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Proton Magnetic Relaxation Study of Oxalic Acid Dihydrate

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Proton magnetic relaxation times T_1, $T_{1\rho}$, and T_{1D} were measured on a single crystal of α-form oxalic acid dihydrate in two modes: temperature dependence at one or two specific crystal orientations, and angular dependence at several temperatures. Results were compared with the calculation based on an isolated three proton system for the assumed modes of motions. The temperature dependence of T_1 and that of $T_{1\rho}$ and T_{1D} in the low temperature range are reasonably accounted for by the 180°-flip of the water molecule. The activation energy for the motion of 43.6 kJ mol^{-1} is obtained. $T_{1\rho}$ and T_{1D} above about 35 °C decreased as the temperature was raised. The comparison of the observed results in this temperature range with the calculated ones suggests that there is exchange motion among the three spins. An activation energy for this motion of 80.8 kJ mol^{-1} is obtained. This three spin exchange motion may be considered as a combination of a jump of carboxyl proton to a higher potential trough corresponding to the ionic configuration and the three-fold reorientation of the hydronium ion thus formed.

Because nuclear magnetic relaxation in a low field can be very effectively caused by a slow nuclear motion, measurement of $T_{1\rho}$ is an important means to study such motion. In the course of $T_{1\rho}$ and T_{1D} measurements on powdered samples of oxalic acid dihydrate, we found a decrease in these relaxation times with temperature which cannot be accounted for by the familiar 180°-flip of the water molecule of hydration. Our primary purpose in this paper is to elucidate the motion responsible for the above finding from the relaxation time study on single crystals.

We will describe first the calculation of relaxation times for assumed modes of motion, then experimental procedures, results of temperature and magnetic-field-direction dependence of relaxation times, and comparison of these results with the calculated values.

Calculation of the Relaxation Rates

The crystal of α-form oxalic acid dihydrate is monoclinic, and its structure is accurately known.[1] Hydrogen atoms in this crystal are incorporated in a hydrogen bond network, as shown in Fig. 1. For simplicity, calculations of relaxation rates are made for an isolated three spin system of H_1, H_2, and H_3. The atomic positions obtained from neutron diffraction studies are used.[2] For proton resonance, an isolated three spin system may be a reasonable approximation, because inter-proton distances within the three spin group are 2.05, 2.12, and 1.53 Å, while those between the adjacent groups are 3 Å or greater, except the $H_3 \cdots H_3'$ value of 2.78 Å.

Calculation of Relaxation Rates due to 180°-Flip of Water Molecule. *Relaxation Rate in the Laboratory Frame*: Along the line of Look and Lowe's standard treatment,[3] the relaxation rate T_1^{-1} due to random modulation of the dipole interaction between the carboxyl proton and two protons of a water molecule executing 180°-flip motion with a probability w_I can easily be calculated as

$$T_1^{-1} = \frac{3}{4}\gamma^4\hbar^2\left\{\frac{\tau_I}{1+\omega_0^2\tau_I^2}[|\chi_{12}^{(1)}|^2+|\chi_{13}^{(1)}|^2 -2\mathrm{Re}(\chi_{12}^{(1)*}\chi_{13}^{(1)})]+\frac{\tau_I}{1+4\omega_0^2\tau_I^2} \times[|\chi_{12}^{(2)}|^2+|\chi_{13}^{(2)}|^2-2\mathrm{Re}(\chi_{12}^{(2)*}\chi_{13}^{(2)})]\right\} \quad (1)$$

where $\tau_I = 1/2w_I$ defines the correlation time of the motion. χ's are given by

$$\left.\begin{aligned}\chi_{\alpha\beta}^{(1)} &= r_{\alpha\beta}^{-3}\sin\theta_{\alpha\beta}\cos\theta_{\alpha\beta}\exp(-i\varphi_{\alpha\beta}),\\ \chi_{\alpha\beta}^{(2)} &= r_{\alpha\beta}^{-3}\sin^2\theta_{\alpha\beta}\exp(-2i\varphi_{\alpha\beta}),\end{aligned}\right\} \quad (2)$$

where $r_{\alpha\beta}$, $\theta_{\alpha\beta}$, and $\varphi_{\alpha\beta}$ are the polar coordinates of a vector joining site α to site β in the coordinate system with its polar axis along the static field H_0, site 1 for carboxyl proton, sites 2 and 3 for those of a water molecule. ω_0 is the Larmor angular frequency and other symbols have their usual meanings.

