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^2H -nuclear magnetic resonance study of the host lattice dynamics in the clathrate of Dianin's compound. Concerted rotational jumps of six hydroxyl groups

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^2H -nuclear magnetic resonance was applied to single crystals of the clathrate of Dianin's compound with ethanol as a guest. The hydroxyl groups of both the host lattice and the guest were deuterated. The temperature dependences of the ^2H spectra and of the quadrupole coupling tensors of the host lattice deuterons provide evidence that these deuterons carry out jumps between two unequally populated sites. These jumps may be visualized as approximate rotations of the hydroxyl groups about the C–O bonds. The occupancies of the two sites were measured and found to follow a Boltzmann distribution at $T > 145\text{ K}$. At lower temperatures the minority sites are overpopulated. The temperature dependence of the jump rate was determined by line shape analyses and relaxation time measurements. From the absence of dipolar fine structure in the ^2H spectra recorded for specially chosen crystal orientations it is concluded that groups of six hydroxyl units carry out their rotational jumps in a concerted manner.

I. INTRODUCTION

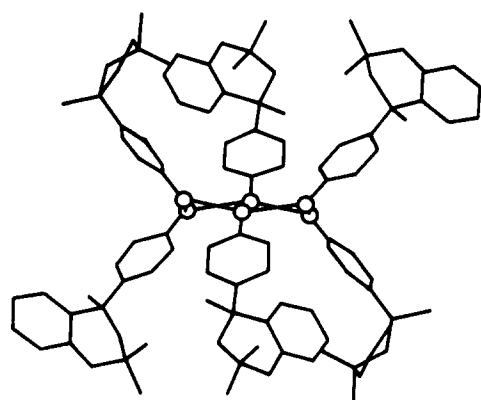
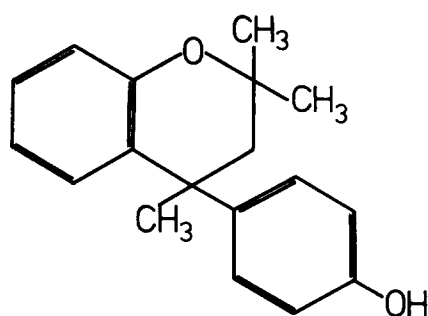
Clathrates consist of a host lattice in which guest molecules are incorporated by steric barriers. In many clathrates these guest molecules are likely to experience great mobility. We applied ^2H nuclear magnetic resonance (NMR) spectroscopy to single crystals of the clathrate of Dianin's compound (4-*p*-hydroxyphenyl-2,2,4-trimethylchroman) with ethanol as a guest. The crystals we used were deuterated in the hydroxyl groups of both the host lattice and the ethanol guest. We found that the mobility of the guest molecules extends to temperatures below the boiling point of nitrogen. Its study requires measurements in a helium cryostat which are currently in progress. Our measurements at $T > 77\text{ K}$ revealed an unusual dynamic process of the host lattice deuterons. Its discussion is the subject of this paper.

Dianin's compound was first prepared by A. P. Dianin in 1914.¹ W. Baker *et al.* showed in 1956 that it forms crystal-line clathrates with a great variety of guests.² The crystal structure of the ethanol, chloroform, and heptanol adducts were established by J. L. Flippen *et al.* by x-ray diffraction.^{3,4} Only tiny differences in the positions of the host lattice atoms were found for these three adducts. The clathrate crystallizes in the trigonal space group $R\bar{3}$. Six host molecules are linked together by hydrogen bonds between their OH groups, building a large complex with alternate chroman molecules pointing up and down as shown in Fig. 1(a). These complexes are stacked on top of each other, forming long chains of "hourglass shaped" cages in which the guest molecules are trapped. The ends of the cages are formed by hexagons of oxygens linked by hydrogen bridges. The distance between two adjacent oxygens is as large as 2.84 Å ,³ the hydrogen bonds must therefore be classified as "weak." Each unit cell contains 18 host molecules and thus three of the hexagons. All these hexagons are magnetically equivalent

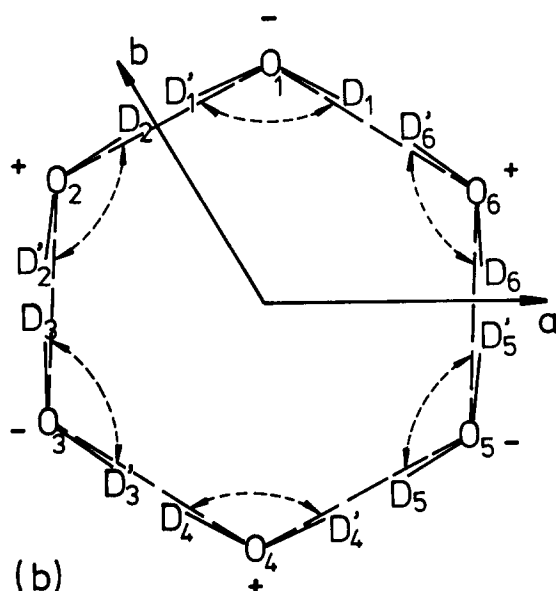
via inversion centers. In our crystals the hydrogens in the hexagons are replaced by deuterons. We found that these deuterons carry out thermally activated jumps between two unequally populated sites in the way sketched in Fig. 1(b). The primed positions (e.g., D'_1) belong to the less populated or minority sites, the unprimed ones to the stronger populated or majority sites. The drawing plane of Fig. 1(b) is perpendicular to the crystal *c* axis which is a threefold rotation axis. An inversion center in the middle of each hexagon renders deuterons on opposite sides magnetically equivalent which reduces the number of magnetically inequivalent deuterons to three. As will be explained in more detail in Sec. III A the jumps can be visualized as approximate rotations of the OD hydroxyl groups about the C–O bonds. The temperature dependences of the occupancies of the two sites and of the jump rates are discussed, respectively, in Sec. III B and III C.

Perhaps the most interesting aspect of the dynamical process studied here is that the six hydroxyl groups in any one of the hexagons appear to carry out their rotational jumps in a concerted manner, and not independently from each other. This is discussed in Sec. III D. We find it astonishing that the rotations of hydroxyl groups in aggregates as large as the hexagon shown in Fig. 1(b) should be coupled to the extent that the hydrogens (deuterons in our case) either sit all in their primed or all in their unprimed positions, as they do.

Concerted jumps of hydrogens are widespread in nature. They have been recognized a long time ago in the infinite three-dimensional lattice of ice which has led to the formulation of the famous ice rules of Pauling.⁵ Gallier *et al.* discuss in a recent paper⁶ on $\text{CsOH} \cdot \text{H}_2\text{O}$ the role of similar rules for the diffusion of hydrogens in a two-dimensional network of hydrogen bonds. On the other end of the scale of



(a)



(b)

FIG. 1. (a) The chroman molecule (Dianin's compound) and the hydrogen bonded six-member complex. The oxygens of the hydroxyl groups are marked by circles. (b) The hexagon formed by the oxygens. The arrows **a** and **b** indicate the directions of the respective primitive lattice vectors. The drawing plane is perpendicular to the *c* axis. The oxygens sit alternately by 0.143 Å above and below this plane. This is indicated by "+" and "-". The deuterons jump between two unequally populated sites. The minority sites are marked by primes.

systems with concerted hydrogen jumps are found dimers of COOH groups the hydrogen dynamics of which has attracted considerable attention recently.⁷⁻¹⁰ Limbach *et al.* have reported on another type of concerted jumps of pairs of hydrogens in a crystalline intramolecularly hydrogen bonded tetraazaannulene.¹¹ The hydrogen dynamics in a hexagon of hydrogen bonds investigated in this work represents a rare but by no means unique intermediate case. Similar concerted jump rotations of hydroxyl groups and water molecules are reported by Betzel *et al.* in their neutron-diffraction work on β -cyclodextrin undecahydrate.¹² Note, however, that this technique does not allow to determine jump rates.

