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DIFFUSION OF WATER MOLECULES IN HYDRATES AND NMR SPECTRA

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The regularities of the temperature variation of PMR spectra of a number of crystal hydrates are determined on the basis of an analysis of the experimental data. It is shown that the regularities can be explained by means of a model of molecular diffusion of H_2O molecules in the crystal lattice. The effect of diffusion in the intramolecular and intermolecular parts of the local magnetic field is considered. Expressions are presented which relate the PMR spectrum parameters with the special arrangement of the water molecules and the diffusion characteristics. It is shown that in all cases in the high-temperature region (in the presence of diffusion) the PMR spectra can be calculated from the experimental data obtained at low temperatures corresponding to a rigid lattice. The experimental data for a number of crystal hydrates are compared with the theoretical concepts developed.

1. INTRODUCTION

THE proton magnetic resonance (PMR) spectra of crystal hydrates at room temperature are in most cases doublets (or sums of several doublets)[1]. This is due to the fact that in H_2O molecules, which are contained in the crystal hydrates, each proton of the water molecule is acted upon, besides the external magnetic field H_0, also by a local field h, equal to

$$h = \pm {}^3/_2 \mu r^{-3}(3\cos^2\theta - 1), \quad (1)$$

and produced by the magnetic moment μ of the other proton of the molecule, located at a distance r. Here θ is the angle between the proton-proton (pp) vector and the direction of H_0. The magnitude of the doublet splitting $\Delta H = 2h$[2], and the anomalous maximum value ΔH_{max} at $\theta = 0°$, for water molecules, amounts as a rule to ~21 Oe.

In addition, it is reported in many papers[3-15] that narrower single doublets were observed, with $\Delta H_{max} = 1–10$ Oe, in NMR spectra of certain crystal hydrates. With decreasing temperature, the spectrum for such crystals broadens, being transformed as a rule into a multicomponent spectrum with $\Delta H \approx 21$ Oe. On this basis, it is customary to assume that the cause of the appearance of narrow doublets is the high mobility of the water molecules in certain hydrates at room temperature. In accordance with the theory of Bloembergen, Purcell, and Pound[16], in the presence of internal mobility, a given nucleus in the crystal is acted upon not by the instantaneous local field h(t), but its time-averaged value $\langle h \rangle$. The averaging of h takes place when the average motion frequency ν_c is approximately equal to or larger than the NMR line width.

Inasmuch as the value of $\langle h \rangle$ is determined by the concrete mechanism of the motion, it is possible to attempt to determine this mechanism from the measured experimental value $\Delta H = 2\langle h \rangle$ and its angular and temperature dependences. Attempts at solving this problem were already undertaken earlier. In particular, Jano[3] relates the narrowing of the spectra in the hydrates to the appearance of two rotational degrees of freedom in the water molecules—rotation around the twofold order axis of the molecule and simultaneous precession of this axis around a certain preferred direction in the crystal. The magnitude of the precession angle determines the magnitude of the splitting ΔH. Ducrot[4] and Pare[5] introduced in their theories the model of a free anisotropy rotational motion of the water molecules, characterized by continuous distribution function of the probabilities of the different orientations of the pp vector relative to the crystal axes. The form of this function determines both the magnitude and the angular dependence of ΔH. In the theory of Tsang and O'Reilly[6] it was proposed that, with a good degree of approximation, the distribution function of the probabilities of the different orientations of the pp vector differs from zero only for certain fixed directions in the crystal.

However, as will be shown below, the aforementioned theories explain satisfactorily only those experimental facts which are connected with the occurrence of the narrow doublet. In addition, it becomes necessary here to introduce different unlikely assumptions, for example, that the ensemble of the water molecules in the crystal is very weakly coupled with the crystal lattice and behaves almost like a free system of molecules capable of rotating. To explain the uniqueness of the doublet it is also necessary to propose that the character of the motion is identical for all the water molecules and does not depend at all on their nearest surrounding. At the same time it is well known[17] that the water molecules are coupled to the lattice by different forces, with a total energy on the order of 10 kcal/mole, which is considerably larger than the energy of the thermal vibrations at ordinary temperatures.