Relaxation Rate in the Rotating Frame: In a same manner $T_{1\rho}^{-1}$ can be calculated for the present case.[3] Since $T_{1\rho} \ll T_1$ in the present experiment, we retain only the dominant terms in the expression of $T_{1\rho}^{-1}$ involving ω_1 and neglect those terms involving ω_0 and $2\omega_0$, where $\omega_1 = \gamma H_1$. $T_{1\rho}^{-1}$ is then given by

$$T_{1\rho}^{-1} = 3\gamma^4\hbar^2\frac{\tau_I}{1+4\omega_1^2\tau_I^2}d_0^2, \quad (3)$$

where

$$d_0 = \frac{1}{4}(\chi_{12}^{(0)} - \chi_{13}^{(0)}), \quad (4)$$

with

$$\chi_{\alpha\beta}^{(0)} = r_{\alpha\beta}^{-3}(1-3\cos^2\theta_{\alpha\beta}). \quad (5)$$

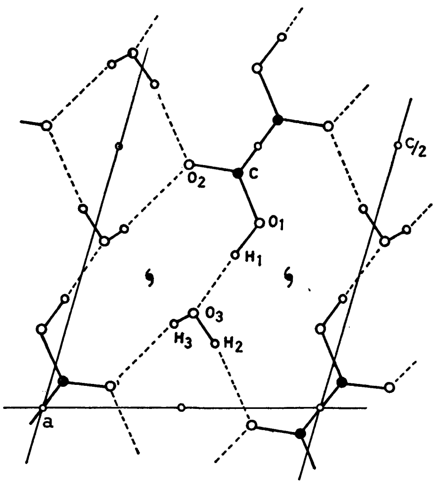


Fig. 1. Crystal structure of α-oxalic acid dihydrate: b axis projection.

When $\omega_1\tau_I \ll 1$, we have

$$T_{1\rho}^{-1} = 3\gamma^4\hbar^2\tau_I d_0^2. \tag{6}$$

Relaxation Rate in the Dipole Field in the Rotating Frame: Because under the conditions of the present measurement of T_{1D}, τ_I is always much smaller than the Larmor period in the local field, we only consider the case of the short correlation time limit. We start from the general perturbation equation of relaxation rate[4] in which the dipole Hamiltonian in the rotating frame is divided into two parts: $\mathscr{H}_{d_0}$, the motion averaged part, and $\mathscr{H}_{d_1}$, the time-varying part (perturbation term).

$$\begin{aligned} T_{1D}^{-1} = &-[2\hbar^2\mathrm{Tr}\{(\mathscr{H}_{d_0})^2\}]^{-1} \\ &\times \int_{-\infty}^{+\infty} \mathrm{d}\tau \mathrm{Tr}\{\langle[\mathscr{H}_{d_1}^*(\tau), \mathscr{H}_{d_0}] \\ &\times [\mathscr{H}_{d_1}^*(0), \mathscr{H}_{d_0}]\rangle\}, \end{aligned} \tag{7}$$

where

$$\mathscr{H}_{d_0} = a_0(D_{IJ}+D_{IK}) + b_0 D_{JK}, \tag{8}$$

$$\mathscr{H}_{d_1} = d(t)(D_{IJ}-D_{IK}), \tag{9}$$

$$\mathscr{H}_{d_1}^*(t) = \exp\left(-i\frac{\mathscr{H}_{d_0}}{\hbar}t\right)\mathscr{H}_{d_1}(t)\exp\left(i\frac{\mathscr{H}_{d_0}}{\hbar}t\right), \tag{10}$$

and

$$\left.\begin{aligned} a_0 &= \frac{1}{4}(\chi_{12}^{(0)} + \chi_{13}^{(0)}), \\ b_0 &= \frac{1}{2}\chi_{23}^{(0)}. \end{aligned}\right\} \tag{11}$$

D_{IJ} *etc.* are of the form,

$$D_{IJ} = \gamma^2\hbar^2(3I_Z J_Z - \boldsymbol{I}\cdot\boldsymbol{J}). \tag{12}$$

I is a spin at site 1, J and K are those flipping between sites 2 and 3, and

$d(t) = d_0$ if J spin is in site 2 at time t,
$= -d_0$ if J spin is in site 3 at time t.

In the short correlation time limit it is permissible to replace $\exp\left(i\frac{\mathscr{H}_{d_0}}{\hbar}t\right)$ in Eq. 10 by 1. We then have

$$\begin{aligned} T_{1D}^{-1} = &-[2\hbar^2\mathrm{Tr}\{(\mathscr{H}_{d_0})\}^2]^{-1}\mathrm{Tr}\{[(D_{IJ}-D_{IK}), \mathscr{H}_{d_0}]^2\} \\ &\times \int_{-\infty}^{+\infty}\langle d(\tau)d(0)\rangle \mathrm{d}t. \end{aligned} \tag{13}$$

The integral gives $2\tau_I d_0^2$. Traces in Eq. 13 are evaluated straightforwardly, leading to the final expression

$$T_{1D}^{-1} = \frac{3}{2}\gamma^4\hbar^2\tau_I d_0^2, \tag{14}$$

which is 1/2 the $T_{1\rho}^{-1}$ of Eq. 6.