II. EXPERIMENTAL

Dianin's compound was synthesized according to Baker *et al.*² and was isolated as the ethanol adduct. In order to prepare clathrate crystals with ethanol-OD (EtOD), the unsolvated compound was prepared first by sublimation applying a running vacuum pump. Single crystals of suitable size ($\sim 6 \times 4 \times 3$ mm) were then grown by slowly lowering the temperature of a saturated EtOD solution ($60^\circ\text{C} \rightarrow 20^\circ\text{C}$; 1°C per day) of Dianin's compound. In the crystals obtained by this procedure the hydrogens of the hydroxyl groups of both the host lattice and the guest are replaced by deuterons. We estimate that the grade of deuteration is larger than 95%.

Two crystals mounted for rotation about the crystal *a* and *c* axis, respectively, were prepared for ^2H -NMR. In what follows these sample crystals will be referred to as the *a* and the *c* crystal. Spectra were recorded at 54.7 MHz by Fourier transformation (FT) of the free-induction decay (FID) following pulses of 1–2 μs duration, corresponding to 30° – 60° flip angles. Dependent on temperature and requirements on signal-to-noise ratio between 50 and 2000 FIDs were accumulated for a spectrum. Pulse repetition times τ were between 100 ms and 2 s. Quadrupole coupling (QC) tensors were measured by recording the orientation dependences of the quadrupole splittings. Two possible QC tensors were initially obtained, because the crystal symmetry is such that the sense of rotation of the crystals could not be determined. We could select the physically meaningful QC tensors by using the empirical fact that for OD groups the principal axis \mathbf{p}_z of the QC tensor corresponding to the eigenvalue with the largest magnitude practically coincides with the bond direction of the deuteron, while the principal axis \mathbf{p}_x corresponding to the intermediate eigenvalue is roughly normal to the C–O–D plane.¹³

For the measurements of the spin lattice relaxation times we used a saturation- Δt - 90° pulse sequence, the saturation part consisting of a string of equally spaced 90° pulses.

III. THE DYNAMICS OF THE HYDROXYL GROUPS

A. Kinematics

^2H -NMR spectra of the two sample crystals were recorded at $77\text{ K} < T < 360\text{ K}$. Figure 2 shows two spectra from the *c* crystal with $\angle(\mathbf{B}_0, \mathbf{a}) = 46.5^\circ$ taken at $T = 283.5\text{ K}$ (bottom) and $T = 305.5\text{ K}$ (top), respectively. At these and higher temperatures the spectra consist of four line

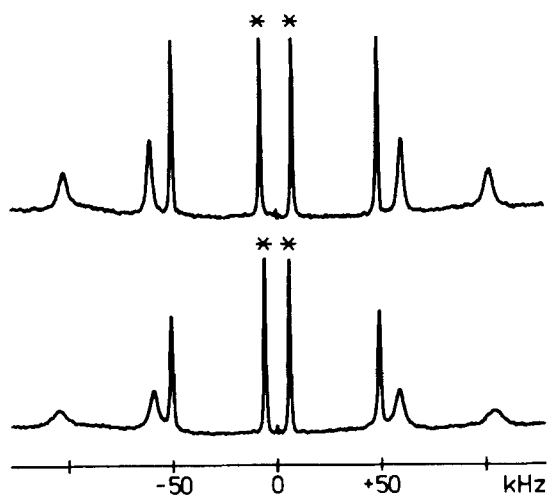


FIG. 2. Two ^2H -NMR spectra from the c crystal. $\angle(\mathbf{B}_0, \mathbf{a}) = 46.5^\circ$, recorded at $T = 305.5$ K (top) and $T = 283.5$ K (bottom). The line pairs marked by stars belong to the ethanol guest. The other lines belong to the host lattice hydroxyl deuterons. These lines get broader on decreasing the temperature. 500 FIDs were accumulated for each spectrum. The pulse duration t_p was $1.5 \mu\text{s}$ corresponding to a 45° pulse. The pulse repetition time τ was 2 s.

pairs. It is quite evident which of them belongs to the deuterons of the ethanol guest: When the c crystal is rotated in the applied field the spectrum always contains one "sharp" line pair whose splitting $\Delta\nu$ is independent of the rotation angle ϕ . At $T = 283.5$ K $|\Delta\nu| = 12$ kHz. This line pair is marked by stars in Fig. 2. It must result from an axially symmetric QC tensor whose "equator" is scanned in the experiment and whose symmetry axis therefore is along c . The size of the quadrupole coupling constant $|\text{QCC}| = \frac{4}{3}|\Delta\nu| = 16$ kHz indicates that the respective QC tensor is a strongly motionally averaged one. A motion which leads to such a strongly averaged, axially symmetric QC tensor with symmetry axis along c is only imaginable for the OD groups of the ethanol guest molecules. Thus, the line pairs marked by stars in Fig. 2 belong to the deuterons of the ethanol molecules.

The other three line pairs must then belong to the OD groups of the host lattice. Both their widths and splittings depend strongly on the rotation angle ϕ of the crystal and on the temperature T , see below.

On cooling the sample the ethanol lines remain sharp down to $T \approx 110$ K. Between 110 and 77 K we find successively line broadening and narrowing, but still only one pair of lines at 77 K. This means that there is still fast motion of the guest molecules on the time scale of the inverse deuteron QC splittings ($\approx 10^{-5}$ s) at the boiling point of nitrogen. We shall discuss this motion under separate cover. From now on we focus attention on the dynamics of the host lattice OD groups. In what follows, lines and QC tensors thus always refer to the deuterons of the host lattice. Their lines get broader on decreasing T down to about 250 K. At temperatures between about 250 and 220 K they get so broad in most crystal orientations that their positions cannot be determined. However, there are special orientations for which one of the line pairs remains sharp over the whole tempera-

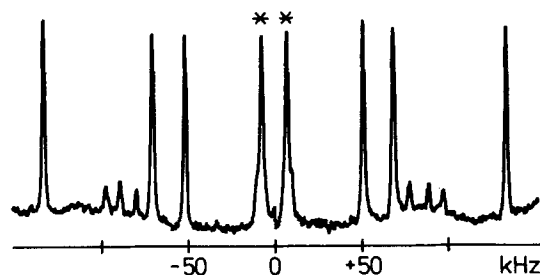


FIG. 3. Spectrum from the c crystal, $\angle(\mathbf{B}_0, \mathbf{a}) = 71.5^\circ$, recorded at $T = 169$ K. The line pair marked by stars belongs to the ethanol guest. There are three "large" and three "small" line pairs from the host lattice deuterons. 500 FIDs were accumulated with $t_p = 1 \mu\text{s}$, $\tau = 2$ s.

