

ANALYSIS OF THE DISPERSION AND ABSORPTION CURVES OF NON-LINEAR  
RELAXATION-REORIENTATION FOR THE MOLECULES OF WATER AND FIBRINOGEN.\*

J. BUCHERT, B. KASPROWICZ-KIELICH and S. KIELICH

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

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ABSTRACT

The behaviour of the dispersion and absorption curves of some non-linear relaxation-reorientation processes is discussed, using the approximation of Debye's rotational diffusion for the molecules of water and fibrinogen, thus: low-frequency second harmonic generation in a DC electric field, non-linear rectification of dielectric frequencies, DC electric field-induced non-linear variations in electric susceptibility, self-induced variations in electric susceptibility in the dielectric frequency range and generation of the third-harmonic of an electromagnetic wave close to frequencies equal to the inverse rotation relaxation times of the molecules of a liquid dielectric.

I. INTRODUCTION

Unceasing progress regarding the influence of intense DC electric fields on the properties of liquid dielectrics [1] also stimulates consideration of the AC case. Work on the linear processes of molecular dielectric relaxation occurring in AC electric fields began in 1929, the year in which Debye published his well-known book [2]. The study of dielectric relaxation provides extensive and highly valuable information on the rotational motions of molecules and macromolecules [3,4] in dielectric fluids. In a previous paper [5], we discussed in full the theory of non-linear relaxational processes using the approximation of

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the rotational diffusion of Debye. Here, the results will be used to describe the dielectric dispersion and absorption of various non-linear processes in the cases of water and fibrinogen molecules.

## II. ELECTRIC POLARISATION OF ORDER 3.

The electric polarisation  $P(E)$  of an isotropic dielectric is a function of odd powers of the AC electric field strength  $E(\omega)$ , where  $\omega$  is the circular frequency of the field. If the dielectric is acted on by three electric fields with frequencies  $\omega_1$ ,  $\omega_2$  and  $\omega_3$ , the first term of non-linear polarisation will depend on the third power of the field and can, in general, be written at the frequency  $\omega_4 = \omega_1 + \omega_2 + \omega_3$  as [4] :

$$P_i^{(3)}(\omega_4) = \chi_{ijkl}^{(3)}(-\omega_4, \omega_1, \omega_2, \omega_3) E_j(\omega_1) E_k(\omega_2) E_l(\omega_3), \quad (1)$$

where  $\chi_{ijkl}^{(3)}$  is the tensor of third-order non-linear susceptibility. The way in which  $\chi_{ijkl}^{(3)}$  depends on both high and low frequencies has been indicated in Ref. [5]. This dependence being of a rather complicated form, we shall simplify our considerations by assuming the isotropic dielectric to contain  $N$  dipolar molecules axially-symmetric electrically, linearly and non-linearly polarizable, and geometrically spherical, in accordance with Debye's assumption. For the experimental set-up when the three electric fields are applied to the dielectric in one direction, e.g. along the  $z$ -axis, we obtain by Eq. (1) :

$$P_z^{(3)}(\omega_4) = \chi^{(-\omega_4, \omega_1, \omega_2, \omega_3)} E_z(\omega_1) E_z(\omega_2) E_z(\omega_3) \quad (2)$$

where  $\chi$  is now the scalar non-linear third-order susceptibility of the isotropic dielectric given, on the basis of previous calculations [5], as follows :

$$\begin{aligned} \chi^{(-\omega_4, \omega_1, \omega_2, \omega_3)} = & \frac{N}{90} \{ 15 c + \\ & + \frac{1}{kT} [ 36 m b A (\omega_1 + \omega_2 + \omega_3) + 4 \gamma^2 B (\omega_1 + \omega_2 + \omega_3) ] + \\ & + \frac{1}{(kT)^2} 8 m^2 \gamma C (\omega_1 + \omega_2 + \omega_3) - \frac{1}{(kT)^3} 2 m^4 D (\omega_1 + \omega_2 + \omega_3) \} \quad (3) \end{aligned}$$

where  $N$  is the number of molecules per unit volume;

