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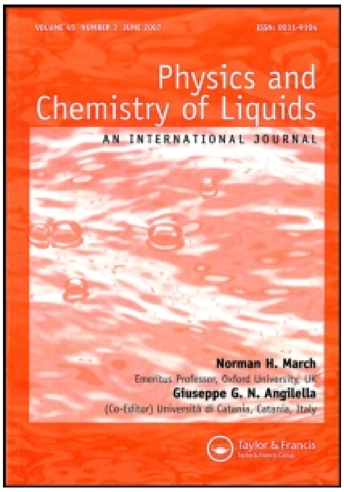

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On the Structure of Liquid Water and the Refractive Indices in Visible Light Region

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The behavior of the state of liquid water is studied by means of changes of refractive indices of the visible light region based on the data of Tilton. A fairly simple model is assumed for the structure of liquid water. Lorentz–Lorenz's formula is employed for the molecular structure of liquid water. The visible light region is taken between the ultra-violet and the infra-red regions, and it is apart from the fundamental absorption bands or lines in both regions. Therefore, even though the contributions from the both regions to the behaviors of the refractive index may play a dominant role, but they can be treated in the simple form of Lorentz–Lorenz's formula. It is found that the behaviors of induced dipoles of liquid water are closely related with molecules and electron clouds. It is also found that when our improved theory is applied, many models of liquid water which have been proposed by many investigators can be understood consistently without any contradiction. It is shown that when ice transforms to liquid water the deformation of electron clouds occurs; the long-range force of water molecules corresponding to melting is changed.

1 INTRODUCTION

A number of investigations have been performed on the structure of liquid water.[1] The structure of liquid water has been roughly explained by the statement that it retains a certain degree of similarity or analogy to ice.

By further investigations, much detailed information on the structure of liquid water, from X-ray diffraction measurements including the effects of temperature,[2–6] those of neutron diffraction including the effects of temperature[7–11] and of high pressure,[12–16] those of electron diffraction[17] and computer simulations[18–21] with various models, has been obtained.

The study of liquid water from the optical measurements of visible light may appear to a a rather old-fashioned method. But some of the results of measurements, especially those of refractive indices of liquid water, have been obtained with very high accuracy (data of 5–8 figures). Reviewing the refractive index data, we can obtain a physical picture of some aspects on the structure of liquid water, as we shall see below.

We have investigated the structure of liquid water by taking into account the temperature and wave length dependence of the refractive index. We have employed a simple structure model, on the assumption of the validity of Lorentz-Lorenz's (Clausius-Mosotti's) formula,

$$\alpha = \frac{3}{4\pi N} \quad \frac{n^2 - 1}{n^2 + 2} = \frac{3}{4\pi N} \quad \frac{\varepsilon - 1}{\varepsilon + 2}$$

for a dipolar substance such as water in the visible light region, where α is polarizability, N the number of molecules per unit weight (1 gram) and ε the dielectric constant.

For dipolar substances whose consituent molecules have large permanent dipole moment, Frölich suggested the following formula,[22]

$$\frac{3(\varepsilon - n_1^2)(2\varepsilon + n_1^2)}{(n_1^2 + 2)} = \left(\frac{4\pi}{3}\right)\frac{\mu^2 N(1 + Z \cdot \overline{\cos\gamma})}{kT},$$

where Z is the number of nearest neighbors, γ the mean value of angles between dipoles of nearest neighbors, n_1 the induced molecular polarization, k Boltzmann constant, μ the permanent dipole moment and T the temperature. Writing

$$\alpha_\mu = \frac{\mu^2}{3kT},$$

$$x = \frac{4\pi N \mu^2 (1 + Z \cdot \overline{\cos\gamma})}{kT},$$

$$y = \frac{(n_1^2 + 2)^2 x}{9 n_1^2},$$

then,

$$2\varepsilon - n_1^2(1 + 3y)\varepsilon - n_1^4 = 0,$$

and

$$\varepsilon = \left(\frac{n_1^2}{4}\right)(1 + 3 \cdot y + 3(1 + (2/3) \cdot y + y^2)^{1/2}).$$

In the case of $\alpha_\mu \ll 1$, ($x \ll 1$ or $y \ll 1$),

$$\varepsilon = n_1^2(1 + y + (1/3) \cdot y)^{1/2} = n_1^2\left(\frac{1 + y}{1 - (1/3) \cdot y}\right).$$

Then,

$$y = \frac{(\varepsilon/n_1^2) - 1}{(\varepsilon/n_1^2) + 2},$$

or

$$x = \left(\frac{9n_1^2}{(n_1^2 + 2)}\right)\left(\frac{(\varepsilon/n_1^2) - 1}{(\varepsilon/n_1^2) + 2}\right).$$

This result is similar to the case of Kirkwood's formula ($n_1^2 = 1$) and Onsager's formula ($Z \cdot \overline{\cos\gamma} = 0$). Thus, for dipolar substances with small permanent dipole moment, Lorentz-Lorenz's formula is valid. However, it is not possible to ascribe the temperature dependence of the refractive index to this small dipole moment. Therefore we have to discuss the temperature dependence of the refractive index on other grounds. The temperature dependence of the refractive index is closely related with the effective number (N_r) of molecules released (not always dissociated or not always free) from the regular configuration structure and μ_{jk}'s of each molecule. N_r depends on the temperature. When a molecule is released, the values of

$$\mu_{jk} = \int \psi_j^* \left(\sum_l e_l r_l\right) \psi_k \mathrm{d}\,\tau$$

of the molecular vibration modes and the electron clouds are changed. Therefore μ_{jk}'s also depend on the temperature.

The purpose of this paper is to investigate the temperature and the ω^2 dependence of $\alpha(T, \omega^2)$, and some aspects of the structure of liquid water based on the simple model of liquid water which we have proposed.

2 WATER MODEL

2.1 Liquid water structure model

General models of liquid water and liquid heavy water are based on the disordered continuous network of hydrogen bonds, and that four hydrogen bonds form by each molecule at approximately tetrahedral angles.

We start from the following fundamental considerations which are different standpoints from the general model of liquid water. The definite number of neighbors of a water molecule cannot occupy the definite number of the sites. This tendency becomes dominant as the temperature rises. That is, liquid water has an almost regular arrangement structure similar to ice *I*, and the tetrahedral structure is still retained. As the temperature rises, some of the constituent molecules of regular arrangement structure are released (not always dissociated or not always free), and these molecules occupy interstitial positions of other regular structures. And, subsequently these molecules connect with the original regular structure. The releases and recombinations of molecules become more frequent as the temperature rises. The life time of the combined state or the released state is a function of the temperature. Near the critical temperature, water has rather the gaseous structure.

TABLE I

Defects in the crystal structure of ice. After H. Granicher

Defect	Orientation Bjerrum defect	Ionization
Form of reaction	$2N \rightleftharpoons D + L$	$2H_2O \rightleftharpoons H_3^+O + OH^-$
Formation energy	0.68 ± 0.04^{ev}	0.96 ± 0.13^{ev}
Activation energy for transfer	0.235 ± 0.01^{ev}	$\simeq 0$ (tunneling)

Considering the values of formation energy and activation energy for transfer of orientation and ionization defects in ice *I*, which are shown in Table I, the number of these defects in the regular structure, in liquid water, is negligible compared with that of release or recombination of a molecule.

Based on the above mentioned water structure model, we have divided liquid water molecules into two classes; the class of released (not always dissociated or not always free) molecules and that of regular arrangement molecules. Two classes represent the statistical states.

2.2 Model of a water molecule

We insist that, in the visible light region, the refractive index is related with the behavior of molecules as well as the structure of liquid water. We shall describe our model of a molecule of liquid water.

1 *Vibration modes of a free molecule* The XY_2- type molecule such as a water molecule has three fundamental vibration modes. Neglecting anharmonic vibrations and interaction of each vibration mode, angular frequencies depend on H—O—H angle. We can infer that the dependence of the frequencies of these fundamental vibration modes on this angle is similar to the case of the molecule in liquid water, and that, this angle depend on *T* by H—H, O—H, O—O and intermolecular interaction, etc.

TABLE II

Fundamental vibration modes of a water molecule in each state

Type	Stretch		Deform.		X–X Sym. Strech	
State	cm^{-1}	ω^2	cm^{-1}	ω^2	cm^{-1}	ω^2
		$\times 10^{29}$		$\times 10^{28}$		$\times 10^{26}$
Vapor	3756	5.006	1595	9.027	—	—
	3651	4.730				
Liquid	3450	4.223	1645	9.601	115	4.69
	3345	3.970				
Solid	3370	4.030	1655	9.719	145	7.46
	3270	3.790				

On the other hand, fundamental vibration modes of gas, liquid and solid state of a water molecule are given in Table II.

2 *Covalent bond and absorption bands of ultra-violet region* The covalent bond of water molecule is the electron bond of hybrid orbitals composed of $2p$-electrons and $(2s)^2$ electron of an O-atom.

Martens's formula[23] about the refractive index of liquid water shows that there is a certain absorption line at $\lambda \sim 1000$ Å ($\omega^2 \sim 300 \cdot 10^{30}$). The value of energy corresponding to this line is almost that of ionization energy of oxygen atom. Therefore, this line is expected to be due to the transition $\sigma \rightarrow \sigma^*$ or $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$, etc. In this case, the principle of Frank–Condon still holds.

