Dynamics of Water in Crystal Hydrates

III. Deuteron Magnetic Resonance and the Motion of Heavy Water Molecules
in $Na_2S_2O_6 \cdot 2\,D_2O$ Single Crystals

S. KETUDAT *, I. BERTHOLD and ALARICH WEISS

Eduard-Zintl-Institut der Technischen Hochschule Darmstadt, Lehrstuhl für Physikalische Chemie

Deuteron magnetic resonance in $Na_2S_2O_6 \cdot 2\,D_2O$ single crystals was investigated in the temperature range $-68\,°C$ to $+80\,°C$. The activation energy for the flipping motion of the heavy water molecule was found to be (9.2 ± 1.5) kcal/mole. The quadrupole coupling constant and the asymmetry parameter in the low temperature case was found to be $e^2\,q\,Q/h = (244 \pm 3)$ kHz, $\eta = 0.103 \pm 0.003$ for gne deuteron and $e^2\,q\,Q/h = (236 \pm 3)$ kHz, $\eta = 0.116 \pm 0.003$ for the other deuteron of the same water molecule. For the fast flipping case at room temperature $e^2\,q\,Q/h = (131 \pm 2)$ kHz and $\eta = 0.77 \pm 0.02$. Good agreements in structural parameters of the water molecule of $Na_2S_2O_6 \cdot 2\,D_2O$ and of $Na_2S_2O_6 \cdot 2\,H_2O$ were found.

It has been shown that the motion of heavy water molecules in crystals could be studied by observing the quadrupole perturbation of the magnetic resonance of the deuterons as a function of temperature [1,2]. The water molecules in the crystal flip about its two-fold axis and this flipping motion could be slowed down or frozen out at low temperatures. This type of study not only reveals the structure and the dynamic behaviour of deuterated water molecules but also the nature of the bond to the deuterium atom. In this investigation, the crystal of sodium dithionate dideuterate $(Na_2S_2O_6 \cdot 2\,D_2O)$ is chosen because the results could be directly compared with those obtained from the proton resonance study of $Na_2S_2O_6 \cdot 2\,H_2O$ [3].

Experimental Procedure

Single crystals were grown from a solution of anhydrous sodium dithionate $(Na_2S_2O_6)$ in heavy water (99.7% D_2O) by slow cooling. Anhydrous sodium dithionate was prepared by the exchange of barium by sodium in the solutions of barium dithionate and sodium sulfate. The $Na_2S_2O_6 \cdot 2\,H_2O$ was recrystallized. Subsequently it was dehydrated to $Na_2S_2O_6$. By slowly cooling $(0.5 - 1.0\,°C$ per day) the saturated solution of sodium dithionate in heavy water from $45\,°C$ to $25\,°C$, clear crystals of several

cubic centimeters in size were obtained in about one month. The crystals grew prismatically along the crystallographic a axis with the forms $\{011\}$, $\{001\}$, $\{101\}$, $\{111\}$ and $\{121\}$.

For room temperature measurements, a suitable crystal was mounted in a goniometer head [4] which could be aligned outside or inside the magnet gap to rotate about any desired axis with an accuracy of better than $\pm 0.5°$.

For measurements at other temperatures, the crystal was first optically aligned on a goniometer head to rotate about the desired axis and was then transferred and glued to a small well-machined plexiglass stick. This plexiglass stick then was fixed to the rf coil form. The crystal together with the coil and rf cable assembly could then be rotated inside a temperature controlled cryostat. In this manner the axis of rotation could be determined to better than $\pm 1°$.

The temperature control has been described previously [1]. The system consists of a long tail glass dewar. A copper tank inside the dewar is filled with the coolant and connected to a large cylindrical copper tail. The sample and the coil are in the tail. Heat can be removed from or added to the sample by conduction through this copper tube tail. By heating this copper tube at its neck with or without coolant in the tank or by controlling the rate of flow of coolant into the tank a desired temperature from

* Present address: Department of Physics, Chulalongkorn University, Bangkok, Thailand.
[1] S. KETUDAT and R. V. POUND, J. Chem. Phys. **26**, 708 [1957]. — S. KETUDAT, Thesis, Harvard University 1957.
[2] T. CHIBA, J. Chem. Phys. **39**, 947 [1963].

