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## Two-dimensional protonic diffusion in a hydrogen-bonded compound CsOH · H<sub>2</sub>O, studied by solid state NMR

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**Résumé.** — L'étude par R.M.N. du césium hydroxide monohydrate CsH<sub>3</sub>O<sub>2</sub> polycristallin révèle une diffusion protonique rapide dans ses phases hautes températures. Par mesure directe, la constante de diffusion est trouvée  $D = 1.2 \times 10^{-5} \exp(-1700/T[\text{K}]) \text{ cm}^2 \cdot \text{s}^{-1}$ . Les données de relaxation du proton et le spectre de deutérium indiquent un fort caractère 2-d pour cette diffusion que l'on montre être de type Grotthus : elle a lieu par des rotations d'ordre trois de l'entité H<sub>3</sub>O<sup>+</sup> combinées avec des sauts du proton le long de l'axe O-O. Le caractère bidimensionnel résulte de la structure en couches et du mécanisme de diffusion.

**Abstract.** — NMR study of polycrystalline caesium hydroxide monohydrate CsH<sub>3</sub>O<sub>2</sub> shows a fast protonic diffusion in its high temperature phases. From a direct measurement, the diffusion constant is  $D = 1.2 \times 10^{-5} \exp(-1700/T [\text{K}]) \text{ cm}^2 \text{ s}^{-1}$ . <sup>1</sup>H relaxation data and <sup>2</sup>H spectrum indicate a strong 2-d character for this diffusion which is shown to be of Grotthus-type : it takes place through threefold H<sub>3</sub>O<sup>+</sup> rotations combined with H jumps along O-O. Two dimensionality comes from the layered structure and the diffusion mechanism.

### Introduction.

The structure of ice was studied by many authors because it is one of the model system for disordered substances. In the ice structure every oxygen is tetrahedrally surrounded by four other oxygens and is bounded to its neighbours by hydrogen bridges. The hydrogen bridges are asymmetric which means that between two oxygens is always situated a hydrogen which has two positions close to one or the other oxygen. Averaged over the whole structure, the two positions on the bridge are populated with the same weight but microscopically the hydrogen arrangement is such that the two ice rules of Pauling are observed : first, on every bridge there is one hydrogen and second, each oxygen has exactly two hydrogen as closest neighbours. These rules are a strong restriction for the arrangement of hydrogen and also for their dynamic behaviour : it is not possible to just shift one hydrogen in one of the bridges. Therefore it seemed us to be of general interest to study the compound Caesium hydroxide monohydrate CsOH · H<sub>2</sub>O which shows some resemblance to the ice structure. It is composed of

hexagonal or nearly hexagonal nets of oxygen atoms with just one hydrogen between the two oxygens, where this hydrogen can have again two possible positions. The different H<sub>3</sub>O<sub>2</sub> nets are then bounded together by Cs layers and due to the large interlayer distance of 4.44 Å no hydrogen bond are form between different layers (Fig. 1). Consequently in this compound there are two dimensional H<sub>3</sub>O<sub>2</sub> nets and one can say that this substance brings the ice problem in two dimensions. The special interest in this substance is caused firstly because the ice rules should be now relaxed and oxygen can on the average have one or two hydrogen neighbours, which should increase the proton mobility quite strongly. This is actually observed with incoherent quasielastic neutron scattering (I.Q.N.S.) [1] and also with nuclear magnetic resonance as reported in this paper. Secondly this compound represents an example of physics in two dimensions which is by itself an interesting fact because a lot of work was performed this last time in the study of 2-d systems.

Whereas below 229 K, CsOH · H<sub>2</sub>O presents a monoclinic structure with chemically unequivalent

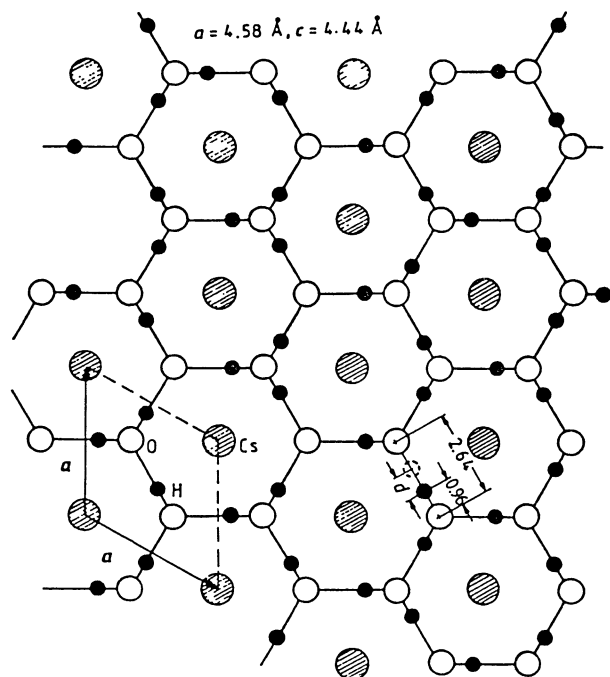


Fig. 1. — Simplified projection of the hexagonal structure ( $T > 340$  K) of  $\text{CsH}_3\text{O}_2$  on to the  $a$ - $a$  plane. ( $a = 4.58$  Å ;  $c = 4.44$  Å).

