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COMPLEX SUSCEPTIBILITY OF LIQUID WATER AS A TWO-POTENTIAL SYSTEM OF REORIENTING POLAR MOLECULES

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Abstract

The theory elaborated in ref. 1 and 2 is applied to the calculation of the liquid water wide-band ($0 < \nu/cm^{-1} < 1000$) dielectric spectra. These comprise the Debye relaxation region at the centimetre/millimetre wavelengths and the two-humped absorption coefficient frequency dependence in the far infrared (FIR) region.

It is supposed that a major part of H_2O molecules, called [L]- particles or [L]- molecules, are bonded by relatively strong H-bonds; [L] - molecules perform librations of relatively small amplitude β (β is about 20°). The remaining molecules called R-molecules have more rotational / translational mobility.

A new microscopic molecular confined rotator / doble well potential (CR DWP) model of liquid water is developed.

The contributions of [L]- and [R]- molecules to the complex permittivity ε are found on the basis of the confined rotator (CR) and the double well potential (DWP) models, with rectangular and $\cos^2\theta$ intermolecular potential profiles, respectively.

It is shown that the CR/DWP model gives a good description of

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the Debye relaxation and a qualitative description of the FIR dielectric spectra of water.

1. INTRODUCTION

As was shown previously [3,4,5], it is possible to use microscopic models of molecular reorientations for the study of the dielectric relaxation in liquids. In this approach the complex dielectric susceptibility $\chi(\omega)$ and permittivity $\varepsilon(\omega)$ are described by simple analytical expressions. The main suggestion of the above theory, namely, that *strong collisions of molecules are regarded as instantaneous,* seems to be more or less acceptable for the gaseous state but its applicability is not quite evident for liquids.

Indeed it was shown by applying in ref.[6] memory function formalism to the Gordon J-diffusion model that for *liquids the collision time* τ_C *exceeds the angular momentum correlation time* τ_J. The result $\tau_C > \tau_J$ was also obtained in ref. 1 for the instantaneous collision approximation, if τ_C denotes a mean half-period of a librational/rotational motion in a conservative potential U, which describes an intermolecular interaction of a given dipole with its neighbours. For a strongly absorbing liquid such as CH_3F the time τ_C was shown to be approximately twice the lifetime τ, where the latter denotes a lifetime of the environment of a given polar molecule. This environment determines a steady-state law of motion and the potential U itself.

Following the approach described in ref. 2 we envisage in this article a more complex situation. We suppose that *two potentials* U_1 and U_2 control reorientations. Using the field model with a $\cos^2\theta$- potential profile, for

which the simplified description of the dielectric response was given in ref. 1., we shall calculate the complex dielectric permittivity $\varepsilon(\omega)$ and absorption coefficient $a(\omega)$ of liquid water.

Indeed according to ref. 4,7,8 it is reasonable to consider in water *two kinds of orientational motion* with the corresponding respective potentials U_1 and U_2. The first potential U_1 describes the librational motion of a major part of H_2O [L]- molecules. These comprise a hydrogen-bonded net and they are responsible for the main ("librational") absorption peak near 700 cm^{-1}. The second potential U_2 is responsible for the "translational" absorption peak near 200 cm^{-1} and causes rotation of the remaining [R]- molecules having greater rotational/translational mobility.

It should be noted that other conceptions also exist on the nature of the translational absorption band [4] but unfortunately these do not give a consistent description of the wide-band dielectric spectra $\varepsilon(\omega)$ and $a(\omega)$ of liquid water. Hence in the present investigation *we suppose that all the wide-band* ($0 < \nu/cm^{-1} < 1000$) *dielectric spectra in water originate from libration/rotation of polar molecules.*

The main purposes of the present study are:

i) to achieve a close *agreement* between the calculated and experimental spectra in the low-frequency region of the Debye relaxation;

ii) to express the free parameters of a molecular model in terms of molecular constants, parameters of the Debye relaxation and the frequencies ν_L and ν_R of translational and librational peaks in the FIR region;

iii) to reduce as far as possible the number of the free parameters of our model; to simplify and formalize the procedure of their evaluation;

iv) to compare the previous confined rotator/extended diffusion (CR/ED) model [8] with the confined rotator/double well potential (CR/DWP) microscopic model of water in order to evaluate the value of intermolecular fields which influence the dipolar [R]-particles.

In the CR model [4,9] the [L]-molecules are regarded as librating between two elastically reflecting walls during a lifetime τ_L. This time and the angular distance 2β between walls (β is the libration amplitude) are the free parameters of the CR model. Thus the CR model is characterized by an infinitely deep rectangular potential well.

The simplified theory [1,10] of the DWP model with the $U(\vartheta) = U_o(1 - \cos^2\vartheta)$ profile is applied to [R]-molecules, ϑ being the angle between the vector $\underset{\sim}{\mu}$ of the dipole moment and the symmetry axis Z of the potential $U(\vartheta)$, which is supposed to exist during some lifetime τ_R in a small local-order volume of a liquid. This potential profile comprises two wells with oppositely directed static fields near the bottoms of the wells, which correspond to the angles $\vartheta = 0$ and $\vartheta = \pi$. Thus we mean that the potential function $U(\vartheta)$ is characterized by the local anisotropy. The dielectric response to reorientation of polar molecules is described by the complex susceptibility $\chi(\omega)$. For an isotropic medium (this is a situation of liquid water) we get the resultant value of $\chi(\omega)$ after the averaging of the dielectric response over all possible Z directions is made.

Previously only the following limiting cases of this DWP model

were used in the study of liquid water spectra:

a) the extended diffusion (ED) model for [R] - molecules, freely rotating between strong collisions [4], and

b) the elastic bond (EB) model for [L]- molecules which were supposed [10,11] to librate in the parabolic potential $U \alpha \theta^2$ with constant angular frequency.

In both approaches, a) and b), the nonlinear law of motion contribution to the susceptibility $\chi(\omega)$ is neglected. We may suppose that the CR/DWP model may give a better description of the liquid water spectrum than that in ref. 8, and may also provide some information about the intermolecular field existing in water. Since the lifetime τ_R of [R]- molecules is rather small, an approximation for DWP model, given in ref. 1, is applicable.

In Sec. 2 we summarize the results of the theory, which later are used for the calculation of the dielectric spectra. In Sec. 3 a method to make an *a priori* estimate of some of the free parameters of a molecular model by employing physical reasoning and experimental data is set forth. Some details of these estimations are given in the Appendix A. In Sec. 4 and 5 we present the results of our calculations. In Appendix B the empirical Liebe, Hufford, Manabe (LHM) formula [12] is presented for the complex permittivity $\varepsilon(\omega)$ of water. This formula is used in the present investigation in order to simplify the comparison results of our theory with experiment and to evaluate some molecular parameters of the CR/DWP model.

2. CONFINED ROTATOR/DOUBLE WELL POTENTIAL (CR/DWP) MODEL

As in ref. 1 and 5 the following formulae are used:

$$a(\nu) = \frac{\omega\varepsilon''}{cn(\omega)} = 4\pi\nu \, \mathrm{Im} \left[\sqrt{\varepsilon^*(\omega)} \right], \qquad (2.1)$$

$$(\varepsilon^* - n_\infty^2)\ (2\varepsilon^* + n_\infty^2) = 12\pi\varepsilon^*\chi^* \quad , \tag{2.2}$$

where (2.1) relates the absorption coefficient $a(\nu)$ to the complex permittivity $\varepsilon(\nu)$ and (2.2) relates the latter to the complex susceptibility $\chi(\nu)$. Here the star denotes the complex conjugate:

$$\chi^*(\nu) = \chi'(\nu) + i\chi''(\nu), \qquad \chi(\nu) = \chi'(\nu) - i\chi''(\nu) \ ,$$

since

$$\varepsilon^*(\nu) = \varepsilon'(\nu) + i\varepsilon''(\nu), \qquad \varepsilon(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu) \ ;$$

the refractive index $n(\omega)$ is given by $n(\omega) = \mathrm{Re}\left[\sqrt{\varepsilon^*(\omega)}\right]$ and n_∞ is the value of $n(\omega)$ in the infrared region.

