

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

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A comparative study of the room temperature D(euteron)MR- and P(roton)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 H₂O, HDO, and the D₂O molecules the following information is obtained: (1) The H₂O 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 $5.1^\circ \pm 0.5^\circ$ out of the plane determined by the hydrogen bond acceptors. (4) The largest principal component of the electric field gradient makes an angle of $53.9^\circ \pm 0.1^\circ$ with the two-fold axis of the D₂O 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 CaSO₄·2H₂O by Pake in 1948.¹ 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.²

In 1957 Ketudat and Pound³ reported the first deuteron magnetic resonance (DMR) study of a fully deuterated hydrate single crystal (Li₂SO₄·D₂O).

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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 up⁴ 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 Ossman⁸ 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 $[\bar{1}\bar{1}\bar{1}]$ faces. The crystal was optically aligned on the goniometer head with either the crystallographic a , b , or c^* ($= a \times b$) 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.

EXPERIMENTAL RESULTS

Qualitative features

The crystal structure of KOMH is fairly accurately known from X-ray⁹ and neutron¹⁰ 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: H₂O, HDO, and D₂O, 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 D₂O-molecules, a fraction 2(1-*x*)*x* HDO-molecules, and a fraction (1-*x*)² H₂O-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 H₂O- 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 H₂O 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 H₂O-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 H₂O and HDO molecules given above, the fraction of deuterons in the KOMH crystal is

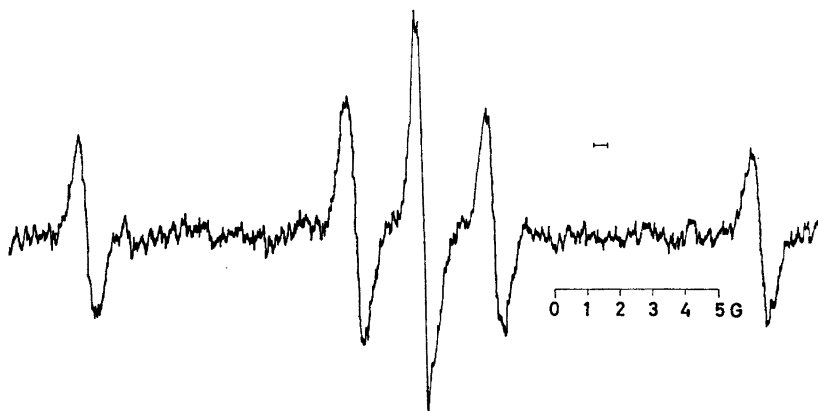


Fig. 1. The PMR-spectrum of partly deuterated potassium oxalate monohydrate. The magnetic field is parallel to the intramolecular proton-proton line. The central line contains a signal from occluded water.

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.² 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.¹¹ 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.⁴ 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*):

$$\Delta H = A + B \cos 2\varphi' + C \sin 2\varphi' = A + D \times \cos 2(\varphi' - \varphi_0') \quad (1)$$

The angle φ' 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 φ_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.

H₂O. The PMR-line splittings are usually written:¹²

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

δ is the angle between R and the plane normal to the axis about which the crystal is rotated, and φ_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

$$A = \alpha(3 \cos^2\delta - 2) \text{ and } D = 3\alpha \cos^2\delta \quad (3)$$

Table 1. Observed and calculated line splittings (all signs omitted).