ture range. For $T < 220$ K we again find lines from the host lattice for all crystal orientations. They get sharper with decreasing temperature. Figure 3 shows a spectrum recorded at $T = 169$ K. The line pair marked by stars belongs to the guest. We find six line pairs from the host lattice, three "large" and three "small" ones. The latter get smaller on decreasing the temperature. The positions of both the large and the small lines are almost independent of T . The described temperature dependence of the ^2H spectra indicates that the host lattice deuterons undergo a jump process between two unequally populated sites. The large lines observed at "low" temperatures belong to the majority, the small ones to the minority sites. If the deuterons are jumping between these sites, and are carrying out no other large scale motion, the "high" temperature line positions must be given by the weighted average of the positions of the large and the small lines observed at low temperatures. Then also the QC tensors $\mathbf{V}^{(i)}$ measured at high temperatures must be the weighted sums of the QC tensors $\mathbf{L}^{(i)}$ and $\mathbf{S}^{(i)}$ belonging to the large and the small lines. In Table I we list the elements of $\mathbf{L}^{(3)}$ and $\mathbf{S}^{(3)}$ measured at $T = 169$ K. They belong, respectively, to the deuterons labeled D_3 , D_6 , and D'_3 , D'_6 in Fig. 1 (b). This assignment is based on the fact that the eigenvectors corresponding to the largest eigenvalues of $\mathbf{L}^{(3)}$ and $\mathbf{S}^{(3)}$ are parallel to the $\text{O}_2\text{--O}_3$ and $\text{O}_3\text{--O}_4$ interconnecting lines to within 2° and 8° , respectively. Remember that D_3 and D_6 as well as D'_3 and D'_6 are magnetically equivalent. The QC tensors of (D_1, D_4) , (D_2, D_5) ; (D'_1, D'_4) , (D'_2, D'_5) are obtained by rotating $\mathbf{L}^{(3)}$ and $\mathbf{S}^{(3)}$ through $\pm 120^\circ$ about the crystal c axis. We denote these QC tensors by $\mathbf{L}^{(1)}$, $\mathbf{L}^{(2)}$ and $\mathbf{S}^{(1)}$, $\mathbf{S}^{(2)}$. The tensor $\mathbf{V}^{(3)}$, whose components are also listed in Table I was measured at $T = 305.5$ K. Again the other two high temperature QC tensors $\mathbf{V}^{(1)}$ and $\mathbf{V}^{(2)}$ are obtained by rotating $\mathbf{V}^{(3)}$ through $\pm 120^\circ$ about c .

At this stage we do not know whether, say, the QC tensor $\mathbf{L}^{(3)}$ belonging to the deuteron D_3 in its majority site must be combined with the minority site QC tensor $\mathbf{S}^{(3)}$ of D'_3 or with $\mathbf{S}^{(2)}$ of D'_2 to give an average tensor $\mathbf{V}^{(i)}$. The first possibility corresponds to the deuteron motion indicated by the dashed arrows in Fig. 1 (b), i.e., rotational jumps of the hydroxyl groups, whereas the second one implies jumps of the deuterons along the $\text{O--D}\cdots\text{O}$ hydrogen bridges. We neither know which of the $\mathbf{V}^{(i)}$, $i = 1, 2, 3$, goes with $\mathbf{L}^{(3)}$. Therefore

TABLE I. Deuteron-QC tensors of the hydroxyl deuterons of Dianin's compound. $V^{(3)}$: motionally averaged QC tensor at 305.5 K. $L^{(3)}$, $S^{(3)}$: QC tensors of the majority and minority sites. These were measured at $T = 169$ K. Note that all components satisfy within small errors the equation $V_{\alpha\beta}^{(3)} = f_L L_{\alpha\beta}^{(3)} + (1 - f_L) S_{\alpha\beta}^{(3)}$ with $f_L = 0.768$.

Tensor	Components ^a [kHz]			Principal values [kHz]	Principal vectors ^a			η^b
					Θ	Φ		
$\mathbf{V}^{(3)}$	− 97.8	− 53.1	34.5	259.6	\mathbf{p}_z :	85.5°	98.0°	0.356
	− 53.1	249.1	37.5	− 83.5	\mathbf{p}_y :	60.8°	5.5°	
	34.5	37.5	− 151.4	− 176.1	\mathbf{p}_x :	29.6°	196.0°	
$\mathbf{L}^{(3)}$	− 160.5	− 3.0	19.7	323.0	\mathbf{p}_z :	82.5°	90.0°	0.123
	− 3.0	314.6	63.1	− 141.6	\mathbf{p}_y :	46.9°	352.9°	
	19.7	63.1	− 154.1	− 181.4	\mathbf{p}_x :	44.1°	187.9°	
$\mathbf{S}^{(3)}$	109.7	− 228.0	89.4	323.9	\mathbf{p}_z :	78.1°	320.3°	0.135
	− 228.0	34.2	− 46.8	− 140.1	\mathbf{p}_y :	49.8°	60.5°	
	89.4	− 46.8	− 143.9	− 183.8	\mathbf{p}_x :	42.6°	217.0°	

^a Tensor components and polar angles in the standard orthonormal system defined by $\mathbf{e}_x \parallel \mathbf{a}$, $\mathbf{e}_z \parallel \mathbf{c}^*$.

^b Asymmetry parameter.

we now attempt to express one of the $V^{(i)}$ as the weighted sum of $L^{(3)}$ and one of the tensors $S^{(2)}$ and $S^{(3)}$:

$$V_{\alpha\beta}^{(i)} = f_L \times L_{\alpha\beta}^{(3)} + f_S \times S_{\alpha\beta}^{(j)}; \quad i = 1, 2, 3; j = 2, 3. \quad (1)$$

f_L and $f_S = 1 - f_L$ are the temperature dependent fractional populations of the majority and the minority sites. With the help of a computer fit routine we searched for the value of f_L which minimizes

$$D_{ij} = \left[\sum_{\alpha > \beta} (V_{\alpha\beta}^{(i)} - f_L \times L_{\alpha\beta}^{(3)} - (1 - f_L) \times S_{\alpha\beta}^{(j)})^2 \right]^{1/2}. \quad (2)$$

For $i = 3$ and $j = 3$ a minimum $D_{33} = 0.43$ kHz is obtained with $f_L = 0.768$. The minima with respect to f_L of D_{ij} for all other combinations of i and j are much larger, the second smallest being $D_{11} = 17.9$ kHz. Moreover they are all obtained for f_L either equal to 1 or to 0 which does not make sense.

The value of $D_{33} = 0.43$ kHz must be compared, on the one hand, with the QCCs of $V^{(3)}$, $L^{(3)}$, and $S^{(3)}$ which are, respectively, 173.0, 215.3, and 215.9 kHz, and, on the other hand, with the experimental errors of the measured tensor components $V_{\alpha\beta}^{(3)}$, $L_{\alpha\beta}^{(3)}$ and $S_{\alpha\beta}^{(3)}$ which are estimated to be ± 0.8 kHz. The low value of D_{33} thus confirms the validity of Eq. (1) for $i = 3, j = 3$ and allows the unambiguous conclusion that the hydroxyl deuterons of the host lattice jump between two unequally populated sites in the way indicated in Fig. 1(b). Deuteron jumps along the O-D \cdots O hydrogen bonds are definitively ruled out.

