

# Proton Spin–Lattice Relaxation in Hexagonal Ice

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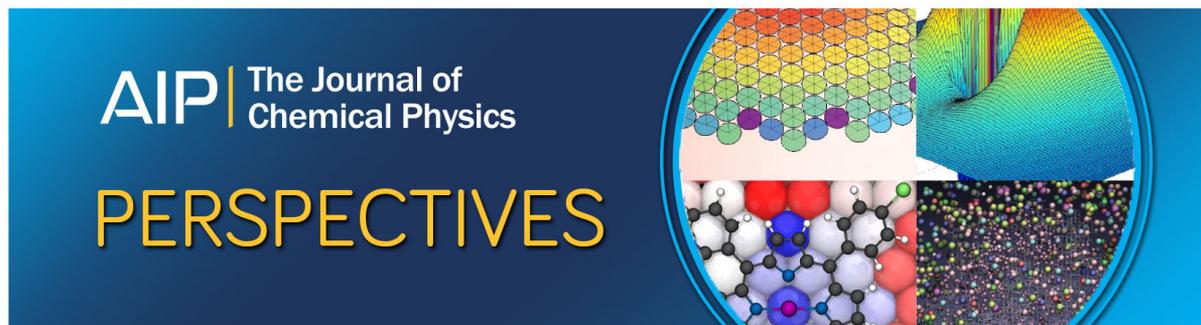
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conflicting experimental results as to the relationship between the proton hfs and the carbon-13 hfs.<sup>14</sup> It is imaginable that perturbations of the  $A_2''$  vibrational mode as well as other modes at low values of  $\theta$  due to surface effects could be responsible for the observed low-temperature decrease in the carbon-13 hfs.

## VI. CONCLUSIONS

The theory of Schrader (I) was developed assuming the methyl radical to be planar and completely free of any surface or matrix interactions. The general trends observed in this study substantiate the theory. Most of the deviations from theory mentioned in Secs. IV and V can be explained in terms of surface interactions except those noticed at higher temperatures. It is probable that matrix effects are of some importance and, therefore, they may have to be included in the development of a theory regarding temperature dependences of hyperfine splittings.

<sup>14</sup> R. W. Fessenden, *J. Phys. Chem.* **71**, 74 (1967).

Further temperature and kinetic ESR studies are in progress in this laboratory in which the effect of changing the chemical composition of the surface of porous glass is being evaluated. It is hoped that information regarding surface effects and trapping sites will be gained. It may be possible to obtain a surface by this method which will exhibit very small interactions with radicals trapped on it. This surface would be of value in checking the theories pertaining to the temperature dependence of hyperfine interactions in free radicals.

## ACKNOWLEDGMENTS

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## Proton Spin-Lattice Relaxation in Hexagonal Ice\* · †

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(Received 27 September 1967)

The results of measurements of the proton spin-lattice relaxation time  $T_1$  in ice are reported. The ice samples were single crystals grown by zone refining at atmospheric pressure. The measured activation energy for the  $T_1$  process is  $14.1 \pm 0.1$  kcal/mole. No anisotropy of  $T_1$  is observed. A theoretical calculation of  $T_1$  is presented, from which molecular displacement times are deduced.

## INTRODUCTION

The atomic and molecular motions in hexagonal ice have been extensively studied by many measuring techniques. Among these are dielectric relaxation,<sup>1,2</sup> electrical conductivity,<sup>3</sup> diffusion,<sup>4</sup> and proton magnetic resonance.<sup>5,6</sup> Each of these measuring techniques is sensitive to a different aspect of atomic and molecular motion, and they are all needed to gain a comprehensive

picture of the internal motions in ice. The models developed from these studies have become increasingly complex.<sup>7,8</sup>

The proton spin-lattice relaxation time measurements by Kume<sup>5</sup> were carried out on polycrystalline ice and used a continuous-wave nuclear magnetic resonance absorption technique. It is known that the internal motions in ice are strongly influenced by minute amounts of impurities,<sup>9</sup> so it seemed desirable to repeat these measurements on high-purity single crystals of ice obtained by zone-refining techniques. These proton spin-lattice relaxation time ( $T_1$ ) measurements have been carried out by pulsed nuclear magnetic resonance techniques. This is considered to be a more accurate and direct way of measuring the absolute value of  $T_1$ . Our interest in this problem has also been spurred by the possibility of finding an orientation dependence of  $T_1$  corresponding to a reported dielectric effect.<sup>1</sup>

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<sup>6</sup> G. J. Krüger, Ph.D. thesis, Technischen Hochschule, Stuttgart, Germany, 1961.

