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Study of Motion of D_2O in $Ba(ClO_3)_2D_2O$ by Transient NMR

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Deuteron spin lattice relaxation time T_1 and the reorientation rate of D_2O have been measured at various temperatures on a single crystal of $Ba(ClO_3)_2D_2O$ by transient nuclear magnetic resonance method. Temperature dependence of T_1 is similar to that of corresponding proton resonance but three to four orders of magnitude smaller than the latter. From the slope of log T_1 *vs.* $1/T$ curve, activation energy of reorientation of D_2O of 6.5—6.8 kcal/mol is obtained in agreement with that from line width transition. Theoretical values of T_1 minima were in good agreement with the observed. Direct measurement of reorientation rate is made by observing a signal recovery from saturation of one of the two deuteron sites of D_2O due to the exchange with unsaturated spins at the other site. The Arrhenius plot of the reorientation rate down to $-170°C$ determined in this manner smoothly connects to that derived from the line width transition. A revision of the previous treatment of line width change is described and the reorientation rates of $Ba(ClO_3)_2D_2O$ are re-evaluated according to this method. A satisfactory agreement is found among the conclusions from the three different types of experiment, T_1, the line width transition and the directly measured reorientation rate. The motion is a random reorientation of D_2O with a rate governed by an activation process of 7 kcal/mol.

In a deuteron magnetic resonance the splitting due to a deuteron quadrupole coupling is usually of the order of 100 kc/sec. If a motion that interchanges two deuterons with different electric field gradient (EFG) components in the direction of H_0 is rapid enough, one gets a splitting corresponding to the averaged EFG of these two deuterons. Thus in hydrates a rapid reorientation of D_2O about its bisector causes the averaged spectra at high temperatures, while at low temperatures the spectra correspond to the stationary deuterons. From the line width change at both the slow and fast exchange limits, the reorientation rate of deuterons can be obtained employing the theory of motional narrowing process.(1) The method has an advantage over the usual line width transition due to dipole interactions in that the separation between the lines can be made as large as 200 kc/sec. However, because of insufficient signal-to-noise ratio usually encountered in deuteron resonances, observation of the broadening process is rather limited to a narrow range of temperatures and the presence of the dipole structure of the lines often imposes additional difficulty in extracting the rate of exchange. An activation energy of 6.5 kcal/mol for the reorientation in $Ba(ClO_3)_2D_2O$ determined in this way is somewhat larger than 5.0 kcal/mol for $Ba(ClO_3)_2H_2O$ determined from the temperature dependence of spin-lattice relaxation time, T_1, by Silvidi *et al.*(2)

It seems therefore worthwhile to study the motion by different method and compare the resulting value of reorientation rate with those obtained from the line width change for $Ba(ClO_3)_2\cdot D_2O$ to examine whether the latter method gives the correct value. The present paper describes the measurements of T_1 and the reorientation rate in D_2O in this suitably simple system. The whole procedure of the present experiment and analysis are similar to the work of Schmidt and Uehling(3) of KD_2PO_4. A refined treatment of the line width transition for the derivation of exchange rate is also given.

Experimental

Single crystals of $Ba(ClO_3)_2D_2O$ are prepared as in the previous study.(1) All measurements were made using a pulse method. The pulse apparatus is of coherent type using Blume's gate circuit(4) operated at a frequency of crystal-controlled 10 Mc. Programmed pulses are furnished by the combination of Tektronix type 162, and 163 generators. The sample coil in a probe is incorporated in a single coil arrangement. Signal was detected by PA-620-L preamplifier and WA-600-D wideband amplifier of Arenberg Ultrasonic Laboratory Inc. Recovery time of the apparatus is about 15 μs. Rf field strength used was such that width of 90° pulse for D was about 15 μs.

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1) T. Chiba, *J. Chem. Phys.*, **39**, 947 (1963).

2) A. A. Silvidi and J. W. McGrath, *ibid.*, **41**, 105 (1964).

3) V. H. Schmidt and E. A. Uehling, *Phys. Rev.*, **126**, 447 (1962).

4) R. Blume, *Rev. Sci Instr.*, **32**, 554 (1961).

