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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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LOW-FREQUENCY INFRARED ABSORPTION SPECTRUM OF THE HYDROGEN BOND IN LIQUID WATER AND CRYSTAL HYDRATES

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As was shown by E. F. Gross, V. I. Val' kov, and A. I. Stekhanov (^{1,2}), in the low-frequency region of the combination-scattering spectrum of ice and of a number of crystal hydrates there is observed a series of weak lines, which they interpreted as belonging to the vibrational spectrum of the hydrogen bond. It was of interest to discover the vibrational spectrum of the hydrogen bond in the low-frequency region of the infrared absorption spectrum of liquid (ordinary and "heavy") water, as well as of a number of crystals containing water of crystallization; this was the subject of the present work, carried out with the aid of the previously developed method and apparatus of long-wavelength infrared spectrometry (^{3,5}).

Fig. 1

1. Low-frequency absorption spectrum of liquid water. Long-wavelength infrared absorption of liquid water and ice was first investigated by Cartwright (^{4}), who, using the "residual rays" method, found a broad structureless absorption band with a center at $60\,\mu$ (170 cm^{-1}), caused by translational vibrations of water molecules along the lines of hydrogen bonds.

Figure 1 presents the transmission (T) and optical-density (D) curves obtained by us in the region 42–$200\,\mu$ for liquid ordinary water (A) and "heavy" water (B), with a layer thickness of 0.013 mm. From these curves it is seen that the broad band of vibrations with a center at 170 cm^{-1} is not simple, but reveals a structure with weakly expressed maxima that are absent in the spectrum of vapor (^{5}). Since the intensities of these bands were close to the noise level, their magnitude and position could be determined as average values from a large number of repeated measurements. If the constants of the quasi-elastic forces of the hydrogen bond in ordinary and "heavy" water are equal, the frequencies of the translational vibrations of ordinary and "heavy" water should be related

Fig. 2

Figure 2: Fig. 2

by—

Table 1

ν, cm^{-1}	232	210	191	175	160	145
H_2O	232	210	191	175	160	145
D_2O	221	196	181	166	156	140
$(\nu_{D_2O}/\nu_{H_2O})^2$	0.91	0.87	0.90	0.90	0.95	0.93

by the ratio $(\nu_{D_2O}/\nu_{H_2O})^2 = M_{H_2O}/M_{D_2O} = 0.90$ (where M denotes molecular masses), which, as is seen from Table 1, is satisfied satisfactorily.

If one considers two isolated water molecules between which a hydrogen bond is formed, then transitions between the various vibrational levels of the hydrogen bond (^{6,7}) will give, in the absorption and combination-scattering spectra, a series of bands with decreasing frequency and intensity, determined by the relation $e^{-E_i/kT}(\nu_i + 1)$. However, it is known that the molecules of liquid water are strongly associated; moreover, as recent investigations have shown (^{8}), almost all possible hydrogen bonds are realized in liquid water. Therefore, in considering the vibrational spectrum of the hydrogen bond it is necessary to take into account the molecular structure of liquid water.

On the basis of X-ray and spectral-investigation data (^{8}) it was shown that the structure of liquid water is well represented by a model in which the water molecules are located at the nodes of a distorted cubic lattice. Each water molecule participates in the formation of four hydrogen bonds and two bonds of the van der Waals type, realized between the oxygen atoms of molecules that do not form hydrogen bonds with one another. Since the interactions between oxygen atoms are small, in calculating translational vibrations one may approximately replace the consideration of such a three-dimensional lattice by a two-dimensional one, in which all possible hydrogen bonds would be realized (Fig. 2). In this model the angle φ between the linear chains must be close to 105°, i.e., to the angle that occurs in an isolated water molecule. Calculation shows (^{9,10}) that the vibrational frequencies ν' of such a two-dimensional lattice, in the case of equality of the horizontal and inclined chains, as occurs in the present case, will be given by the relation:

Fig. 2

$$\nu' = \nu\sqrt{1 \pm \cos\varphi}, \tag{1}$$

where ν are the vibrational frequencies of a linear chain.