[3] I. BERTHOLD and A. WEISS, Z. Phys. Chem. Frankfurt **38**, 140 [1963] ; Z. Naturforschg. **22 a**, 1433, 1440 [1967].
[4] A. WEISS, Z. Naturforschg. **15 a**, 536 [1960].

90 °C to -170 °C can be obtained. Temperature differences over the sample as determined by thermocouples were only a few degrees at the two extremes of the temperature range.

The POUND–KNIGHT–WATKINS [5] spectrometer with frequency sweep produced by a motor-driven tuning capacitor and a 10,000 Gauss constant magnetic field were used. The pair separations of deuteron resonance frequencies, $\Delta \nu$, originating from the quadrupole perturbation on the magnetic resonance, were recorded at $10°$ intervals of rotation about the axis perpendicular to the magnetic field direction. The angular dependence of the pair separation is related to the components of the electric field gradient tensor by the formula [6]

$$\Delta \nu_Z = \frac{3}{4} \frac{e^2 Q}{h} \left[q_{ZZ} + (q_{XX} - q_{YY}) \cos 2\,\Theta_Z \right.$$
$$\left. + 2\,q_{XY} \sin 2\,\Theta_Z \right], \qquad (1)$$

where X, Y and Z are the crystal axes, Z being the axis of rotation and Θ_Z is the angle of rotation of H_0 from the X axis.

In general, if the measurements are made when the crystal is rotated about all three mutually perpendicular axes, all nine (or five independent) components of the tensor can be found by fitting the experimental curve with Eq. (1). Through diagonalization of this tensor the three eigenvalues which give the quadrupole coupling constant

$$e^2 q\,Q/h = e^2 q_{ZZ}\,Q/h$$

the asymmetry parameter $\eta = (q_{XX} - q_{YY})/q_{ZZ}$ and the direction cosines of the principal axes with respect to the crystal axes can be found.

Measurements and Results

a) Room Temperature Measurements

At room temperature (23 °C) the deuteron magnetic resonance signals could only be observed when the angles between the magnetic field direction and the directions [7] of the two OD bonds of the same molecule have the same field gradient tensor. This implies that the molecule flips and the field gradients acting on each deuteron are equal on average.

The frequency difference of pair separation was measured when the crystal was rotated about the axis perpendicular to the magnetic field direction and parallel to the two-fold axis of one of the heavy water molecules. The plot of the pair separation as a function of the angle of the crystal orientation in the magnetic field is shown in Fig. 1. It was found that the direction of the principal axis corresponding to
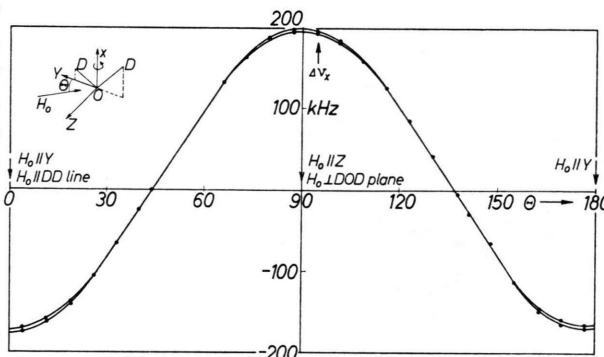

Fig. 1. Pair separations of deuteron resonance lines in $Na_2S_2O_6 \cdot 2\,D_2O$ at room temperature (23 °C).

the largest field gradient component (Z axis) is perpendicular to the plane of the heavy water molecule. In addition the direction corresponding to the middle component (Y axis) is perpendicular to the two-fold axis and lies in the plane of the molecule. The coupling constant and the asymmetry parameter at 23 °C are:

$$e^2 q\,Q/h = (131 \pm 2)\ \text{kHz}; \quad \eta = 0.77 \pm 0.02\,.$$

b) Measurement at -30 °C

At -30 °C the deuteron resonance signals corresponding to "slow flipping" or "static" heavy water molecules could be observed at an arbitrary crystal orientation. The angular dependences of the pair separations when the crystal was rotated about each of the three main axes a, b and c are shown in Fig. 2. It is seen that at an arbitrary angle four pairs of resonance lines originate from deuterons of four non equivalent OD bonds. Therefore two non-equivalent water molecules are observed in agreement with the crystal structure. The diagonalization of the coupling tensors shows that there are (aside from

[5] G. D. WATKINS, Thesis, Harvard University 1952.

