Elektronendichte um eine Ladungseinheit eine chemische Verschiebung des Protonensignals von 9,8 ppm entspricht. Dieser Wert stimmt sehr gut mit den Ergebnissen analoger Betrachtungen an Pyridinderivaten [8] und mit verschiedenen Literaturwerten [9–11] überein.

Die Durchführung dieser Untersuchungen wurde durch Mittel der Deutschen Forschungsgemeinschaft und des Fonds der Chemischen Industrie unterstützt, wofür an dieser Stelle herzlich gedankt wird.

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Dynamics of Water in Crystal Hydrates

I. The ^{1}H-NMR Spectra of $Na_2S_2O_6 \cdot 2\,H_2O$ and $Li_2S_2O_6 \cdot 2\,H_2O$ Single Crystals

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The ^{1}H-NMR spectra of $Na_2S_2O_6 \cdot 2\,H_2O$ and $Li_2S_2O_6 \cdot 2\,H_2O$ single crystals have been investigated at room temperature. The influence on the NMR spectra by the dynamical behaviour of the water molecules is discussed. The direction cosines of the different p—p lines were determined with a modified Pake formula given by Pedersen. The parameters of the librational motions of the water molecules were calculated by the help of infrared data. The equilibrium H—H-distance in the water molecules was found to be 1.52 Å.

The investigation of the nuclear magnetic resonance spectra of protons in crystal hydrates is quite a valuable tool in studying the geometrical arrangement of water molecules in solids. As Pake [1] has shown in his investigation on gypsum, $CaSO_4 \cdot 2\,H_2O$, the informations directly available by this method are the number of crystallographically different positions of water molecules in the unit cell and the lengths and direction cosines of the intramolecular p – p lines of the different water molecules. The equilibrium configuration and the intramolecular distance of the protons are influenced by the vibrational motion of the water molecules. Therefore Pakes theory has to be modified by introducing the dynamical effects of the water molecules. This was shown by Das [2]. The theory of the influence of the dynamical behaviour of water on the ^{1}H-NMR spectra in crystals was given by Pedersen [3]. Unfortunately the determination of the equilibrium lengths and direction cosines of the p – p lines with Pedersens theory is not possible without theoretical assumptions or some further experimental informations.

In this paper we wish to discuss the application of Pedersens theory in interpreting the results of an experimental investigation of ^{1}H-NMR spectra in crystal hydrates. The proton magnetic resonance spectra of sodium dithionate dihydrate, $Na_2S_2O_6 \cdot 2\,H_2O$, and lithium dithionate dihydrate, $Li_2S_2O_6 \cdot 2\,H_2O$, have been studied at room temperature to prove the theoretical arguments. In connection with infrared data the equilibrium distance of the p – p lines could be determined.

Theory

The ^{1}H-NMR spectrum arising from the two protons of one water molecule in a single crystal is characterized by a doublet, whose splitting ΔH (conveniently measured in Gauss) depends on the orientation of the single crystal in the external magnetic field H_0, on the magnetic moment of the proton μ and on the intramolecular distance R_e of the two protons. The magnetic dipolar splitting ΔH due to the magnetic dipolar interaction of the water

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molecule is, as shown by PAKE [1] given by

$$\Delta H = \frac{3\,\mu}{R_e^3}(3\cos^2\delta\cos^2(\varphi-\varphi_0)-1)\,. \qquad (1)$$

φ_0 is the angle between the projection of the intramolecular p – p line on the plane perpendicular to the axis of the crystal and a fixed direction lying in this plane (rotation plane). The direction chosen in the rotation plane may be a crystal axis. φ is the angle between this fixed direction chosen and the direction of the external magnetic field H_0 in the rotation plane. δ is the angle of inclination of the p – p line with regard to the rotation plane. There are two assumptions in deriving the PAKE formula [Eq. (1)]:

1. The water molecules in the crystal are far apart from each other and from nuclei with appreciable magnetic moments. Then the pair of protons in one molecule may be described as an isolated two spin system. 2. The water molecule is rigid and fixed in its position in a rigid lattice.