Angle	^a D ₂ O			^b HDO			D ₂ O			H ₂ O			^{c*} D ₂ O			D ₂ O		
	obs		calc	obs		calc	obs		calc	obs		calc	obs		calc	obs		calc
	obs	calc		obs	calc		obs	calc		obs	calc		obs	calc		obs	calc	
0	5.64	5.85	51.6	50.2	51.6	53.4	5.58	5.48	1.10	1.10	0	4.2	2.57	2.66	236	230.0	236	240.2
5	6.09	5.97	0	5.4	0	10.6	2.60	2.77	0.54	0.54	49	48.3	3.96	3.91	233	233.5	233	234.6
10	5.84	5.85	36.2	39.1	36.2	32.6		0.14	0.01	0.01	92	91.2	5.31	5.15	226	229.8	226	222.0
15	5.47	5.48	74.2	82.0	74.2	75.1	2.25	2.34	0.52	0.52	130	131.7	6.23	6.33	220	219.1	205	202.9
20	4.86	4.87	117.7	121.9	117.7	115.5	4.60	4.58	0.98	0.98	171	168.5	7.25	7.41	202	201.5	178	177.8
25	4.00	3.54	155.0	157.7	155.0	152.6	6.70	6.53	1.38	1.38	204	200.6	8.23	8.36	177	177.7	144	147.6
30	3.11	3.05	187.0	188.2	187.0	185.2	8.12	8.12	1.71	1.71	230	226.9	9.07	9.15	150	148.5	113	113.0
35	1.84	1.88	211.7	212.6	211.7	202.4	9.26	9.31	1.96	1.94	248	246.7	9.80	9.76	118	114.6	77	75.3
40	0.39	0.59	230.0	230.0	230.0	233.3	10.00	10.05	2.08	2.09	259	259.3	10.14	10.16	76	77.1	31	35.5
45	0.88	0.79	248.5	240.1	248.5	247.3	10.28	10.35	2.21	2.14	261	264.3	10.41	10.37	40	37.1	3	5.2
50	2.16	2.21	239.0	242.3	256.0	254.0	10.05	10.13	2.12	2.09	258	261.7	10.37	10.34	0	4.1	44	45.5
55	3.56	3.63	238.0	236.8	257.0	253.2	9.42	9.47	1.95	1.94	249	251.1	10.21	10.09	43	45.2	84	84.2
60	5.03	5.01	223.0	223.6	245.0	244.8	8.12	8.36	1.71	1.71	231	233.9	9.51	9.64	89	85.1	122	120.1
65	6.33	5.79	201.0	203.2	227.0	229.2	6.71	6.84	1.38	1.38	209	209.6	8.96	8.99	129	122.6	154	152.2
70	7.47	7.48	181.0	176.1	206.0	206.9	4.92	4.95	0.98	0.98	181	179.3	8.13	8.15	156	156.3	175	179.4
75	8.41	8.48	143.0	143.3	177.0	178.4	2.67	2.76	0.52	0.52	144	143.9	7.15	7.17	195	185.5	195	201.0
80	9.23	9.30	101.0	105.6	137.0	144.7	0.32	0.32	0.01	0.01	102	104.4	6.15	6.05	214	209.1	214	216.2
85	9.80	9.91	64.6	64.3	106.0	106.8	2.13	2.29	0.54	0.54	66	69.1	4.82	4.87	224	226.5	224	224.7
90	10.21	10.28	21.0	20.6	64.5	65.9	4.75	4.99	1.10	1.10	23	18.2	3.71	3.61	230	237.1	230	226.1
95	10.34	10.40	22.1	24.2	22.1	23.1	7.16	7.70	1.76	1.76	25	25.8	2.28	2.36	236	240.6	225	220.4
100	10.34	10.28	66.3	68.8	18.4	20.2	10.40	10.33	2.25	2.21	69	68.8	1.27	1.12	236	237.0	211	207.9
105	9.98	9.91	108.3	111.6	62.0	62.7	12.80	12.81	2.67	2.72	108	109.3	0.10	0.06	225	226.2	191	188.8
110	9.40	9.30	149.0	151.6	103.8	103.1	14.95	15.05	3.13	3.18	146	146.1	1.08	1.14	208	208.6	164	165.4
115	8.41	7.97	189.0	187.3	142.5	140.1	17.19	17.00	3.60	3.58	179	178.2	2.13	2.08	184	184.9	131	133.5
120	7.56	7.48	216.0	217.9	170.0	172.7	18.75	18.59	3.85	3.91	206	204.5	2.98	2.88	158	155.6	100	98.9
125	6.24	6.21	242.0	242.2	197.0	199.9	19.90	19.77	4.08	4.14	224	224.2	3.58	3.49	125	121.7	65	61.2
130	4.90	5.02	262.0	259.7	217.0	220.8	20.60	20.52	4.23	4.29	238	236.8	4.00	3.89	86	84.2	22	21.4
135	3.64	3.64	275.5	269.7	232.0	234.8	20.85	20.79	4.34	4.34	244	241.9	4.17	4.09	36	44.2	36	19.3
140	2.24	2.21	279.0	272.0	235.0	241.5	20.70	20.60	4.29	4.29	239	239.3	4.13	4.07	0	3.1	53	59.6
145	0.98	0.80	274.5	266.5	237.0	240.7	19.95	19.94	4.10	4.14	230	229.0	3.96	3.82	33	38.1	97	98.3
150	0.29	0.58	259.5	253.3	225.0	232.4	18.85	18.83	3.85	3.91	209	211.5	3.48	3.37	79	78.0	135	134.2
155	1.76	1.36	244.0	232.8	209.5	216.8	17.20	17.31	3.52	3.58	188	187.2	2.62	2.71	113	115.4	167	166.3
160	3.11	3.05	183.5	205.8	217.0	194.4	15.68	15.42	3.27	3.18	160	156.9	1.75	1.88	145	149.2	195	193.5
165	4.37	4.05	152.5	172.9	184.0	165.9	13.18	13.22	2.70	2.72	122	121.4	0.83	0.90	177	178.4	215	215.1
170	5.10	4.87	122.5	135.3	148.0	132.3	10.45	10.78	2.23	2.21	78	82.0	0.39	0.22	200	202.0	230	230.3
175	5.68	5.47	108.5	94.0	84.0	94.4	8.11	8.17	1.75	1.76	38	39.7	0.16	1.40	221	219.4	237	238.8