We note in passing that the kinematics of the deuteron motion indicated in Fig. 1(b) (i.e., rotational jumps of the hydroxyl groups) can also be proved by determining the crystal orientations for which sharp lines are found at any temperature. For those orientations the NMR line positions of one of the deuterons in its majority site must coincide with the NMR line position of the same deuteron in its minority site. Knowing the QC tensors $L^{(i)}$ and $S^{(i)}$ it is an easy matter to calculate those crystal orientations for the two motional models in question. When we compare the resulting orienta-

tions with those for which we actually find sharp line pairs at any temperature it becomes evident once again that the hydroxyl groups carry out rotational jumps.

The positions of the deuterons in both their majority and their minority sites are a compromise between three tendencies: (i) The deuterons seek to optimize their C-O-D bond angles, (ii) they seek to be in a coplanar arrangement with "their" aromatic rings and (iii) they try to form linear O-D \cdots O hydrogen bridges. The deuterons can comply better with these tendencies for the majority than for the minority sites: (i) The C-O-D bond angles are 112.5° for the majority and 116.0° for the minority sites. When calculating these angles we identified \mathbf{p}_z of the deuteron QC tensors with the O-D bond directions, while the C-O bond directions were derived from the x-ray structure data.³ We assume that the heavy oxygen and carbon atoms occupy identical sites before and after a jump of the deuterons. For an undisturbed hydroxyl group we expect the C-O-D bond angle to be equal to the tetrahedral angle of 109.5°. (ii) For a majority site the OD vector points out of the aromatic plane by 9° while this angle is 13° for a minority site. (iii) The O-D \cdots O bond angles are 178° for the majority and 172° for the minority sites. These differences, small as they are, are responsible for the energy difference ΔE and, hence, the unequal occupancies of the majority and the minority sites. The motion of the deuterons can thus be described approximately as a rotation of the hydroxyl groups about the C-O bonds. It is only an *approximate* rotation since the C-O-D bond angles for the majority and the minority sites are slightly different. An estimation of the rotational angle α is obtained by rotating $L^{(3)}$ about the C-O₆ bond direction and comparing the resulting tensor $L^{(3)}(\alpha)$ with $S^{(3)}$. The optimum value for α turns out to be $\alpha_{\text{opt}} = 159^\circ$. The root mean square deviation of the five independent components $L_{\alpha\beta}^{(3)}(\alpha_{\text{opt}})$ from $S_{\alpha\beta}^{(3)}$ is 7.0 kHz. This number once again is small compared with the QCCs of $L^{(3)}$ and $S^{(3)}$, but large compared with D_{33} and indicates that the description of the observed deuteron motion as a rigid rotation of the hydroxyl groups is only approximately cor-

rect. Nevertheless we shall continue to speak about "rotational jumps of the hydroxyl groups" in what follows.

B. Temperature dependence of the occupancies f_L and f_S of the majority and minority sites

As described above we can determine the fractional populations f_L and $f_S = 1 - f_L$ by minimizing D_{33} of Eq. (2). The temperature dependences of f_L and f_S are thus obtained by inserting the $V_{\alpha\beta}^{(3)}$ measured at different temperatures into Eq. (2). We have measured them at $T = 305.5, 323$, and 278 K. Figure 4 shows a plot of $\log(r) = \log(f_L/f_S)$ vs $1/T$.

In the temperature range where the lines get very broad in most crystal orientations it is not possible to determine f_L and f_S . Note that those line pairs which stay "sharp" over the whole temperature range carry no information about f_L and f_S because the positions of the corresponding large and small lines coincide for the respective crystal orientations. In the temperature range where the spectra contain large and small lines the ratio $r(T) = f_L(T)/f_S(T)$ is directly given by the ratio of the intensities of the respective lines. By measuring these intensity ratios we determined $r(T)$ in this temperature range. At each temperature where data were taken the intensity ratios were measured for several crystal orientations and the average of the received values was calculated. The results are also plotted in Fig. 4.

According to Boltzmann we expect

$$r(T) = \exp(\Delta E/kT). \quad (3)$$

Indeed a straight line that passes through $r = 1$ for $1/T = 0$ could be fitted through the first seven data points in Fig. 4 leading to

$$\Delta E = (30.7 \pm 2.0) \text{ meV} \cong (2.96 \pm 0.20) \text{ kJ/mol}.$$

For $T < 145$ K ($1/T > 6.9 \times 10^{-3} \text{ K}^{-1}$) the data deviate distinctly from the Boltzmann-ansatz, the occupancies of the

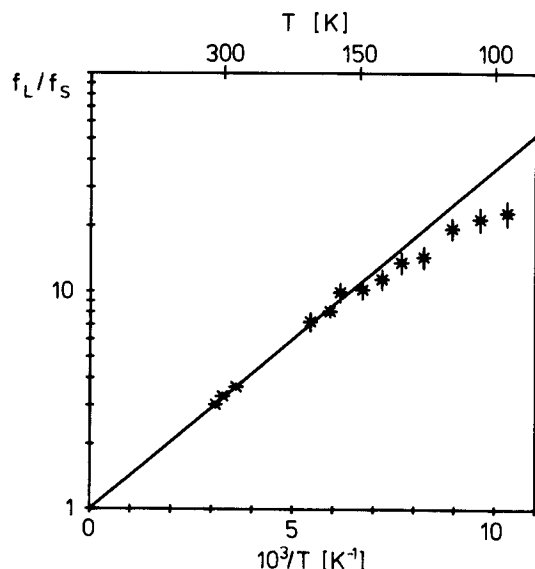


FIG. 4. Plot of $\log[r(T)]$ vs $1/T$. $r(T) = f_L(T)/f_S(T)$ is the ratio of the occupancies of the majority (f_L) and the minority (f_S) sites. A Boltzmann distribution is found for $T > 145$ K. The data deviate distinctly from this distribution at lower temperatures.

minority sites being larger than predicted by Eq. (3). We believe that this observation represents frozen-in overpopulations of the minority sites.

As we shall show in Sec. III D all six hydroxyl groups of one hexagon carry out the rotational jumps in a concerted manner. Thus, ΔE is the energy difference between the configurations "all six deuterons sit in their majority sites" and "all six deuterons sit in their minority sites."

C. Temperature dependence of the jump rates

The NMR-line shape $v(\omega)$ of a nucleus jumping between two positions with resonance frequencies ω_L and ω_S is given by¹⁴

$$v(\omega) = \text{Im} \left(\frac{f_L(\omega - \hat{\omega}_S) + f_S(\omega - \hat{\omega}_L) + i(P_{LS} + P_{SL})}{(\omega - \hat{\omega}_L + iP_{LS})(\omega - \hat{\omega}_S + iP_{SL}) + P_{LS}P_{SL}} \right) \quad (4)$$

with $\hat{\omega}_k = \omega_k - (i/T_2)$ for $k = L, S$. P_{LS} is the jump rate from the majority to the minority site, P_{SL} is defined analogously. P_{LS} and P_{SL} are not independent since detailed balance requires

$$\frac{P_{LS}}{f_S} = \frac{P_{SL}}{f_L}. \quad (5)$$

The correlation time of the motion τ_c is defined by

$$\frac{1}{\tau_c} = P_{LS} + P_{SL}. \quad (6)$$

Equation (4) holds for a deuteron without resolved dipolar or scalar coupling to another nucleus. As we know T_2 from the width $\Delta\omega$ of the lines that stay sharp over the whole temperature range ($\Delta\omega \approx 2\pi \times 1.5$ kHz) and as we have measured f_L and f_S before, the only unknown parameter is P_{LS} , or, equivalently, τ_c . Thus we can determine the jump rates by line shape fitting. Of course these fits can only be carried out at temperatures where the lines are, on the one hand, distinctly exchange broadened, but, on the other hand, not so broad that the observation of the lines becomes virtually impossible. Figure 5 shows four of the fits to demonstrate their quality.

