Prediction of FIR absorption for liquid water with hot HO_2 dipoles as the cause of the translational band

Vladimir I. Gaiduk* and Vladimir V. Gaiduk

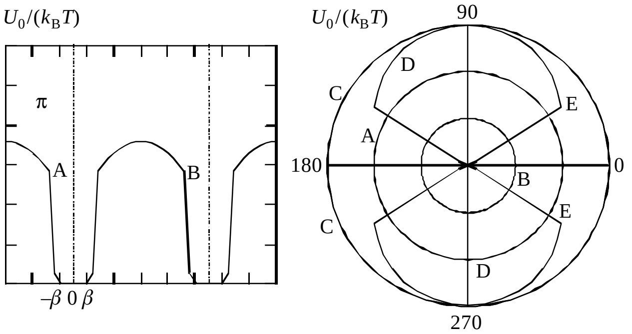
Institute of Radio Engineering and Electronics, Russian Academy of Sciences, 141120 Fryazino, Moscow Region, Russian Federation. E-mail: vig169@ire216.msk.su

The analytic theory of wideband (0–1000 cm^{-1} region) dielectric spectra is elaborated for liquid water; it is assumed that H_2O molecules librate/rotate in a rectangular potential box with flat edges and the librational/translational absorption bands at *ca.* 700 and 200 cm^{-1} are due to slow and fast reorienting particles, respectively.

The study[1–3] of wideband (0–THz) dielectric spectra of liquid water yields valuable information on water structure and the timescales of molecular events. The imaginary peak ε''_D of the complex permittivity $\varepsilon(\omega) = \varepsilon' - i\varepsilon''$ is found in the microwave region while in the FIR spectral region are observed the librational (near 700 cm^{-1}) and the so-called translational (near 200cm^{-1}) absorption bands $\alpha(\omega)$. Here ω is the angular frequency of radiation; the frequency $\nu = \omega/(2\pi c)$ is measured in cm^{-1}, c is the velocity of light. The existence of two absorption peaks is evidence of some bimodalality. Its nature has not yet been established since the molecular theory of this band has not been elaborated. This problem is the main purpose of this communication.

The dielectric spectra of water have been previously described[1–3] using analytical theory elaborated for the combination of the confined rotator (CR) and extended diffusion (ED) models. In each model the energy H of the particles is varied in the interval [0,7] and different types of molecular rotation during lifetime t are considered since two independent molecular fractions (L and R) are introduced, the proportion r- of R-particles being the fitting parameter (the proportion r_L of the other fraction is equal to $1 - r$). The CR model describes the libration of water molecules in a H-bond network. The L-molecules are found in an infinitely deep rectangular potential well. The dielectric response of another (R) fraction is described by the ED model by the consideration of free rotation of dipoles[1–3] (in ref. 2 – by consideration of their rotation in a conservative potential well with the cosine squared profile).

In this communication we attempt to prove the validity of the following suggestion:[4] one can describe the two-humped absorption/low frequency Debye spectrum of liquid water with use of an adequate ('hat') intermolecular potential profile, *i.e.* without employing two independently introduced molecular ensembles. Besides, we suggest a simple calculation that is able to predict, in its main features, the orientational spectrum of liquid water in the frequency region [0,1000 cm^{-1}]. In particular, the influence of temperature T on this spectrum was studied. We also show that it is possible to calculate the critical temperature T_{cr} of liquid water, if one regards T_{cr} to be the point where the employed model of molecular rotation ceases to exist.



(*a*) (*b*)

Figure 1 The geometric scheme pertaining to the double well rectangular potential employed in the hybrid model. Rectangular (*a*) and polar (*b*) coordinate systems. For the spatial configuration Figure (*b*) transforms into two cones joined by the spherical surface.

The so called hybrid model (HM)[5,6] was applied to liquid water that was previously used for the description of 0–THz spectra of simple nonassociated liquids, such as CH_3F. In the HM the potential profile has the form of two rectangular potential boxes with the depth U_0 and angular width 2β. One box is turned relative to the other by the angle π (Figure 1). The two subensembles (L and R) appear inherently in this model. L-molecules, with energy $H < U_0$, perform librations while hot R-particles, with energy $H > U_0$, perform free rotation, their proportion $r = r(U_0,\beta)$ being a function of the well's geometry. The low frequency (Debye) spectrum of a liquid appears to be due to equalization of the induced population of dipoles *via* their transition, under the influence of strong collisions, from one well to another. The mean rotational frequency of L- and R-particles determine the positions n_L and n_R of the two absorption peaks observed in water.

