonlinear response functions [20-22]. It is worth noting that the probability density function (7) has been applied for the description of the spectral line shape of elastic and inelastic light scattering by molecules of liquids reoriented by an external electric field [17, 23]; moreover, a similar formalism can be used for the description of pulse electric field-induced effects of birefringence in liquids [6, 24].

3. Particular cases of application of the theory, and conclusions

Let us begin with the case when the medium is acted on by one, sufficiently intense electric field $E(\omega)$. The nonlinear third-order polarization now consists of a part which oscillates with the frequency of the field, ω , and a part oscillating with the tripled frequency 3ω . The time variations of the polarizations are described by Eqs (22)–(25) with $\omega_1 = \omega_2 = \omega$, $\omega_3 = -\omega$, or $\omega_1 = \omega_2 = \omega_3 = \omega$.

For the component oscillating at 3ω , we obtain:

$$\begin{aligned} \chi^{(1)}(-3\omega; \omega, \omega, \omega; t) = & \frac{N}{V} \left[\frac{1}{10} m(-3\omega) b(\omega, \omega, \omega) Q_{10}(3\omega; t) \right. \\ & + \frac{3}{10} b(-3\omega, \omega, \omega) m(\omega) Q_{10}(\omega; t) \exp(-i2\omega t) \\ & \left. + \frac{2}{45} \gamma(-3\omega, \omega) \gamma(\omega, \omega) Q_{20}(2\omega; t) \exp(-i\omega t) \right], \end{aligned} \quad (27)$$

$$\begin{aligned} \chi^{(2)}(-3\omega; \omega, \omega, \omega; t) = & \frac{1}{45} \frac{N}{V} m(-3\omega) m(\omega) \gamma(\omega, \omega) \\ & \times \{ 3R_{10}(\omega) [Q_{10}(3\omega; t) - Q_{11}(2\omega; t)] - R_{20}(2\omega) [Q_{10}(3\omega; t) - Q_{12}(\omega; t)] \} \\ & + \frac{2}{45} \frac{N}{V} \gamma(-3\omega, \omega) [m(\omega)]^2 R_{10}(\omega) [Q_{20}(2\omega; t) - Q_{21}(\omega; t)] \exp(-i\omega t), \end{aligned} \quad (28)$$

$$\begin{aligned} \chi^{(3)}(-3\omega; \omega, \omega, \omega; t) = & -\frac{1}{45} \frac{N}{V} m(-3\omega) [m(\omega)]^3 R_{10}(\omega) \\ & \times \{ R_{20}(2\omega) [Q_{10}(3\omega; t) - Q_{12}(\omega; t)] - R_{21}(\omega) [Q_{11}(2\omega; t) - Q_{12}(\omega; t)] \}, \end{aligned} \quad (29)$$

whereas for the time-variations of the component at ω we get the following contributions:

$$\begin{aligned} \chi^{(1)}(-\omega; \omega, \omega, -\omega; t) &= \frac{N}{V} \left\{ \frac{1}{10} m(-\omega)b(\omega, \omega, -\omega)Q_{10}(\omega; t) \right. \\ &+ \frac{1}{10} b(-\omega, \omega, \omega)m(-\omega)Q_{10}(-\omega; t) \exp(-i2\omega t) + \frac{1}{5} b(-\omega, -\omega, \omega)m(\omega)Q_{10}(\omega; t) \\ &\left. + \frac{4}{135} [\gamma(-\omega, \omega)]^2 Q_{20}(0; t) + \frac{2}{135} \gamma(-\omega, -\omega)\gamma(\omega, \omega)Q_{20}(2\omega; t) \exp(i\omega t) \right\}, \quad (30) \end{aligned}$$

$$\begin{aligned} \chi^{(2)}(-\omega; \omega, \omega, -\omega; t) &= \frac{N}{135} \frac{N}{V} m(-\omega)m(\omega)\gamma(\omega, -\omega) \\ &\times \frac{1}{2} \{3R_{10}(\omega) [Q_{10}(\omega; t) - Q_{11}(0; t)] - Q_{10}(\omega; t) - Q_{12}(\omega; t)\} \\ &+ \frac{2}{135} \frac{N}{V} m(-\omega)m(-\omega)\gamma(\omega, \omega) \frac{1}{2} \{3R_{10}(-\omega) [Q_{10}(\omega; t) - Q_{11}(2\omega; t)] \\ &\quad - R_{20}(2\omega) [Q_{10}(\omega; t) - Q_{12}(-\omega; t)]\} \\ &+ \frac{2}{135} \frac{N}{V} \{ \gamma(-\omega, \omega)m(\omega)m(-\omega) [R_{10}(-\omega) + R_{10}(\omega)] \\ &\times [Q_{20}(0; t) - Q_{21}(\omega; t)] \exp(-i\omega t) + \gamma(-\omega, -\omega)m(\omega)m(\omega) \\ &\quad \times R_{10}(\omega) [Q_{20}(2\omega; t) - Q_{21}(\omega; t)] \exp(i\omega t) \}, \quad (31) \end{aligned}$$

