Hindered Rotation in Liquid H₂O and D₂O

C. HAWLEY CARTWRIGHT, *Department of Physics, University of Michigan*

(Received March 2, 1936)

THE spectra of molecules in the liquid and vapor state are often so similar that one has often assumed the origin of the absorption to be the same, that is, due to characteristic intramolecular vibrations of the atoms and rotation of the molecules. The lack of fine structure in the part attributed to rotation in liquids was accounted for by a small free path of the translational motions. The absorption spectra of liquid water and water vapor from 1μ to 20μ [1] under low resolution are indeed strikingly similar. It is only as we proceed to longer wave-lengths that the differences become great both in absolute magnitude and the shape of the absorption curves; and these differences cannot be entirely accounted for by the influence of viscosity on an orientation of the permanent dipoles.

Recently it has been found that many properties of liquid could for the first time be successfully explained by assuming a liquid to be more nearly a solid than a dense gas. The molecules of a liquid are thought of as forming a quasi-crystalline structure in which there is no free path at all and the molecules vibrate about slowly displaced equilibrium positions, with a frequency which is about the same as that of the molecules in the solid state.[2] The concept of a quasi-crystalline structure in liquids however does not exclude the possibility of free rotation for, as Pauling has shown, the molecules rotate in certain solids. Whether free or hindered rotation occurs depends on the intermolecular field of potential energy. In the case of liquid water, Debye[3] has calculated from two different types of experimental data that an energy of $10kT$ is necessary to turn a water molecule through 90°. Bernal and Fowler[4] have been able to explain several physical properties of liquid water by assuming a tetrahedral quartz-like structure in which each water molecule is surrounded by four others. From calculating the

intermolecular field of this model,[5, 6] a characteristic frequency is predicted at 60μ due to a mutual vibration between water molecules and a frequency at 20μ due to hindered rotation. The 60μ band should appear only changed by $(20/18)^{\frac{1}{2}}$ in D₂O while the 20μ band should be shifted to longer wave-lengths by the factor $\sqrt{2}$.

We have observed the infrared absorption, reflection and dispersion of liquid H₂O and D₂O and have established the existence of two strong, rather broad bands, one at about 60μ and the other at about 20μ. The 60μ ($\nu = 5 \times 10^{12}$ sec.$^{-1}$ or 160 cm^{-1}) band[7] (1) is practically the same in H₂O and D₂O, (2) is very strongly absorbing (a thickness of 10μ transmits only 30 percent at $\lambda = 60\mu$), (3) is present in ice, (4) disappears for water dissolved in dioxane, (5) increases but slightly the reflecting power and the index of refraction and (6) is Raman active.[5] The 20μ ($\nu = 15 \times 10^{12}$ sec.$^{-1}$ or 500 cm^{-1}) band (1) is shifted by about $\sqrt{2}$ in D₂O, (2) is strongly absorbing, (3) greatly increases the reflecting power (both the absorbing and reflecting powers are much greater than for the fundamental intramolecular vibration bands at 3μ and 6μ), (4) causes anomalous dispersion and (5) is weakly Raman active.

These results are a striking confirmation of the theory by Bernal and Fowler on liquid water although there is a certain difficulty in explaining the strong infrared activity of the 60μ band of hindered translation unless we assume that the surrounding molecules are forced to turn to follow the characteristic intermolecular vibrational frequency.[7] The nature of the two frequencies predicted by Bernal and Fowler, and found experimentally to be strongly infrared active, can perhaps be understood by the following order of magnitude calculation. One may suppose the water molecule to be bound by an intermolecular field. The molecule will then execute vibrations which fall into two main types. One involving a large amplitude of motion of

[1] H. Rubens and E. Ladenburg, Le radium 6, 33 (1909).
[2] E. N. da C. Andrade, Phil. Mag. 17, 497 (1934).
[3] P. Debye, Physik. Zeits. 36, 100, 193 (1935).
[4] J. D. Bernal and R. H. Fowler, J. Chem. Phys. 1, 515 (1933); Trans. Faraday Soc. 29, 1049 (1933).