$m = m_3$  — the dipole moment in the direction of the symmetry axis of the molecule;

- $\gamma = a_{33} - a_{11}$  — the anisotropy of linear polarizability;  
 $b = (2b_{113} + b_{333})/3$  — the mean non-linear polarizability of order 2;  
 $c = \frac{1}{5} c_{\alpha\alpha\beta\beta}$  — the mean non-linear polarizability of order 3  
of the molecule;  
 $k$  — Boltzmann's constant, and  
 $T$  — absolute temperature.

The non-linear relaxation functions are of the form ( $a \neq b \neq c$ ):

$$A(\omega_1 + \omega_2 + \omega_3) = \frac{1}{24} \sum_{abc=1,2,3} [R_1(\omega_a + \omega_b + \omega_c) + 3R_1(\omega_c)]; \quad (4)$$

$$B(\omega_1 + \omega_2 + \omega_3) = \frac{1}{6} \sum_{ab=1,2,3} R_2(\omega_a + \omega_b); \quad (5)$$

$$C(\omega_1 + \omega_2 + \omega_3) = \frac{1}{12} \sum_{abc=1,2,3} \{R_1(\omega_a) R_2(\omega_a + \omega_b) + \\ + \frac{1}{2} [3 R_1(\omega_a) - R_2(\omega_b + \omega_c)] R_1(\omega_a + \omega_b + \omega_c)\}; \quad (6)$$

$$D(\omega_1 + \omega_2 + \omega_3) = \frac{1}{6} \sum_{abc=1,2,3} R_1(\omega_a) R_2(\omega_a + \omega_b) R_1(\omega_a + \omega_b + \omega_c) \quad (7)$$

The relaxational reorientation factors occurring above are:

$$R_i(\omega_a + \omega_b + \omega_c + \dots) = [1 - i(\omega_a + \omega_b + \omega_c + \dots) \tau_i]^{-1} \quad (8)$$

where

$$\tau_i = \frac{1}{i(i+1)D_R} = \frac{2\tau_D}{i(i+1)} \quad (9)$$

is the  $i$ -th relaxation time of the molecule given by the rotational diffusion coefficient  $D_R$  or Debye's dielectric relaxation time  $\tau_D = (2D_R)^{-1}$ .

In Eq. (3) the dependence on frequency is related to relaxation of molecular reorientation only, and is inherent in the non-linear relaxation functions. The dependence of the electric molecular properties on the frequencies, causing electron dispersion, is omitted since electron dispersion occurs at frequencies much higher than those at which the relaxation factors play a role. The frequencies in question are of the order of the inverse rotational relaxation times of the molecules. Electron dispersion has to be taken into account if optical effects [5]

are considered and non-linear Debye dispersion is caused by difference frequencies [6]. Henceforth, we shall neglect the term related to the non-linear polarizability  $c$  of the molecule since it causes no reorientation in the present approximation and gives rise to a constant contribution to the susceptibility tensor (3) of the medium only.

### III. DISPERSION AND ABSORPTION OF DIELECTRIC RELAXATION IN NON-LINEAR PHENOMENA.

The relaxation functions (4) - (7) are, in general, complex, the real and imaginary parts describing, respectively, dispersion and absorption of the process considered. In what follows, we shall give in analytical form the functions describing various temperature contributions to the non-linear susceptibility of order 3 (Eq. (3)) for the individual processes, together with the respective graphs. Also, frequency-dependent functions for the response of the system to the action of an AC electric field will be proposed. The relaxation functions are applied for numerical calculations for substances, the molecular parameters of which were available from other measurements [7]. We selected the water molecule as that of a typically dipolar substance and fibrinogen as representative of one in the non-linear 3rd order susceptibility of which, at room temperature, the contributions from anisotropy in linear polarizability are comparable and compete with those involving the permanent dipole moment. Our discussion will be substantiated on the example of several non-linear effects.

