Deuteron and Proton Magnetic Resonance Study of Partly Deuterated Crystals. I. Potassium Oxalate Monohydrate

BJÖRN PEDERSEN

Sentralinstitutt for industriell forskning, Oslo 3, Norway

A comparative study of the room temperature D(deuteron)MR- and P(proton)MR-spectra of a partly deuterated single crystal of potassium oxalate monohydrate (KOMH) is presented. The DMR-spectra are recorded at 9.1 MHz, and the PMR-spectra at 60 MHz without changing the orientation of the crystal and the magnitude of the magnetic field. By intercomparison of the line splittings observed in the spectra of the H\textsubscript{2}O, HDO, and the D\textsubscript{2}O molecules the following information is obtained: (1) The H\textsubscript{2}O and the HDO molecules are, within 0.2°, vibrating about the same equilibrium position in the lattice, demonstrating the harmonic nature of the potential. (2) The intermediate principal component of the electric field gradient is normal to the molecular plane within 0.5°. (3) The molecular plane is twisted 5.1° ± 0.5° out of the plane determined by the hydrogen bond acceptors. (4) The largest principal component of the electric field gradient makes an angle of 53.9° ± 0.1° with the two-fold axis of the D\textsubscript{2}O molecule; this is close to the direction of the O–D bond.

The quadrupole coupling constant averaged over the vibrating motion is found to be 214 ± 2 kHz and the asymmetry factor 0.076 ± 0.008. Correction for the effects of the torsional oscillations of the water molecule in the lattice increases these values to 224 kHz and 0.11.

One of the first applications of NMR spectroscopy to a problem in structure chemistry was the location of the hydrogen atoms in CaSO\textsubscript{4}.2H\textsubscript{2}O by Pake in 1948. Pake showed that the fine structure observed in the proton magnetic resonance (PMR) spectrum of a hydrate single crystal contains direct information about the orientation and the length of the intramolecular proton-proton distance in the water molecule. Since 1948 the PMR-spectra of about 50 different hydrates have been studied, and the original analysis developed by Pake has been further extended and refined.

In 1957 Ketudat and Pound reported the first deuteron magnetic resonance (DMR) study of a fully deuterated hydrate single crystal (Li\textsubscript{2}SO\textsubscript{4}.D\textsubscript{2}O).

*This work was supported by the Royal Norwegian Council for Scientific and Industrial Research.
They found that the principal directions of the electric field gradient at the deuteron sites are closely related to the orientation of the water molecule in the crystal. At temperatures where the water molecules were not flipping, Ketudat and Pound found that the largest component of the gradient was directed along the O—D bond “within the experimental error”. The interesting perspective this pioneering work opens up has only slowly been further explored.5,6 Recently an interesting relation between the hydrogen bond length and the quadruple coupling constant has been discovered.6,7

We will in this paper point out the advantages to be gained by studying simultaneously the proton and the deuteron magnetic resonance spectra in a partly deuterated single crystal. We will present an unified theoretical analysis of the line splittings observed in the PMR- and DMR-spectra. As an example the experimental room temperature spectra of potassium oxalate monohydrate (KOMH) with a proton/deuteron ratio of approximately 1:1 will be discussed. The PMR-spectra of KOMH has been analyzed in detail earlier,2 and, after the completion of this work, McGrath and Ossman 8 have reported on a deuteron magnetic resonance study of fully deuterated KOMH.

The rate determining step in a magnetic resonance study is usually the growth of a sufficiently large single crystal (volume from 0.1 to 1 cm³). Using a partially deuterated single crystal both the PMR- and the DMR-spectra can be studied by means of only one crystal. The main advantage, however, in using a partly deuterated crystal will be shown to be the reduction of the experimental uncertainty, by about a factor 5—10, in the relative orientation of the electric field gradient and the water molecule, and the increased accuracy enables us to a more detailed discussion of the significance of the obtained results. In addition the HDO molecules add some unique features to the spectra.

EXPERIMENTAL DETAILS

The single crystal used in this study was grown from a saturated solution of potassium oxalate in a 1:1 mixture of heavy and light water by slowly decreasing the temperature. The crystal was in the form of a thick plate bound by the [001], [111], and [111] faces. The crystal was optically aligned on the goniometer head with either the crystallographic a, b, or c* (= a × b) axes parallel to the axis of rotation. The goniometer head was then transferred to a holder in the magnetic field. From this way of orienting the crystal the axis of rotation will not deviate more than 0.1—0.2° from the chosen direction, but the absolute orientation of the crystal in the magnetic field will not be known to more than about 2°. But, as will be shown, the spectra contain information that can be used to check and improve these estimates.

A set of PMR-spectra was recorded using the Varian 60 MHz-probe (V-4331 LP) in a magnetic field of about 14 kG by varying the orientation of the crystal relative to the magnetic field in steps of 5° covering a 180° range. The axis of rotation was always normal to the magnetic field. The magnetic field was swept with a “Field-dial” (Varian), and the sweep was calibrated with a side-band technique.

The 60 MHz-probe was then exchanged with the Varian wide-line probe (V-4230 B 8—16 Mc) operating at 9.1 MHz, and a set of DMR-spectra was recorded at the same settings of the crystal. The crystal and the magnetic field were not altered while the probe was changed. Hence, the orientation of the crystal relative to the magnetic field is the same in both sets of spectra within the accuracy of the crystal holder which is estimated to 0.1°. This uncertainty can be reduced to zero by changing the frequency at each setting or by operating with two frequencies simultaneously. This, however, was not done in the experiments to be discussed here.

Acta Chem. Scand. 22 (1968) No. 2
DEUTERATED CRYSTALS I

EXPERIMENTAL RESULTS

Qualitative features

The crystal structure of KOMH is fairly accurately known from X-ray- and neutron-diffraction studies. The structure has monoclinic symmetry, all water molecules are crystallographic equivalent and are sitting on two-fold axes. The two hydrogen atoms in each water molecule are related by the two-fold axis, and the orientation of the molecule is therefore completely specified by the angle between the plane of the molecule and, say, the a-axis.

A partly deuterated KOMH crystal contains three different molecules: H$_2$O, HDO, and D$_2$O, and each molecular species will give rise to its own characteristic spectrum. If a fraction $x$ of the protons has been replaced by deuterons, then a fraction $x^2$ will be D$_2$O-molecules, a fraction $2(1-x)x$ HDO-molecules, and a fraction $(1-x)^2$ H$_2$O-molecules, assuming all species to be formed with the same probability.