It is noted here that when $\mathscr{H}_{d_0}+\mathscr{H}_Z$ is used instead of $\mathscr{H}_{d_0}$ in Eq. 7, where $\mathscr{H}_Z = -\gamma\hbar H_1(I_x+J_x+K_x)$ is the effective Zeeman Hamiltonian in the rotating frame, a straightforward calculation similar to the above yields

$$T_{1\rho}^{-1} = \frac{3}{2}\gamma^4\hbar^2\tau_I d_0^2(H_L^2+2H_1^2)/(H_L^2+H_1^2), \tag{15}$$

where the local field in the rotating frame H_L is by definition

$$H_L^2 = [3/N\gamma^2\hbar^2 I(I+1)(2I+1)^N]\mathrm{Tr}\{(\mathscr{H}_{d_0})^2\},$$

and expressed in this case as

$$H_L^2 = \frac{1}{2}\gamma^2\hbar^2(2a_0^2+b_0^2). \tag{16}$$

Equations 6 and 14 are the two limiting cases of Eq. 15 for $H_L \ll H_1$ and $H_1 \to 0$, respectively.

Relaxation due to Slow Motional Processes. Relaxation Rate in the Rotating Frame due to Exchange between Carboxyl and Water Protons, or a Three-fold Reorientation: In the present work, in the temperature range where relaxation effects of slow motion appear, we consider the situation where exchange between H_1 and H_2 or H_3 occurs. This may be viewed as a slow three-fold reorientation in addition to the rapid flip motion of the water molecule. We will discuss the actual mode of motion later.

We assume that exchange occurs among the spin arrangements i, ii, and iii with a probability w_{II}.

	site 1	sites 2 and 3
i	I	J, K
ii	J	K, I
iii	K	I, J

Look and Lowe's treatment[3] is again followed and $T_{1\rho}^{-1}$ is expressed by

$$T_{1\rho}^{-1} = \frac{2}{3}\gamma^4\hbar^2(a_0-b_0)^2\frac{\tau_{II}}{1+(4\omega_1\tau_{II}/3)^2}, \tag{17}$$

or

$$T_{1\rho}^{-1} = \frac{3}{8}\gamma^4\hbar^2\frac{(a_0-b_0)^2}{\omega_1^2}\cdot\frac{1}{\tau_{II}} \tag{18}$$

in the limit of slow motion ($\omega_1\tau_{II} \gg 1$). Here we take the correlation time of the exchange motion as $\tau_{II} = 1/w_{II}$.

When $T_{1\rho}^{-1}$ of Eq. 18 is compared with T_{1D}^{-1} of Eq. 24 to be given in the next section, we have

$$T_{1\rho}^{-1}/T_{1D}^{-1} = \frac{3}{4}H_L^2/H_1^2. \tag{19}$$

According to Slichter and Ailion,[5] for the relaxation by slow motion

$$T_{1\rho}^{-1}/T_{1D}^{-1} = H_L^2/(H_1^2+H_L^2), \tag{20}$$

when H_1 is comparable to or less than H_L, and

$$T_{1\rho}^{-1}/T_{1D}^{-1} = \frac{3}{4}H_L^2\bigg/\left(H_1^2+\frac{3}{4}H_L^2\right), \tag{21}$$

when H_1 is sufficiently greater than H_L so that cross-relaxation between the Zeeman and the secular part of the dipole energy in the rotating frame can be neglected. In the present experiment the largest H_L amounts to ≈3.7 G, while the H_1 used is 6.2 G. Rigorously, $T_{1\rho}^{-1}$ of Eq. 18 needs adjustment for H_L due to the relation given by Eq. 20 or 21. These correction factors, however, turn out to be small (estimated to be not more than 20% in the worst case) and are therefore neglected.

Relaxation Rate in the Dipole Field in the Rotating Frame due to Slow Exchange between the Carboxyl and Water Protons: T_{1D}^{-1} in the present case can be given by[5]

$$T_{1D}^{-1} = (1-p)\frac{1}{\tau_{II}}, \tag{22}$$

with

$$(1-p) = \sum_{q,s} A_q(A_q-A_s)/\sum_{q,s} A_q^2, \tag{23}$$

where A's are the lattice part of the dipole interaction (a_0 between sites 1 and 2 or 3, and b_0 between sites

2 and 3), q denotes a spin pair before the reorientational jump and s denotes that after the jump, and the summation is carried out over all possible processes and possible spin pairs. For each jump from one of the arrangements, i, ii, and iii, to another the numerator of Eq. 23 will be given by $(a_0-b_0)^2$ because in the process of i→ii, for instance, one of the three spin pairs (IJ) makes no contribution to it while for the others, (IK) has $a_0(a_0-b_0)$ and (JK) has $b_0(b_0-a_0)$. Each jump contribution to the denominator of Eq. 23 is simply $2a_0^2+b_0^2$; thus we have

$$T_{1D}^{-1} = \frac{(a_0-b_0)^2}{(2a_0^2+b_0^2)}\cdot\frac{1}{\tau_{II}}. \tag{24}$$

Relaxation Rate due to Diffusion. Diffusion of water molecules or carboxyl protons may be another motion which is likely to exist at high temperatures. Here we consider the following two cases of diffusional jump (the three-spin system is considered as before):

Case 1: all dipole interactions are destroyed.