The formulae, based on the linear dielectric response theory,[6] for the absorption $\alpha(\omega)$ and complex permittivity $\varepsilon^* = \varepsilon' + i\varepsilon''$ (* is the complex conjugation symbol). α and ε^* are related as follows

$$\alpha^* = \frac{(\omega/c)\mathrm{Im}(\varepsilon^*)}{\mathrm{Re}(\sqrt{\varepsilon^*})} = \frac{2\pi\nu\varepsilon''}{n}, \qquad (1)$$

where $n \equiv \mathrm{Re}(\sqrt{\varepsilon^*})$ is the refraction index. The dipole moment μ of a molecule in a liquid (water) is related to the moment μ_0 of an isolated molecule:

$$\mu = \mu_0 k_\mu \frac{(n_\infty^2 + 2)}{3} \qquad (2)$$

k_μ is the correction coefficient (k_μ = *ca.* 1.12) and n_∞ is the optical refraction index (n_∞^2 = *ca.* 1.7).

The dielectric response, related to the U potential, is anisotropic and is calculated for the local (during lifetime τ) configuration. This response is characterized by the spectral functions (SF) $K_\parallel(z)$ and $K_\perp(z)$. These correspond to orientations of the radiation amplitude E_m along and across the symmetry axis of the potential U. The argument z of SFs is the dimensionless complex frequency z,

$$z = x + iy; \quad y = \eta/\tau, \quad \eta = [I/(2k_BT)]^{1/2}, \qquad (3)$$

I is the moment of inertia of a molecule that for simplicity we regard to be a linear one, k_B is the Boltzmann constant.

In accordance with usual approach we define I as follows: $1/I = 1/2(1/I_x + 1/I_y)$, where I_x and I_y are the moments of inertia of an asymmetrical top molecule about the principal axis perpendicular to the dipole moment vector. The influence of the molecule form is very important for the description of the discrete rotational spectrum in the water vapour. In the condensed (liquid) state, in which the potential well is deep, the main spectral peculiarities of water are related to the influence of the intermolecular potential on molecular rotation, *viz.* to the

Table 1 Molecular constants[a] of liquid water, the fitted and other parameters of the hybrid model.

	Parameters of the HM						Other quantities					
$T/°\mathrm{C}$	β/degree		u	$U_0/\mathrm{kcal mol^{-1}}$	τ/ps [from (14b)]	k_μ	r	y	$\rho/\mathrm{g cm^{-3}}$	m_L	g	l/Å
	Fitted	from (14a)										
1	17.98	20.84	5.6	3.05	0.851	1.161	0.071	0.052	1.000	16.0	2.24	0.205
27	19.93	21.14	5.7	3.04	0.475	1.118	0.093	0.089	0.999	8.2	2.35	0.209
50	22.09	22.10	4.6	3.0	0.366	1.097	0.122	0.112	0.988	5.7	2.38	0.218

[a] Constants: σ = 2.9 Å, $I = 1.483\times10^{-40}$ g cm^2, μ_0 = 1.84 D.

transformation of almost free rotors into librators. Correspondingly, in water the absorption peak considerably shifts to higher frequencies compared to the position of maximum absorption in vapour. The main object of our theoretical study is the complex orientational susceptibility χ^*. An isotropic polar medium and isothermal collision model (see ref. 6) is given by

$$\chi^*(x) = gGzL(z)[gx + iyL(z)(1 + gxz)]^{-1} \tag{4}$$

The averaged (over all orientations) SF $L(z)$ is given by

$$L(z) = (2/3)\check{K}_\perp + (1/3)\check{K}_{||} + \overset{o}{K}. \tag{5}$$

This SF is applied to an isotropic polar medium. The general approach for the calculation of this $L(z)$ SF is described in ref. 6. For small-amplitude ($\beta < \pi/4$) librations of dipoles in a cone the $\check{K}_\perp$ and $\check{K}_{||}$ SFs were determined in ref. 6; the $\overset{o}{K}$ SF of free rotors was determined in ref. 6 (here the designations are slightly changed compared to ref. 6). Analogous expressions are derived for the SF of the hybrid model (the theory of the HM was elaborated in collaboration with B. M. Tseitlin):