In the course of these investigations we consider the *superpositional calculation scheme* [2,7], in which the susceptibility $\chi^*(\nu)$ is *linearly* related to the susceptibilities $\chi_1^*(\nu)$ and $\chi_2^*(\nu)$ of the two-potential state of a prescribed molecular model; χ_1 and χ_2 correspond to the potentials U_1 and U_2 and these are determined by the *spectral functions* L_1 and L_2 of each model. These represent the dielectric response to the *regular* (*periodic*) rotational motion of a dipole in a corresponding potential well. For the Debye collision model [2,4], where the induced distribution function F depends *explicitly* on the relaxation time τ_D, the resultant susceptibility χ is given by [2]:

$$\chi^*(x) = \chi_1^*(x) + \chi_2^*(x) \quad , \tag{2.3a}$$

$$\chi_1^*(x) = G r_1 L_1(z_1) \left[1 + \frac{\tau_{D1}/\tau_1}{1 - i\omega\tau_{D1}}\right] , \tag{2.3b}$$

$$\chi_2^*(x) = G r_2 L_2(z_2) \left[1 + \frac{\tau_{D2}/\tau_2}{1 - i\omega\tau_{D2}}\right] . \tag{2.3c}$$

Here $G = \mu^2 N/(3k_B T)$, k_B is the Boltzmann constant, μ is a dipole moment of a molecule in a liquid, N is the concentration (number density) of polar molecules, and T is the temperature we denote by N_1 and N_2 the numbers of [L]- and [R]- particles, respectively, so that

$$N_1 + N_2 = N$$

and the ratio of the numbers of the two classes of particles is $r_1 : r_2$, where

$$r_1 = N_1/N \ , \ r_2 = N_2/N.$$

It will be convenient to express r_2 as r, so that r_1 is expressible as 1-r. We denote by τ_{D1} and τ_{D2} relaxation times related to the subensembles associated with the subscripts 1 and 2. Similarly we define the normalized complex frequencies z_1 and z_2 by

$$z_1 = x + iy_1, \ z_2 = x + iy_2, \ x = \eta\omega, \ y_{1,2} = \eta/\tau_{1,2}, \ \eta = \sqrt{I/(2k_BT)},$$

τ_1 and τ_2 are lifetimes in states [L] and [R], respectively, and I is the moment of inertia. It should be noted that the terms in brackets $[..]$ in (2.3b) and (2.3c) represent the dielectric response to the *chaotic* (*Brownian*) *rotational motion* in liquid, just in the same way as this response appears in the Debye theory [13] of the rotational diffusion.

For [L]-*molecules*, i.e. for the *confined rotator model* ([4] Table 4.1)

$$L_1(z) = \sum_{n=1}^{\infty} s_n L_n(z), \quad L_n(z) = 1 + z_n^2 \exp(-z_n^2) E_1(-z_n^2), \tag{2.5}$$

where

$$s_n = \frac{8f^2}{\pi^2} \frac{\sin^2\left[\frac{\pi}{2}(n-f)\right]}{(n^2-f^2)^2}, \ z_n = \frac{zf}{n}, \ f = \frac{2\beta}{\pi}, \ E_1(u) = \int_u^{\infty} \exp(-t)t^{-1}dt.$$

For R-*molecules*, i.e. for the *double well potential model* the following approximation for L(z) is valid [1]:

$$L_2(z_2) = 2L_{DWP}(z_2), \ L_{DWP}(z) = \check{L}(z) + \tilde{L}(z) + \overset{\circ}{L}(z), \tag{2.6}$$

where

$$\check{L}(z) = \frac{\exp(u)}{2\sqrt{\pi}pI_0(u)} \left[\frac{1-(1+3u/2)e^{-3u/2}}{p^2 - z^2} + \frac{1-(1+3u/2 + 9u^2/8)e^{-3u/2}}{2p^2(4p^2 - z^2)} \right]; \tag{2.7}$$

$$\tilde{L}(z) = \frac{2\exp(-u/2)(1-\exp(-7u/6))}{\sqrt{\pi^3}pI_0(u)} \left[\frac{i}{b} + 2ib \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{(n - ib)^2} \right]; \tag{2.8}$$

$$\overset{\circ}{L}(z) = \frac{2e^u}{\sqrt{\pi}I_0(u)} \int_{2p/\sqrt{3}}^{\infty} \frac{S^2\exp(-S^2)dS}{S^2 - z^2} \tag{2.9}$$

and $u = p^2/2$; $b = z/p$. The multiplier 2, relating L_2 and L_{DWP}, is used in order to describe approximately the rotation/libration in

space in terms of the theory, elaborated for planar motion [1,10]. The field parameter p is related to the potential well depth U_o:

$$p = \left[U_o/k_B T\right]^{1/2} \tag{2.10}$$

In this section we replace p by p_2 and U_o by U_{o2}. It should be noted that (2.6) is applicable only if the lifetime τ_2 is sufficiently small or if the normalized frequency y_2 is sufficiently large, namely if [10]

$$y_2 \geqslant (4p_2)^{-1}. \tag{2.11}$$

In a particular case of *free rotation* during lifetime τ_2, we must put $p = 0$, and the DWP model transforms to the extended diffusion (ED) model. The exact (for rotation in space) expression for $L(z)$ is given by ref. 4, p.78, formula (T4.5), namely,

$$L_2(z) = 1 + z^2 \exp(-z^2) E_1(-z^2), \tag{2.12}$$

3. EVALUATION OF A FREE PARAMETERS OF A MICROSCOPIC MODEL

Using formulae of Sec.2, we have calculated dielectric spectra of liquid water at T = 300K and the results will be given in Sec.4. The dipole moment μ of a molecule in a liquid was related to that (μ_o) of an isolated molecule by the equation [5]

$$\mu = \mu_o k_\mu (n_\infty^2 + 2)/3, \tag{3.1}$$

where the factor k_μ is close to unity.

Thus in the *CR/DWP model* we have *8 fitting parameters:*

$$\underbrace{\beta,\ \tau_1,\ \tau_{D1};}_{\text{for [L]-molecules}} \qquad \underbrace{p_2,\ \tau_2,\ r,\ \tau_{D2}}_{\text{for [R]-molecules}} \qquad \text{and } k_\mu. \tag{3.2}$$

We find or evaluate these from the following stipulations:

a) Putting the frequency x = 0 in (2.2) and in (2.3), we may relate some combination of parameters (3.2) to the Kirkwood correlation factor g:

$$\mathcal{E} = (1-r)\left[1 + \frac{\tau_{D1}}{\tau_1}\right]L_1(iy_1) + r\left[1 + \frac{\tau_{D2}}{\tau_2}\right]L_2(iy_2), \qquad (3.3)$$

where

$$\mathcal{E} = \frac{(\varepsilon_s - n_\infty^2)(2\varepsilon_s + n_\infty^2)}{12\pi\varepsilon_s G} \qquad (3.4)$$

and ε_s is the static permittivity.