3 *Oscillator strength* When a molecule is combined with or released from the regular arrangement structure, that is, the hydrogen bond is formed or disappeared, the molecule itself is deformed (change of H—O—H angle). Therefore, the value of oscillator strength f_i of the molecule is changed.

Similarly, when the hydrogen bond is formed or broken, the value of oscillator strength f_λ corresponding to the electron vibration modes of an individual molecule is also changed by the variation of the electron distribution.

With increasing temperature, the probability of release and recombination of hydrogen bonds increases, and the resultant number (N_r) of released molecules increases. Further, with increasing temperature, the regular structure itself may be also changed.

Therefore, f_i, f_λ per molecule are functions of temperature by the intermolecular interactions in both released and regular configuration state.

4 *Line shifts, etc.* Line shifts, line breadth broadening, Stark-effects, collision effects, Doppler effects, etc. are neglected in the following discussion.

5 *Contribution to the refractive index n from all frequency modes except for the main modes* The contribution to n^2 from all frequency modes except for main modes (two groups of modes) is assumed to depend not on frequency but temperature.

6 *Temperature independence of the vacuum ultra-violet absorption line* Tilton *et al.*[24] assumed from their experimental results that the absorption line in vacuum ultra-violet region is independent of temperature. We also follow their assumption.

7 *Hydrogen bond* To the hydrogen bond, there are two contributions from (i) Two electronegative atoms X and Y intervened H atom form the proton donor and acceptor, and produce a static interaction force. (ii) Stabilization by the resonance of structure produces a covalent bond between H and Y. Details of the hydrogen bond are not directly related to our discussion.

8 *Others* The number of released molecules is not always an integer.

Based on the models mentioned in 2.1 and 2.2, we study the refractive index of liquid water in the dipole approximation using Lorentz–Lorenz's formula.

3 GENERAL FORMULA

3.1 General formulas and their transformation

In the visible light region, the refractive index n of liquid water whose molecular orientations are isotropically distributed and molecular configurations are also quasi-isotropical will be given by

$$\begin{aligned} Y(\omega^2, T) &= \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{\rho(T)} \qquad (1) \\ &= \frac{4\pi}{3}\left(\Delta_0 + N \cdot \mathscr{R} \sum_i \alpha_i(\omega^2, T)\right) + \text{const.} \end{aligned}$$

In the above formula, $\mathscr{R}$ denotes the real part, N the number of molecules per unit weight (1 gram), $\rho(T)$ the density of mass at temperature T(°K), ω the angular frequency of a light wave, i the frequency mode number of a molecule, $\Lambda_0 \rightarrow \Delta_0$ the contributions from $\omega \rightarrow \infty$ region, and

$$\alpha_{jk}(\omega^2, T) = \alpha_i(\omega^2, T) = \frac{f_{jk}(e^2/m)}{(\omega_{jk}^2 - \omega^2 + i\gamma_{jk}\omega)}$$
$$= \left(\frac{8\pi^2\nu_{jk}}{3h}\right) \cdot \int \frac{\psi_j^*(\sum_l e_l r_l)\psi_k \, \mathrm{d}\tau}{(\omega_{jk}^2 - \omega^2 + i\gamma_{jk}\omega)},$$

where e is the electric charge, m the mass of particle, ψ_j and ψ_k wave functions and h is Planck's constant. Further, $\nu_{jk} = (E_j - E_k)/h$, r_l ; (x_l, z_l), $\omega = 2\pi\nu$, $\gamma_{jk}(T) \ll \omega$, and μ_{jk} is defined by

$$f_{jk}\left(\frac{e^2}{m}\right) \equiv \left(\frac{8\pi^2\nu_{jk}}{3h}\right)(\mu_{jk})^2, \qquad \mu_{jk} = \int \psi_j^* \left(\sum_l e_l r_l\right) \psi_k \, \mathrm{d}\tau, \tag{2}$$

therefore μ_{jk} is a function of T.

If we write $N_c(T)$ as the effective number of molecules in the state of the regular arrangement and $N_r(T)$ as that of molecules in the state released (not always free or not always fully dissociated) at temperature T, then for N,

$$N = N_c(T) + N_r(T).$$

Further we allocate subscripts ci and $c\lambda$ to the energy level of molecular vibration and the electron energy level of a molecule in the regular arrangement structure, and subscripts ri and $r\lambda$ to those of the molecule in the released state.

If we denote the oscillator strengths f_{ci}, f_{ri}, $f_{c\lambda}$ and $f_{r\lambda}$ corresponding to ci, ri, $c\lambda$ and $r\lambda$ respectively, and write

$$\rho_{ci}(T) = f_{ci}\left(\frac{e^2}{M}\right) \cdot N_c(T), \quad \rho_{ri}(T) = f_{ri}\left(\frac{e^2}{M}\right) \cdot N_r(T),$$

$$\rho_{c\lambda}(T) = f_{c\lambda}\left(\frac{e^2}{m}\right) \cdot N_c(T), \quad \rho_{r\lambda}(T) = f_{r\lambda}\left(\frac{e^2}{m}\right) \cdot N_r(T),$$

then (1) can be written,

$$Y(\omega^2, T) = \left(\frac{4\pi}{3}\right)(\Delta_0$$
$$+ \sum \mathcal{R}\left(\frac{\rho_{ci}(T)}{(\omega_{ci}^2 - \omega^2 + i\gamma_{ci}\omega)} + \frac{\rho_{ri}(T)}{(\omega_{ri}^2 - \omega^2 + i\gamma_{ri}\omega)}\right)$$
$$+ \sum \mathcal{R}\left(\frac{\rho_{c\lambda}(T)}{(\omega_{c\lambda}^2 - \omega^2 + i\gamma_{c\lambda}\omega)} + \frac{\rho_{r\lambda}(T)}{(\omega_{r\lambda}^2 - \omega^2 + i\gamma_{r\lambda}\omega)}\right), \tag{3}$$

where ω_{ci} denotes $\omega_{c,jk}$ and so on.

Now, we divide ci, ri, $c\lambda$ and $r\lambda$ into three groups. The first is the main terms which have a one-to-one correspondence between ci and ri, $c\lambda$ and $r\lambda$. The second is that of the non-main terms which have a one-to-one correspondence. The third is the group which appears or disappears when the molecule combines with or releases from the regular arrangement structure.

And, we allocate new subscripts ci, ri, $c\lambda$ and $r\lambda$ to the members of the first group alone.

From the standpoint of our model, the total contributions from the second and the third groups depend on T, but not on ω^2, therefore these can be written as $\Delta_1(T)$.

Then, we can obtain from (3), with new subscripts,

$$Y(\omega^2, T) = \left(\frac{4\pi}{3}\right)(\Delta_0 + \Delta_1(T)) + \sum_{ci,ri} \mathscr{R}\left(\frac{\rho_{ci}(T)}{(\omega_{ci}^2 - \omega^2 + i\gamma_{ci}\omega)} + \frac{\rho_{ri}(T)}{(\omega_{ri}^2 - \omega^2 + i\gamma_{ri}\omega)}\right) + \sum_{c\lambda,r\lambda} \mathscr{R}\left(\frac{\rho_{c\lambda}(T)}{(\omega_{c\lambda}^2 - \omega^2 + i\gamma_{c\lambda}\omega)} + \frac{\rho_{r\lambda}(T)}{(\omega_{r\lambda}^2 - \omega^2 + i\gamma_{r\lambda}\omega)}\right). \quad (4)$$

Write, $\omega_{ci}^2 - \omega_{ri}^2 = \Delta\omega_i^2$ and $\omega_{c\lambda}^2 - \omega_{r\lambda}^2 = \Delta\omega_\lambda^2$, and put $\gamma_{ci}(T), \gamma_{ri}(T) < \omega$, $\Delta\omega_i^2 < \omega^2$, $\gamma_{c\lambda}(T)$, $\gamma_{r\lambda}(T) < \omega_\lambda$, $\Delta\omega_\lambda^2 < \omega_\lambda^2$, then neglecting these small quantities, finally we obtain,

$$Y(\omega^2, T) = \left(\frac{4\pi}{3}\right)(\Delta_0 + \Delta_1(T)) + \sum_\lambda \frac{\rho_\lambda(T)}{(\omega_\lambda^2 - \omega^2)} - \sum_i \frac{\rho_i(T)}{\omega^2}. \quad (5)$$

where,

$$\rho_i(T) = \rho_{ci}(T) + \rho_{ri}(T),$$
$$\rho_\lambda(T) = \rho_{c\lambda}(T) + \rho_{r\lambda}(T).$$

3.2 Behavior of $Y(\omega^2, T)$ with respect to temperature

If we write $\omega_{ci}^2 = \omega_{ri}^2 = \omega_L^2$ and $\omega_{c\lambda}^2 = \omega_{r\lambda}^2 = \omega_\lambda^2$ in the above formula (4), then we have

$$Y(\omega^2, T) = \left(\frac{4\pi}{3}\right)(\Delta_0 + \Delta_1(T)) + \sum_i \frac{\rho_i(T)}{(\omega_L^2 - \omega^2)} + \sum_\lambda \frac{\rho_\lambda(T)}{(\omega_\lambda^2 - \omega^2)}.$$

Further, if we assume

$$\left(\frac{Y(\omega^2, T_0) - Y(\omega^2, T)}{Y(\omega^2, T_0) - Y(\omega^2, T_{42})}\right) = G(\omega^2, T),$$

where T_0 represents 0°C, we can write for the numerator of $G(\omega^2, T)$,

$$\Delta_1(T_0) - \Delta_1(T) + \sum_i (\rho_i(T_0) - \rho_i(T))/(\omega_L^2 - \omega^2)$$
$$+ \sum_\lambda (\rho_\lambda(T_0) - \rho_\lambda(T))/(\omega_\lambda^2 - \omega^2).$$

A similar relation holds for the denominator of $G(\omega^2, T)$.