<sup>7</sup> A. Steinemann and H. Gränicher, *Helv. Phys. Acta* **30**, 553 (1957).

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<sup>9</sup> C. P. Smyth and C. S. Hitchcock, *J. Am. Chem. Soc.* **54**, 4631 (1932).

## I. EXPERIMENTAL METHOD AND RESULTS

### A. Sample Preparation

The proton spin-lattice relaxation time ( $T_1$ ) measurements reported in this article were made on three single ice crystals, grown and purified by zone refining. The samples were grown and zone refined in 1-cm diam Pyrex tubes. Before use, these tubes were first cleaned with a standard  $H_2SO_4$ -based glass cleaning solution and then rinsed repeatedly for a period of days with  $10^{-6}(\Omega \cdot \text{cm})^{-1}$  water (equilibrium water). The zone-refining process was carried out at an ambient temperature of  $-25^\circ\text{C}$ . The length of the zone was about 1 cm, and the zone was moved along at a speed of 1–2 cm/h. The pass length was about 15 cm, and the  $T_1$  measurements were made 5 cm above the beginning of the passes. Each pass began in a region where the tube was necked down to 2 mm in diameter. This permitted a single crystal to be formed quickly as the zone moved along, and the zone always had a seed of small volume to start from at the beginning of each pass.

### B. Apparatus and Measuring Technique

The pulsed nuclear magnetic resonance apparatus used to carry out the  $T_1$  measurements has been described elsewhere.<sup>10–13</sup> These measurements were carried out at a Larmor frequency of 10.000 Mc/sec, using the following technique. A  $90^\circ$ – $90^\circ$  pulse sequence was applied to the sample (a “ $90^\circ$  pulse” nutates the spins by  $90^\circ$ ) and the free induction decay amplitude  $M(\tau)$  following the second pulse was photographed. ( $\tau$  is the time between the first and second  $90^\circ$  pulses.)  $M(\tau)$  should and was found to obey the equation

$$M(\tau) = M(\infty)[1 - \exp(-\tau/T_1)]. \quad (1)$$

The time constant  $T_1$  was extracted by measuring the slope of the curve of  $\log[M(\infty) - M(\tau)]$  vs  $\tau$ . (The curves were very good straight lines.) The accuracy of these  $T_1$  measurements was about 3%.

The apparatus' temperature control system is described elsewhere.<sup>13</sup> Its stability was about  $0.1^\circ\text{C}$  over the period of time needed to measure the longer  $T_1$ 's. The sample temperature was monitored by two copper-constantin thermocouples located near the sample. The thermocouple voltages were measured using a Leeds and Northrop Type K-3 potentiometer, and the absolute accuracy of the readings was about  $0.1^\circ\text{C}$ . Ice samples were left for an hour at the measuring temperature before  $T_1$  measurements were made, to assure temperature equilibrium. No “annealing effects” were observed when the ice sample was held at the equilibrium temperature for longer periods of time.

<sup>10</sup> I. J. Lowe and R. L. Howard, Rev. Sci. Instr. **33**, 96 (1962).

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<sup>13</sup> D. E. Barnaal, Ph.D. thesis, University of Minnesota, Minneapolis, Minn., 1965 (unpublished).

