Hydrogen Bond Studies

119. A Deuteron Magnetic Resonance Study of Sodium Perchlorate Monohydrate, NaClO₄·H₂O, at 25 °C and -55 °C
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The quadrupole splittings in the deuterium NMR spectrum from single crystals of deuterated sodium perchlorate monohydrate, NaClO₄·D₂O, have been measured at 25 °C and -55 °C. At room temperature, the 180° flip frequency of the D₂O molecules is large compared to the difference between the splittings for the two deuterons. The average quadrupole coupling constant (e²ΩQ/h) and asymmetry parameter η are 134.1(4) kHz and 0.621(5), respectively. At -55 °C, the electric field gradient tensors for each of the two deuterons were observed corresponding to slowly flipping water molecules, and e²ΩQ/h and η for the two deuterons are 231.5(6) and 226.7(6) kHz and 0.196(4) and 0.195(5), respectively. The results indicate that the hydrogen positions in NaClO₄·H₂O are dynamically disordered.

Introduction

An infrared spectroscopic study of sodium perchlorate monohydrate, NaClO₄·H₂O, revealed an unusually high (3550 cm⁻¹) O–H stretching frequency for the water molecule 1. This shows that the water molecule is involved in very weak hydrogen bonding. Recently, the crystal structure of NaClO₄·H₂O was determined at room temperature using X-ray diffraction 2. The structure and some aspects of the dynamics of the water molecule in NaClO₄·H₂O have also been studied at room temperature using neutron diffraction 3. The results of these investigations provide additional support for the idea that the water molecule is very weakly hydrogen bonded. In the neutron diffraction study, very large apparent vibrational amplitudes were observed for the hydrogens in the water molecules; these abnormal amplitudes were discussed in terms of a possible disorder of the hydrogen positions.

A deuteron magnetic resonance study of a solid hydrate reveals the electric field gradient (EFG) tensors at the deuterion sites in the water molecules, and these EFG tensors are very sensitive to the hydrogen bond arrangement. A knowledge of the EFG tensors in NaClO₄·D₂O would therefore provide valuable information on the hydrogen bonding in the compound, as well as resolve the question of a possible disorder. This work forms part of a series of studies of the EFG tensors at the water deuterion sites in different hydrates in progress at this Institute.

Experimental

Commercially obtained NaClO₄·H₂O was heated to about 120 °C to remove the crystallization water and then dissolved in heavy water. Single crystals of NaClO₄·D₂O were obtained from this solution by slowly lowering the temperature by roughly one degree per day. The degree of deuteration was checked by infrared spectroscopy, and found to be not greater than 80%. Since this result was unexpectedly low, the deuteration procedure was carried out a second time, taking even greater care to exclude normal water. The same result was obtained, however. This phenomenon was also observed in the preparation of deuterated crystals of BeSO₄·4D₂O 4. The method normally produces almost completely deuterated single crystals of hydrates 5, but for some reason it works less well for certain hydrates. The isotope effect on the quadrupole coupling constant in HD₂O molecules compared with D₂O molecules has been measured in potassium oxalate monohydrate 6. The effect was small, however, so that the relatively low degree of deuteration is unimportant for our purposes.

Three crystals of roughly the same size (about 5 × 5 × 10 mm³) were sealed into thin-walled glass tubes to prevent decomposition. Each crystal was then mounted on a goniometer head and the crystal orientation determined on a 4-circle X-ray diffractometer. The goniometer head was transferred to the NMR spectrometer without disturbing the crystal orientation and mounted on a device which allows a precise rotation through an angle θ (reproducibility ± 0.1°) about an axis perpendicular to the magnetic field. This procedure for the determination of the crystal rotation axis has proved to be very accurate 3–5. The rotation axis for each of the crys-
Table 1. Rotation axes for the three crystals. The vector components are given in the coordinate system defined by the unit cell axes.

