Polarizability calculations on water, hydrogen, oxygen, and carbon dioxide

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Based on the semiclassical model of damped oscillators, a procedure is developed for the calculation of the dispersion of refractive index, polarizability, and dielectric permeability, which are treated as complex quantities. Using experimental values of refractive indices and employing the frequencies of strong absorption bands, a least squares fit is used to determine oscillator strengths and damping factors. The absorption coefficient and the imaginary part of the refractive index are also calculated at the corresponding wavelengths. The procedure is applied for the cases of water, hydrogen, and oxygen in both the liquid and gaseous states and for gaseous carbon dioxide, and a good agreement is obtained between calculated and observed values of refractive indices. Results are also compared with those of previous calculations. Calculated absorption coefficients agree well with experimental values in the region of absorption bands. The calculated values of oscillator strengths and damping factors are discussed. The previously determined values for the polarizability extrapolated to infinite wavelength agree with the present results for the contribution of the electronic motion to the polarizability, this contribution being about the same for both the liquid and gaseous states of hydrogen, oxygen, and water. The value obtained in the present work for the polarizability of liquid water is about 2.8-fold greater than the results of previous calculations; most of the contribution is due to atomic and molecular motions. Onsager's theory is shown to yield the experimental value of the permanent dipole of water from the dielectric constant of liquid water when our result for the polarizability of liquid water is employed.

I. INTRODUCTION

A knowledge of the polarizability and the dielectric permeability as functions of the frequency of the electric field, i.e., the dispersion law, is required in many theories of intermolecular forces. London[1,2] expresses the intermolecular forces in terms of the polarizabilities in two different formulations:

1. second-order perturbation theory applied to the interaction between two dipoles,

2. a perturbation applied to a system of isotropic harmonic oscillators. London's theory is later applied by Hamaker[3] for the case of condensed media.

In the Lifshitz theory of interactions between macroscopic bodies in condensed media, Lifshitz[4] and later Dzyaloshinskii *et al.*[5] require the representation of the dielectric permeabilities on the imaginary frequency axis. The expression of the polarizabilities on the imaginary frequency axis appears also in Linder's[6] treatment of intermolecular forces based on the method of the fluctuating reaction field, in the article of Jehle *et al.*[7] on intermolecular charge fluctuation interactions in molecular biology, and in Parsegian and Ninham's[8,9] application and extension of the Lifshitz theory.

This list of references is by no means exhaustive; it rather illustrates the role that the polarizability and dielectric permeability play in calculations of intermolecular forces.

Recently Nir, Rein, and Weiss[10] have also applied the Lifshitz theory to some calculations of van der Waals forces across thin films. They concluded that in a water–hydrocarbon system the values of the forces are quite sensitive to variations in the dispersion of the dielectric permeability of water. A procedure was developed in which the polarizability and the dielectric permeability can have imaginary components in the infrared, visible, and ultraviolet regions; the values of the parameters are obtained by least squares calculations using data on refractive indices.

In the present article we extend this procedure, and treat liquid and gaseous water, hydrogen, and oxygen and gaseous carbon dioxide. We focus, however, our attention on the interpretation of the results of calculations on liquid water, since the study of water is of great interest in itself, water being the most common substance in biological systems. In choosing the other substances we had a special interest in hydrogen and oxygen, which are extremely simple cases. Also, we compare the variation of parameters when going from the gaseous to liquid state.

A question of great interest in studies of dielectric permeability and polarizability is the relative contribution to the polarizability of electronic motions and atomic or molecular motions. This problem may be of great relevance for calculations of intermolecular forces. We study this question in the case of liquid water and carbon dioxide by carry-

ing out an extended analysis.

For the purpose of facilitating further discussion we begin the next section with some well-known equations, which in many treatments in the literature are oversimplified by neglecting the complex nature of the polarizability at infrared, visible, and ultraviolet frequencies.

II. SEMICLASSICAL EQUATIONS

A. Introduction

Debye[11] suggested the following expression for the dielectric permeability of a pure substance:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} N \left(\frac{\mu^2/3kT}{1 - i\tau_1\omega} + \alpha \right), \tag{1}$$

in which N is the number of molecules per unit volume, μ is the permanent dipole moment of a single molecule, k is Boltzmann's constant, T is the absolute temperature, τ_1 is the relaxation time of the permanent dipole moment, and α is that part of the polarizability arising from effects other than molecular orientation. The polarizability α is a result of bending and stretching of bonds and of displacement of charges under the effect of an applied field. In Eq. (1) it is implicitly assumed that α is a scalar; in the case of anisotropic substances α is a tensor.

Debye's expression proved to be sufficiently accurate for gases and for many nonpolar liquids. Debye's equation should be modified in the case of polar liquids, particularly in the case of associated liquids such as water, where it fails to account for the value of the static dielectric constant. Improved expressions for the static dielectric permeabilities were suggested by Onsager, [12] Kirkwood, [13,14] and Böttcher. [15-17] However, for optical frequencies starting from the far infrared, the permanent dipoles do not play an important role in contributing to the dielectric constant since they cannot follow the rapidly oscillating electric field; thus Debye's equation may hold also for polar liquids in the optical region.

Equation (1) is obtained when the inner field $\mathbf{F}$ which acts on the molecule is given by

$$\mathbf{F} = \mathbf{E} + (4\pi/3)\,\mathbf{P}, \tag{2}$$

where $\mathbf{E}$ is the external field and $\mathbf{P}$ is the polarization, i.e., the induced dipole moment per unit volume. At optical frequencies Eq. (1) simplifies to

$$(\epsilon - 1)/(\epsilon + 2) = (4\pi/3)\,N\alpha. \tag{3}$$

At optical frequencies and considering ordinary, nonferromagnetic substances $\epsilon = n^2$, where n is the refractive index. Equation (3) may be written as

$$(n^2 - 1)/(n^2 + 2) = (4\pi/3)\,N\alpha, \tag{4}$$

which is the Lorenz–Lorentz equation. [18]

Debye[11] also considered the possibility that the inner field $\mathbf{F}$ in Eq. (2) to be given by

$$\mathbf{F} = \mathbf{E} + (4\pi/3)\,(q + 1)\,\mathbf{P}, \tag{2'}$$

in which q is a certain numerical factor, which is supposed to be a measure of the interaction of neighboring molecules. With Eq. (2') it follows, [11]

$$(n^2 - 1)/[(1 + q)\,n^2 + (2 - q)] = (4\pi/3)N\alpha \tag{4'}$$

B. Derivation of α

The classical equation of motion for a charged oscillator of mass m and charge e under the action of an oscillating field $\mathbf{F} = \mathbf{F}_0 \exp(-i\omega t)$ is[18,19]

$$\ddot{\mathbf{r}} + \gamma\dot{\mathbf{r}} + \omega_0^2\,\mathbf{r} = (e/m)\,\mathbf{F}_0 \exp(-i\omega t), \tag{5}$$

in which γ is a damping factor and ω_0 is an angular eigenfrequency of the undamped motion;

$$\mathbf{r} = \frac{eF_0/m \exp(-i\omega t)}{\omega_0^2 - \omega^2 - i\gamma\omega} \tag{6}$$

Since $\mathbf{m} = e\mathbf{r} = \alpha\mathbf{F}$, where $\mathbf{m}$ is the induced dipole moment, it follows that

$$\alpha = \frac{e^2/m}{\omega_0^2 - \omega^2 - i\gamma\omega}\ , \tag{7}$$

in which ω_0 is interpreted as one of the absorption frequencies. In most cases Eq. (5) has been considered to apply to electrons, the mass m and charge e being then those of an electron. The general trend is to introduce factors f_i—oscillator strengths[20,21]—which mean "effective number of electrons," so that when all absorption frequencies are considered,

$$\alpha = \sum_{i=1}^{p} \frac{f_i e_i^2/m_i}{\omega_i^2 - \omega^2 - i\gamma_i\omega}\ . \tag{8}$$

It is assumed in the classical treatment that the sum of all oscillator strengths equals the number of the electrons per molecule or atom (see Ref. 19).

From Eqs. (4) and (8) we obtain

$$\frac{\bar{n}^2(\omega) - 1}{\bar{n}^2(\omega) + 2} = \beta(\omega)$$

$$= \sum_{i=1}^{p} \frac{C_i}{1 - (\omega/\omega_i)^2 - i\gamma_i\omega/\omega_i^2}\ , \tag{9}$$

where

$$C_i = 4\pi N f_i e_i^2/3\omega_i^2 m_i\ . \tag{10}$$

By $\bar{n}$ we mean a complex refractive index, i.e.,

$$\bar{n} = n + ik, \tag{11}$$

where n is the ordinary refractive index.