Table 2. Experimental parameters (eqn. (1)) referred to arbitrary origo.

Rotation axis	Spectrum of	A (G)	B (G)	C (G)	D (G)	ϕ' (°)	σ_{H} (G)
a	H ₂ O	- 2.21	8.06	1.42	8.19	- 5.0	0.21
	D ₂ O	14.8	35.4	- 254.9	257.3	41.1	7.6
	D ₂ O	6.2	- 59.6	241.1	248.3	52.0	7.2
b	H ₂ O	5.23	0.23	- 15.56	15.56	- 44.6	0.17
	HDO	1.09	0.01	- 3.23	3.23	- 44.9	0.05
	D ₂ O	- 11.2	7.02	- 253.1	253.2	44.2	3.1
c*	H ₂ O	- 3.14	0.48	- 7.23	7.25	- 43.1	0.11
	D ₂ O	- 3.6	233.6	40.7	235.0	5.0	4.0
	D ₂ O	- 7.1	- 233.2	12.2	233.3	- 91.5	4.1

On the other hand:

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

The value of α for the H₂O-molecules in KOMH has been shown to be:²

$$\alpha_{\text{H-H}} = 0.98 (1 - 3\langle\theta_z^2\rangle) \frac{3\mu_{\text{H}}}{2R_e^3} \quad (5)$$

$\langle\theta_z^2\rangle$ is the mean square amplitude of vibration of the H₂O-molecule about its symmetry axis, R_e is the equilibrium intramolecular proton-proton distance, and μ_{H} is the magnetic dipole moment of a proton.

For eqn. (2) to be valid ΔH 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 2α obtained is equal to the value reported earlier, 10.41 (0.03) G, for the undeuterated salt.² The observed values of δ 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 2α and δ . (Standard deviations in brackets).

Rotation axis	2α (G)	δ (°)
a	10.40(0.05)	43.6(0.2)
b	10.33(0.02)	0.0(0.1)
c*	10.39(0.03)	47.0(0.1)

(α) 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.

HDO. 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 α , however, must be changed. A simple extension of the theoretical model on which eqn. (4) is based¹³ should give the following expression for α for the HDO-molecule:

$$\alpha_{\text{H-D}} = 0.98 \left(1 - \frac{3}{1.225} \langle \theta_z^2 \rangle \right) \frac{\mu_{\text{D}}}{R_c^3} \quad (6)$$

where μ_{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_2O -molecule, and has a negligible influence on the averaging process of α from the intramolecular 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 $\alpha_{\text{H-D}}/\alpha_{\text{H-H}}$, 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

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

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 Hahn¹⁵ is too small to have a measurable effect in this case.

D₂O. 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 Volkoff¹⁶ 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 Pound³ found that the largest principal component of the electric field gradient (the z -component) was

directed along the O—D bond. Chiba⁶ 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, φ_0 , and the angle between the z -axis and b , θ_0 .

From general NMR theory it follows that the line splitting, as measured in magnetic field units to first order is given as:⁴

$$\Delta H = \frac{2\pi}{\gamma} \frac{3}{2h} \frac{eQ}{2h} V_{H,H} \quad (7)$$

where $V_{H,H}$ 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:

$$\mathbf{V} = -\frac{1}{2} (1 + \eta) \text{eq } i i - \frac{1}{2} (1 - \eta) \text{eq } j j + \text{eq } k k \quad (8)$$

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

$$V_{H,H} = e_H \cdot \mathbf{V} \cdot e_H \quad (9)$$

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 :

$$\begin{aligned} e_a &= \sin \varphi_0 i + \cos \varphi_0 \cos \theta_0 j + \cos \varphi_0 \sin \theta_0 k \\ e_b &= -\sin \theta_0 j + \cos \theta_0 k \\ e_c &= -\cos \varphi_0 i + \sin \varphi_0 \cos \theta_0 j + \sin \varphi_0 \sin \theta_0 k \end{aligned} \quad (10)$$