[6] G. M. VOLKOFF, Can. J. Phys. **31**, 820 [1953]. — M. H. CoHEN and F. REIF, Solid State Physics (Ed. F. SEITZ and D. TURNBULL), Academic Press Inc., New York 1957, Vol. 5, p. 435.

[7] The OD bond directions were at first postulated and later verified by low temperature measurements to be approximately the same as the OH bonds as determined by the proton resonance study by BERTHOLD and WEISS [3].
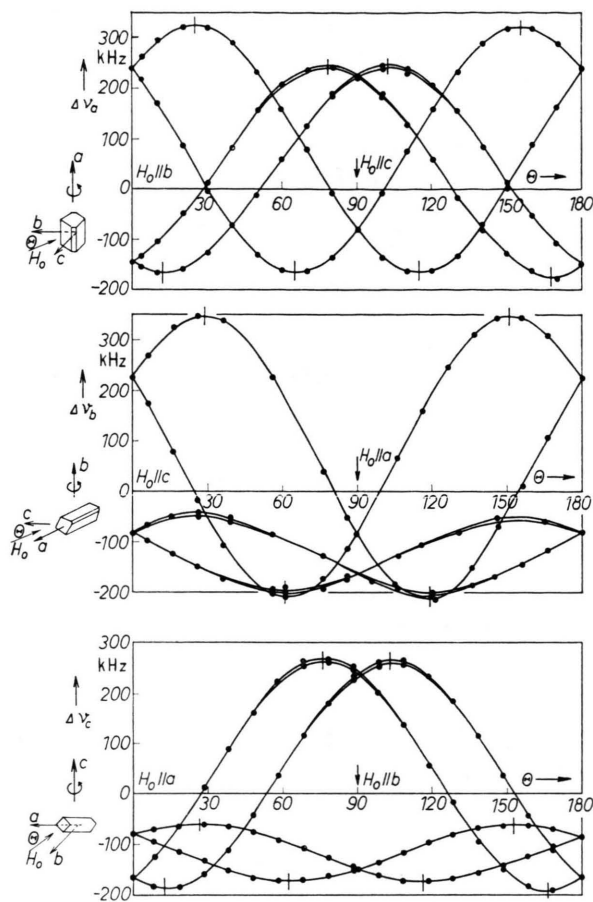
Fig. 2. Pair separations of deuteron resonance lines in Na$_2$S$_2$O$_6 \cdot$ 2 D$_2$O at -30 °C.

the directions of the principal axes) only two types of coupling constants. The two deuterons of each heavy water molecule do not possess the same electric field gradient. These coupling constants and the asymmetry parameter are:

type 1:

$e^2 q Q/h = (244 \pm 3)$ kHz; $\eta = 0.103 \pm 0.003$;

type 2:

$e^2 q Q/h = (236 \pm 3)$ kHz; $\eta = 0.116 \pm 0.003$.