b) In the Debye relaxation region the frequencies are comparatively low and we may put x = 0 in the argument of the spectral functions. Then in the end of the first Debye relaxation region we may put formally $\omega\tau_{D1} \to \infty$ in eq.(2.3) and $\varepsilon' \to \varepsilon_\infty$ in eq.(2.2). Hence we get another equation

$$\mathcal{E}_1 = (1-r)L_1(iy_1) + r\left[1 + \frac{\tau_{D2}}{\tau_2}\right]L_2(iy_2), \qquad (3.5)$$

where

$$\mathcal{E}_1 = \frac{(\varepsilon_\infty - n_\infty^2)(2\varepsilon_\infty + n_\infty^2)}{12\pi\varepsilon_\infty G}. \qquad (3.6)$$

c) Using the results of ref. [1], where the time dependence $\Phi(t)$ of the orientational autocorrelation function of water was calculated, and other physical reasoning we may regard the relaxation time τ_{D1} of [L]-molecules to be close to the experimental value τ_D. Thus, putting $\tau_{D1} = \tau_D$, we may rewrite equations (3.3) and (3.5) in the form:

$$\begin{cases} \tau_1 = (1-r)L_1(iy_1)\tau_D(\mathcal{E} - \mathcal{E}_1)^{-1}, & (3.7) \\ r = \left[\mathcal{E}_1 - L_1(iy_1)\right]\left[\left(1 + \frac{\tau_{D2}}{\tau_2}\right)L_2(iy_2) - L_1(iy_1)\right]^{-1}. & (3.8) \end{cases}$$

Equations (3.7) and (3.8) permit us to express the two free model parameters through other (experimental or molecular) known quantities. A number of other estimates may be made from physical considerations (see Appendix A).

Libration amplitude β *and absorption peak* α_L *in CR model:*

$$\beta \approx (3/2)^{1/2}(4\eta c v_L)^{-1}. \qquad (3.9)$$

$$\alpha_L \approx 32\,(3/2)^{3/2}\exp(-3/2)G(\eta c n_\infty)^{-1}(1-r)\cos^2\beta(1-f^2)^{-2}, \qquad (3.10)$$

where ν_L is the libration peak frequency.

Field parameter p, absorption peak a_R and bandwidth $\delta\nu_R$ at the level 1/2 in DWP model:

$$p \approx \eta\,[(2\pi c\nu_R^2) - \tau_2^{-2}]^{1/2} = \sqrt{x_R^2 - y_2^2}\,, \qquad (3.11)$$

where $x_R = \eta\, 2\pi c\nu_R$

$$a_R \approx 2\pi r G \tau_2 (c\eta^2 n_\infty)^{-1}, \qquad (3.12)$$

$$\delta\nu_R \approx 2\,(\pi c\tau_2)^{-1}. \qquad (3.13)$$

As a rough approximation we may relate $\delta\nu_R$ to the frequencies ν_R and $\nu(a_{min})$, the latter being the frequency of a minimum absorption between the two absorption peaks a_R and a_L in water:

$$\delta\nu_R \cong 2[\nu(a_{min}) - \nu_R]. \qquad (3.14)$$

Finally, according to ref.7 we may accept the approximate relation

$$k_\mu \simeq 1.18 \qquad (3.15)$$

for substitution into (3.1).

These estimations and equations (3.7),(3.8) greately simplify the determination of the fitting constants (/.2) of our molecular model.

4. RESULTS OF CALCULATION

Experimental data and molecular constanrs used in our calculations are presented in Table 1 , while the results of these calculations are summarized in Table 2 and Fig.1-5.

By employing a number of estimations (the solution of transcendental equations (3.7) and (3.8) was obtained by an iteration procedure) we found that we actually ha to fit only the three parameters τ_2 , p_2 , τ_{D2} of a CR/DWP model. These were fitted for good agreement of the theoretical and experimental spectra $a(\omega)$ in the far IR region. As a result it was shown that the lifetime τ_2 must be taken close to

thw life time τ_1 , that is, lifetimes of both kinds of rotational motion are equal o nearly equal. We see from Fig.4 that the curve labelled 1, which corresponds to $\tau_{D2} = 0$ gives better agreement with experiment (curve 4) than does curve 2, for which $\tau_{D2} \neq 0$. Thus it would seem that only the one Debye relaxation process exists in liquid water, and it is determined by [L] -molecules.

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Table 1. Molecular constants and experimental data: liquid water at T = 300K

Molecular constants	Parameters of Debye relaxation (from [12])	Parameters of FIR spectra in cm^{-1} (from [14])
$I = 1.483 \cdot 10^{-40} g \cdot cm^2$	$\varepsilon_s = 77.66$	$\nu_R = 200$
$\rho = 1\ g \cdot cm^{-3}$	$\varepsilon_\infty = 5.211$	$\alpha_R = 1445$
$\mu_o = 1.84 \cdot 10^{-18}$ CGSE units (1.84 Debye)	$\tau_D = 7.88$ ps	$\nu_L = 670$
$n_\infty^2 = 1.7$	$\varepsilon_{\infty 2} = 3.52$	$\alpha_L = 3308$
$M = 18$	$\tau_{D2} = 0.2$ ps	$\alpha_{min} = 1311$
		$\nu(\alpha_{min}) = 260$
		$\Delta\nu_L = 530$

Table 2. Parameters of microscopic CR/DWP and CR/ED models. Liquid water, T = 300 K

Variants	Parameters	CR/DWP	CR/ED
variant A $\tau_2 \neq \tau_1$	τ_1, ps	0.156	0.151
	τ_2, ps	0.212	0.212
	r, %	5.19	8.34
	p	1.45	-
variant B $\tau_2 = \tau_1$	τ, ps	0.155	0.151
	r, %	5.76	8.34
	p	1.57	-
Note: $k_\mu = 1.18$, $\tau_{D1} = \tau_D = 7.88$ ps, $\beta = 20.64^\circ$, $\tau_{D2} = 0$			

Thus we consider two calculational schemes:

Scheme A: $\tau_2 \neq \tau_1$, lifetime τ_1 is determined from eq.(3.7) and (3.8) while the lifetime τ_2 and the field parameter p_2 are fitted.

Scheme B. $\tau_2 = \tau_1$ and p_2 calculated from eq.(3.5),(3.11).

From Fig.1 it is seen that the values of the proportion r and lifetime τ_1, obtained from the solution of the (3.7) and (3.8), actually give the *correct description of the Debye relaxation spectrum* if we use (in obtaining this solution) the experimental values of the parameters τ_D, ε_s and ε_∞. Here points represent results of calculations based on the Liebe-Hufford-Manabe empirical formula [12], see Appendix B. It is important that such a coincidence is obtained quite "automatically".

From Fig.2,3, where the frequency dependencies of absorption $\alpha(\nu)$, real and imaginary parts of the permittivity $\varepsilon^*(\nu)$ are depicted, we see that *in FIR region of the spectrum the theory gives only qualitative agreement* with the experimental data [14]. If the CR/DWP model is used, then the scheme A (with fitted τ_2 and p_2) gives slightly better agreement with the experiment than the scheme B (cf. curves 1 and 2 in Fig.2a). But the latter is simpler, since all free parameters are calculated. The field DWP model, applied to [R]-molecules, is closer to the experiment than the ED model with freely rotating molecules (cf. curves 2 and 3 in Fig.2b). The main disagreement between the theory and experiment is seen in the infrared region near the translational absorption peak ($\nu \cong 40$-200 cm^{-1}), see Fig.2 and 3. From Fig.3b it is evident that the experimental loss curve $\varepsilon''(\nu)$ falls just between the two theoretical ones (for DWP and ED models). We may suppose that some

intermediate value of the intermolecular field (between $p=1.45$ for DWP model and $p=0$ for ED mode) may provide better agreement with the experimen

In Fig.4 we compare the theoretical and experimental plots $\varepsilon''(\varepsilon')$ in the FIR spectral region. It is seen that if the DWP model is applied for [R]-molecules then the introduction of the second Debye relaxation time τ_{D2} increases the disagreement between the theoretical and experimental plots $\varepsilon''(\varepsilon')$ (cf. curve 1 for $\tau_{D2}=0$ with curve 2 for $\tau_{D2}\neq 0$, Fig.4a). On the other *hand*, the ED model, applied to [R]-molecules, is markedly worse than DWP model (cf. curve 1 in Fig.4a with curve 1 in Fig.4b).