In the literature the γ_i's are generally regarded

as very small compared to the ω_i's and hence neglected. This leads of course to an infinite value of α, unobserved experimentally, near any one of the absorption frequencies.

From the real part of Eq. (9) we obtain

$$\frac{(n^2 - k^2 - 1)(n^2 - k^2 + 2) + 4n^2 k^2}{(n^2 - k^2 + 2)^2 + 4n^2 k^2}$$

$$= \mathrm{Re}\beta(\omega) = \sum_{i=1}^{\ell} \frac{C_i[1 - (\omega/\omega_i)^2]}{[1 - (\omega/\omega_i)^2]^2 + (\gamma_i \omega/\omega_i^2)^2} \quad . \quad (12)$$

An analysis of the behavior of the right hand side of Eq. (12) is straightforward. For $\omega \ll \omega_i$ the ith term of the sum tends to remain fairly constant at the value C_i when ω is further decreased. When $\omega < \omega_i$ is being increased the ith term increases (normal dispersion) towards a maximum at $\omega = \omega_i(1 - \gamma_i/\omega_i)^{1/2}$, then decreases (anomalous dispersion) to negative values, passing through zero at $\omega = \omega_i$, reaching a minimum at $\omega = \omega_i(1 + \gamma_i/\omega_i)^{1/2}$, and then tending to zero. Because of the presence of several terms in Eq. (12) this behavior may in fact not be sharply defined. When both the real and imaginary parts of the refractive index are known Eq. (12) may be applied. In gases and in other cases when k is assumed to be much smaller than unity, a simplified version may be used, in which the left hand side of Eq. (12) becomes

$$(n^2 - 1)/(n^2 + 2) = \mathrm{Re}\beta(\omega) \quad (13)$$

The imaginary part of Eq. (9) is

$$\frac{6nk}{(n^2 - k^2 + 2)^2 + 4n^2 k^2}$$

$$= \mathrm{Im}\beta(\omega) = \sum_{i=1}^{\ell} \frac{C_i \gamma_i \omega/\omega_i^2}{[1 - (\omega/\omega_i)^2]^2 + (\gamma_i \omega/\omega_i^2)^2} \quad . \quad (14)$$

The left hand side may be simplified to $(k \ll 1)$

$$6nk/(n^2 + 2)^2 = \mathrm{Im}\beta(\omega). \quad (15)$$

When the right hand side of Eq. (12) is known the right hand side of Eq. (14) is also known; from Eq. (14) the value of $k(\omega)$, the imaginary part of the refractive index, can also be determined.

The quantity $k(\omega)$ determines the absorption of the incident energy.[18,20] The energy of the wave decreases as $\exp(-2\omega kx/C)$, the absorption coefficient $\bar{\mu}$ being:

$$\bar{\mu}(\omega) = 2\omega k(\omega)/C, \quad (16)$$

in which C is the velocity of light in vacuum.

When this somewhat oversimplified treatment of absorption is accepted, values of the absorption coefficients $\bar{\mu}(\omega)$ can be predicted from the representation of the polarizability as a function of the frequency.

III. SEMIEMPIRICAL PROCEDURE FOR CALCULATION OF POLARIZABILITY AND DIELECTRIC PERMEABILITY

When the γ_i's and the ω_i's are regarded as known numbers Eqs. (12) and (13) become a set of linear equations in the C_i's. A choice of m values of measured refractive indices is apparently sufficient to solve for l coefficients where $l = m$. However, it is clear that when the number of observations m is much greater than the number of coefficients l, the solution will be more reliable.

A program has been written which solves for the C_i's, utilizing a linear least squares procedure, for various introduced values of the γ_i's . The input required by the program includes the frequencies of absorption and the measured refractive indices (real or real and imaginary) at the corresponding wavelengths.

One can of course solve for the C_i's when all the γ_i's are set equal to zero. As will be discussed later the agreement between calculated and experimental values is much improved when a particular set of γ_i's, relatively sharply defined, was employed.

It should be pointed out that, according to our procedure of least squares calculations, the quantity which is fitted is not $n(\omega)$ but $\mathrm{Re}\beta(\omega)$. A critical test for the procedure (and for the theory) is that there be a good agreement between observed and calculated values of $n(\omega)$. Accordingly the program calculates for each given value of ω the value of $n(\omega)$ from the relation

$$n^2(\omega) = [1 + 2\,\mathrm{Re}\beta(\omega)]/[1 - \mathrm{Re}\beta(\omega)], \quad (17)$$

which follows from Eq. (13). A more complicated but straightforward relation follows when Eq. (13) is to be used [see Appendix A, Eq. (A1')].

A useful measure for the goodness of the fit is provided by the quantity

$$\Delta_n = (1/m) \sum_{j=1}^{m} [n_0(\omega_j) - n_c(\omega_j)]^2, \quad (18)$$

in which the ω_j's stand for the measured light frequencies and $n_0(\omega_j)$ and $n_c(\omega_j)$ stand for the respective measured and calculated values of the refractive indices. A related measure is the root mean squared error, $\mathrm{RMSE} = \Delta_n^{1/2}$.

The values of the C_i's which appear as parameters in the least squares procedure are not arbitrary but rather restricted. Since they are proportional to the oscillator strengths [see Eq. (10)] they should be positive numbers. In addition, $\sum_{i=1}^{\ell} C_i$ is bounded from above by unity, as is explained below. From Eq. (12) or (13) it is clear that $\mathrm{Re}\beta(\omega)$ is smaller than unity. When the right hand side of Eq. (12) or (13) is considered at low

frequencies $\omega \ll \omega_1$ it is practically equal to the sum of the C_i's. From Eq. (17) it follows that this sum is further bound by the extrapolated value of n^2 to infinite wavelength.

Occasionally, when the number of observations is not sufficient to fix a certain C_i, the resulting value may be a negative number or the sum of the C_i's may exceed the bounding value. In such a case we propose to eliminate the corresponding term from Eq. (12), and to look for a neighboring frequency that would satisfactorily comply with the dispersion law of the refractive index.

From inspection of Eq. (12) it follows that at $\omega \ll \omega_i$ any term i in the summation behaves like a constant C_i. Hence it is clear that a dispersion formula should always include an ultraviolet term, even when ultraviolet data are not available. The coefficient C_{uv} will thus represent a sum of coefficients of many ultraviolet bands. It seems hopeless to obtain refractive index data for all far ultraviolet bands, most of which lie beyond the first ionization limit, and one cannot correspondingly expect to obtain refined predictions for the ultraviolet region. In Appendix B we will discuss how the calculations of forces according to the Lifshitz theory are dependent on knowledge of far ultraviolet dispersion data.

From the point of view of calculations it makes no difference whether Eq. (12) or Eq. (13) is to be used, since calculations are performed with a computer. However, the use of Eq. (12) requires data on the imaginary part of the refractive index as well. In Appendix C we present a table which shows the variation of the left hand side of Eq. (12) (Reβ) with n and k. The errors introduced into Reβ values by neglect of k are less than 0.0005 and 0.0002 for $n = 1.4$ (a typical value of n) and $k = 0.05$ and 0.1, respectively. Such errors in Reβ, i.e., 0.0005 and 0.002, respectively, correspond approximately to errors of 0.0005 and 0.002 in n (for $n = 1.4$), which are reasonably permissible experimental errors in the visible and infrared regions. Thus, neglect of k, i.e., use of Eq. (13) instead of Eq. (12), is permissible as long as k is under 0.05 in the visible region or under 0.1 in the infrared region.

Equation (13) may always be used for gases, since the inequality $k^2 \ll n^2 - 1$ is always satisfied for gases.

IV. RESULTS OF CALCULATIONS ON WATER, HYDROGEN, OXYGEN, AND CARBON DIOXIDE

The first goal is to achieve a good agreement between observed and calculated values of refractive indices at optical frequencies. The representation of the dielectric permeabilities or polarizabilities

on the imaginary frequency axis, which is required for calculations of intermolecular forces, is straightforward once the dispersion law is known[10] (see also Appendix B). The values of the coefficients C_i, the oscillator strengths f_i, and the damping factors γ_i which give the best fit in least squares calculations, are determined; the discussion of these values is postponed to Sec. V.

Calculated values of the absorption coefficients and of the imaginary part of refractive indices are compared with available experimental results.

The contributions of the electronic and atomic or molecular motions to the value of the polarizability α extrapolated to infinite wavelength are also determined.