$$\check{K}_{||}(z) = \frac{24}{\pi^5}C(u,\beta)\beta^4(\sin\beta)^2\int_0^{\sqrt{u}}\frac{t^3e^{-t^2}}{t^2 - (\beta z/\pi)^2}dt, \tag{6}$$

$$\check{K}_\perp(z) = \frac{192}{\pi^5}C(u,\beta)\beta^4(\cos\beta)^2\int_0^{\sqrt{u}}\frac{t^3e^{-t^2}}{t^2 - (2\beta z/\pi)^2}dt, \tag{7}$$

$$\overset{o}{K}(z) = 6e^{-u}C(u,\beta)\int_0^{\infty}\frac{t^3e^{-t^2}}{t^2 - z^2}dt, \tag{8}$$

where

$$u = \frac{U_0}{k_\mathrm{B}T},\ C(u,\beta) = [1 + (e^{-u} - 1)\cos\beta]^{-1},$$

$$G = \frac{\mu^2N}{3k_\mathrm{B}T},\ N = \frac{N_\mathrm{A}\rho}{M}, \tag{9}$$

N_A is the Avogadro constant, N and ρ are the number and mass density, M is the molecular mass. The Kirkwood correlation factor g is calculated with the experimental values of ε_s, n_∞ and G:

$$g = (\varepsilon_\mathrm{s} - n_\infty^2)(2\varepsilon_\mathrm{s} + n_\infty^2)/12\pi G\varepsilon_\mathrm{s}. \tag{10}$$

The complex permittivity ε^* is determined by χ^* and n_∞^2 as the solution of the quadratic equation

$$(\varepsilon^* - n_\infty^2)(2\varepsilon^* + n_\infty^2) - 12\pi\varepsilon^*\chi^* = 0. \tag{11}$$

The proportion r of R-particles is given by

$$r = e^{-u}C(u,\beta). \tag{12}$$

The experiential low frequency $\varepsilon^*(\nu)$ spectrum is taken from ref. 7. In particular, the static permittivity ε_s and the relaxation time τ_D are estimated from the empiric formulae

$$\varepsilon_\mathrm{s}(T) = 77.66 - 103.3\theta,\ \tau_\mathrm{D}(T) = [2\pi\gamma_\mathrm{D}(T)]^{-1}, \tag{13a}$$

$$\gamma_\mathrm{D} = 20.27 + 146.5\theta,\ \theta = 1 - 300/T. \tag{13b}$$

The parameters β, τ, u, k_μ and employed molecular constants are given in Table 1. Having only a few free parameters, we tried to fit the following features of the observed[7–9] dielectric spectra.

(a) The position ν_L of the libration peak. The latter is mainly determined by the libration angle β (β is near 20°). The value α_max of the absorption maximum is corrected by the value of k_μ.

(b) The two-humped absorption curve. This curve appears in theory when the contributions of the free rotors and of the librators are commensurable in the vicinity of the frequency ν_R. The correct result is obtained, if the potential U is rather deep (u = *ca.* 5.5).

(c) The coincidence of the calculated and theoretical positions ν_D of the loss maximum ε''_D. For chosen β and u the calculated ν_D value increases when the lifetime τ rises.

The calculated and observed spectra qualitatively agree (Figure 2). We interpret the fitted parameters of the model as follows.

(A) The libration-band frequency ν_L is close to the mean frequency of librations,[6] since the relation

$$\nu_L \approx \sqrt{(3/2)}[4c\eta\beta]^{-1} \tag{14a}$$

approximately holds.

(B) One may estimate the lifetime τ from the formula[6]

$$\tau(T) = (1/2)\beta^2(T)\tau_\mathrm{D}(T), \tag{14b}$$

that follows from the Debye rotational diffusion theory.[10] The lifetime τ substantially decreases when T rises.