The shape of the PMR-spectrum is determined by the magnetic dipole-dipole coupling within the spin system, and, hence the H$_2$O- and the HDO-molecules will give rise to different PMR-spectra as the proton and the deuteron have different magnetic moment, different spin and different mass. The number of lines in each spectrum will be equal to the multiplicity of the proton and the deuteron spin, respectively. Hence, the PMR-spectrum of H$_2$O consists of a doublet, and the PMR-spectrum of HDO of a triplet. A typical PMR-spectrum is shown in Fig. 1, where the crystal was oriented with the magnetic field approximately parallel to the intramolecular proton-proton vector, $R$. The outermost peaks in the spectrum are due to the H$_2$O-molecules, and the central triplet is due to the HDO-molecules. From the relative heights of the peaks in the spectrum, and the relative fractions of H$_2$O and HDO molecules given above, the fraction of deuterons in the KOMH crystal is

![Fig. 1. The PMR-spectrum of partly deuterated potassium oxalate monohydrate. The magnetic field is parallel to the intramolecular proton-proton line. The central line contains a signal from occluded water.](image)

Acta Chem. Scand. 22 (1968) No. 2
calculated to 0.60, which is slightly higher than the concentration of deuterons in the mother liquid, 0.50.

The line components in the spectrum shown in Fig. 1 are narrower and more symmetric than the line components in the spectrum of the undeuterated salt. The width of the lines in Fig. 1 is only about 1/3 of the width observed previously. This is a result of the deuterium substitution as both the D₂O-molecules and the HDO-molecules are less effective in broadening, and introducing asymmetry, of the line components. The signal/noise of the PMR-spectrum of the partly deuterated salt is therefore approximately the same as the signal/noise observed in the undeuterated salt, as the decrease in the line width compensates for the reduced proton concentration.

The fine structure commonly observed in the DMR-spectrum of hydrates is determined by the coupling between the electric quadrupole moment of the deuteron and the electric field at the deuteron site. The magnetic dipole-dipole coupling should only give rise to a hyperfine structure in the DMR-spectrum. Our DMR-spectra, however, did not show this hyper-fine structure; the spectra obtained with the magnetic field normal to the b-axis consisted of a simple doublet. The only effects noted from the dipole-dipole coupling are that the line components broaden, and the signal/noise is reduced in the regions where the dipole-dipole coupling reaches its maxima. We could therefore not detect separate signals from the HDO- and the D₂O-molecules in the DMR-spectrum, even though this should in principle be possible.

Quantitative results

If all the nuclei at resonance are magnetically equivalent, both the H₂O- and the D₂O-spectra split in only two line components. The line splitting as a function of crystal orientation observed both in the PMR and the DMR spectra can be written (vide infra):

\[ \Delta H = A + B \cos 2\varphi' + C \sin 2\varphi' = A + D \cos 2(\varphi' - \varphi_0') \]  

(1)

The angle \( \varphi' \) in eqn. (1) is the angle between the magnetic field and an arbitrarily chosen reference line.

The interpretation of the parameters \( A, B, C, \) and \( D, \) and \( \varphi_0' \), depends on the coupling giving rise to the fine structure. They will therefore be different for the PMR and the DMR splittings, and we will discuss each one separately.

The parameters in eqn. (1) have been derived from the experimental splittings given in Table 1 by least squares methods as described in appendix I. The results are given in Table 2.

\( H_2O \). The PMR-line splittings are usually written:

\[ \Delta H = 2\alpha[3 \cos^2 \delta \cos^2(\varphi - \varphi_0) - 1] \]  

(2)

\( \delta \) is the angle between \( R \) and the plane normal to the axis about which the crystal is rotated, and \( \varphi_0 \) is the angle between the projection of \( R \) in this plane and the reference line. If eqn. (2) should be identical to eqn. (3) then

\[ A = \alpha(3 \cos^2 \delta - 2) \]  and  \[ D = 3\alpha \cos^2 \delta \]  

(3)

Acta Chem. Scand. 22 (1968) No. 2
Table 1. Observed and calculated line splittings (all signs omitted).