$$\begin{aligned} \chi^{(3)}(-\omega; \omega, \omega, -\omega; t) &= -\frac{1}{135} \frac{N}{V} m(-\omega)m(-\omega)m(\omega)m(\omega) \\ &\times (R_{10}(-\omega) \{ [Q_{10}(\omega; t) - Q_{12}(\omega; t)] - R_{21}(\omega) [Q_{11}(2\omega; t) - Q_{12}(\omega; t)] \}) \\ &+ R_{10}(\omega) \{ R_{20}(2\omega) [Q_{10}(\omega; t) - Q_{12}(-\omega; t)] - R_{21}(\omega) [Q_{11}(0; t) - Q_{12}(-\omega; t)] \} \\ &+ R_{10}(\omega) \{ [Q_{10}(\omega; t) - Q_{12}(\omega; t)] - R_{21}(-\omega) [Q_{11}(0; t) - Q_{12}(\omega; t)] \}. \quad (32) \end{aligned}$$

Eqs (27)–(32) show that the time-variations are dependent on the relaxation times τ_1, τ_2 and (in a rather complicated manner) on the relaxational factors. Moreover, they show that the rise in time of the polarizations at ω and 3ω — which it is our intention to propose for experimental investigation — is of the form of superpositions of exponentials, depending variously on temperature, as well as of non-exponential factors:

$$\lim_{\omega \rightarrow 0} Q_{11}(\omega; t) = \frac{t}{\tau_1} \exp\left(-\frac{t}{\tau_1}\right). \quad (33)$$

For very high frequencies of the electric field (this is the case of laser light) we have $\omega\tau \rightarrow \infty$ and one can assume that

$$\lim_{\omega\tau \rightarrow \infty} R_k(\omega) = \lim_{\substack{\omega\tau \rightarrow \infty \\ k \neq m}} R_{km}(\omega) = 0. \quad (34)$$

The only non-zero contribution is, now,

$$\chi_{\omega}^{(1)} = \frac{4}{135} \frac{N}{V} [\gamma(-\omega, \omega)]^2 \exp(-i\omega t) \left[1 - \exp\left(-\frac{t}{\tau_2}\right) \right], \quad (35)$$

meaning that the setting in of the steady state depends on the relaxation time τ_2 and that the effect moreover depends on electron dispersion of the anisotropy $\gamma(-\omega, \omega)$ of the linear electric polarizability of the molecules. Within this approximation, the rise in time of third-harmonic light generation, related with the tensor of second-order nonlinear electric polarizability c_{ijkl} , does not depend on rotational reorientation of the molecules.

Third-harmonic generation of light has been observed in a variety of molecular media [25–29]. The feasibility of third-harmonic generation at dielectric frequencies by unlocalized electric dipoles in paraelectric media has been suggested in Ref. [30].

We shall now consider dielectric saturation in dipolar liquids [2, 4, 6, 31, 32]. The effect consists in a change in third-order electric susceptibility $\chi(-\omega; \omega, 0, 0; t)$ due to the application of an intense static electric field $E(0)$. The variation can be studied by means of an analyzing electric field $E(\omega)$.

Eqs (22)–(24) lead to the following time-dependence of the quadratic changes in electric susceptibility

$$\begin{aligned} \frac{\Delta\epsilon(\omega; t)}{E^2(0)} &\sim \chi(-\omega; \omega, 0, 0; t), \\ \frac{\Delta\epsilon(\omega; t)}{E^2(0)} &\sim \frac{1}{5} \frac{N}{V} \frac{mb}{kT} \left\{ [1 + R_{10}(\omega)] \exp(-i\omega t) - [\exp(-i\omega t) + R_{10}(\omega)] \exp\left(-\frac{t}{\tau_1}\right) \right\} \\ &+ \frac{2}{135} \frac{N}{V} \frac{\gamma^2}{kT} \left\{ [1 + 2R_{20}(\omega)] \exp(-i\omega t) - [\exp(-i\omega t) + 2R_{20}(\omega)] \exp\left(-\frac{t}{\tau_2}\right) \right\} \\ &+ \frac{2}{135} \frac{N}{V} \frac{m^2\gamma}{(kT)^2} \left\{ [1 + \frac{5}{2} R_{10}(\omega) + R_{20}(\omega) + \frac{3}{2} R_{10}(\omega)R_{10}(\omega)] \exp(-i\omega t) \right. \\ &- [(\frac{3}{2} + 3R_{11}(\omega) + R_{21}(\omega)) \exp(-i\omega t) + 4R_{10}(\omega) - \frac{1}{2} R_{20}(\omega) + \frac{1}{2} R_{12}(\omega) - 3R_{11}(\omega) \\ &+ \frac{3}{2} R_{10}(\omega)R_{10}(\omega) - R_{10}(\omega)R_{20}(\omega)] \exp\left(-\frac{t}{\tau_1}\right) - \frac{3}{2} \left(\frac{t}{\tau_1}\right) R_{10}(\omega) \exp\left(-\frac{t}{\tau_1}\right) \\ &\left. + \frac{1}{2} [(1 + R_{12}(\omega)) \exp(-i\omega t) \right. \\ &\left. + \frac{3}{2} R_{10}(\omega) - \frac{3}{2} R_{20}(\omega) + R_{21}(\omega) - R_{10}(\omega)R_{20}(\omega)] \exp\left(-\frac{t}{\tau_2}\right) \right\} \\ &- \frac{1}{135} \frac{N}{V} \frac{m^4}{(kT)^3} \left\{ [R_{10}(\omega) + R_{10}(\omega)R_{20}(\omega) + R_{10}(\omega)R_{20}(\omega)R_{10}(\omega)] \exp(-i\omega t) \right. \\ &\left. - [\frac{1}{2} R_{11}(\omega) (3 + 2R_{21}(\omega)) \exp(-i\omega t) + \frac{1}{4} R_{10}(\omega) + \frac{1}{2} R_{12}(\omega) - \frac{3}{2} R_{11}(\omega) \right\} \end{aligned}$$

