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## The Absorption of Dipole Liquids in the Visible

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According to the original theory of Debye, the absorption of dipole liquids for electromagnetic waves should rise to a constant value with increasing frequency. Water and the alcohols would then be opaque in the visible. Rocard has taken inertia into account. This results in a decrease of the absorption from the plateau at even higher frequencies. This decrease is, however, too slow to account for the measurements.

According to the elementary Debye theory of dipole liquids,<sup>1</sup> one has

$$\epsilon' - i\epsilon'' = \epsilon_\infty + N \frac{p_0^2}{3kT} \frac{1}{1 + i\omega\tau} = \epsilon_\infty + N \frac{p_0^2}{3kT} \frac{1 - i\omega\tau}{1 + \omega^2\tau^2} \quad (1)$$

If one takes interaction between molecules into account,<sup>2</sup> the result can be written as

$$\epsilon' - i\epsilon'' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \frac{1 - i\omega\tau}{1 + \omega^2\tau^2} \quad (2)$$

where now  $\epsilon_\infty$ ,  $\epsilon_0 - \epsilon_\infty$ , and  $\tau$  are taken from experiment.

The absorption coefficient per cm. for intensity can then be expressed as

$$\alpha = \frac{1}{n} \frac{\omega}{c} \epsilon'' = \frac{\epsilon_0 - \epsilon_\infty}{nc} \frac{\omega^2\tau}{1 + \omega^2\tau^2} \quad (3)$$

provided  $\alpha\lambda$  is small, which is fulfilled for the region to be discussed. Here  $\lambda$  is the vacuum wave length,  $n$  the refractive index. The frequency dependence is the usual one for relaxation phenomena, e.g., ultrasonic waves. For  $\omega\tau \gg 1$

$$\alpha = \frac{\epsilon_0 - \epsilon_\infty}{nc\tau} \quad (4)$$

If one takes for water  $\epsilon_0 - \epsilon_\infty \sim 80$ ,  $\tau = 8 \times 10^{-12}$  sec.,<sup>3</sup>  $n$  (for visible light) = 1.33, one has  $\alpha = 240$  cm.<sup>-1</sup>, i.e., water should be black in layers of a few mm.<sup>4</sup> With slightly different figures this is also true for alcohols.

Hettner<sup>4</sup> has already suggested that this absurd result is due to the neglect of inertia in the original Debye theory. Rocard<sup>5</sup> has taken inertia into account; his formulas are written in a very complicated form, particularly since he includes higher powers of  $p_0E$  (saturation effects). If one drops these higher terms and assumes again that the transition to the liquid changes only the constants, one finds that Rocard's equation takes the simple form

$$\epsilon = \epsilon' - i\epsilon'' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{(1 + \omega^2\tau_1^2)(1 + \omega^2\tau_2^2)} [1 + \frac{\omega^2\tau_1\tau_2 - i\omega(\tau_1 + \tau_2)}{1 + \omega^2\tau_1^2 + \omega^2\tau_2^2}] \quad (5)$$

(1) P. Debye, *Verhandl. deut. physik. Ges.*, **15**, 777 (1913); "Polar Molecules," The Chemical Catalog Co., Dover Publishing Co., New York, N. Y., 1929.

(2) P. Debye, *Physik. Z.*, **36**, 100, 193 (1935); P. Debye and W. Ramm, *Ann. Physik.*, (V) **28**, 28 (1937).

(3) W. Hackel and M. Wien, *Physik. Z.*, **38**, 767 (1937).

(4) C. Hettner, *ibid.*, **38**, 771 (1937). To compare the above figure of 240 with Hettner's, it should be remembered that  $\alpha = 4\pi(nk/\lambda)$ .