<table>
<thead>
<tr>
<th>Angle</th>
<th>H2O</th>
<th>D2O</th>
<th>D3O</th>
<th>H2O</th>
<th>D2O</th>
<th>H2O</th>
<th>D2O</th>
<th>D3O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>obs</td>
<td>obs</td>
<td>obs</td>
<td>obs</td>
<td>obs</td>
<td>obs</td>
<td>obs</td>
<td>obs</td>
</tr>
<tr>
<td>0</td>
<td>5.64</td>
<td>5.85</td>
<td>51.6</td>
<td>50.2</td>
<td>51.6</td>
<td>53.4</td>
<td>5.58</td>
<td>5.48</td>
</tr>
<tr>
<td>5</td>
<td>6.09</td>
<td>5.97</td>
<td>5.4</td>
<td>10.6</td>
<td>2.60</td>
<td>2.77</td>
<td>0.54</td>
<td>0.54</td>
</tr>
<tr>
<td>10</td>
<td>5.84</td>
<td>5.85</td>
<td>36.2</td>
<td>39.1</td>
<td>36.2</td>
<td>32.6</td>
<td>0.14</td>
<td>0.01</td>
</tr>
<tr>
<td>15</td>
<td>5.47</td>
<td>5.48</td>
<td>74.2</td>
<td>82.0</td>
<td>74.2</td>
<td>75.1</td>
<td>2.25</td>
<td>2.34</td>
</tr>
<tr>
<td>20</td>
<td>4.86</td>
<td>4.87</td>
<td>117.1</td>
<td>121.9</td>
<td>117.7</td>
<td>115.5</td>
<td>4.60</td>
<td>4.58</td>
</tr>
<tr>
<td>25</td>
<td>4.00</td>
<td>3.54</td>
<td>155.0</td>
<td>167.1</td>
<td>157.5</td>
<td>152.6</td>
<td>6.70</td>
<td>6.53</td>
</tr>
<tr>
<td>30</td>
<td>3.11</td>
<td>3.05</td>
<td>187.0</td>
<td>188.2</td>
<td>187.0</td>
<td>185.2</td>
<td>8.12</td>
<td>8.12</td>
</tr>
<tr>
<td>35</td>
<td>1.84</td>
<td>1.88</td>
<td>211.7</td>
<td>212.6</td>
<td>211.7</td>
<td>202.4</td>
<td>9.26</td>
<td>9.31</td>
</tr>
<tr>
<td>40</td>
<td>0.39</td>
<td>0.59</td>
<td>230.0</td>
<td>230.0</td>
<td>233.3</td>
<td>10.00</td>
<td>10.05</td>
<td>2.08</td>
</tr>
<tr>
<td>45</td>
<td>0.88</td>
<td>0.79</td>
<td>248.5</td>
<td>240.1</td>
<td>248.5</td>
<td>247.3</td>
<td>10.28</td>
<td>10.35</td>
</tr>
<tr>
<td>50</td>
<td>2.16</td>
<td>2.21</td>
<td>259.0</td>
<td>242.3</td>
<td>256.0</td>
<td>254.0</td>
<td>10.05</td>
<td>10.13</td>
</tr>
<tr>
<td>55</td>
<td>3.56</td>
<td>3.63</td>
<td>258.0</td>
<td>258.5</td>
<td>257.0</td>
<td>253.2</td>
<td>9.42</td>
<td>9.47</td>
</tr>
<tr>
<td>60</td>
<td>5.03</td>
<td>5.01</td>
<td>223.0</td>
<td>245.0</td>
<td>244.8</td>
<td>8.12</td>
<td>8.30</td>
<td>1.71</td>
</tr>
<tr>
<td>65</td>
<td>6.33</td>
<td>5.79</td>
<td>201.0</td>
<td>203.2</td>
<td>227.0</td>
<td>229.2</td>
<td>6.71</td>
<td>6.84</td>
</tr>
<tr>
<td>70</td>
<td>7.47</td>
<td>7.48</td>
<td>181.0</td>
<td>176.1</td>
<td>206.0</td>
<td>206.9</td>
<td>4.92</td>
<td>4.95</td>
</tr>
<tr>
<td>75</td>
<td>8.41</td>
<td>8.48</td>
<td>143.0</td>
<td>143.3</td>
<td>177.0</td>
<td>178.4</td>
<td>2.67</td>
<td>2.76</td>
</tr>
<tr>
<td>80</td>
<td>9.23</td>
<td>9.30</td>
<td>101.0</td>
<td>105.6</td>
<td>137.0</td>
<td>144.7</td>
<td>0.32</td>
<td>0.32</td>
</tr>
<tr>
<td>85</td>
<td>9.80</td>
<td>9.91</td>
<td>64.6</td>
<td>64.3</td>
<td>106.0</td>
<td>106.8</td>
<td>2.13</td>
<td>2.29</td>
</tr>
<tr>
<td>90</td>
<td>10.21</td>
<td>10.28</td>
<td>21.0</td>
<td>20.6</td>
<td>64.5</td>
<td>65.9</td>
<td>4.75</td>
<td>4.99</td>
</tr>
<tr>
<td>95</td>
<td>10.54</td>
<td>10.40</td>
<td>22.1</td>
<td>22.1</td>
<td>23.1</td>
<td>7.18</td>
<td>7.70</td>
<td>1.76</td>
</tr>
<tr>
<td>100</td>
<td>10.34</td>
<td>10.32</td>
<td>66.3</td>
<td>68.8</td>
<td>15.4</td>
<td>20.2</td>
<td>10.40</td>
<td>10.33</td>
</tr>
<tr>
<td>105</td>
<td>9.98</td>
<td>9.91</td>
<td>153.1</td>
<td>116.1</td>
<td>62.0</td>
<td>62.7</td>
<td>12.80</td>
<td>12.81</td>
</tr>
<tr>
<td>110</td>
<td>9.40</td>
<td>9.30</td>
<td>149.0</td>
<td>151.6</td>
<td>103.8</td>
<td>103.1</td>
<td>14.95</td>
<td>15.03</td>
</tr>
<tr>
<td>115</td>
<td>8.41</td>
<td>7.97</td>
<td>189.0</td>
<td>187.3</td>
<td>142.5</td>
<td>140.1</td>
<td>17.19</td>
<td>17.00</td>
</tr>
<tr>
<td>120</td>
<td>7.56</td>
<td>7.48</td>
<td>216.0</td>
<td>217.0</td>
<td>172.7</td>
<td>187.5</td>
<td>18.59</td>
<td>18.59</td>
</tr>
<tr>
<td>125</td>
<td>6.24</td>
<td>6.31</td>
<td>242.0</td>
<td>242.4</td>
<td>197.0</td>
<td>199.8</td>
<td>19.90</td>
<td>19.77</td>
</tr>
<tr>
<td>130</td>
<td>4.90</td>
<td>5.02</td>
<td>262.0</td>
<td>259.7</td>
<td>217.0</td>
<td>220.8</td>
<td>20.60</td>
<td>20.52</td>
</tr>
<tr>
<td>135</td>
<td>3.64</td>
<td>3.64</td>
<td>275.5</td>
<td>279.6</td>
<td>232.0</td>
<td>234.8</td>
<td>20.85</td>
<td>20.79</td>
</tr>
<tr>
<td>140</td>
<td>2.24</td>
<td>2.21</td>
<td>279.0</td>
<td>272.0</td>
<td>235.0</td>
<td>241.5</td>
<td>20.70</td>
<td>20.60</td>
</tr>
<tr>
<td>145</td>
<td>0.88</td>
<td>0.80</td>
<td>274.5</td>
<td>266.5</td>
<td>237.0</td>
<td>240.7</td>
<td>19.95</td>
<td>19.94</td>
</tr>
<tr>
<td>150</td>
<td>0.29</td>
<td>0.58</td>
<td>259.5</td>
<td>253.3</td>
<td>225.0</td>
<td>223.4</td>
<td>18.85</td>
<td>18.83</td>
</tr>
<tr>
<td>155</td>
<td>1.76</td>
<td>1.36</td>
<td>244.0</td>
<td>232.8</td>
<td>209.5</td>
<td>216.8</td>
<td>17.20</td>
<td>17.31</td>
</tr>
<tr>
<td>160</td>
<td>3.11</td>
<td>3.05</td>
<td>183.5</td>
<td>205.8</td>
<td>194.4</td>
<td>155.7</td>
<td>16.42</td>
<td>3.22</td>
</tr>
<tr>
<td>165</td>
<td>4.37</td>
<td>4.05</td>
<td>152.5</td>
<td>172.9</td>
<td>184.0</td>
<td>165.9</td>
<td>13.18</td>
<td>13.22</td>
</tr>
<tr>
<td>170</td>
<td>5.10</td>
<td>4.87</td>
<td>122.5</td>
<td>135.3</td>
<td>148.0</td>
<td>132.3</td>
<td>10.45</td>
<td>10.78</td>
</tr>
<tr>
<td>175</td>
<td>5.68</td>
<td>5.47</td>
<td>108.5</td>
<td>94.0</td>
<td>84.0</td>
<td>94.4</td>
<td>8.11</td>
<td>8.17</td>
</tr>
</tbody>
</table>
Table 2. Experimental parameters (eqn. (1)) referred to arbitrary origo.

