

## Hydrogen Bond Studies. 126. A $^2\text{H}$ NMR Study of $\text{LiClO}_4 \cdot 3\text{D}_2\text{O}$ at 25 and $-71^\circ\text{C}$

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A deuteron magnetic resonance study of a single crystal of  $\text{LiClO}_4 \cdot 3\text{D}_2\text{O}$  at 25 and  $-71^\circ\text{C}$  is reported. The determination of the electric field gradient tensors was based on quadrupole splittings from only one rotation axis.

At  $25^\circ\text{C}$  the observed electric field gradient tensor corresponds to a rapidly flipping water molecule. The quadrupole coupling constant ( $e^2qQ/h$ ) and asymmetry parameter ( $\eta$ ) at the deuteron position were found to be 131.4(2) kHz and 0.758(2), respectively. The principal axis corresponding to the largest eigenvalue deviates by  $4.0(6)^\circ$  from the normal to the water molecule plane.

At  $-71^\circ\text{C}$  the spectra correspond to the slow-flipping limit. The quadrupole coupling constant and asymmetry parameter were found to be 245.2(1) kHz and 0.107(1), respectively. The principal axis corresponding to the largest eigenvalue deviates  $1.8(6)^\circ$  from the O-H direction. The angular displacement is out of the water molecule plane.

The results are consistent with the earlier neutron diffraction and infrared spectroscopic studies.

In hydrated perchlorates, relatively high stretching vibrations of isotopically dilute HDO molecules have been observed,<sup>1,2</sup> corresponding to rather weak hydrogen bonds between the water molecules and the perchlorate ion.  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  serves as a good example. Very long O...O hydrogen bond distances have been observed [ $3.034(2)$ ,\*  $3.093(2)$  and  $3.156(2)$  Å]<sup>3</sup> as well as very high O-D stretching frequencies ( $2641$  and  $2610\text{ cm}^{-1}$ ).<sup>1</sup> A deuteron magnetic resonance study has recently been performed on  $\text{NaClO}_4 \cdot \text{D}_2\text{O}$ .<sup>4</sup> It was shown that the hydrogen atoms are dynamically disordered, causing unexpectedly small quadrupole cou-

pling constants [ $226.7(6)$  and  $231.5(6)$  kHz], and complicating the interpretation of these coupling constants in terms of hydrogen-bond properties. Another perchlorate salt recently studied both by neutron diffraction<sup>5</sup> and IR-spectroscopy<sup>1,6</sup> is  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ .

In  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  there is only one crystallographically independent O-H group with corresponding O...O hydrogen bond distance  $2.989(2)$  Å and O-D stretching frequency  $2619\text{ cm}^{-1}$ . As we are interested in studying the variation of the quadrupole coupling constants in different solid hydrates, and since  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  contains relatively weak hydrogen bonds, we decided to perform a  $^2\text{H}$  NMR study on this hydrate. As  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  belongs to a highly symmetric space group ( $P6_3mc$ , hexagonal), it will also serve as a good example to show some of the advantages of the procedure used at this laboratory<sup>7</sup> for the determination of the electric field gradient (EFG) tensors instead of the method more commonly used elsewhere, as advanced by Volkoff *et al.*<sup>8</sup>

$\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  has recently also been studied by proton wide line NMR as well as relaxation time measurements.<sup>9</sup> An activation energy for a hindered rotation of the water molecule (flip motion) was calculated from  $T_1$  and  $T_{1D}$  relaxation measurements, and found to be 10 kcal/mol. It will be shown that this result is in good agreement with our  $^2\text{H}$  NMR data.

In discussing structural data in this paper, we neglect any differences that might exist between the structures of normal and deuterated  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  as well as temperature effects on the structure.

\* Numbers in parenthesis here and throughout this paper are estimated standard deviations.