hydrogens, above this temperature it has been shown to crystallize in three different hexagonal or pseudo-hexagonal structures [2]. Above 340 K the space group is  $P6/m$  with Cs atoms at the origin and O atoms at  $(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$  and  $(\frac{2}{3}, \frac{1}{3}, \frac{1}{2})$ . In the high temperature phases, there are no distinct  $\text{OH}^-$  and  $\text{H}_2\text{O}$  groups in the layers, i.e. all the H atoms appear to be equivalent. In the following, we will therefore write  $\text{CsH}_3\text{O}_2$  rather than  $\text{CsOH} \cdot \text{H}_2\text{O}$ . I.Q.N.S. experiments have shown the existence of a double well potential for the proton in between two oxygen atoms. The protonic disorder is of a dynamic nature and is well described by a two site jump model corresponding to a non-linear H bond with a bending angle out of the plane of about  $20^\circ$ . The distance between the two sites is then 1 Å and the mean hopping rate for this local motion is found  $8 \times 10^{10} \text{ s}^{-1}$  at 402 K [1].

Owing to its high sensitivity to H large amplitude motions a proton NMR study should give additional information on the proton disorder in this compound. In the present paper, we present NMR experimental results on  $\text{CsH}_3\text{O}_2$  powder which show that the proton dynamical disorder is not limited to jumps over the symmetric double well potential along a O-O line. In fact — on a much longer time-scale — we are dealing with a translational motion over the whole lattice, *via* a Grotthus-type process. It combines in plane rotations of  $\text{H}_3\text{O}^+$  ions and proton transfers from  $\text{H}_3\text{O}^+$  to  $\text{O}^{2-}$  entities. These

motions together with the crystallographic layered structure are responsible for the pure 2-d character of the protonic diffusion.

### Experimental results.

The NMR study was carried out on a BRUKER SXP 4-100 pulse spectrometer at various resonance frequencies  $\nu_0$  between 9 and 90 MHz. Sealed sample tubes were used to avoid thermal decomposition of this highly hygroscopic compound. The temperature was varied and regulated by a standard BRUKER system. It was measured with a thermocouple put in an identical sample tube filled with a non deliquescent salt and set in the NMR probe instead of the studied sample. The temperature was constant to better than 1 K and its gradient in the sample lower than 1 K.

The spin-lattice relaxation time  $T_1$  was measured with the  $180-\tau-90$  pulse sequence. The spin-lattice relaxation time in the rotating frame  $T_{1\rho}$  was determined with the spin-locking method at 60 MHz for the two  $H_1$  field values of 5.9 and 11.8 G. Measurements were performed in the high temperature phases of the compound where translational diffusion of the protons occurs. This motion strongly averages the dipolar interaction between spins and gives a liquid-like proton signal. Its spin-spin relaxation time  $T_2$  was measured by the spin-echo sequence. Below the lowest transition temperature  $T_1 \approx 225$  K, a solid like signal superimposes on the liquid-like component. As the temperature decreases in the monoclinic phase, we observe a gradual transfer of the liquid-like component toward the solid like one, down to about 160 K, where the liquid-like signal becomes unobservable.

We present below the results obtained for the diffusive process in the temperature range from 160 K up to the melting point of the salt (478 K).

1.  $^1\text{H}$  RELAXATION TIMES. — Exponential recovery of the magnetization is observed in the whole temperature range for all the relaxation times.

$T_1$ ,  $T_{1\rho}$  and  $T_2$  are plotted in figure 2.

- $T_{1\rho}$  does not show any noticeable frequency dependence over the whole temperature range.

- Below 250 K,  $T_2$  shows a roughly linear temperature dependence in the semi-log plot *versus*  $1/T$  with an apparent activation energy equal to  $2100 \pm 200$  K. In the highest hexagonal structural phase, above 340 K,  $T_2$  becomes frequency dependent, reaches a plateau (about 30 ms at 60 MHz) and decreases just before the melting point. The  $T_2$  plateau value is higher as the frequency is lower.