A. Liquid Water

We made use of the extensive data collected by Dorsey[22] at a temperature of 20 °C, which include 122 values of refractive indices at the corresponding wavelengths, starting from the far infrared, $\lambda = 152\,\mu$, up to the ultraviolet, $\lambda = 0.1829\,\mu$ (= 1829 Å). (Dorsey's data include also one measurement recorded at 1.54 Å.) The values of the refractive indices which are originally expressed relative to air are transformed to values relative to vacuum with the aid of a table given by Dorsey.[22] The estimated error due to this transformation, which is to be added to the experimental error, is smaller than 0.0005 in absolute magnitude. Values of the imaginary part of the refractive index are obtained from the following sources:

Rusk et al.[23]	2.0–30.3 μ,
Kislovskii[24]	30–117 μ,
Painter et al.[25]	0.1–0.26 μ.

From values of $\bar{\mu}$ [see Eq. (16)] obtained from the International Critical Tables[26] it follows that k values are much smaller than 0.05 throughout the region from 0.18 to 2.50 μ, so that in this range we were completely justified in using Eq. (13), (see discussion in Sec. III).

As outlined in the previous section the first step in the procedure is to determine the absorption frequencies to be used.

In the ultraviolet region we tried all combinations of one, two, or three absorption frequencies in the following set (Herzberg[27]):

$$W = 1.14 \times 10^{16} \text{ rad/sec } (= 1650 \text{ Å}),$$

$$W = 1.507 \times 10^{16} \text{ rad/sec } (= 1250 \text{ Å}),$$

$$W = 1.906 \times 10^{16} \text{ rad/sec } (= 990 \text{ Å}).$$

The last frequency listed corresponds to the first ionization potential,

$\hbar\omega = 12.62$ eV.

For any combination of two or three ultraviolet frequencies tested one of the corresponding coefficients (which is proportional to the corresponding oscillator strength) would turn out to be negative. We therefore had to include only one ultraviolet frequency although the fit was somewhat better when all three frequencies were included. This behavior can be explained by the absence of sufficient number of measurements in the ultraviolet region, especially in the region of the first two uv bands. The best fit with only one absorption frequency in the ultraviolet region was obtained when the frequency which corresponds to the ionization potential was used.

We have also performed calculations using the data of Painter et al.[25] at wavelengths between 1050 and 3000 Å. We had a special interest to use the data of Painter et al. since their measurements cover the range of the first and second absorption frequencies in the ultraviolet region. In addition, they also give results for the imaginary part of refractive indices, so that Eq. (12) was used.

We performed the calculations using the three previously listed absorption frequencies in the ultraviolet region, and ultraviolet data only. According to Painter et al. the center of the first band is significantly shifted to a value of 1510 instead of 1650 Å in the gaseous state; the second band is only slightly shifted to a value of 1290 instead of 1250 Å. The values obtained for the coefficients and damping factors are:

$$C_1 = 0.015 \qquad \gamma_1 = 2.1 \times 10^{15} \text{ rad/sec} \qquad f_1 = 0.07(\lambda_1 = 1510 \text{ Å}),$$
$$C_2 = 0.028 \qquad \gamma_2 = 4.1 \times 10^{15} \text{ rad/sec} \qquad f_2 = 0.17(\lambda_2 = 1290 \text{ Å}),$$
$$C_3 = 0.150 \qquad \gamma_3 = 4.4 \times 10^{15} \text{ rad/sec} \qquad f_3 = 1.53(\lambda_3 = 990 \text{ Å}).$$

The value of the RMSE is 2.5×10^{-2}, which is of about the same value as the experimental error in this case.

We could not match together the far ultraviolet data of Painter et al.[25] and the ultraviolet, visible, and infrared data of Dorsey,[22] due to the fact that the former results are given at a temperature different from 20 °C. (Some of their measurements are performed at a temperature of 1 °C.) It is of interest to point out that the sum (0.193) of three ultraviolet coefficients using the data of Painter et al. is very near the value of the one ultraviolet coefficient 0.202 which is obtained with Dorsey's data.

In the infrared region we employed four absorption frequencies which correspond to absorption bands in liquid water,[28] thus improving the fit obtained when absorption frequencies in the gaseous state were employed.

Table I shows calculated values of refractive indices compared with the measured values. The calculations are based on Eqs. (12), (13), (17) and (A1) with five terms, four in the infrared and one in the ultraviolet.

The five employed absorption frequencies ω_i, the corresponding coefficients C_i, the oscillator strengths f_i, and the damping coefficients γ_i are listed in Table II. In order to save space we include in Table I only 45 cases, skipping the second and third consecutive members of each triad, but including all cases in the far infrared region.

(The wavelength at which the disagreement is largest is included in Table I.) We also compared the results of our calculations with those of two other formulations:

$$n^2 = 1.76253 - 0.0133998 \, \lambda^2$$
$$+ 0.00630957/(\lambda^2 - 0.01588)$$
$$+ 10^{[107.731(0.064156 - \lambda^2) - 5]}, \quad \text{(Dorsey}^{22})$$
$$n^2 = 1.29 + 0.47\lambda^2/[\lambda^2 - (0.119)^2]$$
$$- 0.08\lambda^2/(2.92^2 - \lambda^2), \quad \text{(Kislovskii}^{24})$$

in which λ is the wavelength in microns.

Both authors succeeded in obtaining good agreement between experiment and calculation. However, Kislovskii's representation is best in accounting for the infrared region whereas Dorsey's representation is best for the visible region. Both representations have some deviant points. The sums of the total errors Δ_n [see Eq. (18)] obtained according to their calculations are much greater than in our case for any frequency region chosen.

The agreement between calculated and observed values is very sensitive to the chosen set of damping factors. The value obtained for the RMSE, i.e., $\Delta_n^{1/2}$, is 1.4×10^{-2}. In comparison, when all the γ's are set equal to zero, i.e., the imaginary quantities are neglected, the value of $\Delta_n^{1/2}$ is 1.2×10^{-1}.

The value of 1.4×10^{-2} for the RMSE is above the experimental error in the visible region but

TABLE I. Observed and calculated[a] values of refractive indices of liquid water at corresponding wavelengths ($T = 20\,^\circ$C).

Wavelengths in units of micron	$n_0{}^a$	$n_c{}^a$	$n_c'{}^b$	$(n_0 - n_c)$	$(n_0 - n_c')$
0.000154	1.0000	1.0000	1.0000	0.000	0.000
0.1829	1.4638	1.454	1.453	+0.010	0.011
0.1839	1.4601	1.452	1.451	0.008	0.009
0.1855	1.4553	1.449	1.449	+0.006	0.007
0.1935	1.4360	1.437	1.436	−0.001	0.000
0.2026	1.4199	1.425	1.424	−0.005	−0.004
0.2138	1.4050	1.412	1.412	−0.007	−0.007
0.2195	1.3988	1.407	1.407	−0.008	−0.008
0.2265	1.3926	1.401	1.401	−0.008	−0.008
0.2378	1.3843	1.393	1.393	−0.008	−0.008
0.2568	1.3741	1.381	1.382	−0.008	−0.008
0.2575	1.3737	1.381	1.381	−0.008	−0.008
0.2660	1.3700	1.377	1.377	−0.007	−0.007
0.2894	1.3617	1.368	1.369	−0.007	−0.007
0.3082	1.3569	1.363	1.363	−0.006	−0.006
0.3342	1.3516	1.356	1.357	−0.005	−0.005
0.3602	1.3477	1.352	1.352	−0.004	−0.004
0.3889	1.3443	1.348	1.348	−0.003	−0.004
0.3962	1.3436	1.347	1.347	−0.003	−0.004
0.4047	1.3428	1.346	1.346	−0.003	−0.003
0.4326	1.3403	1.343	1.343	−0.003	−0.003
0.4384	1.3399	1.342	1.343	−0.002	−0.003
0.4800	1.3375	1.339	1.340	−0.002	−0.002
0.4861	1.3372	1.339	1.339	−0.001	−0.002
0.5338	1.3350	1.336	1.336	−0.001	−0.001
0.5770	1.3334	1.334	1.334	0.000	−0.001
0.6563	1.3311	1.331	1.332	0.000	0.000
0.8710	1.3277	1.325	1.326	0.002	−0.002
1.0000	1.3230	1.323	1.323	0.000	0.000
1.256	1.3210	1.317	1.317	0.003	0.003
2.400	1.2750	1.256	1.254	0.019	0.021
2.600	1.2530	1.237	1.235	0.016	0.018
3.200	1.4560	1.400	1.404	0.056	0.052
4.500	1.3430	1.339	1.340	0.005	−0.023
5.500	1.3000	1.295	1.294	+0.005	0.006
6.500	1.3340	1.333	1.333	0.001	0.001
10.00	1.1960	1.220	1.217	−0.023	−0.021
13.00	1.2690	1.232	1.235	+0.037	0.034
18.00	1.505	1.510	1.545	−0.005	−0.040
52.00	1.680	1.678	1.666	0.002	0.014
63.00	1.770	1.764	1.717	0.006	0.053
83.00	1.890	1.913	1.917	−0.023	−0.027
100.00	2.010	1.988	2.007	+0.022	0.003
117.00	2.040	2.040	2.056	−0.000	−0.016
152.00	2.090	2.095	2.083	−0.005	0.007

[a] n_0 is the observed value of n; n_c is the calculated value of n. n_c is determined using four infrared absorption frequencies and one frequency in the ultraviolet region, along with the set of damping factors which give the minimal value of Δn [see Eq. (18)]. The calculation is performed using Eqs. (13) and (17) with parameters listed in Table II, part B.
[b] n_c' is the calculated value of n using Eq. (12) instead of Eq. (13).

not greater than the experimental error in the infrared region. In fact, most of the contribution to the summed error Δ_n arises from a few deviant points, and the errors are quite small throughout all the range, as seen in Table I.

