The Nature of the Translational Band in Far IR Absorption Spectra of Liquid Water and Ice 1

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It is proposed that the 'bimodal' far IR absorption spectra of liquid water and ice 1 can be explained by a specific intermolecular potential and has no direct relation to structural 'defects' of the H-bonded network.

The dielectric spectra of liquid water and ice 1, which comprise the frequency dependences of the complex permittivity $\varepsilon(\nu) = \varepsilon' - i\varepsilon''$ and absorption coefficient $\alpha(\nu) = 4\pi\nu\mathrm{Im}\{[\varepsilon' + i\varepsilon'']^{1/2}\}$, are caused by reorientations of polar H_2O molecules and range up to the IR region [$\nu < 1000\ \mathrm{cm}^{-1}$, $\nu = \omega/(2\pi c)$, where ω is the angular frequency and c is the velocity of light]. In the case of water ε'' passes through[1] a maximum at $\nu_D \approx 1\ \mathrm{cm}^{-1}$ and $\alpha(\nu)$ through translational (α_T) and librational (α_L) maxima at $\nu_T \approx 200\ \mathrm{cm}^{-1}$ and $\nu_L \approx 670\ \mathrm{cm}^{-1}$. In the case of ice the corresponding peaks are narrower[2] and are shifted ($\nu_T \approx 220\ \mathrm{cm}^{-1}$, $\nu_L \approx 840\ \mathrm{cm}^{-1}$). The Debye frequency ν_D falls[3] into the region 10–10^2 kHz.

An empirical formula[1] has been suggested for the permittivity $\varepsilon(\nu)$ of water, while for ice 1 theory is only available in a non-resonant region.[3] A molecular theory of the ice 1 spectra has not yet been elaborated; for liquid water[4–6] and electrolyte[7] solutions a semi-microscopic, two-fractional model has been described, based on linear response theory.[4,8] Here, it was assumed that molecules of the main [L] fraction constitute an H-bonded network and contribute to the absorption peak α_L due to librations. Molecules of another [R] fraction, the nature of which was not identified, have greater rotational mobility and contribute to the absorption peak α_T. In ref. 5 this group was assigned to 'defects' in the H-bonded network. Based on IR spectroscopy Luck introduced two H_2O fractions into his empirical models[9] of systems with hydrogen bonds.

In this communication a hypothesis is proposed concerning the nature of far infrared (FIR) water and ice 1 spectra based on a *unified approach* which develops the ideas in refs. 4–6. We present here qualitative considerations and preliminary estimates. In ice 1 the concentration of [R] defects must be much less than in water. The intensity of the translational band should therefore be substantially reduced if these defects are the cause of the band. Since this prediction has not been confirmed experimentally,[2] we must seek another explanation for the translational band.

We now suggest that the wide band spectra of water and ice 1, as well as their differences from similar spectra[10] of non-associated polar liquids, can be interpreted if some *specific intermolecular potential* $U(\vartheta)$ is used, ϑ being the angular shift of a dipole from the symmetry axis of the potential. It seems that the latter has the profile of an *overturned hat, i.e.*, an almost flat bottomed well at small $|\vartheta|$, and a relatively steep increase of U for greater $|\vartheta|$ which becomes transformed into the plateau $U = U_0$ near the amplitude β_{max}. For such a potential, which *is far from parabolic*, the phase volume Γ_R of the 'hot' [R] particles, having an energy $H > U_0$, may be not much less than the phase volume Γ_L of the 'cold' [L] librators with energy $H < U_0$. As a consequence, the proportion r of [R] particles is a function of the depth U_0 and the profile $U(\vartheta)$ and may be noticeable for a deep well relevant to H-bonded systems ($U_0 > > k_BT$, k_B is the Boltzmann constant). So, [L] and [R] particles are the two possible states of molecular rotation in a single potential well $U(\vartheta)$. By contrast, in previous work,[4–6] [R[and [L] fractions were introduced independently of one another. Thus, if the lifetimes τ_R and τ_L of each sub-ensemble are equal, then the parameters of the Debye relaxation can be related to the free model parameters without the additional assumptions required previously.[6] In Figs. 1–3 we present spectra for three models, calculated based on the theory.[4,6,8]