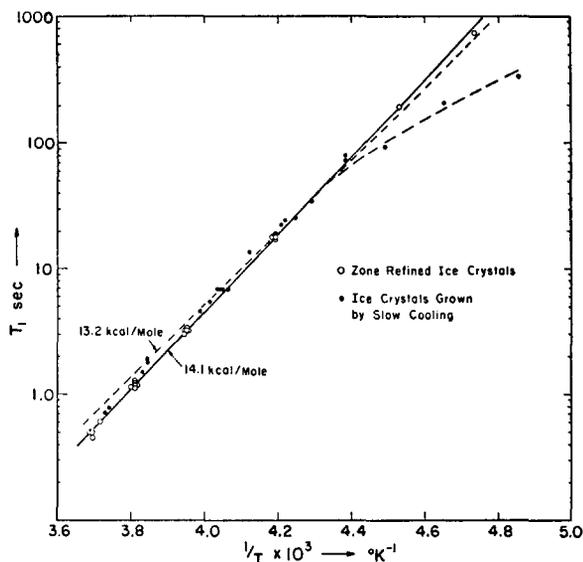


Fig. 1. Log  $T_1$  vs  $T^{-1}$  for protons in ice. Data for zone-refined ice crystals are represented by open circles. Data for ice crystals grown by slow cooling (Ref. 14) are represented by dots.

### C. Experimental Results

Our experimental data is plotted in Fig. 1 in the form of  $\log T_1$  vs  $T^{-1}$ .  $T$  is the absolute temperature of the ice sample. The open circles represent data for the zone-refined ice samples. The small dark circles represent data of earlier measurements made on single crystals of ice. These were cut from large (10-cm diam) slowly grown crystals that were not zone refined. This earlier data is reported in Ref. 14.

The  $\log T_1$  vs  $T^{-1}$  curves for these earlier measurements are linear from  $0^\circ$  to  $-50^\circ\text{C}$ . The curve then bends over at about  $-50^\circ\text{C}$  to a new line of lower slope, and this new slope was found to hold to very large values of  $T_1$ . Below  $-50^\circ\text{C}$ , the  $\log T_1$  vs  $T^{-1}$  curves for these unrefined crystals were not reproducible from sample to sample. It is felt that this was probably due to impurities for two reasons: (1) by adding small amounts of impurities (such as 1 in  $10^6$  of HF), the effect could be greatly increased; (2) the  $\log T_1$  vs  $T^{-1}$  curves of the zone-refined samples do not have a bend in them, and both sets of  $T_1$  data coincide above  $-50^\circ\text{C}$ .

For measurements below  $-50^\circ\text{C}$  on the clean end of the zone-refined samples (the starting end),  $T_1$  increased with each zone-refining pass made on the ice sample, up to the 10th pass. The  $T_1$  of the dirty end of the sample got shorter with each zone-refining pass. All the data plotted in Fig. 1 for zone-refined ice crystals are for crystals on which 10 zone-refining passes have been made. These measurements were made with the  $c$  axis (optical axis) both parallel and perpendicular to the applied static magnetic field  $B_0$  by rotating the sample. Careful measurements were made at  $-2.5^\circ$ ,  $-10.2^\circ$ ,

<sup>14</sup> D. E. Barnaal, M. S. thesis, University of Minnesota, Minneapolis, Minn., 1962 (unpublished).

−20.3°, and −34.0°C to look for any anisotropy of  $T_1$ . The variation of  $T_1$  between the two directions for all these measurements was less than 2%.

From the data plotted in Fig. 1, it appears that for sufficiently pure ice crystals, only a single activation energy for the  $T_1$  process is observed down to at least −60°C. A least-squares fit of a straight line to the data in Fig. 1 for the zone-refined ice crystals yields a value of  $14.1 \pm 0.1$  kcal/mole for this activation energy ( $0.611 \pm 0.004$  eV/molecule).

## II. THEORETICAL CALCULATION OF $T_1$ IN ICE

### A. Models of Proton Motions in Ice

Large-amplitude atomic and molecular motions, with an appreciable Fourier component near the Larmor frequency, are an effective spin-lattice relaxation mechanism.<sup>15</sup> There is ample evidence, such as from dielectric relaxation studies, for such motions for protons in ice. A review and bibliography of this subject is given in Ref. 16. There have been many suggested mechanisms for proton motion in ice, some of which are listed below.