Figure 1 shows that $Y(\omega^2, T)$ is related with temperature, where n's are the absolute refractive indices (at 1 atmosphere) obtained from Tilton's

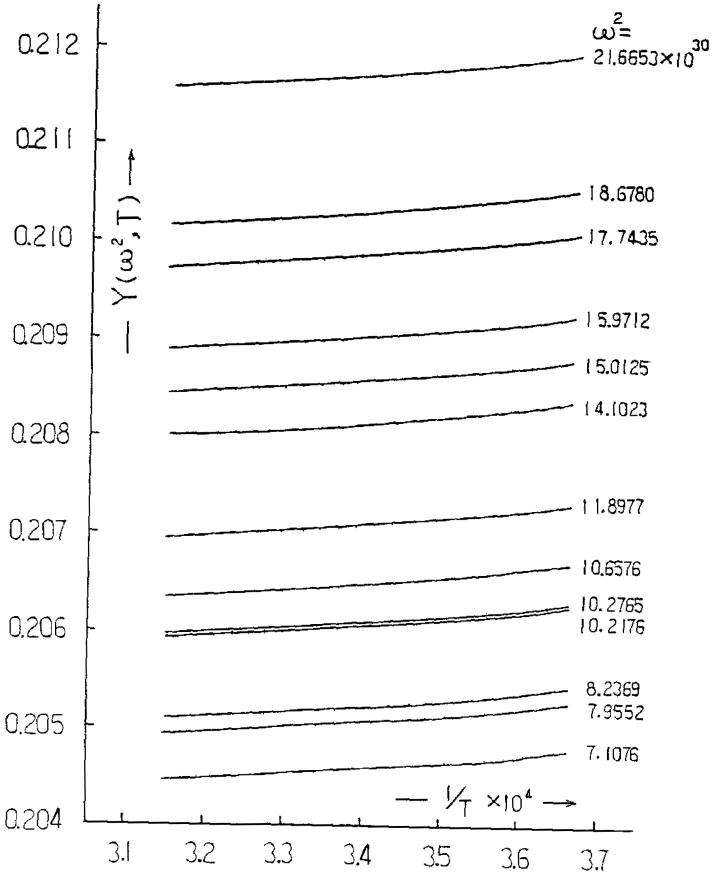

FIGURE 1 $Y(\omega^2, T)$——$1/T$ curves obtained from Table III.

TABLE III

Values of $Y(\omega^2, T) = (n^2 - 1)/(n^2 + 2)(1/\rho(T))$ for each temperature θ°C. n's are the absolute values of refractive indices obtained from Tilton and Taylor's results using Tilton's correction formula

	He	He	H	Na	He	Hg	Hg	He	H	He	He	Hg	Hg
λ(Å)	7065.2	6678.1	6562.8	5892.6	5875.6	5769.6	5460.7	5015.7	4861.3	4713.1	4471.5	4358.3	4046.6
ω^2	$\times 10^{30}$ 7.1076	7.9552	8.2369	10.2176	10.2765	10.6576	11.8977	14.1023	15.0125	15.9712	17.7435	18.6780	21.6653
θ	0.204	0.205	0.205	0.206	0.206	0.206	0.207	0.208	0.208	0.209	0.210	0.210	0.211
0	7887	2761	4325	4736	5036	6956	3090	3725	8054	2596	0974	5382	9558
2	7628	2496	4058	4460	4760	6678	2808	3437	7763	2305	0678	5085	9256
4	7383	2246	3806	4198	4498	6414	2541	3165	7489	2029	0400	4805	8972
6	7151	2008	3567	3951	4251	6167	2288	2907	7260	1768	0136	4540	8706
8	6933	1785	3342	3716	4016	5930	2049	2663	6985	1520	0.209 9887	4289	8450
10	6727	1572	3128	3495	3795	5708	1823	2432	6752	1286	9651	4053	8211
12	6532	1374	2929	3286	3586	5498	1610	2214	6533	1065	9428	3830	7987
14	6362	1187	2740	3090	3388	5304	1408	2008	6326	0858	9219	3619	7776
16	6179	1010	2562	2904	3202	5113	1218	1815	6130	0662	9021	3421	7577
18	5950	0844	2395	2730	3028	4937	1039	1632	5947	0477	8835	3235	7390
20	5864	0689	2239	2565	2864	4772	0871	1460	5774	0304	8661	3059	7215
22	5727	0544	2092	2483	2710	4617	0713	1298	5598	0141	8497	2896	7052
24	5530	0408	1947	2268	2566	4472	0565	1147	5460	0.208 9988	8343	2743	6897
26	5474	0282	1827	2133	2501	4336	0426	1006	5317	9845	8201	2599	6756
28	5360	0165	1708	2007	2305	4209	0297	0874	5186	9712	8067	2466	6693

30	5255	0.204 0055	1598	1891	1851	4010	0178	0751	5061	9588	7943	2341	6500
32	5159	9955	1495	1783	2080	3983	0.206 0066	0637	4947	9473	7827	2227	6387
34	5070	9863	1402	1683	1981	3881	9963	0531	4841	9367	7722	2121	6282
36	4989	9777	1317	1591	1888	3788	9868	0435	4744	9269	7624	2023	6168
38	4917	9700	1238	1507	1804	3686	9781	0347	4655	9179	7535	1934	6098
40	4851	9631	1166	1430	1728	3626	9702	0266	4573	9098	7453	1852	6019
42	4793	9569	1104	1362	1659	3556	9631	0192	4500	9025	7379	1780	5948
44	4738	9510	1044	1297	1594	3490	9563	0123	4431	8955	7310	1711	5881
46	4698	9466	0999	1247	1544	3440	9511	0092	4378	8902	7257	1658	5830
48	4649	9413	0945	1187	1485	3381	9450	0007	4315	8839	7231	1596	5770
50	4611	9372	0903	1141	1142	3333	9401	0.207 9957	4264	8789	7145	1547	5722
52	4587	9344	0874	1107	1108	3299	9366	9921	4228	8754	7110	1513	5689
54	4557	9309	0838	1067	1069	3258	9324	9878	4186	8711	7068	1471	5649
56	4520	9269	0797	1021	1034	3211	9277	9830	4138	8663	7021	1424	5604
58	4521	9265	0793	1013	1014	3203	9267	9820	4127	8653	7011	1415	5596
60	4496	9237	0763	0979	0980	3170	9232	9785	4092	8618	6978	1381	5564

TABLE IV

Values of $(Y(\omega^2, T_0) - Y(\omega^2, T))/(Y(\omega^2, T_0) - Y(\omega^2, T_{42}))$ for each temperature θ°C

	He	He	H	Na	He	Hg	Hg	He	H	He	He	Hg	Hg
λ(Å)	7065.2	6678.1	6562.8	5892.6	5875.6	5769.6	5460.7	5015.7	4861.3	4713.1	4471.5	4358.3	4046.6
	$\times 10^{30}$												
ω^2	7.1076	7.9552	8.2369	10.2176	10.2765	10.6576	11.8977	14.1023	15.0125	15.9712	17.7435	18.6780	21.6653
θ													
0	0	0	0	0	0	0	0	0	0	0	0	0	0
2	0.08371	0.08302	0.08289	0.08182	0.08173	0.08176	0.08153	0.08151	0.08188	0.08149	0.08234	0.08245	0.08366
4	0.16290	0.16134	0.16113	0.15945	0.15931	0.15941	0.15872	0.15851	0.15898	0.15878	0.15967	0.16019	0.16233
6	0.23756	0.23590	0.23533	0.23266	0.23245	0.23206	0.23186	0.23153	0.23185	0.23187	0.23310	0.23376	0.23657
8	0.30834	0.30576	0.30518	0.30231	0.30204	0.30176	0.30095	0.30059	0.30079	0.30132	0.30236	0.30344	0.30693
10	0.37492	0.37249	0.37162	0.36781	0.36749	0.36706	0.36629	0.36598	0.36635	0.36684	0.36801	0.36896	0.37313
12	0.43794	0.43452	0.43341	0.42976	0.42938	0.42882	0.42787	0.42768	0.42797	0.42873	0.43004	0.43087	0.43518
14	0.49677	0.49311	0.49208	0.48785	0.48801	0.48588	0.48627	0.48599	0.48621	0.48670	0.48818	0.48945	0.49363
16	0.55204	0.54856	0.54735	0.54298	0.54309	0.54206	0.54120	0.54062	0.54136	0.54159	0.54325	0.54442	0.54875
18	0.60375	0.60056	0.59919	0.59455	0.59461	0.59382	0.59295	0.59241	0.59285	0.59339	0.59499	0.59606	0.60055
20	0.65385	0.64912	0.64762	0.64345	0.64317	0.64235	0.64151	0.64110	0.64153	0.64184	0.64339	0.64492	0.64349
22	0.69813	0.69455	0.69326	0.68880	0.68878	0.68794	0.68719	0.68695	0.69105	0.68748	0.68901	0.69017	0.69418
24	0.74047	0.73716	0.73828	0.73148	0.73142	0.73059	0.72998	0.72969	0.72988	0.73033	0.73185	0.73265	0.73712
26	0.77990	0.77663	0.77554	0.77149	0.77110	0.77059	0.77016	0.76960	0.77012	0.77037	0.77135	0.77263	0.77618
28	0.81674	0.81328	0.81248	0.80883	0.80871	0.80794	0.80746	0.80696	0.80698	0.80762	0.80862	0.80955	0.81302