<table>
<thead>
<tr>
<th>Crystal No</th>
<th>Rotation axis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.05714</td>
</tr>
<tr>
<td></td>
<td>-0.06305</td>
</tr>
<tr>
<td></td>
<td>-0.01084</td>
</tr>
<tr>
<td>2</td>
<td>-0.02336</td>
</tr>
<tr>
<td></td>
<td>0.16854</td>
</tr>
<tr>
<td></td>
<td>-0.00138</td>
</tr>
<tr>
<td>3</td>
<td>0.06441</td>
</tr>
<tr>
<td></td>
<td>0.00407</td>
</tr>
<tr>
<td></td>
<td>0.00034</td>
</tr>
</tbody>
</table>

The audio frequency modulation amplitude was about 0.5 mT and the r.f. field was held below saturation level. To increase the signal-to-noise ratio, about 100 spectra per crystal orientation were accumulated in an IBM-1800 computer. The low temperature was obtained by blowing a cold nitrogen gas-stream on the crystals. The magnetic field was swept with a Fieldial unit at rates varying between 5 and 10 mT/min.

The magnetic field sweep was calibrated by recording the positions of the deuteron signal from a water sample at various frequencies measured with a frequency counter. The reproducibility of the sweep rate was better then 0.1% over the whole period of data collection. The linearity of the part of the sweep used was better than 0.3% of the total sweep width.

**Results**

The diffraction studies on NaClO$_4$·H$_2$O have demonstrated that the structure, shown in Fig. 1, belongs to the monoclinic space group C2/c, \((a = 15.5422(13), b = 5.5399(5), c = 11.0455(11), \beta = 110.666(8), Z = 8)\). There are eight symmetry related water molecules in the unit cell, forming two groups of four molecules, and all the molecules within each group producing identical spectra. A DMR-spectrum will therefore contain four doublets if the water molecules undergo no flipping motion or flip at a sufficiently low rate. On the basis of signal-to-noise considerations, \(-55^\circ C\) was found to be the most convenient temperature for studying the EFG tensors of the "static" water molecule. As the number of splittings was small, no difficulties arose in assigning a given splitting to the correct deuteron and symmetry operation.

The method for calculating the EFG tensors from the observed quadrupole splittings has been described briefly in Reference 5. The eigenvalues and eigenvectors of the crystallographically independent EFG tensors were obtained in a least-squares analysis of the observed splittings calculated on an IBM 370/155 computer using the program QSPL3. The analysis of the data from 25°C was based on 98 observed splittings and the r.m.s. deviation between observed and calculated splittings (from the final EFG tensors) was 0.18 mT. Corresponding quantities at \(-55^\circ C\) were 179 observations and 0.22 mT, respectively. At each temperature, all data from all three crystals were used simultaneously in the analysis, including splittings from symmetry related EFG tensors.

The calculated eigenvalues and eigenvectors at \(-55^\circ C\) and 25°C are given in Table 2 and Table 3, respectively. A comparison between crystal-

![Fig. 1. A stereoscopic illustration of the structure of NaClO$_4$·H$_2$O. The two water molecules which are magnetically non-equivalent with respect to the external magnetic field are shaded. The figure is based on parameters from Reference 3.](image)
Table 2. Eigenvalues and eigenvectors of the EFG tensor for the two deuterons at −55 °C. The vector components are given in the coordinate system defined by the unit cell axes.

<table>
<thead>
<tr>
<th>Eigenvalues (kHz)</th>
<th>Eigenvectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₁</td>
<td></td>
</tr>
<tr>
<td>−93.1 (6)</td>
<td>0.0103 (8)</td>
</tr>
<tr>
<td>−138.4 (7)</td>
<td>0.0649 (1)</td>
</tr>
<tr>
<td>231.5 (6)</td>
<td>−0.0203 (1)</td>
</tr>
<tr>
<td>−91.2 (7)</td>
<td>0.0149 (7)</td>
</tr>
<tr>
<td>−135.5 (7)</td>
<td>0.0643 (1)</td>
</tr>
<tr>
<td>226.7 (6)</td>
<td>0.0192 (1)</td>
</tr>
</tbody>
</table>

| D₂                |              |
| −135.5 (7)        | 0.0149 (7)   |
| 226.7 (6)         | 0.0192 (1)   |

* Numbers in parenthesis here and in the following are estimated standard deviations in the least significant digits.

Table 3. Eigenvalues and eigenvectors of the averaged EFG tensor at 25 °C together with the mean value of the two tensors in Table 2. The components are given in the coordinate system defined by the unit cell axes.