<table>
<thead>
<tr>
<th>Rotation axis</th>
<th>Spectrum of</th>
<th>A (G)</th>
<th>B (G)</th>
<th>C (G)</th>
<th>D (G)</th>
<th>φ' (°)</th>
<th>σ_H (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>H_2O</td>
<td>2.21</td>
<td>8.06</td>
<td>1.42</td>
<td>8.19</td>
<td>5.0</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>D_2O</td>
<td>14.8</td>
<td>35.4</td>
<td>-254.9</td>
<td>257.3</td>
<td>41.1</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>D_4O</td>
<td>6.2</td>
<td>-59.6</td>
<td>241.1</td>
<td>248.3</td>
<td>52.0</td>
<td>7.2</td>
</tr>
<tr>
<td>b</td>
<td>H_2O</td>
<td>5.23</td>
<td>0.23</td>
<td>-15.56</td>
<td>15.56</td>
<td>-44.6</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>HDO</td>
<td>1.09</td>
<td>0.01</td>
<td>-3.23</td>
<td>3.23</td>
<td>-44.9</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>D_2O</td>
<td>-11.2</td>
<td>7.02</td>
<td>-253.1</td>
<td>253.2</td>
<td>44.2</td>
<td>3.1</td>
</tr>
<tr>
<td>c*</td>
<td>H_2O</td>
<td>-3.14</td>
<td>0.48</td>
<td>-7.23</td>
<td>7.25</td>
<td>-43.1</td>
<td>0.11</td>
</tr>
<tr>
<td></td>
<td>D_2O</td>
<td>-3.6</td>
<td>233.6</td>
<td>40.7</td>
<td>235.0</td>
<td>5.0</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>D_4O</td>
<td>-7.1</td>
<td>-233.2</td>
<td>12.2</td>
<td>233.3</td>
<td>-91.5</td>
<td>4.1</td>
</tr>
</tbody>
</table>

On the other hand:

\[
2\alpha = D - A \quad \text{and} \quad \delta = \arccos \left( \frac{3(D-A)}{2D} \right) \tag{4}
\]

The value of \(\alpha\) for the H_2O-molecules in KOMH has been shown to be:²

\[
\alpha_{H-H} = 0.98 \left(1 - 3\langle \theta_z^2 \rangle \right) \frac{3\mu_H}{2R_e^3} \tag{5}
\]

\(\langle \theta_z^2 \rangle\) is the mean square amplitude of vibration of the H_2O-molecule about its symmetry axis, \(R_e\) is the equilibrium intramolecular proton-proton distance, and \(\mu_H\) is the magnetic dipole moment of a proton.

For eqn. (2) to be valid \(\Delta H\) should be measured between the centres of gravity of the two line components.¹¹ However, in the case to be discussed here the line components look symmetrical, and the analysis is therefore based on the max-max line splittings (i.e. the distance between the two points where the recorded spectrum cuts through the base line).

From the data in Table 2 and eqn. (3) we find the results given in Table 3.

The value of \(2\alpha\) obtained is equal to the value reported earlier, 10.41 (0.03) G, for the undeuterated salt.² The observed values of \(\delta\) tell us that the H—H vector is normal to the b-axis and makes an angle of 47.0° (c*) or 46.4°

Table 3. Experimental values of \(2\alpha\) and \(\delta\). (Standard deviations in brackets).

<table>
<thead>
<tr>
<th>Rotation axis</th>
<th>(2\alpha) (G)</th>
<th>(\delta) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>10.40(0.05)</td>
<td>43.6(0.2)</td>
</tr>
<tr>
<td>b</td>
<td>10.33(0.02)</td>
<td>0.0(0.1)</td>
</tr>
<tr>
<td>c*</td>
<td>10.39(0.03)</td>
<td>47.0(0.1)</td>
</tr>
</tbody>
</table>

*Acta Chem. Scand. 22 (1968) No. 2*
(a) with the a-axis. The difference between the two latter values is probably
significant, and tells us that the rotation axis might deviate by some tenths
of a degree from the chosen directions.

$HD\dot{O}$. The PMR line splitting observed in the triplet spectrum of the
HDO-molecules as measured between the two outermost peaks, is also given
by eqn. (2), and hence eqns. (3) and (4) are still valid. The expression for $\alpha$
however, must be changed. A simple extension of the theoretical model on
which eqn. (4) is based$^{13}$ should give the following expression for $\alpha$ for the
HDO-molecule:

$$\alpha_{H-D} = 0.98 \left(1 - \frac{3}{1.225} \langle \theta_z^2 \rangle \right) \frac{\mu_D}{R_e^3} \tag{6}$$

where $\mu_D$ is the magnetic moment of a deuteron. In the derivation of eqn. (6)
we have assumed that the exchange of a proton with a deuteron in a water
molecule only changes the rigid body vibration of the H$_2$O-molecule, and
has a negligible influence on the averaging process of $\alpha$ from the intramolec-
ular vibrations (giving rise to the factor 0.98).

Due to the small splitting only the b-axis data, where the splitting reaches
its maximum value, have been measured. Using eqn. (4) we find

$$2\alpha = 2.14 \pm 0.01 \, \text{G}$$

We can now calculate the splitting ratio $\alpha_{H-D}/\alpha_{H-H}$, using the value of
$$\langle \theta_z^2 \rangle = 0.0311 \, \text{rad}^2$$ estimated earlier from a calculation by McGrath and
Paine,$^{14}$ and compare the calculated value with the experimental ratio

$$\left(\frac{\alpha_{H-D}}{\alpha_{H-H}}\right)_{\text{calc}} = 0.2086 \quad \left(\frac{\alpha_{H-D}}{\alpha_{H-H}}\right)_{\text{exp}} = 0.2072 \pm 0.0007$$

The calculated and observed ratios are in good agreement, supporting the
estimated value of $\langle \theta_z^2 \rangle$. (If we ignore completely the different vibrating
motion of the two molecules, we calculate the ratio to 0.2047, i.e., a significantly
smaller value). The nuclear dipole field quenching of integer spins recently
discussed by Leppelmeier and Hahn$^{15}$ is too small to have a measurable
effect in this case.

$D_2O$. Eqn. (1) is commonly used as the basis in the analysis of DMR-
spectra,$^{16}$ and usually the line splittings are analyzed by means of the Volkoff$^{16}$
matrix-method by using data obtained by rotating the crystal about three
mutually perpendicular axes. However, as it will be shown in this study one of
the sources of uncertainty in the data is that the chosen axes are not necessarily
exactly orthogonal to each other. It would therefore be better to have analytical
expressions for the coefficients in eqn. (1) in terms of the angles specifying
the relative orientation of the principal axes of the electric field gradient and
the crystallographic axes a, b, and c$^*$. Due to some simplifying features of
the crystal structure of KOMH and a reasonable assumption, to be tested in
the subsequent analysis, theoretical expressions for the coefficients will now
be derived.

As stated in the introduction Ketudat and Pound$^3$ found that the largest
principal component of the electric field gradient (the z-component) was

Acta Chem. Scand. 22 (1968) No. 2
directed along the O—D bond. Chiba has concluded that the intermediate component (the x-component) seems to be orthogonal to the molecular plane and, hence, the smallest component (the y-component) is in the molecular plane and normal to the O—D bond. (Of symmetry reasons the latter two requirements are fulfilled by the isolated water molecule). If these rules are applied to KOMH the x-axis is expected to be orthogonal to the b-axis. We will therefore evaluate the parameters in eqn. (1) for rotation of the crystal about the a-, b-, and c*-axis. When the x-axis is normal to the b-axis two angles are sufficient to specify the orientation of the principal axes relative to the crystallographic axes: The angle between the yz-plane and the a-axis, \( \varphi_0 \), and the angle between the z-axis and b, \( \theta_0 \).