It is clear that the first assumption certainly is an approximation. If we assume that the substance is diamagnetic, the effective magnetic field seen by one proton of the water molecule is not only given by the external field H_0 and the local magnetic field created by the second proton of the same water molecule but also by the next nearest neighbours with magnetic moments. Besides the intramolecular dipole-dipole interaction between both protons of the water molecule we have to take into consideration the intermolecular interactions. In many cases the inter-interaction is much smaller than the intra-interaction. Then we can treat the inter-interaction in first approximation as a small perturbation, which influences only the line shape of the NMR lines but not the line position. The influence of a weak inter-interaction on the line shape causes an asymmetric broadening of the absorption signals. Therefore, the distance of the two maxima in the doublet is no longer a direct measure for ΔH in the PAKE equation [Eq. (1)]. HOLCOMB and PEDERSEN [4] have shown, that in such cases the distance between the centers of gravity of the two absorption signals is identical with the doublet splitting of an isolated pair of protons. The center of gravity of an NMR line is given by the first moment

$$\bar{\nu}-\nu_0=\overline{\Delta\nu}=\int_0^\infty(\nu_{nn'}-\nu_0)\,f(\nu)\,\mathrm{d}\nu\Big/\int_0^\infty f(\nu)\,\mathrm{d}\nu\,. \qquad (2\,a)$$

Finally the splitting of the doublet is

$$M_1 = 2\,\overline{\Delta\nu}/\gamma = \Delta H\,. \qquad (2\,b)$$

M_1 is the first moment measured in Gauss. The approximation used in the application of Eq. (2 b) is valid as long as the ratio $R_{\text{inter}}/R_{\text{intra}}$ is larger than 1.6. The substances investigated in this paper fulfill this condition. This was found by an investigation of the proton positions in sodium dithionate dihydrate under the assumption of static water molecules [5, 6] and should also be true for the lithium dithionate dihydrate, since both substances have the same crystal structure and quite similar lattice constants (see the following paper).

During the last years different groups working on NMR spectroscopy of crystal hydrates [2, 3, 7, 8] have shown, that the dynamical behaviour of the water molecules in crystal hydrates has to be considered in interpreting the results of ^{1}H-NMR investigations. The problem of the dynamics of the water molecules was intensively discussed by PEDERSEN [3]. The vibrations of the water molecules influence the distance and the direction cosines of the p – p line in applying Eq. (1) for the calculation of the equilibrium arrangement of the water molecules. Therefore the PAKE formula has to be modified. One has to find the interpretation of the time averaged NMR spectra. The vibrational motions may be divided into two classes: a) the symmetric OH-stretching modes and bending modes acting only on the HH distance, and b) the torsional modes changing only the direction cosines of the p – p lines. The asymmetric stretching modes are not considered here. The influence of the OH-stretching and bending vibrations of the water molecules on the distance was discussed by many authors. The correction term given by PEDERSEN is: $R_e^3 = 0.98 \cdot R^3$. The torsional vibrations are not as simple to introduce into the PAKE equation. This problem was treated by PEDERSEN [3]. He considered the special arrangement that

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[6] M. VAN MEERSCHE, J. M. DEREPPE, and P. W. LOBO, Acta Cryst. **16**, 95 [1963].
[7] J. W. MCGRATH and A. A. SILVIDI, J. Chem. Phys. **29**, 104 [1958].
[8] T. CHIBA, J. Chem. Phys. **39**, 947 [1963].

the projection of the p – p lines of the water molecule on the rotation plane is parallel to the crystal axis which was set to be the fixed direction defining the angle φ. Therefore the angle φ_0 is zero. The modified PAKE equation he finds, is:

$$M_1 = 0.98 \frac{3\mu}{R_e^3} \{3(1 - \langle \Theta_x^2 \rangle - 2\langle \Theta_z^2 \rangle)\cos^2 \delta^* \cos^2 \varphi + 3(\langle \Theta_x^2 \rangle - \langle \Theta_z^2 \rangle) \cos^2 \delta_n \cos^2(\varphi - \varphi_n) + 3\langle \Theta_z^2 \rangle - 1\} . \quad (3)$$

The angle δ^* in Eq. (3) has the same meaning as δ in Eq. (1). The angle φ is already explained in Eq. (1). δ_n is the angle between the twofold axis of the water molecule and the rotation plane; φ_n is the angle between the projection of the twofold axis of the water molecule on the rotation plane and the fixed direction in this plane defining the angle φ. Eq. (3) takes into account the torsional motions of the water molecule by the introduction of the torsional parameters $\langle \Theta_x^2 \rangle$ and $\langle \Theta_z^2 \rangle$. The mean square amplitude of the torsional motion of the p – p line around the twofold axis of the water molecule is $\langle \Theta_z^2 \rangle$ and around the axis of inertia perpendicular to the HOH plane $\langle \Theta_x^2 \rangle$. The third torsional motion, characterized by $\langle \Theta_y^2 \rangle$, has no influence on the ^{1}H-NMR spectra since this motion does not change the direction cosines of the p – p lines. The torsional parameters are expressed in units of [rad]^2. In the general case of non-special direction of the p – p line of the water molecules in the crystal the angle between the projection of the p – p line on the rotation plane and the fixed direction in this plane has to be introduced. This angle is called φ_0^*. For $\varphi_0^* \neq 0$ the first moment M_1 is given by

$$M_1 = 0.98 \frac{3\mu}{R_e^3} \{3(1 - \langle \Theta_x^2 \rangle - 2\langle \Theta_z^2 \rangle) \cos^2 \delta^* \cos^2(\varphi - \varphi_0^*) + 3(\langle \Theta_x^2 \rangle - \langle \Theta_z^2 \rangle) \cos^2 \delta_n \cos^2(\varphi - \varphi_n) + 3\langle \Theta_z^2 \rangle - 1\} . \quad (4)$$