In Fig.5 we compare the contributions of [L]- and [R]-molecules to the complex susceptibility and absorption. As is seen, the latter contribute to the loss and absorption more than [L]-molecules only in a relatively narrow band near 200 cm^{-1}.

5. CONCLUSION

A microscopic molecular model , based on an analytical description of *two kinds of rotational motion* of H_2O molecules, is elaborated. The central idea of the suggested calculation scheme is that *H-bonded [L]-molecules are responsible* in liquid water for almost all static susceptibility χ_s and for the main loss peak ε''_D.

ε''_D

The CR/DWP model gives a *quantitative* description of the Debye relaxation at microwaves and a *qualitative* one in the FIR region ($\nu < 1000$ cm^{-1}). Some spectral peculiarities in the Debye and FIR regions are related to the fitted parameters (3.2) of the model.

In our work the lifetimes τ_1 and τ_2 of both rotational states are equal or nearly equal. This means that both the local order potentials U_1 and U_2 probably change *simultaneously* because of the

Brownian motion.

If we use the definition of a collision time τ_c introduced in ref. 1 , we find that

$$\tau_c=\eta/y_c, \quad \text{where } y_c(p)=\pi^{-3/2}\exp(p^2/2)\left[I_0(p^2/2)\right]^{-1} \qquad (5.1)$$

For [R]-molecules in the scheme A we have:

$$y_c(1.45)=0.396, \text{ that is } \tau_{cR}=0.107 \text{ ps} \sim \tau_R. \qquad (5.2)$$

Using data of Appendix B we find for [L]-molecules:

$$y_c(4.384)=1.376, \text{ that is } \tau_{cL}=0.03 \text{ ps} \sim 5\tau_L. \qquad (5.3)$$

Hence, the lifetime τ_R is close to the collision time τ_c while the lifetime τ_L H-bonded molecules is much longer than the collision time τ_c . On the contrary, in simple (nonassociated) liquids, such as CH_3F , the collision time is twice the lifetime [1] . So, we may conclude that librations in liquid water exist in much more distinct form than in liquids without H-bonds.

The field DWP model with $\cos^2\theta$-potential profile gives the better description of the [R]-molecules dielectric response than the ED model. To the value p=1.45 of the field parameter corresponds the potential well depth $U_0 \cong 2k_BT$. The amplitude of rotation, β_R, of [R]-molecules may be evaluated as [10]

$$\beta_R = (p)^{-1}\sqrt{\pi/2} \qquad \text{or at } p = 1.45 \qquad \beta_R \cong 50^\circ.$$

Thus the rotational mobility in this sub-ensemble is approximately twice that of the [L]-molecules.

In Sec.4 it was suggested that for smaller values of p (or of the intermolecular potential U_0) the theory may better agree with the experiment in the vicinity of the translational peak . This idea was confirmed on the example of $\alpha(\nu)$ frequency dependence after this work was finished. So it seems that for [R]-molecules the effective intermolecular field U_0 may be near k_BT or still less

than this value.

The CR model with the infinitely high rectangular potential well gives the bandwidth of the FIR librational peak exceeding the experimental one (see Fig.2). On the other hand, as it may be shown, the proper (at $\tau \to \infty$) bandwidth of a simple $\cos^2\theta$-potential well is too narrow for liquid water and this cannot be applied to describe the dielectric response of [L]-molecules. So there is a need to elaborate a new model for [L]-librators with $U(\theta)$ profile which may be in some sense intermediate between the two above-mentioned potential wells.

Appendix A. EVALUATION OF THE FREE MODEL PARAMETERS

In the vicinity of the *translational absorption peak* we retain for simplicity only the susceptibility χ_2 due to [R]-molecules. To a first approximation we may write :

$$\varepsilon''(\nu) = n_\infty + 4\pi\chi_2''(\nu); \qquad \alpha(\nu) = \frac{\omega\varepsilon''}{cn_\infty} = \frac{4\pi\omega\chi_2''(\omega)}{cn_\infty},$$

$$\chi_2 = GL_2(z_2), \qquad L_2(z_2) = \frac{1}{p^2 - z^2} = \frac{1}{2p}\left[\frac{1}{p-z} + \frac{1}{p+z}\right].$$

Omitting the non-resonant term $(p+z)^{-1}$ we derive the formula for the absorption coefficient:

$$\alpha(x) = \frac{4\pi Gr}{c\eta n_\infty}\,\mathrm{Im}\left[\frac{x}{p^2 - z^2}\right] = \frac{4\pi Gr\varphi(x)}{c\eta n_\infty}; \quad \varphi_2(x) = \frac{2xy_2}{p^2 - x^2 + y_2^2 + 4x^2y_2^2}. \qquad (A1)$$

This function of x reaches its maximum value $(2y_2)^{-1}$ at $x = x_R$, where $x_R = 2\pi\eta c\nu_R = \sqrt{p^2 + y_2^2}$. Thus,

$$\alpha_R = \frac{2\pi rG}{c\eta n_\infty y_2} = \frac{2\pi rG\tau_2}{c\eta^2 n_\infty}, \qquad (A2)$$

$$p = \sqrt{\tau_R^2 - (\eta/\tau_2)^2}. \qquad (A3)$$

The bandwidth of the function $\varphi_2(x)$ on the level 1/2 is found from the condition

$$\varphi_2\left[x \mp \frac{\Delta x}{2}\right] = \frac{1}{4y_2}, \text{ hence } x_R \mp \frac{\Delta x}{2} = \sqrt{x_R^2 + y_2^2} \mp 2y_2 ; \quad (A4)$$

$$\Delta x_R = 2\pi\eta c\Delta\nu_R = \sqrt{x_R^2+y_2^2} = 4y_2 = 4\eta/\tau_2. \quad (A5)$$

Thus, we have got estimations (3.11)-(3.14).

In the vicinity of a librational peak ν_L we retain only $\chi_1(x)$ term in (2.3a):

$$\alpha(\nu) = \frac{\omega\varepsilon''}{cn_\infty} = \frac{4\pi x\chi_1''(x)}{cn_\infty\eta}.$$

For simplicity we examine the limit $y \to 0$ and retain only the first term of the sum in (2.5). Since $x_1 = f\cdot x$, we have

$$x\chi_1^*(x) = Gf^{-1}x_1 \operatorname{Im}\left\{a_1[1+x_1^2\exp(-x_1^2)E_1(-x_1^2-i0)]\right\}.$$

Since $E_1(-t-i0) = i\pi - Ei(t)$, we obtain for $y=0$:

$$x\chi_1''(x) = \pi f^{-1}G(1-r)a_1\varphi_1(x_L); \qquad \varphi_1(x_L) = x_L^3\exp(-x_L^2).$$

The $\varphi_1(x_L)$ function goes through its maximum

$$\max\{\varphi_1(x_L)\} = (3/2)^{3/2}\exp(-3/2) \quad \text{at } x_m = \sqrt{3/2} = fx_L = \frac{2\beta}{\pi}\, 2\pi\eta c\nu_L. \quad (A6)$$

This estimation gives the relation (3.9) of β to ν_L.