#### A. Dispersion and absorption of the change in electric susceptibility $\chi(-\omega, \omega, 0, 0)$ due to an intense static electric field.

By insertion of  $\omega_1 = \omega$  and  $\omega_2 = \omega_3 = 0$  in Eqs. (3) - (8), we obtain for the non-linear relaxation function of the dielectric saturation effect :

$$A(\omega) = \frac{1}{2} [1 + R_1(\omega)] \quad (10)$$

$$B(\omega) = \frac{1}{3} [1 + 2 R_2(\omega)] \quad (11)$$

$$C(\omega) = \frac{1}{6} \{1 + R_2(\omega) + R_1(\omega) R_2(\omega) + [3 - R_2(\omega)] R_1(\omega) + \frac{1}{2} [3 R_1(\omega) - 1] R_1(\omega)\} \quad (12)$$

$$D(\omega) = \frac{1}{3} [1 + R_2(\omega) + R_1(\omega) R_2(\omega)] R_1(\omega) \quad (13)$$

Graphs of the real and imaginary parts of the preceding functions are shown in Fig. 1 versus  $\omega\tau_2$ .

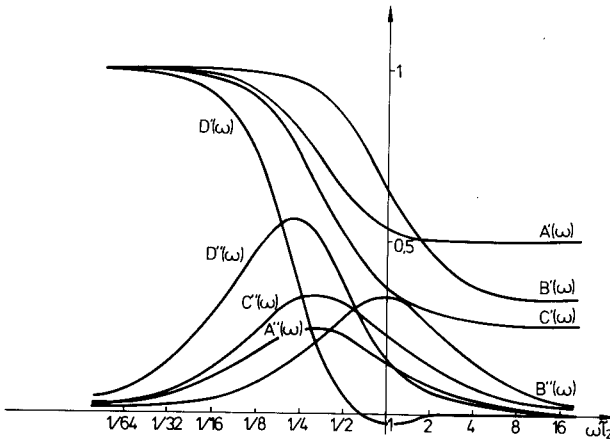


Fig. 1. Temperature-dependent contributions to dispersion and absorption of the susceptibility  $\chi(-\omega, \omega, 0, 0)$ .

The dispersion curves related to the linear and non-linear molecular polarizabilities at high frequencies  $\omega\tau_2 \gg 1$  contribute to dielectric saturation contrary to the term in the fourth power of the dipole moment, the reorientation of which cannot keep pace with the field frequency.

The curves of Fig. 1 et seq. are normalized to the DC field dielectric saturation value. The curves marked with primed letters are for dispersion, and those with double-primed ones for absorption of non-linear processes.

B. Dispersion and absorption of the susceptibility  $\chi(-2, \omega, \omega, 0)$  for the case of second-harmonic generation in the presence of a static electric field.

If  $\omega_1 = \omega_2 = \omega$  and  $\omega_3 = 0$ , the reorientation functions (3) - (8) take a form well adapted to numerical calculations :

$$A(2\omega) = \frac{1}{4} [1 + 2 R_1(\omega) + R_1(2\omega)] \quad (14)$$

$$B(2\omega) = \frac{1}{3} [2 R_2(\omega) + R_2(2\omega)] \quad (15)$$

$$C(2\omega) = \frac{1}{6} \{ 2 R_1(\omega) R_2(\omega) + R_1(\omega) R_2(2\omega) + [3 R_1(\omega) - R_2(\omega)] R_1(2\omega) + \frac{1}{2} [3 - R_2(2\omega)] R_1(2\omega) \} \quad (16)$$

$$D(2\omega) = \frac{1}{3} [R_1(\omega) R_2(2\omega) + R_1(\omega) R_2(\omega) + R_2(\omega)] R_1(2\omega) \quad (17)$$

The respective curves are plotted in Fig. 2.