This equation holds for a CARTESIAN coordinate system. Inserting $\varphi_0^* = 0°$, PEDERSENS result [Eq. (3)] follows. The different angles in Eq. (4) are explained in Fig. 1. From the NMR experiment one can

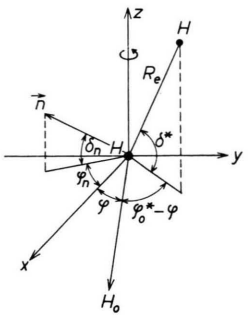

Fig. 1. The coordinate system defining the angles in Eq. (4).

deduce the first moment M_1 as a function of the angle φ. Eq. (4) contains the angles δ^*, φ_0^*, δ_n, φ_n together with the parameters $\langle \Theta_x^2 \rangle$, $\langle \Theta_z^2 \rangle$ and R_e. The torsional parameters $\langle \Theta_x^2 \rangle$ and $\langle \Theta_z^2 \rangle$ as well as the equilibrium distance R_e are constants and independent of the coordinate system chosen, while the angles δ^*, φ_0^*, δ_n and φ_n are connected with the rotation axes.

In a general case one has to discuss separately the determination of φ_0^* for each problem. The problem is much easier to solve for the special cases $\varphi_n = \varphi_0^*$ or $\varphi_n = 90° + \varphi_0^*$. Under this assumption the correction term in Eq. (4) $\cos^2 \delta_n \cos^2(\varphi - \varphi_n)$ is in phase or 90° out of phase with the main part of the splitting function $\cos^2 \delta^* \cos^2(\varphi - \varphi_0^*)$ in this equation. Then the angles φ_0^* may be determined from the maximum splitting. If there is an angle difference $\varepsilon \neq 0°$ or $\neq 90°$ between φ_n and φ_0^* one can show that the accuracy in determining the angle φ_0^* from the maximum splitting decreases with increasing ε. It is rather difficult to derive an analytical expression for the accuracy in φ_0^*, since the accuracy does not only depend on ε but on the values of δ^*, δ_n and φ_n too. Concerning the problems studied here the angles φ_n and δ_n were known approximately ($\pm 5°$) by a former determination of the proton positions in the unit cell of $Na_2S_2O_6 \cdot 2\,H_2O$ (l. c. [5]). In this study ^{1}H-NMR was also used, but the normal PAKE equation without any correction for vibrational motions was the background for the interpretation of the experimental results. From the direction cosines of the p – p lines, and the knowledge of the H-bridge bonding, an approximate analysis about the positions of protons in the cell could be made. From this information we found that the condition $\varphi_n = \varphi_0^*$ or $\varphi_n = 90° + \varphi_0^*$ was not exactly fulfilled. The deviation angles were

found to be 8°, 0.5° and 31.5° for the rotation around the crystallographic axes *a*, *b* and *c* respectively. The accuracy in φ_0^* for the rotation around *a* and *b* axis was $\pm 0.5°$ and somewhat lower for the third axis. A control of the accuracy in φ_0^* is given by the relation:

$$\mathrm{tg}[\varphi_{0b}^*]_a \cdot \mathrm{tg}[\varphi_{0c}^*]_b \cdot \mathrm{tg}[\varphi_{0a}^*]_c = 1\,. \qquad (5)$$

This relation is valid for a CARTESIAN coordinate system of axes *a*, *b* and *c* where the subscript of the bracket defines the rotation axis and the subscript of φ_0^* inside the bracket the fixed direction determining the rotation angle φ. The angles φ_0^* are connected with the angles δ^* by simple geometrical relations as

$$\mathrm{ctg}\,\delta_a^* = \mathrm{tg}[\varphi_{0a}^*]_c / \cos[\varphi_{0b}^*]_a\,, \qquad (6)$$

so that the angles of inclination of the p – p lines on the different rotation planes may be calculated. Further relations are shown in Fig. 2 and can easily be transferred into trigonometric equations.

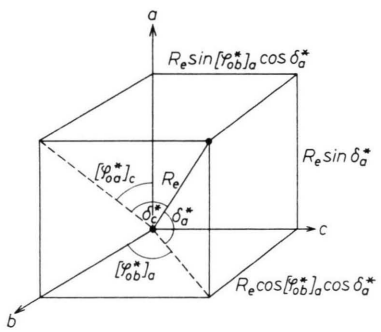

Fig. 2. Relations between the direction cosines of the p – p line and the crystal axes.