(C) In the interval [1, 50 °C] the well-depth U_0 is nearly constant (U_0 = *ca.* 3kcal mol^{-1}) and is commensurable with the energy of H-bond (about 5 kcal mol^{-1}). The constancy of U_0 corresponds to the known picture of a rigid water structure.

(D) The rise of T from 1 to 50 °C is accompanied by the weakening of water structure since the proportion r of hot particles doubles and the number m_L of librations during the lifetime τ decreases 3 times (see Table 1); $m_\mathrm{L} = y_\mathrm{c}/(2y)$, where

$$y_\mathrm{c} = C(u,\beta)\left[\sin\beta\left(\frac{\sqrt{\pi}}{2}\mathrm{erf}(\sqrt{u}) - \sqrt{u}e^{-u}\right) + \frac{\sqrt{\pi}}{2}e^{-u}\right]. \tag{15}$$

Consequently, the rotational mobility of some H_2O molecules, *viz.* of R-particles, in this T-interval significantly increases although the water structure is relatively hard.

The drawbacks of the HM probably result from the roughness of the chosen intermolecular potential profile, *i.e.*

(1) Too slow transition of the absorption curve $\alpha(\nu)$ to the transparency near 1000 cm^{-1} [*cf.* solid/dashed curves in Figure 2(a)].

(2) The calculated absorption minimum between 200 and 300 cm^{-1} is deeper than that observed experimentally, *cf.* solid and dashed curves for T = 27 °C, Figure 2(a).