From general NMR theory it follows that the line splitting, as measured in magnetic field units to first order is given as:

\[
\Delta H = \frac{2\pi}{\gamma} \frac{3}{2h} eQ V_{HH}
\]  

(7)

where \( V_{HH} \) is the component of the electric field gradient in the direction of the external magnetic field \( H_0 \). We can write the electric field gradient as a dyadic:

\[
V = -\frac{1}{2} (1 + \eta) e_1 i + \frac{1}{2} (1 - \eta) e_2 j + e_3 k
\]  

(8)

when \( \eta \) is the asymmetry factor, and eq the z-component of the electric field gradient. We define a unit vector along \( H \): \( e_H \), then

\[
V_{HH} = e_H \cdot V \cdot e_H
\]  

(9)

We can now define unit vectors along a, b, and c* as \( e_a \), \( e_b \), and \( e_c \) respectively, and express these in terms of the unit vectors in the principal axis coordinate system \( i, j, k \):

\[
e_a = \sin \varphi_0 i + \cos \varphi_0 \cos \theta_0 j + \cos \varphi_0 \sin \theta_0 k
\]

\[
e_b = -\sin \theta_0 j + \cos \theta_0 k
\]

\[
e_c = -\cos \varphi_0 i + \sin \varphi_0 \cdot \cos \theta_0 j + \sin \theta_0 \sin \phi_0 \sin \theta_0 k
\]  

(10)

We can now calculate \( V_{HH} \) from eqn. (9) by expressing \( e_H \) in the principal axis coordinate system by means of eqn. (10). \( e_H \) will depend on which axis the crystal is rotated about, and we will give the expressions for each of the three axes separately:

\textit{a as rotation axis:}

Then \( e_H = \cos \varphi e_a + \sin \varphi e_c \)

If we use eqn. (10), insert in eqn. (9) using eqn. (8), we obtain after some rearrangement:

\[
A_a = -E(\sin \varphi_0) + F
\]

\[
B_a = E(\sin \varphi_0) + F
\]

\[
C_a = C(\sin \varphi_0)
\]  

(11)

*Acta Chem. Scand.* 22 (1968) No. 2
DEUTERATED CRYSTALS I

\[ C(\sin \varphi_0) = K(3 - \eta) \sin \varphi_0 \sin 2\theta_0 \]  
\[ E(\sin \varphi_0) = K[(3 - \eta) \sin^2 \varphi_0 \cos^2 \theta_0 + (1 + (1 + \eta) - (3 + \eta) \sin^2 \varphi_0) \cos 2\theta_0 + \eta + 1] \]  
\[ F = \frac{1}{2} K[(3 - \eta) \cos 2\theta_0 + \eta + 1] \]  
\[ K = \frac{2\pi}{\gamma} \frac{e^2 Q}{\hbar} \]

b as rotation axis:

Then \( e_\text{H} = \cos \varphi \ e_\alpha + \sin \varphi \ e_\epsilon \)

Inserting as above we obtain:

\[ A_b = -F \]
\[ D_b = 1/2 \ K[-(3 - \eta) \cos 2\theta_0 + 3\eta + 3] \]  

(16)

c* as rotation axis:

Then \( e_\text{H} = \cos \varphi \ e_\alpha + \sin \varphi \ e_\beta \)

Inserting as above we obtain:

\[ A_\epsilon = -E(\cos \varphi_0) + F \]
\[ B_\epsilon = E(\cos \varphi_0) + F \]
\[ C_\epsilon = C(\cos \varphi_0) \]

(17)

We will use eqns. (11), (16), and (17) as the basis for interpretation of the data. We will only point out first that in KOMH the two deuterons are not in general magnetically equivalent even though they are crystallographically equivalent. However, the electric field gradient at one deuteron in one particular water molecule is related to the gradient at the other deuteron by a two-fold axis. Hence, the components of the electric field gradient at each site are identical, but the orientations of the principal axes are different at the two sites. Due to the symmetry the orientation at one site is obtained from the other by exchanging \( \varphi_0 \) with \( \varphi_0 + \pi \), leaving \( \theta_0 \) unchanged. From eqns. (11), (16), and (17) it follows that only two line components are observed when we rotate the crystal about the b-axis, but rotating the crystal about any of the other two axes gives us four line components where the two line splittings are described by the same A and B, but the factor C changes sign. This conclusion can be shown to be independent of the particular orientation of the principal axes (here x-axis normal to the b-axis), but it will be only if the rotation axis is orthogonal to the b-axis. This fact will be used later to test whether or not the rotation axes used in this study really are parallel to the intended directions.

The same situation has also been analyzed by McGrath and Ossman and their eqns. (4) and (5) are equal to our eqns. (11) and (16). However, the underlying assumptions are not clearly stated in their paper.

Before we can use the developed equations we have to transform the experimental results from the angle of rotation measured from an arbitrary origo, \( \varphi_0' \), to the angle referred to the same axes as chosen as reference lines in the just derived equations, \( \varphi \). This can be done, based on the fact that the four line components observed when we rotate the crystal about the a or the

Acta Chem. Scand. 22 (1968) No. 2
$c^*$ axis must collapse to only two when the external magnetic field is parallel to the $b$-axis. Hence;

$$\Delta H_1(\varphi') = \Delta H_2(\varphi')$$

then

$$\varphi = \varphi' - \varphi_0 = 0$$

where $\varphi_0$ is the angle from the reference line to the $b$-axis. This property has been used to obtain the data given in Table 4.

This technique can not be used in finding any of the axes when the crystal is rotated about the $b$-axis. But from the line splittings measured by rotating the crystal about the other two axes, we know the values of the line splittings to be found when the magnetic field is parallel to either the $a$-axis (from the $c^*$-data) or the $c^*$-axis (from the $a$-data). These two fixed points have been used to transform the $b$-axis line splittings to the $a$-axis as reference axis. These parameters are also given in Table 4.

From the data in this table it is evident that the two line splittings observed, rotating the crystal about the $a$-axis and the $c^*$-axis, are not simply described by the same $A$, $B$, and $|C|$. It is nearly true for the $c^*$-axis parameters, but for the $a$-axis parameters the deviations are larger. This shows that the rotation axis in the latter case deviates significantly from the $a$-axis and from being orthogonal to the $b$-axis. This is understandable from the knowledge of the shape of the crystal used in this study. Due to the presence of the well developed [001] face on the crystal, it was much easier to orient the crystal for rotation about the $c^*$-axis than about the $a$-axis.