The direction of the principal axes corresponding to the largest field gradient component (Z axis) is approximately along the O$_W$O direction and within a few degrees from the OH bond as determined by the proton resonance study [3]. The axis corresponding to the middle component (Y axis) is approximately

perpendicular to the plane of the water molecule. Direction cosines of pertinent axes are tabulated in Table 2. It should be stressed at this point that our deuteron magnetic resonance study determines neither the position of the deuterium atom nor do we know that the Z axis of the field gradient points exactly along the OD bond. However, the fact that one deuteron lies in a different electric field gradient from the other of the same heavy water molecule tells us that the flipping is considerably slower than at ambient temperatures.

c) Measurements of the Activation Energy of the Flipping Motion

To obtain the activation energy of the flipping motion, the line widths at various temperatures were observed in the manner similar to CHIBA [2] based on the theory by GUTOWSKY et al. [8] and by ABRAGAM [9]. At low temperatures where the flipping motion or the exchange rate of the two deuterons is slow, each deuteron of a water molecule has its own resonance frequency since the two field gradients are different and the line width is predominantly GAUSSIAN. As the temperature is raised, the line width becomes broader. In the temperature range where the flipping or exchange frequency is approximately the same as the frequency difference of the two deuterons $|\nu_1 - \nu_2|$ the lines are very broad and overlapping and therefore unobservable. At high temperatures where the flipping rate is fast compared with the aforementioned frequency difference, deuterons see and share the average field gradient and the line-width again becomes narrow. The line-width measured between the points of maximum slope of the absorption line $\Delta\nu_{msl}$ in the region near the transition is given by

$$\Delta\nu_{msl} = (1/\sqrt{3\,\pi})\{\sqrt{2\,\pi}(\Delta\nu_{msl})_G + \nu_{ex}\}$$
$$\text{for } \nu_{ex} \ll |\nu_1 - \nu_2|, \qquad (2)$$

and

$$\Delta\nu_{msl} = (1/\sqrt{3\,\pi})\{\sqrt{2\,\pi}(\Delta\nu_{msl})_G + \tfrac{1}{2}\pi^2(\nu_1 - \nu_2)^2/\nu_{ex}\}$$
$$\text{for } \nu_{ex} \gg |\nu_1 - \nu_2|, \qquad (3)$$

where $(\Delta\nu_{msl})_G$ is the "static" line width at very low temperatures. The flipping or exchange frequency ν_{ex} can be determined directly from the line width measured as:

$$\nu_{ex} = \sqrt{3\,\pi}(\Delta\nu_{msl}) - \sqrt{2\,\pi^2}(\Delta\nu_{msl})_G \qquad (4)$$

[8] H. S. GUTOWSKY, D. W. McCALL, and C. P. SLICHTER, J. Chem. Phys. **21**, 279 [1953].

[9] A. ABRAGAM, The Principles of Nuclear Magnetism, Oxford University Press, London 1961.

for the "static" case,

$$\nu_{ex} = \frac{\pi^2}{2} \frac{(\nu_1 - \nu_2)^2}{\sqrt{3}\,\pi(\Delta\nu_{msl}) - \sqrt{2}\,\pi(\Delta\nu_{msl})_G} \qquad (5)$$

for the "fast flipping" case.

The flipping frequency is related classically to the temperature as

$$\nu_{ex} = \nu_\infty \, e^{-V_0/kT} \,.$$

To minimize the error and the uncertainty in the line width measurements the signal was observed at the orientation where the deuteron dipole-dipole fine structure splitting is zero. Unfortunely even at +80 °C the signals corresponding to the fast flipping mode could hardly be observed. Only data in the temperature range between +15 °C to −68 °C, corresponding to the "static" or "slow flipping" mode could be obtained. Consequently, the uncertainty in the determination of the energy is somewhat large. The plot of the logarithm of the flipping frequency ν_{ex} as a function of the inverse temperature is shown in Fig. 3. In the experiment, the line width measured between the points of maximum slope, $\Delta\nu_{msl}$, was determined at various temperatures. The static line width, $(\Delta\nu_{msl})_G$, was obtained by plotting $\log \sqrt{3}\,\pi(\Delta\nu_{msl})$ versus the inverse temperature. It is seen that at lower temperatures (the upper curve of Fig. 3) the curve levels off. This asymptotic value then determines the static line-width. When $(\Delta\nu_{msl})_G$ was obtained, $\log(\nu_{ex})$ as calculated from Eq. (4) and Eq. (5) was plotted again to give the lower curve in Fig. 3. The activation energy V_0 is seen to be $V_0 = (9.2 \pm 1.5)\,\text{kcal/mole}$.