$$\begin{aligned}
& +\frac{1}{2} R_{20}(\omega) - \frac{1}{2} R_{21}(\omega) + \frac{3}{2} R_{10}(\omega) R_{20}(\omega) + R_{10}(\omega) R_{20}(\omega) R_{10}(\omega) - R_{11}(\omega) R_{21}(\omega)] \\
& \times \exp\left(-\frac{t}{\tau_1}\right) + \left[\frac{1}{2} R_{12}(\omega) \exp(-i\omega t) - \frac{3}{4} R_{10}(\omega) + \frac{1}{2} R_{20}(\omega) - \frac{1}{2} R_{21}(\omega)\right. \\
& \left. + \frac{1}{2} R_{10}(\omega) R_{20}(\omega)\right] \exp\left(-\frac{t}{\tau_2}\right) - \frac{3}{2} R_{10}(\omega) \left(\frac{t}{\tau_1}\right) \exp\left(-\frac{t}{\tau_1}\right) \Big\}. \quad (36)
\end{aligned}$$

Above, we have neglected the dependence of the molecular polarizability parameters on Lorentz-Voigt electron dispersion [6].

By (36), the time-variations of dielectric saturation in liquids depend, in a rather highly complicated way, on the two relaxation times τ_1 and τ_2 . In the following two particular cases, however, the situation becomes considerably simpler:

(1) if the analyzing electric field is static in time, or if its vibration frequency is low $\left(\omega \ll \frac{1}{\tau_2}\right)$,

(2) when considering nonlinear dispersion and absorption of dielectric saturation in the steady state i.e. at moments of time $t \gg \tau_1$ subsequent to the switching on of external electric fields (τ_1 being the rotational relaxation time).

In the former case we have the relation:

$$\lim_{\substack{\omega \rightarrow 0 \\ k \neq m}} R_{km}(\omega) = \frac{k(k+1)}{k(k+1) - m(m+1)}, \quad (37)$$

with which we derive from Eq. (36) the simpler formula:

$$\begin{aligned}
\frac{\Delta\varepsilon\left(\omega \ll \frac{1}{\tau_2}; t\right)}{E^2(0)} & \sim \frac{2}{5} \frac{N}{V} \frac{mb}{kT} A\left(\omega \ll \frac{1}{\tau_2}; t\right) + \frac{2}{4^5} \frac{N}{V} \frac{\gamma^2}{kT} B\left(\omega \ll \frac{1}{\tau_2}; t\right) \\
& + \frac{4}{4^5} \frac{N}{V} \frac{m^2\gamma}{(kT)^2} C\left(\omega \ll \frac{1}{\tau_2}; t\right) - \frac{1}{4^5} \frac{N}{V} \frac{m^4}{(kT)^3} D\left(\omega \ll \frac{1}{\tau_2}; t\right), \quad (38)
\end{aligned}$$

involving the following relaxation functions:

$$A\left(\omega \ll \frac{1}{\tau_2}; t\right) = 1 - \exp\left(-\frac{t}{\tau_1}\right), \quad (39)$$

$$B\left(\omega \ll \frac{1}{\tau_2}; t\right) = 1 - \exp\left(-\frac{t}{\tau_2}\right), \quad (40)$$

$$C\left(\omega \ll \frac{1}{\tau_2}; t\right) = 1 - \frac{9}{8} \exp\left(-\frac{t}{\tau_1}\right) + \frac{1}{8} \exp\left(-\frac{t}{\tau_2}\right) - \frac{1}{2} \left(\frac{t}{\tau_1}\right) \exp\left(-\frac{t}{\tau_1}\right), \quad (41)$$

$$D\left(\omega \ll \frac{1}{\tau_2}; t\right) = 1 - \frac{3}{4} \exp\left(-\frac{t}{\tau_1}\right) - \frac{1}{4} \exp\left(-\frac{t}{\tau_2}\right) - \frac{3}{2} \left(\frac{t}{\tau_1}\right) \exp\left(-\frac{t}{\tau_1}\right). \quad (42)$$