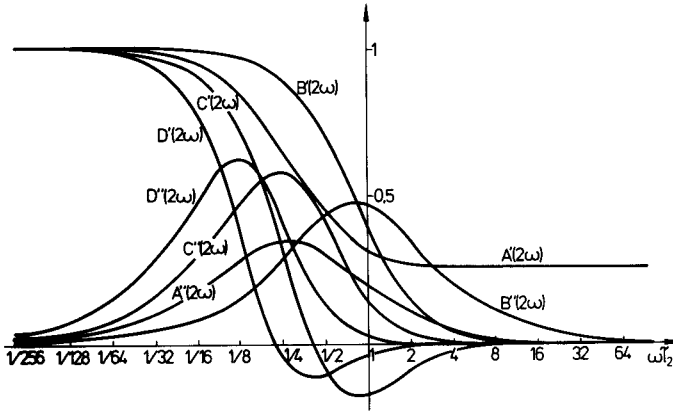


Fig. 2. Temperature-dependent contributions to dispersion and absorption of the susceptibility  $\chi(-2\omega, \omega, \omega, 0)$ .

The curves of  $C'(2\omega)$  and  $D'(2\omega)$  specifically exhibit a change in sign of the dispersion. On passing through a minimum, they tend to zero thus making relaxational dispersion resemble resonance dispersion.

C. Dispersion and absorption of non-linear dielectric frequency rectification in the presence of a static electric field:

$$\chi(-0, \omega, -\omega, 0).$$

It is feasible to perform observations of non-linear rectification of dielectric frequencies when  $\omega_1 = \omega$ ,  $\omega_2 = -\omega$ , and  $\omega_3 = 0$ . Eqs. (3) - (8) now become :

$$A(0) = \frac{1}{4} [2 + R_1(-\omega) + R_1(\omega)] \quad (18)$$

$$B(0) = \frac{1}{3} [1 + R_2(\omega) + R_2(-\omega)] \quad (19)$$

$$C(0) = \frac{1}{6} \{1 + R_1(-\omega) R_2(-\omega) + R_1(\omega) + R_2(\omega) + \frac{1}{2} [3 R_1(\omega) + 3 R_1(-\omega) - R_2(\omega) - R_2(-\omega)]\} \quad (20)$$

$$D(0) = \frac{1}{3} [R_1(\omega) + R_2(\omega) + R_1(-\omega) R_2(-\omega)] \quad (21)$$

Curves illustrating the behaviour of these contributions to the non-linear susceptibility  $\chi(-0, \omega, -\omega, 0)$  are shown in Fig. 3.

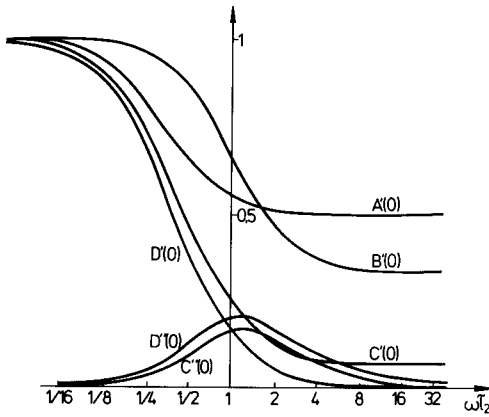


Fig. 3. Temperature-dependent contributions to dispersion and absorption of the susceptibility  $\chi(-0, \omega, -\omega, 0)$ .

D. Dispersion and absorption of self-induced variations in the non-linear susceptibility  $\chi(-\omega, \omega, \omega, -\omega)$ .