We also performed calculations which neglect k values. The RMSE in this case is 1.3×10^{-2}, i.e., no improvement in terms of the error occurs when

Eq. (12) is used instead of Eq. (13). The resulting parameter values are included in Table II, which shows coefficients do not differ appreciably whether Eq. (12) or Eq. (13) is being used.

We would like to mention briefly some more calculations on liquid water at different temperatures.

At 24 °C we made use of the following sources of data: Tilton and Taylor,[29] $\lambda = 0.4 - 0.725\ \mu$, Querry et al.,[30] $\lambda = 2 - 20\ \mu$. In the ultraviolet region we made use of Dorsey's[22] values. Although the individual experimental and calculated values of refractive indices were different from the values at 20 °C, the set of parameters (C_i's and γ_i's) turned out to be almost the same, thus verifying independently the previous results. We also performed separate calculations in the region 2.00–30.3 μ using the extensive data of Rusk et al.,[23] at 25 °C, consisting of 174 values of both the real and imaginary part of the refractive index. The resulting values for the parameters are very close to those obtained using Dorsey's data, at 20 °C.

In our calculations we also tried to determine whether there is any advantage in using Eq. (4') instead of the Lorenz–Lorentz equation, Eq. (4). We varied q between 1.5 and −1.5. [The case $q = -1$ corresponds to setting the inner field F equal to the external field E as is seen from Eq.

TABLE II. Absorption frequencies, oscillator strengths, and damping factors for liquid water.

λ_i Absorption wavelength in units of micron	$C_i{}^a$	$f_i{}^b$ Oscillator strength	γ_i Damping coefficient in units of rad/sec	$\alpha_i(0)^b$ Contribution to static polarizability in units of cm³
A. $T = 20\,^\circ$C				
51.8	0.154	5.73×10^{-6}	5×10^{13}	1.099×10^{-24}
14.3	0.186	9.10×10^{-5}	1.0×10^{14}	1.327×10^{-24}
6.08	0.004	10.6×10^{-6}	2.6×10^{13}	0.028×10^{-24}
2.86	0.020	2.4×10^{-4}	1.3×10^{14}	0.143×10^{-24}
0.099	0.202	2.07	5.9×10^{15}	1.446×10^{-24}
B. $T = 20\,^\circ$C				
51.8	0.156	5.82×10^{-6}	4.6×10^{13}	1.115×10^{-24}
14.3	0.172	8.42×10^{-5}	1.0×10^{14}	1.228×10^{-24}
6.08	0.004	9.97×10^{-6}	2.5×10^{13}	0.026×10^{-24}
2.86	0.019	2.3×10^{-4}	1.3×10^{14}	0.136×10^{-24}
0.099	0.202	2.066	5.2×10^{15}	1.442×10^{-24}

[a] The coefficients C_i, $(i = 1 \cdots 5)$ are defined in Eqs. (9), (12), and (13). See also Eq. (10) for relation between C_i's and oscillator strengths f_i's. The parameters which appear in part A are obtained with the inclusion of data on the imaginary part of the refractive index, k [see Eq. (12)].
[b] Oscillator strengths f_i are calculated from the C_i by substituting the electronic charge and mass in Eq. (10). Polarizabilities extrapolated to infinite wavelength, $\alpha_i(0)$, are obtained from the C_i by using Eqs. (8), (9), and (10). Parameters in part B result from a neglect of k, using Eq. (13).

TABLE III. Observed and calculated values of imaginary part of refractive index and absorption coefficient in liquid water.[a]

Wavelengths in units of micron	k_0	k_c	$\bar{\mu}_0 (\times 10^3)$	$\bar{\mu}_c (\times 10^3)$
2.87	0.225	0.254		11.11
2.92	0.281	0.246		10.59
2.96	0.291	0.220		9.35
3.01	0.269	0.183	7.33	7.63
3.12	0.194	0.114		4.60
4.39	0.008	0.016		0.47
4.59	0.012	0.016	0.45	0.45
4.90	0.015	0.017		0.44
5.15	0.013	0.019		0.47
5.32	0.009	0.021	0.3	0.50
5.75	0.023	0.039	0.9	0.85
5.95	0.072	0.090		0.90
6.10	0.139	0.152	2.53	3.13
6.33	0.064	0.064		1.26
6.76	0.033	0.039	0.88	0.73
8.06	0.031	0.058	0.78	0.91
11.6	0.160	0.212		2.30
17.9	0.416	0.398	2.99	2.79
23.8	0.402	0.299		1.58
30.3	0.380	0.301		1.25

[a] Observed values of imaginary part of refractive index, k, and absorption coefficient, $\bar{\mu}_0$, are given in Refs. 23 and 26, respectively. Calculated values are obtained by using Eqs. (14) and (16) (with five terms).

(2′).] The agreement between calculated and observed values of n is significantly better when q in Eq. (4′) is zero, which reduces to the Lorenz–Lorentz equation.

1. Calculation of Absorption Coefficient and Imaginary Part of Refractive Index

It is obvious that in order to predict values of $k(\omega)$ and $\bar{\mu}(\omega)$ from a knowledge of the real part of the refractive index, detailed information on the location of band centers is required. In addition, a sufficient number of values of refractive indices in the vicinity of the bands should be available.

In performing the calculations we observed that a fair prediction was obtained for values of $k(\omega)$ and $\mu(\omega)$ at the centers of the peaks, but that the calculated values did not decrease sufficiently rapidly when moving away from the band centers. Most of the difficulty is due to a large contribution of the ultraviolet band, which is not so critical in the infrared region.

In Table III we compare calculated values of the imaginary part of the refractive index and absorption coefficients with observed values in the infrared region.

In summarizing this part of the work we state

that values of $k(\omega)$ or $\bar{\mu}(\omega)$ in the vicinity of the absorption bands can be predicted within an order of magnitude with the simple theory given in Eqs. (14) and (16). The exact decrease of absorption coefficients when moving away from the center of a band is yet to be determined.

2. Polarizability at Infinite Wavelength

From Eqs. (4) and (9) directly arises the relation $\alpha(\omega) = 3/4\pi N \beta(\omega)$, which at $\omega = 0$ becomes $\alpha(0) = (3/4\pi N) \sum_{i=1}^{p} C_i$, where $\alpha(0)$ is the polarizability at infinite wavelength and N is the number of molecules per unit volume. We may write the last relation as $\alpha(0) = \sum_{i=1}^{p} \alpha_i(0)$, where $\alpha_i(0) = (3/4\pi N) C_i$. From the C_i values (see Table II) we obtain immediately the individual contributions to the value of $\alpha(0)$. Since absorption frequencies in the ultraviolet region represent electronic energy levels, the value of $\alpha_5(0)$ (We refer to the results listed in Tables I and II.) represents the contribution of the electronic motions to the polarizability at infinite wavelength. On the other hand the absorption frequencies in the infrared region represent energy levels of atomic and molecular motions.[28] Thus the sum $\sum_{i=1}^{4} \alpha_i(0)$ is the contribution of the atomic and molecular motions to the polarizability at infinite wavelength.

Our resulting value for $\alpha_5(0)$ is 1.45×10^{-24} cm^2, whereas the total $\alpha(0)$ is 2.8 times larger than $\alpha_5(0)$, being 4.04×10^{-24} cm^3. The values recorded for $\alpha(0)$ in the literature are: Sänger and Steiger,[31] $\alpha(0) = 1.43 \times 10^{-24}$ cm^3, Moelwyn-Hughes,[32] $\alpha(0) = 1.444 \times 10^{-24}$ cm^3, and $\alpha(0) = 1.68 \times 10^{-24}$ cm^3. The experimental evaluation of the static polarizability $\alpha(0)$ was obtained by extrapolating the dispersion formula of the refractive index to zero frequency.[32] The previously obtained values of $\alpha(0)$ for liquid water have apparently resulted from neglect of infrared terms in the dispersion formula, thus neglecting atomic and molecular contributions to the static polarizability. We observe that the previously recorded values for $\alpha(0)$ coincide with our value of $\alpha_5(0)$, but we obtain in addition the contribution of the infrared bands to the static polarizability, $\sum_{i=1}^{4} \alpha_i(0)$, which is 1.8 times larger than the contribution of the ultraviolet bands to the static polarizability. Thus, the most important contribution to the static polarizability of water is the atomic and molecular polarizability. With the introduction of the present value obtained for $\alpha(0)$ in the expressions[2,3,6] for intermolecular energies, the results may significantly change for the case of water.