By Eqs (38)—(42), the time-variations of dielectric saturation for experimental observation are superpositions of exponential terms and a term of the form $\left(\frac{t}{\tau_1}\right) \exp\left(-\frac{t}{\tau_1}\right)$. They should be accessible to investigation — and hence the molecular relaxation times τ_1 and τ_2 as well — by performing experiments with appropriately chosen nondipolar, or strongly dipolar liquids.

The relaxations (39)—(42) visualize the competitive roles of the various temperature-dependent contributions in dielectric saturation. They show that the rise in time of the polarization due to permanent dipole moment reorientation is slower than the changes

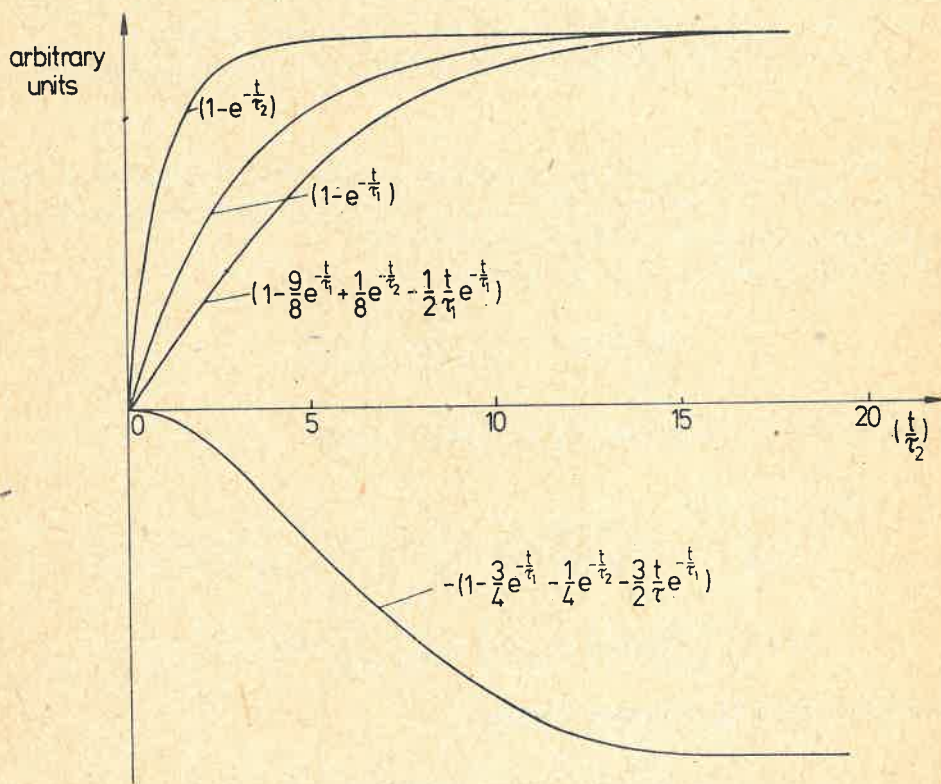


Fig. 1. Normalized time-rise functions for different molecular contributions to quadratic variations in dielectric saturation in liquids calculated from Eqs (39)—(42), versus $\left(\frac{t}{\tau_2}\right)$

caused by reorientation of the anisotropy in electric polarizability of the molecule. Fig. 1 shows the different time-evolutions of the relaxation functions (39)—(42) vs the parameter $\left(\frac{t}{\tau_2}\right)$; the plots were prepared taking $\tau_1 = 3\tau_2$ in accordance with Debye's rotational diffusion approximation, τ_2 denoting the relaxation time of electric birefringence [34—36].

In the latter case ($\omega; t \gg \tau_1$), the shape of the relaxation functions A, B, C, D can be calculated either by performing a symmetrization for the frequencies $\omega_1 = \omega, \omega_2 = \omega_3 = 0$ in Eqs (15)–(18), or by going over to $t \rightarrow \infty$ in Eq. (36). We now obtain:

$$A(\omega; t \gg \tau_1) = \frac{1}{2} [1 + R_{10}(\omega)], \quad (43)$$

$$B(\omega; t \gg \tau_1) = \frac{1}{3} [1 + 2R_{20}(\omega)], \quad (44)$$

$$C(\omega; t \gg \tau_1) = \frac{1}{6} [1 + \frac{5}{2} R_{10}(\omega) + R_{20}(\omega) + \frac{3}{2} R_{10}(\omega)R_{10}(\omega)], \quad (45)$$

$$D(\omega; t \gg \tau_1) = \frac{1}{3} [1 + R_{20}(\omega) + R_{10}(\omega)R_{20}(\omega)]R_{10}(\omega). \quad (46)$$