Case 2: dipole interactions between carboxyl protons and water protons are destroyed but that within the water molecule is retained. As will be described later, these diffusion mechanisms do not give satisfactory angular dependence of relaxation rates; thus only the proportionality relations resulting from these mechanisms, which are necessary for later discussion, will be presented.

When an expression for relaxation rate by slow motion similar to Eq. 22 is applied, we have for Case 1,

$$T_{1D}^{-1} \propto \frac{2a_0^2+b_0^2}{2a_0^2+b_0^2}\cdot\frac{1}{\tau_d} = \frac{1}{\tau_d}, \tag{25}$$

independent of the field direction, because the entire dipole interaction is destroyed by a diffusional jump. τ_d denotes the correlation time for diffusion. From the relation of $T_{1\rho}^{-1}$ and T_{1D}^{-1} mentioned before we can expect to have an approximate relation:

$$T_{1\rho}^{-1} \propto \frac{2a_0^2+b_0^2}{\omega_1^2}\cdot\frac{1}{\tau_d}. \tag{26}$$

A similar argument for Case 2 leads to

$$T_{1D}^{-1} \propto \frac{2a_0^2}{2a_0^2+b_0^2}\cdot\frac{1}{\tau_d}, \tag{27}$$

and

$$T_{1\rho}^{-1} \propto \frac{a_0^2}{\omega_1^2}\cdot\frac{1}{\tau_d}. \tag{28}$$

Experimental

Single crystals of α-form oxalic acid dihydrate $(COOH)_2\cdot 2H_2O$ are grown by slowly cooling a saturated aqueous solution. The crystal is mounted on a teflon holder which fits in the probe head. Alignment of the crystalline axes in the probe head is made visually. The alignment error is estimated to be less than 2°. Measurements are made at the Larmor frequency of 30 MHz. A single coil coupling arrangement is used. Recovery time of the receiving system is about 8 μs. T_1 is measured by 90° pulse comb-90° pulse sequence. For rotating frame experiments the spin locking state is prepared by turning on H_1 slowly (in a time of ≈ 1 ms), and at the same time the initially offset rf frequency is swept to the exact resonance.

Accuracy of the relaxation time measurement depends strongly on the appearance of free induction decay signals. In most unfavorable cases the error in the relaxation time probably amounts to 20%, but in most cases the estimated error is 10% or less.

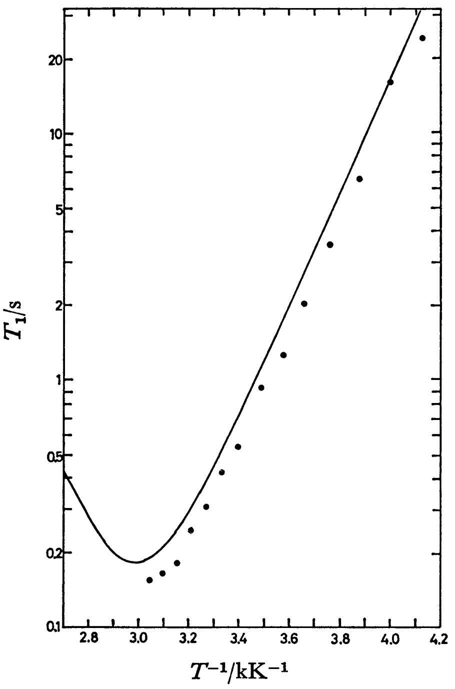


Fig. 2. Temperature dependence of T_1 at $\varphi_H=172°$, φ_H being defined in the text.

Temperature control below room temperature is made by regulation of intermittent flushing of liquid nitrogen directly onto the thick-wall copper shield casing of the sample coil.[6)]

Results

T_1. Temperature dependence of T_1 as shown in Fig. 2 is measured at $\varphi_H=172°$, where φ_H denotes the angle of rotation of H_0 from the a axis toward the c axis in the ac plane. To avoid damage of the sample due to dehydration the measurement is not carried out to the point of T_1 minimum. However, from the appearance of Fig. 2, we estimate this to occur at about 61 °C. The theoretical T_1 curve of Eq. 1 with τ_I of Arrhenius form is fit to the observed one in the following two respects: (1) the slope of log T_1 against $1/T$, and (2) the temperature of the T_1 minimum. The following parameters are obtained:

$$\left.\begin{aligned} \tau_I &= 4.37\times 10^{-16}\exp(\Delta E_I/RT), \\ \Delta E_I &= 43.6\,\mathrm{kJ\,mol^{-1}}. \end{aligned}\right\} \tag{29}$$

The calculated T_1 from Eq. 1, also shown in Fig. 2, is in satisfactory agreement with the observed value, considering that only isolated three-proton system is taken into account.

In Fig. 3, T_1^{-1} at 1.4 °C with H_0 in the ac plane, and that with H_0 in the b axis are compared with the theoretical curve with τ_I of Eq. 29. The agreement is generally satisfactory.

