

The Chemical Society

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SYMPOSIUM No. 11

NEWER ASPECTS OF MOLECULAR RELAXATION PROCESSES

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11 C. Barker and J. Yarwood* *University of Durham, UK*

Studies of ion-ion and ion-molecule interactions using far infra-red interferometry

* Reading Author

† Not preprinted

Molecular Relaxation Times from Time-variations of Dispersion and Absorption of Third-order Electric Polarisation in Liquids

BY WŁADYSŁAW ALEXIEWICZ, JANUSZ BUCHERT and STANISŁAW KIELICH

Nonlinear Optics Division, Institute of Physics,
A. Mickiewicz University, 60-780 Poznan, Poland

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Processes involving an increase in nonlinear 3rd order electric polarisation in dipolar liquids by the action of external electric fields are considered in the approximation of Debye's rotational diffusion model of geometrically spherical molecules. For times comparable with the Debye times of molecular orientation, we show that the dispersion and absorption of the above effects are described by the well known Debye factors $R_i(\omega)$ and supplementary factors $R_{ik}(\omega)$, and that the setting in of steady state polarisation depends on the relaxation times τ_1, τ_2 . We perform a detailed analysis of the case of quadratic changes in electric permittivity in a static electric field.

Recently, a classical theory has appeared concerning nonlinear processes of molecular relaxation in strong electric fields of both low and high frequencies and describing the dispersion and absorption of third-order polarisation of liquid dielectrics in terms of Debye molecular rotational diffusion and Lorentz-Voigt electron dispersion.^{1,2}

For an experimental system in which three electric fields with the frequencies $\omega_1, \omega_2, \omega_3$ are applied to the dielectric in the same direction, i.e., along the z -axis, the nonlinear electric polarisation of third order, $P_z^{(3)}(\omega_4)$, is given generally at the frequency $\omega_4 = \omega_1 + \omega_2 + \omega_3$ by:

$$P_z^{(3)}(\omega_4; t) = \chi(-\omega_4, \omega_1, \omega_2, \omega_3; t) E_z(\omega_1) E_z(\omega_2) E_z(\omega_3), \quad (1)$$

where χ is the scalar nonlinear third-order susceptibility of the isotropic dielectric; the dependence of χ on the electric field frequencies is considered in ref. (3). The time-variable electric field is given by:

$$E_z(t) = \sum_{a=\pm(1,2,3)} E_z(\omega_a) \exp(-i\omega_a t). \quad (2)$$

Here, by taking into consideration the dependence of the susceptibility tensor χ on time, we extend the theory to processes of increase and decrease in nonlinear polarisation caused by the imposition and removal of electric fields. In this way, we obtain a description of the dynamics of numerous nonlinear processes, such as third-harmonic generation, with the nonlinear susceptibility $\chi(-3\omega, \omega, \omega, \omega; t)$; second-harmonic generation in the presence of a static electric field, $\chi(-2\omega, \omega, \omega, 0; t)$; nonlinear rectification of optical and electric frequencies, $\chi(-0, \omega, -\omega, 0; t)$; self-induced changes in electric susceptibility, $\chi(-\omega, \omega, \omega, -\omega; t)$; and quadratic changes in electric permittivity $\Delta\epsilon(\omega, t)/E^2 \sim \chi(-\omega, \omega, 0, 0; t)$ in a strong static electric field.

THEORETICAL

Consider an isotropic dielectric, the N noninteracting axially symmetric molecules of which possess a permanent dipole moment m parallel to the symmetry z -axis, the tensor components $a_{xx} = a_{yy} \neq a_{zz}$ of linear electric polarisability, and the tensor components $b_{zzz}, b_{xxx} = b_{yyy}$ of electric hyperpolarisability. We are interested in the time-variations of polarisation due to the switching on of AC electric fields. We calculate these time-variations by determining the probability distribution function of orientation, $f(\theta, t)$, from Debye's rotational diffusion equation:⁴

$$\frac{1}{D} \frac{\partial f}{\partial t} = \nabla^2_{\Omega} f + \frac{1}{kT} \nabla_{\Omega} [f(\nabla_{\Omega} u)], \quad (3)$$

with: ∇_{Ω} — the angular part of the spatial derivation operator, D — the rotational diffusion coefficient of a molecule with spherical geometry, and