30	0.85068	0.84774	0.84663	0.84321	0.84306	0.84265	0.84186	0.84178	0.84219	0.84234	0.84312	0.84425	0.84709
32	0.88171	0.87907	0.87861	0.87522	0.87533	0.87441	0.87424	0.87404	0.87423	0.87454	0.87538	0.87590	0.87839
34	0.91047	0.90789	0.90748	0.90486	0.90465	0.90441	0.90402	0.90405	0.90405	0.90423	0.90459	0.90533	0.90748
36	0.93665	0.93484	0.93387	0.93213	0.93219	0.93176	0.93148	0.93122	0.93135	0.93167	0.93185	0.93254	0.93407
38	0.95992	0.95896	0.95840	0.95702	0.95706	0.95676	0.95663	0.95613	0.95639	0.95687	0.95661	0.95725	0.95845
40	0.98125	0.98058	0.98075	0.97985	0.97957	0.97941	0.97947	0.97905	0.97946	0.97956	0.97941	0.98001	0.98033
42	1	1	1	1	1	1	1	1	1	1	1	1	1
44	1.01778	1.01848	1.01863	1.01927	1.01925	1.01941	1.01966	1.01953	1.01941	1.01960	1.01919	1.01916	1.01856
46	1.03070	1.03227	1.03260	1.03408	1.03405	1.03412	1.03469	1.02830	1.03433	1.03444	1.03394	1.03387	1.03269
48	1.04654	1.04887	1.04936	1.05187	1.05153	1.05147	1.05233	1.05236	1.05205	1.05209	1.04117	1.05108	1.04931
50	1.05882	1.06172	1.06240	1.06550	1.06574	1.06559	1.06649	1.06652	1.06640	1.06609	1.06509	1.06469	1.06260
52	1.06658	1.07049	1.07141	1.07558	1.07610	1.07559	1.07661	1.07671	1.07653	1.07589	1.07483	1.07413	1.07175
54	1.07628	1.08145	1.08258	1.08743	1.08765	1.08765	1.08875	1.08888	1.08835	1.08793	1.08651	1.08579	1.08283
56	1.11086	1.09399	1.09531	1.10107	1.10127	1.10147	1.10234	1.10246	1.10186	1.10137	1.09958	1.09883	1.09529
58	1.11021	1.09524	1.09655	1.10344	1.10364	1.10382	1.10523	1.10529	1.10495	1.10417	1.10236	1.10133	1.09751
60	1.09632	1.10401	1.10587	1.11352	1.11134	1.11353	1.11535	1.11520	1.11480	1.11397	1.11154	1.11077	1.10637

data[4] using correction formulas shown in his another paper.[25] The values of $Y(\omega^2, T)$ are shown in Table III.

From Table III, we can obtain the values of $G(\omega^2, T)$ and the curve of the mean values of $G(\omega^2, T)$ which are shown in Table IV and Figure 2 respectively, for $T_0 = 0(°C)$ and $T_{42} = 42(°C)$. We can find that $G(\omega^2, T)$ does not almost depend on ω^2.

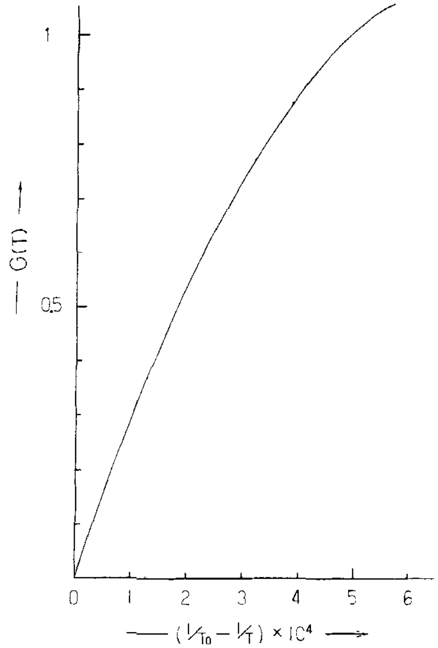

FIGURE 2 Curves of $(T(\omega^2, T_0) - (Y(\omega^2, T))/(Y(\omega^2, T_0) - (Y(\omega^2, T_{42}))$——$(1/T_0 - 1/T)$, obtained from the mean values of Table II.

From these results, we can write

$$Y(\omega^2, T) = Z(T)Y(\omega^2),$$

$$G(T) = \left(\frac{Z(T_0) - Z(T)}{Z(T_0) - Z(T_{42})}\right),$$

with satisfactory accuracy, and $Z(T)$, similar to $G(T)$, is shown approximately in the form of

$$Z(T) \sim A(T - T_0) - B(T - T_0)^2.$$

Further, when $G(\omega^2, T)$ is independent of ω^2, we can obtain

$$
\begin{aligned}
G(T) &= \left(\frac{\Delta_1(T_0) - \Delta_1(T)}{\Delta_1(T_0) - \Delta_1(T_{42})}\right) \\
&= \sum_i \left(\frac{\rho_i(T_0) - \rho_i(T)}{\sum_i \rho_i(T_0) - \rho_i(T_{42})}\right) \\
&= \sum_\lambda \left(\frac{\rho_\lambda(T_0) - \rho_\lambda(T)}{\sum_\lambda \rho_\lambda(T_0) - \rho_\lambda(T_{42})}\right)
\end{aligned}
\tag{6}
$$

and these relations are expected to hold for our results and to be useful to the study of the validity of the approach.

4 COMPARISON WITH EMPIRICAL FORMULA

Further, we transform the formula (5) to obtain numerical values of $\Delta(T)$, ω_λ^2, $\rho_\lambda(T)$ and $\sum_i \rho_i(T)$ by comparing with the empirical formula.

Put

$$
\Delta(T) = \Delta_0 + \Delta_1(T),
$$

$$
4\pi\rho(T)g^+(T) = \frac{4\pi\rho(T)g(T)}{(1 - (4\pi/3)\rho(T)\Delta(T))},
$$

for an arbitrary function $g(T)$, then

$$
\begin{aligned}
n^2 = 1 &+ \frac{4\pi\rho(T)\Delta^+(T)}{D} \\
&+ (4\pi)\rho(T)\sum_\lambda \frac{(\rho_\lambda^+(T)/(\omega_\lambda^2 - \omega^2))}{D} \\
&- (4\pi)\rho(T)\sum_i \frac{(\rho_i^+(T)/\omega^2)}{D},
\end{aligned}
$$

$$
D = 1 - \left(\frac{4\pi}{3}\right)\rho(T)\sum_\lambda \frac{\rho_\lambda^+(T)}{(\omega_\lambda^2 - \omega^2)} + \left(\frac{4\pi}{3}\right)\rho(T)\sum_i \frac{\rho_i^+(T)}{\omega^2}.
$$

For λ, if we assume that λ's are reduced to one level, then we have finally

$$
\begin{aligned}
n^2 = 1 &+ 4\pi\rho(T)\Delta^+(T) + 4\pi\rho(T)\rho_\lambda^+(T) \\
&\times \left(\frac{1 + (4\pi/3)\rho(T)\Delta^+(T)}{(\omega_\lambda^2 - \omega^2 - (4\pi/3)\rho(T)\rho_\lambda^+(T)}\right) \\
&- \left(\frac{4\pi\rho(T)\sum_i \rho_i^+(T)}{\omega^2}\right)\left\{1 + \left(\frac{4\pi}{3}\right)\rho(T)\Delta^+(T)\right\} \\
&\times \{1 + (8\pi/3)\rho(T)\rho_\lambda(T)/(\omega_\lambda^2 - \omega^2 - (4\pi/3)\rho(T)\rho_\lambda(T)) \\
&+ ((4\pi/3)\rho(T)\rho_\lambda(T))^2/(\omega_\lambda^2 - \omega^2 - (4\pi/3)\rho(T)\rho_\lambda(T))^2\}
\end{aligned}
\tag{7}
$$

Neglecting ω^2 in the last curl bracket of the above formula, we obtain finally the formula comparable with the empirical formula.

The empirical formula of the refractive index of liquid water in the region $0.224\mu < \lambda < 1.256\mu$ at 18°C is given by[26]

$$n^2 = -0.013414\,\lambda^2 + 1.76148 + 0.0065438/(\lambda^2 - (0.11512)^2), \qquad (8)$$

where λ (unit is micron) is a wavelength.