We shall show below that a consistent explanation of all the observed features of the NMR spectra of hydrates with mobile water molecules can be obtained by starting from the model of molecular diffusion of the water of crystallization.

2. MAIN EXPERIMENTAL DATA

The table lists some of the characteristics of the NMR spectra of a number of hydrates containing

At the same time, the model of Tsang and O'Reilly[6] is in principle free of these shortcomings, although the question of the temperature dependence of ΔH is not considered in[6]. It is easy to see that a suitable choice of a discrete number of orientations, over which $\langle h \rangle$ can be averaged, can explain the narrowing of the spectra, the character of the angular dependence, and the absence of a temperature dependence of ΔH, if the discrete series of admissible orientations of the pp vector does not change with temperature. It should be noted, however, that the model of[6] was constructed for a specific case of a ferroelectric (potassium ferrocyanide) with "repolarization" motions of the H_2O molecules. Most of the considered hydrates are not ferroelectric, and therefore the applicability of the Tsang and O'Reilly theory to them is doubtful. Moreover, the model of[6] cannot explain the narrowing of the doublet components. Indeed, in accordance with the results of a structure analysis of the hydrates, the distance between the water molecules usually amounts to ~2.8 Å. The minimum magnitude of the intermolecular interaction, which determines the width of the components, will take place when the molecules rotate isotropically. The value of h in this case can be calculated from formula (1) if we assume that r = 2.8 Å and that both protons are located in the center of the rotating H_2O molecule. A calculation[15] gives a mean value $h \approx 1-2$ Oe, which is larger by one order of magnitude than the observed widths of the components. It is therefore clear that the width of the doublet components should not change with increasing temperature, starting with a certain value of the temperature, and cannot go lower than a certain minimum value (~1 Oe). We note that the obtained conclusion that it is impossible to explain the width of the components and the exponential decrease of this width with increasing temperature pertains equally well also to the models of[3-5], in which rotation of the water molecule at fixed sites is proposed.

3. DOUBLET STRUCTURE OF THE SPECTRA

We now propose that the H_2O molecules diffuse in the hydrates under consideration. This assumption agrees with such well known facts as the dehydration and rehydration, which are based on the assumption that there exists an effective mechanism whereby the water molecules diffuse through the crystal lattice.

It should be expected that for most crystals the most probable is the hole mechanism of diffusion, using molecular vacancies after Schottky. The equilibrium concentration d of the vacancies is determined by the relation

$$d = N_v / N = \exp(-\Delta E_v / kT), \tag{3}$$

where N_V is the number of vacancies in the crystal, N the total number of molecules, and ΔE_V the energy of vacancy production[18]. For H_2O molecules, $\Delta E_V \approx 5$ kcal/mole. This yields $d \approx 10^{-4}$ at room temperature. The average lifetime of the vacancy at a given site, calculated in accordance with the usual formulas[18], amounts to $\sim 10^{-8}$ sec (at T = 300°K). From this it follows, when (3) is taken into account, that at room temperature each H_2O molecule changes its localization point, on the average, 10^4 times. In accordance with the theory[16], this leads to a dynamic narrowing of the NMR spectrum. It is clear that the change of ΔE_V can shift this temperature in either direction. In each of the sites successively occupied during the diffusion process, the molecule should be oriented in a manner characteristic for the given site, for example such as to produce the strongest hydrogen bonds. In other words, the diffusing molecule runs through a set of positions and orientations which it encounters in the lattice. If the time of transition from one site to another is much shorter than the lifetime of the molecule at each site, as is usually the case, then the time averaging of the local field reduces simply to a mean value $\langle h \rangle$ for ensemble of molecules, in accordance with their positions and orientations of the pp vectors in the "rigid" lattice of the crystal.