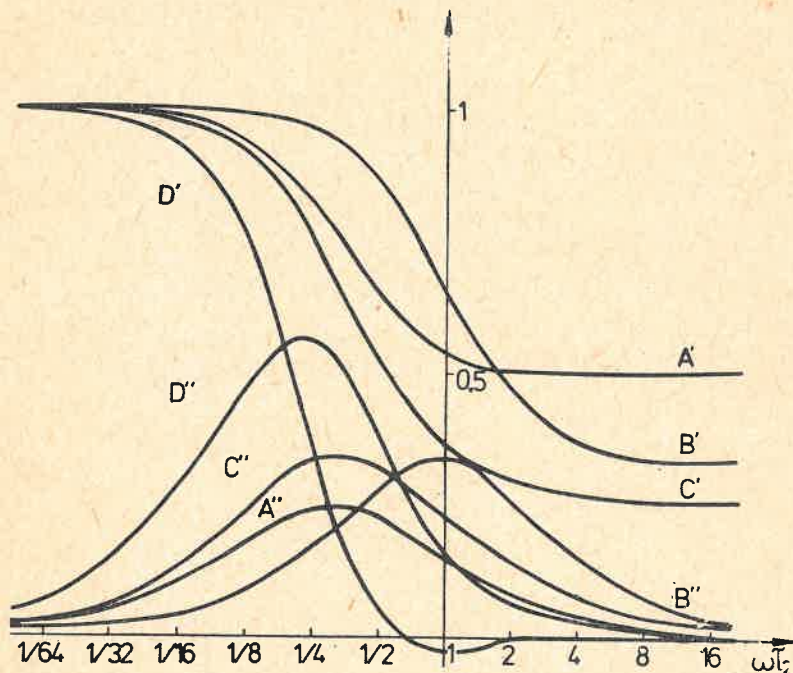


Fig. 2. Normalized dispersion A', B', C', D' and absorption A'', B'', C'', D'' curves for different molecular contributions to quadratic variations in dielectric saturations from Eqs (43)–(46), versus $\omega\tau_2$

By applying Eq. (19), we resolve the functions (43)–(46) into a real part, describing dispersion, and an imaginary part, describing absorption of dielectric saturation $\frac{\Delta\epsilon(\omega; t \gg \tau_1)}{E^2(0)}$.

$$\frac{\Delta\epsilon(\omega; t \gg \tau_1)}{E^2(0)}$$

The dispersion and absorption functions are plotted vs $\omega\tau_2$ in Fig. 2.

In order to visualize the evolution in time of the changes in electric saturation following the switching on of external electric fields, or the evolution of dispersion and absorption in a system of non-interacting dipolar, linearly polarizable molecules ($m \neq 0, \gamma \neq 0, b = c = 0$), we introduce (as in Ref. [36]) the dimensionless molecular parameter

$$r = \frac{m^4}{(kT)^3} : \frac{m^2\gamma}{(kT)^2} = \frac{1}{kT} \frac{m^2}{\gamma}. \quad (47)$$

For molecules with a small permanent dipole (or non-dipolar ones) r is close to zero. For strongly dipolar ones, r differs strongly from zero. The sign of r depends on that of $\gamma = a_{zz} - a_{xx}$, the electric polarizability anisotropy.

By (14) we have, on applying Eq. (47), for $b = c = 0$:

$$\frac{\Delta\epsilon(\omega; t)}{E^2(0)} \sim \frac{1}{4^{5/2}} \frac{N}{V} \frac{m^4}{(kT)^3} \left\{ 2 \left(\frac{1}{r} \right)^2 B(\omega; t) + \frac{4}{r} C(\omega; t) - D(\omega; t) \right\}, \quad (48)$$

and the functions $B(\omega; t)$, $C(\omega; t)$, $D(\omega; t)$ go over respectively into (40)—(42), or (44)—(46), for the two cases considered above. Their explicit form is to be obtained by comparing Eqs (48) and (36).

As shown in Figs 3a—5a for positive r and in Figs 3b—5b for $r < 0$, recourse can be had to Eq. (48) for performing an analysis of the time-variations or dispersion and absorption of the electric saturation for molecular systems characterized by different values of the parameter r . The strongly different time- and dispersional characteristics of the terms related with the dipole moment and polarizability anisotropy (Figs 1, 2) cause the responses of systems to externally applied electric fields to differ in shape strongly and thus to render apparent the competitive nature of the various molecular contributions. Eq. (48) shows that the magnitude of electric saturation, attained by the system after a sufficiently long time $t \gg \tau_1$ subsequent on its immersion in slowly variable electric fields ($\omega \ll \frac{1}{\tau_1}$), amounts to:

$$\frac{\Delta\epsilon\left(\omega \ll \frac{1}{\tau_1}; t \gg \tau_1\right)}{E^2(0)} \sim \frac{1}{4^{5/2}} \frac{N}{V} \frac{m^4}{(kT)^3} \left(\frac{2}{r^2} - \frac{4}{r} + 1 \right), \quad (49)$$