One possible source of proton motion in ice can be that of lattice molecular vacancies hopping through the ice lattice. In this model, a given H<sub>2</sub>O molecule performs a random walk through the lattice as a result of displacements by visiting vacancies. At each jump of the molecule, the molecule rotates to a new direction such that the protons have positions at the new site consistent with the Bernal-Fowler coordination rules (hydrogen-bonded oxygens, with one H on each O-O bond, 2 H atoms near each O). Gränicher,<sup>16</sup> maintains that this cannot be an effective dielectric relaxation mechanism. There is no doubt however that it can be an effective  $T_1$  mechanism. The only question is whether there exists a sufficient number of these molecular vacancies and whether they have a high enough mobility to produce a reasonable jump rate for the H<sub>2</sub>O molecules.

A second possible source for proton motion in ice is the rotation and ionization defects postulated by Bjerrum.<sup>17</sup> The rotation defect is formed by an H<sub>2</sub>O molecule rotating through 120° about an O-H···O bond to form a doubly occupied O-H·H-O bond and an empty O···O bond. Each of these defects can then travel through the lattice by successive rotations of the neighboring molecules. When a molecule is visited by one of these defects, it is reoriented by 120° about one of its O-H···O bonds. The ionic defect is formed by a proton migrating along a bond from one H<sub>2</sub>O molecule to a neighboring H<sub>2</sub>O molecule (both of which are neutral), to produce an H<sub>3</sub>O<sup>+</sup> ion and a OH<sup>-</sup> ion. By

further proton translations, each of these ions can migrate through the crystal.

A somewhat more involved defect has been proposed by Haas.<sup>8</sup> He suggests that an interstitial molecule may hop along with a Bjerrum defect for a few steps, or even exchange with the lattice molecule undergoing rotation at each step.

### B. Calculation of $T_1$

All of the models listed in the previous section for large amplitude molecular motions in ice have the protons in fixed spatial configurations until a defect visits their neighborhood. In the presence of the defect, the protons move to new sites. The transition time for this move is short in comparison to a Larmor period ( $10^{-7}$  sec) and to the time between transitions, and for the purposes of computing  $T_1$ , it may be taken as instantaneous. All that matters in computing  $T_1$  is the *relative* displacement of the protons, and as discussed by Eisenstadt and Redfield<sup>18a</sup> the relationship between relative nuclear displacements and visits by defects can be very complicated. Ignoring these complications, we shall assume there exists a mean jump frequency for interacting pairs of protons, and denote it by  $\nu$ .

Figure 1 shows that  $\log T_1 \propto T^{-1}$ . This suggests that over the temperature range for which  $T_1$  measurements were carried out,  $\omega_0/\nu \gg 1$ , where  $\omega_0 = \gamma B_0 = 2\pi \times$  Larmor frequency and  $\gamma$  is the proton magnetogyric ratio. We have also measured  $T_1$  as a function of  $\omega_0/2\pi$  down to  $76 \times 10^3$  Hz and found that it is proportional to  $\omega_0^2$ . This further supports  $\omega_0/\nu \gg 1$ . For this long-correlation time hopping-model case, a formula for the spin-lattice relaxation time  $T_1$  is found in Eisenstadt and Redfield<sup>18a</sup> [Eqs. (12) plus (26)], and in Torrey.<sup>18b</sup> It is written below in a slightly modified notation so that some of the arguments that follow are more transparent,

$$1/T_1 = \{ \gamma^4 \hbar^2 [3I(I+1)] / 2N \} \times \sum_{i \neq j} [\kappa_{ij}^{(1)}(\omega_0) + \kappa_{ij}^{(2)}(2\omega_0)]. \quad (2)$$