The calculation for translational vibrations of linear chains (^{10}) leads to the result that, as a consequence of interactions, each of the vibrational levels of an isolated hydrogen bond is split into N components, where N is the number of hydrogen bonds in the chain, and the vibrational frequencies ν_j of the chain are approximately expressed by the relation:

$$\nu_j^2 = \frac{k\chi}{\pi^2(k+\chi)}\frac{1}{M}\sin^2\frac{j\pi}{2(N+1)} = \nu_0^2\sin^2\frac{j\pi}{2(N+1)}, \tag{2}$$

where k and χ are the quasi-elastic constants of the chemical bond O–H and of the hydrogen bond H $\cdots$ O, respectively, M is the mass of the molecule, and $j = 1, \ldots, N$.

The most intense will be the so-called limiting transitions, corresponding to the limiting frequencies ν_0, when $\sin^2\frac{j\pi}{2(N+1)} \to 1$. In addition, all maximum frequencies for chains with different numbers of hydrogen bonds, beginning with $N = 10$, will practically coincide and tend to the value of the limiting frequency. Therefore, in the case of long chains in the vibrational spectrum there can apparently appear, in the form of separate bands, only bands due to transitions close to the limiting ones.

Upon passing to the two-dimensional model shown in Fig. 2, each of the limiting frequencies ν_0, according to expression (1), is split into two components ν_1' and ν_2', connected with ν_0 by the relations: $\nu_1' = 1.12\nu_0$ and $\nu_2' = 0.86\nu_0$. Of these, as shown in (^{9}), the high-frequency component will be the more intense.

If the highest-frequency band observed experimentally (232 cm^{-1} for H_2O) is assigned to the frequency ν_1', then the corresponding frequency of the limiting transition in the linear chain ν_0 will be 207 cm^{-1}, and the frequency ν_2' will be ...

178 cm^{-1}. In accordance with this, the frequency of the fundamental vibrational quantum of the dimer ν_0', obtained from (2) for $j = 1$ and $N = 1$ and related to the frequency ν_0 by the expression $\nu_0' = 0.707\,\nu_0$, proves to be equal to 146.5 cm^{-1}. Similarly, all the bands observed experimentally may be taken as ν_1' and the corresponding frequencies ν, the frequencies of the limiting transitions ν_0, and the vibrational frequencies of an isolated hydrogen bond ν_0' may be determined. All these frequency values for the vibrational spectrum of the hydrogen bond in ordinary and "heavy" water are given in Table 2*.

It is seen from the table that all the frequencies are grouped around the values obtained experimentally, and each of the experimental bands may be due to different vibrations. In liquid water, apparently only the vibrations ν_1 and ν_2 occur. Hence it is clear why the broad band of translational vibrations of liquid water has a maximum at 170 cm^{-1}, although the experimentally observed bands lie in a higher-frequency region. These bands are due to transitions close to limiting ones; however, still higher-frequency continuum transitions

Fig. 3

Figure 3: Fig. 3

also occur, which strongly overlap and make their contribution to the overall intensity distribution of the broad absorption band of translational vibrations.

Table 2

H_2O	H_2O	H_2O	H_2O	D_2O	D_2O	D_2O	D_2O
ν_1', cm^{-1}	ν_0, cm^{-1}	ν_2', cm^{-1}	ν_0', cm^{-1}	ν_1', cm^{-1}	ν_0, cm^{-1}	ν_2', cm^{-1}	ν_0', cm^{-1}
232	207	178	146.5	221	197.5	170	139.5
210	187.5	161	133	196	175	150.5	124
191	170.5	147	121	181	161.5	139	114
175	156	134	110	166	148	127	105
160	143	123	101	156	139	120	98
145	130	112	92	140	125	108	88

The proposed interpretation also makes it possible, by the known formula for the vibrations of a harmonic oscillator, to calculate the quasi-elastic constant of the hydrogen bond, which, when allowance is made for the anharmonicity of the vibrations—easily obtained from the data of Table 2—turns out to be approximately equal to $1.4 \cdot 10^4$ dyn/cm for liquid ordinary and "heavy" water. Naturally, the same result can also be obtained from formula (2).