Another means for establishing the jump rates is given by measuring the spin lattice relaxation rate T_1^{-1} . If it is dominated by a two-sites jump process of the deuteron, it may be expressed as¹⁵

$$\frac{1}{T_1} = \frac{4\pi^2}{9} \left\{ \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} (V_{xz}^{\beta^2} + V_{yz}^{\beta^2}) + \frac{\tau_c}{1 + 4\omega_0^2 \tau_c^2} \times [(V_{xx}^{\beta^2} - V_{yy}^{\beta^2})^2 + 4V_{xy}^{\beta^2}] \right\}. \quad (7)$$

ω_0 is the Larmor frequency and the $V_{ij}^{\beta^2}$ are the components of the fluctuating QC tensor defined by

$$\mathbf{V}^{\beta^2} = (f_L f_S)^{1/2} (\mathbf{L}^{(3)} - \mathbf{S}^{(3)}) \quad (8)$$

and expressed in the laboratory frame. As $\mathbf{L}^{(3)}$, $\mathbf{S}^{(3)}$, f_L and f_S have been measured before, \mathbf{V}^{β^2} is a known tensor.

To check the validity of Eq. (7) in our case we measured the orientation dependence of T_1 for the c crystal at $T = 323$ K. The results are shown in Fig. 6. Solving Eq. (7) for τ_c

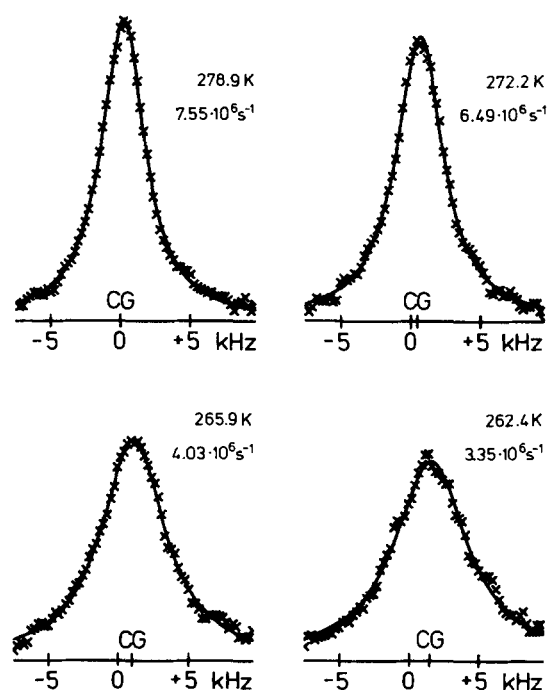


FIG. 5. Line shape analyses of the host lattice ^2H lines according to Eq. (4). The temperature at which each spectrum was recorded and the best value for $1/\tau_c = P_{LS} + P_{SL}$ are given with each spectrum. The origin of the frequency axis is set arbitrarily at the center of gravity (CG) of the line at $T = 278.9$ K. Note that the CGs of the lines shift on changing the temperature.

leads to a fourth order equation which does not have a unique solution. However, we already know the order of magnitude of τ_c from the line fits and therefore can easily select the physically meaningful solution. The solid line in Fig. 6 corresponds to Eq. (7) with $\tau_c = 2.55 \times 10^{-8}$ s. As we find good agreement between measurement and theory we conclude that the relaxation is actually dominated by the jumps. This is true at least at $T = 323$ K.

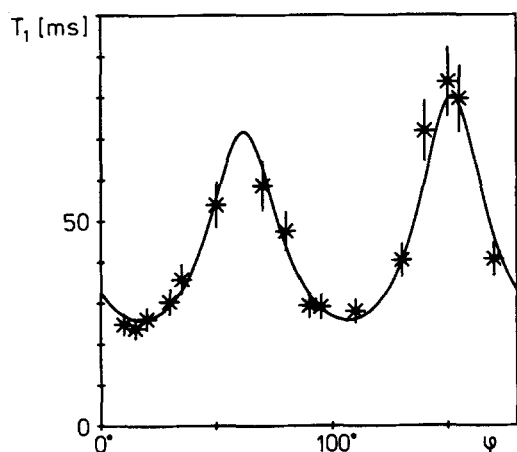


FIG. 6. Angular dependence of T_1 for the c crystal at $T = 323$ K. $\phi = 81.5^\circ$ corresponds to $B_0 \parallel a$. Estimated errors are $\pm 10\%$. The solid line corresponds to Eq. (7) with $\tau_c = 2.55 \times 10^{-8}$ s.

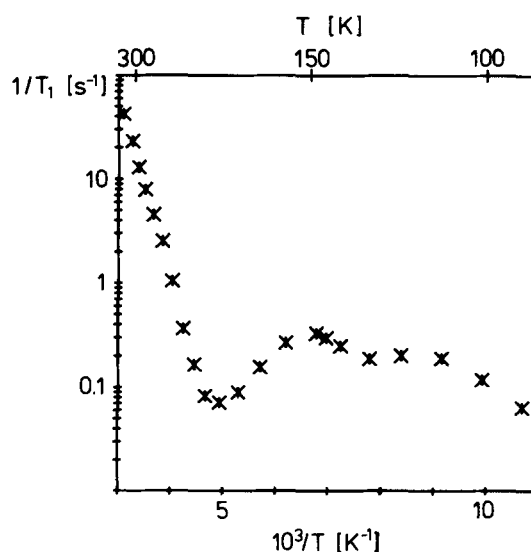


FIG. 7. Temperature dependence of the relaxation rate $1/T_1$. The relaxation is dominated by the two-sites jumps of the deuterons for $1/T < 4.6 \times 10^{-3} \text{ K}^{-1}$ ($T > 217$ K). At lower temperatures other relaxation processes take over. Vertical bars indicate estimated errors.