B. Water Vapor

The dispersion data of water vapor include measurements of refractive indices at wavelengths

TABLE IV. Observed and calculated values of refractive indices of water vapor[a] at corresponding wavelengths.

Wavelength in units of micron	$10^6 \times (n_0 - 1)$[b]	$10^6 \times (n_c - 1)$[b]	$10^6 \times (n_0 - n_c)$[b]
0.26	8.04	7.96	0.08
0.27	7.92	7.91	0.01
0.28	7.79	7.71	0.08
0.29	7.84	7.83	0.01
0.30	7.77	7.75	0.02
0.31	7.75	7.76	− 0.01
0.36	7.63	7.63	0.00
0.40	7.53	7.56	− 0.03
0.43	7.56	7.52	0.04
0.58	7.46	7.41	0.05
0.59	7.38	7.40	− 0.02
0.61	7.41	7.40	0.01
0.63	7.46	7.39	0.07
0.64	7.28	7.18	0.10
0.65	7.36	7.38	− 0.02
0.67	7.33	7.37	0.04
0.72	7.38	7.36	0.02
0.74	7.36	7.35	0.01
0.79	7.32	7.34	− 0.02
0.81	7.33	7.34	− 0.01
0.83	7.33	7.34	− 0.01
0.84	7.33	7.34	− 0.01
0.86	7.41	7.33	0.08
0.436	256.9	257	− 0.008
0.447	256.3	256	− 0.023
0.468	255.4	255	0.032
0.480	254.9	255	0.036
0.508	253.8	254	− 0.025
0.546	252.7	253	− 0.009
0.588	251.7	252	− 0.022
0.644	250.7	251	0.019

[a] The first set of data listed is given by Newbound[33] at 25°C. The second set is given by Cuthbertson and Cuthbertson[32] at 0°C.

[b] n_0 and n_c indicate the observed and calculated values of refractive index, respectively.

varying from 0.26 to 0.86 μ. The sources used by us are: C. Cuthbertson and M. Cuthbertson,[33] at 0 °C and 1 atm., and K. Newbound,[34] at 22.25 °C and 24.94 mm Hg.

Due to the absence of dispersion data for water vapor in both the ultraviolet and infrared regions, we used in our program only one absorption frequency. (The fit was not improved when two absorption frequencies were used.) The absorption frequency we employed is $\omega_{uv} = 1.898 \times 10^{16}$ rad/sec, which corresponds to the value of 12.56 eV for the ionization potential of water vapor (Price[35]). The results of our calculations compared with measured values are given in Table IV. By varying the values of γ, the damping factor, we found a local minimum in $\Delta_n^{1/2}$ at $\gamma = 7 \times 10^{15}$ rad/sec, using Cuthbertson's data. Using the resulting coefficient C

$= 1.637 \times 10^{-4}$ and $N = 2.686 \times 10^{19}$ molecules/cm³, the value obtained for the oscillator strength is 2.07, and $\alpha(0)$ is 1.456×10^{-24} cm³ [see Eq. (10)]. Newbound's data showed a minimum in $\Delta_n^{1/2}$ at $\gamma = 1.1 \times 10^{16}$ rad/sec, with an oscillator strength of 2.03, and $\alpha(0) = 1.431 \times 10^{-24}$ cm³. (N equals 0.809 $\times 10^{18}$ molecules/cm³.)

The agreement between calculated and experimental values of refractive indices obtained by us was compared with that obtained when the following formulas proposed by Cuthbertson and Cutherbertson[33] and Newbound[34] were used; their formulas are:

1. $(n_0 - 1) = 2.62707 \times 10^{27}/(10697 \times 10^{27} - \nu^2)$

(Cuthbertson's equation at 0 °C and 1 atm, using ν as the light frequency in sec⁻¹.)

2. $[(n - 1)/\rho] \times 10^7 = 3.0198 + 0.16365\lambda^{-2}$
$$+ 0.000133\lambda^{-4}$$

(Newbound's equation at 22.25 °C and 24.94 mm Hg, in which ρ is the gas density in g/m³.)

The fit of these dispersion formulas with measured values of the refractive index n_0 was computed at corresponding wavelengths and compared with data given in the papers of Cuthbertson and Cuthbertson[32] and Newbound,[33] giving differences between calculated and measured values, $|n_0 - n_c|$, of about 10^{-5} and 10^{-6} in the first and second cases, respectively. In the present work, we obtain better agreement with values of $|n_0 - n_c|$ varying between 1×10^{-7} and 1×10^{-8}. Our results indicate that this improvement was due mainly to the introduction of damping factors.

Our results indicate that the RMSE was decreased by more than an order of magnitude due to the introduction of the damping factor. (It should be mentioned, however, that the RMSE was relatively insensitive to values of γ between 10^{15} to 10^{16} rad/sec.) It is remarkable that the values for the oscillator strengths derived from the two sets of water vapor data coincide with the value obtained for f_5 in the case of liquid water. Also, the values obtained for $\alpha(0)$ coincide with the value obtained for $\alpha_5(0)$ in the case of liquid water. As discussed previously, this agreement indicates that the contribution of the electronic motion to the polarizability is the same in both the liquid and gaseous states of water. Since we still do not have sufficient data for the dispersion in the infrared region, we are not able to determine the contribution of the atomic and molecular motions to the polarizability.

C. Hydrogen

1. Gaseous Hydrogen

The dispersion data consist of 29 measurements of refractive index at the corresponding wavelengths

in the ultraviolet and visible regions and two measurements in the near-infrared region. The data are given for 0 °C and 1 atm (International Critical Tables, Vol. VII[26b]).

Molecular hydrogen does not have any absorption bands in its electronic spectrum (Herzberg[36]), but only discrete lines. In such a case we do not expect to obtain an improvement in the accuracy of our calculations with the introduction of damping factors. In fact, variation of values of γ showed no dependence of the fit of calculated values of n to observed values of n on the assumed value of γ.

We performed two calculations. In the first case we used only one frequency, $\omega = 2.344 \times 10^{16}$ rad/sec, which corresponds to the ionization potential 15.43 eV. (Herzberg[36]). The RMSE is about 10^{-16}. The resulting parameters are: $C = 9.19 \times 10^{-5}$, $f = 1.77$, and $\alpha(0) = 0.818 \times 10^{-24}$ cm^3 (using $N = 2.686 \times 10^{19}$ molecules/cm^3). The value of $\alpha(0)$ agrees well with the previously obtained value of 0.81×10^{-24} cm^3 (London[2]).

In the second case we used the two frequencies which appear in the dispersion formula proposed by Schüler and Wolf[37]: $\omega_1 = 1.999 \times 10^{16}$ rad/sec and $\omega_2 = 2.565 \times 10^{16}$ rad/sec. The RMSE is 3.8×10^{-8}, i.e., slightly better than according to the fit of the dispersion formula of Schüler and Wolf (RMSE $= 4.7 \times 10^{-8}$).

The resulting parameters are:

$$C_1 = 6.004 \times 10^{-5}, \quad f_1 = 0.841,$$

$$\alpha_1(0) = 0.534 \times 10^{-24} \text{ cm}^3,$$

$$C_2 = 3.065 \times 10^{-5}, \quad f_2 = 0.707,$$

$$\alpha_2(0) = 0.273 \times 10^{-24} \text{ cm}^3.$$

The sum of $\alpha_1(0)$ and $\alpha_2(0)$ gives 0.807×10^{-24} cm^3, which agrees well with the value obtained using the ionization potential and with the previously obtained value (London[2]).

2. Liquid Hydrogen

The dispersion data include measurements at only three wavelengths in the visible, (Johns and Wilhelm[38]), at 20.41 °K (the boiling point) and 1 atm. We used the same absorption frequency as in the gaseous state, $\omega = 2.344 \times 10^{16}$ rad/sec. As in the gaseous state results were insensitive to γ, so the value $\gamma = 0$ was chosen. The value of $\Delta_n^{1/2}$ is 4×10^{-4}, which is about the experimental error, 0.0003 (Johns and Wilhelm[38]).

The resulting values for oscillator strength and static polarizability are very close to those obtained by us for the gaseous state. The values of the resulting parameters are: $C = 0.0716$, $f = 1.755$,

$\alpha(0) = 0.810 \times 10^{-24}$ cm^3 (using $N = 2.111 \times 10^{22}$ molecules/cm^3).