The local magnetic field acting on the given proton i, consists of the sum of the intramolecular and intermolecular parts h^{ia} and h^{ie}:

$$h = h^{ia} + h = \pm \mu r^{-3} (3\cos^2\theta_i - 1) + \sum_{j=1}^{2N-2} \left[\pm \frac{3}{2} \mu R_{ij}^{-3} (3\cos^2\theta_{ij} - 1) \right] \tag{4}$$

where θ_i is the angle between $\mathbf{H}_0$ and the pp vector of the water molecule containing the proton i, R_{ij} is the distance from the given proton to the proton of the other water molecule, θ_{ij} is the angle between $\mathbf{R}_{ij}$ and H_0, and N is the total number of molecules. The symbol ± denotes that the local field can be either positive or negative, in accordance with the two possible orientations of the magnetic moment. Since $r \approx 1.6$ Å and $R \geq 2.8$ Å, we find that for water molecules h^{ia} is larger by approximately one order of magnitude than h^{ie}. Thus, the predominant influence on h in (4) is exerted by the first term, which leads to a splitting of the spectrum into two components with $\Delta H = 2h$. The second term leads to a broadening of these components.

In the general case, the motion of the water molecules that take part in the diffusion can be represented as an aggregate of parallel transfers between sites fixed in the lattice, and rotations from one fixed orientation in one site to another fixed orientation in the other site.

Let us consider the influence of diffusion on h^{ia}. Parallel transfer does not change the values of r and θ_i, and therefore only rotation need be taken into account. If the pp vector of the water molecules assumes during the diffusion process m positions allowed by the structure, each characterized by a relative weight p_i, then the average value of the intramolecular part of the local field will be

$$\langle h^{ia} \rangle = \sum_{i=1}^{m} p_i h_i = \pm \sum_{i=1}^{m} p_i \left[\frac{3}{2} \mu r^{-3} (3\cos^2\theta_i - 1) \right], \qquad \sum_{i=1}^{m} p_i = 1. \tag{5}$$

Thus, calculation of $\langle h^{ia} \rangle$ reduces to a calculation of the influence of the aggregate of possible rotations of the molecules on the NMR spectrum, as in the case of the reorientation (hindered rotation) in solids.

In concrete systems, the calculation reduces to the following three possibilities:

Hydrate	Transition temperature °C	$f(\gamma, \varphi) = \frac{\Delta H}{K}$ $T = 20°$ C	K, Oe	Angles measured from direction		Reference
				γ	φ	
Edingtonite $BaAl_2Si_3O_{10} \cdot 4H_2O$	—50 to —20	$3\cos^2\gamma - 1$	4,6	[001]	—	[7]
Heulandite $CaAl_2Si_6O_{16} \cdot 5H_2O$	—40 to —10	»	4,0	[010]	—	[8]
Chabazite $CaAl_2Si_4O_{12} \cdot 6H_2O$	—100 to —40	»	0,6	[001]	—	[4]
Harmotome $BaAl_2Si_4O_{12} \cdot 6H_2O$	—60 to —30	»	2,4	[001]	—	[9]
Collagen (moisture 50%)	—40 to 20	»	0,4	Fiber axis	—	[10]
$K_4Fe(CN)_6 \cdot 3H_2O$	—80 to —20	$\sin^2\gamma \sin 2\varphi$	4,6	[010]	[100]	[6, 11–14]
$MgCl_2 \cdot 6H_2O$	—30 to 0	$\sin 2\varphi$	5,1	Rotation around the axis of a needle crystal		[3]
$CaI_2 \cdot 6H_2O$	—60 to —20	$\sim \sin 2\varphi$	2,2	Axis not indicated		[3]
Desmine $CaAl_2Si_7O_{18} \cdot 7H_2O$	—130 to —90	$3(3\cos^2\gamma - 1) + \sin^2\gamma \cos 2\varphi$	0,85	[100]	[001]	[5]

mobile water molecules at room temperature. These characteristics give an idea of the values of ΔH customarily encountered in such cases and their angular dependences and the temperatures of the transitions from the broad NMR spectra that are characteristic of low temperatures to narrow doublets.