The ^{1}H-NMR single crystal investigations of the complete orthogonal set of rotation axes *a*, *b*, *c* leads to the angles φ_0^* and δ^* of the different p – p lines in the cell. In connection with the approximate values for φ_n and δ_n a functional relationship between $\langle\Theta_z^2\rangle$ and $\langle\Theta_x^2\rangle$ is now available. Out of the two special experimental points at $\varphi = \varphi_0^*$ (M_{1+}) and $\varphi = 90° + \varphi_0^*$ (M_{1-}) the prefactor $0.98 \cdot (3\,\mu)\, R_e^{-3}$ can be eliminated. It is obtained:

$$\langle\Theta_z^2\rangle = A + B \cdot \langle\Theta_x^2\rangle\,,$$

where A and B are constants and independent from the rotation axes chosen. For the determination of $\langle\Theta_x^2\rangle$ and $\langle\Theta_z^2\rangle$ and finally R_e we need a second relation between the torsional parameters or the direct knowledge of one of this parameters. PEDERSEN[3] found a relation between $\langle\Theta_z^2\rangle$ and the potential barrier V_0 for the twisting mode:

$$\langle\Theta_z^2\rangle = 0.2\, V_0^{-1/2} \left\{ \frac{1}{2} + \frac{1}{\exp(201\sqrt{V_0/T}) - 1} \right\}. \qquad (7)$$

Eq. (7) was derived under the assumption of a potential energy function of the form $V_z = V_0 \cdot \sin^2\alpha$, where α defines the torsional angle. V_z approximates a harmonic potential when α is small. The potential barrier may be obtained by measuring the temperature dependence of the spin lattice relaxation time T_1 or by line width measurements of deuteron magnetic resonance spectra. The first method was applied in literature on $CaSO_4 \cdot 2\,H_2O$ [9], $Li_2SO_4 \cdot H_2O$ [9] and $Ba(ClO_3)_2 \cdot H_2O$ [10], the second on $Ba(ClO_3)_2 \cdot D_2O$ [8]. The values found for the potential barrier V_0 are in the region between 5.0 and 7.3 kcal/mole. For $Ba(ClO_3)_2 \cdot H_2O$ a value of 5.0 and for $Ba(ClO_3)_2 \cdot D_2O$ a value of 6.6 kcal/mole was found. This is quite an interesting point as it possibly shows that the potential barrier in the deuterated compound is somewhat higher – the bridge bonding stronger. Finally the potential barrier should be a function of the length of the bridging bonds. Under this assumption Eq. (7) is only valid for weak hydrogen bonds. The potential barrier V_0 in Eq. (7) can be related to the twisting frequency ν_z and the moment of inertia J_z approximately by

$$V_0 = \tfrac{1}{2} J_z (2\pi\nu_z)^2.$$

A reasonable value for V_0 as discussed by PEDERSEN is 6.5 kcal/mole if the water molecule is bound to two oxygen atoms. By inserting this value in Eq. (7) it is seen that at 300 °K $\langle\Theta_z^2\rangle = 0.056$. From the general formula for the torsional vibrations

$$\langle\Theta_i^2\rangle = \frac{h\nu_i}{f_i} \left\{ \frac{1}{2} + \frac{1}{\exp(h\nu_i/kT) - 1} \right\} \qquad (8)$$

one gets an expression for the ratio $\langle\Theta_x^2\rangle / \langle\Theta_z^2\rangle$:

$$\frac{\langle\Theta_x^2\rangle}{\langle\Theta_z^2\rangle} = \frac{\nu_x}{\nu_z} \frac{f_z}{f_x} \left\{ \frac{\frac{1}{2} + 1/(\exp(h\nu_x/kT) - 1)}{\frac{1}{2} + 1/(\exp(h\nu_z/kT) - 1)} \right\}.$$

Inserting for the force constant $f_i = J_i \cdot (2\pi\nu_i)^2$, where J_i is the moment of inertia, we get:

$$\frac{\langle\Theta_x^2\rangle}{\langle\Theta_z^2\rangle} = \frac{\nu_z}{\nu_x} \frac{J_z}{J_x} \left\{ \frac{\frac{1}{2} + 1/(\exp(h\nu_x/kT) - 1)}{\frac{1}{2} + 1/(\exp(h\nu_z/kT) - 1)} \right\}. \qquad (9)$$

The proportionality $f_i \sim J_i \cdot \nu_i^2$ is an assumption which holds only for weak bridging bonds (exact only for