D. Oxygen

1. Gaseous Oxygen

The dispersion data of gaseous oxygen we used include 56 measurements of the refractive index in the visible and ultraviolet regions, at wavelengths from 0.192 to 0.59 μ, at 0 °C and 1 atm (Ladenburg and Wolfsohn[39]).

We performed two calculations. (1) In the first case we used only one frequency, $\omega = 1.854 \times 10^{16}$ rad/sec, which corresponds to the ionization potential (Herzberg[36]). The value of $\Delta_n^{1/2}$ is 3×10^{-6}. The values of the parameters are: $\gamma = 4 \times 10^{15}$ rad/sec, $C = 1.73 \times 10^{-4}$, $f = 2.09$, and $\alpha(0) = 1.542 \times 10^{-24}$ cm^3.

(2) The value of $\Delta_n^{1/2}$ is 8×10^{-8} which is the same value as the dispersion formula of Wolfsohn and Ladenburg[39]), this value being below the experimental error. The values of the parameters are:

$$\lambda_1 = 1899 \text{ Å}, \quad \gamma_1 = 1 \times 10^{16} \text{ rad/sec}, \quad C_1 = 1.73 \times 10^{-6},$$

$$f_1 = 5.98 \times 10^{-3}, \quad \alpha_1(0) = 0.015 \times 10^{-24} \text{ cm}^3,$$

$$\lambda_2 = 1450 \text{ Å}, \quad \gamma_2 = 5 \times 10^{14} \text{ rad/sec}, \quad C_2 = 3.73 \times 10^{-5},$$

$$f_2 = 0.215, \quad \alpha_2(0) = 0.331 \times 10^{-24} \text{ cm}^3,$$

$$\lambda_3 = 544 \text{ Å}, \quad \gamma_3 = 3 \times 10^{15} \text{ rad/sec}, \quad C_3 = 1.38 \times 10^{-4},$$

$$f_3 = 5.784, \quad \alpha_3(0) = 1.224 \times 10^{-24} \text{ cm}^3.$$

The sum $\alpha(0)$ is 1.570×10^{-24} cm^3, which agrees well with the result obtained from our one term formula and coincides with the previously obtained value (London[2]). Our value for the oscillator strength of the second band, $f_2 = 0.215$, agrees well with a previously recorded value 0.193, which was obtained from absorption data (Ladenburg et al.[40]).

2. Liquid Oxygen

The data we used consist of three measurements in the visible region, at 90.21 °K, (the boiling point of oxygen) and at 1 atm (Johns and Wilhelm[38]). We employed only one frequency, the same as in the one-term formula for the gaseous state. The value of $\Delta_n^{1/2}$ is 4.1×10^{-4}, which is below the experimental error. The values of the parameters are:

$$\gamma = 1.1 \times 10^{16} \text{ rad/sec}, \quad C = 0.139,$$

$$\alpha(0) = 1.552 \times 10^{-24} \text{ cm}^3$$

(using $N = 2.15 \times 10^{22}$ molecules/cm^3). The value obtained for the static polarizability is very close to that obtained for it in the gaseous state of oxygen.

E. Carbon Dioxide

The dispersion data for gaseous carbon dioxide include measurements of refractive indices at wavelengths varying from 0.238 to 13.75 μ. We used the dispersion data at 0 °C and 1 atm. (Fuchs[41]; Statescu[42]; Cuthbertson and Cuthbertson[43]; International Critical Tables[26b]). The data include 54 measurements in the visible and ultraviolet region and 49 measurements in the infrared region. We employed one absorption frequency in the ultraviolet, $\omega = 2.175 \times 10^{16}$ rad/sec, which corresponds to the ionization potential of gaseous carbon dioxide, 14 eV (Fuchs[41]), and two absorption frequencies in the infrared, at wavelengths 4.29 and 14.7 μ. There is another band at 2.75 μ but insufficiency of data prevented us from including another term in the dispersion formula.

The value of $\Delta_n^{1/2}$ we obtain is 2×10^{-5}. We also compared our results with two previously obtained dispersion formulas. The one-term dispersion formula of Cuthbertson and Cuthbertson,[43] yields a value $\Delta_n^{1/2} = 1.2 \times 10^{-4}$, whereas the four-term formula of Fuchs[41], which includes two infrared terms, results in $\Delta_n^{1/2} = 7 \times 10^{-5}$. We obtain a better over-all fit but the previous dispersion formulas are somewhat better in the visible region. The improved fit we obtain is largely due to the introduction of damping factors, which help in reducing $\Delta_n^{1/2}$ by about a factor of 2.

The resulting parameters are:

$\lambda_1 = 4.29 \mu$, $\gamma_1 = 10^{12}$ rad/sec, $C_1 = 1.60 \times 10^{-5}$,

$\qquad f_1 = 8.96 \times 10^{-6}$ $\alpha_1(0) = 0.142 \times 10^{-24}$ cm^3,

$\lambda_2 = 14.7 \mu$, $\gamma_2 = 1.1 \times 10^{13}$ rad/sec, $C_2 = 1.89 \times 10^{-5}$,

$\qquad f_2 = 1.27 \times 10^{-4}$ $\alpha_2(0) = 0.168 \times 10^{-24}$ cm^3,

$\lambda_3 = 0.087 \mu$, $\gamma_3 = 5 \times 10^{15}$ rad/sec, $C_3 = 2.89 \times 10^{-4}$,

$\qquad f_3 = 4.78$, $\alpha_3(0) = 2.564 \times 10^{-24}$ cm^3.

From this $\alpha(0) = 2.87 \times 10^{-24}$ cm^3, which is in good agreement with the previously obtained value, $\alpha(0) = 2.86 \times 10^{-24}$ cm^3 (London[2]). The atomic polarizability in this case is about 10% of the total static polarizability.

V. DISCUSSION

A. Oscillator Strengths

By the application of time-dependent perturbation theory it is obtained[19] that

$$\alpha(\omega) = (2/\hbar) \sum_i \omega_i m_{x_{i0}}^2 / (\omega_i^2 - \omega^2), \qquad (19)$$

where $\hbar$ is Planck's constant divided by 2π, $m_{x_{i0}}$ is the matrix element of the X component of the electric dipole between the ground state 0 and an ex-

cited state i, and ω_i indicates an absorption frequency from the ground state to the state i. In Eq. (19) the imaginary part of the polarizability is neglected; we therefore will compare it with the corresponding semiclassical expression, Eq. (8), in which damping is neglected. We thus obtain

$$f_i = \omega_i |m_{x_{i0}}|^2 2m_i / \hbar e_i^2$$
$$= \omega_i |m_{i0}|^2 2m_i / 3\hbar e_i^2 \qquad (20)$$

On the other hand Eq. (10) provides the values of the oscillator strengths f_i in terms of the coefficients C_i. The calculated values of the oscillator strengths in the case of liquid water (with five terms) are listed in Table II, parts A and B.

The first observation to be made is that f_5 is much larger than the sum of all other oscillator strengths. By making use of Eq. (20) for $i = 5$ the value of $|m_{x_{50}}|$ turns out to be 3.7×10^{-18} esu, i.e., about twice the magnitude of the permanent electric dipole moment.[11] Hence the value obtained by us for f_5 is certainly too large.

The second observation is that the sum of oscillator strengths, 2.04, is much lower than 10, which is the number of electrons in a water molecule.

Let us first discuss the question of the sum of oscillator strengths. Note that f_i is proportional to the product $C_i \omega_i^2$. If ω_i is a frequency in the far ultraviolet region f_i may turn out to be considerable when C_i is very small. As discussed in Sec. III, the sum of the C_i's should be bound by about 1/2, say, in order to satisfy Eq. (17) at low frequencies. However, this sum may still preserve its present value by splitting the value of C_5 between C_5, C_6, $C_7 \cdots$, where the indices 5, 6, $7 \cdots$ designate, in our case, coefficients in the ultraviolet region. Thus, due to the proportionality between f_i and $C_i \omega_i^2$ the sum of oscillator strengths may increase to a value of ten without affecting the sum of the C_i's, when more absorption frequencies in the far ultraviolet are considered. In fact, the inclusion of a single ultraviolet term in our calculation on liquid water with Dorsey's[22] data was merely a result of not having sufficient ultraviolet dispersion data.

This question of the sum of oscillator strengths is connected with the observation that f_5 turns out to be too large. This happens because C_5 absorbs the missing coefficients C_6, $C_7 \cdots$. In the previous section (IV. A) we mentioned that when the data of Painter et al.[25] were employed with three frequencies in the ultraviolet region the value of C_5 was split between three coefficients. It is noteworthy that recent results[44] by a different method, i.e., by an integration over absorption bands up to a value of $E_0 = 14.6$ eV, yield a value of approxi-

mately unity for the summed oscillator strengths.