Here  $I$ ,  $\gamma$ , and  $\omega_0$  are the spin, the magnetogyric ratio, and  $2\pi \times$  Larmor frequency, respectively, of the nuclear species in the calculation, which for this case is the proton.  $N$  is the number of nuclei of type I in the solid, and the summation is over all the nuclei of type I in the solid,

$$\kappa_{ij}^{(q)}(\omega) = (2\nu/\omega^2) \sum_{X,Y} P_{i,j}(X,Y) F^{(q)}(X,Y) [F^{(q)}(X,Y) - \sum_{W,Z} F^{(q)}(W,Z) * P_{i,j}^{(1)}(X,Y;W,Z)], \quad (3)$$

$$F^{(1)}(X,Y) = r^{-3} \sin\theta \cos\theta \exp(-i\phi), \quad (4)$$

$$F^{(2)}(X,Y) = r^{-3} \sin^2\theta \exp(-2i\phi). \quad (5)$$

$X$ ,  $Y$ ,  $W$ , and  $Z$  are equilibrium lattice positions for the

<sup>15</sup> A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon Press, Oxford, England, 1961).

<sup>16</sup> H. Gränicher, *Physik Kondensierten Materie* **1**, 1 (1963).

<sup>17</sup> N. Bjerrum, *Science* **115**, 385 (1952).

<sup>18</sup> (a) M. Eisenstadt and A. G. Redfield, *Phys. Rev.* **132**, 635 (1963); (b) H. C. Torrey, *ibid.* **92**, 962 (1953).

nuclei of species I in the solid. The  $r$ ,  $\theta$ , and  $\phi$  in Eqs. (4) and (5) are the polar coordinates of the vector connecting positions  $X$  and  $Y$  in the lattice; the polar axis of the system is along the applied magnetic field, and the azimuthal plane is arbitrary.  $P_{i,i}(X, Y)$  is the probability of finding nucleus  $i$  at lattice site  $X$  and nucleus  $j$  at lattice site  $Y$ .  $P_{i,j}^{(1)}(X, Y; W, Z)$  is the probability that if nucleus  $i$  is at site  $X$  and nucleus  $j$  is at site  $Y$  initially, nucleus  $i$  is at site  $W$  and nucleus  $j$  is at site  $Z$  after *one* visit of a lattice defect.

In two different ways, Eqs. (1)–(5) show that lattice sites  $X$  and  $Y$  which are closest to one another make the dominant contribution to the spin-lattice relaxation process. The first way is that  $F^{(q)}$  comes in quadratically, so that each term in Eq. (3) contains a  $r^{-6}$  term. A crude measure of how important the nearest-neighbor sites are can be gained from a comparison of the contribution to the NMR line-shape second moment of nearest-neighbor protons to all other protons in the crystal. {This comparison is reasonable because of the similarity of  $[F^{(q)}(X, Y)]^2$  to terms in the second-

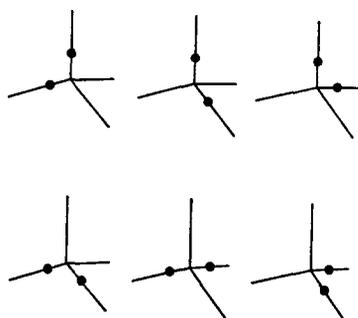


FIG. 2. The six possible arrangements of the hydrogen atoms around the central oxygen atom.

moment formula.<sup>15</sup> A detailed computation carried out in Ref. 19 shows that the intramolecular contribution to the second moment in ice is about 56% of the total second moment, and is thus dominant for that case. The second way is that in Eq. (3) appears the term

$$F^{(q)}(X, Y) - \sum_{W,Z} F^{(q)}(W, Z) P_{i,j}^{(1)}(X, Y; W, Z). \quad (6)$$

In one visit of a defect, spins  $i$  and  $j$  cannot move very far, so that  $W$  is near  $X$ , and  $Z$  is near  $Y$ . If  $X$  and  $Y$  are far apart then  $F^{(q)}(X, Y) \approx F^{(q)}(W, Z)$  and the expression listed in Eq. (6) is close to zero. Only when  $X$  and  $Y$  are close together can one visit of a defect significantly change the relative coordinates of nuclei  $i$  and  $j$ , and thus have the expression in Eq. (6) make a large contribution to  $T_1$ . We estimate that a  $T_1$  computation for ice which considers only nearest-neighbor lattice sites in the sum in Eq. (3) should yield a value that is not larger by 20% than the  $T_1$  value obtained when the complete sum is carried out. Considering the

TABLE I. Comparison of the time between rotational jumps of the  $H_2O$  molecule in ice as derived from proton spin-lattice relaxation-time measurements and dielectric relaxation-time measurements.