(5) Y. Rocard, *J. phys. radium*, (VII) **4**, 247 (1933).

or

$$\alpha = \frac{\epsilon_0 - \epsilon_\infty}{nc} \frac{\omega^2(\tau_1 + \tau_2)}{(1 + \omega^2\tau_1^2)(1 + \omega^2\tau_2^2)} \quad (6)$$

Here  $\tau_1$  is the Debye frictional relaxation time

$$\tau_1 = \frac{4\pi\eta a^3}{kT} \quad (7')$$

while  $\tau_2$  is a new relaxation time ( $I$ , moment of inertia)

$$\tau_2 = \frac{I}{8\pi\eta a^3} \quad (7'')$$

Therefore

$$\tau_1\tau_2 = \frac{I}{2kT} \quad (8')$$

We will determine  $\tau_1$  from experiment ( $8 \times 10^{-12}$  sec.) and assume (8') to remain valid in the liquid. If one takes for  $I$  the geometrical average of the three moments of inertia of water, and sets  $T = 295^\circ$ , one finds

$$\tau_2 = 2.8 \times 10^{-14} \text{ sec.} \ll \tau_1 \quad (8'')$$

Considering the frequency dependence of  $\alpha$  in (6), one finds it the same form as in the usual dispersion theory with heavy damping, where

$$\alpha = A \frac{\omega}{c} \frac{\omega\omega'}{(\omega_0^2 - \omega^2)^2 + \omega^2\omega'^2} = \frac{A}{c} \frac{\omega^2\omega'}{\omega_0^4 + \omega^2(\omega'^2 - 2\omega_0^2) + \omega^4} \quad (9)$$

since (6) can be written

$$\alpha = \frac{\epsilon_0 - \epsilon_\infty}{nc} \frac{\tau_1 + \tau_2}{\tau_1^2\tau_2^2} \frac{\omega^2}{\left(\frac{1}{\tau_1\tau_2}\right)^2 + \omega^2\left(\frac{1}{\tau_1^2} + \frac{1}{\tau_2^2}\right) + \omega^4} \quad (10)$$

Therefore

$$\omega_0^2 = \frac{1}{\tau_1\tau_2}$$

and

$$\omega' = \frac{1}{\tau_1} + \frac{1}{\tau_2}$$

Since  $\tau_1 \gg \tau_2$ ,  $\alpha$  rises from

$$\alpha = \frac{\epsilon_0 - \epsilon_\infty}{nc} \omega^2(\tau_1 + \tau_2) \sim \frac{\epsilon_0 - \epsilon_\infty}{nc} \tau_1\omega^2 \quad (11)$$

TABLE I  
 ABSORPTION IN WATER IN THE NEAR-INFRARED AND VISIBLE

$\lambda$ in $\mu$	2.2	1.67	1.08	0.8	0.7	0.65	0.594	0.580
$\bar{\nu}$	4500	5100	9300	12500	14300	15400	16800	17200
$\alpha_{\text{exptl}}$	17	5	0.13	0.02	0.006	0.0035	0.002	0.001
$\alpha_{\text{calcd}} (1)$	4.2	0.34	0.1	0.05	0.042	0.037	0.031	0.029
$\alpha_{\text{calcd}} (2)$	0.12	0.01	0.003	0.0015	0.0012	0.001	0.00086	0.00080

for  $\omega\tau \ll 1$ , *i.e.*, the value of the original Debye theory, to a plateau

$$\alpha = \frac{\epsilon_0 - \epsilon_\infty}{nc\tau_1} \frac{\tau_1 + \tau_2}{\tau_1} \sim \frac{\epsilon_0 - \epsilon_\infty}{nc\tau_1} \quad (12)$$

*i.e.*, again the Debye value (4), for the range  $\omega\tau_2 \ll 1 \ll \omega\tau_1$ . But for  $\omega\tau_2 > 1$ , it drops again according to

$$\alpha = \frac{\epsilon_0 - \epsilon_\infty}{nc\tau_1} \frac{\tau_1 + \tau_2}{\tau_1} \frac{1}{1 + \omega^2\tau_2^2} \sim \frac{\epsilon_0 - \epsilon_\infty}{nc\tau_1} \frac{1}{1 + \omega^2\tau_2^2} \quad (13)$$

If we introduce the wave number  $\bar{\nu} = \omega/2\pi c$  and the wave number at which the second drop is half-completed

$$\bar{\nu}_2 = \frac{1}{2\pi\tau_2 c} \quad (14)$$

Equation 13 can be rewritten

$$\alpha = \frac{\epsilon_0 - \epsilon_\infty}{nc\tau_1} \left[ 1 + \left( \frac{\bar{\nu}}{\bar{\nu}_2} \right)^2 \right]^{-1} \quad (15)$$

The value of  $\tau_2$  given in (8') corresponds to  $\bar{\nu}_2 = 190 \text{ cm.}^{-1}$ . If the mutual interactions in the liquid should affect (8') one would expect an increase in the effective moment of inertia, *i.e.*, a decrease in  $\bar{\nu}_2$ .