Fig. 3

2. Low-frequency infrared absorption spectra of crystal hydrates. In connection with the study of the vibrational spectrum of the hydrogen bond, absorption spectra of a number of crystal-hydrate powders were obtained in the region 42-200 μ, at temperatures +20° and −175°: $CaSO_4 \cdot 2H_2O$, $Na_2CO_3 \cdot 10H_2O$, $CuSO_4 \cdot 5H_2O$, $Li_2SO_4 \cdot H_2O$, and $(CO_2CHOH)_2 \cdot NaK \cdot 4H_2O$. As an example, Fig. 3 gives the transmission of crystalline gypsum at a temperature of −175°. Curves 1 and 2 characterize the transmission of gypsum before and after its dehydration at a temperature of +180° for 4 hours. The disappearance of the absorption bands 221; 192; 175; 160; 145; 130 and 118 cm^{-1} upon dehydration of gypsum shows that these bands are due to water molecules weakly bound to the main crystal lattice ([11]).

[*] According to work ([12]), in the higher-frequency region of the water spectrum there is no selective absorption that could be assigned to the series of bands under consideration.

In work [(2)], only the frequencies 110, 122, 132, and 146 cm^{-1} were assigned to the vibrational spectrum of the hydrogen bond of crystallization water in gypsum; however, in [(13)] it was shown that the intensity and polarization of these lines depend on the orientation of the gypsum crystal, which led the author to abandon the interpretation of these bands as belonging to the vibrational spectrum of the hydrogen bond. Indeed, the changes observed in (13) in the spectra cannot be explained on the basis of ideas about the presence of an isolated hydrogen bond in the crystal. These changes are apparently associated with a more complex association of water molecules in the crystal.

Table 3

$CaSO_4$ $2H_2O$	Na_2CO_3 $10H_2O$	$CuSO_4$ $5H_2O$	Li_2SO_4 H_2O	$(CO_2CHOH)_2$ × NaK $4H_2O$
	308 *	280 *		353 *
	265 *	252 *		270 *
	235 *			233 *
221		220 *	218	
	207			208
			195	
192				190
		185	185	
175	175			176
160		160		160
			150	
145	145	148		145
130	133	130		137
118	116		116	115
		111		
	107		108	
	102	100		
			67 *	

Note. The spectra of $CaSO_4$ $2H_2O$ and Li_2SO_4 H_2O in the frequency range above 230 cm^{-1} were not obtained; bands marked with an asterisk were obtained only at room temperature.

Table 3 gives a summary of the frequencies of all absorption bands observed in the infrared spectra of the crystals studied at room temperature and at −175°. The interpretation of all the bands obtained is at present difficult. Some of these bands apparently belong to the vibrational spectrum of the hydrogen bond. It should be emphasized, however, that in interpreting the spectra of crystal hydrates in each individual case, including the case of gypsum, it is necessary to take into account both the vibrations of the main crystal lattice and the vibrations of the molecules of crystallization water, bearing in mind the type of hydrogen bond formed in the crystal and the possible association of water molecules.

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CITED LITERATURE

1. E. F. Gross, V. I. Val' kov, DAN, **68**, 473, 1013 (1949); **74**, 453 (1950); **81**, 761 (1951).
2. A. I. Stekhanov, DAN, **92**, 281 (1953).
3. N. G. Yaroslavskii, B. A. Zheldub, A. E. Stanevich, *Optics and Spectroscopy*, **1**, 507 (1956).
4. C. H. Cartwright, *Nature*, **136**, 181 (1935).
5. N. G. Yaroslavskii, A. E. Stanevich, *Optics and Spectroscopy*, **5**, 384 (1958).
6. M. V. Vol' kenshtein, M. A. El' yashevich, B. I. Stepanov, *Molecular Vibrations*, Moscow-Leningrad, 1949.
7. N. D. Sokolov, *Advances in Physical Sciences*, **57**, 205 (1958).
8. C. L. Eck, H. Mendel, *Proc. Roy. Soc.*, **A247**, 472 (1958).
9. O. P. Girin, *Optics and Spectroscopy*, **9**, 5, 673 (1960).
10. B. I. Stepanov, O. P. Girin, *Proceedings of the State Optical Institute*, **23**, issue 139 (1953).
11. J. D. Bernal, *Advances in Chemistry*, **25**, 643 (1956).
12. E. K. Plyler, N. Acquista, *J. Opt. Soc. Am.*, **44**, 505 (1954).
13. A. I. Stekhanov, DAN, **100**, 685 (1955).

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