This formula will be rewritten as

$$\begin{aligned} n^2 &= m_0 + \frac{m'\omega'^2}{(\omega'^2 - \omega^2)} - m''\omega''^2/\omega^2 \\ &\div m_0 + \frac{m'\omega'^2}{(\omega'^2 - \omega^2)} + m''\omega''^2/(\omega''^2 - \omega^2), \\ m_0 &= 1.26770,\ m'\omega'^2 = 132.20 \cdot 10^{30} \\ m''\omega''^2 &= 4.7004 \cdot 10^{28},\ \omega'^2 = 267.73 \cdot 10^{30},\ \omega = 2\pi c/\lambda. \end{aligned}$$

Comparing (7) with (8),

$$\omega_\lambda^2 - \left(\frac{4\pi}{3}\right)\rho(T)\,\rho_\lambda^+(T) = 267.73 \cdot 10^{30},$$

$$1 + 4\pi\rho(T)\Delta^+(T) = 1.26770,$$

$$4\pi\rho(T)\rho_\lambda^+(T)(1 + \left(\frac{4\pi}{3}\right)\rho(T)\Delta^+(T)) = 132.20 \cdot 10^{30},$$

$$\begin{aligned} &4\pi\rho(T)\sum_i \rho_i^+(T)(1 + \left(\frac{4\pi}{3}\right)\rho(T)\Delta^+(T)) \\ &\times \{1 + (8\pi/3)\rho(T)\rho_\lambda(T)/(\omega_\lambda^2 - (4\pi/3)\rho(T)\rho_\lambda(T)) \\ &+ ((4\pi/3)\rho(T)\rho_\lambda(T))^2/(\omega_\lambda^2 - (4\pi/3)\rho(T)\rho_\lambda(T))^2\} \\ &= 4.7004 \cdot 10^{28}. \end{aligned}$$

Therefore,

$$4\pi\rho(T)\Delta^+(T) = 0.26670,\ \omega_\lambda^2 = 308.19 \cdot 10^{30},$$
$$4\pi\rho(T)\rho_\lambda^+(T) = 121.4 \cdot 10^{30},\ 4\pi\rho(T)\sum_i \rho_i^+(T) = 3.257 \cdot 10^{28}.$$

For the mass density of liquid water $\rho(T) = 0.9986248$ at 18°C, we obtain

$$\Delta(T) = 0.01952,\ \omega_\lambda^2 = 308.19 \cdot 10^{30},$$
$$\rho_\lambda(T) = 8.885 \cdot 10^{30},\ \sum_i \rho_i = 2.38_5 \cdot 10^{27}. \qquad (9)$$

Hereafter, this value of ω_λ^2 is used as the same constant for liquid water and ice in our model.

5 RELATION AND TEMPERATURE

Write,

$$\begin{aligned} \Delta_0 &= \delta_0 \cdot N_c(T) + \delta_0 \cdot N_r(T) = \delta_0 \cdot N, \\ \Delta(T) &= \delta_c \cdot N_c(T) + \delta_r \cdot N_r(T), \\ \rho_i(T) &= f_{ci}(T) \cdot N - (f_{ci}(T) - f_{ri}(T)) \cdot N_r(T), \end{aligned}$$

etc., (4) is given by

$$\begin{aligned} Y(\omega^2, T) = \left(\frac{4\pi}{3}\right) & (\delta_0 \cdot N + \delta_c(T) \cdot N - (\delta_c(T) - \delta_c(T)) \cdot N_r(T) \\ & + \sum \mathscr{R}\left(\frac{f_{ci}(T)}{(\omega_{ci}^2 - \omega^2 + i\gamma_{ci}\omega)}\right) \cdot N \\ & - \left(\frac{f_{ci}(T)}{(\omega_{ci}^2 - \omega^2 + i\gamma_{ci}\omega)} - \frac{f_{ri}(T)}{(\omega_{ri}^2 - \omega^2 + i\gamma_{ri}\omega)}\right) \cdot N_r(T) \\ & + \sum \mathscr{R}\left(\frac{f_{c\lambda}(T)}{(\omega_{c\lambda}^2 - \omega^2 + i\gamma_{c\lambda}\omega)}\right) \cdot N \\ & - \left(\frac{f_{c\lambda}(T)}{(\omega_{c\lambda}^2 - \omega^2 + i\gamma_{c\lambda}\omega)} - \frac{f_{r\lambda}(T)}{(\omega_{r\lambda}^2 - \omega^2 + i\gamma_{r\lambda}\omega)}\right) \cdot N_r(T). \end{aligned}$$

In the above formula, we assume ω_{ci}^2 and ω_{ri}^2 to be equal to ω_L^2 whose value is the simple arithmetical mean of two values of the molecular vibration modes of liquid state in Table 2, and assume reduced one level mode for λ's, then obtain for liquid water ($\omega_L^2 = 4.096 \cdot 10^{29}$ and $\omega_\lambda^2 = 308.19 \cdot 10^{30}$)

$$Y(\omega^2, T) = \left(\frac{4\pi}{3}\right)\left(\Delta_0 + \Delta_1(T) + \frac{\sum_i \rho_i(T)}{(\omega_L^2 - \omega^2)} + \frac{\rho_\lambda(T)}{(\omega_\lambda^2 - \omega^2)}\right).$$

Similarly, if we assume ω_{ci}^2 of ice to be equal to ω_c^2 whose value is the simple arithmetical mean of two values of the molecular vibration modes of solid state in Table 2, then for ice ($\omega_c^2 = 3.910 \cdot 10^{29}$ and $\omega_\lambda^2 = 308.19 \cdot 10^{30}$) obtain

$$Y(\omega^2, T) = \left(\frac{4\pi}{3}\right)\left(\Delta_0 + \Delta_1(T) + \sum_i \frac{\rho_i(T)}{(\omega_c^2 - \omega^2)} + \frac{\rho_\lambda(T)}{(\omega_\lambda^2 - \omega^2)}\right),$$

TABLE V

Values of $\Delta_0+\Delta_1(T)$, $\sum_i\rho_i(T)$, $\rho_\lambda(T)$——θ°C.

θ	$\Delta_0+\Delta_1(T)$	$\sum_i\rho_i(T)$	$\rho_\lambda(T)$
	$\times 10^{-2}$	$\times 10^{27}$	$\times 10^{30}$
Ice	1.869_1	2.174_8	9.407_3
0	1.939_4	1.928_1	8.967_5
4	1.938_4	1.911_8	8.956_9
6	1.938_1	1.904_8	8.965_0
10	1.936_8	1.888_9	8.965_0
14	1.935_4	1.872_9	8.966_0
16	1.934_3	1.864_1	8.967_4
20	1.932_7	1.848_9	8.969_5
24	1.930_8	1.833_0	8.972_5
26	1.929_7	1.824_2	8.974_6
30	1.925_6	1.797_2	8.985_9
34	1.925_4	1.792_7	8.983_3
36	1.924_4	1.785_7	8.985_3
40	1.920_9	1.764_7	8.994_1
42	1.923_4	1.773_2	8.986_4

where the subscript C represents the crystal (solid) state and therefore

$$\Delta_0 + \Delta_1(T) = \delta_0\cdot N + \delta_c^c\cdot N,$$

$$\sum_i \rho_i^c = \sum f_{ci}^c\cdot N,\quad \rho_\lambda^c = f_{c\lambda}^c\cdot N.$$

From Table III and the above formula, we can obtain Table V by the least squares method. The curves obtained from Table V are shown in Figures 3, 4 and 5.

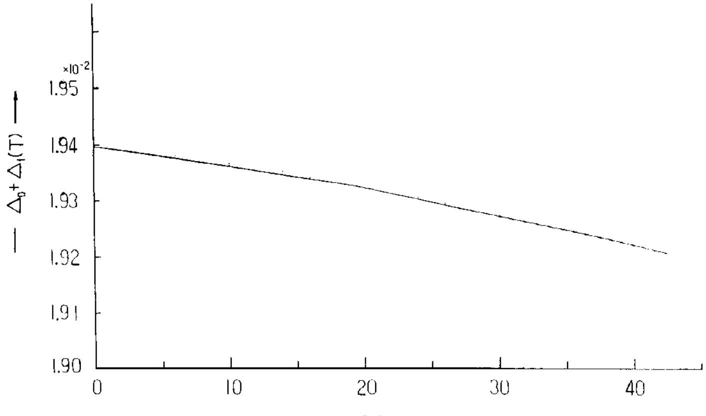

FIGURE 3 Curve of $\Delta_0 + \Delta_1(T)$——θ°C, obtained from Table V.

