Proton and Deuteron NMR Study on Single Crystals of $Na_2ZnCl_4 \cdot 3\,H_2O$ ($Na_2ZnCl_4 \cdot 3\,D_2O$)

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Single crystal ^{1}H- and ^{2}H-NMR spectra of $Na_2ZnCl_4 \cdot 3\,H_2O$ and $Na_2ZnCl_4 \cdot 3\,D_2O$, respectively, were studied. The following results have been obtained: The positions of the hydrogens and deuterons are described in the space group $C_{3v}^2 - P\,31m$ with one formula unit in the unit cell. The point positions are: $H_I(D_I)$ in 3m: $x = 0.455 \pm 4$, $y = 0$, $z = 0.556 \pm 5$; $H_{II}(D_{II})$ in 3m: $x = 0.675 \pm 4$, $y = 0$, $z = 0.466 \pm 5$. The angle H–O–H (D–O–D) is 107.0° and the H–H distance is 1.603 ± 3 Å. Including dynamical corrections, the equilibrium positions are: $H_I(D_I)$: $x = 0.459 \pm 4$, $y = 0$, $z = 0.550 \pm 5$; $H_{II}(D_{II})$: $x = 0.669 \pm 4$, $y = 0$, $z = 0.464 \pm 5$. The H–H distance is then 1.537 ± 5 Å. From the ^{2}H-NMR the nuclear quadrupole coupling constant of the deuterons is at $T = 22$ °C: $e^2qQ/h = 132.0 \pm 1.0$ kHz; $\eta = 0.754 \pm 5$. The major principal axis of the electric field gradient tensor is perpendicular to the twofold axis of the molecule D_2O. At $T = -25$ °C for the two deuteron atoms of one molecule D_2O, the values $(e^2qQ/h)_I = 239.7 \pm 1.0$ kHz; $\eta_I = 0.118 \pm 2$; $(e^2qQ/h)_{II} = 235.9 \pm 1.0$ kHz; $\eta_{II} = 0.125 \pm 2$ have been found. Here the intermediate principal axis of the FGT is perpendicular to the H–O–H plane. The direction cosines of the FGTs have been determined. The activation energy for the flipping process was found to be 12.7 kcal. mol^{-1}. The possible hydrogen bonds O–H ... Cl are discussed.

Introduction

In connection with investigations of hydrogen bonds in crystal hydrates[1,2] it was of interest to study the hydrogen positions and the hydrogen bond in crystals of $Na_2ZnCl_4 \cdot 3\,H_2O$ and $Na_2ZnCl_4 \cdot 3\,D_2O$, respectively. Except for the positions of the hydrogen atoms, the crystal structure of $Na_2ZnCl_4 \cdot 3\,H_2O$ is well known[3,4]. The compound crystallizes at room temperature with the space group C_{3v}^2-P 31m and may therefore be of interest in optical devices. The phonon spectrum of $Na_2ZnCl_4 \cdot 3\,H_2O$ and of $Na_2ZnCl_4 \cdot 3\,D_2O$ has recently been studied[5]. ^{35}Cl-NQR experiments on polycrystalline samples are reported in the literature[6] and single crystal studies of the electric field gradients in $Na_2ZnCl_4 \cdot 3\,H_2O$ by ^{23}Na- and ^{35}Cl-NMR are available[7,8]. The Mn^{2+}-EPR spectrum of $Na_2ZnCl_4 \cdot 3\,H_2O$:Mn^{2+} was studied by Schlaak and Weiss[9] (see the following paper) in order to get information about the electric field at the center of the $MnCl_4^{2-}$-ion within this system.

Experimental

Single crystals of $Na_2ZnCl_4 \cdot 3\,H_2O$ were grown from saturated aqueous solutions containing NaCl and $ZnCl_2$ in the molar ratio of approx. 1.6:1. As observed by Brehler[3], the crystals grow as elongated prisms and needles with the prism axis [001]. The hexagonal zone {100} and the basis {001} are favored, although the trigonal prism {110} was also observed. Some crystals developed {111}-faces, especially during the last period of their growing. The crystal growth was achieved by slow cooling of the solution within a closed system. Small seeds of the crystals were fixed on glass rods and inserted into the thermostatized saturated solution of appropriate composition. The crystal growth was started at 35–37 °C and the solution cooled at a rate of approx. 0.2°/day. Crystals of the size of 1–3 cm^3 have been obtained in this way. The same procedure was applied in growing crystals of $Na_2ZnCl_4 \cdot 3\,D_2O$. Special care was taken in preventing exchange of D_2O with atmospheric H_2O.

Differential thermoanalysis of $Na_2ZnCl_4 \cdot 3\,H_2O$ showed two peaks at 80.3 ± 0.5 °C and 98.1 ± 0.5 °C, respectively. We assign the phase transformation $Na_2ZnCl_4 \cdot 3\,H_2O \rightarrow Na_2ZnCl_4 \cdot H_2O + 2\,(H_2O)_g$ and $Na_2ZnCl_4 \cdot H_2O \rightarrow Na_2ZnCl_4 + (H_2O)_g$ to these two peaks.

The ^{1}H-NMR spectra

For the NMR experiments, the axes [001], [010], and [210] were chosen as an orthogonal set of crystal axes (Figure 1). Crystals with a shape appropriate for the NMR experiments were

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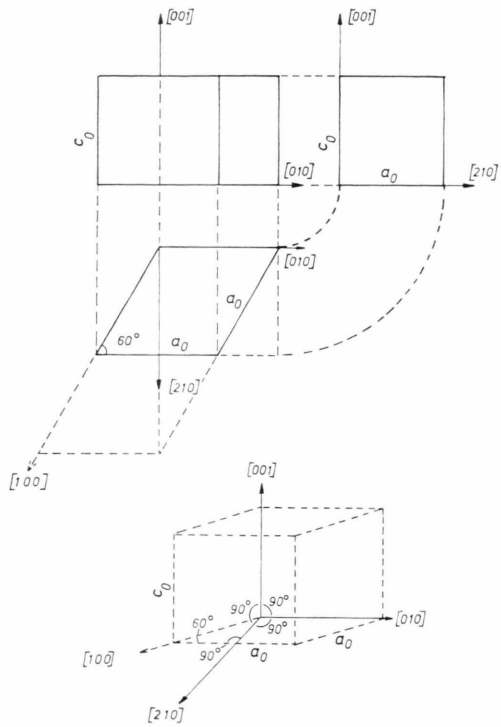


Fig. 1. Orthogonal set of axes and unit cell of $Na_2ZnCl_4 \cdot 3\ H_2O$ ($Na_2ZnCl_4 \cdot 3\ D_2O$). The hexagonal axes are shown too.

mounted on a glass rod, which in turn was attached to a goniometer head. As the crystals are hygroscopic in air with a relative humidity of $\geqq 30\%$ they had to be protected with a thin layer of vaseline. The adjustment with an optical two circle goniometer was thus difficult and misalignments in the order of 1° to 3° had to be taken into account. To correct such misalignments, a numerical method, explained in Appendix I, was applied. For the NMR experiments the goniometer head with the single crystal was fixed on a one circle goniometer which was mounted on the base of the electromagnet with its axis of rotation perpendicular to the symmetry axis of the magnetic field H_0[10]. Three different crystals were rotated within the magnetic field H_0 through 180° about the crystal axes [001], [010], and [210], respectively.

With the aid of a Varian V 4210 A wide line spectrometer and a Varian V 3900-12″ magnet with field control (Fielddial Mark II), the ^{1}H-NMR spectra were recorded at a fixed frequency of 15.644 MHz using the field sweep, which was checked for linearity and rated magnitude. The linearity was found to be accurate to $\pm$ 0.1 Gauss. A sweep speed of 2G/minute, a modulation frequency of 40 Hz for ΔH_0, a modulation amplitude of 0.98 G, and a time constant of 3 seconds were chosen for the experiments. The ^{1}H-NMR spectra were recorded in steps of 3° ([010] and [210] as axes of rotation) or 2° ([001] as axis of rotation) within the range of $0° \leqq \varphi \leqq 180°$. In Fig. 2, a typical ^{1}H-NMR spectrum of $Na_2ZnCl_4 \cdot 3\ H_2O$ is shown.