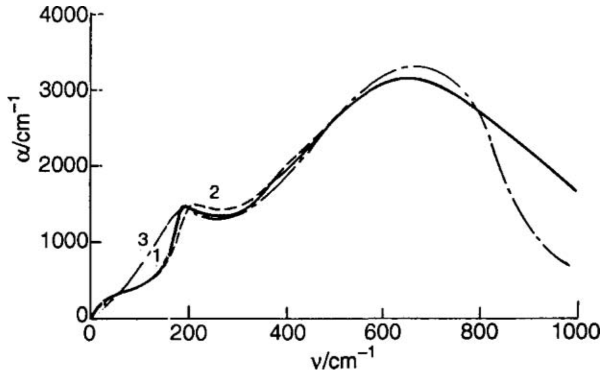

Fig. 1 The frequency dependence of the absorption coefficient: 1, 2 calculated for two fractional model; 3 from the experiment.[11] The parameters of a model: $\beta = 20.6°$; for the curve 1: $\tau_L = 0.152$ ps, $\tau_R = 0.114$ ps, $r = 7.32\%$, the field parameter $p = [U_0/(k_BT)]^{1/2} = 0.67$; for the curve: $\tau_L = \tau_R = 0.155$ ps, $r = 5.76\%$, $p = 0.67$. Liquid water at $T = 300$ K.

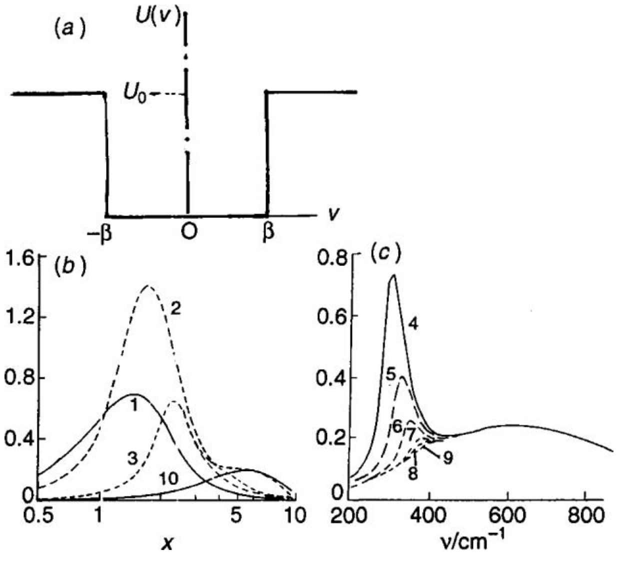

Fig. 2 The scheme of a hybrid confined rotator / extended diffusion model (*a*) and the frequency dependences of the FIR absorption coefficient (in dimensionless units) at various relative well depths $u = U_0/(k_BT)$. For curves 1, 2, . . . , 10 the depth $u = 0, 1.5, 4, 5, 6, 7, 8, 8.5, 9, 10$; the libration amplitude $\beta = \pi/8$. (*a*) The normalized collision frequency $y = [I/(2k_BT)]^{1/2} = 0.5$, the radiation frequency is expressed in dimensionless units $x = \eta\omega$, where $\eta = (I/(2k_BT)]^{1/2}$, I is the moment of inertia of an H_2O molecule; (*b*) $y = 0.15$, the radiation frequency is expressed in cm^{-1}.

The two-fractional model I for liquid water is now discussed (Fig. 1, calculations performed by V. V. Gaiduk). We suppose that [L] molecules librate freely in a rectangular, infinitely-deep potential well and that [R] molecules librate/rotate in a two-well potential with a profile $\cos^2\vartheta$. The theory agrees with experiment for equal (or close) lifetimes τ_L and τ_R (≈ 0.15 ps) with the proportion $r = 5$–8% at $T = 300$ K. The width $\Delta\nu_L$ of the librational band exceeds the experimental[11] one (*cf.* curves 1–3 in