## EXPERIMENTAL DETAILS

*Preparation.*  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  was synthesized from commercial  $\text{Li}_2\text{CO}_3$  and perchloric acid ( $\text{HClO}_4$ ) dissolved in water. Deuterated  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$  was prepared by dissolving anhydrous  $\text{LiClO}_4$  in heavy water (99.99%  $\text{D}_2\text{O}$ ). A single crystal of  $\text{LiClO}_4 \cdot 3\text{D}_2\text{O}$  was grown in a desiccator employing dried  $\text{P}_2\text{O}_5$  as a desiccant. After a few weeks a well shaped flat crystal was obtained. The crystal was cut to an approximate size of  $4 \times 3 \times 10 \text{ mm}^3$  and sealed into a glass tube to prevent decomposition. The degree of deuteration in the crystal was calculated from the relative intensities of the O–H and O–D stretching bands in an infrared spectrum, using the intensity weighting factors 1.0 and 2.0, respectively. The degree of deuteration was found to be 94%.

*$^2\text{H}$  NMR spectra.* The single crystal of  $\text{LiClO}_4 \cdot 3\text{D}_2\text{O}$  was mounted on a goniometer head in such a way that the axis of rotation was tilted a few degrees away from the  $c$ -axis. The rotation axis was then determined on a 4-circle X-ray diffractometer and found to be  $-0.0276a + 0.0170b + 0.1748c$ , where  $a$ ,  $b$  and  $c$  are the unit cell axes.

The crystal was then transferred to a modified Varian wide-line NMR spectrometer without changing its orientation relative to the goniometer head. The crystal was rotated systematically in the magnetic field through an angle  $\phi$  in steps of  $5^\circ$  from  $0$  to  $180^\circ$  about the goniometer head axis. The precision in the setting of the angle  $\phi$  was  $\pm 0.05^\circ$ .

Deuteron magnetic resonance spectra were recorded at a crystal stabilized frequency of 7.0 MHz. The magnetic field was swept with a Varian Fieldial unit and the sweep rate was 5 and 10 mT/min. The field sweep was calibrated regularly by recording the position of the deuteron signals from a water sample ( $\text{D}_2\text{O}$ ) at various frequencies, and measuring these frequencies with a frequency counter. The reproducibility of the sweep rate was 0.1% over the whole data collection. The linearity of the utilized portion of the sweep was better than 0.3% of the total sweep.

In order to improve the signal-to-noise ratios, all spectra were time-averaged using an IBM 1800 computer. The rf amplitude was kept low enough to avoid saturation effects.

One data set was collected at room-temperature ( $25^\circ\text{C}$ ) where the water molecules reorient rapidly enough around their two-fold pseudosymmetry axes (flipping motion) to produce  $^2\text{H}$  NMR signals from an averaged EFG tensor. The signals were unexpectedly broad, however. This was probably due to the water molecules not having reached a sufficiently high flip rate to produce the high temperature limiting spectrum containing narrow lines. It is well

known that the  $^2\text{H}$  NMR signals will be considerably broadened in the temperature range corresponding to the transition from the high temperature spectrum from rapidly flipping water molecules to the low temperature spectrum from "static" water molecules. This has been discussed in detail in Ref. 10. However, the spectra observed at  $25^\circ\text{C}$  were judged to be sufficiently close to the high temperature limiting shape to allow a determination of the motionally averaged EFG tensor. No attempts were therefore made to produce narrower lines by increasing the temperature.

A second data set was collected at  $-71^\circ\text{C}$  where very narrow lines were observed from "static" water molecules. The temperature region for the line shape transition is correlated to the activation energy of the hindered rotation of the water molecule.<sup>11,12</sup> In Ref. 12 the following expression is given for the activation energy,  $E_a$ , in terms of the centre temperature,  $T$ , of the line shape transition region:

$$E_a = \frac{0.0374T}{1 - 0.00137T}$$

For the case of  $\text{LiClO}_4 \cdot 3\text{D}_2\text{O}$  a lower limit of  $T$  is  $-71^\circ\text{C}$  providing an estimate of the lower limit for the activation energy of 10.4 kcal/mol. This is consistent with the value of 10 kcal/mol obtained from relaxation measurements.<sup>9</sup>

The low temperature was obtained by using a cold nitrogen gas stream and measured with a copper-constantan thermocouple.