$T_{1\rho}$ and T_{1D}. The temperature dependence of $T_{1\rho}$ and T_{1D} is measured at $\varphi_H=47°$ and 172° where the free induction decay signal is not exceedingly short,

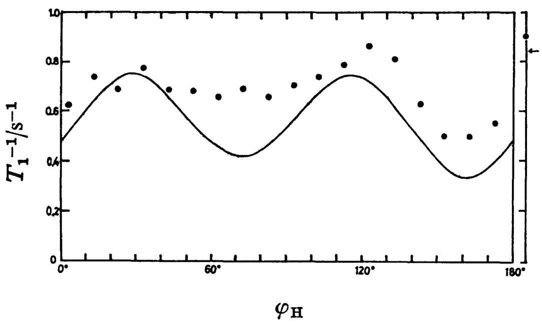


Fig. 3. Angular dependence of T^{-1} at 1.4 °C. The calculated curve from Eq. 1 is also shown. The value with H_0 along the b axis is shown at the far-right of the figure; an arrow indicates a calculated value.

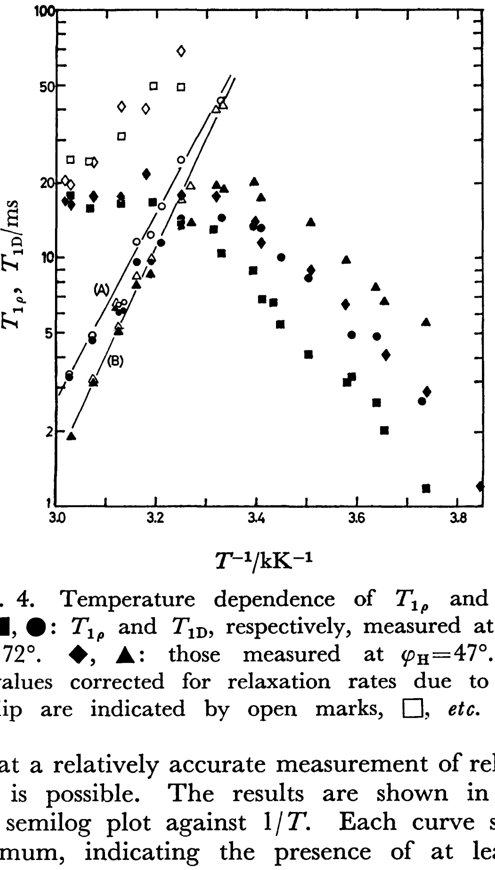


Fig. 4. Temperature dependence of $T_{1\rho}$ and T_{1D}. ■, ●: $T_{1\rho}$ and T_{1D}, respectively, measured at $\varphi_H = 172°$. ◆, ▲: those measured at $\varphi_H = 47°$. The values corrected for relaxation rates due to 180°-flip are indicated by open marks, □, *etc.*

so that a relatively accurate measurement of relaxation time is possible. The results are shown in Fig. 4 as a semilog plot against $1/T$. Each curve shows a maximum, indicating the presence of at least two different modes of motion.

Positively Temperature Dependent Range. The slopes of the curves in this range are nearly the same as that of Fig. 2. This indicates that the relaxation times are governed by the fast 180°-flip of water molecule ($\tau_I \gamma H_1 \ll 1$ or $\tau_I \gamma H_L \ll 1$). The ΔE_I values derived from $T_{1\rho}$, ≈ 47 kJ mol^{-1} ($\varphi_H = 172°$), and ≈ 41 kJ mol^{-1} ($\varphi_H = 47°$) are in satisfactory agreement with ΔE_I of Eq. 29. Calculated $T_{1\rho}$ and T_{1D} from Eqs. 6 and 14 with τ_I from Eq. 28 are a factor of about 1.5 greater than the observed values of $\varphi_H = 172°$ and a factor of about 2.2 greater than those of $\varphi_H = 47°$.

The angular dependences of $T_{1\rho}^{-1}$ and T_{1D}^{-1} measured at 0 °C are shown in Fig. 5. Calculated angular dependences due to fast 180°-flip from Eqs. 6 and 14 with Eq. 28 are also shown in the same figure.

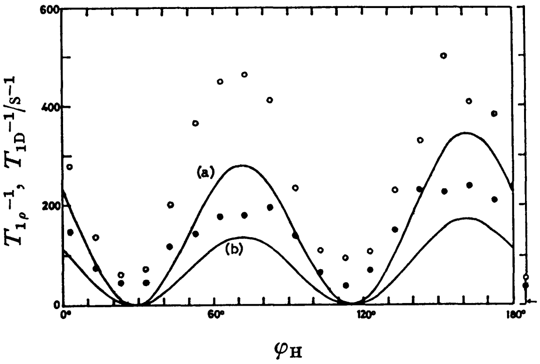


Fig. 5. Angular dependence of $T_{1\rho}^{-1}$(○) and T_{1D}^{-1} (●) at 0 °C. (a): $T_{1\rho}^{-1}$ from Eq. 6, (b): T_{1D}^{-1} from Eq. 14. Values at the b axis are presented at the far-right (calculated $T_{1\rho}^{-1}$ value indicated by an arrow).