The changes of the NMR spectra of these hydrates with changing temperature are characterized by the following regularities:

a) No matter how complicated the NMR spectrum of a given hydrate may be at low temperatures, the transition to the narrow spectrum always results in a single doublet with a relation $\Delta H = Kf(\gamma, \varphi)$ that is characteristic of the given crystal; γ and φ characterize the orientation of H_0 relative to the axes of the crystal.

b) At a given crystal orientation, ΔH does not depend on the temperature.

c) The doublet components are very narrow (within 0.1–0.01 Oe), and the width of the components decreases approximately exponentially with increasing temperature.

d) An unusually strong temperature dependence of the width of the PMR spectra is observed in the temperature region below the transition.

Figure 1 shows by way of illustration of these premises, the PMR obtained by us for desmine ($CaAl_2Si_7O_{18} \cdot 7H_2O$) and some of their characteristics at different temperatures.

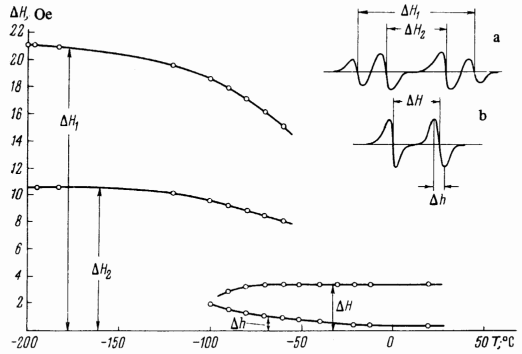

FIG. 1. Schematic form of the PMR spectra of desmine at −196°C (a) and + 20°C (b), and the temperature dependence of the doublet splittings of the spectra. Field $\mathbf{H}_0 \parallel [010]$.

The only one of the important regularities listed above explained satisfactorily in the[3-6] is the appearance of a narrow doublet for specific crystals. It is appropriate to note here that the possibility of introducing different mechanisms of averaging the local field is explained in[3-6] as being due to the fact that, generally speaking, there exists an infinite number of angular distribution functions for the probability density of different orientations of the pp vector in the crystal, for which the average values of the local field is equal to a specified value. Therefore the choice of the correct model should be based on additional physical data.

The table gives information concerning the dependence of ΔH on the orientation of the crystal relative to the external magnetic field for different hydrates. We see that there are at least three different types of angular dependence. The precession model introduced by Jano[3] admits of only one type of angular dependence

$$\Delta H = K(3\cos^2\gamma - 1), \tag{2}$$

where K is a coefficient determined by the precession angle and by interproton distance in the H_2O molecule, and γ is the angle between the precession axis and the external field H_0. Consequently, the appearance of hydrates with other types of angular dependence can in general not be explained within the framework of the Jano theory[3].

The absence of a temperature dependence of ΔH in the temperature region above the transition is likewise difficult to reconcile with the Jano model[3]. The change of the temperature should, generally speaking, lead to a change in the precession angle, and consequently in ΔH. In the models of Ducrot[4] and Pare[5] it is also to be expected that the angular distribution function of the pp vector changes with changing temperature, since this dependence should be isotropic at extremely high temperatures.

Thus, the models of[3-5] cannot be readily reconciled with the absence of a temperature dependence of ΔH.

1) The orientations of the pp vectors at the localization points of the water molecule are connected by twofold symmetry axes. In this case we have[19]

$$\langle h^{ia}\rangle = \pm{}^3/_2\mu r^{-3}[{}^3/_2\cos^2\delta(1+\cos 2\varphi\cos 2\alpha)-1], \tag{6}$$

where 2α is the angle between the pp vectors, φ is the angle between the twofold axis and the projection of the magnetic field on the plane of the pp vectors, and δ is the angle of inclination of the magnetic field to this plane.