$T$ (°C)	$W^{-1}=2\tau_D$ (seconds)	$\nu^{-1}$ (seconds)	$W^{-1}/\nu^{-1}$
-3	$5 \times 10^{-5}$	$2.5 \times 10^{-6}$	20
-10	$1 \times 10^{-4}$	$5.5 \times 10^{-6}$	18
-36	$1.8 \times 10^{-3}$	$1.1 \times 10^{-4}$	16.4

somewhat indefinite relation of  $\nu$  to the visits of lattice defects, and the unknown nature of the defects involved in the  $T_1$  process, a more extensive evaluation of the sums in Eq. (3) does not seem warranted.

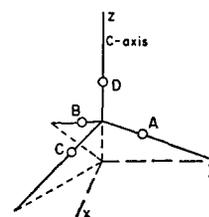
On the basis of the above arguments, we have evaluated the  $T_1$  for ice using Eqs. (2)–(5) for a model in which an  $H_2O$  molecule does a random walk between the six possible orientations shown in Fig. 2. This hopping motion can be induced by the random visits of lattice vacancies, orientation defects or Haas-type defects. In this model,  $\nu$  can be interpreted as the mean jump frequency of the molecule between its various equilibrium positions. For this calculation, the H–O–H angle is set at  $109^\circ 28'$ , and the O–H bond length is set at 1.0 Å. (See Ref. 13 for further details of the calculation.) The lattice sums are evaluated for the cases of  $B_0$  parallel to the  $c$  axis, and  $B_0$  perpendicular to the  $c$  axis and along the “ $y$  axis” (see Fig. 3). The results are, that for a Larmor frequency of 10 MHz,

$$T_1 = 2.14 \times 10^5 \nu^{-1} \quad (7)$$

for *both* field directions. (The units for both  $T_1$  and  $\nu^{-1}$  are seconds.) Thus, no anisotropy for  $T_1$  is calculated in this model; and none was observed experimentally by us. A crude evaluation of Eq. (3) for the ionic defect model suggests that a slightly larger constant than the one in Eq. (7) would be obtained.

Equation (7) can be used to obtain  $\nu$  for the  $H_2O$  molecule in ice from experimental  $T_1$  data. A similar quantity, the molecular rotational probability per unit time, denoted by  $W$ , is used in dielectric relaxation theory. Steinemann and Gränicher<sup>7</sup> have interpreted the dielectric relaxation time  $T_D$  to be related to  $W$  by  $W^{-1} = 2T_D$ . Listed for several temperatures in Table I are values of  $W^{-1}$  obtained from dielectric relaxation

FIG. 3. The labeling of the proton positions for the  $T_1$  calculation in ice, and the choice of rectangular axes.



<sup>19</sup> D. E. Barnaal and I. J. Lowe, J. Chem. Phys. **46**, 4800 (1967).

measurements, and values of  $\nu^{-1}$  obtained from  $T_1$  measurements.

### III. DISCUSSION

Our spin-lattice relaxation-time measurements of protons in ice lead us to conclude that the motional process causing the relaxation is accurately described by a single activation energy of  $14.1 \pm 0.1$  kcal/mole ( $0.611 \pm 0.004$  eV) over the range of temperatures ( $0^\circ$  to  $-60^\circ\text{C}$ ) at which the measurements were carried out. The pulsed NMR measurements of Kruger<sup>6</sup> yield a value of 0.59 eV for the same parameter. This is reasonably close agreement. We believe our value to be slightly closer to the true value for pure ice however, because of the larger temperature span over which we were able to carry out our  $T_1$  measurements and the careful preparation our samples received. The continuous-wave NMR measurements of Kume<sup>5</sup> yield a value of 0.44 eV. The large difference between Kume's value and ours (and also Kruger's) is possibly due to the known difficulties involved in the measurement of  $T_1$  using cw-NMR techniques.