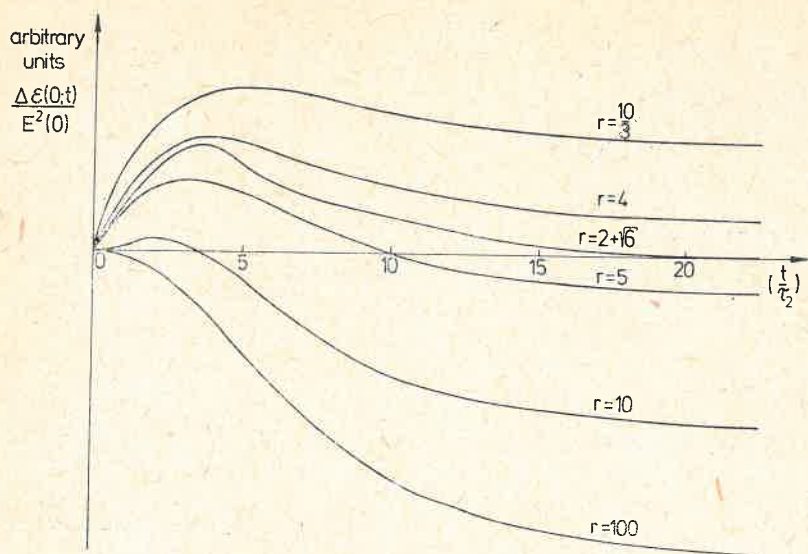
since now we have:

$$B\left(\omega \ll \frac{1}{\tau_1}; t \gg \tau_1\right) = C\left(\omega \ll \frac{1}{\tau_1}; t \gg \tau_1\right) = D\left(\omega \ll \frac{1}{\tau_1}; t \gg \tau_1\right) = 1. \quad (50)$$

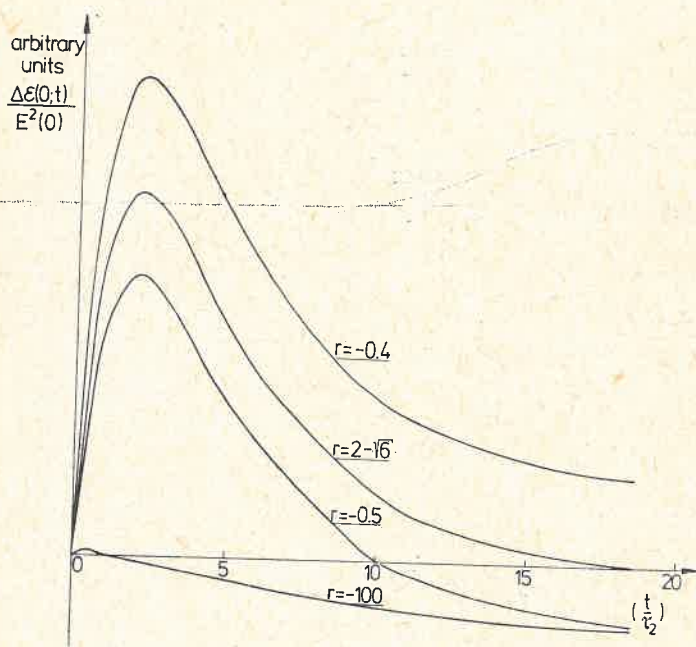
Eq. (49) shows moreover that for the two values of r :

$$r_{1,2} = 2 \pm \sqrt{6} \quad (51)$$

the electric saturation curves take a rather specific shape. In the case of slowly variable fields and measurements after a considerable lapse of time, $\Delta\epsilon$ becomes zero. We have $\Delta\epsilon \neq 0$ only in the short time range (Figs 3a, 3b) and for $t \gg \tau_2$ when the analyzing frequency is comparable to or larger than the inverse rotational relaxation time (Figs 4a, 4b, 5a, 5b). Also noteworthy and highly characteristic are the dispersion and absorption curves and time-variations of electric saturation, which exhibit an anomalous rise or decrease in $\Delta\epsilon$ for certain values of $\frac{t}{\tau_2}$ or $\omega\tau_2$ due to competition between the contributions from the dipole moment and polarizability anisotropy and to their different signs. In



a



b

Fig. 3. Time dependence of $\frac{\Delta\epsilon\left(\omega \ll \frac{1}{\tau_1}; t\right)}{E^2(0)}$ for some values of the molecular parameter r ; (a) $r > 0$,
(b) $r < 0$