The bandwidth Δx_L of the librational peak is found from the equation

$$\varphi_1\left[x_m \mp \frac{f\Delta x_L}{2}\right] = \frac{1}{2}(3/2)^{3/2}\exp(-3/2),$$

that is

$$f\Delta x_L \approx 1.162, \quad \Delta\nu_L \approx \frac{\Delta x_L}{2\pi c\eta} \simeq 636 \text{ cm}^{-1}. \quad (A7)$$

For the chosen value of β the bandwidth $\Delta\nu_L$ defined in (A7) is greater than experimental value $\simeq 570$ cm^{-1}.

Noting that $a_1/f = [8f/\pi^2]\sin^2\left[\frac{\pi}{2} - \beta\right]\cdot\left[1 - f^2\right]^{-2}$,

we obtain the estimation (3.10) for the peak absorption:

$$\alpha_L = \frac{4G}{c\eta n_\infty}(1-r)\frac{8}{f}\cos^2\beta\cdot\left[1 - f^2\right]^{-2}(3/2)^{3/2}\exp(-3/2). \quad (A8)$$

To estimate the static (at $x=0$) value of the spectral function, we write :

$$L_1(iy_1) = \sum_{n=1}^{\infty} s_n\left[1 - y_n^2 \exp(y_n^2)\, E_1(y_n^2)\right] \text{ and [4] } \sum_{n=1}^{\infty} s_n = 1 - \frac{\sin^2\beta}{\beta^2}.$$

At small β and $y \to 0$ the sum reduces to $(2/3)y^2$, so

$$L_1(iy_1) \approx \frac{2}{3}\beta^2. \qquad \text{(A9)}$$

Now we apply for example these formulae to liquid water at T=300K. Using the data from Table 1, we calculate the time scale η and a number of dimensionless parameters:

η=0.0423 ps, G=1.938, g=2.11, g_1=0.112, x_R=1.594.

From (3.9) we find: β=0.36, i.e. β=20.6°. Since $\delta\nu_R \cong 120$ cm^{-1}, we may estimate τ_2 and r from (3.14) and (3.12): τ_2=0.177 ps and r=0.047. Thus, $p = p_2 = 1.592$. We may take $\tau_1 = \tau_2 \cong 0.2$ ps.

The self-consistency of these estimations is evident if we calculate the peak absorption (3.10): $\nu_L \simeq 1442$ cm^{-1}, which is close to the experimental value 1445 cm^{-1}. On the other hand, the values of τ_1 and r found from the more accurate equations (3.7), (3.8) and the fitted value of p also agree with the above estimated quantities.

Appendix B. THE EMPIRICAL LIEBE-HUFFORD-MANABE (LHM) FORMULA FOR THE COMPLEX PERMITTIVITY OF LIQUID WATER

An analytical empirical description of $\epsilon^*(\omega)$ applicable to liquid water over wide range of frequencies and temperature has been suggested by Liebe, Hufford and Manabe [12]. Their LHM formula comprises two Debye (relaxational) terms and two resonance (Lorentz) ones:

$$\varepsilon^* = \varepsilon_s - f\left(\frac{\varepsilon_s - \varepsilon_{\infty 1}}{i\gamma_1 + f} + \frac{\varepsilon_s - \varepsilon_{\infty 2}}{i\gamma_2 + f}\right) + \sum_{j=1,2}\left(\frac{A_j}{f_j^2 - f^2 - i\Gamma_j f} - \frac{A_j}{f_j^2}\right) \qquad \text{(B1)}$$

where $f=\omega/(2\pi)=\nu c$ is the frequency in Hz (this should not be confused

with the normalized libration amplitude $f=2\beta/\pi$ in the CR model),

$$\varepsilon_s=77.66-103.3\theta,\quad \varepsilon_{\infty 1}=0.0671\varepsilon_s,\qquad \varepsilon_{\infty 2}=3.52+7.52\theta,$$

$$\gamma_1=(20.2+146.4\theta+316\theta^2)\cdot 10^9,\qquad \gamma_2=39.8\gamma_1,$$

$$f_1=5.11\cdot 10^{12},\qquad f_2=18.2\cdot 10^{12},\qquad (B2)$$

$$\Gamma_1=4.46\cdot 10^{12},\qquad \Gamma_2=15.4\cdot 10^{12},$$

$$A_1=25.03\cdot 10^{24},\qquad A_2=282.4\cdot 10^{24},$$

$$\theta=1-\frac{300}{T}=\frac{300}{273.15+T\,C^{\circ}},\quad \text{so}\quad \tau_{D1}=\frac{1}{2\pi\gamma_1},\quad \tau_{D2}=\frac{1}{2\pi\gamma_2}.$$

It follows from (B1) that at T=300K (or θ=0) the relaxation times of the first (main) and the second (if this exists) Debye regions and the corresponding values $\varepsilon_{\infty 1}$ and $\varepsilon_{\infty 2}$ are, respectively:

τ_{D1}= 7.88 ps, $\varepsilon_{\infty 1}$=5.21 and τ_{D2} = 0.2 ps, $\varepsilon_{\infty 2}$= 3.52

On the other hand, in the Lorentz line approximation, for which $L\cong(p^2 - z^2)$, we may estimate , using the empirical parameters (B2), some the field parameters of our DWP model:

$$p_R = 2\pi\eta\sqrt{f_1^2 - \gamma_1^2/4} = 1.22 \quad .$$

At the frequency ν_R of a translational absorption peak we may put approximately $A_1 = 4\pi Gr/(2\pi\eta)^2$, from which we estimate the proportion r of [R]-particles: r = 0.073.

For the librational band (in terms of LHM we use subscript 2 in this case) similar estimations give:

$$p_L = 2\pi\eta\sqrt{f_2^2 - \gamma_2^2/4} = 4.384;\ \beta_L= \sqrt{\pi/2}\ p_L^{-1} = 0.286 \quad (\beta_L=16.4^{\circ}).$$

These estimations agree with that, given in Sec.3 and in the Appendix A, although they are independent of the latter. Thus, we may relate some of the parameters of (B1) approximation to a number of the physical characteristics of a molecular model.

It should be noted that in Sec.4 we use the notation τ_D and ε_∞ instead of τ_{D1} and $\varepsilon_{\infty 1}$.

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CAPTIONS FOR FIGURES

Fig.1. Dielectric spectra of liquid water in the relaxation region: real part of the permittivity $\varepsilon'(\nu)$ (a) and the loss curve $\varepsilon''(\nu)$ (b). Calculations for the CR/DWP model (solid lines 1) and CR/ED model (dashed lines 2). Curve 3 - experiment [14].

Fig.2. Absorption coefficient $\alpha(\nu)$ frequency dependence: for the CR/DWP model (a) and the CR/ED model (b).

Curves 1 and 2 - CR/DWP model for schemes A and B; points 3 - experiment [14]; curve 4 - CR/ED model for scheme A.

Fig.3. $\varepsilon'(\nu)$ (a) and $\varepsilon''(\nu)$ (b) plots in submillimeter and FIR regions. All notation as in Fig.2.

Fig.4. $\varepsilon''(\varepsilon')$ plot for the CR/DWP model (a) and the CR/ED model (b). Curves 1 and 2 - the results of calculation for the relaxation time τ_{D2} equal to zero (1) and to 0.2 ps (2). Points 3 - for experimental data [14]. Curves 4 - for the LHM empirical formula [12]. The two marks in the abscissa axis ε' correspond to the values [12] ε_∞ and $\varepsilon_{2\infty}$ of the main and the second Debye regions.