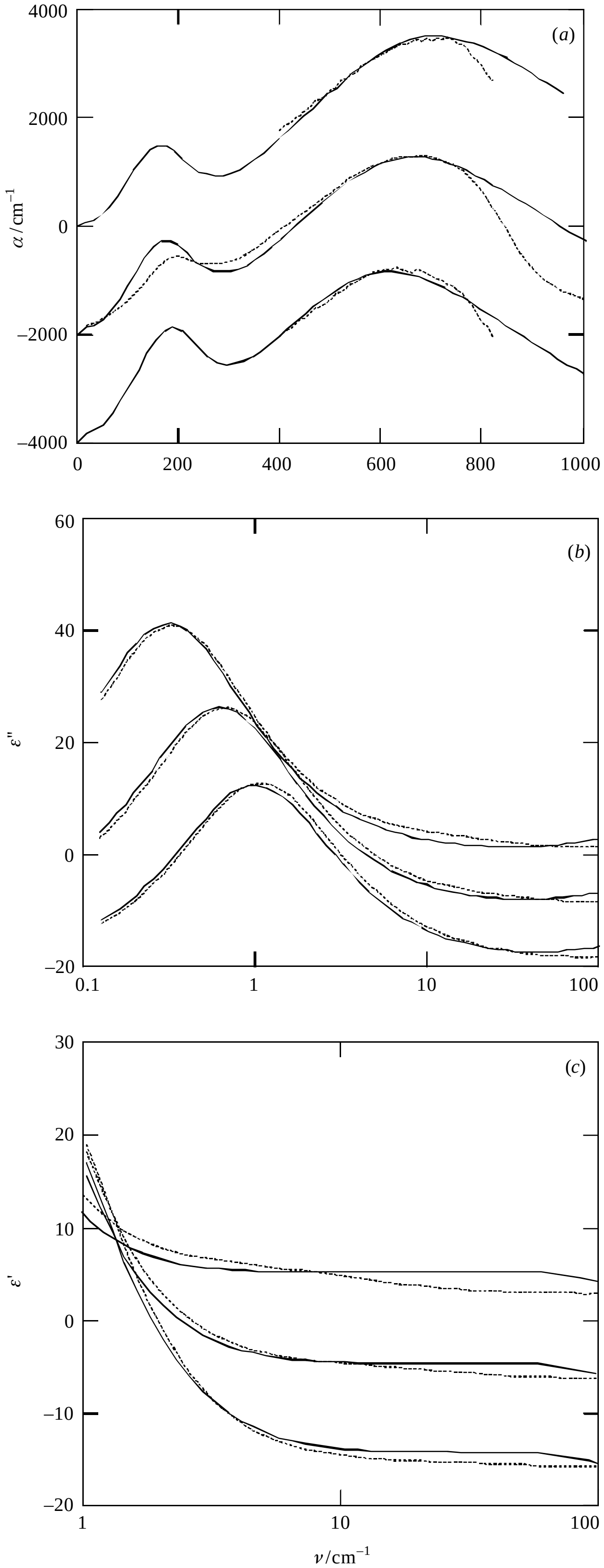


Figure 2 FIR absorption (a) and low frequency (Debye) spectra of the permittivity components ε', ε'' (b),(c). Liquid water for T = 1, 27 and 50 °C; for the last two temperatures the curves are shifted downwards. Solid lines–calculation for the hybrid model, dashed lines – observed data.[7–9]

(3) For the range $\nu \in [10, 100\,\mathrm{cm}^{-1}]$ the calculated submillimeter absorption is less than the observed one. This property of the HM probably confirms the idea[7] that the second Debye relaxation region exists in water. However, an alternative physical mechanism may be responsible for this ‘excess’ absorption.

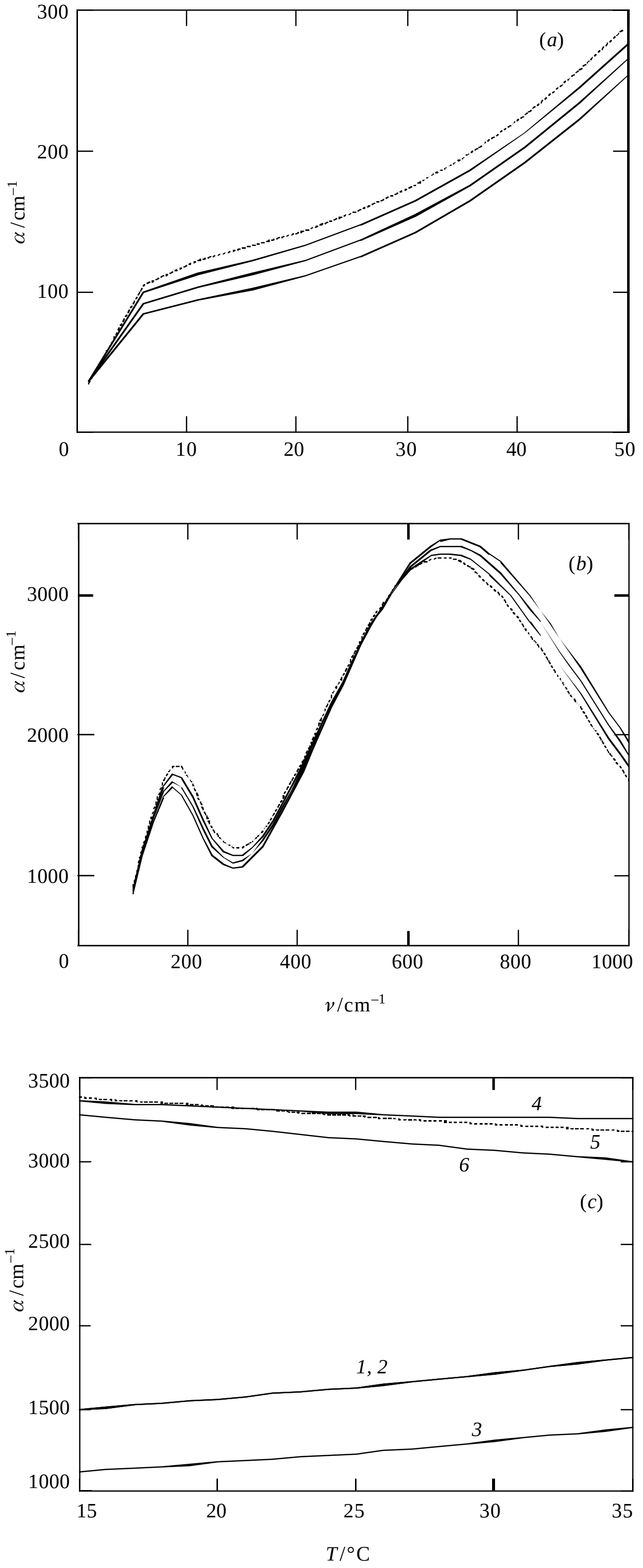


Figure 3 The predicted frequency (a), (b) and temperature (c) dependencies of the absorption coefficient in water. (a), (b): dashed lines for T = 25°C, solid lines for T = 20, 15 and 10°C; (c): curves *1, 2, 3, 4, 5* and *6* for ν =150, 200, 250, 650, 700 and 750 cm^{-1}.