The omission of more frequencies in the far ultraviolet is responsible for the high values of f_5 and $|m_{50}|$ and for the small value of the sum of oscillator strengths.

It should be stressed that due to the proportionality between f_i and $C_i\omega_i^2$ the contribution to the sum of oscillator strengths from additional frequencies at longer wavelengths, i.e., in the infrared region, is unlikely to be considerable.

As previously indicated the oscillator strengths which correspond to the infrared bands in liquid water, ω_1 to ω_4, turn out to be very small, although the absorption peaks are high and broad. It is known[24,28] that these absorption bands correspond to oscillatory motion of particles with masses which are several orders of magnitude larger than the electronic mass. When Eq. (10) is used with masses which correspond to the respective mode of vibration and with a unit electronic charge, the values of the oscillator strengths turn out to range from 0.1 to 1 instead of 4×10^{-6} to 2×10^{-4}.

To be more specific we will cite the assignments proposed for the four bands. According to Ref. 24 and Ref. 28 (pp. 228–231), ω_1 and ω_2 correspond to intermolecular motions. The band centered at ω_3 is due to bending of the H–O–H bonds. This band overlaps a weak broad band having a maximum at 2125 cm^{-1}, which has no analog in the gaseous state and is often called the association band. The band centered at ω_4 corresponds to a stretching frequency of the O–H bond. This band is in fact composed of the fundamental symmetric and asymmetric stretching modes. Absence of more data has prevented us from more detailed analysis of this band.

In all cases, i.e., hydrogen, oxygen, and water, ultraviolet oscillator strengths do not differ between the liquid and gaseous states. This is consistent with the picture that the electronic motion does not depend strongly on the intermolecular surroundings and is not affected much by intermolecular forces.

It should be however mentioned that the first ultraviolet band in liquid water is appreciably shifted from its position in the gaseous state. Thus, the agreement between the results for the ultraviolet oscillator strength in the liquid and gaseous states of water may arise for ultraviolet bands whose oscillator strengths are absorbed in the value of f_5.

At present we do not have any information on the oscillator strengths for the gaseous state of water in the infrared region. As mentioned before there

is at least one band in the liquid state which has no analog in the gaseous state.

B. Damping Factors

The damping factor γ in Eq. (5) is a sum of radiation damping γ_r and collision or interaction damping γ_b. γ is the inverse of the relaxation time of the oscillator in the classical formulation, or of the energy level in the semiquantum formulation.[19] It is shown[18,19] that γ equals the linewidth when the Doppler effect is not taken into account.

The classical result for γ_r,[18,19] i.e., $\gamma_r = \frac{2}{3}(e^2\omega^2/mc^3)$ yields a value of about 2×10^9 rad/sec when ω is equal to 1.9×10^{16} rad/sec. and e and m are the electronic charge and mass, respectively. For frequencies in the infrared region γ_r is much smaller. The quantum mechanical analog of γ_r, the natural linewidth, is less than 10^9 rad/sec. These values are negligibly small compared with the observed band widths in the liquid state, which are larger than 10^{13} rad/sec. This means that γ essentially equals γ_b, i.e., γ represents collision or interaction broadening. The damping factor which appears in Eq. (5) does not include Doppler broadening, but the widths of observed bands are several orders of magnitude larger than widths due to the Doppler effect.[19]

In the following we show that our values for the damping factors agree fairly with observed widths of bands. Since absorption intensity of bands is in general plotted versus λ, the wavelength, the widths $\Delta\omega$ are obtained from the relation $\Delta\omega = \Delta\lambda 2\pi C/\lambda^2$. For liquid water, $\Delta\omega_1 = 4\times10^{13}$ rad/sec (Ref. 24) whereas $\gamma_1 = 5.0\times10^{13}$ rad/sec;

$$\Delta\omega_2 = 6\times10^{13} \text{ rad/sec}, \quad \gamma_2 = 1.0\times10^{14} \text{ rad/sec},$$

$$\Delta\omega_3 = 10^{14} \text{ rad/sec}, \quad \gamma_3 = 2.6\times10^{13} \text{ rad/sec},$$

$$\Delta\omega_4 = 7\times10^{13} \text{ rad/sec}, \quad \gamma_4 = 1.3\times10^{14} \text{ rad/sec}$$

(see Ref. 28, p. 230).

As previously mentioned, the absorption band in the ultraviolet, ω_5, includes at least three absorption bands so it is expected that we obtain a large value for γ_5. The width $\Delta\omega$ of one of these three bands, which has a peak at 1510 Å, is about 10^{15} rad/sec, whereas we obtain $\gamma_5 = 5.9\times10^{15}$ rad/sec.

Our value for the damping factor of the 4.3 μ band in CO_2, $\gamma = 11\times10^{12}$ rad/sec, is close to the half-bandwidth $\Delta\omega = 8.5\times10^{12}$. In the case of hydrogen where bands are very narrow no improvement was obtained by employing damping factors. It should be noted that no attempt has been made to determine γ values which agree with observed bandwidths. We only looked for a set of damping factors which would give the best fit of calculated to observed values of refractive index. In doing so we

wanted to test the power of the theory and the procedure on several representative cases. In further work it may be recommended to limit the individual γ values in some range of values centered at the corresponding bandwidths.

C. Application of Onsager's Theory to Liquid Water

Onsager developed a set of equations based on the idea that in considering orientation effects the reaction field of the permanent dipole should not be taken into account, since it is parallel to the instantaneous orientation of the permanent dipole. In developing the equations, the polarizability of the molecule was expressed in terms of an "internal refractive index" n,

$$\alpha = [(n^2 - 1)/(n^2 + 2)] a^3, \tag{21}$$

where a is the radius of a spherical molecule in a liquid.

The application of Onsager's equations to the case of liquid water resulted in a value of 3.10^{-18} esu for the permanent dipole moment, whereas the experimental value (from vapor measurements) is 1.84×10^{-18} esu. Hence it has been concluded that the theory is still unsatisfactory for the case of water or associated liquids in general. We find it of interest to point out that when we apply Onsager's theory, using our values for the polarizability of liquid water, we obtain values of the permanent dipole moment of water which are close to the experimental values.

Following Böttcher, [17] Onsager's equation for the case of a pure liquid can be written in the form

$$(\epsilon - 1)(2\epsilon + 1)/12\pi\epsilon = N\alpha/(1 - f\alpha) + N\mu^2/(1 - f\alpha)^2 3kT, \tag{22}$$

in which f is the factor of the reaction field,

$$f = 1/a^3 \times (2\epsilon - 2)/(2\epsilon + 1). \tag{23}$$

Another relation used by Onsager and Böttcher for liquids is

$$(4\pi N/3)a^3 = 1. \tag{24}$$

When Eqs. (21)–(24) are used for the case of liquid water (at $T = 293°$, $\epsilon = 80.4$) it turns out that μ is approximately 3×10^{-18} esu. About the same result is obtained when Eq. (21) is avoided by substituting the value $\alpha = 1.44 \times 10^{-24}$ cm³ previously recorded in the literature.

Making use of Eqs. (22) to (24) we obtain: for $\alpha = 4.04 \times 10^{-24}$ cm³, (See Table II, part A), $\mu = 1.70 \times 10^{-18}$ esu; for $\alpha = 3.947 \times 10^{-24}$ cm³, (See Table II, part B), $\mu = 1.75 \times 10^{-18}$ esu. These values are close to the experimental value $\mu = 1.84 \times 10^{-18}$ esu.

So far we have shown that Onsager's theory gives good predictions for liquid water at 20 °C. Since Onsager's theory predicts an approximate linear decrease of ϵ with $1/T$ we would tend to believe that a good agreement will be also obtained at other temperatures. However, before we have more data to determine α at other temperatures we cannot say whether the agreement obtained is fortuitous or not. We would speculate that the same improved agreement with experiment of Onsager's theory, would be obtained in the case of alcohols if larger values of α will be employed.

D. Conclusion

The main goal of this work is to establish a procedure to determine with sufficient precision the complex polarizability and dielectric permeability at optical frequencies. These quantities may be used to calculate intermolecular forces.

A good agreement between calculated and measured values of refractive indices is obtained for all substances treated.

We would like to summarize our results in some conclusions:

1. The Lorenz–Lorentz equation [Eq. (4)] seems to hold for all substances, including liquid water throughout all the optical region.

2. The inclusion of an imaginary part in the expression for the polarizability in the form of damping factors improves the fit. [Its inclusion was necessary to prevent infinitely high values of $\alpha(\omega)$ at resonance frequencies.]