2) The orientations of the pp vectors of the water molecules in the crystal are connected by threefold, fourfold, or sixfold symmetry axes. In this case it is possible to use for the calculation of $\langle h^{ia}\rangle$ the formula of Gutowsky and Pake[20], derived for the case of reorientation around these axes:

$$\langle h^{ia}\rangle = \pm{}^3/_4\mu r^{-3}(3\cos^2\alpha-1)(3\cos^2\beta-1), \tag{7}$$

where β is the angle between the axis and H_0, and α is the angle between the axis and the pp vector.

3) Crystals in which the pp vector is at the localization points of the water molecules are not connected by symmetry elements. In this case it is necessary to average over all the different h_i in accordance with the general formula (5).

It is important to note that $\langle h\rangle$ is directly connected with the aggregate of θ_i and p_i, which can be obtained from the NMR spectra in the temperature region below the transition temperature. For a sufficiently low temperature, when the diffusion is too slow for time averaging of the local fields, each of the allowed positions of the H_2O molecules gives, in accordance with (1), its own doublet, and their relative intensities and angular dependences can be readily determined experimentally.

Consequently, on the basis of the experimental data on the NMR spectra below the transition temperature, it is possible to calculate theoretically, by means of formula (5), the angular dependence of the doublet splitting of the spectra in the presence of molecular diffusion. The agreement between the obtained theoretical dependence and the one measured in experiment above the transition temperature can serve as one of the proofs of the correctness of the chosen interpretation.

To verify this conclusion, we have investigated in detail the NMR spectra of certain single-crystal hydrates.

Desmine. From an analysis of the spectra recorded at −196°C, it was found with the aid of formula (1) that in desmine $^3/_7$ of all the pp vectors are oriented parallel to the [001] direction, $^3/_7$ parallel to the [010] direction, and $^1/_7$ at angles ±55° to the [100] direction in the (001) plane. Their arrangement relative to the crystal axes is shown schematically in Fig. 2. For arbitrary orientations of the magnetic field, characterized by the angles γ and φ, and of the i-th pp vector, the orientation of which is determined by the angles γ_i and φ_i, we have

$$\cos\theta_i = \cos\gamma_i\cos\gamma + \sin\gamma_i\sin\gamma\cos(\varphi_i-\varphi)$$

(θ_i—angle between the i-th pp vector and H_0). Using this formula, we can easily show that for desmine

$$\Delta H = 2\langle h^{ia}\rangle = 3\mu r^{-3}\cdot{}^1/_7[3(3\cos^2\gamma-1)+\sin^2\gamma\cos 2\varphi], \tag{8}$$

the result of the calculation, apart from a constant factor, coincides with the experimental result (Fig. 3) obtained at room temperature in[5] and confirmed by us. The outward difference between expression (8) and the empirical formula given in[5] is due to our choice of another coordinate system, which is more convenient for us. The theoretical value of the coefficient $K = 3\mu r^{-3}\,(^1/_7) = 1.5$ Oe is larger than the experimental value 0.85 Oe. The possible cause of the difference is discussed below.

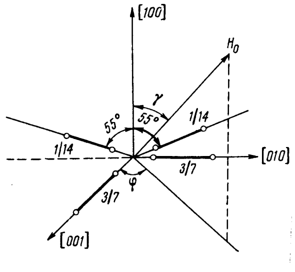

FIG. 2

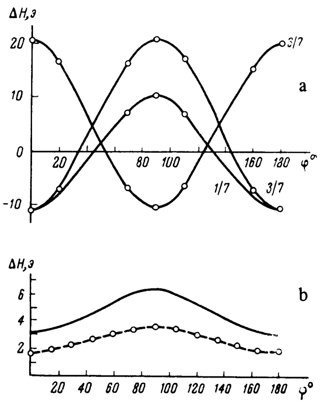

FIG 3

FIG. 2. Designation of the angles and arrangement of the pp vectors relative to the principal axes of desmine. The numbers denote the relative number of pp-vectors.