Fig.5. Contributions of [L]- and [R]- molecules to the real part of the susceptibility $\chi'(x)$, to the loss $\chi''(x)$(a,b) and to the normalized absorption $x\chi''(x)$ (c). Curves 1′,1″ and 1 for [L]-molecules; curves 2′,2″ and 2 for [R]- molecules. Scheme A.

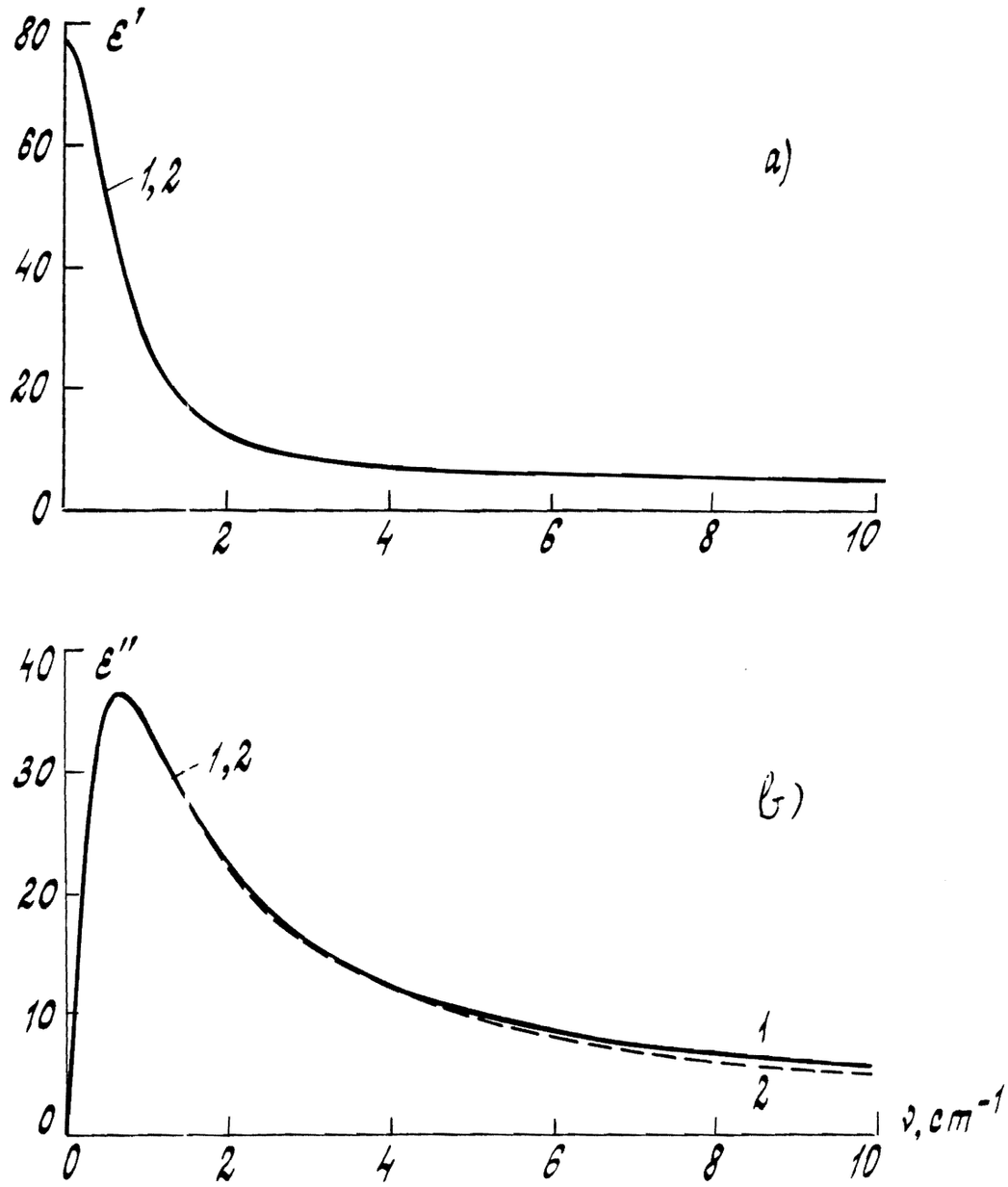
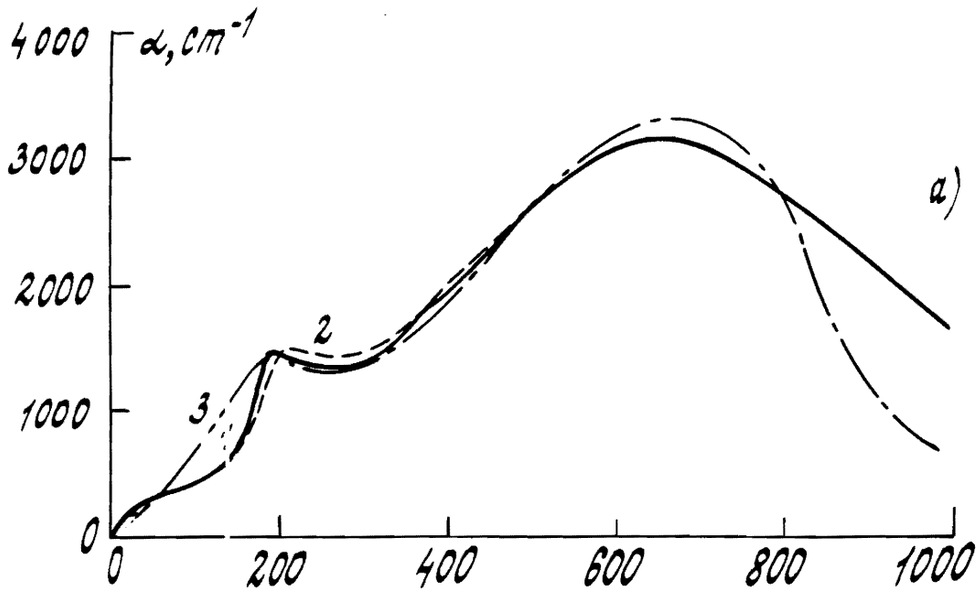