Results and Discussion

Measurement of T_1. $Ba(ClO_3)_2D_2O$ crystal is monoclinic. Bisector of D_1OD_2 is a two-fold axis parallel to the crystallographic b axis.[5] D has nearly axially symmetric EFG about the D-O direction.[1]

For a deuteron nuclear spin $I=1$, therefore, an inclusion of a quadrupole interaction gives three unequally-spaced Zeemen levels. If only one of the two transitions (say, $m=1\rightarrow0$) is saturated, the recovery to the equilibrium cannot in general be represented by a single exponential function. If $P_1 \neq P_2$ as is generally the case, where P_1 is the thermal transition probability of $\Delta m=\pm1$ and P_2 is that of $\Delta m=\pm2$, unique T_1 can be defined only when three levels become equidistant as

$$1/T_1 = 2P_2 + P_1 \qquad (1)$$

Therefore, the measurement of T_1 is to be made for the crystal orientation where the quadrupole splitting is zero. Moreover, in the present case, because of the rapid exchange motion of D_1 and D_2 at high temperatures, in order to be able to observe T_1 for a wide temperature range the crystal orientation must be so chosen that the quadrupole splitting vanishes both for D_1 and D_2. There are two directions specified as direction I and II in Fig. 1 where this condition is met. The observed T_1 in these directions at various temperatures are plotted in Fig. 2. A typical V-shaped curve indicates that the reorientation with the jump rate ν_j governed by Arrhenius equation is a principal relaxation mechanism. The activation energy (in kcal/mol) is obtained from the slopes at the high and low temperature sides of the T_1 minimum as,

H_0 direction	High temp. side	Low temp. side	Averaged
I	6.1	6.9	6.5
II	6.85	6.8	6.8

These values are in good agreement with that of 7.0 kcal/mol from the line width transition.

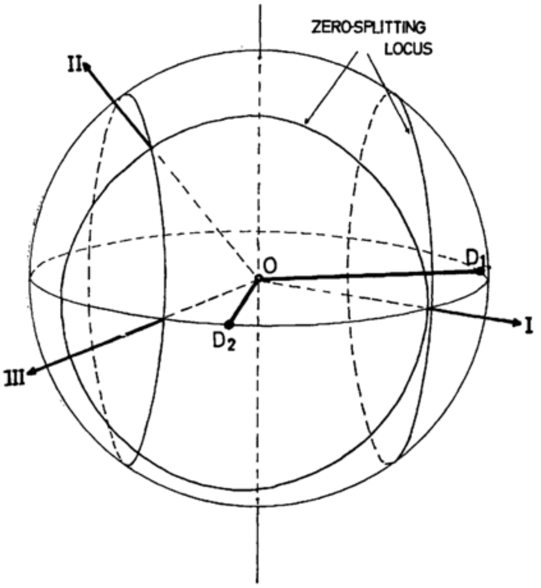

Fig. 1. Directions of magnetic field relative to the orientation of the D_2O molecule in the present study: Direction I and II for the measurement of T_1, Direction III for the direct measurement of jump rate.

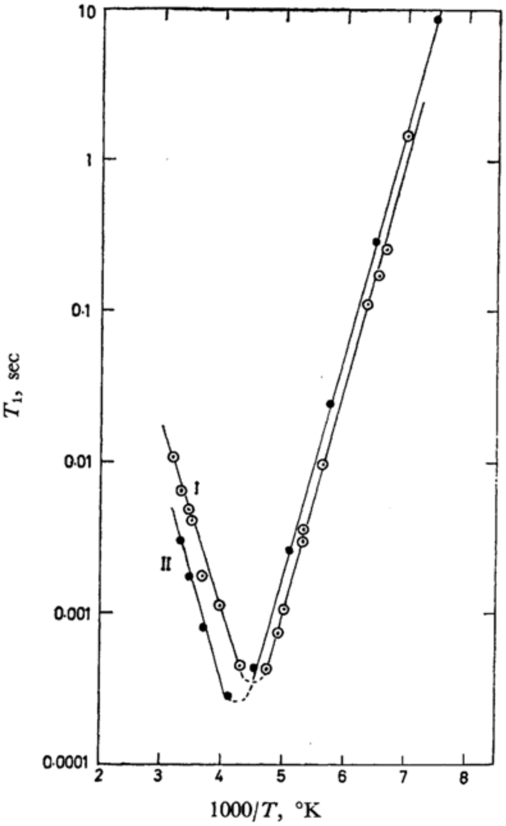

Fig. 2. Temperature dependence of T_1.
⊙ Measured in Direction I.
● Measured in Direction II.