[5] M. Magat, J. de phys. et rad. 5, 347 (1934).
[6] J. D. Bernal and G. Tamm, Nature 136, 229 (1935).
[7] C. H. Cartwright, Nature 136, 181 (1935).

the hydrogen atoms and one involving a large amplitude of motion of the oxygen atom. These vibrations are of course in addition to the three interatomic oscillations which appear in the near infrared. Assuming harmonic oscillations of a water molecule about the axis of smallest moment of inertia ($I = 0.998 \times 10^{-40}$; this would give the highest frequency, be infrared active and be practically only a motion of the hydrogen atoms), we obtain for the 20μ band in H_2O or the 28μ band in D_2O, according to the formula $\nu = 1/2\pi(K/I)^{\frac{1}{2}}$, a value of $K = 9 \times 10^{-13}$ dyne-cm or $22kT$. The water molecule would therefore be hindered from oscillating through an angle of about $\pm 27°$. If we assume that the oxygen atoms

vibrate in the same field as was found for the hydrogen atoms, the wave-length of the natural vibration period of the oxygen atoms would be 57μ, which agrees well with the experimental data. The amplitude of the vibrations of the oxygen atoms would be about 0.15A.

The results obtained experimentally when compounded with the Bernal and Fowler model of liquid water or when interpreted with an order of magnitude calculation show clearly that at room temperature the molecules in liquid water are hindered by a strong intermolecular field from executing a free rotational motion.

I am pleased to thank Professor Dennison for his helpful suggestions.

A Method for the Determination of the Selective Absorption Regions of Slow Neutrons

D. F. Weekes, M. Stanley Livingston and H. A. Bethe, *Department of Physics, Cornell University*
(Received March 4, 1936)

FERMI and Amaldi[1] and Szilard[2] have demonstrated that each element which shows a strong capture absorption of slow neutrons absorbs neutrons of a characteristic energy. These bands of selective absorption were originally assumed to be in the thermal or near-thermal region. Rasetti and Fink[3] have shown, however, that there is no temperature effect on these bands except for cadmium.

According to the Wigner-Breit[4] theory the selective absorption is explained as a resonance phenomenon. It is assumed that the nucleus which is formed by the capture of the neutron has some excited level whose energy is equal to that of the original nucleus plus a neutron of a certain energy E_0. If a neutron of this energy falls on the nucleus there may be a nonradiative transition (inverse "Auger-effect") into the above-mentioned excited state. This excited state will then, after a certain time, go over into the ground state with the emission of radiation rather

than disintegrate again with the emission of a neutron. The theory, therefore, explains also the large observed ratio of capture to scattering in strongly absorbing elements.

The probability of capture of a neutron of energy E is, according to this theory, given by:

$$\sigma_c = (a/E^{\frac{1}{2}}) \cdot (\gamma/(E-E_0)^2 + \gamma^2), \qquad (1)$$

where γ is the natural breadth of the energy level at E_0 as determined by its lifetime against radiation, and a, E_0 and γ are constants characteristic of the element. γ is estimated to be of the order 1 to 50 volts and E_0 of from 0 to 1000 volts. The capture cross section has, according to Eq. (1), two maxima, one at a very low energy (thermal) and one near E_0.

It is obvious that the velocity selectors for neutrons of thermal energies in use at present[5] cannot be readily extended to this energy region. We wish to propose here a simple experiment designed to measure these energies, which depends on a few relatively safe assumptions. The main assumption is that in certain elements (e.g., B and Li) the absorption is inversely propor-

[1] Amaldi and Fermi, Ricerca Scientifica VI–II, Nos. 9–10 (1935).
[2] Szilard, Nature 136, 950 (1935).
[3] Rasetti and Fink, Bull. Am. Phys. Soc., New York Meeting, Vol. 11, Nos. 1, 28 (Feb., 1936).
[4] Wigner and Breit, Bull. Am. Phys. Soc., New York Meeting, Vol. 11, No. 30 (Feb., 1936).
[5] Fink, Dunning, Pegram and Mitchell, Phys. Rev. 49, 103 (1936).