Fig. 1


4000
3000
2000
1000
0
α, cm⁻¹
a)
2
3
0
200
400
600
800
1000

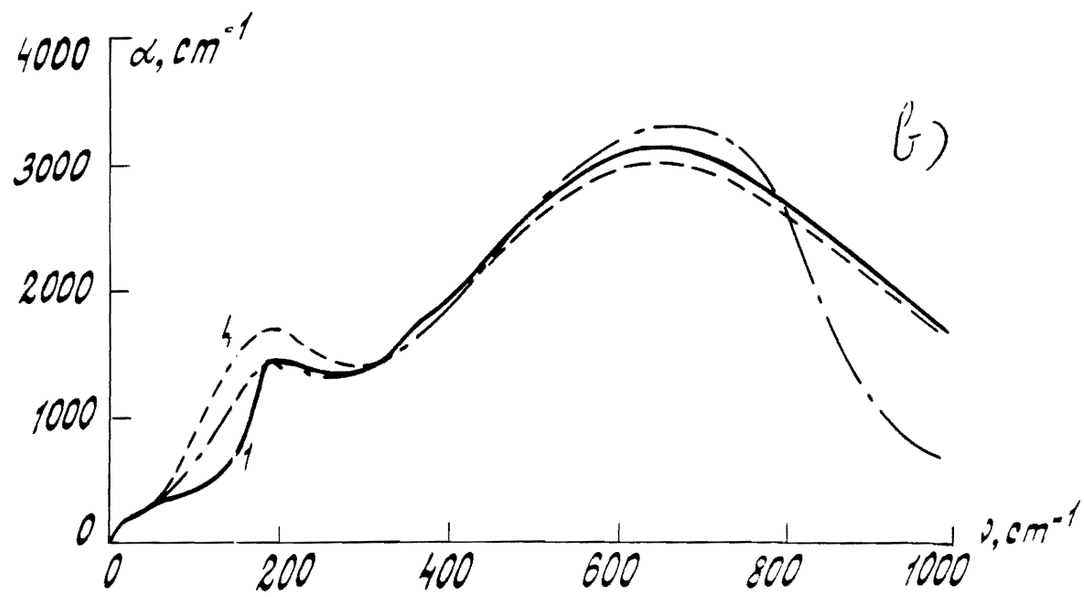
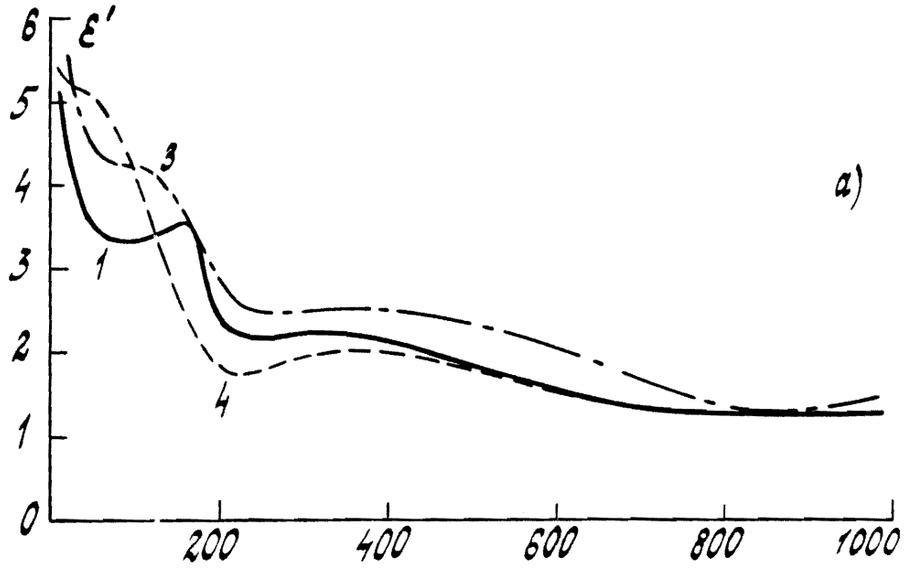

4000
3000
2000
1000
0
α, cm⁻¹
b)
4
1
0
200
400
600
800
1000
ν, cm⁻¹

Fig. 2


ε'
a)
1
3
4
0
1
2
3
4
5
6
200
400
600
800
1000

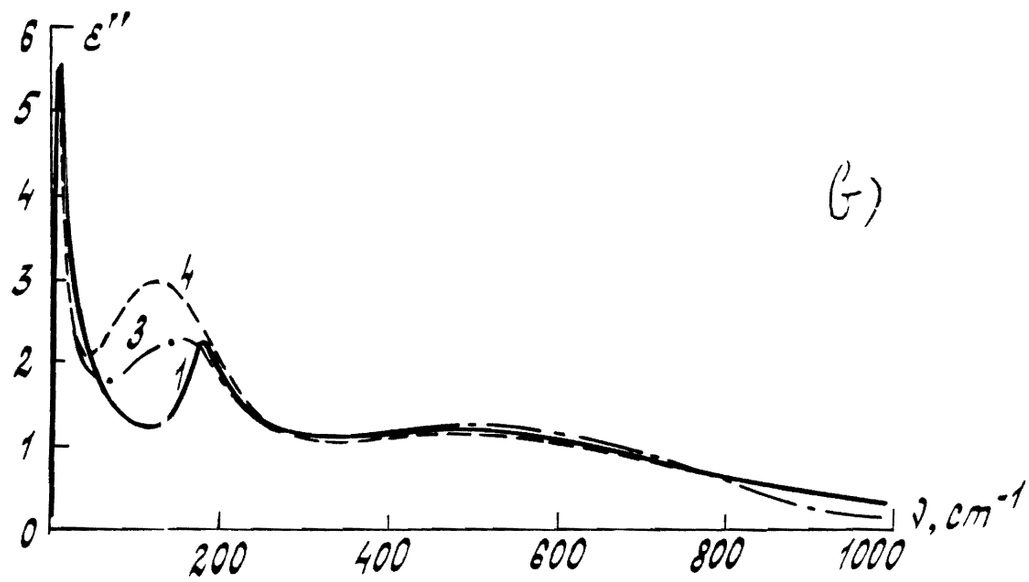
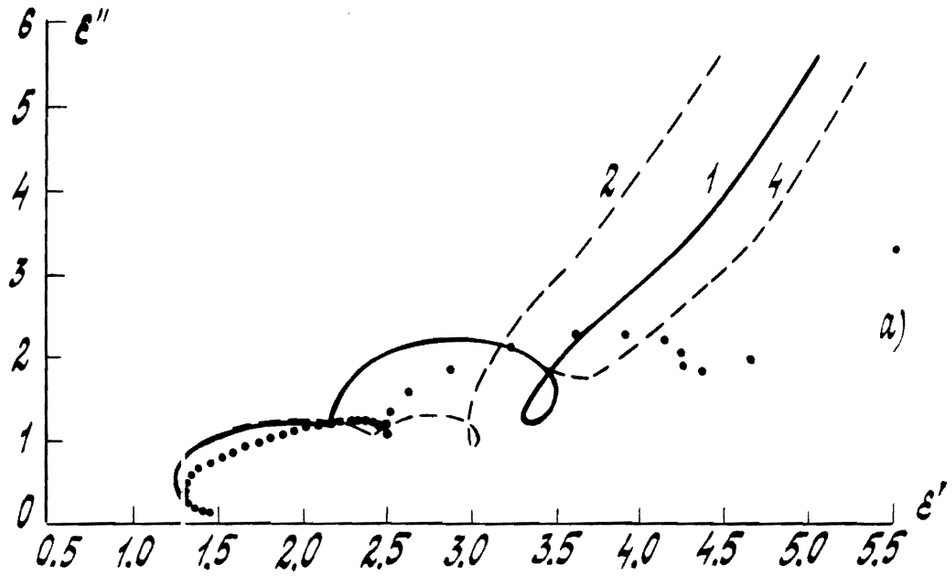

ε''
б)
1
3
4
0
1
2
3
4
5
6
200
400
600
800
1000
ν, cm⁻¹

Fig. 3


ε''
ε'
0
1
2
3
4
5
6
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
1
2
4
a)