## RESULTS AND DISCUSSION

The crystal structure of  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ , shown in Fig. 1, belongs to the hexagonal space group  $P6_3mc$  [ $a = 7.719(2)$ ,  $c = 5.455(2) \text{ \AA}$ ],<sup>5</sup> with twelve asymmetric units in the unit cell. There is only one crystallographically independent O–H group, as the water oxygen is situated on a mirror plane, perpendicular to the molecular plane. On the other hand, all twelve EFG tensors at the deuteron positions in the unit cell are magnetically non-equivalent for a general orientation of the crystal relative to the magnetic field. Hence, a maximum of twelve pairs of lines will appear at low temperatures when the water molecules flip sufficiently slowly, and six pairs at high temperatures, when the water molecules flip more rapidly. For the latter case, two of the EFG eigenvectors are in the mirror plane.

The  $^2\text{H}$  NMR spectra were analyzed by using the least-squares program QSPL3<sup>7</sup> in a procedure that has been described elsewhere.<sup>13</sup> The most widely used method to calculate the EFG tensors is the

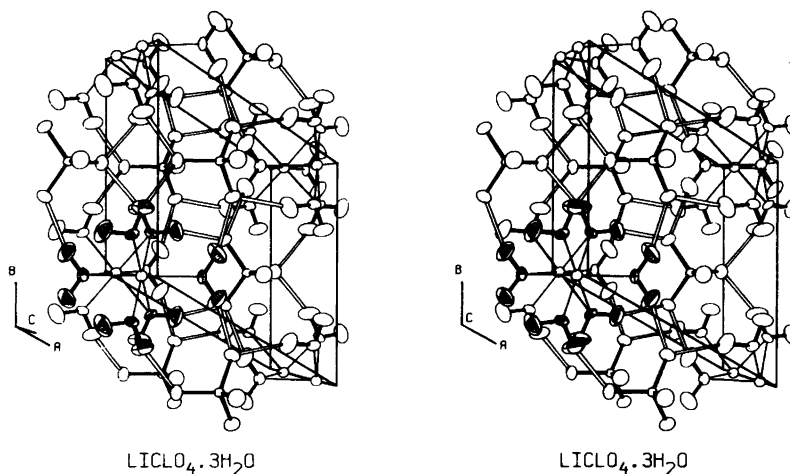


Fig. 1. A stereoscopic illustration of the crystal structure of  $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ , as given in Ref. 5. The six water molecules which are non-equivalent with respect to the external magnetic field are shaded.

method of Volkoff *et al.*<sup>8</sup> This method necessitates that the crystal be rotated in a magnetic field about three mutually orthogonal axes; the most common choice for these uses the crystallographic axes (*e.g.*,  $a$ ,  $b$  and  $c^*$  for a monoclinic case). The disadvantages of this method are: (1) it fails to make explicit use of the information contained in the crystal symmetry; (2) ambiguities arise in the derived EFG tensors for certain choices of rotation axes; and (3) there can be difficulties in aligning the crystals along three orthogonal axes. The last point can be a severe problem when the crystal faces are poorly developed and optical alignment is used.

A method to calculate the EFG tensors has recently been proposed by El Saffar<sup>14</sup> for making use of the information from symmetry related EFG tensors. The method is based on observations of DMR splittings from only one rotation axis, provided that the observed rotation patterns are not related by a mirror plane. The method is applicable to all crystal classes except triclinic, and uses some of the information in the symmetry related splittings, but not all.

It can be shown that, for all symmetry classes except triclinic, it is also possible to extract at least partial information about the crystal orientation relative the magnetic field from the symmetry related DMR splittings. For symmetries higher than monoclinic the rotation axes and EFG tensors can, in fact, be simultaneously determined from the NMR data. One can therefore make use of crystal sym-

metry to correct for misalignments of the crystal, a problem that has often been discussed in the literature. It can also be shown that, for monoclinic and triclinic crystal classes, it is possible to determine some of the rotation axes (*e.g.* if one rotation axis of three is unknown, this axis may be derived from the NMR data). A procedure has been developed in this laboratory which makes full use of all crystal symmetry in the determination of EFG tensors and, where possible, also allows a simultaneous determination of the crystal orientation to be made. The procedure has been implemented in the computer program QSPL3, and the determination of the EFG tensors in  $\text{LiClO}_4 \cdot 3\text{D}_2\text{O}$  serves as a good example of the possibilities which this procedure offers.