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free water molecules). The ratio of the moments of inertia for a water molecule may be calculated if the geometry of the molecule is known. For the HOH bond angle of $105 \pm 5°$ we find:

$$J_z/J_x = 0.66 \pm 0.03 .$$

With this ratio from Eq. (9) follows:

$$\langle \Theta_x^2 \rangle / \langle \Theta_z^2 \rangle = (0.66 \pm 0.03)\,(\nu_z/\nu_x)\,\Gamma(T). \quad (10)$$

$\Gamma(T)$ stands for the BOLTZMANN part in Eq. (9). This equation is useful when the torsional frequencies (twisting and rocking) are known. Sometimes it is possible to get informations about these frequencies from IR or/and RAMAN experiments. In our case the frequency ν_x was available from IR spectra, while ν_z was assumed by comparison with the torsional modes of $Ba(ClO_3)_2 \cdot D_2O$ given by CHIBA [8]. If we assume that the potential barrier for the hindered rotation around the twofold axis (z-axis) is lower than for the x axis (rocking motion) the ratio ν_z/ν_x is less than unity. In such cases the ratio $\langle \Theta_x^2 \rangle / \langle \Theta_z^2 \rangle$ is lower than 0.66. For $Ba(ClO_3)_2 \cdot D_2O$ CHIBA has found from line width measurements of the D resonance as function of temperature a value $\langle \Theta_x^2 \rangle / \langle \Theta_z^2 \rangle$ of 0.42 at 300 °K.

Results

We have investigated the magnetic resonance spectra of the proton in sodium- and lithium dithionate dihydrate single crystals by turning the crystals around the three principal crystallographic axes at room temperature. A somewhat modified POUND–KNIGHT–WATKINS spectrometer [11] was mostly used. For lithium dithionate dihydrate, $Li_2S_2O_6 \cdot 2\,H_2O$, a ROBINSON [12] oscillator was found to be more sensitive. The $Na_2S_2O_6 \cdot 2\,H_2O$ single crystals were grown by a controlled cooling of a saturated solution of $Na_2S_2O_6$ in the temperature range between 45 °C and 25 °C. The crystals are clear and stable in air. By filing and cutting, cylindrical samples 2 – 3 cm long and about 2 cm in diameter were prepared for the NMR experiments. The samples prepared in this way were glued on a teflon holder by help of a phosphate cement and optically adjusted on a goniometer head. $Li_2S_2O_6 \cdot 2\,H_2O$ is hygroscopic under normal conditions. Single crystals of this compound were grown at constant temperature by concentrating the solution in a closed and temperature controlled system over $CaCl_2$. In contact with solution the dihydrate is stable only above 24 °C. Below this temperature a second phase (tetrahydrate) precipitates.

The ^{1}H-NMR spectra of both compounds investigated, $Na_2S_2O_6 \cdot 2\,H_2O$ and $Li_2S_2O_6 \cdot 2\,H_2O$, consisted of four peaks when the crystals were turned around a main crystal axis. This multiplicity is in accordance with the symmetry operations of the space group D_{2h}^{16} – Pnma [5]. The spectra of the two water molecules not identical in the NMR experiments differ by the transformation $\varphi_0^* \longleftrightarrow -\varphi_0^*$ in Eq. (4).

a) $Na_2S_2O_6 \cdot 2\,H_2O$

In Fig. 3 the first moment M_1 is given as a function of the rotation angle φ for sodium dithionate dihydrate when the crystals are turned around the crystallographic axes a, b, c. When the first moment is plotted as a function of $\cos^2(\varphi \mp \varphi_0^*)$ a straight

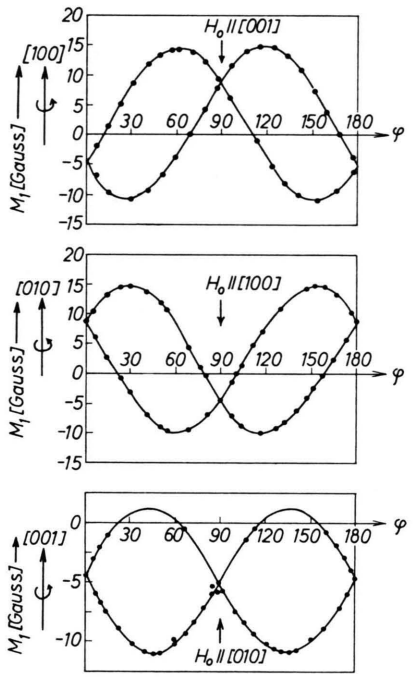

Fig. 3. ^{1}H-NMR spectra of $Na_2S_2O_6 \cdot 2\,H_2O$. The first moment M_1 as a function of the rotation angle φ.

line should be expected [this follows from Eq. (4)]. For the three crystallographic main axes this behaviour was confirmed (Fig. 4). The angles φ_0^* were

[11] R. V. POUND, Progr. Nucl. Phys. **2**, 21 [1952].