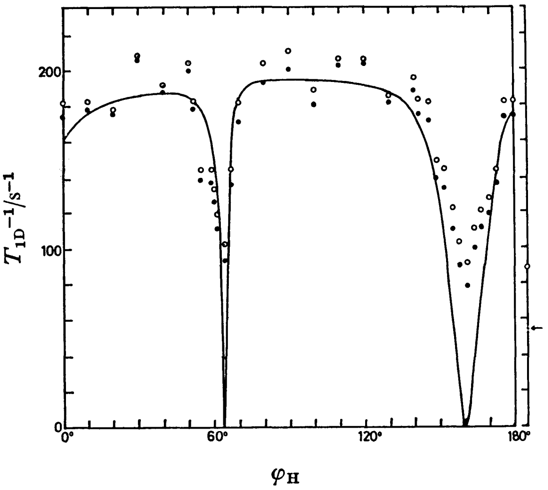


Fig. 6. Angular dependence of T_{1D}^{-1} at 47 °C (solid circles) with H_0 in the ac plane and along the b axis, the latter being shown at the far-right of the figure. Open circles are those corrected for contribution from 180°-flip motion. Calculated curve from Eq. 24 is also shown.

The agreement with the experimental values is generally satisfactory. Discrepancies may be partly ascribed to the assumption of the isolated three spin system.[7]

Negatively Temperature Dependent Range. At temperatures above the T_{1D} maximum, relaxation rates due to the high-temperature-mode motion are estimated by subtracting the contribution due to the 180°-flip motion of water molecule from the observed relaxation rates. The latter values are estimated by extrapolating relaxation rates from the low temperature values, by assuming the activation energy determined above. The corrected values are also shown in Fig. 4. An average value of activation energy for the high-temperature-mode motion of 80.8 kJ mol^{-1} is obtained from lines (A) and (B) fit to the temperature dependence of T_{1D} of Fig. 4. The same trend at high temperatures is apparent for both $T_{1\rho}$ and T_{1D} but the high temperature mode motion has less effect on $T_{1\rho}$. Therefore, $T_{1\rho}$ data are not used for deriving the activation energy.

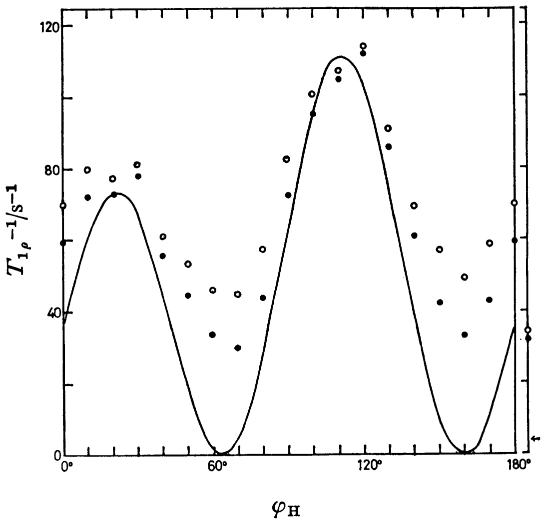


Fig. 7. Angular dependence of $T_{1\rho}^{-1}$ at 55.3 °C (solid circles) with H_0 in the ac plane and along the b axis. Open circles are values corrected for contribution from 180°-flip motion. Calculated curve from Eq. 18 is also shown.

To understand the mode of motion responsible for the high temperature relaxation, angular dependences of T_{1D} at 47 °C and $T_{1\rho}$ at 55.3 °C are measured. These relaxation rates are shown in Figs. 6 and 7. Also shown in these figure are the rates corrected for the small contribution due to the 180°-flip. The amounts of correction at these temperatures are assumed to be the fraction theoretically expected from the temperature variation in correlation time of the relaxation rates of Fig. 5 at 0 °C.

Theoretical curves of the angular dependence of relaxation rates due to carboxyl–water proton exchange motion from Eqs. 18 and 24 are also shown in Figs. 6 and 7. Numerical values of τ_{II} used in drawing these curves are to be described later. Except for the field direction in which the second moment of the three spin system becomes very small and where such an approximation is by no means a good one, the agreement of angular dependence between observed T_{1D}^{-1} and the one calculated for the three spin exchange motion appears excellent. The observed angular dependence of $T_{1\rho}^{-1}$ in Fig. 7 is also in satisfactory agreement with the curve for the exchange mechanism.

Before concluding that the exchange mechanism is the high temperature motional mode of this crystal, however, we need to examine whether a diffusion mechanism can also explain the observed results. The angular dependences of diffusion mechanisms expected from relations (25)—(28) are shown in Fig. 8. Diffusional motion of Case 2 can be definitely eliminated from the appearance of the curve. As for Case 1, though T_{1D}^{-1} from (25), which is angular independent, disagrees with the observed curve of Fig. 6, two dips on the curve which are located around the second moment minimum might be a consequence of inappropriate assumption of the isolated three spin system at these angles. Unfortunately, this cannot be decided by the angular dependence of $T_{1\rho}^{-1}$, because the curves of Fig. 7 and Fig. 8 (d) have similar appearance.