$$\begin{aligned} u(\theta, t) &= - \sum_{s=0}^{\infty} u_s(t) P_s(\theta) \\ &= -mP_1(\theta)E_z(t) - [aP_0(\theta) + \frac{1}{3}\gamma P_2(\theta)]E_z^2(t) \\ &\quad - [\frac{1}{15}bP_4(\theta) + \frac{1}{15}\kappa P_3(\theta)]E_z^3(t) + \dots \end{aligned} \quad (4)$$

the potential energy of an axially symmetric molecule in the external field $E_z(t)$. Above, $a = \frac{1}{3}(a_{zz} + 2a_{xx})$ is the mean linear polarisability of the molecule; $\gamma = a_{zz} - a_{xx}$ the anisotropy of its linear polarisability; $b = (b_{zzz} + 2b_{xxx})/3$ its mean hyperpolarisability; and $\kappa = b_{zzz} - 3b_{xxx}$ the anisotropy of its hyperpolarisability. The $P_i(\theta)$ are Legendre polynomials, dependent on the polar angle θ .

Eqn (3) can be solved by statistical perturbation calculus applying the highly useful method of Racah algebra.⁵ To this aim, we have recourse to the following series expansion in Legendre polynomials and successive powers of $1/kT$, the reciprocal of the energy of thermal motion of the molecules:

$$f(\theta, t) = \sum_n \sum_l \left(\frac{1}{kT} \right)^n A_l^{(n)}(t) P_l(\theta). \quad (5)$$

The expansion (5), on insertion into eqn (3), yields a set of differential equations of the form:

$$\begin{aligned} \frac{1}{D} \frac{\partial A_l^{(n)}(t)}{\partial t} &= -l(l+1)A_l^{(n)}(t) - \\ &\quad - \frac{1}{2} \sum_{l', s} u_s(t) A_{l'}^{(n-s)}(t) [l'(l'+1) - l(l+1) - s(s+1)] \begin{bmatrix} s & l' & l \\ 0 & 0 & 0 \end{bmatrix}. \end{aligned} \quad (6)$$

Eqn (6) enables us to find the explicit form of the dynamical coefficients $A_l^{(n)}(t)$.⁷

Above, $\begin{bmatrix} s & l' & l \\ 0 & 0 & 0 \end{bmatrix}$ denote the Clebsch-Gordan coefficients; summation over the indices l', s is restricted by the triangle inequality.⁵

In the zero'th approximation of perturbation calculus, we obtain from (6) the equation of free rotational diffusion of spherical top molecules:⁶

$$\frac{\partial A_l^{(0)}(t)}{\partial t} = -l(l+1)DA_l^{(0)}(t) \quad (7)$$

with the well known solution:

$$A_l^{(0)}(t) = \text{const} \cdot \exp\left(-\frac{t}{\tau_l}\right), \quad (8)$$

the τ_l being rotation ^{rel}relaxation times, related to the rotational diffusion coefficient D as follows:

$$\tau_l = [l(l+1)D]^{-1} = \frac{2\tau_1}{l(l+1)}, \quad (9)$$

where τ_1 is Debye's relaxation time.

For $n \geq 1$, eqn (6) has the solution:

$$A^{(n)}(t) = -D \exp(-t/\tau_1) \sum_{l'} \frac{l'(l'+1) - l(l+1) - s(s+1)}{2} \begin{bmatrix} s & l' & l \\ 0 & 0 & 0 \end{bmatrix}^2 \int_0^t A^{(n-1)}(t) u_s(t) \exp(+t/\tau_1) dt. \quad (10)$$

If integration in (10) is performed from 0 to ∞ , the distribution function thus obtained corresponds to the steady state attained by the liquid dielectric after a sufficiently long time subsequent to the moment at which the external electric fields were switched on or removed. The case in question has been dealt with in full detail in ref (1)–(3).