A strong AC field causes self-induction of variations in non-linear susceptibility at the frequency  $\omega$  if  $\omega_1 = \omega_2 = \omega$  and  $\omega_3 = -\omega$ . The relaxational reorientation functions now are :

$$A(\omega) = \frac{1}{4} [3 R_1(\omega) + R_1(-\omega)] \quad (22)$$

$$B(\omega) = \frac{1}{3} [2 + R_2(\omega)] \quad (23)$$

$$C(\omega) = \frac{1}{6} \{R_1(\omega) + R_1(-\omega) + R_1(\omega) R_2(2\omega) + [3 R_1(\omega) - 1] R_1(\omega) + \frac{1}{2} [3 R_1(-\omega) - R_2(2\omega)] R_1(\omega)\} \quad (24)$$

$$D(\omega) = \frac{1}{3} [R_1(\omega) + R_1(-\omega) + R_1(\omega) R_2(2\omega)] R_1(\omega) \quad (25)$$

Their real and imaginary parts are plotted in Fig. 4.

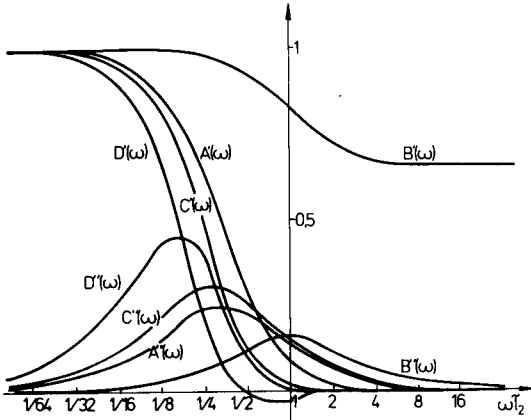


Fig. 4. Temperature-dependent contributions to dispersion and absorption of the susceptibility  $\chi(-\omega, \omega, -\omega, \omega)$ .

Here, too, we find a change in sign for dispersion of the factor  $D'(\omega)$ . In high frequency fields, a contribution to the 3rd order susceptibility tensor arises from the factor related with the squared anisotropy in linear molecular polarizability. This contribution is proportional to the inverse temperature.

E. Dispersion and absorption of the non-linear susceptibility  $\chi(-3\omega, \omega, \omega, \omega)$  in the process of third-harmonic generation at dielectric frequencies.

Likewise to 3rd harmonic generation of light (optical frequencies), THG at dielectric frequencies is a subject of study. The process is described by the relaxation functions (3) - (8) for  $\omega_1 = \omega_2 = \omega_3 = \omega$  :

$$A(3\omega) = \frac{1}{4} [3 R_1(\omega) + R_1(3\omega)] \quad (26)$$

$$B(3\omega) = R_2(2\omega) \quad (27)$$

$$C(3\omega) = \frac{1}{2} \{R_1(\omega) R_2(2\omega) + \frac{1}{2} [3 R_1(\omega) - R_2(2\omega)] R_1(3\omega)\} \quad (28)$$



$$D(3\omega) = R_1(\omega) R_2(2\omega) R_1(3\omega) \quad (29)$$

plotted in Fig. 5.

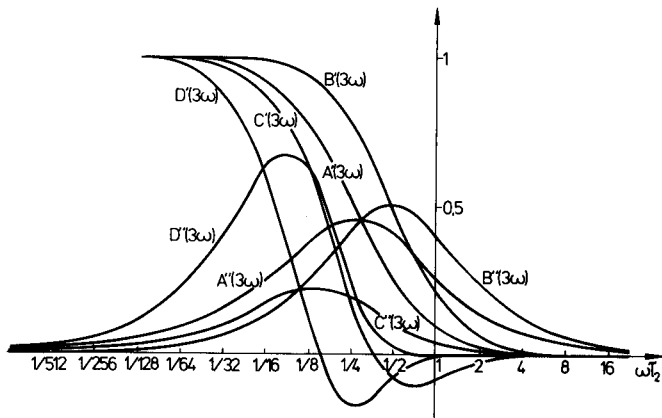


Fig. 5. Temperature-dependent contributions to dispersion and absorption of the susceptibility  $\chi(-3\omega, \omega, \omega, \omega)$ .