- $T_1$  presents the well known V-shaped temperature dependence, passing through a minimum dependent on the frequency. On the low temperature side of the minimum, the linear part of the  $T_1$  curves

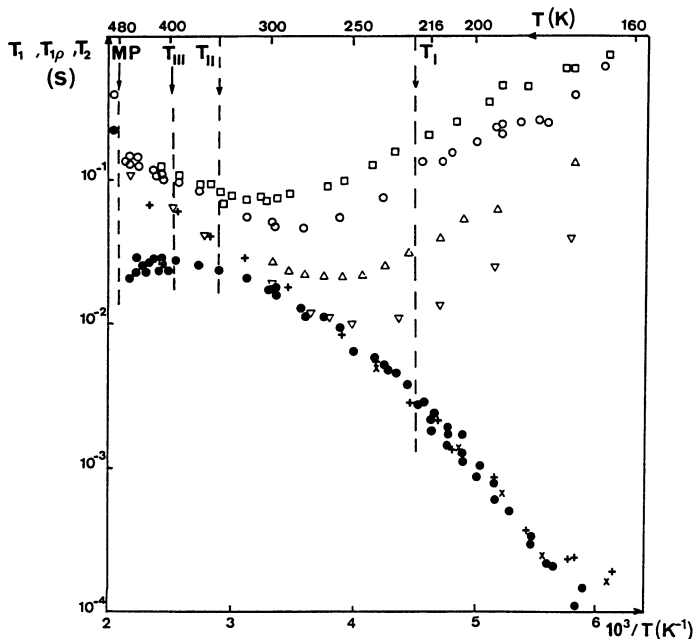


Fig. 2. — <sup>1</sup>H relaxation times  $T_1$ ,  $T_{1\rho}$ ,  $T_2$  plotted versus  $1/T$ :  $\square$   $T_1$ , 90 MHz;  $\circ$   $T_1$ , 60 MHz;  $\triangle$   $T_1$ , 25 MHz;  $\nabla$   $T_1$ , 12 MHz;  $\bullet$   $T_2$ , 60 MHz;  $+$   $T_{1\rho}$ , 60 MHz,  $H_1 = 11.8$  G;  $\times$ ,  $H_1 = 5.9$  G; MP: melting point;  $T_I$ ,  $T_{II}$ ,  $T_{III}$ : transition phases temperatures.

gives, whatever the frequency, the same apparent activation energy equal to  $980 \pm 50$  K. The  $T_1^{-1}$  frequency dependence below the minimum is plotted in figure 3 for the two temperatures 192 and 172 K. A unique relaxation process contributes to the spin-lattice relaxation rate according to :

$$T_1^{-1} \approx A \nu_0^{-1.5} \tag{1}$$

The slope  $A$  amounts to  $17.6 \pm 1$  and  $9.5 \pm$

$0.5 \times 10^{11} (s^{2.5})$  at 192 and 172 K respectively, from which an activation energy, again equal to  $\approx 1000$  K, is obtained. At the lowest resonance frequency studied (9 MHz), a departure from this relation is obvious, especially at 192 K. The proximity of the  $T_1$  minimum, observed at 250 K for this low frequency, is likely to be the origin of this disagreement.

On the high temperature side of the  $T_1$  minimum,

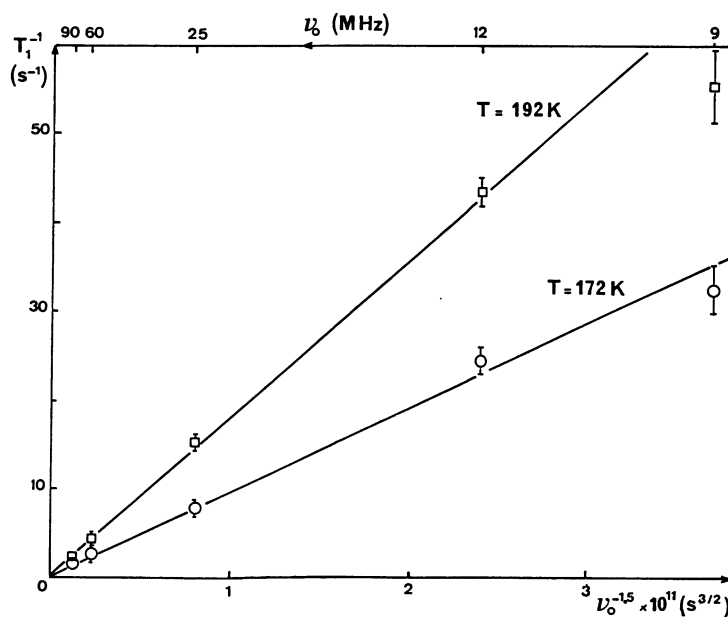


Fig. 3. — Frequency dependence of the spin-lattice relaxation rate  $T_1^{-1}$  observed at 172 and 192 K between 9 and 90 MHz plotted versus  $\nu_0^{-1.5}$ . Full lines: linear dependence followed in this frequency range.