The curve is similar to the one obtained from the proton resonance in $Ba(ClO_3)_2H_2O$ by Silvidi and McGrath,[2] but T_1 is 3 to 4 orders of magnitude smaller in the present case indicating predominant quadrupolar relaxation mechanism of deuteron. Theoretical values of T_1 minimum are calculated as follows.

The matrix elements of quadrupole interaction Hamiltonian are given as

$$(m\pm1|\mathscr{H}_Q|m) = \frac{eQ}{4I(2I-1)} \times(2m\pm1)[(I\pm m+1)(I\mp m)]^{1/2}(\varphi_{xz}\mp i\varphi_{yz}) \qquad (2)$$

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5) G. Kartha, *Acta Cryst.*, **5**, 845 (1952).

$$(m\pm2|\mathscr{H}_Q|m)=\frac{eQ}{8I(2I-1)}$$
$$\times[(I\pm m)(I\mp m-1)(I\pm m-1)(I\pm m+2)]$$
$$\times(\varphi_{xx}-\varphi_{yy}\mp2i\varphi_{xy}) \quad (3)$$

where φ's represent the matrix elements of EFG tensor. The z axis is taken along H_0. φ's which are different for the D_1 and D_2 of D_1OD_2, fluctuate with the random flip of D_2O, and cause relaxation among different m levels.

Denoting the mean lifetime of a deuteron in one of the site by τ, the autocorrelation function of the fluctuating φ can be written as

$$\langle\varphi(0)\varphi^*(t)\rangle=\varphi_\Delta{}^2\exp(-2t/\tau), \quad (4)$$

where

$$\varphi_\Delta=[\varphi(D_1)-\varphi(D_2)]/2, \quad (5)$$

and $\varphi(D_1)$ and $\varphi(D_2)$ are φ at D_1 and D_2 respectively. Corresponding spectral density $J(\omega)$ is given by

$$J(\omega)=|\varphi_\Delta|^2 j(\omega), \quad (6)$$

$$j(\omega)=4\tau/(1+4\omega^2\tau^2). \quad (7)$$

The transition probabilities of 1→0 and 1→−1 due to this motion are

$$P_1=\hbar^2|A_1|^2J(\omega), \quad (8)$$

$$P_2=\hbar^2|A_2|^2J(\omega), \quad (9)$$

where A_1 and A_2 represent spin parts of (2) and (3), respectively. T_1 is given by Eq. (1). To calculate T_1 in the direction I, the quadrupole coupling tensor $(eQ/h)q$ of D in the principal axis system as determined in Ref. 1 is transformed into the coordinate system where the z axis is along H_0 and the x axis perpendicular to the molecular plane. By the 180° flip motion the yz element changes as $\varphi_{yz}\rightarrow-\varphi_{yz}$. All the other elements are unchanged by the motion. $|(eQ/h)\varphi_{yz}|=167$ kc/sec. Then from (1), (2), (6), and (8)

$$1/T_1=(1/8\hbar^2)(167\times10^3h)^2j(\omega). \quad (10)$$

Similarly in the direction II, when transformed into the coordinate system where z is along H_0 and x along bisector of D_2O, only the xy and xz elements of EFG tensor change by the flip motion, namely,

$$\varphi_{xy}\rightarrow-\varphi_{xy} \quad \text{and} \quad \varphi_{xz}\rightarrow-\varphi_{xz}.$$

$$|(eQ/h)\varphi_{xy}|=117\ \text{kc/sec},$$

and $$|(eQ/h)\varphi_{xz}|=119\ \text{kc/sec},$$

T_1 in this case will be,

$$1/T_1=(1/8\hbar^2)(119\times10^3h)^2j(\omega)$$
$$+(1/4\hbar^2)(117\times10^3h)^2j(2\omega). \quad (11)$$

The T_1 minimum and corresponding ν_j from (10) and (11) are 0.45 msec and $3.1\times10^7\ \text{sec}^{-1}$ for the direction I, and 0.24 msec and $4.5\times10^7\ \text{sec}^{-1}$ for the direction II respectively. Observed T_1 minimum values are about 0.4 msec and 0.3 msec for the directions I and II, respectively. The agreement between the calculated and the observed is quite satisfactory. The parallel shift of the curve I from curve II of Fig. 2 is in the right direction, but a few times larger than that expected from the theory. ν_j at the T_1 minima are indicated in Fig. 3 of ν_j *versus* $1/T$ curve.