Discussion and Comparison of Results with the Hydrated Crystal and Others

The crystal structure of $Na_2S_2O_6 \cdot 2\,H_2O$ has been determined by X-rays by MARTINEZ et al. [10] and later refined by us (see paper II). The orthorhombic unit cell contains four molecules (formula units). Consequently, there are eight water molecules in a unit cell.

The cell projection on the $b\,c$ plane is shown in Fig. 2 of paper II (see p. 1442). The sulfur atoms and two oxygen atoms of the $S_2O_6^{--}$ group are situated in the position 4c [11], and the other atoms in position 8d. The hydrogen atoms of the water molecules are bonded to the oxygen atoms of the $S_2O_6^{--}$ group so that a chain of $[S_2O_6^{--} \cdot 2\,H_2O]_\infty$ is formed along the direction of the a axis. In magnetic resonance study, with the magnetic field direction perpendicular to the crystal axis, the rotation axis, the plane of symmetry and the center of symmetry reduces the number of non-equivalent molecules by a factor of two. Thus there are only two non-equivalent heavy water molecules or four non-equivalent OD bonds in an unit cell.

To check the differences, if any, in the lattice parameters of the hydrate and deuterate crystals, measurements of the quadrupole interaction of sodium in the deuterate crystal were carried out at room temperature. Within the experimental error of $\pm 2\,\text{kHz}$ in frequency and $\pm 0.5°$ in crystal alignment it was found to be the same as in the hydrate crystal [12]. According to our calculation of the electric field gradient at the sodium nucleus in $Na_2S_2O_6 \cdot 2\,H_2O$ on a point charge model, the water molecule contributed more than 70% to the field gradient. Consequently, as no difference in the
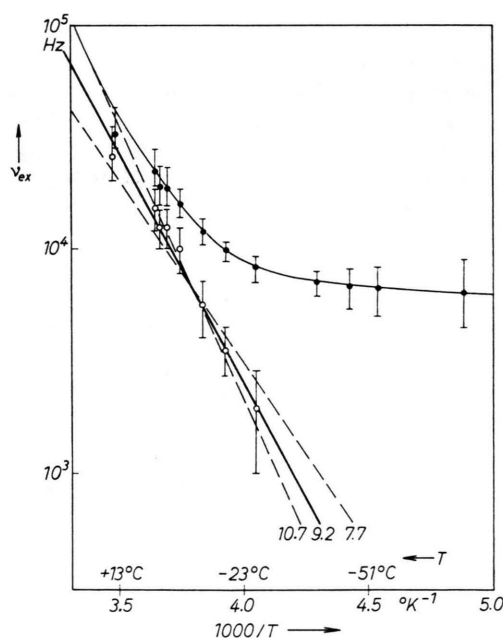

Fig. 3. A semilog plot of flipping frequency versus $1/T$.

[10] S. MARTINEZ, S. GARCIA-BLANCO, and L. RIVOIR, Acta Cryst. **9**, 145 [1956].

[11] International Tables for X-ray Crystallography, Vol. 1, The Kynoch Press, Birmingham 1952.

[12] I. BERTHOLD and A. WEISS, Ber. Bunsenges. Physik. Chem. **68**, 640 [1964].

quadrupole interactions of sodium in the hydrate and deuterate crystal was found, it is reasonable to assume that the lattice parameters in the two crystals are identical.
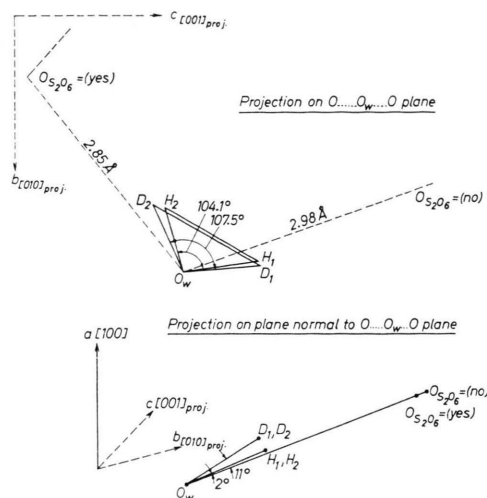

Fig. 4. Projection of water molecule in $Na_2S_2O_6 \cdot 2\ D_2O$ and in $Na_2S_2O_6 \cdot 2\ H_2O$.