Standard methods of statistical averaging with the distribution function (5) and dynamical coefficients (10) lead to the result that the increase in polarisation due to the application of the AC electric fields at the moment of time $t = 0$ is described, with accuracy to $E_2^3(t)$, by the temperature-dependent contributions to the tensor of 3rd order susceptibility:

$$\chi = \frac{1}{kT} \chi^{(1)} + \left(\frac{1}{kT} \right)^2 \chi^{(2)} + \left(\frac{1}{kT} \right)^3 \chi^{(3)} + \dots \quad (11)$$

where:

$$\begin{aligned} \chi^{(1)} = \frac{N}{V} \mathbf{S}_{abc} [& \frac{1}{15} m(-\omega_{abc}) b(\omega_a, \omega_b, \omega_c) Q_{10}(\omega_{abc}; t) + \\ & + \frac{1}{15} b(-\omega_{abc}, \omega_a, \omega_b) m(\omega_c) \exp(-i\omega_a t) Q_{10}(\omega_c; t) + \\ & + \frac{2}{45} \gamma(-\omega_{abc}, \omega_a) \gamma(\omega_b, \omega_c) \exp(-i\omega_a t) Q_{20}(\omega_{bc}; t)], \quad (12) \end{aligned}$$

$$\begin{aligned} \chi^{(2)} = \frac{2}{45} \frac{N}{V} \mathbf{S}_{abc} \{ & m(-\omega_{abc}) m(\omega_a) \gamma(\omega_b, \omega_c) \frac{1}{2} \{ 3R_{10}(\omega_a) [Q_{10}(\omega_{abc}; t) - Q_{11}(\omega_{bc}; t)] \\ & + R_{20}(\omega_{bc}) [Q_{10}(\omega_{abc}; t) - Q_{12}(\omega_a; t)] \} + \gamma(-\omega_{abc}, \omega_a) m(\omega_b) m(\omega_c) R_{10}(\omega_c) \\ & [Q_{20}(\omega_{bc}; t) - Q_{21}(\omega_b; t)] \exp(-i\omega_a t) \}, \quad (13) \end{aligned}$$

$$\begin{aligned} \chi^{(3)} = -\frac{1}{45} \frac{N}{V} \mathbf{S}_{abc} m(-\omega_{abc}) m(\omega_a) m(\omega_b) m(\omega_c) R_{10}(\omega_c) \{ & R_{20}(\omega_{bc}) \\ & [Q_{10}(\omega_{abc}; t) - Q_{12}(\omega_a; t)] - R_{21}(\omega_b) [Q_{11}(\omega_{ab}; t) - Q_{12}(\omega_a; t)] \}, \quad (14) \end{aligned}$$

where we have introduced the time-dependent relaxational functions:

$$R_{lk}(\omega_{abc}; t) = R_{lk}(\omega_{abc}) [\exp(-i\omega_{abc}t - t/\tau_k) - \exp(-t/\tau_1)]. \quad (15)$$

\mathbf{S}_{abc} is the operator of symmetrisation over the frequencies $\omega_a, \omega_b, \omega_c$. Eqn (12)–(15), moreover, take into account the dependence of the molecular parameters on frequency since, in optical fields, Lorentz-Voigt dispersion can also occur for very high frequencies. One has also to give consideration to the factors oscillating with the frequencies of the external fields; their vanishing with increasing polarisation depends on the molecular relaxation times τ_1, τ_2 and dispersional factors:⁷

$$R_{lk}(\omega_{abc}) = (1 - \tau_l/\tau_k - i\omega_{abc}\tau_l)^{-1}. \quad (16)$$

The latter, at $k = 0$, go over into the Debye factors $R_i(\omega_{abc}) = (1 - i\omega_{abc}\tau_i)^{-1}$ discussed in ref. (1)–(4), which define the dispersion and absorption of the effects in steady states (for $t = \infty$).

APPLICATIONS AND CONCLUSIONS

The preceding results provide a coherent description of time-dependent nonlinear relaxation effects in the approximation of Debye rotational diffusion taking into account processes of time-dependent growth of polarisation from the moment of application of external fields onwards. This is of especial significance in relation to measurements of the dielectric and optical properties of molecules by pulse technique, when the times necessary for switching the field on can be comparable with the Debye rotational relaxation times and when difference frequencies between various laser modes can cause nonlinear Debye dispersion in the optical range.