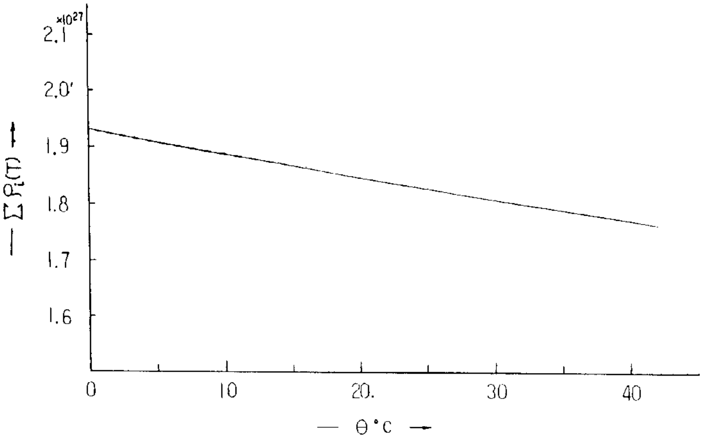

FIGURE 4 Curve of $\sum_i \rho_i(T)$——θ°C, obtained from Table V.

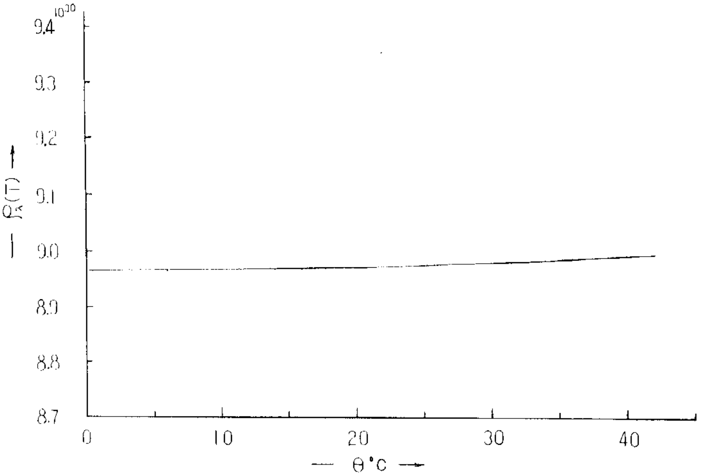

FIGURE 5 Curve of $\rho_\lambda(T)$——θ°C, obtained from Table V.

Further, using the values of Table V, we obtain the temperature dependence of $\Delta_0 + \Delta_1(T)$, $\sum_i \rho_i(T)$ and $\rho_\lambda(T)$ up to the order of $(T - T_0)^2$ by the least squares method, and the results are

$$\Delta_0 + \Delta_1(T) = 1.93 \cdot 10^{-2} - 3.14 \cdot 10^{-6}(T - T_0) - 3.05 \cdot 10^{-8}(T - T_0)2, \tag{10}$$

$$\sum_i \rho_i(T) = 1.93 \cdot 10^{27} - 4.40 \cdot 10^{24}(T - T_0) + 1.05 \cdot 10^{22}(T - T_0)^2, \tag{11}$$

$$\rho_\lambda(T) = 8.96 \cdot 10^{30} - 6.71 \cdot 10^{25}(T - T_0) + 1.71 \cdot 10^{25}(T - T_0)^2. \tag{12}$$

Therefore,

$$\begin{aligned} \Delta_0 + \Delta_1(T_{42}) &= 1.92_1 \cdot 10^{-2}, \\ \sum_i \rho_i(T_{42}) &= 1.76_4 \cdot 10^{27}, \\ \rho_\lambda(T_{42}) &= 8.99_3 \cdot 10^{30}. \end{aligned} \tag{13}$$

and these values are approximately equal to the values of (9), but some discrepancy exists for $\sum_i \rho_i(T)$.

From (10), (11), (12) and (13), we can inspect the relation (6), and obtained results are shown in Table VI. Their curves for $G_{\Delta_1}(T)$, $G_{\rho_i}(T)$ and $G_{\rho_\lambda}(T)$ are illustrated in Figure 6. From these results, we can see that these three curves are in good agreement with each other in order of magnitude.

TABLE VI

Values of $G_{\Delta_1}(T)$, $G_{\rho_i}(T)$, $G_{\rho\lambda}(T)$ —θ°C.

$G(T)$ θ	$G_{\Delta_1}(T)$	$G_{\rho_i}(T)$	$G_{\rho\lambda}(T)$
0	0	0	0
4	0.07	0.11	0.00
6	0.11	0.16	0.01
10	0.19	0.26	0.04
14	0.27	0.36	0.09
16	0.31	0.41	0.12
20	0.40	0.50	0.20
24	0.50	0.60	0.30
26	0.55	0.65	0.36
30	0.66	0.74	0.49
34	0.76	0.83	0.64
36	0.82	0.87	0.72
40	0.94	0.96	0.90
42	1	1	1

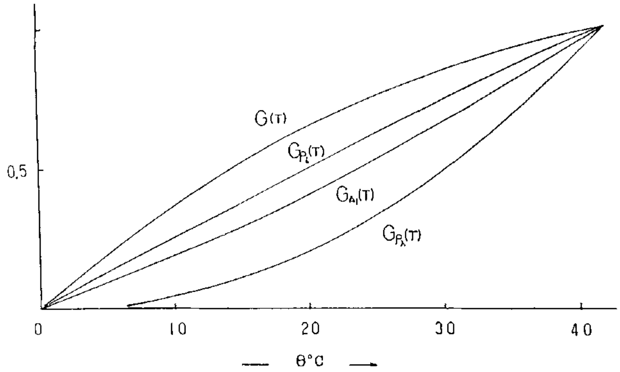

FIGURE 6 Curves of $G(T)$, $G_{\Delta_i}(T)$, $G_{\rho i}(T)$ and $G_{\rho\lambda}(T)$——θ°C, obtained from Table VI.

6 THE TEMPERATURE DEPENDENCE

Since $Y(\omega^2, T)$ is a smooth function of T, we can write

$$Y(\omega^2, T) = Y(\omega^2, T_0) + \left(\frac{\mathrm{d}\,Y(\omega^2, T)}{\mathrm{d}T}\right)_{T=T_0}(T - T_0)$$
$$+ \left(\frac{1}{2}\right)\left(\frac{\mathrm{d}^2 Y(\omega^2, T)}{\mathrm{d}T^2}\right)_{T=T_0}(T - T_0)^2 + \cdots$$

If we use the notation σ as a representative of f_i, f_λ, and δ, and Q a representative of $\Delta(T)$, $\sum_i \rho_i(T)$ and $\rho_\lambda(T)$ in the above formula, then

$$Q(\omega^2, T)_{T=T_0} = \sigma_c(T_0)\cdot N - (\sigma_c(T_0) - \sigma_r(T_0)\cdot N_r(T_0), \tag{14}$$

$$\begin{aligned} Q'(\omega^2, T)_{T=T_0} = {} & (\sigma_c'(T)\cdot N - (\sigma_c(T) - \sigma_r(T))'\cdot N_r(T) \\ & - (\sigma_c(T) - \sigma_r(T))\cdot N_r'(T))_{T=T_0}, \end{aligned} \tag{15}$$

$$\begin{aligned} Q''(\omega^2, T)_{T=T_0} = {} & (\sigma_c''(T)\cdot N - (\sigma_c(T) - \sigma_r(T)''\cdot N_r(T) \\ & -2(\sigma_c(T) - \sigma_r(T))'\cdot N_r'(T) - (\sigma_c(T) - \sigma_r(T))\cdot N_r''(T))_{T=T_0}. \end{aligned} \tag{16}$$

where the superscript ′ denotes d/dT.

According to Luck,[27] in the region 0 ~ 170°C, for $\lambda = 0.9483$ and 1.140 (micron),
$N_r(T_0)/N = 0.0889$, $(1/N)\mathrm{d}N_r(T)/\mathrm{d}T = 1.155\cdot 10^{-3}$ (Const.).

If we assume that these values are still valid in the region of wavelength of interest, then

$$N_r'(T) = K(\text{Const.}), \frac{K}{N_r(T_0)} = 1.29_9\cdot 10^{-2}.$$

Therefore, from (16),

$$Q''(\omega^2, T)_{T=T_0} \approx (\sigma_c''(T) \cdot N - (\sigma_c(T) - \sigma_r(T))'' \cdot N_r(T) - 2(\sigma_c(T) - \sigma_r(T))' \cdot N_r'(T))_{T=T_0},$$

further when σ'' is negligible,

$$Q''(\omega^2, T)_{T=T_0} \sim -2((\sigma_c(T) - \sigma_r(T))' \cdot N_r'(T))_{T=T_0}. \tag{17}$$

Assuming that the right-hand side of (17) is equal to $-2A$,

$$(\sigma_c(T) - \sigma_r(T))'_{T=T_0} \cdot N_r(T_0) = \frac{A \cdot N_r(T_0)}{K}, \tag{18}$$

and assuming the right-hand side of (15) is equal to B, then from (18), we have

$$(\sigma_c'(T) \cdot N - (\sigma_c(T) - \sigma_r(T)) \cdot N_r'(T))_{T=T_0} = B + N_r(T_0) \cdot \frac{A}{K}. \tag{19}$$

Further, assuming the right-hand side of (14) is equal to C, then

$$(\sigma_c(T_0) - \sigma_r(T_0)) \cdot N_r(T_0) = \sigma_c(T_0) \cdot N - C. \tag{20}$$

Therefore, from (19), (20), we obtain

$$\sigma_c'(T)_{T=T_0} \cdot N - (\sigma_c(T_0) - C) \cdot \frac{K}{N_r(T_0)} = B + N_r(T_0) \cdot \frac{A}{K}. \tag{21}$$

A's, B's and C's are the values given by (10), (11) and (12).