**Table 4.** Experimental parameters in eqn. (1) transformed to known origo. (Standard deviations in brackets).

<table>
<thead>
<tr>
<th>Rotation axis</th>
<th>Reference axis</th>
<th>Spectrum of</th>
<th>$A$ (G)</th>
<th>$B$ (G)</th>
<th>$C$ (G)</th>
<th>$D$ (G)</th>
<th>$\varphi_0$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$b$</td>
<td>$H_2O$</td>
<td>2.26</td>
<td></td>
<td>8.36</td>
<td>90.0</td>
<td>(0.04)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$D_2O$</td>
<td>14.8</td>
<td>9.0</td>
<td>257.1</td>
<td>257.3</td>
<td>(1.3)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1.8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$D_4O$</td>
<td>6.2</td>
<td>17.4</td>
<td>-244.7</td>
<td>248.3</td>
<td>(1.2)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(1.7)</td>
</tr>
<tr>
<td>$b$</td>
<td>$a$</td>
<td>$H_2O$</td>
<td>5.23</td>
<td></td>
<td></td>
<td>15.68</td>
<td>(0.03)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$HDO$</td>
<td>1.09</td>
<td></td>
<td></td>
<td>2.33</td>
<td>(0.01)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.01)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$D_2O$</td>
<td>-11.2</td>
<td></td>
<td></td>
<td>253.2</td>
<td>(0.5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.7)</td>
</tr>
<tr>
<td>$c^*$</td>
<td>$b$</td>
<td>$H_2O$</td>
<td>-3.20</td>
<td></td>
<td></td>
<td>7.39</td>
<td>(0.02)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$D_2O$</td>
<td>-3.6</td>
<td>24.6</td>
<td>-233.7</td>
<td>235.0</td>
<td>(0.7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.9)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$D_4O$</td>
<td>7.1</td>
<td>27.5</td>
<td>231.7</td>
<td>233.3</td>
<td>(0.7)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(0.9)</td>
</tr>
</tbody>
</table>

*Acta Chem. Scand.* 22 (1968) No. 2
Only a slight misorientation gives rise to deviations between the parameters of the magnitude observed. From the simple form of eqn. (16) it is easily found that the parameters $A$ and $D$ change with about 7 G per degree deviation between the rotation axis and the $b$-axis. If this estimate is typical the deviations observed in the $a$-axis case should indicate that the rotation axis and the $a$-axis make an angle of about $0.5^\circ$. Similarly, the $c^*$-axis should not deviate with more than $0.2^\circ$ from the rotation axis. The angle between the $b$-axis and the rotation axis is probably not larger than this, because here a deviation also shows up in a doubling of the number of components in the spectrum. In the subsequent analysis we will, therefore, rely mostly on the $b$-axis and the $c^*$-axis data.

Using the experimental values of the coefficients $C_a$, $C_b$, $A_a$ and $D_b$ and the developed equations, we calculate that

$$\theta_0 = 47.0^\circ \pm 0.2^\circ \quad \theta_0 = 53.9^\circ \pm 0.1^\circ \quad K = 122.8 \pm 1.0 \text{ G}$$

$$\frac{e^2qQ}{h} = 214 \pm 2 \text{ kHz} \quad \eta = 0.076 \pm 0.008$$

From these values we can calculate the values of the other coefficients and they are given in Table 5.

**Table 5. Observed and calculated coefficients (in G).**

<table>
<thead>
<tr>
<th>Rotation axis</th>
<th>$A$</th>
<th>$B$</th>
<th>$C$</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>obs</td>
<td>calc</td>
<td>obs</td>
<td>calc</td>
</tr>
<tr>
<td>$a$</td>
<td>15</td>
<td>14.3</td>
<td>9</td>
<td>7.7</td>
</tr>
<tr>
<td>$b$</td>
<td>-11</td>
<td>-11.2</td>
<td>17</td>
<td>7.7</td>
</tr>
<tr>
<td>$c^*$</td>
<td>-4</td>
<td>-3.3</td>
<td>25</td>
<td>25.3</td>
</tr>
</tbody>
</table>

From the data in Table 5 it can be seen that the calculated values of $A_a$ and $B_a$ are in excellent agreement with the observed values. The deviations are somewhat larger for $A_b$ and $B_b$, but these parameters are somewhat more uncertain, as pointed out above. The internal consistency of the calculated and observed parameters therefore strongly suggests that the $x$-axis is normal to the $b$-axis as assumed, at least within, say, $0.2^\circ$.

The parameters given above are average values averaged over the librational oscillations and the intramolecular vibrations of the water molecule. In appendix II it is shown how the librational oscillations affect the line splitting and how to derive the "equilibrium" values of the parameters (neglecting the effects of the intramolecular vibrations). We assume that the librational vibrations are harmonic. The motion will then not change the orientation of the principal axes, but only the magnitude of the coupling constant and the asymmetry parameter. Hence, the given values of $\phi_0$ and $\theta_0$ specify the equilibrium values of these parameters. Using the final equation in appen-

*Acta Chem. Scand. 22 (1968) No. 2*
dix II, together with the estimated mean-square amplitudes of vibration, we obtain:

\[
\left( \frac{e^2 q Q}{\hbar} \right)_0 = 224 \text{ kHz} \quad \eta_0 = 0.11
\]

It is not given any uncertainty limits on these values, as these depends on the uncertainty of the vibrational correction which is difficult to estimate. In particular the value of \(\eta\) seems to be sensitive to small changes in the mean-square amplitudes of vibrations.

**DISCUSSION**

From the analysis of the line splitting data given above it is evident that several independent values of some of the parameters specifying the orientation of the water molecule and the electric field gradient in KOMH have been deduced from the data. We will first discuss the internal consistency of these values and what they can tell us about the nature of the torsional oscillations of the water molecules in KOMH. We will then discuss the orientation of the electric field gradient relative to the orientation of the water molecule, and conclude with a discussion of the observed coupling constants.

It seems to be a general property of hydrates that the water molecules are executing a temperature activated flip motion about their two-fold axis.\(^3,6\) In KOMH the activation energy hindering this motion is calculated to be fairly high, 14 kcal/mole.\(^6\) As a consequence, the D\(_2\)O molecules are not flipping fast enough at room temperature to make the two deuterons magnetically equivalent, as have been observed in all other hydrates studied earlier.\(^3,5,6,17\)

The orientation of the water molecule in KOMH is determined by a single parameter; the angle between the equilibrium position of the molecular plane and the \(a\)-axis, \(\varphi_0\). \(\varphi_0\) is not necessarily equal for the H\(_2\)O, HDO, and the D\(_2\)O molecules, because the motions of these molecules in the lattice are not equal. Due to the different moments of inertia the amplitude of vibration will decrease from H\(_2\)O to HDO to D\(_2\)O if the environment is supposed not to change.\(^18\) Only if the water molecule is vibrating in a harmonic potential well will \(\varphi_0\) be the same for all three molecular species. Now, in this study we can only directly observe \(\varphi_0\) for the H\(_2\)O and the HDO molecules from the PMR-spectra. We have found the following values:

<table>
<thead>
<tr>
<th></th>
<th>(\varphi_0)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>46.4 (0.2)</td>
<td>(from (\delta) (a)-axis)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>47.0 (0.1)</td>
<td>(from (\delta) (c^*)-axis)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>46.9 (0.1)</td>
<td>(\varphi_0) (b)-axis)</td>
<td></td>
</tr>
<tr>
<td>HDO</td>
<td>46.6 (0.1)</td>
<td>(\varphi_0) (b)-axis)</td>
<td></td>
</tr>
</tbody>
</table>

The weighted mean value of \(\varphi_0\) for H\(_2\)O is 46.8° ± 0.1, which is not significantly different from the value of \(\varphi_0\) observed for the HDO-molecule: 46.6° ± 0.1. Hence, we can say that within the experimental uncertainty the H\(_2\)O and HDO
are vibrating about the same equilibrium position. Remembering that the
rms vibration amplitude of the H₂O molecule is about 10°, this information
tells us that the harmonic approximation seems to be a realistic description
of the torsional vibrations. The validity of this approximation receives
additional experimental support from the agreement between the observed
and the calculated ratio of the PMR line splittings of the HDO and the H₂O
molecules, as given above.

The positions of all the atoms, except hydrogen, have been determined
earlier by Pedersen from three-dimensional X-ray diffraction data. Fig. 2
shows the coordination around the water molecule as found in her study with
the water molecule oriented as found here. From this figure it is clear that the
water molecule is twisted out of the plane determined by the water oxygen
and the two hydrogen bond acceptor atoms. The angle between the hydrogen
bond acceptor plane and the a-axis is 41.7 ± 0.5°. Hence, the angle between
the molecular plane and the acceptor plane is 5.1° ± 0.5°. Chidambaram,
Sequeira, and Sikka in their neutron diffraction study of KOMH found an
angle of 4.5° ± 3.5°. McGrath and Paine calculated an angle of 1.5° as the
minimum in electrostatic potential energy using a point charge model. A simi-
lar theoretical model has been used by Baur on a number of hydrates, and
his results indicate that the calculated minimum in electrostatic energy of
a H atom in a water molecule deviates on the average 0.1 Å from the observed
position. To increase the accuracy of the calculation other contributions to
the potential energy have to be taken into account.

φ₀ for the DMR-data refers to the angle between the yz-plane of the principal
axes of the electric field gradient and the a-axis. For this parameter we have
found the following values:

47.3 (0.1) (φ₀ b-axis)
47.0 (0.2) (ratio C₄/C₃)

Acta Chem. Scand. 22 (1968) No. 2
Due to the additional uncertainty in the angles from the rotation axis deviating about 0.2° from the sought direction, we can not say that the yz-plane is significantly shifted away from the plane of the molecule.

McGrath and Ossman 8 find 43.9° ± 1.0° and 45.0° which probably are not significantly different from our result, but these fairly large deviations very likely reflect the uncertainty in determining the electric field gradient relative to the crystallographic axes from DMR-spectra only.

In an isolated water molecule the molecular plane defines the yz-plane for symmetry reasons. When the molecule is bound in a solid it is reasonable to look at the field gradient at each deuteron site as consisting of two terms: a modified intramolecular term and a crystal term. The intramolecular gradient will be modified because the molecule is likely to be polarized, and the shape of the molecule can be altered due to intercrystalline forces. It is therefore somewhat surprising, on the basis of the asymmetric coordination shown in Fig. 2, that the yz-plane is so close to the plane of the molecule in KOMH. But further discussion of this point must wait until a quantitative calculation of the field gradient at the deuteron site in a trapped molecule has been made. At the moment it seems to be fairly difficult to get reliable results even on the isolated molecule.7,21 McGrath and Ossman 8 have given a rough estimate of the crystal term from a point charge model taking into account the closest neighbours. They find that the crystal term leads to a decrease in the coupling constant and the asymmetry factor by about 10%.

The observed angle between the z-axis and the b-axis, 53.9° ± 0.1°, is close to the O—D bond direction. In the isolated D₂O molecule the O—D distance has been found to be 0.9572 Å.22 In a solid this distance can be stretched under the influence of hydrogen bond formation.23 In the earlier PMR-study of KOMH we found R = 1.534 ± 0.003 Å. The maximum value of the angle between the O—D bond and the b-axis will therefore be 53.2° ± 0.2°. In the isolated water molecule (HDO) Posener 24 found that the z-axis was parallel to the O—D bond within the experimental uncertainty (1.2°). Due to this uncertainty it is not possible to say whether 1) the direction of the z-axis has changed when the molecule is bound in KOMH or 2) if the direction of the z-axis deviates significantly from the O—D bond. At present, therefore, even though the z-axis can be located relative to the orientation of the H₂O-molecule with an estimated standard deviation of about 0.5°, it is not possible to locate the direction if the O—D bond with more than an accuracy of 1 to 2°. Both our knowledge of the electric field gradient in the isolated molecule and the effect of the environments on this gradient have to be improved before the direction of the O—D bond can be determined more accurately from DMR-spectra.

The observed values of the coupling constant, 214 kHz, and the asymmetry factor, 0.076, are reasonable values compared to earlier determinations in other hydrates 8 and the values found by McGrath and Ossman 8 209.7 ± 2.5 kHz and 0.090 ± 0.020.

The torsional oscillations have been shown to increase the coupling constant from 214 to 224 kHz. In Ba(ClO₃)₂·H₂O the correction raised the value of the coupling constant from 244 kHz (at −130°C) to 270 kHz. These values, however, are not true equilibrium values as no correction for the intramolecular
vibrations has been made. For the isolated water molecule the coupling constant has been found to be about 315 kHz.\textsuperscript{34,35} The relative importance of 1) the intramolecular vibration correction, 2) the stretching of the $O-D$ bond,$^7$ and 3) the redistribution of the lone-pair electrons$^8$ in reducing the coupling constant from the value observed in the isolated molecule to the value for the molecule when bound in a hydrate still seems to be an open question, and further theoretical work is needed to clarify the situation.

Acknowledgement. I would like to thank Mrs. M. Jerve for extensive technical assistance, and Professor I. Rosenquist for placing an optical goniometer at my disposal.