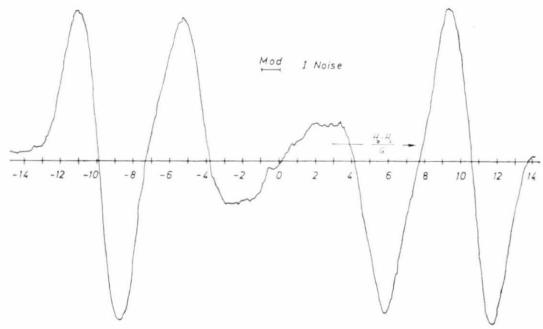


Fig. 2. Single crystal ^{1}H-NMR spectrum of $Na_2ZnCl_4 \cdot 3\ H_2O$. Rotation axis is [210]; the angle $\varphi\{H_0, [001]\}$ is 73°. H_0 is the external field, H_L the Larmor field for free protons.

In a solid, the dipolar interaction between nuclei results in a splitting (or broadening) of the NMR lines (Pake[11]). Restricting the problem to the protons in a crystal hydrate, the splitting is given by:

$$\Delta H = (3\mu/r_{12}^3)[3\cos^2\delta\cos^2(\varphi - \varphi_0) - 1]. \quad (1)$$

Here μ is the magnetic moment of the proton and r_{12} is the distance between the two protons 1 and 2 within one water molecule. The angles δ, φ and φ_0 are explained in Figure 3a. Equation (1) is exact for an isolated two proton system. As long as the minimum intermolecular distance $(r_{12})_{\text{inter}}$ of protons belonging to different H_2O molecules is considerably larger than the intramolecular distance $(r_{12})_{\text{intra}}$ within the H_2O molecule, $(r_{12})_{\text{inter}}/(r_{12})_{\text{intra}} \geqq 1.6$, the Pake formula (1) can be used in its simple form[12,1]. This condition is fulfilled in our experiment and, therefore, Eq. (1) was used without any corrections.

From the study of the doublet splitting ΔH as a function of the angles δ and φ the direction of the intramolecular H-H-vector and its length can be deduced. The three water molecules in the unit cell ($Z = 1$) of $Na_2ZnCl_4 \cdot 3\ H_2O$ are inequivalent with respect to the NMR experiment. The spectra taken with [001] and [010], respectively, as axes of rotation show three pairs of ^{1}H-NMR lines with the

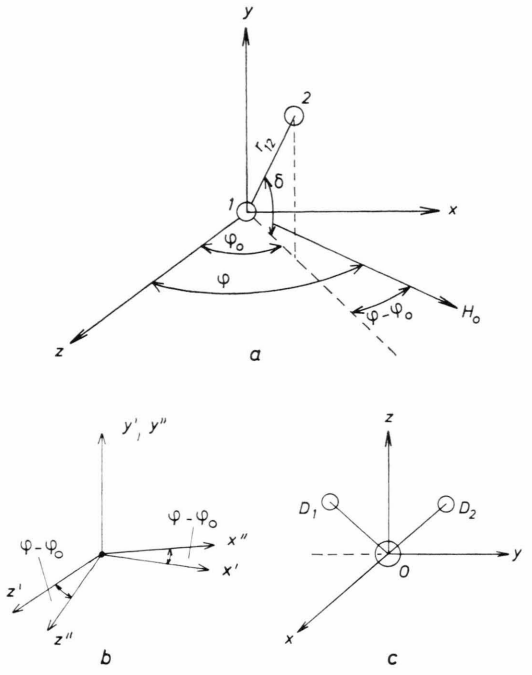


Fig. 3. a) Definition of the angles between the intramolecular H-H-vector, r_{12}, the external magnetic field H_0, and the rotation axis y. — b) Laboratory coordinate system x', y', z', and crystal axes system x'', y'', z'', chosen for the ^{2}H-NMR experiments on $Na_2ZnCl_4 \cdot 3\,D_2O$. Special situation: [210] is the rotation axis. — c) Internal coordinate system of a molecule D_2O.

maximum pair splitting of 17 G ([001] as axis of rotation) and 13—14 G ([010] as axis of rotation). Small inclusions of mother liquid gave for some crystals an additional weak signal at $H_0 = H_L$ due to free water molecules.

The ^{1}H-NMR spectra with [010] and [001] as axes of rotation are badly resolved. The lines overlap over a wide range of angles φ. Therefore, minor use was made of these spectra in determining r_{12} and the angles δ and φ_0. In Figs. 4 and 5, the line splittings ΔH for the rotation around [001] and [010] are shown.

With [210] as axis of rotation, two of the three proton pairs are equivalent with respect to the ^{1}H-NMR (see Discussion) and the maximum splitting found is about 10 G. For the third proton pair the maximum splitting is 20.6 G. The proton-proton vector of this particular water molecule is perpendicular to the crystal axis [210] and well resolved doublets over wide ranges of angles are found. In this case misalignments of 2° to 3° of the axis of rotation with respect to the crystal axis [210] have no significant influence on the ^{1}H-NMR spectrum. Thus the results obtained for this proton pair have mainly been used in calculating the direction and the length of the intramolecular H-H-vector. In Fig. 6, the ^{1}H-NMR rotation pattern for the axis of rotation [210] is shown.

When rotating around the axes [210] and [010], respectively, the position of the axis [001] was determined with the aid of the ^{23}Na-NMR spectrum. The principal axis V_{ZZ} of the electric field gradient tensor at the site of the ^{23}Na is identical with the axis [001]. In this way, the accuracy in determining the angle between the H-H-vector and the axis [001] was significantly improved. The final results of the ^{1}H-NMR experiments are given in Table 1.

Table 1. Results from ^{1}H-NMR spectroscopy on $Na_2ZnCl_4 \cdot 3\,H_2O$.

a) Intramolecular H-H-distance r_{12} (within one molecule H_2O): $r(H \ldots H) = 1.603 \pm 0.003$ Å.

b) Angle δ between the plane (001) and the H-H-vector (for all three water molecules):
$\delta\{H \ldots H, (001)\} = 19.4 \pm 0.1°$.

c) Angles between the crystal planes and the H-H-vector:
Molecule 1: $\vartheta\{H \ldots H, (100)\} = 0° \pm 0.3°$,
Molecule 2: $\vartheta\{H \ldots H, (010)\} = 0° \pm 0.3°$,
Molecule 3: $\vartheta\{H \ldots H, (110)\} = 0° \pm 0.3°$.

d) Angles between the crystal axes and the H-H-vector r_{12} (molecule 1):
$\alpha = \alpha\{r_{12}, [001]\} = 70.6° \pm 0.1°$,
$\beta = \beta\{r_{12}, [210]\} = 90°$,
$\gamma = \gamma\{r_{12}, [010]\} = 19.4° \pm 0.1°$.

The ^{2}H-NMR spectra

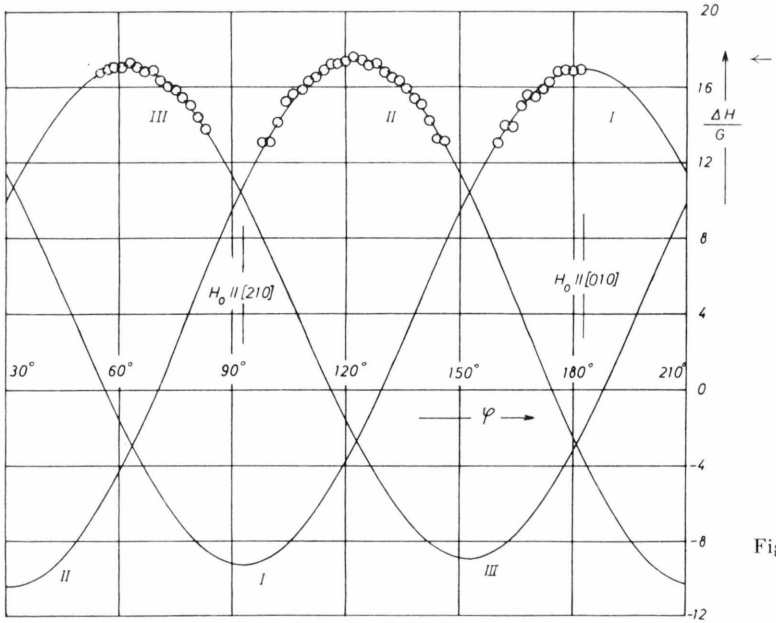
In magnetic fields of the order of 10^4 G, the splitting of a D-NMR line due to nuclear quadrupole interactions is satisfactorily described by the first order perturbation theory[13]:

$$\Delta\nu = \frac{3(2m-1)}{2I(2I-1)} \frac{e^2qQ}{h} \frac{V_{z'z'}}{eq}. \qquad (2)$$