<table>
<thead>
<tr>
<th>Eigenvalues (kHz)</th>
<th>Eigenvectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exp. data at 25 °C</td>
<td></td>
</tr>
<tr>
<td>−25.4 (3)</td>
<td>0.0006 (1)</td>
</tr>
<tr>
<td>−108.7 (4)</td>
<td>−0.0250 (1)</td>
</tr>
<tr>
<td>134.1 (4)</td>
<td>0.0640 (1)</td>
</tr>
</tbody>
</table>

| Mean value of the EFG tensors at −55 °C | 0.0009 | 0.1444 | −0.0539 |
| Mean value of the EFG tensors at 25 °C  | 0.0244 | 0.1019 | 0.0554  |
|                                         | 0.0643 | 0.0367 | 0.0582  |

Table 4. Some structural quantities related to the EFG tensor at the deuteron nuclei. \( \alpha_1 \), \( \alpha_2 \) and \( \alpha_3 \) are the angles between the \( z \)-principal axis and the \( O-H, H \ldots O \) and \( O \ldots O \) vectors. \( \beta \) is the angle between the \( y \)-principal axis and the normal to the water molecule plane. The crystallographic data are taken from Reference 3.

<table>
<thead>
<tr>
<th>Deuteron</th>
<th>Hydrogen-bond angle</th>
<th>O−H (Å)</th>
<th>H⋯O (Å)</th>
<th>O⋯O (Å)</th>
<th>( e^2 q Q / h ) (kHz)</th>
<th>( \eta ) (°)</th>
<th>( \beta ) (°)</th>
<th>( \alpha_1 ) (°)</th>
<th>( \alpha_2 ) (°)</th>
<th>( \alpha_3 ) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D₁</td>
<td>140.4 (9)</td>
<td>0.905 (6)</td>
<td>2.389 (7)</td>
<td>3.141 (3)</td>
<td>231.5 (6)</td>
<td>0.196 (4)</td>
<td>3.5 (1.1)</td>
<td>2.1 (7)</td>
<td>41.5 (2)</td>
<td>31.0 (1)</td>
</tr>
<tr>
<td></td>
<td>135.2 (9)</td>
<td>2.378 (10)</td>
<td>3.087 (3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>42.0 (2)</td>
</tr>
<tr>
<td>D₂</td>
<td>155.5 (7)</td>
<td>0.935 (7)</td>
<td>2.152 (8)</td>
<td>3.028 (3)</td>
<td>226.7 (6)</td>
<td>0.195 (5)</td>
<td>0.2 (1.0)</td>
<td>1.0 (5)</td>
<td>25.2 (2)</td>
<td>17.9 (1)</td>
</tr>
<tr>
<td></td>
<td>122.0 (7)</td>
<td>2.733 (7)</td>
<td>3.325 (3)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>57.1 (2)</td>
</tr>
</tbody>
</table>
Table 5. Some representative quadrupole coupling constants and asymmetry parameters of EFG tensors for deuterium in hydrates. The first reference relates to the distance and the second to the NMR data.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{O}\ldots\text{O} ) (Å)</th>
<th>( e^2 q Q/h )</th>
<th>( \eta )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaDC(_2)O(_4)·D(_2)O</td>
<td>2.808</td>
<td>228.5</td>
<td>0.127</td>
<td>8, 9</td>
</tr>
<tr>
<td>LiHCOO·D(_2)O</td>
<td>2.714</td>
<td>198.7</td>
<td>0.060</td>
<td>10, 5</td>
</tr>
<tr>
<td>Li(_2)SO(_4)·D(_2)O</td>
<td>2.37</td>
<td>236.7</td>
<td>0.091</td>
<td>11, 4</td>
</tr>
<tr>
<td>Ba(C(_2)0(_3))(_2)·D(_2)O</td>
<td>2.891</td>
<td>243.5</td>
<td>0.074</td>
<td>12, 13</td>
</tr>
<tr>
<td>Na(_2)S(_2)O(_3)·2D(_2)O</td>
<td>2.85</td>
<td>236</td>
<td>0.116</td>
<td>14, 15</td>
</tr>
<tr>
<td>K(_2)CO(_3)·D(_2)O</td>
<td>2.754</td>
<td>209.7</td>
<td>0.090</td>
<td>16, 17</td>
</tr>
</tbody>
</table>

\( \text{H}_2\text{O} \) for which normal EFG tensors were found in a DMR study\(^9\).