(4) The theory of an isotopic effect (the coincidence of the translational peak ν_R in ordinary and heavy water) is worthy of special study. The HM cannot explain this effect. Our preliminary consideration shows that one needs to employ for this purpose a hat potential with curved brims (not with flat

edges as it was assumed in the present study). We hope to return later to this question.

The following calculation scheme is suggested for the prediction of dielectric spectra in water ($0 < T < 50$°C).

(*1*) Formulae (1)–(11) are employed.

(*2*) U_0 and k_μ are kept constant ($3.05\ \mathrm{kcal\,mol^{-1}}$ and 1.12, respectively).

(*3*) The libration amplitude β is found by the interpolation of the values presented in Table 1.

(*4*) The relaxation time τ_D and the lifetime τ are calculated from equations (13) and (14*b*), respectively.

First example. For $T \in [15, 30°\mathrm{C}]$ and $\nu \in [1, 100\ \mathrm{cm^{-1}}]$ the absorption $\alpha(\nu)$ is calculated. In this region the Debye spectrum transforms into quasi-resonance. It is seen from Figure 3(*a*) that the absorption rises monotonically when T increases. For $\nu \in [5, 30\,\mathrm{cm^{-1}}]$ the Debye-like plateau gives way to an intensive ‘over- Debye’ absorption.

Second example. $\alpha(\nu)$ was calculated for the same temperature interval and $\nu \in [100, 1000\ \mathrm{cm^{-1}}]$, where the translational (near α_R) band transfers to the librational (near α_L) one. It can be seen from Figure 3(*b*),(*c*) that with the rise of T the α_R-peak increases and the α_L-peak decreases. Figuratively speaking, the increase of the ‘vapour’ fraction in water accompanies the melting of its ‘ice’ fraction.

Let us consider finally the ‘rotational’ cell model of a liquid. We can express[5,6] the libration angle β by a few steady-state parameters, *viz.*

$$\beta(T) = \frac{\pi}{8}\sqrt{\frac{m_\mathrm{H}M}{I}}\left(\left[\frac{M}{N_\mathrm{A}\rho(T)}\right]^{1/3} - \sigma\right), \qquad (16)$$

(comparing with refs. 5,6 the formula is slightly simplified). Here m_H is the proton mass and σ is the effective diameter of a molecule. We choose the σ value ($\sigma = ca.\ 2.9$ Å) from the demand that for $T = 50$ °C the estimated and above fitted β values should coincide (*ca.* 22.1°). This cell model is applicable for $T > 50$ °C when the density ρ and the amplitude β substantially alter with the rise of T (Figure 4). One may wait from physical reasoning that the maximum libration angle β_max is about $\pi/2$. For water this β-value is reached if temperature $T_\mathrm{max} = 628$ K, just near the critical temperature $T_\mathrm{cr} = 647$ K, the difference being only 3%. One may also determine T_cr by this way in nonassociated liquids.[12]

We have found that for $T < 50$ °C the rotational cell model gives qualitative estimations (see Figure 4) since equation (16) yields β amplitudes which vary with T more slowly than those fitted for the HM. Consequently, for low temperatures ($T < 50$ °C) molecular rotation is determined sooner by the ice-like tetrahedral water structure; molecular dynamics in this case does not correspond to a simple gas-like picture of molecular rotation that determined the liquid cell model.

Thus, we have discovered the physical mechanism responsible for the existence of *R*-particles. The latter was always[1–3] employed for the calculation of the orientational spectrum in water. *R*-molecules have an elevated rotational mobility and inherently appear in the hybrid model as over-barrier ‘hot’ particles. These molecules are the cause of the ‘translational’ absorption peak near $\nu_R = ca.\ 200\ \mathrm{cm^{-1}}$. In frames of the HM we have elaborated a simple method for the prediction of wideband ($\nu < 1000\ \mathrm{cm^{-1}}$) dielectric spectra of $\alpha(\nu)$, $\varepsilon'(\nu)$, $\varepsilon''(\nu)$ and $n(\nu)$, *i.e.* of absorption, components of permittivity and of refraction index. We have also shown that the critical temperature T_cr corresponds to that limiting state of a liquid, in which the libration amplitude β reaches its maximum possible value $\beta_\mathrm{max} \approx \pi/2$.