$\Delta\nu$ is the frequency splitting $\nu' - \nu''$ between a pair of satellites, and $V_{z'z'}$ is the component of the electric field gradient tensor, FGT, in the direction of the external magnetic field H_0. m is the magnetic quantum number, I the nuclear spin, eQ the nuclear quadrupole moment, and eq is the major principal axis of the FGT. For deuterium with the spin $I = 1$, this equation is reduced to:

$$\Delta\nu = \frac{3}{2} \frac{eQ}{h} V_{z'z'}. \qquad (3)$$

x', y', z' are the Cartesian axes of the laboratory coordinate system, with z' defined as the direction



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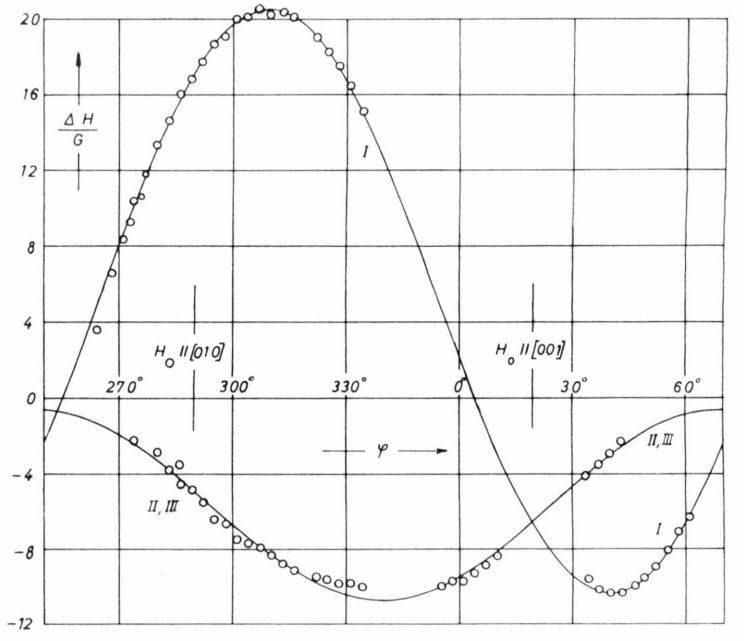
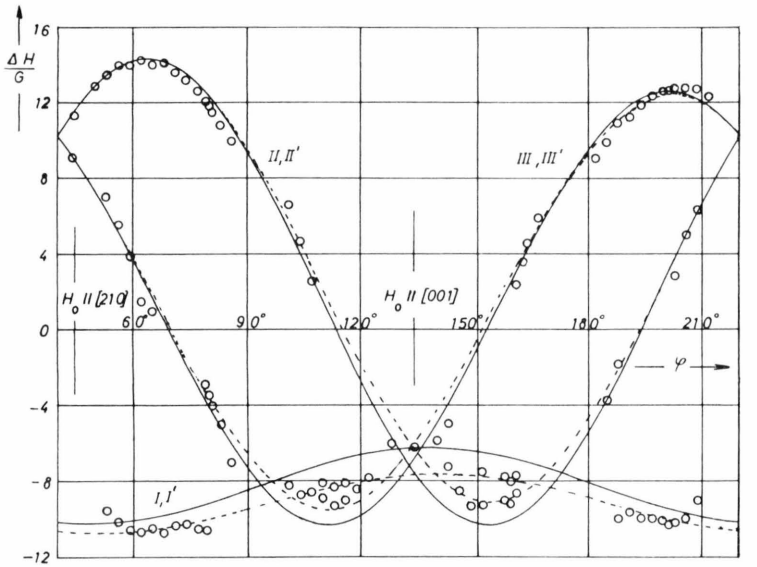


Fig. 6 →



← Fig. 5

Fig. 4. Pake curves, $\Delta H = f(\varphi)$, for the ^{1}H-NMR spectrum in $Na_2ZnCl_4 \cdot 3\ H_2O$. Rotation axis is [001]. The 3 H_2O molecules corresponding to the curves I, II, III are located on the crystal planes (100), (010), and ($\bar{1}$10), respectively.

Fig. 5. Pake curves, $\Delta H = f(\varphi)$, for the ^{1}H-NMR spectrum in $Na_2ZnCl_4 \cdot 3\ H_2O$. Rotation axis is [010]. The dashed curves are gained by the mean squares adjustment to the experimental points. The heavy drawn curves are corrected for line overlap. The 3 H_2O molecules corresponding to the curves I, II, III are located on the crystal planes (100), (010) ,and ($\bar{1}$10), respectively.

Fig. 6. Pake curves, $\Delta H = f(\varphi)$, for the ^{1}H-NMR spectrum in $Na_2ZnCl_4 \cdot 3\ H_2O$. Rotation axis is [210]. The two curves I, and II, III correspond to the water molecules located on the crystal planes (100) and (010), ($\bar{1}$10), respectively.

of the magnetic field H_0, y' as the rotation axis and x' perpendicular to both of them. Furthermore, a crystal axes system is defined by x'', y'', and z''. $V_{z'z'}$ can be expressed by the components of the principal axes of the FGT with respect to the crystal axes. Using y'' as the rotation axis ($y'' = y'$) we have[13]:

$$V_{z'z'} = \tfrac{1}{2}(V_{x''x''} + V_{z''z''}) + \tfrac{1}{2}(V_{z''z''} - V_{x''x''}) \cos 2\varphi + V_{x''z''} \sin 2\varphi. \quad (4)$$

For this work we have chosen the crystal axes $x'' = [001]$, $y'' = [210]$ and $z'' = [010]$ in turn as rotation axes (see Figure 3b). Similar relations corresponding to Eq. (4) can be found by cyclic permutation of the indices if x'' and z'' are used as rotation axes.

With the definitions

$$a = -\tfrac{1}{2} V_{y''y''}; \quad b = -V_{x''x''} - \tfrac{1}{2} V_{y''y''}; \quad c = V_{x''z''}$$

and with

$$V_{x''x''} + V_{y''y''} + V_{z''z''} = 0;$$

it follows

$$V_{z'z'} = a + b \cos 2\varphi + c \sin 2\varphi\,, \quad (5)$$

and

$$\Delta\nu = A + B \cos 2\varphi + C \sin 2\varphi\,, \quad (6)$$

with

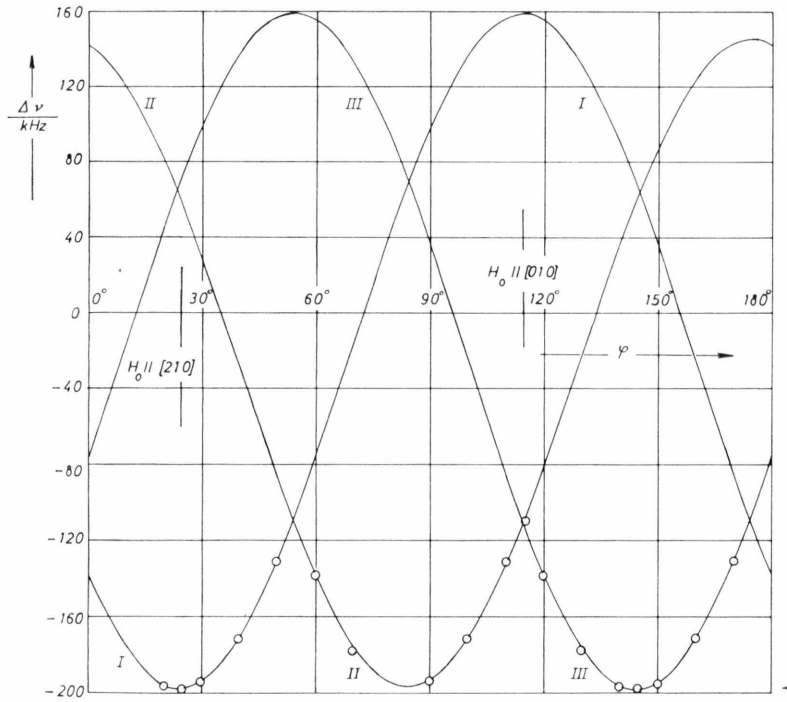
$$A = k\,a,\ B = k\,b,\ \text{and}\ C = k\,c\ ;\ k = \tfrac{3}{2}(eQ/2)$$

^{2}H-NMR studies on single crystals of $Na_2ZnCl_4 \cdot 3\ D_2O$ were carried out at room temperature (22 °C) and at − 25 °C. In the latter case a simple device was used by means of which a cold stream of nitrogen cooled the crystal. The temperature was determined with the aid of three thermocouples fastened above, on, and below the crystal. A temperature constancy of ± 2 °C over the sample was sufficient, as temperature effects on the D-NMR spectrum at − 25 °C are small. At an external field H_0 of 17125 G, ^{2}H-NMR spectra were recorded for both temperatures (22 °C and − 25 °C) and for both rotation axes [001] and [010]. At 17395 G, the ^{2}H-NMR spectrum was also studied for both temperatures, choosing the axis [210] as the rotation axis. In all cases H_0 was kept constant and the frequency of the oscillator was swept in recording the spectrum for a particular rotation angle. Frequency marks with a distance of 10 kHz were produced with the aid of a quartz stabilized spectrum generator.[29] A time constant of 3 sec for the lock-in amplifier was sufficient for the D-NMR work.