3. The absorption coefficients, $\bar{\mu}(\omega)$, and imaginary part of refractive index, $k(\omega)$, are predicted fairly well at the peaks of absorption bands and up to an order of magnitude inside the infrared absorption bands. The simple semiclassical theory of polarizability as due to the motion of bound and damped oscillators is insufficient to predict the values of $k(\omega)$ and $\bar{\mu}(\omega)$ for frequencies outside the bands.

4. Damping factors, γ_i, which yield the minimal error in the least square calculations agree within a factor of one to three with the corresponding bandwidths, in accord with the semiclassical picture.

5. The contribution of electronic motion to the polarizability extrapolated to infinite wavelength is about the same in both the liquid and gaseous states of water, hydrogen and oxygen.

6. Liquid water has the peculiar feature that the atomic and molecular motions contribute the major part to the polarizability extrapolated to infinite wavelengths. Significantly different values may therefore emerge in future calculations of in-

termolecular forces in water-containing systems.

7. Onsager's theory is shown to yield the experimental value of the permanent dipole of water from the dielectric constant and polarizability of liquid water.

When comparing the results for the substances treated, i. e., gaseous and liquid water, hydrogen, oxygen, gaseous carbon dioxide, and also our preliminary results for benzene, carbon disulfide, and carbon monoxide[46] we find out that liquid water is unique in its possessing an extremely high value of the atomic and molecular polarizability, which is obtained by an extrapolation of the infrared polarizability to infinite wavelength. In this framework of our study we do not attempt to provide an explanation to that, but rather point out that the high value of atomic polarizability can be regarded as one more anomaly of liquid water. We would speculate that it is related to the role of hydrogen bonds in the structure of liquid water.

With our value of the static polarizability Onsager's theory is now satisfactory for liquid water.

We will attempt to extend this work to other substances. In fact we have already preliminary encouraging results for glass and work is being done on benzene, carbon disulfide and carbon monoxide. It is also possible to extend the treatment and to improve the results for water when more abundant and precise data for both the real and imaginary part of the refractive index become available.

It will be of interest to perform similar studies at different temperatures, and for other associated liquids.

A recent quantum mechanical calculation (Hartree–Fock SCF) of the electronic polarizability of water[45] gives values from 0.509×10^{-24} cm^3 (with a basis of 7 atomic orbitals) to 1.13×10^{-24} cm^3 (with a basis of 27 atomic orbitals) for the static polarizability. Our use of an IEHT ground state wavefunction and employment of configuration interaction with nine configurations yields a value of the static polarizability close to that obtained previously with the same size of the basis set.

It seems that for the purpose of polarizability calculations employment of our semiclassical method developed in the present work is advantageous over quantum mechanical calculations even for gases.

APPENDIX A

Equation (12) is a quadratic equation in n^2, whose solution is

$$n^2 = [-B + (B^2 - 4AC)^{1/2}]/2A \tag{A1}$$

in which,

$$A = 1 - \text{Re}(\beta)$$

$$B = (1 + 2k^2) - \beta 2(k^2 + 2)$$

$$C = (2 - k^2)[-k^2 - 1 - \text{Re}(\beta)(2 - k^2)]$$

Eq. (A1) reduces to Eq. (17) when k approaches zero.

APPENDIX B. CALCULATION OF DISPERSION FORCES ACCORDING TO THE LIFSHITZ THEORY

We illustrate here how to obtain the dielectric permeability on the imaginary frequency axis and show how this quantity is related to calculation of dispersion forces according to the Lifshitz theory. [4,5]

The equation for the attractive force F acting on a unit area of each of two semiinfinite slabs which are separated by a gap of width d, the gap being occupied by a substance different from that of the slabs, is[4,5,9,10]

$$F = \hbar \bar{w}/8\pi^2 d^3$$

$$\bar{w} = \int_0^\infty \left[\frac{\epsilon_1(i\xi) - \epsilon_2(i\xi)}{\epsilon_1(i\xi) + \epsilon_2(i\xi)}\right]^2 \exp(-2d\xi \sqrt{\epsilon_2(i\xi)} /C)$$

$$\times (1 + 2d\xi \epsilon_2^{1/2}(i\xi) + 2(d\xi/c)^2 \epsilon_2(i\xi))d\xi, \tag{B1}$$

where $\epsilon_1(i\xi)$ and $\epsilon_2(i\xi)$ are the dielectric permeabilities of the media evaluated on the imaginary frequency axis. Due to the decaying exponent the contribution from large frequencies, say, beyond 10^{17} rad/sec, is negligibly small so that detailed knowledge of $\epsilon(i\xi)$ in this region is not critical when d is assumed to be around 1000 Å [Eq. (B1) refers to $T = 0\,°K.$]

On the imaginary frequency axis, $w = i\xi$, both

TABLE V. Variation of the dielectric permeability of liquid water on the imaginary frequency axis.

w (rad/sec)	$\epsilon(iw)$ [Eq. (13)]	$\epsilon(iw)$ [Eq. (12)]	$\epsilon(iw)$ (ultraviolet terms)
2.0×10^{14}	2.072	2.093	2.023
2.0×10^{15}	1.735	1.733	1.695
2.0×10^{16}	1.277	1.273	1.248
2.0×10^{17}	1.005	1.005	1.005

TABLE VI. Values of real β for different values[a] of n and k.

n	$k = 0$	0.01	0.05	0.1	0.2	0.5	1
1.1	0.0654	0.0654	0.0654	0.0669	0.0715	0.1095	0.3182
1.3	0.1870	0.1870	0.1874	0.1888	0.1944	0.2369	0.4234
1.4	0.2424	0.2424	0.2429	0.2443	0.2500	0.2922	0.4651
1.5	0.2941	0.2941	0.2946	0.2960	0.3016	0.3425	0.5016
1.7	0.3865	0.3865	0.3869	0.3882	0.3934	0.4300	0.5628
2.0	0.5000	0.5000	0.5003	0.5014	0.5055	0.5346	0.6341

[a] Calculations of real β are performed according to Eq. (12). The case $k = 0$ corresponds to using Eq. (13).

α, β, and ϵ are real. From Eq. (9) it follows that

$$\beta(i\xi) = \sum \frac{C_i}{[1 + (\omega/\omega_i)^2 + \gamma_i \omega/\omega_i^2]} \tag{B2}$$

and

$$\epsilon(i\xi) = [1 + 2\beta(i\xi)] / [1 - \beta(i\xi)]. \tag{B3}$$

In Table V we present values of $\epsilon(i\xi)$ of liquid water which result from three sets of parameters:

1. Calculation according to Eq. (13) with five coefficients.

2. Calculation according to Eq. (12) with five coefficients.

3. Calculation according to Eq. (12) with seven coefficients, the uv coefficient C_3 being split between C_5, C_6 and C_7, where the coefficients C_5, C_6, C_7 are obtained by using two ultraviolet bands.

It should be mentioned that in Case 3 we used the same infrared parameters as in Case 1. Also, Case 1 and 2 correspond to a temperature of 20 °C, whereas in Case 3 the ultraviolet parameters correspond to a temperature of 1 °C.

The results indicate that for the purpose of calculating dispersion forces according to Eq. (B1) there is not an appreciable difference between the three sets of values. In fact the difference between the first and the second set is about 1% in the infrared and less than 0.1% in the ultraviolet region.

In order to illustrate how critical is the detailed spectral information in the far ultraviolet region for the purpose of force calculations at small values of d we consider the hypothetical system water–vacuum–water.

From the analysis in Sec. III it follows that the result for the sum of coefficients C_i in the ultraviolet region will be independent of the last (largest) effective ultraviolet absorption frequency employed. By shifting this effective absorption frequency the values of $\epsilon(i\omega) - 1$ in the infrared and visible regions will not be significantly affected.

On the other hand a blue shift of the effective ultraviolet absorption frequency will lead to a relative significant increase in the value of $\epsilon(i\omega) - 1$ in the ultraviolet region. As a result such a blue shift will yield larger values of $\bar{w}$ and F in Eq. (B1). For instance, when a value of $\omega_{uv} = 3 \times 10^{16}$ rad/sec is used and $d = 50$ Å, F becomes 1.8×10^5 dyn/cm^2 instead of 1.2×10^5 obtained with $\omega = 1.906 \times 10^{16}$ rad/sec. For $\omega_{uv} = 5 \times 10^{16}$ rad/sec F becomes 2.8×10^5 dyn/cm^2. Hence the uncertainty in the calculations may reach a factor of two at small distances of separation. We have however to point out that the agreement with experimental values of refractive indices of the results of calculations of the semiempirical method worsens with a blue shift of the effective ultraviolet frequency.

APPENDIX C

We present a table which illustrates the variation of the right hand side of Eqs. (12) and (13) with different values of n and k (see Table VI).

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