Here (as in SHG in a DC electric field — Fig. 2) the dispersion curves of  $C'(3\omega)$  and  $D'(3\omega)$  exhibit a change in sign. However, at frequencies high by comparison to the inverse relaxation times of molecular reorientation, the macroscopic susceptibility of the medium is described solely by the contributions due to the 3rd order non-linear polarizability  $c$  of the molecule formula (3), since all temperature-dependent contributions tend to zero. Moreover, due to non-linearity of the relaxation functions, absorption still increases towards higher frequencies in some cases after the dispersion curve has fallen to zero.

#### IV. DISCUSSION and RESULTS

Most of the preceding dispersion curves could be interpreted as functions, analytically described by simple Debye relaxation factors with a single relaxation time involving, according to the situation, doubled and tripled frequencies of the external field. However, with regard to the respective absorption curves, the above interpretation is found to be unsound. In fact, absorption maxima exhibit relative heights both larger and less than 0.5, leading to Cole-Cole diagrams

differing from regular semi-circles, as should be the case on the interaction-less model assumed here. Moreover, the inflection point of the dispersion curve often occurs at a frequency different from that of the absorption maximum. Also, due to non-linearity of the relaxation functions, absorption in some cases still takes place at higher frequencies where dispersion is no longer non-zero.

Dispersion and absorption of the preceding non-linear processes for systems of polar, linearly and non-linearly polarizable molecules are discussed for water and fibrinogen (Figs. 6-10), for which the numerical values of molecular parameters are taken from Ref [7].

Water, as one sees from the graphs, behaves like a typical dipolar liquid. The factor proportional to  $m^4/(kT)^3$  predominates over the others, and decidedly governs the behaviour of the dispersion and absorption curves. At low frequencies, as long as molecular reorientation keeps pace with the external field, we observe negative dielectric saturation.

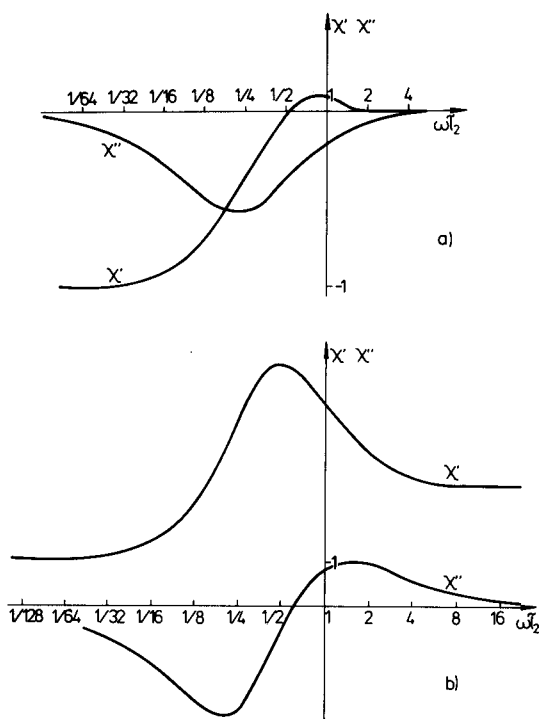


Fig. 6. Dispersion and absorption of the susceptibility  $\chi(-\omega, \omega, 0, 0)$  for : (a) a system of water molecules; (b) a system of fibrinogen molecules.

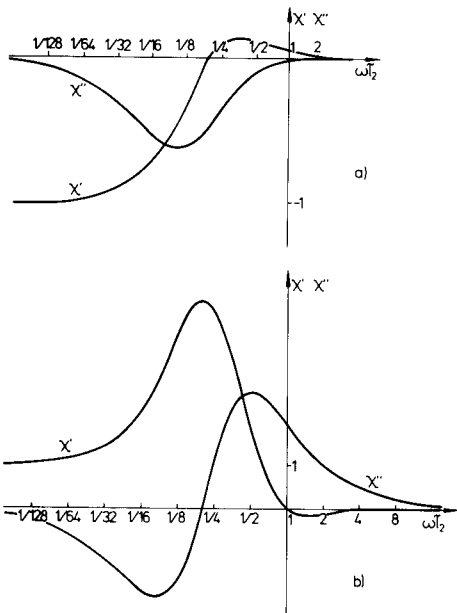


Fig. 7. Dispersion and absorption of the susceptibility  $\chi(-2\omega, \omega, \omega, 0)$  for : (a) a system of water molecules; (b) a system of fibrinogen molecules.