The EFG tensors at 25 and  $-71^\circ\text{C}$  were calculated as follows: the orientation of the EFG tensors were estimated from the structural data,<sup>5</sup> and the quadrupole coupling constants from the hydrogen-bond distances. Putting the asymmetry parameters equal to 0.1 at  $-71^\circ\text{C}$  and 0.9 at  $25^\circ\text{C}$ , rotation patterns were generated for both the high and low temperature cases for the rotation axis given above. These rotation patterns agreed very well with those obtained experimentally, and it was possible to assign all the rotation patterns to the appropriate symmetry operations.

All data (in all 620 observations) at both 25 and  $-71^\circ\text{C}$  were then used simultaneously in the refinement of the two EFG tensors, the rotation axis and the angle,  $\theta$ , between the rotation axis and the

Table 1. Calculated eigenvalues and eigenvectors of the EFG tensors at 25 and  $-71$  °C, and rotation axis for  $\text{LiClO}_4 \cdot 3\text{D}_2\text{O}$ . The components of the vectors are given in the coordinate system defined by the unit cell axes.

Eigenvalues		Eigenvectors	
25 °C			
- 15.9(1)	-0.07477(1)	0.07477(1)	0.00430(39)
-115.5(2)	0.12955	0.12955	0
131.4(2)	-0.00175(16)	0.00175(16)	-0.18327(1)
$\eta=0.758(2)$			
$-71$ °C			
-109.5(1)	-0.01704(5)	-0.13721(2)	-0.00264(149)
-135.7(1)	-0.00349(16)	0.00048(111)	-0.18324(2)
245.2(1)	0.14858(1)	0.05958(3)	-0.00461(10)
$\eta=0.107(1)$			
Rotation axis		0.17511(7)	
0.02689(20)	-0.01699(20)		