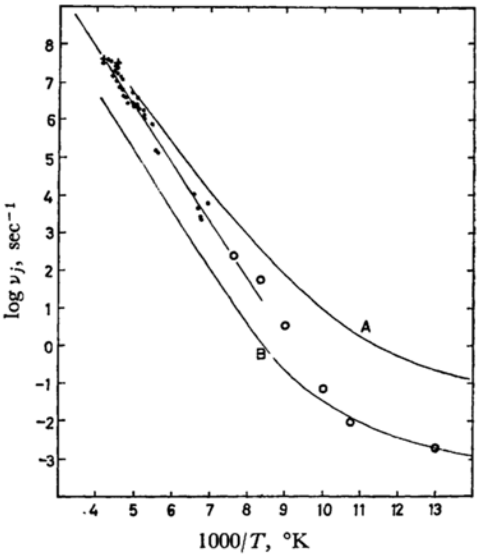

Fig. 3. Temperature dependence of jump rate ν_j determined from T_1 minimum, +, from direct measurement, ○, and from the line width change, ●. Curves A and B are theoretical ones from quantum mechanical tunneling process with potential barrier of 6.17 and 7.61 kcal/mol, respectively.

Direct Reorientation Rate Measurement. The rate of reorientation or the jump rate of a deuteron from the site 1 to site 2 can be directly measured in the following experiment, if one observes a recovery from saturation of a signal of site 1 by diffusion of site 2 spins, which has been kept in thermal equilibrium. Suppose the crystal is oriented in such a way that the signal of site 1 is unsplit, while that of site 2 has large splitting. We apply two 90° pulses in succession at the Larmor frequency. The first pulse saturates site 1 line. Then the magnitude of the Bloch decay signal after the second pulse shows a recovery due to the diffusion of unsaturated spins from the site 2 to site 1 by reorientation in addition to the recovery by spin-lattice relaxation. The method is applicable when T_2 is much shorter than this recovery time, that is, the two successive Bloch decay signals can be well separated. Also the rf pulse strength H_1 should be such that $\gamma H_1\ll2\pi\Delta\nu$, where $\Delta\nu$ is the frequency difference between the two sites, in order that the rf pulse has negligible effect on the site 2 nuclei. Direct measurement of τ, the lifetime in one of the sites, $(\tau=1/\nu_j)$, is made when $\tau\ll T_1$ and $\tau\ll T_{12}$, the latter being the condition that the cross-relaxation time T_{12} due to spin flip between the two sites should be negligible. This method has been applied to study the jump rate between bonds of deuterons in KD_2PO_4 by Schmidt and Uehling.[3] The relation of jump rate with recovery time constant given in Appendix I of their paper exactly applies to the present case, and the recovery time constant$=\tau/2=1/2\nu_j$. In order to avoid the error due to possible nonlinearity in the observed signal amplitude, they used the following method. Three 90° pulses are applied in succession, the time interval being t_1 between the first and second pulses, and t_2 between the first and third. t_1 is varied while t_2 is fixed at a value $t_2 \gg \tau$. t_1 is so adjusted that the Bloch decay signals after the second and the third pulses are made to have equal height. Then τ is given by $t_1=(\ln 3)\tau$. We used this method, and also two 90° pulse sequence, where the signal height following the second pulse is compared with the first one to observe the exponential growth. The measurement was done with H_0 in the direction III shown in Fig. 1, where site 1 line is at the Larmor frequency and $\Delta\nu$ is about 150 kc/sec. In $Ba(ClO_3)_2D_2O$, lines of stationary water molecule are observed below -120°C, and this is well below the temperature of the T_1 minimum. Since quadrupole relaxation due to reorientation is a principal relaxation mechanism, and the quadrupole interaction is only a small perturbation to the Zeeman energy, the inequality $T_1 \gg \tau$ holds. Therefore, the direct measurement of jump rate is applicable below -120°C. At very low temperatures, however, T_1 gets so large that it is necessary to irradiate the crystal with γ ray to bring T_1 to the workable range. Thus after this treatment, T_1 measured at direction I is about 90 sec at liquid nitrogen temperature, and stays nearly constant up to the temperature where relaxation due to the motion becomes appreciable (~ -140°C). The observed recovery is found to be much faster than 90 sec except at liquid nitrogen temperature where it becomes comparable to 90 sec. With this sample, we can conclude that the condition $\tau \ll T_1$, T_{12} is valid down to -170°C since T_{12} should be nearly constant, and T_1 due to paramagnetic centers is also rather insensitive to temperature variation, whereas the observed recovery gets much longer at the liquid nitrogen temperature. To estimate τ at the liquid nitrogen temperature, the observed recovery curve is compared with the calculated one with various τ values assuming $T_1=90$ sec, same as in direction I. If τ of 5 min at liquid nitrogen temperature thus obtained is correct, a bend in the plot of $\log \nu_j$ *vs.* $1/T$ would show a departure from the Arrhenius equation, and indicate quantum mechanical tunnel effect. ν_j calculated from the tunnelling process shown in the figure suggests that such a bend is quite probable.