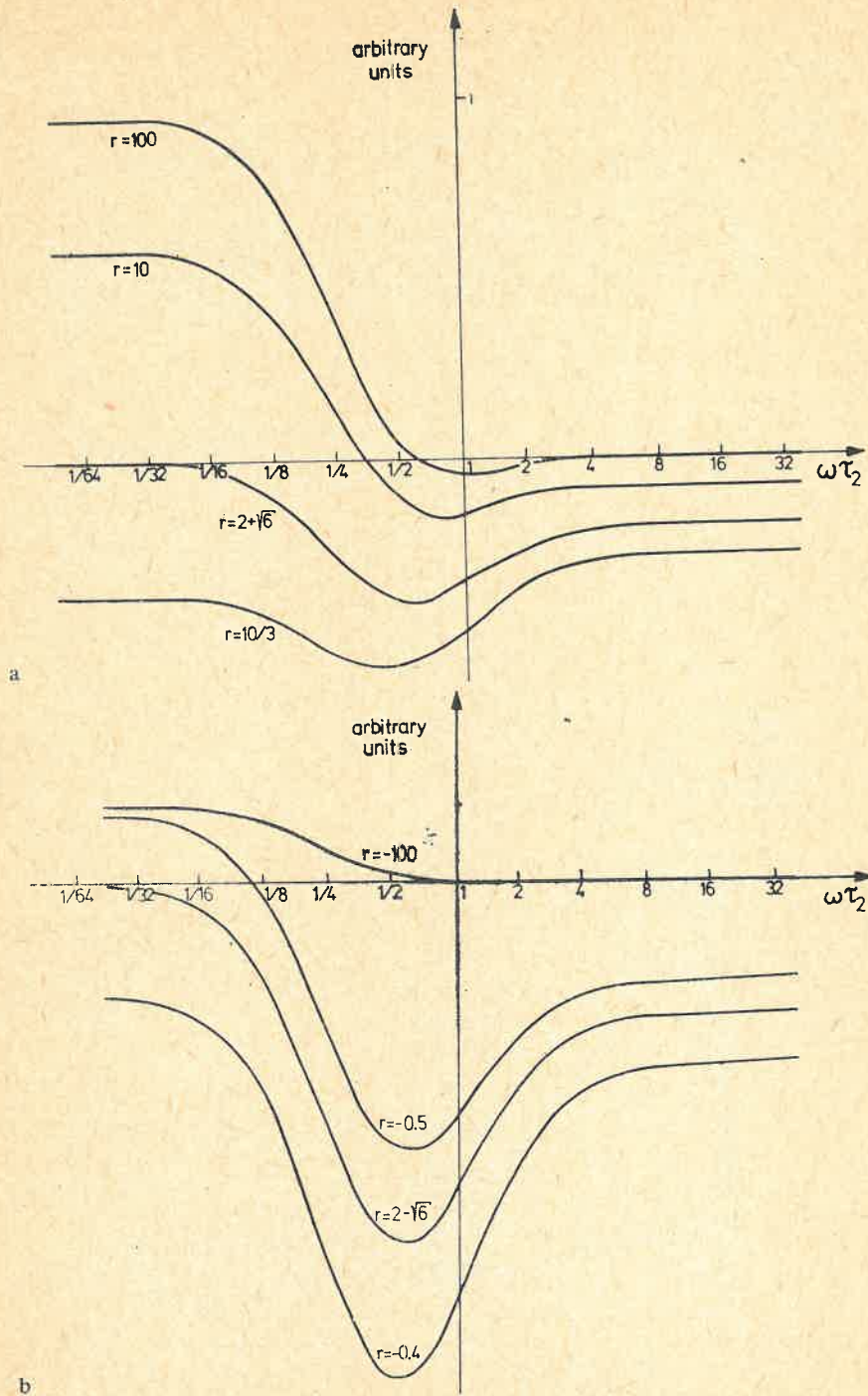


Fig. 4. Dispersion curves of $\text{Re} \left\{ \frac{\Delta\epsilon(\omega; t \gg \tau_2)}{E^2(0)} \right\}$ for some values of the molecular parameter r ; (a) $r > 0$, (b) $r < 0$