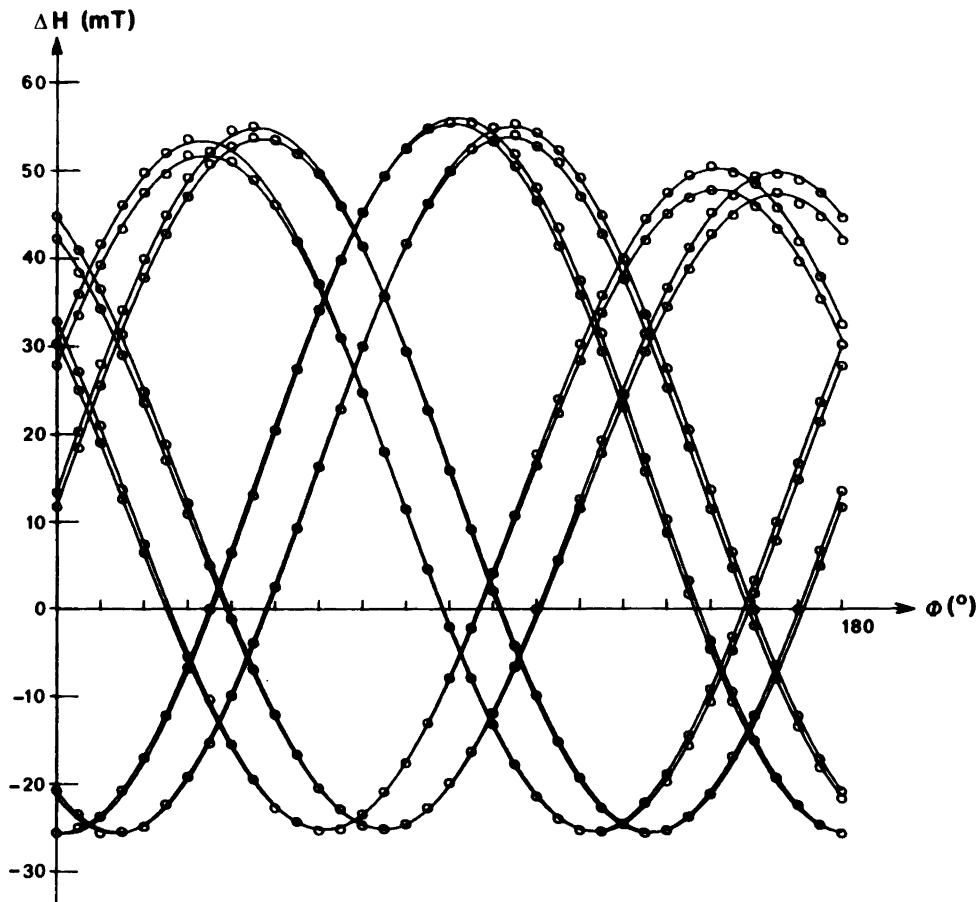


Fig. 2. Rotation patterns based on parameters given in Table 1 at  $-71$  °C. The circles are experimental  $^2\text{H}$  NMR-splittings.

Table 2. Some structural quantities related to the EFG tensor at  $-71^\circ\text{C}$  at the deuterium nuclei.  $\alpha_1$ ,  $\alpha_2$  and  $\alpha_3$  are the angles between the  $z$ -principal axis and the  $\text{O}-\text{H}$ ,  $\text{H}\cdots\text{O}$  and  $\text{O}\cdots\text{O}$  vectors.  $\beta$  is the angle between the  $y$ -principal axis and the normal to the plane of the water molecule. Structural data are taken from Ref. 5.

Hydrogen bond angle $\text{O}-\text{H}\cdots\text{O}$ ( $^\circ$ )	163.6(8)
$\text{O}-\text{H}$ ( $\text{\AA}$ )	0.972(7)
$\text{H}\cdots\text{O}$ ( $\text{\AA}$ )	2.044(7)
$\text{O}\cdots\text{O}$ ( $\text{\AA}$ )	2.989(2)
$e^2qQ/h$ (kHz)	245.2(1)
$\eta$	0.107(1)
$\alpha_1$ ( $^\circ$ )	1.8(6)
$\alpha_2$ ( $^\circ$ )	10.1(5)
$\alpha_3$ ( $^\circ$ )	8.2(1)
$\beta$ ( $^\circ$ )	3.8(4)

external magnetic field. The estimated EFG tensors were used as start parameters in this procedure. The angle  $\theta$  did not deviate significantly from  $90^\circ$ . The calculated EFG tensors and the rotation axis are given in Table 1. The refined rotation axis deviates by less than  $0.4^\circ$  from the one obtained from the diffractometer data. The rotation patterns based on the parameters in Table 1 at  $-71^\circ\text{C}$  are given in Fig. 2, together with the experimental  $^2\text{H}$  NMR splittings. The overlap of some of the curves is due to the small angle ( $1.4^\circ$ ) between the  $z$ -principal axis and the  $(\bar{2}10)$  glide plane.

The root-mean-square deviation between observed and calculated splittings was 0.29 mT for the 620 observations. The single EFG tensor associated with one water molecule at  $25^\circ\text{C}$  is very close to the average of the two symmetry related tensors of the same water molecule at  $-71^\circ\text{C}$ . The deviations are probably caused by differences in the vibrational motions at the two temperatures. The  $z$ -principal axis at  $25^\circ\text{C}$  forms an angle of  $4.0(6)^\circ$  with the normal to the water molecule plane, and the  $y$ -principal axis is along the (110) direction as a consequence of the crystal symmetry. This is exactly along the  $\text{D}\cdots\text{D}$  direction in the water molecule.

The  $z$ -principal axis at  $-71^\circ\text{C}$  forms an angle  $1.8(6)^\circ$  with the  $\text{O}-\text{H}$  direction. The angular displacement is out of the water molecule plane. In Table 2, the EFG tensor and some structural quantities are compared. The results are in good agreement with earlier results reported for other hydrates. The deuteron quadrupole coupling constant is one of the largest reported so far for a water molecule in a solid hydrate. This is in excellent agreement

with the very long hydrogen bonds and the high value of  $\text{O}-\text{D}$  stretching frequency. The correlation between these quantities is discussed more extensively in Ref. 15.

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