FIG.3. Angular dependences of the doublet splittings of PMR spectra of desmine at −196°C (a) and at +20°C (b). The rotation axes is [100], the angles are measured from the [010] direction. ○ – experimental points, number on the curve denote the relative intensity of the line; the solid curves were calculated by the formula of Pake (a) and from formula (5) (b); dashed curve—angular dependence of ΔH in accordance with formula (5) with allowance for the vibrations of the H_2) molecules.

Heulandite. The NMR experimental spectra at −196°C have shown that in the structure of this crystal $^2/_5$ of all the pp vectors are oriented parallel to [010], $^2/_5$ lie in the (001) plane at angles ±35° to [010], and $^1/_5$ in the (001) plane at angles ±55° to the [010] direction. Averaging yields

$$\Delta H = 6.3(3\cos^2\gamma-1)\ \text{Oe} \tag{9}$$

The angle γ is reckoned here from the [010] direction. The angular part of the obtained expression agrees fully with experiment, which, however, yields a numerical coefficient of 4.0 Oe in (9)[8].

Our analysis of the experimental data for edingtonite, potassium ferrocyanide, natrolite, apophyllite, and other crystal hydrates has shown that in all cases the angular dependence of the spectra in the temperature region above the transition temperature is likewise completely determined by the arrangement of the pp vectors at low temperature, in accordance with formulas (5)–(7).

4. VIBRATIONS OF WATER MOLECULES

As already mentioned, in the investigated substances an appreciable change (20–25%) was observed in the magnitude of the doublet splittings in a relatively narrow temperature interval in the temperature region directly close to the transition (Fig. 1). Inasmuch as the form of the spectrum remains unchanged in this case, such changes can be attributed to be the vibrations of the water molecules. Indeed, as shown by Pedersen[21], in the presence of libration vibrations of the water molecules, the angular part of the formula (1), as a result of averaging over the vibrational motion, can be represented in the form

$$\langle(3\cos^2\theta-1)\rangle=[1-C\langle\alpha^2\rangle](3\cos^2\theta-1), \tag{10}$$

where $\langle\alpha^2\rangle$ is the mean square of the amplitude of the vibration about the twofold axis of the molecule, $C = 2-3$ is a coefficient that depends on the form of the barrier for the vibrations. The quantity $\langle\alpha^2\rangle$ is connected with the temperature by the relation

$$\langle\alpha^2\rangle=\frac{\hbar}{I\omega}\left\{\frac{1}{2}+\left[\exp\left(\frac{\hbar\omega}{kT}\right)-1\right]^{-1}\right\} \tag{10a}$$

$$=0.2V_{\text{vib}}^{-1/2}\left\{\frac{1}{2}+\left[\exp\left(\frac{201V_{\text{vib}}^{1/2}}{T}\right)-1\right]^{-1}\right\},$$

where I is the moment of inertia of the H_2O molecule, ω the circular frequency of the vibrations of the H_2O molecules, V_{vib} the height of the potential barrier for the vibrations in kcal/mole, and T the absolute temperature. Therefore, with increasing temperature, the doublet splitting $\Delta H_{1,2} = \Delta H^0_{1,2}(1 - C\langle\alpha^2\rangle)$ ($\Delta H^0_{1,2}$—splitting at $\langle\alpha^2\rangle = 0$) should decrease, but the form of the spectrum should remain unchanged.

As seen from Fig. 1, the noted regularities are satisfied, but in such an approach it is somewhat difficult to explain the magnitude of the decrease of $\Delta H_{1,2}$. At a relative decrease of the doublet splittings by 25%, the formulas presented above yield $\langle\alpha^2\rangle^{1/2}$ 20° and $V_{\text{vib}} \sim 0.5$ kcal/mole for desmine (the same value of V_{vib} is obtained for potassium ferrocyanide[6]). The obtained value of V_{vib} seems to be much too low compared with the height of the energy barrier for diffusion, V_{dif}, which can be estimated on the basis of the relation[22]

$$V_{\text{dif}}=37\,T_{\text{tr}}\ \text{cal}$$

where T_{tr} is the temperature (deg K) of the transition from the broad to the narrow spectrum of NMR. For water molecules in desmine, V_{dif} 8 kcal/mole, which is comparable with the energy of the hydrogen bonds. We can expect the height of the barrier for the vibrations of the water molecules to have approximately the magnitude, but a decrease by one order of magnitude is very unlikely.