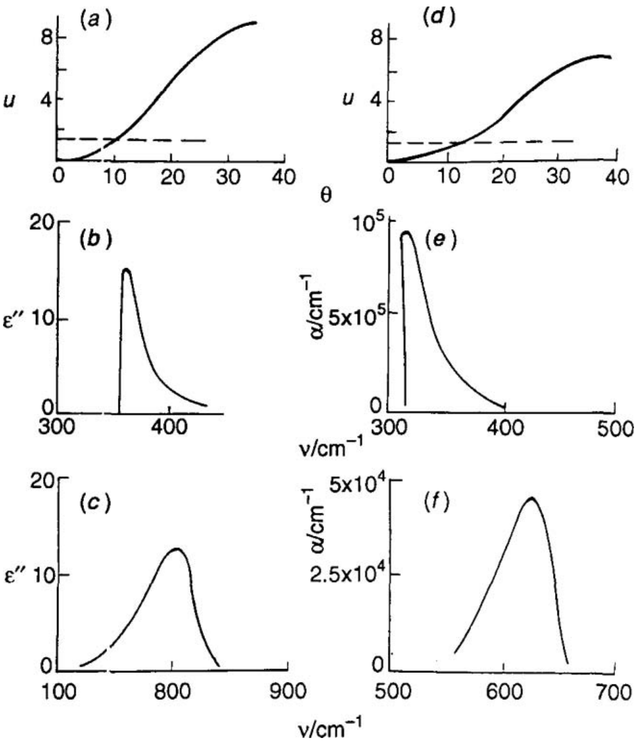

Fig. 3 The potential profile $U(\vartheta)$ as the polynomial of the 4th power (*a*, *d*) and the corresponding calculated spectra of dielectric loss (*b*, *c*) and absorption (*e*, *f*) in the FIR spectral region. Ice 1 at 0 °C (*a*, *b*, *c*) and liquid water at 0 °C (*d*, *e*, *f*). [R] band (*b*, *e*) and [L] band (*c*, *f*). For the potential of Fig. (*a*): $p=7$, $k=16$, $<\beta>=10°$, $<U>=1.5k_BT$, $r=2\%$; for the potential of Fig. (*d*), $p=5.5$, $k=13$, $<\beta>=12°$, $<U>=1.2k_BT$, $r=10\%$.

Fig. 1 at $\nu > 400$ cm^{-1}). This drawback specifically excludes the applicability of this model to ice 1.

Under the supposition that the well depth is finite (and equal to U_0) let us consider *model II* – the hybrid confined rotator / extended diffusion model (HM).[8,10] Fig. 2 shows the form of the potential well and the FIR loss / absorption spectrum. If we take *two* similar potential wells, having different depths and widths, then for the two fractional HM/HM model so 'constructed' we may obtain results similar to those shown in Fig. 1. We prefer, however, to mark here an essentially new property of an HM: for $u=U_0/(k_BT)$ near 5–7 the theory predicts a *two-humped* absorption spectrum (like that in liquid water), where the high frequency band is due to low-energy librators ($H_L < U_0$) and the low-frequency band is due to rotors with energy $H_R > U_0$. For the first group of particles we account for the effect of the potential well but ignore it for the second group, assuming free rotation of [R] particles during lifetime τ. Their proportion *r* depends on the well depth U_0 and on its width 2β, the effects being observed even for $u \gg 1$, see Table 1. This result has as its basis the proportionality of *r* to the integral $\int \exp[-H_R/(k_BT)]d\Gamma$ over the phase volume Γ_R of [R] particles and not to their Boltzmann factor $\exp[-H_R/(k_BT)]$. (Note that in a planar model $d\Gamma$ is proportional to the product $dH_L.dT_L$, not to dH_L alone). The lower the value of β (and the libration period T_L, which is proportional to β) the more slowly *r* decreases when *u* rises. Thus, one can in essence interpret the FIR water spectrum by using a *single potential* $U(\vartheta)$. But the HM cannot give as satisfactory an agreement with experiment as the previous two fractional models. The HM is also inapplicable to ice 1 because the calculated bandwidth $\Delta\nu_L$ is too great.

Comparing the data[6] with curves 1 and 2 in Fig. 1, we notice that for a sufficiently large lifetime τ the bandwidth Δν is *less* if a molecule rotates in some intermolecular potential well $U(\vartheta)$ than when $U=$ const. In a strong conservative potential (at $u \gg 1$) Δν becomes very small.

Table 1 Estimate of the proportion *r* of hindered rotors for a hybrid confined rotator/extended diffusion model.