As seen from the structure and the proton resonance study, the two deuterium (or hydrogen) atoms of the water molecule are bonded differently to the two oxygen, of the $S_2O_6^{--}$ group (see Fig. 2 of paper II and Fig. 4). The deuterium of type 1 is bonded between the oxygen of its own molecule and one of the oxygens of the $S_2O_6^{--}$ group which is *not* bonded to another deuteron, whereas the deuteron of type 2 is bonded to one of the oxygens of the di-

Type of D	e^2qQ/h kHz	η	$O_{S_2O_6} =$ bonded to another D	$O_W \ldots O_{S_2O_6}$ distance
1	244 ± 3	0.103 ± 0.003	no	2.98 Å
2	236 ± 3	0.116 ± 0.003	yes	2.85 Å

Table 1. Results of deuteron magnetic resonance investigations in $Na_2S_2O_6 \cdot 2\ D_2O$ single crystals at $-30\ °C$.

thionate ion which is *also* bonded to another deuteron. The $O_W \ldots O_{S_2O_6}^-$ distances of these two types are different. Therefore one may expect that the quadrupole coupling constant for each deuteron of the water molecule should be different as we report here. These results are tabulated in Table 1.

It is seen that the quadrupole coupling constant of the deuterium belonging to the larger OO distance is larger, than that of the deuterium belonging to the shorter OO distance. This agrees qualitatively with the results of SALEM [13] who found the relationship between the electric field gradient and force constant for stretching modes of diatomic systems, which in this case is a function of OO distance.

In first approximation, assuming the principal axis corresponding to the largest component of the electric field gradient being along the OD bond, several comparisons with the proton resonance data can be made. Taking the water molecule whose oxygen coordinate is (0.758; 0.456; 0.313), the projection of water molecules on the OO_WO plane is shown in Fig. 4. The summarized results are given in Table 2.

Quantity to be compared	Deuterate crystal	Hydrate crystal
Direction cosines of OD_1 or OH_1	$(+0.4630;\ -0.1740;\ +0.8687)$	$(+0.3234;\ -0.1935;\ +0.9268)$
Corresponding angles with respect to a, b and c axes	$(+62°;\quad -80°; +30°)$	$(+71°;\quad -79°; +22°)$
Direction cosines of OD_2 or OH_2	$(-0.2270;\ -0.8860;\ -0.4044)$	$(-0.1811;\ -0.9601;\ -0.2131)$
Corresponding angles with respect to a, b and c axes	$(-77°;\quad -28°; -66°)$	$(-80°;\quad -16°; -78°)$
Bond angle D_1OD_2 or H_1OH_2	107.5°	104.1°
$O \cdots O \cdots O$ angle	109.5°	109.5°
Distance DD or HH	1.55 Å	1.52 Å
Angle between the plane of water molecule and the OOO plane	11°	2°
Bond bending angle OD_1O or OH_1O	159°	167°
Bond bending angle OD_2O or OH_2O	163°	160°
Coordinates of D_1 or H_1	$(0.828; 0.441\quad ; 0.391)$	$(0.821; 0.437\quad ; 0.393)$
Coordinates of D_2 or H_2	$(0.724; 0.377\quad ; 0.277)$	$(0.716; 0.377\quad ; 0.280)$
Angle between H_1H_2 and D_1D_2	0°	
Angle between D_1OD_2 and H_1OH_2 plane	9°	

Table 2. Comparison of results on water molecules of $Na_2S_2O_6 \cdot 2\ H_2O$ and $Na_2S_2O_6 \cdot 2\ D_2O$.

[13] L. SALEM, J. Chem. Phys. **38**, 1227 [1963].