2) It has been suggested that the asymmetry parameter of the EFG tensor of a deuteron will increase as a result of participation in a non-linear hydrogen bond\(^{18, 19}\). In NaClO\(_4\)·D\(_2\)O, each O—H group points towards two hydrogen bond acceptors (a bifurcated bond, cf. Fig. 2) which are not collinear with the O—H direction. Both will therefore add to the non-axiality of the EFG tensors. This effect cannot be excluded from being at least partially responsible for the high \( \eta \) in the present case. It is difficult to make a quantitative estimate of the importance of this effect, however.

3) The most probable major contribution to the non-axiality is related to the very large apparent vibrational amplitudes for the hydrogens observed in the neutron diffraction study. Independent of whether these apparent vibrational amplitudes are due to actual vibrations or to a dynamical disorder, they will strongly affect the observed EFG tensors. Furthermore, by far the largest amplitude was in the plane of the water molecule. A librational motion in this plane, \( i.e. \) about the eigenvector \( y \) of the equilibrium EFG tensor, will not affect the eigenvalue \( V_{yy} \) but will reduce the observed eigenvalues \( V_{zz} \) and \( V_{xz} \). The average of \( \eta = (V_{yy} - |V_{xz}|) / V_{zz} \) will therefore increase as a result of such a motion, as is actually observed. An estimate of the effect of a libration which is predominantly in the plane of the water molecule may be obtained as follows. If \( \theta_x, \theta_y \) and \( \theta_z \) represent rotational displacement coordinates about the equilibrium eigenvectors \( x, y \) and \( z \), then the relation \(^{20}\) between the average EFG components \( \langle V_{ij} \rangle \), the equilibrium values \( V_{zz} \) and \( \eta^0 \) and the mean square amplitudes of libration gives that

\[
\frac{\langle V_{xx} \rangle - \langle V_{yy} \rangle}{\langle V_{zz} \rangle} = \frac{V_{zz}^0}{\langle V_{zz} \rangle} \cdot \left[ \eta_0 \left( 1 - \frac{1}{3} (\langle \theta_x^2 \rangle + \langle \theta_y^2 \rangle) - 2 \langle \theta_z^2 \rangle \right) \right] + \frac{2}{3} \left( \langle \theta_y^2 \rangle - \langle \theta_z^2 \rangle \right). \tag{1}
\]

Note that, strictly speaking, the left-hand side of this relation is not in general the asymmetry parameter \( \langle \eta \rangle \) of the average EFG tensor. This is because the eigenvectors of the average EFG tensor will not in general coincide with those of the equilibrium EFG tensor. Therefore, since \( \langle V_{xx} \rangle, \langle V_{yy} \rangle \) and \( \langle V_{zz} \rangle \) are components of the average EFG tensor referred to the equilibrium eigenvectors \( x, y \) and \( z \), these averaged quantities will not be eigenvalues of the average EFG tensor and they will not define \( \langle \eta \rangle \). However, for the special case where the librational modes correspond to rotations about axes parallel to \( x, y \) and \( z \), the eigenvectors for the average EFG tensor will coincide with \( x, y \) and \( z \), and we can write \( \langle \eta \rangle = (\langle V_{xx} \rangle - \langle V_{yy} \rangle) / \langle V_{zz} \rangle \). In our case, the major motion is about an axis normal to the plane of the water molecule, \( i.e. \) roughly about \( y \). The averaged EFG eigenvectors will therefore probably not differ much from the equilibrium values, and we may take Eq. (1) as an estimate of \( \langle \eta \rangle \). Thus

\[
\langle \eta \rangle \approx \frac{V_{zz}^0}{\langle V_{zz} \rangle} \cdot \eta_0 \left( 1 - \frac{1}{3} (\langle \theta_x^2 \rangle + \langle \theta_y^2 \rangle) - 2 \langle \theta_z^2 \rangle - 2 \eta_0 \langle \theta_z^2 \rangle \right). \nonumber
\]