^{2}H-NMR at 22 °C

In crystals of $Na_2ZnCl_4 \cdot 3\ D_2O$ at 22 °C, the 180 degree reorientation frequency (flipping frequency) of the D_2O molecule about its twofold axis is higher than the quadrupole interaction frequency $\Delta\nu = \nu' - \nu''$. The water molecule undergoes a flipping motion about its twofold axis[14,15,2]. This motion is not fast enough to allow the observation of signals for all possible orientations of the crystal with respect to the external magnetic field H_0. With [001] as the rotation axis signals could be observed only within a restricted angular range of about ± 25° from the positions $\varphi = 0°$, $\varphi = 60°$, and $\varphi = 120°$ (with $\varphi = 0°$ at $[210] \parallel H_0$). Within each of these three angular ranges only the signals from one of the three D_2O molecules of the unit cell were observable. The D—O—D plane of one of the three water molecules in the unit cell is at the position $\varphi = 0°$ perpendicular to H_0. At the positions $\varphi = 60°$ and $\varphi = 120°$ the same situation results in turn for the two other D_2O molecules.

For the interpretation of the D-NMR results we define a coordinate system connected to the water molecule (see Figure 3c). The plane of the water molecule is the (zy)-plane of this coordinate system and the z-axis is also the twofold axis of the molecule. The x-axis is perpendicular to the plane of the molecule. If a water molecule lies with one of the axes x, y, or z, parallel to H_0, deuterium signals are obtained, even if the hindered rotation about the twofold axis (z-axis) is not very fast compared with the quadrupole splitting $\Delta\nu = \nu' - \nu''$[14,15,16,17]. The reason for this is the dependence of the dynamical line width on the term $\cos^2\Theta_1 - \cos^2\Theta_2$, Θ_1 and Θ_2 being the angles between the largest principal axis of the deuterium FGT 1 and 2, respectively, and the direction of H_0. If the rotation frequency is comparable with $\Delta\nu$, and the term $\cos^2\Theta_1 - \cos^2\Theta_2$ is not almost zero, the lines are considerably broadened and disappear in the noise. In particular, we expect lines to be observed at or near the positions $H_0 \parallel x$, $H_0 \parallel y$, and $H_0 \parallel z$, or at any position where the rotation axis is parallel or nearly parallel to z or y (see Figure 3c). For the rotation about the axis [001] one expects lines to be observed over a wide angular range departing from the position $H_0 \parallel x$ for each of the three water molecules in the unit cell. This is due to the small angle (19.4°) between the axis [001] and the twofold axes of the water molecules.



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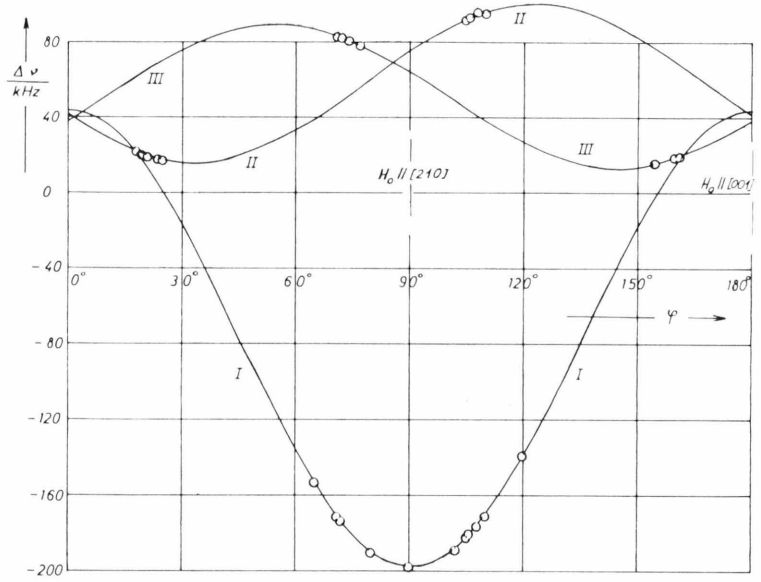
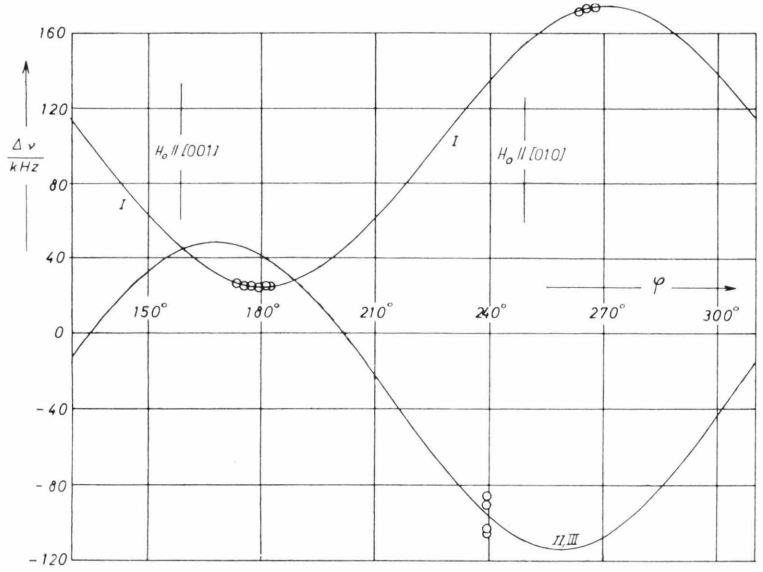


Fig. 8



← Fig. 9

Fig. 7. ^{2}H-quadrupole splitting $\Delta\nu = \nu' - \nu''$ in $Na_2ZnCl_4 \cdot 3\ D_2O$ at $T = 22\,^\circ C$. Rotation axis is [001]. The curves I, II, III correspond to the molecules D_2O lying on the planes (100), (010), and ($\bar{1}$10), respectively.

Fig. 8. ^{2}H-quadrupole splitting $\Delta\nu = \nu' - \nu''$ in $Na_2ZnCl_4 \cdot 3\ D_2O$ at $T = 22\,^\circ C$. Rotation axis is [010]. The curves I, II, III correspond to the molecules D_2O lying on the planes (100), (010), and ($\bar{1}$10), respectively.

Fig. 9. ^{2}H-quadrupole splitting $\Delta\nu = \nu' - \nu''$ in $Na_2ZnCl_4 \cdot 3\ D_2O$ at $T = 22\,^\circ C$. Rotation axis is [210]. The curves I, II, III correspond to the molecules D_2O lying on the planes (100), (010), and ($\bar{1}$10), respectively.

Rotating about the axis [010], we expect good signal to noise ratio only for the water molecule lying on the plane (100). The other two molecules will give observable D-NMR signals only in a much smaller angular range.

Finally, the rotation about the [210] axis will give observable deuterium signals for the water molecule lying on the plane (100) in a small angular range near $H_0 \parallel y$ and $H_0 \parallel z$. The other two molecules will give observable signals only in a small angular range.

These conclusions drawn from the ^{1}H-NMR results are well confirmed by the D-NMR experiments. In Figs. 7, 8, and 9, the rotation patterns for the three selected axes are shown. The signals show a fine (triplet) structure which has been explained by Ketudat[15] as arising from the motion of the water molecule. Chiba[16] explained the fine structure by assuming dipolar effects. The results obtained from D-NMR at 22 °C are given in Table 2.

Table 2. Results from ^{2}H-NMR spectroscopy on $Na_2ZnCl_4 \cdot 3\ D_2O$ at $T = 22$ °C ("fast" flipping D_2O molecules).

a) Principal components of the ^{2}H-FGT.
$\pm\ V_{XX} = 24.4 \pm 0.5$ kHz,
$\pm\ V_{YY} = 173.6 \pm 1.5$ kHz,
$\mp\ V_{ZZ} = 198.0 \pm 0.5$ kHz.
The coordinate system X, Y, Z defines the principal axes of the FGT and is different from the molecule coordinate system x, y, z.

b) $|e^2qQ/h| = 132.0 \pm 1.0$ kHz,
$\eta = (V_{XX} - V_{YY})/V_{ZZ} = 0.754 \pm 0.005$.

c) The direction cosines for the molecule D_2O lying on the plane (100) are:

	[210]	[010]	[001]
V_{XX}	0	0.355 ± 25	0.935 ± 9
V_{YY}	0	0.935 ± 9	0.355 ± 25
V_{ZZ}	1	0	0

The direction cosines of the two other molecules within the unit cell may be obtained by application of the symmetry operations of the space group.