$T_1$  is slightly frequency dependent, as shown on the semi-log plot of the figure 4 at three temperatures in the range 380-420 K. Such a behaviour has been previously observed in some compounds where diffusion of the guest molecular species ( $H_2O$ ,  $NH_3$ ) in the host lattice is two-dimensional in character [3-5]. It is expected that two-dimensional diffusion leads to a greater persistence of the spatial correlation than in three dimensions. Thus the long time behaviour of the spin correlation function depends crucially on the dimensionality of the system. Some authors have predicted the logarithmic divergence of the spin-lattice relaxation rate in the low-frequency-high temperature limit [6-10].

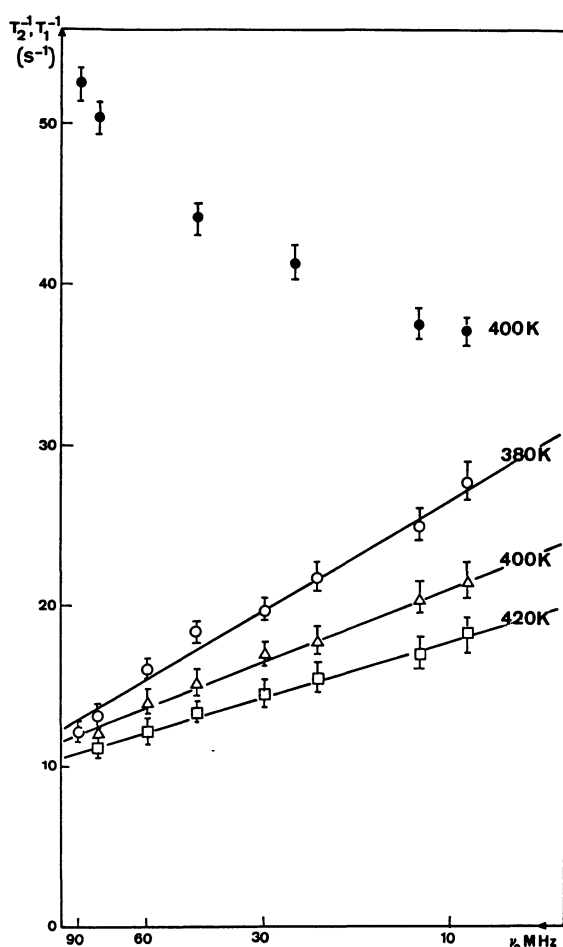


Fig. 4. — Frequency dependence of the relaxation rates  $T_1^{-1}$  (blank characters) and  $T_2^{-1}$  (black circles) observed at high temperatures plotted versus  $\log_{10} \nu_0$ ; full lines: logarithmic dependence followed in this frequency range by the spin-lattice relaxation.

• Spin lattice as well as spin-spin proton relaxation times, present no noticeable anomaly or discontinuity or change in slope for any of the three phase transitions, the temperatures of which observed by a thermal study (2), are respectively 229, 340 and

398 K. Let us note that this is even true for the lowest one which manifests itself only by the appearance of a *solid-like* component in the FID.

2. TRANSLATIONAL DIFFUSION CONSTANT. — In the high temperature structural phases, above 340 K, proton diffusion becomes so fast that it can be observed directly by NMR. It is well known that the HAHN echo amplitude  $M(2\tau, G)$  depends on the diffusion constant  $D$ , according to [11]:

$$M(2\tau, G) = M(0, G) \exp\left(-\frac{2\tau}{T_2} - \frac{2}{3} \gamma^2 G^2 D \tau^3\right). \quad (2)$$

The above relation is valid for an isotropic and unrestricted diffusion and a uniform field gradient  $G$ . Diffusion thus strongly affects the echoes envelope, above all at large  $\tau$  values. If the diffusion takes place in a bounded medium, as is the case for small size powder grains, (2) is no longer satisfied and is replaced by a linear dependence with  $\tau$  at large  $\tau$  [12, 13]. In our case, the  $\tau^3$  dependence is well fitted in the whole temperature range where diffusion is observable and the limited size of the powder grains plays no role. It is believed that proton diffusion is two-dimensional in nature in  $CsH_3O_2$ , so the above expression (2) should be corrected for its anisotropic character. However, owing to the limited precision of our measurements, such a theoretical adjustment was not tried. In the absence of a pulse field gradient equipment, the measurement of the diffusion constant used a large steady field gradient, obtained by moving the NMR probe outside the central part of the magnet air gap. Calibration of the field gradient was derived from a similar study on a water sample; its diffusion constant is well known:  $D_{\text{water}}$  equals  $2.3 \pm 0.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  at 298 K [14, 15]. Several field gradients were used. They give consistent  $D$  results. To overcome the  $T_2$  dependence of the echo amplitude, we have plotted versus  $\tau^3$  on a logarithmic scale the ratio  $\frac{M(2\tau, G_1)}{M(2\tau, G_2)}$  instead of  $\frac{M(2\tau, G)}{M(0, G)}$ ,  $G_1$  and  $G_2$  being two very different  $G$  values. In spite of this careful process, the accuracy of our results is rather low ( $\pm 20\%$ ). This is due mainly to a distribution of the gradient over the sample and over the time of measurement.