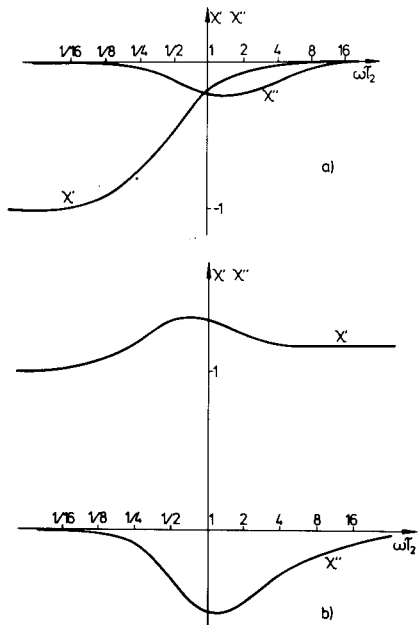


Fig. 8. Dispersion and absorption of the susceptibility  $\chi(-0, \omega, -\omega, 0)$  for : (a) a system of water molecules; (b) a system of fibrinogen molecules.

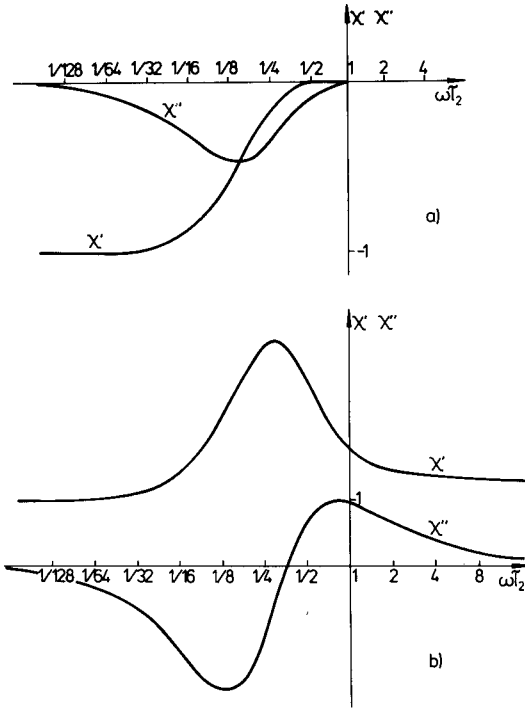


Fig. 9. Dispersion and absorption of the susceptibility  $\chi(-\omega, \omega, -\omega, \omega)$  for : (a) a system of water molecules; (b) a system of fibrinogen molecules.

Above  $10^{12}$  Hz, when the dipole moment lags behind the field oscillations, saturation tends to zero. At even higher frequencies, the non-linear susceptibility changes to positive, because reorientation by polarizability anisotropy (the relaxation time of which amounts to one-third of that of the permanent dipole moment) becomes predominant. This is obvious on the dispersion graphs of the temperature contributions. Dispersion related to the dipole moment tends to zero more steeply than dispersion of the factors related to the anisotropy of polarizability.