To obtain the numerical values of σ_c's, σ_r's, etc., we must use the numerical values of ice[28] given in Table V in addition to (10), (11) and (12).

In the case of ice, we use the notation σ^c instead of σ. For the difference between σ_c^c(crystal) and σ_c(regular arrangement structure), this can be written

$$\sigma_c^c - \sigma_c(T_0) = \phi(T_0).$$

If $\phi(T_0)$ is a function of $N_r(T_0)$ and a certain parameter related with the phase transition, we can write approximately

$$\phi(T_0) = -\int_0^{N_r(T_0)} \left(\frac{\partial \sigma}{\partial N}\right) \cdot \mathrm{d}N + \eta = \xi + \eta,$$

that is,

$$\delta_c^c - \delta_c(T_0) = \phi_\delta(T_0) = \xi_\delta + \eta_\delta,$$

$$f_{ci}^c - f_{ci}(T_0) = \phi_i(T_0) = \xi_i + \eta_i,$$

$$f_{c\lambda}^c - f_{c\lambda}(T_0) = \phi_\lambda(T_0) = \xi_\lambda + \eta_\lambda.$$

When $\phi_\delta(T_0)$, $\phi_i(T_0)$ and $\phi_\lambda(T_0)$ are given, using data of ice and formulas (10), (11) and (12),

$$\delta_c(T_0) - \delta_r(T_0), f_{ci}(T_0) - f_{ri}(T_0), f_{c\lambda}(T_0) - f_{r\lambda}(T_0),$$

can be obtained assuming that, for ice, Lorentz–Lorentz's formula is valid.

There are some problems in using the data of liquid water and ice. For both data, measuring instruments, laboratory conditions etc. are different. Hence, some discrepancies and errors may exist in the values used. Nevertheless we can expect that these values are useful for qualitative purposes.

If we put

$$V^{\mathrm{I}} = \sigma_c^c \cdot N,$$

$$V^{\mathrm{II}} = \sigma_c(T_0) \cdot N - \frac{\sigma_c'(T)_{T=T_0} \cdot N \cdot N_r(T_0)}{K},$$

then,

$$V^{\mathrm{I}} - V^{\mathrm{II}} = (\sigma_c^c - \sigma_c(T_0)) \cdot N + \frac{\sigma_c'(T)_{T=T_0} \cdot N \cdot N_r(T_0)}{K}$$

$$= \phi(T_0) \cdot N + \frac{\sigma_c'(T)_{T=T_0} \cdot N \cdot N_r(T_0)}{K} \qquad (22)$$

Since we have no knowledge of ξ's and η's, we must be satisfied with using an approximation ϕ's $= 0$. The physical meaning of this approximation is as follows; since ξ's $= 0$ is equivalent to $\partial\sigma_c/\partial N_r(T) = 0$, then

$$\sigma_c'(T) = \left(\frac{\partial\sigma_c}{\partial N_r(T)}\right)\left(\frac{\mathrm{d}N_r(T)}{\mathrm{d}T}\right) + \frac{\partial\sigma_c}{\partial T} = \frac{\partial\sigma_c}{\partial T}.$$

That is, the effect on σ_c due to the increase in $N_r(T)$ is neglected. Further, the variation of η due to the phase transition is also neglected.

From the standpoint of refractive index, by using this numerical approximation, the regular arrangement structure in liquid water at 0°C is regarded as the same as that of ice *I*.

Therefore, putting the numerical values obtained from the right-hand side of (21) into (22), we obtain

$$V_\delta^{\mathrm{I}} - V_\delta^{\mathrm{II}} 0.0186_9 - 0.0194_6 = \frac{\sigma_c'(T)_{T=T_0} \cdot N_r(T_0) \cdot N}{K},$$

$$V_i^{\mathrm{I}} - V_i^{\mathrm{II}} = 2.1_7 \cdot 10^{27} - 2.3_8 \cdot 10^{27} = \sum_i \frac{f_{ci}'(T)_{T=T_0} \cdot N_r(T_0) \cdot N}{K},$$

$$V_\lambda^{\mathrm{I}} - V_\lambda^{\mathrm{II}} = 9.40_7 \cdot 10^{30} - 9.07_2 \cdot 10^{30} = \frac{f_{c\lambda}'(T)_{T=T_0} \cdot N_r(T_0) \cdot N}{K}.$$

TABLE VII

Obtained values of the quantities related with our discussions

$$\delta_c(T_0)N = 0.0186_9 \quad , \{\delta_c(T_0) - \delta_r(T_0)\}N_r(T_0) = -0.707_1 \cdot 10^{-3}$$
$$f_{ci}(T_0)N = 2.1_7 \cdot 10^{27} \quad , \{f_{ci}(T_0) - f_{ri}(T_0)\}N_r(T_0) = 2.4_4 \cdot 10^{26}$$
$$f_{c\lambda}(T_0)N = 9.40_7 \cdot 10^{30}, \{f_{c\lambda}(T_0) - f_{T\lambda}(T_0)\}N_r(T_0) = 0.44_2 \cdot 10^{30}$$

$$\delta'_c(T)_{T=T_0}N = -9.98 \cdot 10^{-6}, \delta'_r(T)_{T=T_0}N = -3.56 \cdot 10^{-5}$$
$$f'_{c\,i}(T)_{T=T_0}N = -2.0_4 \cdot 10^{24}, f'_{ri}(T)_{T=T_0}N = 7.1_0 \cdot 10^{24}$$
$$f'_{c\lambda}(T)_{T=T_0}N = 4.35_6 \cdot 10^{27}, \; f'_{r\lambda}(T)_{T=T_0}N = 1.87_1 \cdot 10^{28}$$

$$\{\delta_c(T) - \delta_r(T)\}_{T=T_0}N_r(T_0) = 2.35_1 \cdot 10^{-6}$$
$$\{f_{ci}(T) - f_{ri}(T)\}'_{T=T_0}N_r(T_0) = -8.2_2 \cdot 10^{23}$$
$$\{f_{c\lambda}(T) - f_{r\lambda}(T)\}'_{T=T_0}N_r(T_0) = -1.31_8 \cdot 10^{27}$$

$$\{\delta_c(T_0) - \delta_r(T_0)\}K = -9.18_6 \cdot 10^{-6}, \{\delta_c(T) - \delta_r(T)\}'_{T=T_0}K = 3.05_4 \cdot 10^{-8}$$
$$\{f_{ci}(T_0) - f_{ri}(T_0)\}K = 3.1_8 \cdot 10^{24}, \quad \{f_{ci}(T) - f_{ri}(T)\}'_{T=T_0}K = 1.0_6 \cdot 10^{22}$$
$$\{f_{c\lambda}(T_0) - f_{r\lambda}(T_0)\}K = 5.74_0 \cdot 10^{27}, \quad \{f_{c\lambda}(T) - f_{ry}(T)\}'_{T=T_0}K = -1.71_2 \cdot 10^{25}$$

Further, the quantities needed in our discussions can be calculated. Results thus obtained are shown in Table VII.

σ's are positive constants from their definition. In the above results, $\sum_i(f_{ci}(T_0) - f_{ri}(T_0)) \cdot N = 2.75_0 \cdot 10^{27}$ and $\sum_i f_{ci}(T_0) \cdot N = 2.17 \cdot 10^{27}$, therefore $\sum_i f_{ri}(T_0) \cdot N = -0.57 \cdot 10^{27}$. This is a contradiction to the definition (formula (2)). It will be proper to assume as $\sum_i f_{ri}(T_0) \sim 0$.

7 DISCUSSION

7.1 Model and formula

As we have already mentioned, the relation (6) holds in order of magnitude for liquid water. This shows, even though it is not direct, the adequacy of using our model and Lorentz–Lorentz's formula for liquid water.

7.2 $\Delta_1(T)$

In general, the degree of freedom of a molecule in the state of the regular arrangement is smaller than that of a free molecule in the state of gas. When a molecule is released from the regular arrangement state, the degree of freedom increases.

From the definition of $\Delta_1(T)$, $\delta_c \cdot N = \delta_c(T_0) \cdot N(= 0.0187) < \delta_r(T_0) \cdot N$ $(=0.0267)$ reflects this situation. As temperature rises from T_0, $\delta_c(T)$ and $\delta_r(T)$ decrease, and for the rate of increment,

$$\delta'_c(T)_{T=T_0} \cdot N(= -1.00 \cdot 10^{-5}) > \delta'_r(T)_{T=T_0} \cdot N(= -3.56 \cdot 10^{-5}).$$

7.3 $\Sigma_i \rho_i(T)$

Curves of $\sum_i \rho_i(T)/\sum_i \rho_i(T_0)$ derived from (11) are shown in Figure 7. On the other hand, Pople[29,30] discussed the dielectric constant by applying his bent model to Kirkwood's formula

$$(1/4\pi)(\varepsilon - 1)V = (3\varepsilon N_0/(2\varepsilon + 1))(\alpha_m + \boldsymbol{\mu}\cdot\bar{\boldsymbol{\mu}}/3kT),$$

where N_0 is the Avogadro's number, $\bar{\boldsymbol{\mu}}$ the average dipole moment of a macroscopic spherical specimen of the dielectric, immersed in an infinite medium of its own dielectric constant when one of its dipoles is fixed in a specified orientation $\boldsymbol{\mu}$, ε the dielectric constant, α_m the polarizability of the molecule, V_M the molal volume.