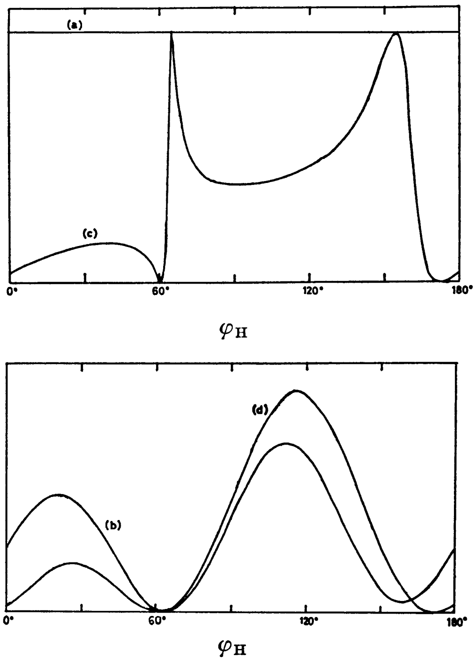


Fig. 8. Angular dependence of T_{1D}^{-1} and $T_{1\rho}^{-1}$, in the ac plane from assumed diffusional mechanisms. (a) and (b) represent T_{1D}^{-1} and $T_{1\rho}^{-1}$, respectively, for Case 1 ((25) and (27)). (c) and (d) represent T_{1D}^{-1} and $T_{1\rho}^{-1}$, respectively, for Case 2 ((26) and (28)). Each curve is drawn to arbitrary scale.

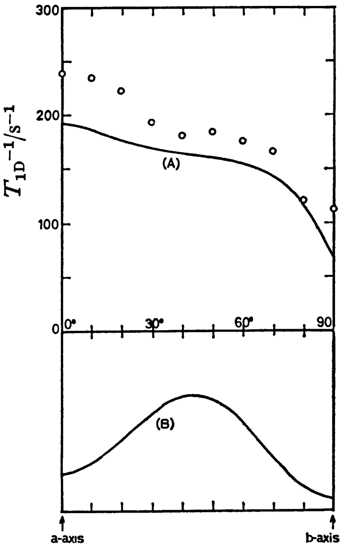


Fig. 9. T_{1D}^{-1} at 49 °C as H_0 is rotated from the a to b axis. (A): Calculated curve from Eq. 24. (B): calculated angular dependence of second moment (scale arbitrary); this curve is to show no extremely small values of H_L is present in these directions.

In order to draw a definite conclusion to this problem, the angular dependence of T_{1D} with H_0 in the ab plane is measured. In this case the three spin system has two different orientations with respect to H_0, and T_{1D}^{-1} is calculated as the mean value for these two orientations, as shown in Fig. 9. It is noted that the theoretical T_{1D}^{-1} due to three spin exchange motion decreases steadily as the field is rotated from the a axis to the b axis. The observed values of T_{1D}^{-1}, also shown in Fig. 9, are in satisfactory agreement with the curve calculated for the exchange mechanism,[8] but they disagree with the diffusional motion of Case 1, where a constant value over the whole range is expected. A diffusion mechanism is therefore excluded.

From the maximum value of T_{1D}^{-1} at 47 °C of Fig. 6, $\tau_{II}=7.7$ ms is obtained using Eq. 24. With this τ_{II} and the activation energy obtained above, we have

$$\left.\begin{aligned} \tau_{II} &= 5.3 \times 10^{-16} \exp(\Delta E_{II}/RT), \\ \Delta E_{II} &= 80.8\,\text{kJ mol}^{-1}. \end{aligned}\right\} \qquad (30)$$

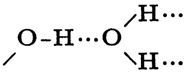
Similarly, from the maximum value of $T_{1\rho}^{-1}$ at 55.3 °C of Fig. 7, $\tau_{II}=2.8$ ms is obtained using Eq. 18; this is in fair agreement with 3.5 ms at that temperature from Eq. 30.

Discussion

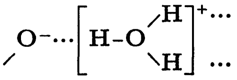
T_1 and the low temperature part of $T_{1\rho}$ and T_{1D} are consistently explained by a 180°-flip motion of water molecule. The activation energy for this motion has been obtained from the temperature dependence of T_1 of the deuteron in the α-form $(COOD)_2 \cdot 2D_2O$ crystal to be 9.7 kcal mol^{-1} (=40.6 kJ mol^{-1}).[9] There is a small difference in ΔE_I of the previous report from the present result; this may be ascribed to experimental error rather than indicating an isotope effect.[10]

While relaxation rates in the rotating frame are most sensitive to slow motion at $H_1 \rightarrow 0$, for a rapid motion this is not the case. As seen in Eqs. 6 and 14, T_{1D} is twice the $T_{1\rho}$ in the case of rapid two-fold reorientation.[11] The relation may be utilized to detect slow motion in the presence of rapid reorientation, for $T_{1D}/T_{1\rho}$ may be a sensitive measure of additional slow motional processes.