[12] F. N. ROBINSON, J. Sci. Instr. **36**, 482 [1958].

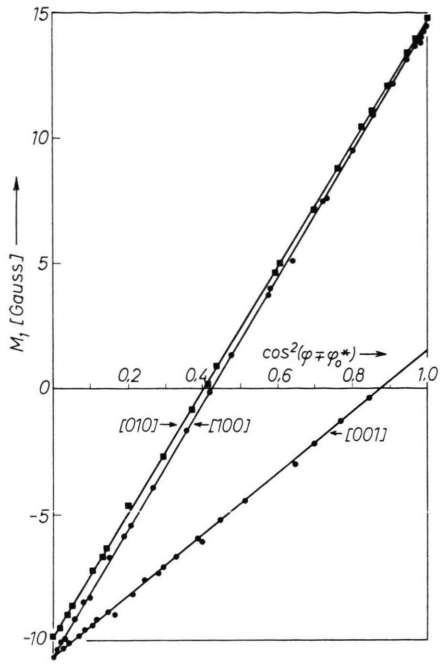

Fig. 4. ^{1}H-NMR spectra of $Na_2S_2O_6 \cdot 2\,H_2O$. The first moment M_1 as a function of $\cos^2(\varphi \pm \varphi_0^*)$.

determined from the maximum splittings of M_1 with an IBM 7090 computer in the manner already discussed. The angles δ^* were calculated using Eq. (6). The results are given in Table 1 together with φ_0, δ and the approximate angles φ_n and δ_n calculated from Eq. (1) (see ref. [5]).

The standard deviation in φ_0^*, δ^* and δ is $\pm 0.5°$, in φ_n and δ_n $\pm 5°$. As one can see from Table 1, the angles φ_0 and δ are not influenced by the dynamical behaviour of the water molecules (compare φ_0^*, δ^*) in our case. Inserting the angles given in Table 1 into Eq. (4) a relation between $\langle \Theta_x^2 \rangle$ and $\langle \Theta_z^2 \rangle$ was found. This relation was calculated on an IBM 7090 computer by standard least squares methods using all experimental points of the splitting curves. We found:

a-axis rotation: $\langle \Theta_z^2 \rangle = 0.038 + 0.89 \langle \Theta_x^2 \rangle$;

b-axis rotation: $\langle \Theta_z^2 \rangle = 0.034 + 0.94 \langle \Theta_x^2 \rangle$.

For the *c*-axis rotation the inaccuracy in the first moments M_1 was high for such angles φ where the splitting was small; therefore the accuracy in getting a functional relation between $\langle \Theta_z^2 \rangle$ and $\langle \Theta_x^2 \rangle$ is critical and poor. From *a*- and *b*-axis rotation a mean value of

$$\langle \Theta_z^2 \rangle = 0.036 + 0.91 \langle \Theta_x^2 \rangle$$

within an accuracy of 10% results. Eq. (9) together with Eq. (11) makes a determination of $\langle \Theta_x^2 \rangle$ and $\langle \Theta_z^2 \rangle$ possible. We tried to find the unknown torsional frequencies in Eq. (9) by IR spectroscopy. Comparing the IR spectra of $Na_2S_2O_6$, $Na_2S_2O_6 \cdot 2\,H_2O$ and $N_2S_2O_6 \cdot 2\,D_2O$ the frequency ν_x was found to be (463 ± 5) cm^{-1} (see the following paper), which is quite near to the frequency ν_x (H_2O) for $Ba(ClO_3)_2 \cdot H_2O$ (466 cm^{-1}) given by PEDERSEN [3]. The torsional frequency ν_z could not be assigned. We assumed that this frequency is equal or near to ν_z of $Ba(ClO_3)_2 \cdot H_2O$ which was calculated from CHIBA's data as 353 cm^{-1}. Inserting those values in Eq. (9), the ratio $\langle \Theta_x^2 \rangle / \langle \Theta_z^2 \rangle$ for room temperature was found to be 0.45 ± 0.03. In connection with the experimentally found relation between $\langle \Theta_z^2 \rangle$ and $\langle \Theta_x^2 \rangle$ we obtained:

$$\langle \Theta_x^2 \rangle = 0.027 \pm 0.003; \qquad \langle \Theta_z^2 \rangle = 0.061 \pm 0.006\,.$$

The height of the potential barrier V_0 is determined by Eq. (7). With $\langle \Theta_z^2 \rangle = 0.061 \pm 0.006$ at room temperature a value of $V_0 = (6.0 \pm 1)$ kcal/mole follows. Inserting the torsional parameters and the angles given in Table 1 into Eq. (4) an equilibrium H – H distance in the water molecule of

$$R_e = (1.515 \pm 0.015)\ \text{Å}$$

was calculated for $Na_2S_2O_6 \cdot 2\,H_2O$. The equilibrium distance R_e between the two protons of the water molecules in the crystalline hydrate is identical with the value given for free water in the gase phase (1.514 Å [13]).

axis	φ_0^*	δ^*	φ_n	δ_n	φ_0	δ
a	±61°27′	±26°10′	158°	11°	±61,5°	±26,5°
b	±29°03′	±25°28′	29°	66°	±29°	±25,5°
c	±44°13′	±52°02′	102°	21°	±44°	±52°

Table 1.