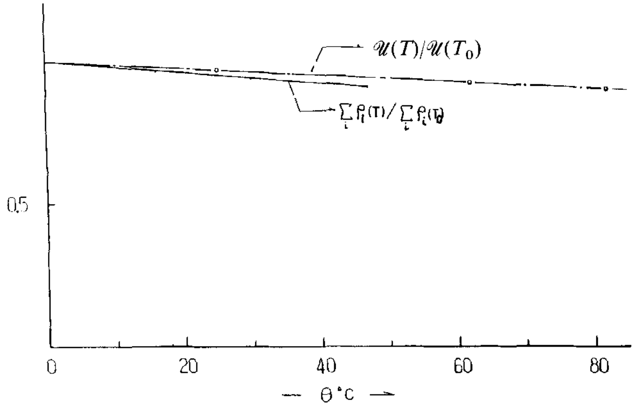

FIGURE 7 Curves of $\mathcal{U}(T)/\mathcal{U}(T_0)$ and $\sum_i \rho_i(T)/\sum_i \rho_i(T_0)$——θ°C.

Pople divided the neighbors of the fixed molecule into shells, and wrote

$$\boldsymbol{\mu}\cdot\bar{\boldsymbol{\mu}} = \mu^2(1 + \sum_j N_j(\cos\gamma_j)) = \mathcal{U}(T),$$

where N_j is the number of particles in the j-th shell and γ_j shows the angle between the molecular axis of a molecule in the shell and that of a fixed central molecule.

Using the bent model, considering up to 3 for j in the above formula and taking the 1st neighbors for $\mu(T)$, he calculated $\mathcal{U}(T)$. The curves of $\sum_i \rho_i(T)/\sum_i \rho(T_0)$ and $\mathcal{U}(T)/\mathcal{U}(T_0)$ are shown in Figure 7. The curves of $\sum_i \rho_i(T)/\sum_i \rho_i(T_0)$ and $\mathcal{U}(T)/\mathcal{U}(T_0)$ can be seen to agree with each other.

Considering the physical picture of $\sum_i \rho_i(T)$, even though this is the quantity of the visible light region, $\sum_i \rho_i(T)$ will have relation with $\mathcal{U}(T)$, and therefore this good agreement is not fortuitous.

Further, from the standpoint of $f_{ri}(T)$, we have

$$\sum_i f^c_{ci} \cdot N = \sum_i \; f_{ci}(T_0) \cdot N = 2.17 \cdot 10^{27}, \sum_i f_{ri}(T_0) \cdot N \sim 0.$$

and these expressions represent that the released molecule is in the state of $\int \psi_j^* \sum er\psi_k \mathrm{d}\tau \sim 0$ or that $\psi_j \rightarrow \psi_k$ transition is forbidden. As temperature rises from T_0, $\sum_i f_{ri}(T)$ increases and $\sum_i f_{ci}(T)$ decreases, that is

$$\sum_i f'_{ri}(T)_{T=T_0} \cdot N = 7.1_0 \cdot 10^{24}, \sum_i f'_{ci}(T)_{T=T_0} \cdot N = -2.0_4 \, 10^{24}.$$

From the standpoint of $\sum_i \rho_i(T)$, $N_r(T)$ must be taken account. As $\sum_i \rho_i(T_0)$ is given by (14), from $\sum_i f_{ri}(T_0) \sim 0$, we have

$$\sum_i \rho_i(T_0) \approx \sum_i f_{ci}(T_0) \cdot N_c(T_0),$$

and from Table VII,

$$-\sum_i (f_{ci}(T_0) - f_{ri}(T_0)) \cdot N_r(T_0) + \sum_i f'_{ci}(T)_{T=T_0} \cdot N = -5.2 \cdot 10^{24},$$

$$\sum_i f'_{ri}(T) \cdot N_r(T_0) = 0.6 \cdot 10^{24},$$

where $\sum_i f'_{ri}(T)_{T=T_0} \cdot N_r(T_0)$ is neglected in (15). Then we can obtain approximately, taking account of $\sum_i \rho''_i(T)_{T=T_0} \ll \sum_i \rho'_i(T)_{T=T_0}$,

$$\sum_i \rho'_i(T)_{T=T_0} \approx \sum_i f'_{ci}(T)_{T=T_0} \cdot N_c(T_0) - \sum_i f_{ci}(T_0) \cdot K.$$

Therefore, $\sum_i \rho_i(T)$ behaves as if $N_r(T) = 0$ for the variation of T, that is

$$\sum_i \rho_i(T) = \sum_i \rho_i(T_0) + \sum_i \rho'_i(T)_{T=T_0}(T - T_0)$$

$$\approx \sum_i (f_{ci}(T_0) \cdot N_c(T_0) + (f'_{ci}(T)_{T=T_0} \cdot N_c(T_0) - f_{ci}(T_0) \cdot K)(T - T_0))$$

$$= \sum_i \left(\frac{f_{ci}(T_0) \cdot N_c(T_0)}{N} + \left(\frac{f'_{ci}(T)_{T=T_0} \cdot N_c(T_0)}{N} - \frac{f_{ci}(T_0) \cdot K}{N} \right) \right) (T - T_0) N.$$

From the above formula, it is clear that $\sum_i \rho_i(T)$ behaves as if all the molecules of liquid water were in the regular arrangement structure, and hence, the bent model is valid. Of course, the behaviors of $\sum_i \rho_i(T)$ is including the effects from intra molecular atom interactions and inter molecular interactions.

7.4 $\rho_\lambda(T)$

$\rho_\lambda(T)$ is the polarizability by electron clouds as assumed previously.

For a molecule in the state of regular arrangement, $f_c \cdot N = f_{c\lambda}(T_0) \cdot N = 9.4_1 \, 10^{30}$. On the other hand, for a molecule in the state of release, $f_{r\lambda}(T_0) \cdot N =$

$4.4_4 \cdot 10^{30}$. Therefore, when a molecule is released, $\sum er$ or μ_{jk} of electrons concerned with the λ mode decreases.

When temperature rises from T_0, $\sum er$ or μ_{jk} of electrons concerned with the λ mode in both states increases, because

$$f'_{c\lambda} \cdot N = 0.436 \cdot 10^{28} \text{ and } f'_{r\lambda} \cdot N = 1.87 \cdot 10^{28}.$$

Therefore, when the phase transition (ice to liquid water) occurs, ρ^c_λ is reduced to $\rho_{c\lambda}(T_0)$, but with rising of T from T_0, $\rho_{c\lambda}(T)$ increases.

Different from the case of $\sum_i \rho_i(T)$, $f_{r\lambda}(T_0)$ and $f'_{r\lambda}(T)_{T=T_0}$ are not negligible compared with $f_{c\lambda}(T_0)$ and $f'_{c\lambda}(T)_{T=T_0}$ respectively, even though $f_{r\lambda}(T_0) < f_{c\lambda}(T_0)$ and $f'_{r\lambda}(T)_{T=T_0} < f'_{c\lambda}(T)_{T=T_0}$. And the value of $(f_{r\lambda}(T) - f_{r\lambda}(T))'_{T=T_0} \cdot K$ is not so small as to be negligible. Then, for $\rho_\lambda(T)$, we cannot neglect the contributions from the released molecules.

Thus, for $\rho_\lambda(T)$, the bent model is not acceptable from the standpoint of our model. But it seems that there is a possibility for $\rho_\lambda(T)$ to be related to the forces responsible for long-range order, whose break-down corresponds to melting.

8 SUMMARY

We have studied the refractive index of liquid water, assuming a simple structure model and setting up several assumptions and approximations.

Observed data of refractive indices of liquid water used in our discussion are measured to 8 figures, while those of ice are available to 5 figures. The discussion of accuracy of the observed data is not satisfactory. But at present we must be satisfied with their data, expecting more precise data to be forthcoming in future. In addition, for the assumed value of ω_λ^2 and for the neglected values of γ_{jk}, etc., the situation is similar to the case of refractive indices. However, the values of refractive indices obtained with respect to each vibration mode seem to be reasonable.

Because the visible light region is taken between the ultra-violet and infrared regions, the refractive index of the visible light has contributions from molecular states and electron states in each molecule. But the contributions from both states are only those of the dominant absorption bands or lines making it simpler to treat the contributions from them.

Studying the refractive index of liquid water, we have been able to relate this to the behavior of molecules and that of electron clouds, especially that of the induced dipoles of molecules and electron clouds.

For molecule, we obtained $\sum_i f_{ri}(T) \cdot N_r(T) \sim 0$; then the bent model is acceptable. Further detailed investigations are necessary for this subject from other physical points of view.

For electron clouds, when ice transforms to liquid water, the variation of induced dipoles of electron clouds is perceptible. This suggests the change of the long-range force. Hence, the most prominent difference between ice and liquid water seems to be the difference between electron cloud distributions, because electron clouds have the dominant contributions not only to $\rho_\lambda(T)$ but also to $\Delta_1(T)$ (refer to formulas (3) and (4)).

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