The angle between the direction of V_{ZZ} and the axis [210] is zero. This finding is in agreement with other works on fast flipping water molecules in crystals where also the largest principal axis of the FGT was found to be perpendicular to the twofold axis of the molecule and perpendicular to its plane[2]. From the D-NMR the angle between the direction [010] and V_{YY} is found to be $20.8° \pm 1.5°$, which is also the angle between the direction [001] and V_{XX}. The deviation from the value of $19.4° \pm 0.1°$ found for the angle between the H-H-vector and the axis [010] is not significant, since the accuracy of the D-NMR is somewhat less. (The D-NMR value was gained from the rotation pattern around [210]. Therefore, only a restricted amount of data was available as shown in Figure 9.)

^2H-NMR at -25 °C

At -25 °C the hindered motion of the water molecule about its twofold axis is slower than the quadrupole interaction frequency. Each deuterium atom gives a NMR doublet, correponding to the D-NMR spectrum of a stationary molecule D_2O. Therefore, in general a total number of six lines is expected. Spectra were recorded at intervals of 10°. Many spectra did not show the total number of six lines, as superimpositions of lines occurred.

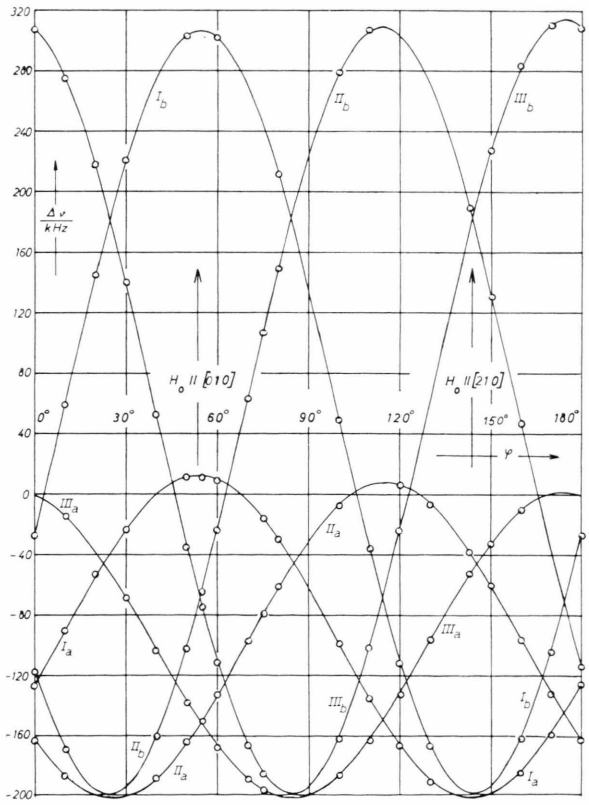


Fig. 10. ^{2}H-quadrupole splitting $\Delta\nu = \nu' - \nu''$ in $Na_2ZnCl_4 \cdot 3\ D_2O$ at $T = -25$ °C. Rotation axis is [001]. The curves I, II, and III correspond to the water molecules on the planes (100), (010), and ($\bar{1}$10), respectively. To differentiate between the two atoms D_I and D_{II} within one molecule, the indices a and b are used.

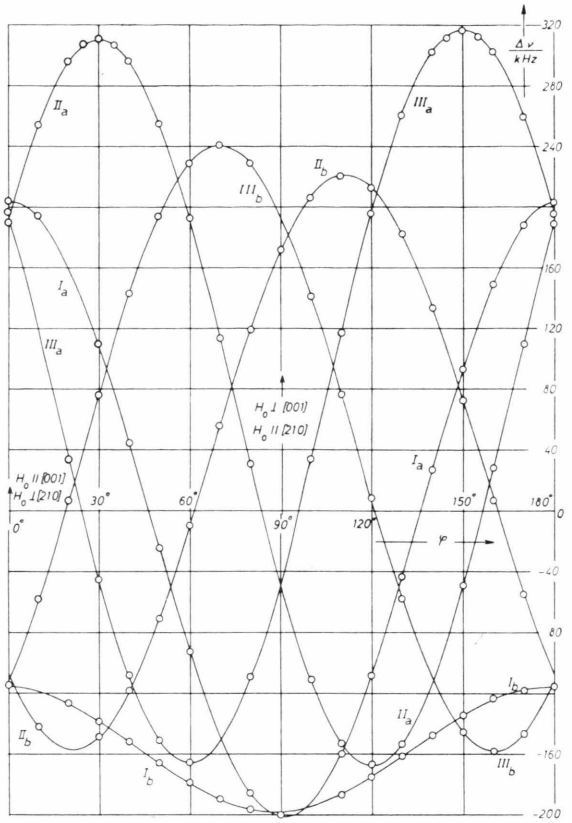


Fig. 11. ^{2}H-quadrupole splitting $\Delta\nu = \nu' - \nu''$ in $Na_2ZnCl_4 \cdot 3\ D_2O$ at $T = -25\,^\circ C$. Rotation axis is [010]. The curves I, II, and III correspond to the water molecules on the planes (100), (010), and ($\bar{1}$10), respectively. To differentiate between the two atoms D_I and D_{II} within one molecule, the indices a and b are used.

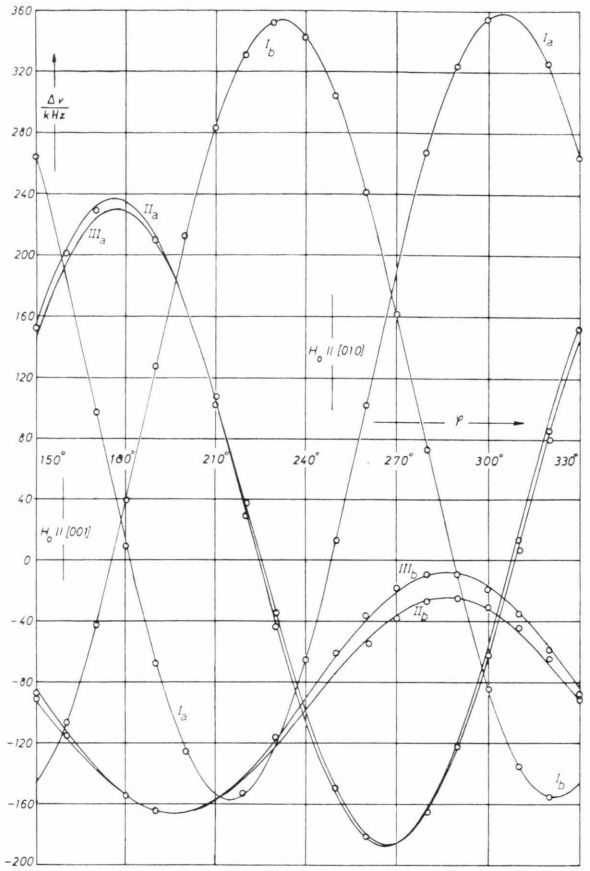


Fig. 12. ^{2}H-quadrupole splitting $\Delta\nu = \nu' - \nu''$ in $Na_2ZnCl_4 \cdot 3\ D_2O$ at $T = -25\,^\circ C$. Rotation axis is [210]. The curves I, II, and III correspond to the water molecules on the planes (100), (010), and ($\bar{1}$10), respectively. To differentiate between the two atoms D_I and D_{II} within one molecule, the indices a and b are used.

In Figs. 10, 11, and 12, the rotation patterns for the rotation axes [001], [010], and [210], respectively, are shown. Misalignments where taken into account by the method shown in Appendix I.

As the two deuterium atoms of the water molecule have different environments, the FGTs at their positions are slightly different. To differentiate, they are called D_I and D_{II} and the results are given in Table 3.

The largest principal axis of the FGT (D_I) includes an angle of $55.8^\circ \pm 0.1^\circ$ with the axis [010]. The angle between V_{ZZ} (D_{II}) and [010] is $17.2^\circ \pm 0.1^\circ$. The intermediate principal axes $V_{YY}(D_I)$ and $V_{YY}(D_{II})$ are parallel to [210] and, therefore, perpendicular to the plane of the molecule D_2O.