On the other hand, inasmuch as the water molecules vibrate at the localization points with the frequency of the normal vibrations ($\sim 10^{12}$ sec^{-1}), we should substitute in (5) the values of h^{ia} averaged over the libration oscillations in accordance with (10). Thus, allowance for the vibrations leads to a decrease of the calculated value of ΔH of the narrow doublet. Here, however, ΔH should depend on $\langle\alpha^2\rangle$ and consequently on the temperature, whereas no such dependence is actually observed.

The noted contradictions can be resolved by noting that the described vibrations are connected with the diffusion process. In the temperature region below the transition, this can be seen, in particular, directly from the spectra. Although at these temperatures $\nu_c \lesssim 10^4$ Hz, some fraction of the molecules moves with a frequency $\nu_c \gtrsim 10^4$ Hz, leading to the appearance of a narrower doublet, characteristic of high temperatures, against the background of the broad spectrum corresponding to the rigid lattice. With increasing temperature, the intensity of this doublet increases, and the intensity and the width of the broad part of the spectrum decrease.

It can be assumed that after the transition from one localization point to another, the H_2O molecule gives up its excess energy to the lattice within a time $\Delta\tau$, during which the amplitude of its oscillations greatly exceeds the amplitude of the thermal vibrations. Obviously, the contribution of these vibrations to $\langle h^{ia}\rangle$ at $\Delta\tau < \Delta t$ will be proportional to the ratio $\Delta\tau/\Delta t$, where Δt is the lifetime of the molecule at the given site. With increasing temperature, Δt decreases and when $\Delta t \lesssim \Delta\tau$ the contribution of the excess vibrations no longer depends on Δt, and consequently on the temperature. Inasmuch as in the region of the appreciable decrease of the doublet splittings $\Delta t \approx 10^{-8}$ sec, it follows therefore that $\Delta\tau \approx 10^{-8}$ sec, too. This value is larger by several order of magnitude than the usual time of "emission" of the excess energy of the molecules, but the feasibility of such an effect in principle has been predicted theoretically[23].

Thus, the introduction of excess vibrations connected with diffusion makes it possible to explain satisfactorily both the temperature dependence of $\Delta H_{1,2}$ of the doublet splittings in the pre-transition region, and the magnitude and absence of a temperature dependence of ΔH in the temperature region above the transition. It is assumed here that when (5) is used to calculate the local field averaged as the result of the diffusion, the excess oscillations are first taken into account with the aid of formula (10). The amplitudes of these vibrations can be determined on the basis of the temperature dependence of $\Delta H_{1,2}$ in the pre-transition region or (more accurately) from the relation $[1 - C\langle\alpha^2\rangle] = \Delta H_{\text{exp}}/\Delta H_{\text{theor}}$.

5. WIDTH OF THE DOUBLET COMPONENTS

It is clear diffusion will decrease the intermolecular part of the local field h^{ie}, since both θ_{ij} and R_{ij} will change in (4). In principle, the averaging of the intermolecular part must be carried out in the same manner as for the intramolecular part, but the problem is greatly complicated here by the need for taking into account a large number of small terms and different configurations over which the averaging is carried out.