The measured activation energy for the reorientation of the electric dipoles in ice is reported<sup>2</sup> as  $13.2 \pm 0.05$  kcal/mole. This measured activation energy value and our own, are fairly close together, but *well* outside the limits of experimental error set on the two values. It is possible that there is a systematic error in one or the other sets of measurements. It is also possible that proton magnetic relaxation in ice is dominated by one type of motion, and dielectric relaxation in ice by another type of motion, each having its own activation energy. Consistent with this second interpretation is the comparison in Table I of the time between rotational jumps of the  $\text{H}_2\text{O}$  molecule in ice as derived from proton spin-lattice relaxation time measurements and dielectric relaxation-time measurements. It shows the time between jumps of the  $\text{H}_2\text{O}$  molecule to be 20 times shorter at  $-3^\circ\text{C}$  and 16 times shorter at  $-36^\circ\text{C}$  when derived from proton spin-lattice relaxation measurements than when derived from dielectric relaxation time measurements. While the  $T_1$  calculation we have carried out is fairly crude, we cannot think of anything we can do to the calculation, either by adding in more terms to the sum, or changing distances between protons in some realistic fashion, or changing the model for jumping, that would decrease the jump rate by more than a factor of 2. This would still leave a factor of 10 difference to be explained. A possible solution to this difference in jump times is that the dielectric relaxation time has not been correctly related to the jump frequency. However, any new theory that brings compatibility between the derived jump times would also have to explain the difference in measured activation energies, assuming that this difference is real.

A crude measure of proton jump rates in ice can be obtained from the temperature dependence of the

motional lengthening of the free induction decay (fid) shape. This corresponds to the narrowing of the cw absorption line. The fid shape begins to change and lengthen from its rigid lattice shape when the average time between jumps of a proton pair approaches the time duration of the fid shape. The ice fid shape<sup>19</sup> has a nominal length of 15–30  $\mu\text{sec}$  (depending how one wants to define it, since the ice line shape is complex), and one should therefore expect this shape to start lengthening when the average time between jumps for a proton pair is in the region of 15–30  $\mu\text{sec}$ . It is experimentally found<sup>19</sup> that the ice fid shape begins to narrow at about  $-25^\circ\text{C}$ , implying, therefore, a jump time per proton pair of 15–30  $\mu\text{sec}$ . The calculated jump time at  $-25^\circ\text{C}$  from our  $T_1$  measurements, is 29  $\mu\text{sec}$  which is consistent with the fid-shape lengthening results. The proton jump time at  $-25^\circ\text{C}$ , as deduced from dielectric measurements, is 500  $\mu\text{sec}$ . The fid-shape method of measuring proton jump rates lends further support to the values deduced from  $T_1$  measurements.

In conclusion, it can be pointed out that Onsager and Runnels<sup>20</sup> have decided that for ice "the observed diffusion is an order of magnitude faster than the dielectric relaxation if discussed on equivalent terms." The diffusion experiments<sup>4a</sup> for  $^{18}\text{O}$ , deuterium, and tritium in ice yield a diffusion constant  $D$  of  $10^{-10}$   $\text{cm}^2/\text{sec}$  at  $-2^\circ\text{C}$ . If one assumes  $D=L^2/(6\tau)$  and lets the jump distance  $L$  be the O–O bond length, then the computed value of  $\tau$  is 1.2  $\mu\text{sec}$  at  $-2^\circ\text{C}$ . This compares reasonably well with the value of 2.3  $\mu\text{sec}$  computed from  $T_1$  using Eq. (7). The most recent measurement<sup>21</sup> of the activation energy for the diffusion of tritium in ice is  $0.62 \pm 0.03$  eV. This is the same value for the proton  $T_1$  in ice to within quoted experimental errors. This close agreement of jump times and activation energies suggests that the proton diffusion mechanism in ice is also the proton  $T_1$  mechanism. Whether this is true or not is still uncertain in our minds for there is also evidence against this interpretation. The proton  $T_1$  is very sensitive to doping impurities<sup>19</sup> such as HF, while tritium diffusion in ice is not.<sup>22,23</sup> We think that more experimental work on this point is needed before a definite conclusion can be drawn.

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