We can now calculate $V_{H,H}$ 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:

a as rotation axis:

$$\text{Then } e_H = \cos \varphi e_b + \sin \varphi e_c$$

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

$$\begin{aligned} A_a &= -E(\sin \varphi_0) + F \\ B_a &= E(\sin \varphi_0) + F \\ C_a &= C(\sin \varphi_0) \end{aligned} \quad (11)$$

$$C(\sin \varphi_0) = K(3-\eta) \sin \varphi_0 \sin 2\theta_0 \quad (12)$$

$$E(\sin \varphi_0) = K[(3-\eta) \sin^2 \varphi_0 \cos^2 \theta_0 + (1 + (1 + \eta) - (3 + \eta) \sin^2 \varphi_0)] \quad (13)$$

$$F = \frac{1}{2}K[(3-\eta) \cos 2\theta_0 + \eta + 1] \quad (14)$$

$$K = \frac{2\pi}{\gamma} \frac{3}{8} \frac{e^2 q Q}{h} \quad (15)$$

b as rotation axis:

$$\text{Then } e_H = \cos \varphi e_a + \sin \varphi e_c$$

Inserting as above we obtain:

$$\begin{aligned} A_b &= -F \\ D_b &= 1/2 K[-(3-\eta) \cos 2\theta_0 + 3\eta + 3] \end{aligned} \quad (16)$$

*c** as rotation axis:

$$\text{Then } e_H = \cos \varphi e_a + \sin \varphi e_b$$

Inserting as above we obtain:

$$\begin{aligned} A_c &= -E(\cos \varphi_0) + F \\ B_c &= E(\cos \varphi_0) + F \\ C_c &= C(\cos \varphi_0) \end{aligned} \quad (17)$$

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 φ_0 with $\varphi_0 + \pi$, leaving θ_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 true only if the rotation axis is orthogonal to the *b*-axis.¹⁶ 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 Ossman⁸ 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, φ_0' , to the angle referred to the same axes as chosen as reference lines in the just derived equations, φ . This can be done, based on the fact that the four line components observed when we rotate the crystal about the *a* or the

c^* axis must collapse to only two when the external magnetic field is parallel to the b -axis. Hence;

$$\begin{aligned} \text{when} \quad & \Delta H_1(\varphi') = \Delta H_2(\varphi') \\ \text{then} \quad & \varphi = \varphi' - \varphi_0 = 0 \end{aligned}$$

where φ_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).

Rotation axis	Reference axis	Spectrum of	A (G)	B (G)	C (G)	D (G)	φ_0 (°)
a	b	H ₂ O	- 2.26 (0.04)			8.36 (0.05)	90.0 (0.2)
		D ₂ O	14.8 (1.3)	9.0 (1.8)	257.1 (1.8)	257.3 (1.8)	44.0 (0.2)
		D ₂ O	6.2 (1.2)	17.4 (1.7)	-244.7 (1.7)	248.3 (1.7)	-43.0 (0.2)
b	a	H ₂ O	5.23 (0.03)			15.68 (0.04)	46.9 (0.1)
		HDO	1.09 (0.01)			3.23 (0.01)	46.6 (0.1)
		D ₂ O	-11.2 (0.5)			253.2 (0.7)	47.3 (0.1)
c^*	b	H ₂ O	- 3.20 (0.02)			7.39 (0.03)	90.1 (0.1)
		D ₂ O	- 3.6 (0.7)	24.6 (0.9)	-233.7 (0.9)	235.0 (0.9)	-42.0 (0.1)
		D ₂ O	- 7.1 (0.7)	27.5 (0.9)	231.7 (0.9)	233.3 (0.9)	41.6 (0.1)

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° . Similarly, the c^* -axis should not deviate with more than 0.2° 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_b and D_b and the developed equations, we calculate that

$$\varphi_0 = 47.0^\circ \pm 0.2^\circ \quad \theta_0 = 53.9^\circ \pm 0.1^\circ \quad K = 122.8 \pm 1.0 \text{ G}$$

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

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).