Dynamics of the Water Molecule in $Na_2ZnCl_4 \cdot 3\ H_2O$ ($Na_2ZnCl_4 \cdot 3\ D_2O$)

The effect of the motion of nuclear spins on the line shape has been treated generally by Anderson [18] and Kubo [19]. Chiba [16], and Chiba and Kakiuchi [20] expanded the theories of Anderson and Kubo to the case where the electric field gradient tensors of the two deuterium atoms of a D_2O molecule are averaged by the reorientational motion of the molecule about its bisectrix. According to Chiba [16], at the temperature of the slow exchange limit, $|\nu_1 - \nu_2| \gg \nu_R$ the line width δ can be expressed in terms of the dipolar line width, δ_0, and of the reorientation frequency ν_R:

$$\delta = \delta_0 + \nu_R\,. \qquad (7)$$

Table 3. Results from ^{2}H-NMR spectroscopy on $Na_2ZnCl_4 \cdot 3\ D_2O$ at $T = -25\,^\circ C$ ("rigid" D_2O molecules).

a) The principal components of the F G Ts at $-25\,^\circ C$:

D_I $\mp V_{XX} = 158.5 \pm 0.5$ kHz
$\mp V_{YY} = 201.1 \pm 0.5$ kHz
$\pm V_{ZZ} = 359.6 \pm 0.8$ kHz
D_{II} $\mp V_{XX} = 154.9 \pm 0.5$ kHz
$\mp V_{YY} = 199.0 \pm 0.5$ kHz
$\pm V_{ZZ} = 353.9 \pm 0.5$ kHz

b) $(e^2qQ/h)_{DI} = 239.7 \pm 1.0$ kHz;
$\eta_{DI} = 0.118 \pm 0.002$
$(e^2qQ/h)_{DII} = 235.9 \pm 1.0$ kHz
$\eta_{DII} = 0.125 \pm 0.002$.

c) Direction cosines for the water molecule in the plane (100):

D_I	[210]	[010]	[001]
V_{XX}	0	0.8269 ± 9	0.5623 ± 12
V_{YY}	1	0	0
V_{ZZ}	0	0.5623 ± 12	0.8269 ± 9

D_{II}	[210]	[010]	[001]
V_{XX}	0	0.2952 ± 16	0.9554 ± 5
V_{YY}	1	0	0
V_{ZZ}	0	0.9554 ± 5	0.2952 ± 16

The direction cosines of the two other molecules within the unit cell may be obtained by application of the symmetry operations of the space group.

$|\nu_1 - \nu_2|$ is the difference between the two resonance frequencies for the stationary deuterons.

At the temperature of the fast exchange limit, $|\nu_1 - \nu_2| \ll \nu_R$, the line width, δ, is given by:

$$\delta = \delta_0 + \tfrac{1}{2}\pi^2[(\nu_1 - \nu_2)^2/\nu_R]. \qquad (8)$$

The line width has been corrected by a factor k, which accounts for the line shape[16]. This factor k is $(2\pi)^{1/2} \approx 2.5$ for Gaussian line shape, and $\sqrt{3} \cdot \pi \approx 5.4$ for Lorentzian line shape. It is assumed that the original line shape, is Gaussian where motional effects are negligible. Using equations (7) and (8) and a value $k = 2.5$, the reorientational frequencies were calculated from the line widths measured at different temperatures.

The temperature dependence of the reorientation frequency is assumed to be governed by an activation process:

$$\nu_R = \nu_0 \exp\{-V_0/kT\}. \qquad (9)$$

For comparison, the temperature dependences of the reorientation frequency of a classical rotator were calculated for different activation energies V_0 and also for a tunneling mechanism with fixed activation energy. The results are shown in Figure 13. From the line fitting of the experimental points $V_0 = 12.7$ kcal/mole follows.

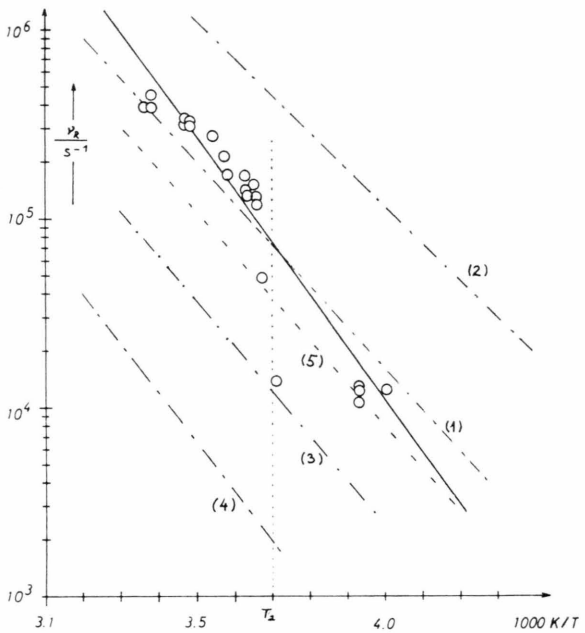


Fig. 13. Reorientation frequency ν_R from ^{2}H-NMR line width measurements on $Na_2ZnCl_4 \cdot 3\ D_2O$ as a function of $1/T$. The curves (1), (2), (3), and (4) correspond to $V_0/(\text{kcal} \cdot \text{mole}^{-1}) = 10$, 9, 11, and 12, respectively. The line (5) is calculated assuming a tunneling mechanism with $V_0 = 11$ kcal $\cdot$ mole^{-1}. $T_2 \triangleq T_a$. The position of the dashed curves 1—5 within the diagram is arbitrary.

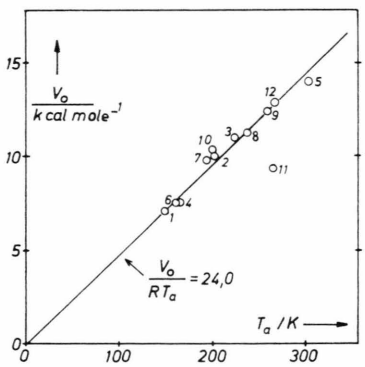


Fig. 14. Plot of V_0 as a function of the temperature T_a (T_a is the temperature of complete disappearence of the signal.) The points belonging to the different substances are:

1) $Ba(ClO_3)_2 \cdot D_2O$[16]; (2) α-$(COOD)_2 \cdot 2\ D_2O$[21];
3) β-$(COOD)_2 \cdot 2\ D_2O$[17]; (4) $NiSiF_6 \cdot 6\ D_2O$[22];
5) $(KCOO)_2 \cdot D_2O$[23]; (6) ... (10) belong to the different water molecules in $CuSO_4 \cdot 5\ D_2O$[17];
11) $Na_2S_2O_6 \cdot 2\ D_2O$[2]; (12) $Na_2ZnCl_4 \cdot 3\ D_2O$ (this work).

The temperature T_a, given in Fig. 13, indicates the region where the lines are too broad to be observed, and where $|\nu_1 - \nu_2|$ is comparable with ν_R. Soda and Chiba[17] have indicated an interesting empirical relation between this temperature T_a and the activation energy V_0: $V_0/RT_a = 24.0$. In Fig. 14, the relation $T_a = f(V_0/RT_a)$ is shown for some substances, including $Na_2ZnCl_4 \cdot 3\ D_2O$.

Spin-Lattice Relaxation Time T_1

Information on the reorientational motion may be gained by measuring the spin-lattice relaxation time of the proton as a function of the temperature. According to the BPP-theory[24] in the formulation of Kubo and Tomita[25], the reorientational motion may be described by a unique correlation time τ,

$$1/T_1 = C\{[\omega_0\tau/(1+\omega_0^2\tau^2)] + [4\omega_0\tau/(1+4\omega_0^2\tau^2)]\}, \quad (10)$$

with ω_0 as the Larmor frequency; the constant C can be obtained from the minimum value of T_1 ($\omega_0\tau = 0.615$). The temperature dependence of τ is given by

$$\tau = \tau_0 \exp\{E/RT\}. \quad (11)$$

Proton spin relaxation times were measured by the 180°—90° technique as well as by the n 90°—90° technique, using a Bruker pulse-NMR-spectrometer at a fixed frequency of 34 MHz. The crystals were oriented with [001] $\parallel H_0$ and [001] $\perp H_0$. In Fig. 15 the experimental results are shown.

The well known V-shape is encountered only in a small region of $T_1 = f(1/T)$ and the assumption of a single correlation time is probably not satisfactory for $Na_2ZnCl_4 \cdot 3\ H_2O$. Nevertheless, with $(T_1)_{min} = 0.047$ sec at $T = 300$ K, the temperature dependence of the correlation time has been calculated, wherefrom an activation energy of 7.8 kcal/mole followed.