To establish the temperature dependence of τ_c we measured T_1 of a line pair that stays sharp at any temperature. The results are shown in Fig. 7. Using Eq. (7) together with Eqs. (5) and (6) we calculated the values of the jump rates from the measured relaxation times at $T > 210$ K. Figure 8 shows a plot of $\log(P_{LS})$ and $\log(P_{SL})$ vs. $1/T$. Data points derived from T_1 measurements are marked by stars, while those obtained by line fits are marked by circles. The fact that a fit of a straight line through the data points is possible proves that the jump rates follow an Arrhenius-ansatz in the temperature range in question:

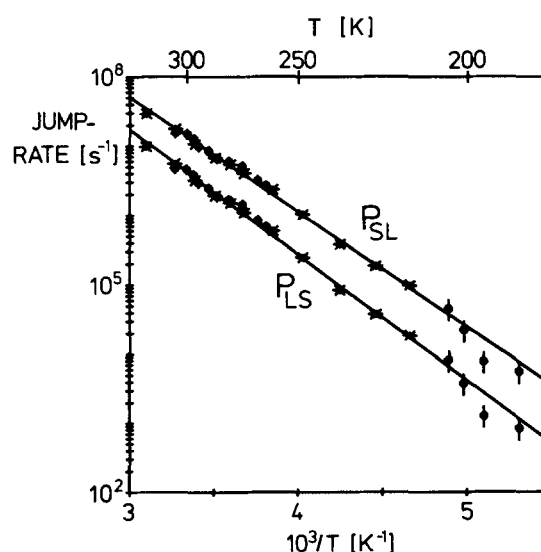


FIG. 8. Temperature dependences of the jump rates P_{SL} (top) and P_{LS} (bottom). Data points derived from T_1 measurements are marked by stars, those obtained by line shape analyses by circles. Note the excellent agreement between the two sets of data. The jump rates obey an Arrhenius law over the whole investigated temperature range. The two fitted straight lines are not parallel to each other, cf. Eq. (9).

$$P_{LS} = \frac{1}{\tau_0} \exp \left[- \left(E_a + \frac{\Delta E}{2} \right) / kT \right];$$

$$P_{SL} = \frac{1}{\tau_0} \exp \left[- \left(E_a - \frac{\Delta E}{2} \right) / kT \right].$$

Here we used $P_{SL} = f_L/f_S \times P_{LS} = \exp(\Delta E/kT) \times P_{LS}$ according to Eqs. (3) and (5). From the fit we obtain $1/\tau_0 = 3.6 \times 10^{12} \text{ s}^{-1}$, $E_a + \Delta E/2 = 359.1 \text{ meV}$, $E_a - \Delta E/2 = 328.7 \text{ meV}$ and thus:

$$E_a = (343 \pm 10) \text{ meV} \cong (33.1 \pm 1.0) \text{ kJ/mol}.$$

E_a is the activation energy. It can be interpreted as the height of an energy barrier that hinders the six deuterons to jump together from one site to the other. This is illustrated in Fig. 9.

Note that in no temperature range the plot of $\log(1/T_1)$ vs $1/T$ is linear, see Fig. 7. For $1/T < 4.6 \times 10^{-3} \text{ K}^{-1}$ ($T > 217 \text{ K}$) this is due to the fact that the relaxation is affected by both the temperature dependence of the occupancies f_L and f_S and the decrease of the transition probabilities P_{LS} and P_{SL} , which follow the Arrhenius equation down to at least $T = 188 \text{ K}$ ($1/T = 5.3 \times 10^{-3} \text{ K}^{-1}$). The strong deviation of $\log(1/T_1)$ vs $1/T$ from linearity for $T < 217 \text{ K}$ ($1/T > 4.6 \times 10^{-3} \text{ K}^{-1}$) is evidence that a relaxation process competing with the two-sites jumps takes over. This process is probably related with the motions of the guest molecules.

Finally we would like to draw the reader's attention to the fact that the agreement between the P_{LS} and P_{SL} derived, on the one hand, from relaxation and, on the other hand, from line shape analyses is excellent at temperatures where the two-sites jump process does dominate the deuteron relaxation (see Fig. 8). Note that all parameters except P_{LS} and P_{SL} entering Eqs. (4) and (7) have been measured independently. This is true in particular of $\mathbf{V}^H = (f_L f_S)^{1/2} (\mathbf{L}^{(3)} - \mathbf{S}^{(3)})$. Stressing this point is worthwhile since Sparks *et al.* in their recent powder work on the side chain dynamics of crystalline L -[3,3- $^2\text{H}_2$] methionine¹⁶ find it both necessary and logical to introduce a correction factor for reconciling correlation times derived, respectively, from relaxation measurements and from line shape analyses.

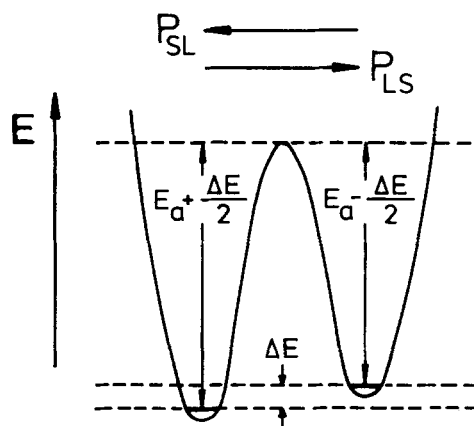


FIG. 9. Double minimum potential and meaning of the energies E_a and ΔE . The deeper and higher minima belong, respectively, to the configurations "all six deuterons in their majority sites" and "all six deuterons in their minority sites." P_{LS} and P_{SL} are the jump rates for the concerted jumps of all six deuterons.

D. Independent or concerted rotational jumps of the hydroxyl groups?

In this section we discuss the question whether the six hydroxyl groups in one of the hexagons [see Fig. 1(b)] carry out their rotational jumps in a concerted manner or independently from each other. Concerted means in this context that all six deuterons change their sites in a time that is short compared with the mean time each of them stays in either its majority or minority site.

If the deuterons jumped completely independently, they would come very close to each other occasionally. Assuming that the O-D bond length is 0.96 \AA ¹⁷ a distance of 0.93 \AA results for, e.g., the sites D_6 and D'_1 [see Fig. 1(b)]. While rotational jumps of six hydroxyl groups in concert are a remarkable phenomenon it is also quite unlikely that two deuterons sit as close as 0.93 \AA to each other for a considerable time. As discussed in Sec. III C the residence time in the minority sites is about 10^{-7} s at room temperature and increases to about 10^{-4} s at $T = 190 \text{ K}$. To decide experimentally whether the hydroxyl groups carry out their rotational jumps independently or in a concerted manner we draw on the fact that the dipolar coupling of two deuterons at close distance would affect the form of the ^2H -NMR spectrum. Calculating this form for an arbitrary jump rate is a complicated problem, because in general we have to consider six deuterons each of them coupled to its next two neighbors in a time dependent manner. We therefore restrict ourselves to calculating the splittings to be expected in the limiting cases of very slow and very fast motion for independent jumps and considering special crystal orientations for which these splittings should be maximal.

For very slow motion, i.e., at very low temperatures, we basically face a static problem. A deuteron sitting in the minority site together with the neighboring deuteron in the majority site forms a fairly isolated, strongly coupled pair of deuterons. This case can be treated readily.¹⁸ The secular part of its Hamiltonian is $H_{\text{sec}} = H_Q + H_D$ with

$$H_Q = H_{Q1} + H_{Q2} = \hbar 3 A_1 I_{z1}^2 + \hbar 3 A_2 I_{z2}^2 \quad (10)$$

and

$$H_D = \hbar D [I_{z1} I_{z2} - \frac{1}{4} (I_1^- I_2^+ + I_1^+ I_2^-)], \quad (11)$$

where, for $i = 1, 2$,

$$A_i = \frac{e^2 Q_1 q_i}{8 \hbar} (3 \cos^2 \theta_i - 1 + \eta_i \sin^2 \theta_i \cos 2\Phi_i); \quad (12)$$