In general, the agreement between the deuterium and proton studies is good, especially with regard to the DD and HH directions which agree extremely well. It is interesting to note that the DOD angle is larger than the HOH angle (Table 3). This is found to be the case for other crystals in which both proton and deuterium resonance have been observed. As pointed out earlier, the field gradient axis does not necessarily lie along the bond direction, and from the electrostatic point of view it can be shown that the angle between the two principal axes of the field gradients at the position of the two deuterons is larger than the bond angle.

Substance	DOD or HOH angle	Ref.	Activation energy [kcal/mole]	Ref.
$Li_2SO_4 \cdot H_2O$	110.6°	a	7.3 ± 0.8	f
$Li_2SO_4 \cdot D_2O$	108°		—	
$Ba(ClO_3)_2 \cdot H_2O$	105°	b	5.0 ± (0.4)	g, h
$Ba(ClO_3)_2 \cdot D_2O$	110°	c	6.6 ± (0.2)	c
$Na_2S_2O_6 \cdot 2 H_2O$	104.1°	d	6.0 ± 1.0	d
$Na_2S_2O_6 \cdot 2 D_2O$	107.5°	e	9.2 ± 1.5	e

a W. C. HAMILTON, Acta Cryst. 15, 353 [1962].
b J. W. McGRATH and A. A. SILVIDI, J. Chem. Phys. 34, 322 [1961].
c T. CHIBA, J. Chem. Phys. 39, 947 [1963].
d I. BERTHOLD and A. WEISS, Z. Naturforschg. 22 a, 1433, 1440 [1967].
e This investigation.
f D. F. HOLCOMB and B. PEDERSEN, J. Chem. Phys. 36, 3270 [1962].
g B. PEDERSEN, J. Chem. Phys. 41, 122 [1964].
h A. A. SILVIDI, J. M. McGRATH, and D. F. HOLCOMB, J. Chem. Phys. 41, 105 [1964].

Table 3. List of DOD and HOH angles and activation energy for flipping motion in three substances.

It is not surprising to see that the average bond-bending angle (Table 2) is nearer to 180° for the proton case because the position of the protons in paper II were fixed by the minimum of the bond bending under the restraint that the p—p distance and direction were kept constant. When the OD distance is assumed to be 0.96 Å and the deuteron is placed on the principal axis of the maximum field gradient component, the agreement between the co-ordinates of the hydrogen and the deuterium atoms is good (see Table 2).

It is of interest to focus our attention on the dynamic behaviour of the heavy water molecule. As pointed out earlier, at room temperature the deuteron resonance signals could only be observed when the angles between the magnetic field direction and the directions of the two OD bonds of the same molecule where the same. The result indicates qualitatively that even at room temperature the flipping motion of the heavy water molecule in the $Na_2S_2O_6 \cdot 2 D_2O$ crystal is much slower than that in $Li_2SO_4 \cdot D_2O$ [1] and in $Ba(ClO_3)_2 \cdot D_2O$ [2]. The value of the activation energy of the flipping motion of the heavy water molecule for sodium dithionate dideuterate of (9.2 ± 1.5) kcal/mole is somewhat higher than (7.3 ± 0.8) kcal/mole found for $Li_2SO_4 \cdot H_2O$ by PEDERSON [14] and (6.6 ± 0.2) kcal/mole found in $Ba(ClO_3)_2 \cdot D_2O$ by CHIBA [2], and even higher than (6.0 ± 1.0) kcal/mole found in $Na_2S_2O_6 \cdot 2 H_2O$ (paper I). If the difference in the activation energy for the flipping motion of the heavy water molecule (D_2O) and that of the water molecule (H_2O) is significant and real, it would confirm the idea, that the deuterium bond is stronger than the hydrogen bond. Unfortunately in this crystal we cannot measure the resonance signals at the two extremes of the motion, i. e. the fast flipping and the slow flipping. It will be worthwhile to investigate and compare the activation energy of the flipping motion of the water molecule in other suitable hydrate and deuterate crystals.

14 B. PEDERSEN, J. Chem. Phys. 41, 122 [1964].