Figure 5 shows the temperature dependence of  $D$  which seems roughly linear on a semi-log plot as expected for a thermally activated process:

$$D = D_0 \exp(-E_d/kT) \quad (3)$$

$D_0$  and  $E_d$  can only be estimated:  $E_d/k \approx 1700 \pm 200$  K. The self diffusion constant at 400 K,  $D \approx 1.8 \pm 0.3 \times 10^{-7} \text{ cm}^2/\text{s}$ , yields a value of  $D_0 \approx 1.2 \times 10^{-5} \text{ cm}^2/\text{s}$ .

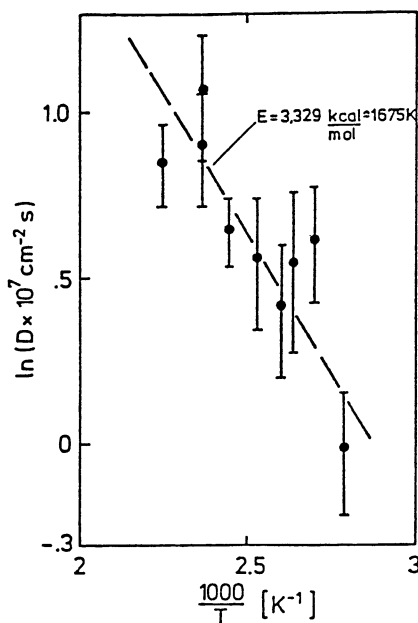


Fig. 5. — Measured diffusion constant  $D$  plotted versus  $1/T$ ; full line: linear dependence giving the activation energy  $E_d = 1\,700$  K.

3. DEUTERON SPECTRA. — The  $^2\text{H}$  spectrum obtained at 13.82 MHz and room temperature is presented in figure 6. It consists of two narrow lines of almost equal amplitude separated by a difference  $\Delta\nu$  in resonance frequency equal to  $56.5 \pm 0.5$  KHz. It is a direct proof of the anisotropy for the motion of the deuteron spins. Otherwise for an isotropic motion, a single sharp resonance line would be observed close to the heavy water resonance frequency. The typical powder pattern is not observed mainly for the very low value of the motionally averaged dipolar coupling between the  $D$  spins gives a very small line broadening (experimental linewidth equal to  $700\text{ s}^{-1}$ , about ten times larger than the inhomogeneous broadening of the Zeeman field).

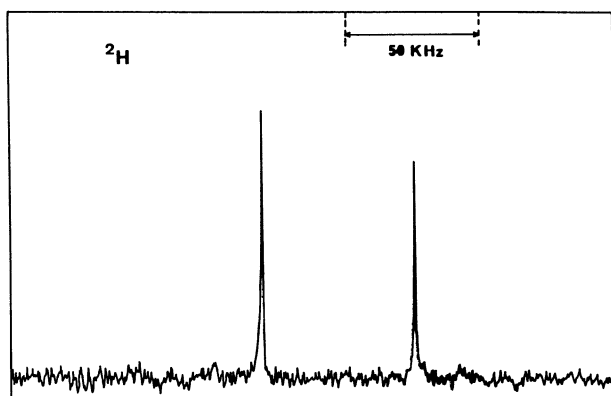


Fig. 6. —  $^2\text{H}$  resonance spectrum at 300 K. The two narrow lines are separated by  $\Delta\nu = 56.5$  KHz. Frequency: 13.82 MHz.

Furthermore the long delay time ( $100\ \mu\text{s}$ ) used, owing to the large dead time of the receiver and to the ringing, does not allow to reproduce correctly the small wings of the powder spectrum. The deuteron spectrum corresponds to an axial symmetry of the electric field gradient tensor with a quadrupolar coupling constant (QCC) of  $75 \pm 1$  KHz. This is very near to the QCC observed in deuterated hydronium perchlorate [16], where  $\text{D}_3\text{O}^+$  ions reorients around their threefold axis.

Deuteron spectra at room temperature implied fast  $\text{D}_3\text{O}^+$  reorientations around the  $C_3$  axis of the hydronium ions. From this last point, two features of the diffusion process can be derived: diffusion is anisotropic and it takes place through  $\text{D}_3\text{O}^+$  rotations. Since jumps of the proton over the double well potential between adjacent oxygen atoms have already been shown to exist by quasielastic neutron scattering [1], we suggest that the diffusion mechanism combines the two above basic motions (rotation and jump) and thus is of the Grotthus type [17].