APPENDIX I. EXPERIMENTAL PARAMETERS DERIVED BY LEAST SQUARES METHODS

The experimental line splittings are given in Table 1. The experimental line splittings have been fitted to eqn. (1) by means of a least squares procedure. We have measured $\Delta H$ in steps of $5^\circ$ from 0 to 175$^\circ$. In regions where the fine structure collapses the line splittings have been obtained by interpolation. When such a complete set of line splittings is available, it is fairly easy to show that the least squares formulas for the coefficients get relatively simple, and we will therefore give them here:

$$A = \frac{1}{n} \sum \Delta H_i$$
$$B = \frac{\sum \Delta H_i \cos 2\phi_i}{\sum \cos^2 2\phi_i}$$
$$C = \frac{\sum \Delta H_i \sin 2\phi_i}{\sum \sin^2 2\phi_i}$$

Here $n$ is the number of line splittings, and $\Delta H_i$ the line splitting measured at $\phi_i = i\delta$ where $\delta$ is the step. Hence, here where $\delta = 5^\circ$, $n = 36$ and

$$A = \frac{1}{36} \sum \Delta H_i$$
$$B = \frac{1}{18} \sum \Delta H_i \cos 2\phi_i$$
$$C = \frac{1}{18} \sum \Delta H_i \sin 2\phi_i$$

The standard deviations in these coefficients are also easily calculated:

$$\sigma_A = \frac{1}{n^{\frac{1}{2}}} \sigma_H = 0.167 \sigma_H$$
$$\sigma_B = \frac{1}{(\sum \cos^2 2\phi_i)^{\frac{1}{2}}} \sigma_H = 0.236 \sigma_H$$
$$\sigma_C = \sigma_B$$
$$\sigma_R = \left[ \frac{\sum (\Delta H(\phi_i) - \Delta H_i)^2}{n-3} \right]^{\frac{1}{2}} = 0.374 \left[ \sum (\Delta H(\phi_i) - \Delta H_i)^2 \right]^{\frac{1}{2}}$$

_Acta Chem. Scand._ 22 (1968) No. 2
These formulas have been used in the calculation of the coefficients and the standard deviations given in Table 2. A detailed comparison between observed and calculated line splittings have been made in Table 1.

APPENDIX II. EQUILIBRIUM VALUES OF THE ELECTRIC FIELD GRADIENT

We will in this appendix average the electric field gradient over the torsional oscillations of the water molecule. A similar calculation has been done earlier by Chiba.5

The water molecule is assumed to perform three independent, torsional oscillations of small amplitude: the twisting oscillation about the two-fold axis, the rocking oscillation about an axis normal to the molecular plane, and the waving oscillation about an axis orthogonal to the other two. The mean square amplitudes will be denoted: \( \langle \theta_t^2 \rangle \), \( \langle \theta_r^2 \rangle \), and \( \langle \theta_w^2 \rangle \), respectively. We will assume that these oscillations are harmonic. This motion will then not displace the directions of the principal axes of the electric field gradient. The motion will therefore only affect the coupling constant and the asymmetry factor. To determine these two unknowns, we will look at the effect of the motion on the line splitting observed when rotating the crystal about the \( b \)-axis.

We must start by evaluating the line-splitting when the \( x \)-axis is making an angle of \( \delta \) with the \( b \)-axis. The angles \( \varphi_0 \), \( \theta_0 \), and \( \delta \) can then be regarded as the three Euler-angles specifying the orientation of \( xyz \) relative to \( ab c^* \). Using standard formulas we find:

\[
\Delta H_b = 2K_0 \left[ -(1-\eta_0)(\cos(\varphi-\varphi_0) \cos \theta_0 + \cos \delta \sin \delta \cdot \sin(\varphi-\varphi_0))^2 
- (1 + \eta) \sin^2 \delta \sin^2(\varphi-\varphi_0) 
+ 2[\cos(\varphi-\varphi_0) \times \sin \theta - \cos \delta \cos \theta_0 \times \sin(\varphi-\varphi_0)]^2 \right]
\]

Because we have assumed the vibrations to be independent, we can average \( \Delta H \) over the three vibrations separately. Furthermore, if we turn the molecule an angle \( \alpha \) away from the equilibrium position then in the three possible cases:

- **twist**
  \( \varphi_0 = \varphi_0 + \alpha \quad \theta = \theta_0 \quad \delta = \frac{\pi}{2} \)

- **rock**
  \( \varphi_0 = \varphi_0 \quad \theta = \theta_0 + \alpha \quad \delta = \frac{\pi}{2} \)

- **wave**
  \( \varphi_0 = \varphi_0 \quad \theta = \theta_0 \quad \delta = \frac{\pi}{2} + \alpha \)

It is then straightforward to get the final answer assuming the oscillations to be of small amplitude and keeping terms up to \( \alpha^2 \):

\[
\Delta \tilde{H}_b = \tilde{A}_b + \tilde{D}_b \cos 2(\varphi-\varphi_0)
\]

where

\[
\tilde{A}_b = K_0(3-\eta_0)(1-2\langle \theta_r^2 \rangle - \langle \theta_w^2 \rangle \sin^2 \theta_0 + (3-\eta_0)\langle \theta_r^2 \rangle 
+ (3+\eta_0)\langle \theta_w^2 \rangle - 2)
\]

\[
\tilde{D}_b = K_0(3-\eta_0)(1-2\langle \theta_r^2 \rangle - 2\langle \theta_r^2 \rangle + \langle \theta_w^2 \rangle \sin^2 \theta_0 + (3-\eta_0)\langle \theta_r^2 \rangle 
- (3+\eta_0)\langle \theta_w^2 \rangle + 2 \eta_0 (1-2\langle \theta_r^2 \rangle ))
\]

*Acta Chem. Scand.* 22 (1968) No. 2
The mean-square amplitudes of vibration are not known for KOMH. Earlier we have concluded from the PMR-spectra that \( \langle \theta^2 \rangle = \langle \theta^2 \rangle \), and we have calculated \( \langle \theta^2 \rangle \) from the shape of the potential well as calculated by McGrath and Paine.\(^\text{14}\) However, Prask and Boutin\(^\text{27}\) have recently studied the inelastic scattering of cold neutrons from both deuterated and undeuterated KOMH. They interpreted the spectrum of the deuterated salt in terms of the following wave numbers:

\[
\nu_t = 450 \text{ cm}^{-1}, \quad \nu_r = 370 \text{ cm}^{-1}, \quad \text{and} \quad \nu_w = 505 \text{ cm}^{-1}
\]

From the knowledge of the different moments of inertia of the \( \text{D}_4\text{O} \)-molecule \( (I_t = 3.85, I_r = 5.77, I_w = 1.82 \text{ in units } 10^{-40} \text{ g cm}^2)\),\(^\text{22}\) we can calculate the mean square amplitudes from the following expression, valid for a harmonic oscillator

\[
\langle \theta^2 \rangle = \frac{\hbar}{4\pi^2 I_x^2} \left[ \frac{1}{2} + \left( \frac{\nu^2}{(kT)(kT)} \right) \right]
\]

We obtain

\[
\langle \theta_t^2 \rangle = 0.020 \text{ rad}^2 \quad \langle \theta_r^2 \rangle = 0.018 \text{ rad}^2 \quad \langle \theta_w^2 \rangle = 0.036 \text{ rad}^2
\]

REFERENCES

18. Pedersen, B. F. (unpublished) has found that the lattice parameters of KOMH change by less than 0.1 % on complete deuteration.

Received August 15, 1967.

Acta Chem. Scand. 22 (1968) No. 2