To estimate the decrease of the intermolecular interaction (and the width of the doublet components), let us consider the magnitude of the local magnetic field produced at the point i by the magnetic moment of the proton located at the point j. In the static case, the local field is of the order of (formula (4))

$$h_j^{ie}\sim\mu R_{ij}^{-3}.$$

The quantity h_j^{ie} determines the characteristic frequency ν_j^{ie} of the motion[16], above which averaging of the local field takes place:

$$\nu_j^{ie} \approx \frac{1}{2\pi}\gamma h^{ie} \approx \frac{1}{2\pi}\gamma\mu R_{ij}^{-3}. \tag{12}$$

We see that this frequency decreases rapidly with increasing R_{ij}. In order for a narrow doublet to appear, as noted above, averaging should take place of the intramolecular part of the local field, i.e., the correlation frequency ν_c^{ia} of the diffusion motion of the molecule of the water should be

$$\nu_c^{ia} \gtrsim \frac{1}{2\pi}\gamma\mu r^{-3}. \tag{13}$$

Since $r < R_{ij}$, we get $\nu_c^{ia} > \nu_c^{ie}$ by a factor n_j, where

$$n_j = \nu_c^{ia}/\nu_j^{ie} = (R_{ij}/r)^3 \tag{14}$$

We see therefore that if the frequency of motion has reached the value ν_c^{ia} at which averaging of h^{ia} takes place, then for each field h^{ie} it is larger by a factor n_j than the corresponding frequency ν_j^{ie}. Within the time $\tau_j^{ie} = (2\pi\nu_i^{ie})^{-1}$, the molecule whose proton is located at the site j will change places n_j times. In the case of random "wandering," this molecule can "visit" the sites located in a sphere with a radius on the order of[18]

$$\rho_j = a n_j^{1/2} = a(R/r)^{3/2}, \tag{15}$$

where a is the distance between the nearest sites.

Thus, a proton located at the instant of time $t = 0$ at a site j, is effectively "smeared out" over a sphere of radius ρ_j at the end of the time interval $t = \tau_j^{ie}$ for the point i. In calculating the time-averaged value of $\langle h^{ie}\rangle$ it is necessary to calculate the mean value of ρ_j, which this quantity takes on in the time interval from $t = 0$ to $t = \tau_j^{ie}$.

It is easy to see that $\langle\rho_j\rangle \gtrsim R_{ij}$ for all R_{ij}. Averaging over a sphere of this radius greatly decreases h^{ie} compared with its value for the "rigid" lattice. If we assume that the decrease of h^{ie} is proportional to the radius of the "averaging" sphere, we can determine from this the character of the temperature dependence of $\langle h^{ie}\rangle$ and consequently the width of the components of the doublet $\Delta h(T)$. Indeed, the average frequency of motion ν_c (frequency of change of place) increases with the temperature like $\exp(-V_{dif}/kT)$, where k is the Boltzmann constant and T is the absolute temperature). This increase does not change $\langle h^{ia}\rangle$, since no new values of p_i and θ_i are obtained here. At the same time, for $\langle h^{ie}\rangle$, the increase of ν_c leads to an increase of ρ_j, i.e., to the appearance of new positions over which the averaging of h^{ie} takes place, and consequently to the experimentally observed exponential decrease of the width of the doublet components.

6. CONCLUSION

The foregoing analysis and estimates offer, in our opinion, sufficiently convincing evidence that all the features of the temperature changes of the NMR spectra of a number of hydrates can be explained on the basis of the model of molecular diffusion of water. The use of the developed approach may be useful for the study of molecular diffusion over regular vacancies in a lattice, which is difficult by other methods. Naturally, the use of the NMR method for the investigation of molecular diffusion in solids is not limited to the case of the diffusion of H_2O molecules; this method is equally applicable to an investigation of the diffusion of other molecules and molecular ions. It follows directly from this analysis that it is of value to the study of the crystal structure of matter and of molecular vibrations, since such characteristics determine the most important features of the NMR spectra not only in the low-temperature but also in the high-temperature region.

An investigation of "irregular" defects in a lattice is also promising. If such defects, which are arranged at random, can be used for diffusion, then the local field h^{ia} may become averaged out to zero as a result of the disordered fluctuations of p_i and θ_i. This leads to the appearance of a narrow structureless line, the intensity of which is proportional to the number of the defects. The observation of such an effect was reported earlier[22].

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