It seems that our idea that hot H_2O dipoles are the origin of the translational band does not contradict the other (see *e.g.*, ref. 13) reasoning according to which this band is related to intermolecular vibrations of H-bonded H_2O and D_2O molecules. These vibrations accompany the rotational motion of H_2O dipoles. Unfortunately, the existing H-bond theory is not capable of describing the wideband dielectric spectra of water even if on the level of this study.

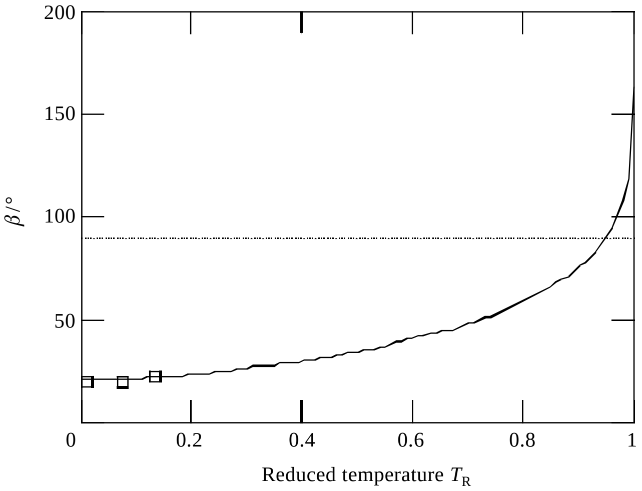


Figure 4 The temperature dependence of the libration amplitude β obtained for the rotational cell model of water. Points – the β-values fitted for the hybrid model at T =1, 27 and 50 °C (from left to right).

The elaboration of the method capable to predict the water spectra/its critical temperature was accomplished in frames of the grant no. 95-03-0-8214a, while the potential well effect on spectra was studied in frames of the grant no. 96-05-65379. Both grants were supported by the Russian Foundation for Basic Research.

References

1 V. I. Gaiduk, T. A. Novskova and V. V. Brekhovskikh, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 1975.

2 V. I. Gaiduk and V. V. Gaiduk, *Physica A*, 1995, **222**, 46.

3 V. I. Gaiduk, V. D. Gus’kova and T. A. Novskova, *Izvestiya Vyssh. Uchebn. Zaved., Radiofiz.*, 1988, **31**, 799 (in Russian).

4 V. I. Gaiduk, *Mendeleev Commun.*, 1994, 15.

5 V. I. Gaiduk, T. A. Novskova and V. V. Brekhovskikh, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 559.

6 V. I. Gaiduk and B. M. Tseitlin, *Adv. Chem. Phys.*, 1994, **87**, 125.

7 H. J. Liebe, J. A. Hufford and T. Manabe, *J. Infrared and Millimeter Waves*, 1991, **12**, 659.

8 H. D. Downing and D. Williams, *J. Geophys. Res.*, 1975, **80**, 1656.

9 L. W. Pinkley, P. P. Sethna and D. Williams, *J. Opt. Soc. Am.*, 1976, **67**, 494.

10 P. Debye, *Polyarnye moleculy* (*Polar molecules*), GONTI, Moscow–Leningrad, 1931 (in Russian).

11 I. T. Goronoskii, Yu. P. Nazarenko and E. F. Necryach, *Kratkii spravochnik khimika* (*Short handbook of chemist*), ed. O. D. Kurilenko, Naukova Dumka, Kiev, 1965 (in Russian).

12 V. V. Brekhovskikh and V. I. Gaiduk, *Radiotekhnika i Elektronika* (in press) (in Russian).

13 B. Curnutte and J. Bandeker, *J. Mol. Spectrosc.*, 1972, **41**, 500.

Received: Moscow, 27th September 1996
Cambridge, 17th January 1997; Com. 6/06667D