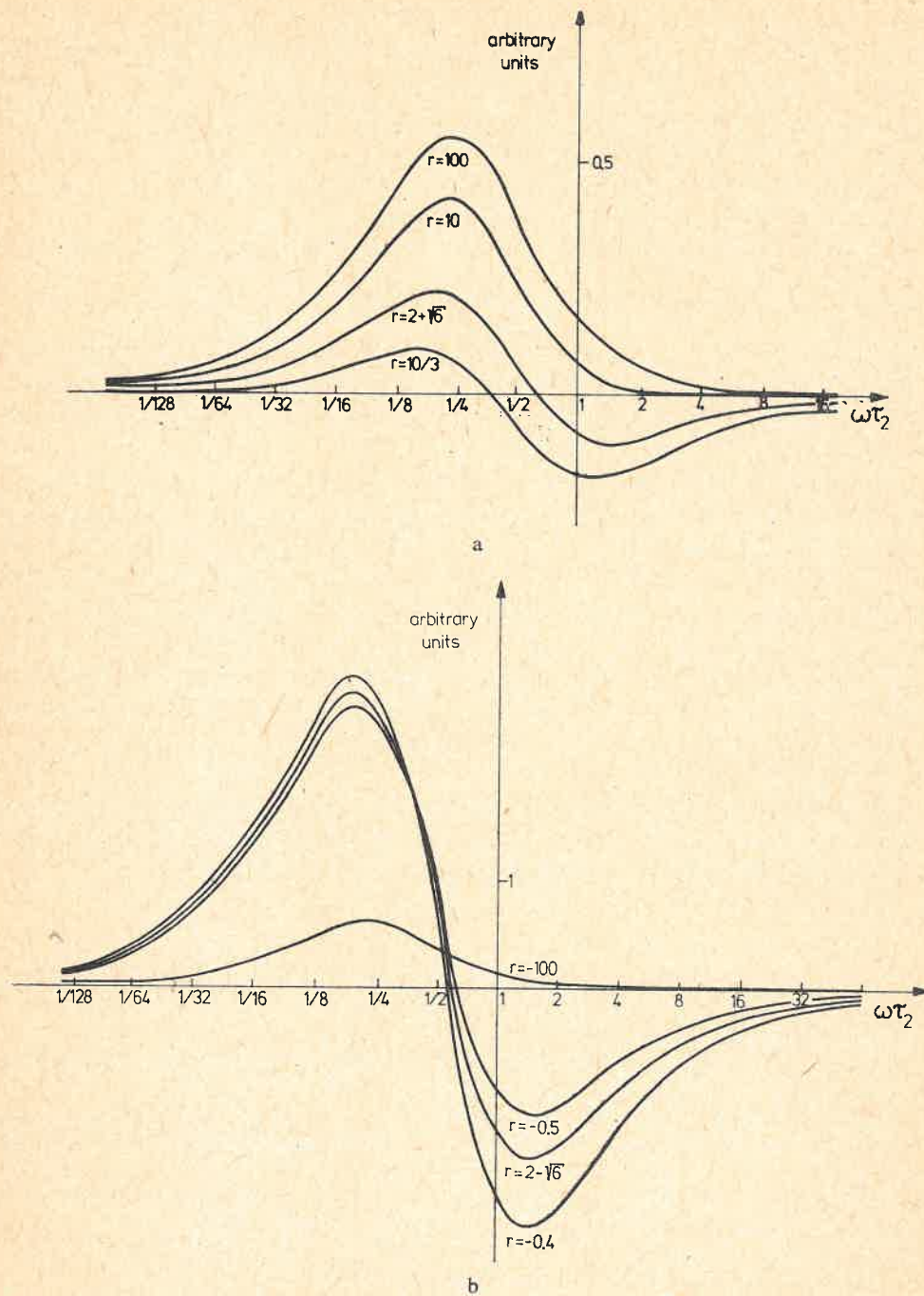


Fig. 5. Absorption curves of $\text{Im} \left\{ \frac{\Delta\epsilon(\omega; t \gg \tau_2)}{E^2(0)} \right\}$ for some values of the molecular parameter r ; (a) $r > 0$
 (b) $r < 0$

the case of molecules for which the values of r fulfil the inequality $r_2 < r < r_1$, the effect of electric saturation undergoes a change in sign during the time process whereby the polarization of the medium tends to the steady state, or if the frequency of the analyzing field is made to vary appropriately. Similarly, a change in sign is to be observed when investigating the absorption curves (Figs 5a, 5b).

The nonlinear effects given by Eqs (22)—(24) are also accessible to this treatment, as done in Refs [6, 7] for dispersion and absorption.

Noteworthy are the latest results on electric saturation in liquids [32] and studies [33] of quadratic changes in the nonlinear electric susceptibility $\frac{\Delta\epsilon(\omega; t \gg \tau_2)}{E^2(0)}$ in solutions of ϵ -caprolactam in cyclohexane under the action of an intense static electric field taking into account dispersion and absorption of the measuring field over the frequency range from 2 to 100 MHz. It is to be hoped that this kind of work can soon be extended to time-variations of dielectric saturation.

All in all, from the present considerations, the variations in time of third-order electric polarization in liquids are characterized by a complicated dependence on the dispersional, relaxational and electric properties of the molecules. By having recourse to the model of Debye's rotational relaxation, we have obtained in Eqs (20)—(25) a consistent description of third-order polarization as a function of time. Our results permit a detailed analysis of the time-evolution of a wide variety of phenomena, as done above for the induction of fundamental and third-harmonic nonlinear polarization as well as for the process leading to a steady state of quadratic variations in nonlinear electric susceptibility. The same procedure can be applied with regard to the evolution in time of relaxation processes, related with other nonlinear effects.

The present, rapid progress in pulse technique will most probably permit the extension of dielectric studies of molecules in liquids to the determination of the time-variations of dispersion and absorption of various nonlinear relaxational processes.

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