Since the lines are narrow while $\Delta\nu$, the separation between the lines of D_1 and D_2, is large, the cross-relaxation between D_1 and D_2 is probably ineffective. It should be definitely ineffective from the formalism of Bloembergen *et al.*[6] However, to get an experimental justification for excluding cross-relaxation process at liquid nitrogen temperature, we measured the recovery at the crystal orientation where $\Delta\nu$ is about 80 kc/sec. Unless the recovery rate changes drastically, the cross-relaxation could be neglected.*2 In this case the recovery at liquid nitrogen temperature is found to be shorter by a factor of about 3 than the other case. However, that this is not due to the cross-relaxation is seen from the fact that the recovery toward a full intensity is observed instead of one half as expected from the cross-relaxation process. This shortening of recovery can be understood as the T_1 diminution due to cross-relaxation to the Ba nuclei which have short T_1 due to a quadrupole interaction. Using a quadrupole coupling tensor for ^{135}Ba and ^{137}Ba by Nakamura and Enokiya[7] the transition frequencies of Ba in the present experiment are calculated. The result turned out that one of the transitions falls in fact almost at 10 Mc. The whole task for such an experiment is rather involved. Moreover, transition frequencies of Ba resonances depend in a complex manner on crystal orientation, and the Ba quadrupole coupling and its temperature dependence have been determined only at higher temperatures, which situation makes the estimation of exact transition frequencies in the present experiment difficult. For this reason no further experiment on this line is made.

Values of ν_j determined in the present work are to be compared with those from the line width change. In the following a revision of the previous treatment[1] of line width transition will be described.

A random motion of atoms has an effect both on the quadrupole splitting and on dipole structure. It would be possible to derive a reorientation rate by comparing the observed broadened spectra with the numerically calculated one at each particular case taking into account the effect of motion on both quadrupole and dipole interaction in an exact fashion according to the theory of motional broadening.[8] However, poor quality of the observed line shape prevents the analysis of detailed line shape, and also the fact that the observations have to be made at various orientations of the crystal (that is, various values of quadrupole and dipole interactions) which requires much

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*2 The authors are indebted to Professor C. P. Slichter for suggesting this measurement.

6) N. Bloembergen, S. Shapiro, P. S. Pershan and J. O. Artman, *Phys. Rev.*, **114**, 445 (1959).

7) S. Nakamura and H. Enokiya, *J. Phys. Soc. Japan*, **18**, 183 (1963).

8) A. Abragam, "The Principles of Nuclear Magnetism," Chapter X, Section II—IV, Oxford University Press, Oxford (1961).

too laborious calculations, this exact method seems to be impractical.

Generally signal-to-noise ratio of the broadened spectra is such that, 1) spectra can only be observed at the fast and slow exchange limits of the quadrupole broadening, 2) the only quantity which can be measured with a reasonable accuracy is the signal amplitude of the derivative curve between the points of maximum and minimum slopes of the absorption line. This signal amplitude will be denoted by S.

Since in general practice, one measures the line broadening where the quadrupole interaction is much larger than the dipole interaction the effect of motion upon the dipole width is relatively small (particularly so in the 180° flip of a water molecule where the intramolecular dipole interaction is unaffected by the motion). The change in dipole line width should therefore take place at the temperature range different from those of quadrupole structure. It may then be permissible to assume that the dipole width is invariant under the present condition of observation.

To derive an exact effect on quadrupole broadening it is, however, necessary to separate this effect from the dipole structure. Since S depends on the line width strongly (as the inverse square of the width if the dipole width is absent*[3]) the following procedure will be used.