[13] W. S. BENEDICT, N. GAILAR, and E. K. PLYLER, J. Chem. Phys. **24**, 1139 [1956].

b) $Li_2S_2O_6 \cdot 2\,H_2O$

The ^{1}H-NMR spectra measurements on $Li_2S_2O_6 \cdot 2\,H_2O$ were found to be equivalent in multiplicity in comparison with the sodium compound. An investigation of the structure of lithium dithionate dihydrate (see the following paper) showed, that the lithium and sodium compounds are isotypic. The determination of the ^{1}H-doublet splittings in $Li_2S_2O_6 \cdot 2\,H_2O$ were somewhat more complicated by a free water signal resulting from the free H_2O of the non exact stoichiometric hydrate. This signal was independent of the crystal orientation. The doublet splittings of the different H_2O molecules in the unit cell are shown for *a*-, *b*-, and *c*-axis rotation in Fig. 5.

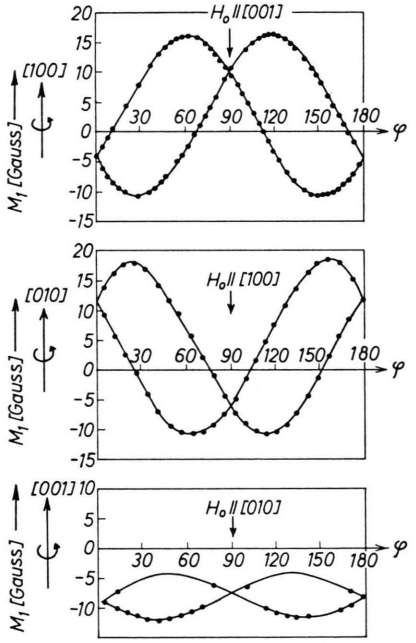

Fig. 5. ^{1}H-NMR spectra of $Li_2S_2O_6 \cdot 2\,H_2O$. The first moment M_1 as a function of the rotation angle φ.

Plots of the first moment as a function of $\cos^2(\varphi \pm \varphi_0^*)$ are given in Figs. 6 and 7. From those diagrams one can see, that for *b*-axis rotation Eq. (4) is not valid. We have not found by what type of perturbation the deviation from Eq. (4) is caused. We suspect that there is a lithium specific coupling term, which is comparable to the HH-coupling terms. Similar effects have been found in the ^{1}H-NMR spectra of $Li_2SO_4 \cdot H_2O$ [7, 14]. The determination of the angles φ_0^* for the different axes were not affected by this perturbation. The angles δ^* were calculated in the same way as described for the sodium compound. The results are given in Table 2. Since the crystal structure of $Na_2S_2O_6 \cdot 2\,H_2O$ and $Li_2S_2O_6 \cdot H_2O$ are the same, the angles δ_n and φ_n can be transferred from the results for the Na salt to the Li salt.

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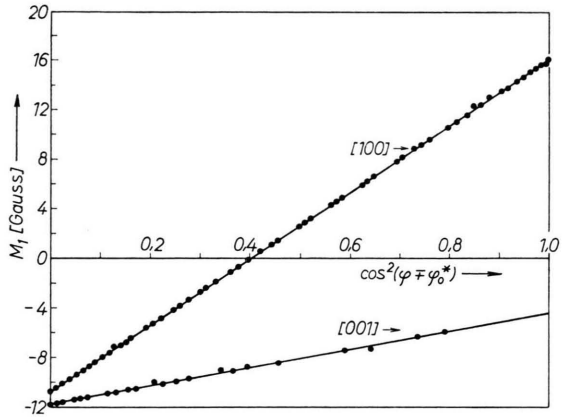

Fig. 6. ^{1}H-NMR spectra of $Li_2S_2O_6 \cdot 2\,H_2O$. The first moment M_1 as a function of $(\varphi \pm \varphi_0^*)$. Rotation axes: $a = [100]$ and $c = [001]$.