Discussion

The ^{1}H-NMR spectra in $Na_2ZnCl_4 \cdot 3\ H_2O$ and the ^{2}H-NMR spectra in $Na_2ZnCl_4 \cdot 3\ D_2O$ clearly revealed that the water molecules are located on the planes (100), (010), and (110). The vector H-H within a H_2O molecule forms an angle of 19.4° ± 0.1° with the plane (001). From the ^{2}H-NMR at 22 °C we find an angle of 90°—(20.8° ± 1.5°) between the plane (001) and the twofold axis of the

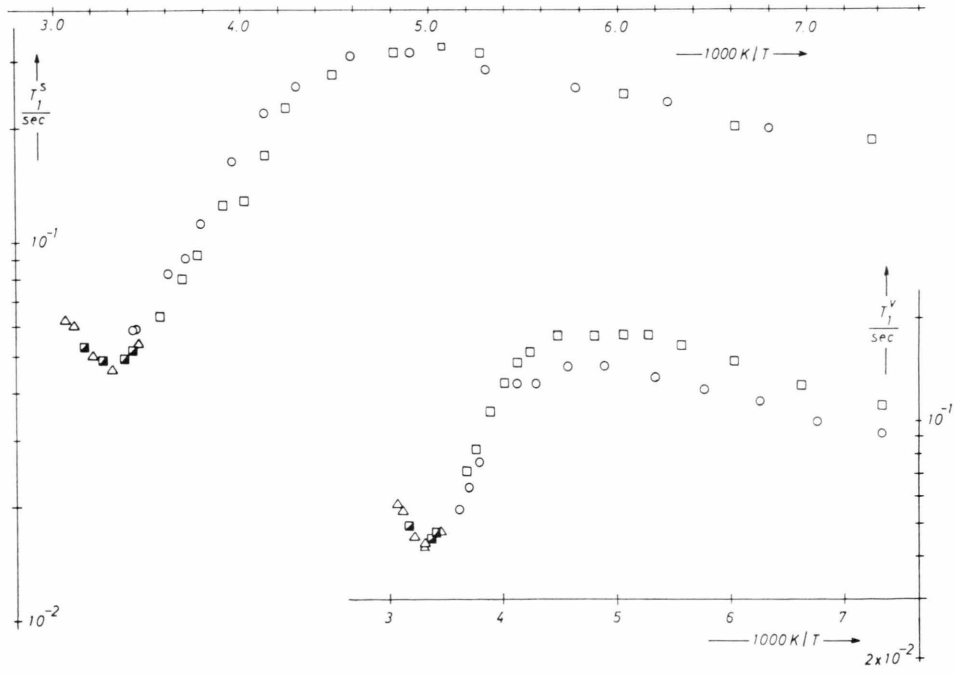


Fig. 15. Spin-lattice relaxation time T_1 for ^{1}H in $Na_2ZnCl_4 \cdot 3\ H_2O$ as a function of $1/T$. T_1^s was determined by the n 90°—90°-pulse sequence; T_1^v was measured with the aid of the 180°—90°-pulse sequence. ○: $H_0 \perp 001$; □, △, ◢: $H_0 \parallel$ [001] for different series of measurements.

molecule D_2O. Using the ^{2}H-NMR data at $-25\,^\circ$C we can calculate the angle between the *D-D*-vector of a D_2O molecule and the plane (001) with the following assumptions:

a) The direction of the largest principal axis of the FGT is the O—D direction,

b) The two O—D bond lengths within one molecule are equal, and

c) The small difference in the quadrupole coupling constants for D_I (239.7 kHz) and D_{II} (235.9 kHz) is due to the external components (crystal field effect) of the FGT and not to differences in the O—D bonds. This is also true for the difference between η_I (0.118) and η_{II} (0.125).

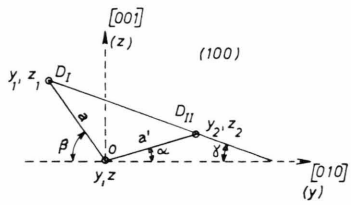


Fig. 16. Geometry of the D_2O molecule at the plane (100) with respect to the axes [001] and [010].

Figure 16 shows the D_2O molecule lying on the plane (100). Since a is equal to a', it follows:

$$\tan\gamma = (\sin\beta - \sin\alpha)/(\cos\beta + \cos\alpha)\,.$$

Inserting the values of α and β (Table 3), an angle of $\gamma = 19.3^\circ \pm 0.1^\circ$ is calculated, which is in good agreement with the angle between the *H-H*-vector and the plane (001).

The ^{1}H-NMR spectrum gives a *H-H* distance which is influenced by the dynamics of the water molecule. It was shown by Pedersen[26] that smaller *H-H* distances r_e result if the torsional motions of the water molecules in the lattice are considered. Using the activation energy of 12.7 kcal/mole found from the ^{2}H-NMR experiments, an equilibrium value of 1.537 Å is found for the intramolecular *H-H* distance in $Na_2ZnCl_4 \cdot 3\,H_2O$. For comparison, the r_e value of the molecules D_2O, HDO, H_2O is 1.514 ± 1 Å[27].

In Table 4, the parameters for the hydrogen atoms in the unit cell of $Na_2ZnCl_4 \cdot 3\,H_2O$ are given for the intramolecular *H-H* distance of H_2O as found from the NMR experiments, and (in brackets) for the equilibrium distance $r_e = 1.537$ Å. Also the atomic positions for the heavy ions Na, Zn, Cl, and O, are listed as given by Trunz[4]. From the atomic coordinates some of the interatomic distances of the next nearest neighbors in the lattice are calculated and listed (Table 4). Within the limits of error of our investigations, the atomic coordinates of the deuterium atoms are identical with the ^{1}H positions.

Table 4. Atomic coordinates of $Na_2ZnCl_4 \cdot 3\,H_2O$ ($Na_2ZnCl_4 \cdot 3\,D_2O$).

$Na_2ZnCl_4 \cdot 3\,H_2O$; Space Group: C_3^2—P 31m; $Z = 1$			
Atom	No. of Positions	Point Symmetry	Positions
Na	2	3	1/3, 2/3, z; 2/3, 1/3, z; $z = 0.192 \pm 0.003$
Zn	1	3 m	0, 0, z; $z = 0$
Cl_I	1	3 m	0, 0, z; $z = 0.389 \pm 0.004$
Cl_{II}	3	m	x, 0, z; 0, x, z; x, x, z; $x = 0.318 \pm 0.001$; $z = 0.902 \pm 0.001$
O	3	m	$x = 0.537 \pm 0.003$; $z = 0.417 \pm 0.004$
H_I	3	m	$x = 0.455 \pm 0.004$; $(x = 0.459 \pm 0.004)$; $z = 0.556 \pm 0.005$; $(z = 0.550 \pm 0.005)$
H_{II}	3	m	$x = 0.675 \pm 0.004$; $(x = 0.669 \pm 0.004)$; $z = 0.466 \pm 0.005$; $(z = 0.464 \pm 0.005)$

Interatomic distances in $Na_2ZnCl_4 \cdot 3\,H_2O$

Atoms	Distance (Å)	
H_I—O	0.999	(0.959)
H_{II}—O	0.994	(0.954)
H_I—Cl_{II}	2.27	
H_{II}—Cl_I	2.28	
Zn—Cl_{II}	2.26	
Zn—Cl_I	2.32	
$\sphericalangle$ H—O—H	107°0′	

Within the limits of error, the same coordinates and distances are assigned to the atoms in $Na_2ZnCl_4 \cdot 3\,D_2O$.

In Fig. 17, the water molecule situated in the plane (100) is shown together with its next nearest neighbors. Two short distances H ... Cl are found: a) $H_I \ldots Cl_{II} = 2.27$ Å, and b) $H_{II} \ldots Cl_I = 2.28$ Å. Assuming these two short H ... Cl distances to be the directions of the hydrogen bond O—H ... Cl, it is found that the angles O—H ... Cl are 170.2° and 151.0°, respectively. A single hydrogen bond $H_I \ldots Cl_{II}$ is formed, while each Cl_I-atom has hydrogen bonds to three different atoms H_{II}.