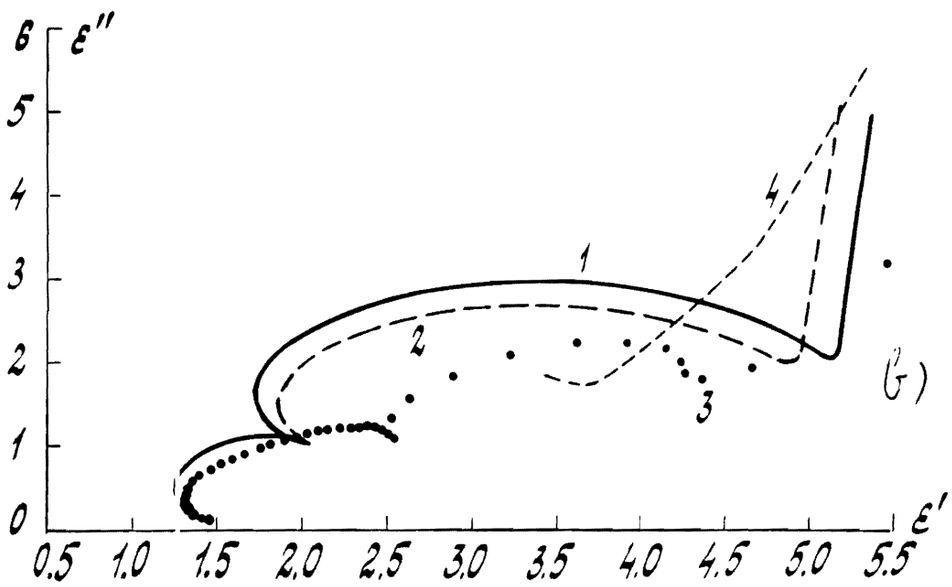

ε''
ε'
0
1
2
3
4
5
6
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
1
2
3
4
б)

Fig. 4

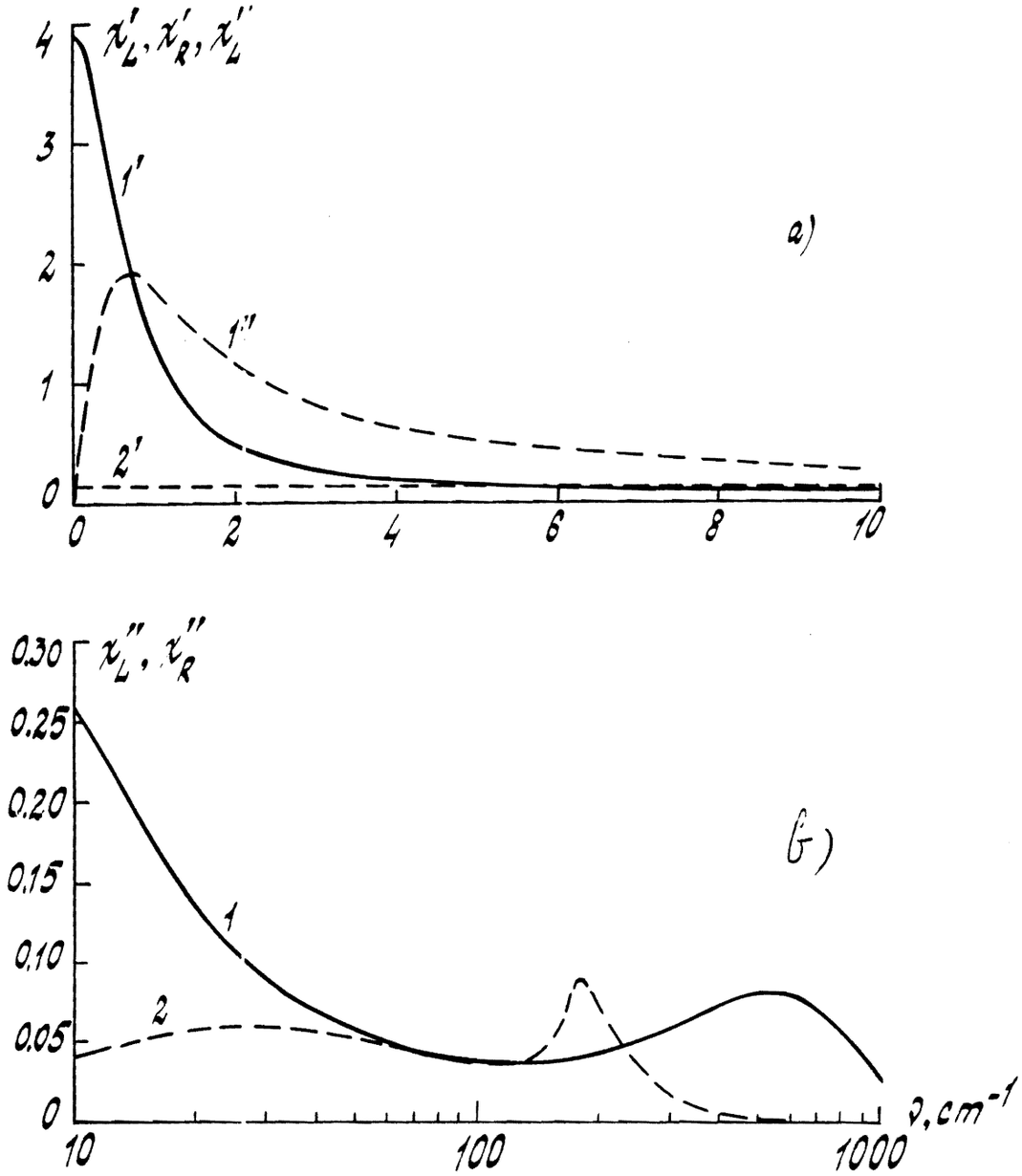

$\chi'_L, \chi'_R, \chi'_L$
4
3
2
1
0
1'
1''
2'
a)
0
2
4
6
8
10
χ''_L, χ''_R
0.30
0.25
0.20
0.15
0.10
0.05
0
1
2
б)
10
100
1000
ν, cm^{-1}

Fig. 5 a, б

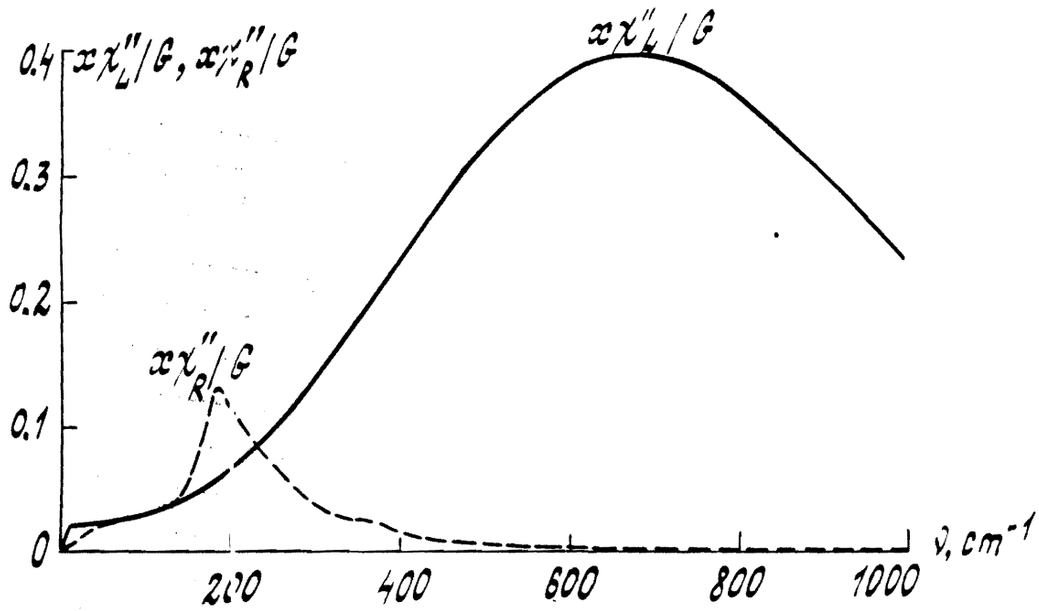

0.4
0.3
0.2
0.1
0
$x\chi''_L/G$, $x\chi''_R/G$
$x\chi''_L/G$
$x\chi''_R/G$
200
400
600
800
1000
ν, cm^{-1}

Fig. 5c