The case dealt with in the present study revealed an interesting three spin exchange motion in a system in which H_3O^+ is not formed. It seems more reasonable to consider this motion as involving the following excited configuration rather than a simple three-fold reorientation. The system in the ground configuration (I) is first excited to the excited configuration (II),



(I)



(II)

followed by a three-fold reorientation of H_3O^+ in that state, and then it returns to (I). Schematic illustration of the potential curve of the system is shown in Fig. 10. The observed ΔE_{II} may be interpreted as the sum of E_1+E_3 if $E_2 \leq E_3$, or interpreted as E_1+E_2 if $E_2 > E_3$; in the latter case the jump of the carboxyl proton to the upper state and the three-fold reorientation take place in one step. The activation energy for the three-fold reorientation of H_3O^+ is reported to be 4.82 kcal mol^{-1} (=20.17 kJ mol^{-1}) in H_3O^+-ClO_4^-,[12] and that of 34 kJ mol^{-1} is obtained for $H_3O^+HSO_4^-$ from our T_1 measurement.[13] Though the interpretation of the energy relations given here is very approximate, with E_3 in the range of activation energy of H_3O^+ reorientation quoted above, a reasonable estimate of the upper limit of E_1 may be around 60 kJ mol^{-1}.

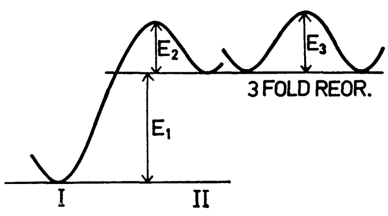


Fig. 10. Schematic illustration of the potential curves for water and carboxyl proton exchange motion.

The mechanism of motion proposed above involves jumps between unequal levels of the carboxyl proton. Usually in a case like this the motion is relatively ineffective for relaxation due to the short residence time in the less stable site.[14] In the present case, however, the carboxyl proton which moved to the high energy site can exchange position with the water protons by the three-fold reorientation and therefore the whole sequence can provide an efficient mechanism for relaxation.[15]

From the positive temperature dependence of the deuteron quadrupole coupling of carboxyl deuteron in deuterated oxalic acid dihydrate, a weakening of the hydrogen bond with temperature is suggested.[9] If this is the case it would result in an increase in the activation energy ΔE_{II} with temperature. However, if such an effect is taken into consideration, the resulting pre-exponential factor, τ_{II}^0, becomes unreasonably small. For instance, a linear temperature dependence of ΔE_{II} of only 4.2 kJ mol^{-1}/100 °C leads to ΔE_{II} at 350 K of 88 kJ mol^{-1} and τ_{II}^0 of 10^{-17}. Though there seems to be thus some incongruity between the previous deuteron resonance result and the present work, for which at the moment no explanation is available, we conclude that ΔE_{II} of Eq. 30 is substantially correct and that the positive temperature dependence in ΔE_{II}, if it exists, is not large.

The chemical shift of oxalic acid dihydrate at room temperature has been measured by high resolution NMR in solids.[16] Because the chemical shift spectrum is also sensitive to slow motional processes, it is hoped that such study will be extended to higher temperatures to see if supporting results can be obtained.

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7) For the calculation of $T_{1\rho}^{-1}$, Eq. 6 is used throughout, and no correction (Eq. 15) due to nonvanishing H_L is made. In directions where $T_{1\rho}^{-1}$ becomes large, H_L is relatively

small, and the theoretical curve is not greatly influenced by this correction.

8) Some discrepancy of theoretical and observed T_{1D}^{-1} is seen in the vicinity of the a axis direction. This might be due to a small error in crystal orientation, because crystal setting in this case was more difficult than in the case of the b axis rotation. Therefore, theoretical curves for up to 10° misalignment in the a axis were also examined and found not to affect the above conclusion.

9) T. Chiba, *Bull. Chem. Soc. Jpn.*, **44**, 1703 (1971).

10) We calculated the deuteron T_1 at the experimental conditions of the previous measurement, using the quadrupole coupling tensor and τ_I of Eq. 29. The calculation reproduced the measured values rather satisfactorily.

11) The same relation can be seen to hold for rapid reorientation of an isolated three-spin system (T. Chiba, unpublished).

12) D. E. O'Reilly, E. M. Peterson, and J. M. Williams, *J. Chem. Phys.*, **54**, 96 (1971).

13) T. Chiba, unpublished.

14) D. C. Look and I. J. Lowe, *J. Chem. Phys.*, **44**, 3437 (1966).

15) A case somewhat like the present one is found in the work of D. E. O'Reilly *et al.* on chloroauric acid tetrahydrate [*J. Chem. Phys.*, **55**, 5629 (1971)]. Here the proton motion in $(H_5O_2)^+$ of the jump between symmetric double minimum equilibrium positions plus hydronium reorientation is treated.

16) S. Sagnowski, S. Aravamudhan, and U. Haeberlen, *J. Chem. Phys.*, **66**, 4697 (1977), and Refs. 1 and 2 quoted therein.