A width between the maximum slopes, $\Delta\nu_{\mathrm{ms}0}$, and a signal intensity S_0 is defined at the point where the exchange motion is either sufficiently rapid or sufficiently slow so that practically no motional broadening is involved in the line shape.

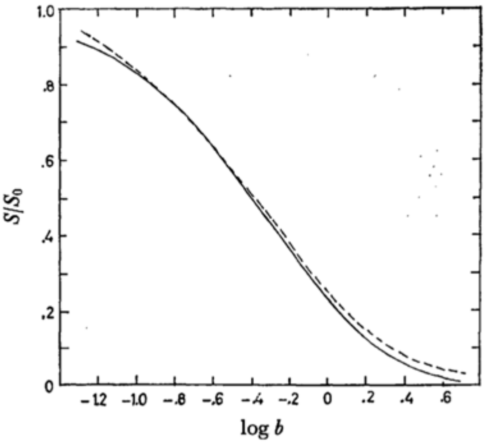

Fig. 4. Diminution of derivative signal intensity (S/S_0) due to broadening.
—— Gaussian line (half width $(\ln 2)^{1/2}$) broadened inhomogeneously by Lorentzian curve (half width b).
---- Lorentzian line (half width 1) broadened to half width $1+b$.

Numerical calculation of line shape is made, assuming a Gaussian dipole line shape (half maximum half width $(\ln 2)^{1/2}$) and each component of it is further broadened by a Lorentzian line shape of a given width (half maximum half width b). Then S/S_0 has a dependence on the line width parameter b as shown in Fig. 4. From the observed S/S_0, b is read off. $\Delta\nu_{\mathrm{M}}$ $(=1/(2\pi T_2{}')$, the half width due to motion) is obtained as,

$$\Delta\nu_{\mathrm{M}} = \Delta\nu_{\mathrm{ms}0} \times b/\sqrt{2},$$

a factor $1/\sqrt{2}$ coming from the normalization.

S and S_0 are obtained at different temperatures, and the signal height may therefore vary with temperature, according to various factors such as sensitivity of the instrument, the relaxation time, the Boltzmann factor, and the thermal noise, but difference between the temperatures of observation of S and S_0 is usually not so large to give serious effect.

If the original line is approximately Lorentzian with T_2 as in the case of certain paramagnetic substances, added breadth by motion can be separated by use of the similar curve also shown in Fig. 4, through the formula $\Delta\nu_{\mathrm{M}}=\Delta\nu_{\mathrm{ms}0}\times b\times 2\sqrt{3}$. $\Delta\nu_{\mathrm{M}}$ is related to the jump rate in the case of 180° flip of a water molecule as $\Delta\nu_{\mathrm{M}}=\nu_j/2\pi$ for the slow exchange limit, and $\Delta\nu_{\mathrm{M}}=(\pi/4)\times(\Delta\nu^2/\nu_j)$ for the fast exchange limit.

The above procedure is applied to the case of $\mathrm{Ba(ClO_3)_2D_2O}$. In Fig. 3 is shown the revised result including some added experimental points. The activation energy is 7.0 kcal slightly higher than the previous value, and the pre-exponential factor is 10^{14-15}.

As shown in Fig. 3, a satisfactory agreement is found among the experimental results of T_1, line width and jump rate, interpreted as due to random 180° flip of $\mathrm{D_2O}$ with a rate $\nu_j \propto \exp(-\Delta E/\boldsymbol{R}T)$, ΔE being 7 kcal/mol. Such a simple picture of the motion is probably true in case of this crystal. In this connection it is interesting to note that the good agreement of the frequency of twisting mode of $\mathrm{D_2O}$ derived from the recent neutron scattering experiment on this compound by Prask and Boutin[9] with those from ΔE with the assumption of cosine type potential.

Finally, it may safely be said that the present results give also a support to the reliability of deriving activation energy of the motion from the line width transition of quadrupole splitting by the procedure described above.

We are grateful to Assistant Professor Kiyoshi Kume of Tokyo Metropolitan University for many helpful comments for the construction of the pulse apparatus.

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*[3] Previous treatment (Ref. 1) is inadequate since $S/N \propto 1/\Delta\nu$ is assumed.

9) H. J. Prask and H. Boutin, *J. Chem. Phys.*, **45**, 699 (1966).