Rotation axis	A		B		C		D	
	obs	calc	obs	calc	obs	calc	obs	calc
a	15 6	14.3	9 17	7.7	257 -245	250.9		
b	-11	-11.2					253	253.4
c^*	-4 -7	-3.3	25 28	25.3	-234 232	234.0		

From the data in Table 5 it can be seen that the calculated values of A_c and B_c are in excellent agreement with the observed values. The deviations are somewhat larger for A_a and B_a , 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° .

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 φ_0 and θ_0 specify the equilibrium values of these parameters. Using the final equation in appen-

dix II, together with the estimated mean-square amplitudes of vibration, we obtain:

$$\left(\frac{e^2qQ}{h}\right)_0 = 224 \text{ kHz } \eta_0 = 0.11$$

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 η 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.^{3,5} In KOMH the activation energy hindering this motion is calculated to be fairly high, 14 kcal/mole.¹⁴ As a consequence, the D₂O 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, φ_0 . φ_0 is not necessarily equal for the H₂O, HDO, and the D₂O 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 H₂O to HDO to D₂O if the environment is supposed not to change.¹⁸ Only if the water molecule is vibrating in a harmonic potential well will φ_0 be the same for all three molecular species. Now, in this study we can only directly observe φ_0 for the H₂O and the HDO molecules from the PMR-spectra. We have found the following values:

φ_0		
H ₂ O	46.4 (0.2)	(from δ <i>a</i> -axis)
	47.0 (0.1)	(from δ <i>c</i> *-axis)
	46.9 (0.1)	(φ_0 <i>b</i> -axis)
HDO	46.6 (0.1)	(φ_0 <i>b</i> -axis)

The weighted mean value of φ_0 for H₂O is $46.8^\circ \pm 0.1$, which is not significantly different from the value of φ_0 observed for the HDO-molecule: $46.6^\circ \pm 0.1$. Hence, we can say that within the experimental uncertainty the H₂O and HDO

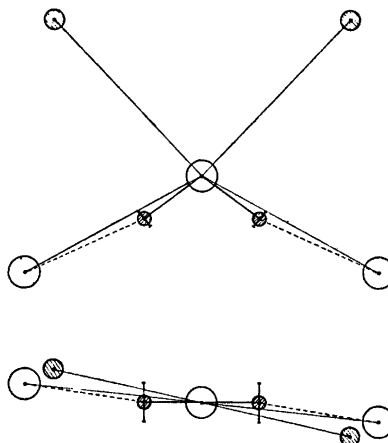


Fig. 2. The coordination about the water molecule in potassium oxalate monohydrate as seen normal to the plane of the water molecule (above) and along the *b*-axis (below).

are vibrating about the same equilibrium position. Remembering that the rms vibration amplitude of the H_2O molecule is about 10° , this information tells us that the harmonic approximation seems to be a realistic description of the torsional vibrations.¹⁴ 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 H_2O molecules, as given above.

The positions of all the atoms, except hydrogen, have been determined earlier by Pedersen⁹ 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 $41.7 \pm 0.5^\circ$.⁹ Hence, the angle between the molecular plane and the acceptor plane is $5.1^\circ \pm 0.5^\circ$. Chidambaram, Sequeira, and Sikka¹⁰ in their neutron diffraction study of KOMH found an angle of $4.3^\circ \pm 3.5^\circ$. McGrath and Paine calculated an angle of 1.5° as the minimum in electrostatic potential energy using a point charge model. A similar theoretical model has been used by Baur¹⁹ 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.²⁰

φ_0 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:

$$\begin{array}{ll} 47.3 (0.1) & (\varphi_0 \text{ } b\text{-axis}) \\ 47.0 (0.2) & (\text{ratio } C_a/C_c) \end{array}$$

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 Ossman⁸ find $43.9^\circ \pm 1.0^\circ$ 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.⁵ 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 Ossman⁸ 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, $53.9^\circ \pm 0.1^\circ$, is close to the O—D bond direction. In the isolated D_2O molecule the O—D distance has been found to be 0.9572 \AA .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 $R = 1.534 \pm 0.003 \text{ \AA}$.² The maximum value of the angle between the O—D bond and the b -axis will therefore be $53.2^\circ \pm 0.2^\circ$. In the isolated water molecule (HDO) Posener²⁴ 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 H_2O -molecule with an estimated standard deviation of about 0.5° , it is not possible to locate the direction of 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 hydrates⁸ and the values found by McGrath and Ossman⁸ 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 $Ba(ClO_3)_2 \cdot H_2O$ the correction raised the value of the coupling constant from 244 kHz (at $-130^\circ C$) to 270 kHz.⁵ 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.^{24,25} 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 electrons⁵ 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.