Since \( \eta_0 \approx 0.1 \)

\[
\langle \eta \rangle \approx \frac{V_{zz}^0}{\langle V_{zz} \rangle} \cdot \eta_0 + \frac{2}{3} (\langle \theta_y^2 \rangle - \langle \theta_z^2 \rangle) - 2 \eta_0 \langle \theta_z^2 \rangle. \nonumber
\]
Since \( \langle \theta_x^2 \rangle \gg \langle \theta_z^2 \rangle \), \( \langle \theta_z^2 \rangle \) and \( \eta_0 \approx 0.1 \), the most important correction term in the bracket is \( \frac{3}{2} (\langle \theta_x^2 \rangle - \langle \theta_z^2 \rangle) \). Neglecting the term \( 2 \eta_0 \langle \theta_z^2 \rangle \), taking 250 kHz as a lower limit for \( V^0_{zz} \) and taking \( \eta_0 = 0.1 \), a rough estimate of the \( \langle \theta_x^2 \rangle - \langle \theta_z^2 \rangle \) value required to give the observed \( \langle \eta \rangle = 0.2 \) would be 0.06 rad\(^2\). This is considerably smaller than the amplitudes observed in the neutron diffraction study.

We thus conclude that the in-plane motion of the water molecule is sufficiently large to account for the abnormal asymmetry parameter, at least at room temperature.

**The possibility of Disorder**

The neutron diffraction study of NaClO\(_4\)-H\(_2\)O\(^3\) showed a remarkably large r.m.s. amplitude of displacement of the hydrogens in the plane of the water molecule, as shown in Figure 2. This result can either be due to disorder in the hydrogen positions or to an extremely large librational motion in the water molecule plane (a large rocking mode). In the first case, the water molecule will have at least two possible equilibrium orientations, related by a rotation about an axis roughly normal to the plane of the water molecule. In the second case, however, there will be just one equilibrium orientation. Furthermore, if disorder is the predominant cause of the large in-plane amplitude, it is most probably dynamical, i.e. the water molecule performs random jumps between the possible equilibrium positions. For it to be a static disorder, additional splittings should be observed, at least at certain crystal orientations.

The measured EFG tensor at 25 °C is compared in Table 3 with the EFG tensor obtained as the mean value of the two EFG tensors measured at −55 °C. It is clear that these two tensors are very similar. The temperature dependence of the EFG tensor is thus rather small. This result is not compatible with the suggestion that the very large orientational freedom of the water molecule observed with neutron diffraction is due to a rocking vibration. Such a large librational amplitude would correspond to a very low vibrational frequency, and therefore to a large temperature dependence both of the librational amplitude and the vibrationally averaged EFG tensor. On the other hand, if the hydrogens are disordered, the temperature dependence of the vibrational amplitude is expected to be small; the major effect of a temperature change would be to alter the jump rate between the possible equilibrium orientations of the water molecule. Our data therefore favour an interpretation in terms of dynamical disorder rather than large vibrational amplitude.

It should also be noted that, in the neutron diffraction study, a crude estimate of the librational frequency corresponding to the observed amplitudes gave the value 146 cm\(^{-1}\). This is considerably below any observed rotational vibration for a water molecule. Taken together with our results, this provides additional evidence for the disorder in spite of the many approximations involved in the vibrational analysis.

In the IR study of NaClO\(_4\)-H\(_2\)O\(^1\) very narrow O–D stretching bands were observed down to −165 °C. This indicates either that the water molecule is ordered or, if disorder exists, that the disorder is between orientations of the water molecule which produce very closely similar O–D stretching frequencies. The observed IR spectra are thus compatible both with a disordered structure and with a large in-plane vibration. In our view, however, the total experimental evidence favours a disordered structure.

It is rather unfortunate that this apparent disorder exists in NaClO\(_4\)-H\(_2\)O since it would be very interesting to know the EFG tensors at the deuteron sites in this very weakly hydrogen-bonded water molecule. It is probably impossible to resolve the EFG tensors for the disordered deuterons even if the temperature is decreased further, since the jumps between two adjacent positions are likely to be hindered by a very low activation energy, and would therefore be very difficult to “freeze-in”. However, if the various equilibrium hydrogen positions can be resolved by low-temperature neutron diffraction, it will be possible (with some approximations) to calculate \( e^2 q Q/h \) for each of the equilibrium orientations of the water molecules in NaClO\(_4\)-D\(_2\)O.

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