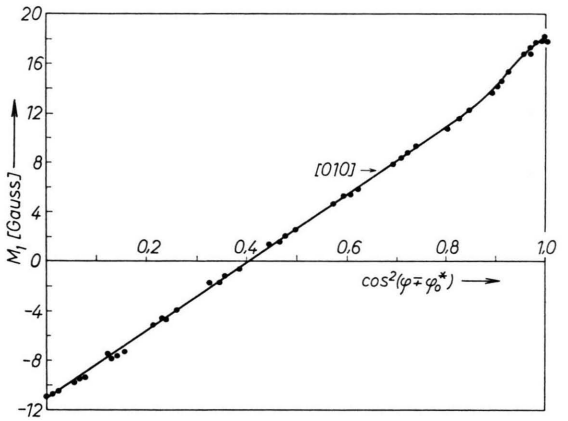

Fig. 7. ^{1}H-NMR spectra of $Li_2S_2O_6 \cdot 2\,H_2O$. The first moment M_1 as a function of $(\varphi \pm \varphi_0^*)$. Rotation axis: $b = [010]$.

axis	φ_0^*	δ^*
a	$\pm 61°39'$	$\pm 21°54'$
b	$\pm 24°36'$	$\pm 26°09'$
c	$\pm 40°45'$	$\pm 54°42'$

Table 2.

The experimental error in φ_0^* and δ^* is $\pm 0.5°$. The condition

$$\mathrm{tg}[\varphi^*_{0b}]_a \cdot \mathrm{tg}[\varphi^*_{0c}]_b \cdot \mathrm{tg}[\varphi^*_{0a}]_c = 1$$

is fulfilled within the experimental error. For the calculation of the torsional parameters by least squares fit we used only the a-axis rotation to suppress the strange behaviour of nonlinearity for b-axis rotation (compare Fig. 7). Using the value φ_n and δ_n given for $Na_2S_2O_6 \cdot 2\,H_2O$ for $Li_2S_2O_6 \cdot 2\,H_2O$, from the a-axis rotation the relation

$$\langle \Theta_z^2 \rangle = 0.033 + 0.90 \langle \Theta_x^2 \rangle \qquad (12)$$

was found. Comparing this relation for the lithium compound with the sodium result

$$\langle \Theta_z^2 \rangle = 0.034 + 0.91 \langle \Theta_x^2 \rangle$$

both expressions are identical within the experimental error of 10%. Additionally the torsional frequency ν_x of the lithium salt found by IR spectroscopy is the same as for the sodium compound. Consequently the torsional parameters, the height of the potential barrier, and the equilibrium p – p distance for the H_2O molecules of lithium dithionate dihydrate are:

$\langle \Theta_x^2 \rangle = 0.027 \pm 0.003$; $\langle \Theta_z^2 \rangle = 0.061 \pm 0.006$; $V_0 = (6.0 \pm 1)$ kcal/mole and $R_e = (1.515 \pm 0.015)$ Å.

Conclusions

The results of the ^{1}H-NMR investigations on $Na_2S_2O_6 \cdot 2\,H_2O$ and $Li_2S_2O_6 \cdot 2\,H_2O$ at room temperature show that the influence of the dynamical behaviour of the water molecules in the crystals changes the value of the intramolecular HH distance remarkably. The influence can be studied only if other physical arguments like IR spectra or the temperature dependence of the NMR spectra are available besides the room temperature NMR experiments. The consequences of the dynamics of H_2O in the crystals on the determination of the proton positions and the interpretation of the hydrogen bonds are discussed in the following paper.

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Dynamics of Water in Crystal Hydrates

II. The Crystal Structure of $Na_2S_2O_6 \cdot 2\,H_2O$ and $Li_2S_2O_6 \cdot 2\,H_2O$

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The crystal structure of $Na_2S_2O_6 \cdot 2\,H_2O$ has been refined by means of single crystal X-ray intensity data. The structure of the isotypic $Li_2S_2O_6 \cdot 2\,H_2O$ was also determined by single crystal studies. Two dimensional differential Fourier synthesis revealed the approximate positions of the hydrogen atoms. From ^{1}H-NMR investigations, the crystal structure, and information gained by IR spectroscopy the complete atomic arrangement in these two substances was obtained. The influence of the dynamical behaviour of the water molecules is taken into account in determining the hydrogen positions.

Although there are already data available on the crystal structure of $Na_2S_2O_6 \cdot 2\,H_2O$ from NMR spectroscopy[1–3] and X-ray analysis[4], the calculation of the electric field gradient on the lattice sites of ^{23}Na and ^{7}Li nuclei demands a knowledge of the atomic coordinates as accurate as possible. Since we are interested in understanding the nuclear quadrupole coupling tensor of ^{23}Na in $Na_2S_2O_6 \cdot 2\,H_2O$ in magnitude and orientation, a redetermination of the crystal structure of $Na_2S_2O_6 \cdot 2\,H_2O$ was undertaken. Accordingly the interpretation of the NQR experiments on ^{7}Li in single crystals of $Li_2S_2O_6 \cdot 2\,H_2O$ is

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