#### Discussion.

The experimental results have directly shown that translational diffusion of the hydrogen atom occurs in the lattice. Both  $^1\text{H}$  spin-spin  $T_2$  and spin-lattice relaxation in the rotating frame  $T_{1\rho}$  are due to this translational motion. On the contrary, spin-lattice relaxation in the laboratory frame could *a priori* be due to an other process since, in the same temperature range, its apparent activation energy is much lower ( $\approx 1\,000$  K instead of  $\approx 2\,100$  K for  $T_2$  or  $T_{1\rho}$  temperature dependence). This apparent disagreement will be discussed in the following and we will show that the  $T_1$  relaxation is also due to the translational diffusion of the H spins. For this we must call upon a theoretical model to draw from the measured relaxation rates the mean rest time  $\tau_d$  between two diffusion jumps and to compare the related diffusion constant given by:

$$D = \frac{l^2}{4\tau_d} \quad (4)$$

where  $l$  is the jump distance to the next neighbour place, with the measured  $D$  value.

1. GENERAL ANALYSIS FOR THE PROTONIC DIFFUSIVE PROCESS. — In a previous approach, we have analyzed the data within the frame of a general diffusive model developed by Torrey [18]. Although valid only for a random walk isotropic diffusion this theory presents the valuable advantages to determine the absolute values of the relaxation rate in the whole temperature and frequency range and not only for high frequency or low frequency limits.

In figure 7 we show both the experimental  $T_1$  values measured at four resonance frequencies

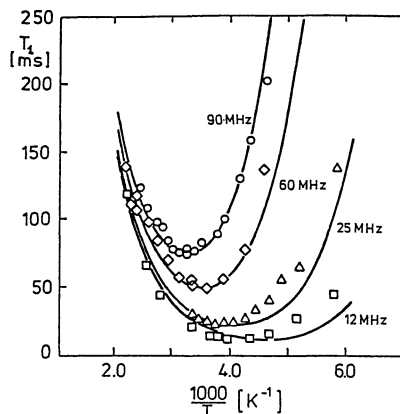


Fig. 7. — Measured  $T_1$  plotted versus  $1/T$  at four frequencies ; full lines : Torrey theory best fit.

90, 60, 25 and 12 MHz and the lines which result from a detailed study [19]. These curves have been fitted to the experimental points by using only two fit parameters which describe the temperature dependence of the mean residence time  $\tau_d$  :

$$\tau_d = \tau_{d\infty} \exp(E_d/kT). \quad (5)$$

The values  $\tau_{d\infty} = 1.21 \times 10^{-11}$  s and  $E_d = 1590$  K result from the best fit.

Now, let us discuss the main features of the Torrey fit of our  $T_1$  experimental study :

— a very good agreement is found between experimental and calculated  $T_1$  minimum values at each frequency studied. For example at 60 MHz, the respective values are 47.0 and 47.8 ms. We observe simply at the lowest frequencies — 25 and 12 MHz — a slight shift of the temperature minima between the calculated curve and the experimental one. Recall that the two fit parameters,  $E_d$  and  $\tau_{d\infty}$ , allow to describe at the best the  $T_1$  temperature dependence but have no influence on the  $T_1$  minima values. So the Torrey theory, adapted to our case, predicts properly the absolute  $T_1$  minimum values, without any adjustable parameter ;

— the activation energy  $E_d = 1590$  K derived from the fit is in rather good agreement with the one observed by the diffusion constant measurements ( $E \approx 1700$  K). Moreover, the calculated diffusion constant at 400 K, obtained from (4) with  $l = 2.286$  Å and  $1/\tau_d$  given by (5), equals  $2.03 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup>, close to the experimental value  $D = 1.8 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup> ;

— although the Torrey theory gives a good agreement with the measured diffusion constant and  $T_1$  minima, it fails, as expected, at low temperature and low frequency (see Fig. 7). The two-dimensional character of the diffusion, not treated by Torrey, becomes highly significant and modifies the temperature and frequency behaviours. So, we must call

upon another theoretical description which takes into account the dimensionality of the diffusion.

2. TWO-DIMENSIONAL CHEMICALLY REACTIVE PROCESS MODEL. — Fries [10] has presented an extended theory which describes the translational diffusive process without any consideration of the structure of the individual disorder. It takes into account correlations between chemically reacting groups of atoms. They can be in an *associated* and in a *disassociated* state. Fries introduces four parameters, whose values influence strongly the frequency and temperature dependences of the mathematical solution : the minimum distances  $b$  and  $b_a$  between interacting spins, in the associated and disassociated state respectively ; the association and dissociation rates  $w_a$  and  $w$ .

Fries theory is interesting for the two following reasons :

— it predicts an  $\omega_0^{-3/2} T_1^{-1}$  frequency dependence for the high frequency limit, as observed on the low temperature side of our experimental data ;

— it is indeed conceivable that diffusion in CsH<sub>3</sub>O<sub>2</sub> takes place through a reaction between the OH<sup>-</sup> and H<sub>2</sub>O groups with the appearance of an associated state H<sub>3</sub>O<sup>+</sup>.