To gain information on the hydrogen bonds in $Na_2ZnCl_4 \cdot 3\,H_2O$ and $Na_2ZnCl_4 \cdot 3\,D_2O$, the NQR spectra of ^{35}Cl and ^{37}Cl belonging to the atoms

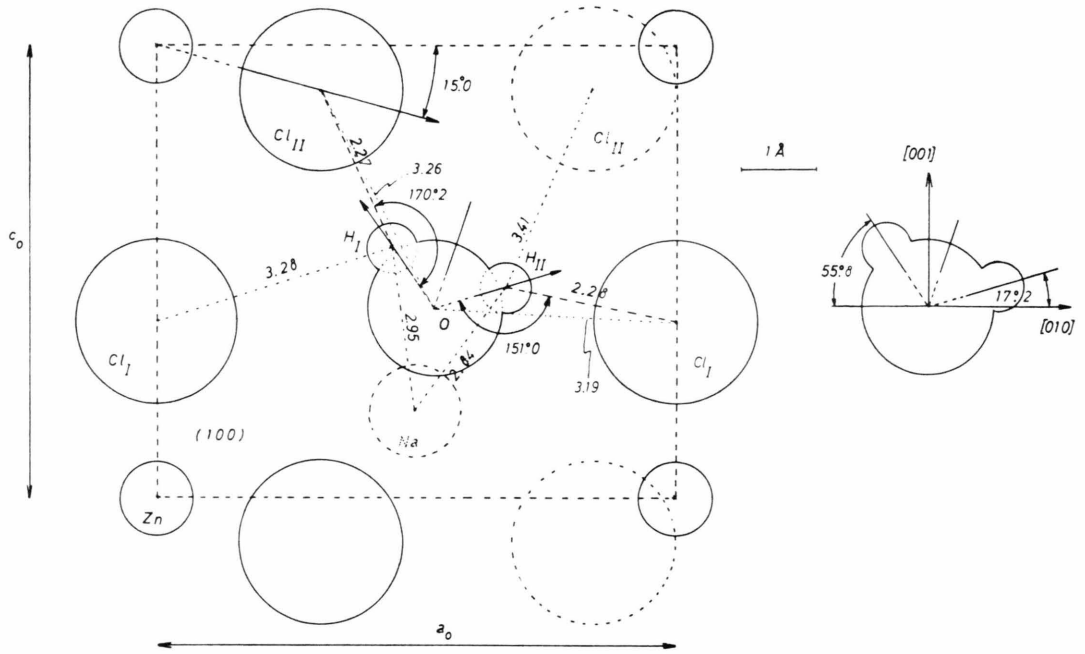


Fig. 17. H_2O (D_2O) molecule on the plane (100) of $Na_2ZnCl_4 \cdot 3\,H_2O$ (D_2O) and its nearest neighbors.

Table 5. Results of $^{35}Cl(^{37}Cl)$-NQR spectroscopy on $Na_2ZnCl_4 \cdot 3\,H_2O$ and $Na_2ZnCl_4 \cdot 3\,D_2O$.

$\nu(^{35}Cl_{II})$/kHz; $(T/°C)$	$\nu(^{37}Cl_{II})$/kHz; $(T/°C)$
$Na_2ZnCl_4 \cdot 3\,H_2O$	
9147.5 ± 2; (26.8 ± 1)	7210.2 ± 3; (26.3 ± 2)
9151.3 ± 3; (22.9 ± 2)	
$Na_2ZnCl_4 \cdot 3\,D_2O$	
9144.6 ± 3; (26.8 ± 1)	7208.2 ± 4; (26.4 ± 2)
9147.5 ± 4; (22.8 ± 2)	
$Na_2ZnCl_4 \cdot 3\,H_2O$:	
$\nu\,^{35}Cl_{II}/\nu\,^{37}Cl_{II} = 1.2688$; $(T = 26.3\,°C)$	
$Na_2ZnCl_4 \cdot 3\,D_2O$:	
$\nu\,^{35}Cl_{II}/\nu\,^{37}Cl_{II} = 1.2687$; $(T = 26.4\,°C)$	

(ions) Cl_{II} were investigated on polycrystalline samples. The results are shown in Table 5. Only very small shifts in the NQR resonance frequencies were found due to the substitution H ↔ D. This shows that the hydrogen bonds O—H ... Cl and O—D ... Cl are very similar. However, no conclusions can be drawn about the strength of the hydrogen bond from such experiments as shown by Pies and Weiss[28].

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Appendix I

Given the laboratory coordinate system x', y', and z' (see Fig. 18), z' is the direction of H_0, y' is the axis of rotation, and x' is perpendicular to both z' and y'. For the position of the crystal axes it is assumed that [001] ≙ x'' is parallel to x', [210] ≙ y'' is parallel to y', and [010] ≙ z'' is parallel to z'.

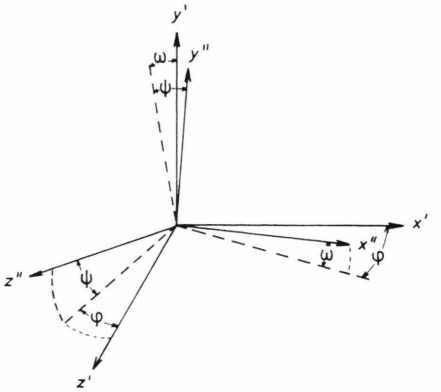

Fig. 18. System of coordinates and angles used in correcting misalignments of the crystal.

Any orientation of the crystal can be realized with respect to the laboratory system by the following rotations: 1. around y'' by the angle φ (in negative direction); 2. around z'' by the angle ω

(positive direction); 3. around x'' by the angle ψ (negative direction).

When rotating around one of the crystal axes (Fig. 18), the following special values for ψ and ω follow:

Rotation Axis	Angle of Rotation = φ	
	ψ	ω
[210]	0	0
[010]	90	0
[001]	0	90

In terms of φ, ω and ψ the FGT component in the $z' \triangleq H_0$-direction is:

$$V_{z'z'} = a + b\cos 2\varphi + c\sin 2\varphi\,, \qquad \text{(I,1)}$$

with

$$\begin{aligned} a = {} & \frac{V_{x''x''} - V_{y''y''}}{2}\cos^2\omega \\ & + \frac{\sin^2\psi\cos^2\omega}{2}(2V_{y''y''} + V_{x''x''}) \\ & - V_{x''x''} - \sin\psi\cos\omega\sin\omega\, V_{z''z''}\,, \\ b = {} & -V_{x''x''} - \frac{V_{y''y''}}{2} \\ & + \frac{\sin^2\omega}{2}(V_{x''x''} - V_{y''y''}) \\ & + \sin\psi\cos\omega\sin\omega\, V_{x''z''} \qquad \text{(I,2)} \\ & + \frac{\sin^2\psi}{2}(\sin^2\omega + 1)(2V_{y''y''} + V_{x''x''})\,, \\ c = {} & \cos\psi\sin\psi\sin\omega(2V_{y''y''} + V_{x''x''}) \\ & + \cos\psi\cos\omega\, V_{x''z''}\,. \end{aligned}$$

For the special case $\psi = \omega = 0$, from (I,2) the equations given by Volkoff, Petch and Smellie[13] follow.

To illustrate the method, we consider the three atoms D_{I} in the unit cell of $Na_2ZnCl_4 \cdot 3\,D_2O$. The atom $D_{\mathrm{I}}^{(1)}$ is situated on the plane (100), $D_{\mathrm{I}}^{(2)}$ on the plane (010), and $D_{\mathrm{I}}^{(3)}$ on the plane ($\bar{1}10$). The components of the FGT in the z' direction (direction of H_0) of these three atoms are connected by the angle ψ.

The angle ψ corresponds to the D_{I} atom on the plane (100) ($D_{\mathrm{I}}^{(1)}$), the angle $\psi + 120°$ to the D_{I} atom on the plane (010) ($D_{\mathrm{I}}^{(2)}$), and the angle $\psi + 240°$ to the D_{I} atom on the plane (110) ($D_{\mathrm{I}}^{(3)}$).

For each atom we define the sum z ($z^{(1)}$, $z^{(2)}$, and $z^{(3)}$):

$$\begin{aligned} z \equiv a + b &= \sin^2\psi\, V_{y''y''} + \cos^2\psi\, V_{z''z''} \\ &= V_{y''y''} - (2V_{y''y''} + V_{x''x''})\cos^2\psi\,. \end{aligned}$$

Then the angle ψ is:

$$\tan\psi = -p \pm \sqrt{p^2 + 1}$$

with

$$p \equiv \frac{z^{(3)} + z^{(2)} - 2z^{(1)}}{\sqrt{3}\,(z^{(3)} - z^{(2)})}\,.$$

The angle ω is then obtained by inserting ψ back into Equation (I,2).

The position of the axis [001] can be determined by comparing the results for the D_{I} and D_{II} atoms or by ^{23}Na-NMR, as stated before.

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