$$D = \frac{\gamma^2 \hbar}{r_{12}^3} (1 - 3 \cos^2 \theta_{12}). \quad (13)$$

\mathbf{r}_{12} is the vector from the first to the second deuteron, $\theta_{12} = \angle(\mathbf{B}_0, \mathbf{r}_{12})$. θ_i, Φ_i are the polar angles of the applied field \mathbf{B}_0 in the principal axes system of the QC tensor of the i th deuteron. The remaining symbols have their usual meanings. In the limiting case $|A_1| - |A_2| \gg D$ the spectrum consists of four symmetric 1:1:1 triplets, centered at the positions of the resonances of the uncoupled deuterons. The splitting of two adjacent components of any triplet equals D . In other cases the dipolar fine structure consists of asymmetric triplets with line splittings between D and $2D$. Now we can discuss the form of the spectra for independent jumps in

the temperature range where small lines are found. Assuming that the jump rates still obey the Arrhenius law at, say, $T = 170$ K we have: $P_{LS}(170 \text{ K}) = 70 \text{ s}^{-1}$ and $P_{SL}(170 \text{ K}) = 565 \text{ s}^{-1}$. For two deuterons being 0.93 \AA apart $D = (1 - 3 \cos^2 \theta_{12}) * 2\pi * 3.5 \text{ kHz}$. Thus at least for crystal orientations such that $|\cos \theta_{12}| \approx 1$ the *slow motion regime* $D \gg P_{SL}$ applies for $T < 170 \text{ K}$. In the model of independent jumps a deuteron sitting in its minority site will be very close to its neighboring deuteron for an average time fraction given by $f_L(T)$, because for this time fraction the neighboring deuteron will sit in its majority site. The resonance of the deuterons in the minority sites will be inhomogeneous, the fraction $f_L(T)$ of any small line being affected by the dipolar coupling to the neighboring deuteron. At $T = 170 \text{ K}$ this fraction is $f_L \approx 0.89$ and it increases with decreasing temperature, see Sec. III B. We recorded several spectra at $T < 170 \text{ K}$ for a crystal orientation with $|\cos \theta_{12}| \approx 1$ and $|A_1| - |A_2| \gg D$ for one of the deuterons. An example is shown in Fig. 10. The line pair for which $|\cos \theta_{12}| \approx 1$ is marked by arrows. For independent jumps we would expect these small lines to split into triplets, the splitting between two adjacent components being about 7 kHz . The width $\Delta\nu \approx 2.5 \text{ kHz}$ of these lines is somewhat larger than that of the other small lines, $\Delta\nu \approx 1.5 \text{ kHz}$, but there is certainly no splitting of the predicted size. As a matter of fact dipolar fine structure of the small lines is not found at any temperature for any crystal orientation. Thus we conclude that at least at low temperatures the deuterons do not jump independently from each other. If, in contrast, they carry out their jumps in a concerted manner they never come very close to each other for a sizable fraction of time so we do not expect a resolvable dipolar splitting, in agreement with the experiment.

Next we consider the regime of very fast motion. To simplify the situation and to enlarge the expected effect we recorded spectra of a 30% deuterated crystal. We take for granted that the protonated hydroxyl groups carry out the same rotational jumps as their deuterated counterparts. The crystal could be rotated about the c axis. We chose the special orientation sketched in Fig. 11 for which the calculation

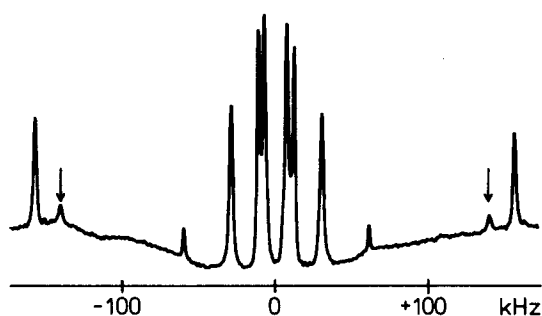


FIG. 10. Spectrum from the c crystal recorded at $T = 169 \text{ K}$. The crystal orientation was chosen such that in the hypothetical case of independent jumps the lines marked by arrows would split into symmetric triplets with line splittings of about 7 kHz between adjacent components. No such dipolar fine structure is observed. Therefore independent jumps are ruled out at "low" temperatures. 500 FIDs were accumulated for the spectrum with $t_p = 2 \mu\text{s}$, $\tau = 2 \text{ s}$.

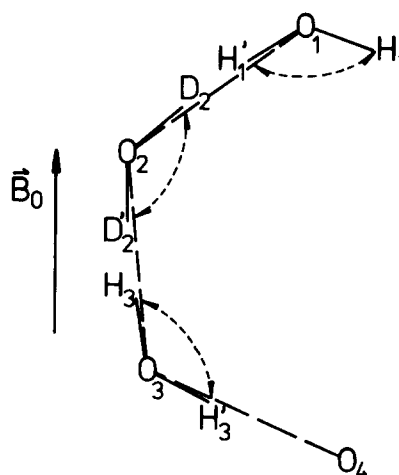


FIG. 11. The special orientation of the 30% deuterated crystal chosen to answer the question whether or not the six deuterons jump independently at "high" temperatures. The angle between \mathbf{B}_0 and $\mathbf{D}_2\mathbf{H}_1$ is close to the magic angle $\theta_{\text{mag}} = 54.7^\circ$. Hence the dipolar coupling between \mathbf{D}_2 and the nucleus in position 1 can be neglected. As $\angle(\mathbf{B}_0, \mathbf{D}_2\mathbf{H}_3)$ is small the dipolar interaction between deuteron 2 and proton 3 is nearly maximal.

of the expected spectrum becomes particularly easy. We consider the deuteron jumping between positions D_2 and D'_2 . The angle between \mathbf{B}_0 and $\mathbf{D}_2\mathbf{H}_1$ (or $\mathbf{D}_2\mathbf{D}'_1$ if there is a deuteron in position 1) is close to the magic angle $\theta_{\text{mag}} = 54.7^\circ$ which means that the dipolar coupling between \mathbf{D}_2 and the nucleus in position 1 can be neglected. Let us assume that there is a proton in position 3. As $\angle(\mathbf{D}'_2\mathbf{H}_3, \mathbf{B}_0) \approx 5^\circ$, the dipolar interaction between \mathbf{D}'_2 and \mathbf{H}_3 is nearly maximal. Now consider the Hamiltonian for deuteron 2. For fast motion we have to consider the averaged Hamiltonian \bar{H} taking into account the possible positions of deuteron 2 and proton 3.

$$\bar{H} = \hbar \bar{A} 3I_z^2 + \hbar f_S f_L^* D I_z S_z, \quad (14)$$

with

$$D = \frac{\gamma_P \gamma_D \hbar}{r_{23}^3} (1 - 3 \cos^2 \theta_{23}) \quad (15)$$

and

$$\bar{A} = f_L A_L + f_S A_S. \quad (16)$$

\mathbf{r}_{23} is the vector from deuteron 2 to proton 3, $\theta_{23} = \angle(\mathbf{r}_{23}, \mathbf{B}_0)$, f_L^* is the fractional population of the proton in the majority site and S_z is the z component of the proton's spin operator. This Hamiltonian leads to a spectrum consisting of two doublets at \bar{A} and $-\bar{A}$ with doublet splitting of $S = f_S f_L^* D$. Assuming $f_L = f_L^*$ and inserting $f_L(357 \text{ K}) = 0.73$, $r_{23} = 0.93 \text{ \AA}$ and $\theta_{23} = 5^\circ$ we obtain $S = 2\pi \times 17.8 \text{ kHz}$. In our crystal only 70% of the \mathbf{H}_3 positions are occupied by a proton, the remaining ones by a deuteron. Therefore we should find a superposition of the calculated doublets and of triplets with smaller splittings resulting from deuteron-deuteron coupling. The spectrum shown in Fig. 12 was recorded at $T = 357 \text{ K}$. We are certainly in the *fast motion regime* $P_{LS} > (A_L - A_S)^2 / S^{19}$ since