The expression of the spin-lattice relaxation rate obtained by Fries for the high frequency limit ( $\omega_0 \tau_d \gg 1$ ) depends on the value of the association rate  $w_a$ . When the condition  $w_a/b \gg (\omega_0/\tau_d)^{1/2}$  is satisfied, thus for a large association rate,  $T_1^{-1}$  is simply given by :

$$T_1^{-1} = C \tau_d^{-1/2} \omega_0^{-3/2}. \quad (6)$$

The apparent activation energy in  $T_1$  experiments is half its actual value. This result removes the apparent discrepancy previously pointed out concerning the measured activation energies.

In figure 8, we present the result of the fit to the

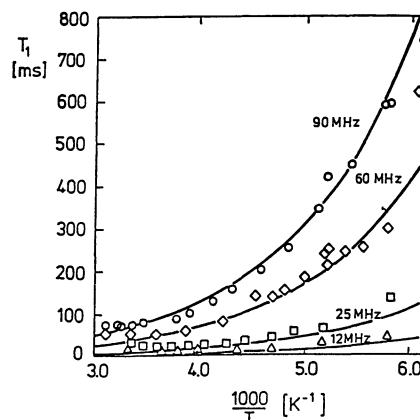


Fig. 8. — Measured  $T_1$  plotted versus  $1/T$  at four frequency ; full lines : Fries theory best fit.

experimental data. The  $T_1$  temperature dependence is well described at each frequency in this low temperature range.  $E_d$  given by the fit, amounts to 1 780 K, in good agreement with the value (1 700 K) observed directly at high temperature by the diffusion constant measurements. Hence the value of  $E_d$  seems to persist over the whole temperature range studied and the slight structural changes observed at the transition temperatures around 340 and 398 K do not affect the barrier hindering the diffusive process. As we have shown above, diffusion occurs through threefold H<sub>3</sub>O<sup>+</sup> reorientations. The observed activation energy is thus likely the potential barrier of these C<sub>3</sub> rotations. Values reported in the literature for this process depend on the compound and vary between 1 000 K and 4 200 K [16, 20, 21]. Our value lies in this range and agrees with this assignment.

**3. FAST DIFFUSION LIMIT.** — In the low frequency limit ( $\omega_0 \tau_d \ll 1$ ), Fries's paper predicts, whatever the value of the association rate, a logarithmic dependence of the spin-lattice relaxation rate. Only a qualitative description is provided and no practical application can be made.

Such dependence is also given by other authors [3, 6, 9] for a two-dimensional diffusive motion and seems typical of this process. The result of the work of two of them [9, 3] allows to calculate the  $T_1^{-1}$  variation with frequency.

Sholl [9] expressed  $T_1^{-1}$  as function of the diffusion constant  $D$  :

$$T_1^{-1} = B \text{Ln } \omega_0^{-1} \quad (7)$$

with

$$B = \frac{\gamma^4 \hbar^2 I(I+1)}{16 \pi D} n_c \sigma \left( \sum_{\alpha} r_{\alpha}^{-3} \right)^2 \quad (8)$$

$n_c$  : concentration of spins on the two-dimensional lattice whose lattice sites are  $r_{\alpha}$  ;

$\sigma$  : area per lattice site.

$D$  is given by equation (3). By putting its value in (8), we obtain at the three temperatures where the frequency dependence was experimentally determined (380, 400 and 420 K) a slope  $B$  equal respectively to 5.8, 4.7 and 3.8 s<sup>-1</sup>. The experimental slopes measured on the plots of the figure 4 are respectively 5.3 ; 4.1 and 3.0 s<sup>-1</sup> in good agreement with the calculated values.

Silbernagel *et al.* [3] expressed this slope with the intermolecular contribution  $M_{2\text{inter}}$  to the resonance line second moment :

$$B \approx 0.53 M_{2\text{inter}} \tau_d \quad (9)$$

$M_{2\text{inter}}$  is given by the lattice sum :

$$M_{2\text{inter}} = \frac{9}{20} \gamma^4 \hbar^2 \sum_j r_{ij}^{-6} \quad (10)$$

$\sum_j r_{ij}^{-6} = 0.0349 \text{ \AA}^{-6}$  for the CsH<sub>3</sub>O<sub>2</sub> hexagonal lattice ;  $\tau_d$  is derived from (3) and (4). Thus, we find, at the three temperatures — 380, 400 and 420 K — a slope equal respectively to 4.4, 3.5 ; 2.9 s<sup>-1</sup>, very close to the measured values. Here also a good agreement is obtained. This is likely rather fortuitous, given the limited accuracy of our measurements and the simplifying assumptions involved in each of the theoretical expressions. One can say, however, that these results support again the two-dimensional character of the diffusion in CsH<sub>3</sub>O<sub>2</sub>.