Future dielectric studies of the relaxation times of molecules need not be restricted to dispersion and absorption measurements of nonlinear effects but can extend to determinations of the time-variations of dispersion and absorption. For example, we have the following formulae for the quadratic variations in electric permittivity in the presence of a strong, static electric field (for the sake of clarity, we omit the frequency-dependence of the molecular parameters, assuming electron dispersion to be absent):

$$\begin{aligned} \frac{\Delta\epsilon(\omega; t)}{E^2} \sim & \frac{1}{3} \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{1}{135} \frac{\gamma^2}{kT} \left\{ [1 + 2R_{20}(\omega)] \exp(-i\omega t) - \right. \\ & \left. [\exp(-i\omega t) + 2R_{20}(\omega)] \exp\left(-\frac{t}{\tau_2}\right) \right\} \\ & + \frac{1}{135} \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. \\ & - \left\{ \frac{3}{2} + 3R_{11}(\omega) + R_{21}(\omega) \right\} \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) \left. \right\} \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) \right\} \exp\left(-\frac{t}{\tau_2}\right) \left. \right\} \\ & - \frac{1}{135} \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) \right. \\ & + \frac{1}{4}R_{10}(\omega) + \frac{1}{2}R_{12}(\omega) - \frac{3}{2}R_{11}(\omega) + \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) \left. \right\} \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(-t/\tau_2) - \frac{3}{2}R_{10}(\omega)(t/\tau_1) \exp(-t/\tau_1) \left. \right\}. \quad (17) \end{aligned}$$

We have thus resolved each of the temperature-dependent contributions into a part describing the steady state ($t = \infty$) and parts which decrease with τ_1 and τ_2 and describe the increase in polarisation of the medium. The latter are characterised by the occurrence, in addition to factors oscillating with the frequency of the measuring field,

of non-oscillating factors decreasing in time exponentially and unexponentially, with dispersion given by the function $R_R(\omega)$. Other effects, described by the susceptibility χ , also involve these non-oscillating factors, e.g., the effects of rectification of dielectric and optical frequencies, of the emergence of constant polarisation of isotropic bodies under illumination, and of dielectric saturation.

The method used by us for the determination of the distribution function from Debye's kinetic diffusion equation is well adapted to extension by taking intermolecular interactions into account^{8,9} as well as to application within the framework of the more general response function method.¹⁰⁻¹²

The distribution function, determined from eqn (5), can serve as well for calculations of orientation time-autocorrelation tensors in effects of linear and nonlinear light scattering¹³ and for spectral line shape determinations in elastic and inelastic scattering of light by molecules of liquids oriented by the action of an external electric field.^{7,14} A similar description can be used for pulse electric field-induced effects of birefringence in liquids.^{1,11,15}

¹ B. Kasprowicz-Kielich and S. Kielich, *Adv. Mol. Relax. Proc.*, 1975, **7**, 275.

² B. Kasprowicz-Kielich, S. Kielich and J. R. Lalanne, *Molecular Motions in Liquids*, ed. J. Lascombe (D. Reidel, Dordrecht, Holland, 1974), p. 563.

³ J. Buchert, B. Kasprowicz-Kielich and S. Kielich, *Adv. Mol. Relax. Proc.*, 1976, **8**, 0000.

⁴ P. Debye, *Polare Molekülen* (Hirzel, Leipzig, 1929).

⁵ M. E. Rose, *Elementary Theory of Angular Momentum* (Wiley, New York, 1957).

⁶ L. D. Favro, *Phys. Rev.*, 1960, **119**, 53.

⁷ W. Alexiewicz, J. Buchert and S. Kielich, *J. Polymer Sci. (Polymer Symp.)*, 1976, **00**, 0000.

⁸ R. Zwanzig, *J. Chem. Phys.*, 1963, **38**, 2766.

⁹ R. H. Cole, *Mol. Phys.*, 1974, **27**, 1.

¹⁰ R. Kubo, *J. Phys. Soc. Japan*, 1957, **12**, 570.

¹¹ R. Pecora, *J. Chem. Phys.*, 1969, **50**, 2650.

¹² B. J. Berne, *Physical Chemistry*, ed. Eyring, Henderson and Jost (Academic Press, N.Y., 1971), Vol. VIII B, p. 539.

¹³ P. D. Maker, *Phys. Rev.*, 1970, **A1**, 923.

¹⁴ W. Alexiewicz, J. Buchert and S. Kielich, *Proc. Fifth International Conference on Raman Spectroscopy* (Freiburg, 1976), p. 378.

¹⁵ I. L. Fabelinskii, *Usp. Fiz. Nauk*, 1971, **104**, 77.