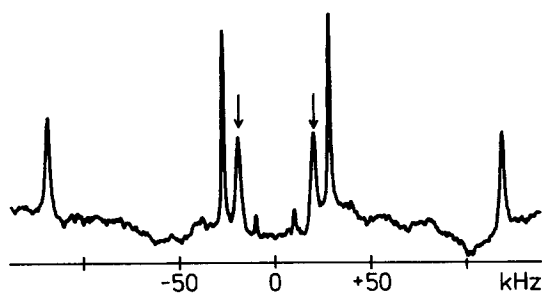


FIG. 12. Spectrum from the 30% deuterated crystal recorded at $T = 357$ K. In the hypothetical case of independent jumps of the six deuterons in one hexagon the lines marked by arrows would split into doublets with a splitting of about 17.8 kHz. No such dipolar fine structure is found. We conclude that the six deuterons do not jump independently also at "high" temperatures. 2000 FIDs were accumulated for the spectrum with $t_p = 2 \mu\text{s}$, $\tau = 100$ ms. The small interior line pair belongs to the ethanol guest. These lines are small because T_1 is much greater than 100 ms for the ethanol guest at $T = 357$ K. The strong baseline distortions are due to coherent disturbances which build up when very many FIDs need to be accumulated which is the case for the only 30% deuterated crystal.

$P_{LS} = 3.2 \times 10^7 \text{ s}^{-1}$ at $T = 357$ K, while $(A_L - A_S)^2/S = 2.4 \times 10^6 \text{ s}^{-1}$ for the line pair from deuteron 2 which is marked by arrows in Fig. 12. No dipolar fine structure is found. From this we infer that also at high temperatures the deuterons do not jump independently from each other. As we do not find any sign of dipolar fine structure in our spectra at any temperature for any crystal orientation we would like to conclude that the rotational jumps of the hydroxyl groups occur in a concerted manner over the whole temperature range.

Of course one could argue that there might be some correlation between the rotational jumps of the six hydroxyl groups, but that this correlation is not strong enough to permit only concerted jumps of all six deuterons. However, in this case the ^2H spectra should display dipolar splittings in a similar manner as discussed above. The line splittings would be of the same size as calculated above whereas the intensities of the components would depend on the strength of the correlation. Only in the case of very strong correlation, which means concerted rotational jumps of all six hydroxyl groups, will there be no dipolar fine structure, in agreement with the experimental data.

In order to find out whether the jump rates of the deuterons are different in the 30% and in the fully deuterated crystals we measured the spin lattice relaxation times for three different orientations of the 30% deuterated crystal at $T = 305.5$ K. Within the experimental error of $\pm 10\%$ the same results as for the fully deuterated crystal were obtained. Thus, there is no significant difference of the jump rates in the two crystals. As we are dealing with concerted jumps, which in the case of the 30% deuterated crystal involve a majority of protonated hydroxyl groups, this result suggests that protonated hydroxyl groups jump at essentially the same rate as deuterated ones.

Finally we would like to emphasize how important the use of single crystals has been for this study. The ^2H -NMR spectra obtainable from a polycrystalline sample of Dianin's

compound with ethanol as a guest are superposition of Pake patterns from the host lattice on the one hand and from the guest on the other hand, which would have to be separated first. In the present case this seems to be a tractable task. From the asymmetry parameters and quadrupole coupling constants obtainable from high temperature host lattice Pake patterns one would clearly conclude that the deuterons undergo some kind of motion. The low temperature spectra, however, would just be Pake patterns of static hydroxyl deuterons, since the QC tensors of the deuterons in their majority and in their minority sites are almost indistinguishable, apart from rotations. Thus, it would be quite difficult to unravel the kinematics of the motions and in any event one would have to resort to motional models. Even if one had guessed correctly the kinematics it would still be hard to distinguish between independent or concerted jumps, since the effects of the dipolar coupling on the Pake patterns to be expected in the case of independent jumps would be small and hardly conclusive.

We believe that the advantage of single crystal over powder ^2H -NMR studies is of particular importance in case of dynamical processes that involve strongly unequal occupancies of different sites.

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- ¹A. P. Dianin and J. Russ, *Phys. Chem. Soc.* **46**, 1310 (1914).
- ²W. Baker, A. J. Floyd, J. F. W. McOmie, G. Pope, A. S. Weaving, and J. H. Wild, *J. Chem. Soc.* **1956**, 2010.
- ³J. L. Flippen, J. Karle, and I. L. Karle, *J. Am. Chem. Soc.* **92**, 3749 (1970).
- ⁴J. L. Flippen and J. Karle, *J. Phys. Chem.* **75**, 3566 (1971).
- ⁵L. Pauling, *J. Am. Chem. Soc.* **57**, 2680 (1935).
- ⁶J. Gallier, B. Toudic, M. Stahn, R. E. Lechner, and H. Dachs, *J. Phys. (France)* **49**, 949 (1988).
- ⁷W. Scheubel, H. Zimmermann, and U. Haeberlen, *J. Magn. Reson.* **80**, 401 (1988).
- ⁸T. Agaki, F. Imashiro, T. Terao, N. Hirota, and S. Hayashi, *Chem. Phys. Lett.* **139**, 331 (1987).
- ⁹R. Meyer and R. R. Ernst, *J. Chem. Phys.* **86**, 784 (1987).
- ¹⁰T. P. Jarvie, A. M. Thayer, J. M. Miller, and A. Pines, *J. Phys. Chem.* **91**, 2240 (1987).
- ¹¹H. H. Limbach, B. Wehrle, H. Zimmermann, R. D. Kendrick, and C. S. Yannoni, *Angew. Chem. Int. Ed. Engl.* **26**, 247 (1987).
- ¹²C. Betzel, W. Saenger, B. E. Hingerty, and G. M. Brown, *J. Am. Chem. Soc.* **106**, 7545 (1984).
- ¹³R. Blinc, in *The Hydrogen Bond II*, edited by P. Schuster, G. Zundel, and C. Sandorfy (North-Holland, Amsterdam, 1976).
- ¹⁴A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance* (Harper & Row, New York, 1969).
- ¹⁵S. Benz, U. Haeberlen, and J. Tengenfeldt, *J. Magn. Reson.* **66**, 125 (1986).
- ¹⁶S. W. Sparks, N. Budhu, P. E. Young, and D. A. Torchia, *J. Am. Chem. Soc.* **110**, 3359 (1988).
- ¹⁷*CRC Handbook of Chemistry and Physics*, 64th ed., edited by R. C. Weast (CRC, Boca Raton, FL, 1983).
- ¹⁸C. Müller, S. Idziak, N. Pislewski, and U. Haeberlen, *J. Magn. Reson.* **47**, 227 (1982).
- ¹⁹A. Keller, S. Benz, and U. Haeberlen, *J. Magn. Reson.* **72**, 434 (1987).