Equation 15 describes a decrease of the absorption coefficient from the constant value (12) with increasing frequency, but this decrease is rather slow. *E.g.*, to a 5000-fold decrease in  $\alpha$ , from the half-way point, one needs a 100-fold increase in  $\bar{\nu}$ , to  $\bar{\nu} = 19,000$ .

One cannot get the experimental data easily. For  $\omega\tau_1 < 1$ , the Debye and therefore the Rocard expressions are well satisfied.<sup>4</sup> However, at higher frequencies, vibrational absorptions are superposed. In Table I the minima between vibrational absorption maxima from Curcio and Petty's<sup>6</sup> data have been used, but these numbers are probably too large since they contain unknown contributions from the bands. Sulli-

van's<sup>7</sup> data are too large because of scattering (by a factor of about 2) but probably do not contain band contributions. In Table I  $\alpha_{\text{calcd}} (1)$  is calculated from (15) with  $\bar{\nu}_2 = 190$ ,  $\alpha_{\text{calcd}} (2)$  with  $\bar{\nu}_2 = 32$ . At the high frequency end, the absorption  $\alpha_{\text{calcd}} (1)$ , calculated with  $\bar{\nu}_2 = 190$ , is too large, perhaps by a factor 36, so a second calculation  $\alpha_{\text{calcd}} (2)$  was made with  $\bar{\nu}_2 = 190/6 = 32$ ; this means that  $\tau_2$  and the effective moment of inertia  $I$  are six times larger, which seems not unreasonable. But it is clear that the theory cannot explain the abrupt drop in absorption, which does occur, *e.g.*, by a factor 20 in the wave number interval 12,500–17,300. For either value of  $\bar{\nu}_2$ , there should be a minimum in absorption between  $\bar{\nu}_2$  and the onset of vibrational absorption. Measurements are needed in this region.

For heavy water,<sup>7</sup> one should expect  $\tau_1$  to be the same, but the effective moment of inertia  $I$ , whether affected by coupling or not, to be twice as large; this means that  $\bar{\nu}_2$  should be half that for light water, and the absorption in the range considered one-quarter that in light water (Table II).

 TABLE II  
 ABSORPTION OF HEAVY WATER IN THE VISIBLE<sup>a</sup>

$\lambda$ in $\mu$	0.8	0.7	0.65	0.58
$\alpha_{\text{exptl}}$	7.5	4.5	3.4	$4.9 \times 10^{-4}$

<sup>a</sup> See ref. 7.

The only explanation which comes to mind at present for the behavior between  $\lambda = 2.2$  and  $0.6 \mu$  is a dipole absorption corresponding about to  $\alpha_{\text{calcd}} (2)$  on which is superposed an unresolved absorption due to higher vibrational combination bands, together with weak companion bands due to libration.<sup>8</sup> Such absorption might drop rather sharply on the high frequency side. For alcohols, the absorption on the plateau should be less than in water since  $\epsilon_0 - \epsilon_\infty$  is smaller and  $\tau_1$  larger than in the latter.  $\tau_2$  ought to be smaller than in water if only the HO group rotates, *i.e.*, if  $I$  is about the same. If the whole molecules rotates, one cannot predict values for  $\tau_2$ . There seem to be almost no experimental data for that region.

(7) S. Sullivan, *ibid.*, **53**, 962 (1963). <sup>4</sup>

(8) R. G. Gordon, *J. Chem. Phys.*, **38**, 1724 (1963); **39**, 2783 (1963).

(6) J. A. Curcio and C. C. Petty, *J. Opt. Soc. Am.*, **41**, 302 (1951).