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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 ΔH in steps of 5° from 0 to 175° . 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:

$$A = \frac{1}{n} \sum \Delta H_i$$

$$B = \frac{\sum_i \Delta H_i \cos 2\varphi_i}{\sum_i \cos^2 2\varphi_i}$$

$$C = \frac{\sum_i \Delta H_i \sin 2\varphi_i}{\sum_i \sin^2 2\varphi_i}$$

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

$$A = \frac{1}{36} \sum \Delta H_i \quad B = \frac{1}{18} \sum \Delta H_i \cos 2\varphi_i \quad \text{and} \quad C = \frac{1}{18} \sum \Delta H_i \sin 2\varphi_i$$

The standard deviations in these coefficients are also easily calculated:

$$\sigma_A = \frac{1}{n^{1/2}} \sigma_H = 0.167 \sigma_H$$

$$\sigma_B = \frac{1}{(\sum \cos^2 2\varphi_i)^{1/2}} \sigma_H = 0.236 \sigma_H$$

$$\sigma_C = \sigma_B$$

$$\sigma_H = \left[\frac{\sum (\Delta H(\varphi_i) - \Delta H_i)^2}{n-3} \right]^{1/2} = 0.374 [\sum (\Delta H(\varphi_i) - \Delta H_i)^2]^{1/2}$$

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 δ with the b -axis. The angles φ_0 , θ_0 , and δ can then be regarded as the three Euler-angles specifying the orientation of xyz relative to $a b c^*$. Using standard formulas²⁶ we find:

$$\begin{aligned} \Delta H_b = 2K_0\{ & -(1-\eta_0)[\cos(\varphi-\varphi_0) \cos \theta_0 + \cos \delta \sin \delta_0 \cdot \sin(\varphi-\varphi_0)]^2 \\ & -(1+\eta) \sin^2 \delta \sin^2(\varphi-\varphi_0) \\ & + 2[\cos(\varphi-\varphi_0) \times \sin \theta - \cos \delta \cos \theta_0 \times \sin(\varphi-\varphi_0)]^2 \} \end{aligned}$$

Because we have assumed the vibrations to be independent, we can average ΔH over the three vibrations separately. Furthermore, if we turn the molecule an angle α away from the equilibrium position then in the three possible cases:

twist	$\varphi_0 = \varphi_0 + \alpha$	$\theta = \theta_0$	$\delta = \frac{\pi}{2}$
rock	$\varphi_0 = \varphi_0$	$\theta_0 = \theta_0 + \alpha$	$\delta = \frac{\pi}{2}$
wave	$\varphi_0 = \varphi_0$	$\theta_0 = \theta_0$	$\delta = \frac{\pi}{2} + \alpha$

It is then straight forward to get the final answer assuming the oscillations to be of small amplitude and keeping terms up to α^2 :

$$\Delta \bar{H}_b = \bar{A}_b + \bar{D}_b \cos 2(\varphi - \varphi_0)$$

where
$$A_b = K_0[(3-\eta_0)(1-2\langle\theta_r^2\rangle - \langle\theta_w^2\rangle)\sin^2\theta_0 + (3-\eta_0)\langle\theta_r^2\rangle + (3+\eta_0)\langle\theta_w^2\rangle - 2]$$

$$D_b = K_0[(3-\eta_0)(1-2\langle\theta_r^2\rangle - 2\langle\theta_t^2\rangle + \langle\theta_w^2\rangle)\sin^2\theta_0 + (3-\eta_0)\langle\theta_r^2\rangle - (3+\eta_0)\langle\theta_w^2\rangle + 2\eta_0(1-2\langle\theta_t^2\rangle)]$$

The mean-square amplitudes of vibration are not known for KOMH. Earlier we have concluded from the PMR-spectra that $\langle \theta_r^2 \rangle \approx \langle \theta_t^2 \rangle$, and we have calculated $\langle \theta_t^2 \rangle$ from the shape of the potential well as calculated by McGrath and Paine.¹⁴ However, Prask and Boutin²⁷ 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 D₂O-molecule ($I_t = 3.85$, $I_r = 5.77$, $I_w = 1.82$ in units 10^{-40} g cm²),²² we can calculate the mean square amplitudes from the following expression, valid for a harmonic oscillator

$$\langle \theta_x^2 \rangle = \frac{h}{4\pi^2 I_x \nu_x} \left[\frac{1}{2} + (\exp(h\nu_x/(kT)) - 1)^{-1} \right]$$

We obtain

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

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