In the case of fibrinogen, the factors related to the anisotropy of polarizability play a more important role from the outset. They are comparable to the  $m^4/(kT)^3$  factor, but are opposite in sign. This leads to a specific shape of the curves. The case of dispersion and absorption measurements in fibrinogen at dielectric frequencies is of particular interest: the real part of  $\chi$  (the third-order susceptibility tensor) increases anomalously at electric field frequencies close to the inverse

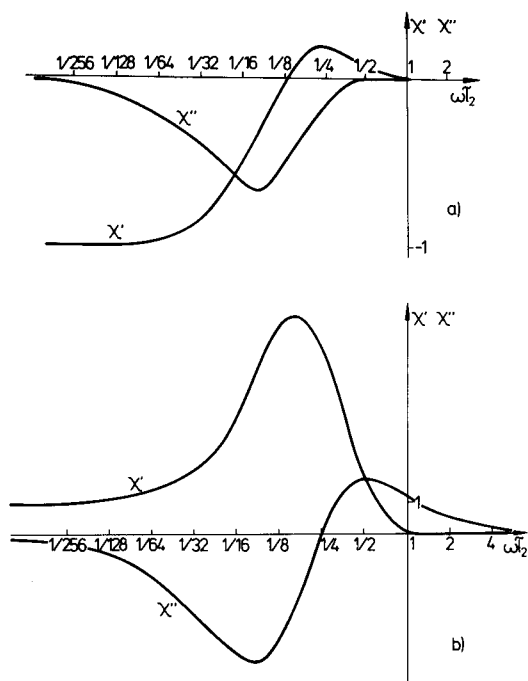


Fig. 10. Dispersion and absorption of the susceptibility  $\chi(-3\omega, \omega, \omega, \omega)$  for : (a) a system of water molecules; (b) a system of fibrinogen molecules.

relaxation time  $\tau_2^{-1}$ , and the imaginary part of  $\chi$  undergoes a change in sign (Figs. 6b, 7b, 9b, 10b). Conditions particularly propitious for the generation of harmonics will exist when the absorption is zero and the fundamental frequency is damped out at detection.

These highly specific curve shapes were obtained by an appropriate choice of the substances and performing "computer experiments" for room temperature. For fibrinogen, the anomalous non-Debye shape of the dispersion and absorption curves is due to the comparable values of  $\gamma m^2 / (kT)^2$  and  $m^4 / (kT)^3$  and their mutually shifted dispersions. Predictably, the same effects can also be achieved in other substances at higher temperatures as the two denominators contain different powers of  $T$ .

Dispersion measurements of the quantity  $\Delta\epsilon(\omega)/(E^2)$ , proportional to the fourth rank tensor of non-linear permittivity of the medium, are even now performed in some ranges of frequency [5]. If performed throughout a wide range of frequencies, taking into account the non-linearity of the relaxation functions, they will enable a rather good

separation of the factors affecting the change in non-linear susceptibility to be obtained. The recently reported studies [8] of changes in  $\Delta\epsilon(\omega)/(E^2)$  under the action of an intense static electric field taking into account dispersion and absorption of the measuring field seem particularly promising in this respect. It is desirable to continue these studies by having recourse to picosecond laser pulses, and to intensity modulation of the intense linearly polarized beam of a laser at varying frequencies measuring the variations in light refractive index as a function of the modulating frequency.

## REFERENCES

- 1 S. Kielich, in "Dielectric and Related Molecular Processes", ed. M. Davies, Chem. Soc. London, 1972, Vol. I, Chapter 7 and references therein.
- 2 P. Debye, "Polare Molekeln", Hirzel, Leipzig, 1929.
- 3 G. Boudouris, Riv. Nuovo Cimento, Serie I, 1 (1969) 1.
- 4 B. Kasproicz-Kielich, S. Kielich, J.R. Lalanne, in "Molecular Motions in Liquids", ed. J. Lascombe, Reidel, Dordrecht, 1974, p. 563.
- 5 B. Kasproicz-Kielich, S. Kielich, Advances Mol. Relaxation Processes, 7 (1975) 275 and references therein.
- 6 N. Bloembergen, P. Lallemand, Phys. Rev. Lett., 16 (1966) 81.
- 7 S. Kielich, Acta Phys. Polon., A37 (1970) 447.
- 8 L. Hellemans, L. De Maeyer, J. Chem. Phys., 63 (1975) 3490.