Well depth $U_0/(k_BT)$	0	1.5	3	5	7	10
r at $\beta=\pi/3$	1	0.463	0.136	0.020	0.003	1.362×10^{-4}
r at $\beta=\pi/8$	1	0.697	0.295	0.051	0.007	3.631×10^{-4}

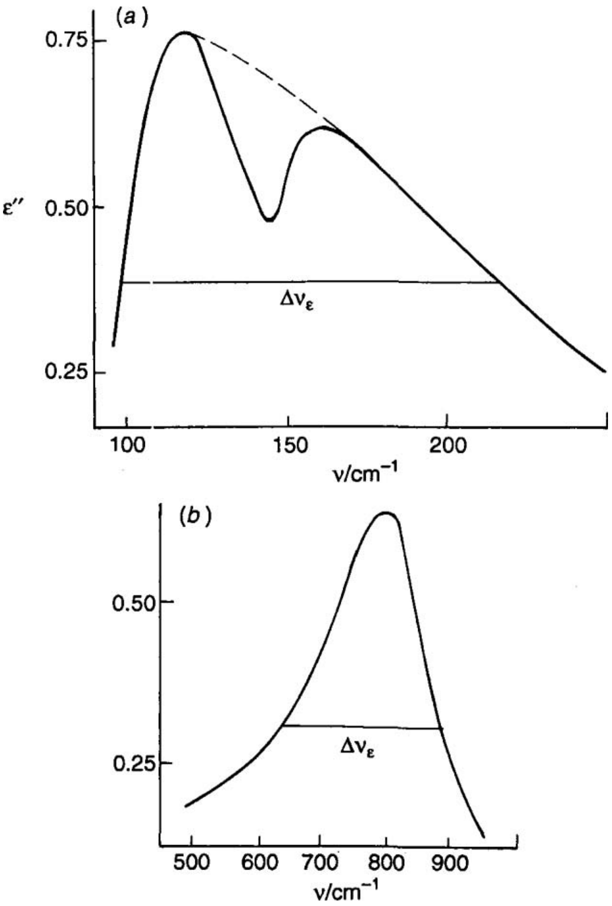

Fig. 4 The picture of the translational (*a*) and librational (*b*) bands in ice 1 as determined from the data.[2] Horizontal line: the bandwidth at the level $\frac{1}{2}$.

We shall now consider *model III*, taking some specific potential profile $u(\vartheta)=p^2[\vartheta^2-(k/12)\vartheta^4]$, which is obtained as an expansion over ϑ of $u(\vartheta)=[U_0/(k_BT)]$ $(I-\cos^n\vartheta)$ (two terms being retained in the series and $k=3n-2$; an analytical theory was elaborated by B. M. Tseitlin). The theory predicts the appearance of *two separate absorption peaks* for appropriately fitted *p* and *k* values. This result contrasts with the case of an infinitely-deep rectangular well, when only one absorption or loss maximum appears in the FIR spectral region. The two-humped spectra are illustrated in Fig. 3, the left hand side of which roughly relates to ice 1 and the right hand side spectrum to liquid water. The parameters *p* and *k* of the potential are fitted so as to make the intensities of the [R] and [L] bands nearly equal. The dotted lines in Fig. 3(*a*) and 3(*d*) correspond to the mean potential energy of a dipole. The mean amplitude $<\beta>$ is *ca.* 10° for ice and 12° for water, the last value being approximately two times less than for the rectangular well. For ice 1 the theoretical curves are *narrower* than the experimental ones[2] shown in Fig. 4; this is all the more true for the case of water [*cf.* Fig. 3(*e*) and 3(*f*) with Fig. 1]. Correspondingly, the theoretical intensities of the librational/translational peaks are much greater than the experimental ones.

The calculations presented here show the relation of FIR spectra to the potential profile $U(\vartheta)$. The 'true' potential well may be supposed to be intermediate between a rectangular well [Fig. 2(*a*)] and a well pictured in Fig. 3(*a*) and 3(*d*). In fact, we have arrived at a distinctive 'continuous' model of liquid water and ice 1 in which the FIR translational/librational dielectric loss (absorption) maxima appears simultaneously. This standpoint is confirmed by the fact that the translational band is 'hot' since the number of hindered rotators increases substantially with a decrease in U_0. The fitted values of U_0 (Figs. 2, 3) are of the order of the energy of an H-bond. This result, the hat-like profile $U(\vartheta)$ and the fitted (Fig. 1) values of the lifetimes τ are confirmed independently by computer simulations.[12–14]

Our theory has been elaborated for a gas of independent particles rotating under steric restrictions since we have taken into consideration only reorientations of isolated dipoles in some averaged (over time) intermolecular field generated by nearby particles. Other mechanisms may be also important, *e.g.* related to collective excitations.[15] The latter may cause the splitting of the translational band in ice 1 [see Fig. 4(*a*)].

The author is grateful to N. D. Sokolov and G. G. Malenkov for their interest in this work and for helpful discussions.

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Received: Moscow, 22nd September 1993
Cambridge, 2nd November 1993; Com. 3/06129I