**4. SPIN-SPIN RELAXATION RESULTS.** — Two experimental features remain to be explained :

— the large temperature dependence observed on  $T_2$  measurements below 250 K, giving an apparent activation energy  $\approx 2$  100 K instead of the lower value ( $\approx 1$  700 K) derived both from  $D$  experimental study and from Fries's theory fit of the  $T_1$  data ;

— the  $T_2$  plateau and its frequency dependence in the highest temperature phases (Fig. 4).

• Consider the first point. The low dimensionality affects the spin correlation functions. As a result, the well-known expression of the spin-spin relaxation rate in the motional narrowing regime :

$$T_2^{-1} = M_2 \tau_d \quad (11)$$

could no longer apply [8]. In (11),  $M_2$  is the resonance line second moment at the onset of the motional narrowing. For a two dimensional diffusive process and the same limiting conditions (i.e.  $\omega_0^{-2} \ll \tau_d^2 \ll M_2^{-1}$ ), Richards [7] replaces the above relation (11) by the following :

$$T_2^{-1} = M_2 \tau_d \text{Ln } (M_2 \tau_d^2)^{-1} . \quad (12)$$

As the temperature increases,  $\tau_d$  decreases (see (5)) and  $T_2^{-1}$  decreases faster. If (12) is actually satisfied, a  $T_2$  semi-log plot *versus*  $1/T$  would no longer show a linear dependence with a slope equal to the true activation energy of the motion. Since the logarithm is a slowly varying function, the plotted curve would deviate not much from a straight line and the apparent activation energy would be not very different from the true one, but only slightly higher. That is exactly what was observed between 160 K and 230 K (Fig. 2). Accordingly the greater  $E_d$  value derived from  $T_2$  data in this temperature range is expected for a 2-d diffusive motion.

• A  $T_2$  plateau at high temperature has often been reported in fast protonic conductors [22-25]. Chemical shift line broadening is not considered since it is removed by the used Hahn-pulse sequence. The above observation is then related to the diffusion and can have different origins, such as internal field



gradients, low dimensionality of the motion, paramagnetic impurities. Let us consider successively each of these possible contributions.

Demagnetization field gradients, due to the irregular shape, size and packing of the particles in powder samples gives this levelling of  $T_2$  at high temperature [25]. This is easily explained if we look at the equation (2), used above for the determination of the diffusion constant. In this later case, the NMR probe was moved in a large external field gradient to increase the diffusion contribution to the echo decay (second term of the exponential in (2)) and to give it a sufficient extent. But for the  $T_2$  measurements, the probe was in the central part of the magnet air gap with the best homogeneous magnetic field. Its gradient can be estimated from the echo half-width observed on a water sample. It was lower than  $1 \text{ G cm}^{-1}$ . If we put in the probe the  $\text{CsH}_3\text{O}_2$  sample instead of the water sample, the width of the echo was not appreciably reduced. The internal field gradient is thus comparable for the two samples. Such a gradient value is much too low to affect the echo amplitude, even for the largest  $\tau$  values ( $\approx 50 \text{ ms}$ ). Besides, if actually the diffusion contributed to the echo decay, the  $\tau^3$  dependence would be verified and not the  $\tau$  dependence experimentally observed at all temperatures where  $T_2$  was determined.

Effects of low dimensionality on the spin-spin relaxation rate would be to yield a logarithmic divergence with frequency, as for  $T_1^{-1}$  in the low frequency limit, since both relaxation rates depend on the same spectral density functions. However, application to the zero frequency gives an infinite  $T_2^{-1}$  value. Some authors introduced a cut-off frequency to overcome this difficulty [3]. Others predicted a finite value when the limited size of the particle is taken into account [26]. In any case where a theoretical expression is available,  $T_2$  would increase with frequency, which disagrees with the experimental observation.

The presence of paramagnetic impurities can give, as observed on  $\text{PbF}_2$  [27-29], and *anomalous*  $T_2$  temperature dependence with a  $T_2$  minimum in the high temperature diffusive phase. No frequency dependence is expected for this contribution. Of course, another origin of the  $T_2$  behaviour could be the appearance of a small 3-d character of the proton diffusion, on approaching the melting temperature.

However this should not give the observed  $T_2$  frequency dependence. Finally as anyone of the above assumptions agrees with our experimental study, the occurrence of the plateau remains unclear.

### Conclusion.

$^1\text{H}$  nuclear magnetic relaxation in  $\text{CsH}_3\text{O}_2$  is provided by a translational diffusion process of the hydrogen atoms, which takes place through  $\text{H}_3\text{O}^+$  molecular reorientations alternating with proton jumps between the two wells of the O-O double-well potential. The measured diffusion constant amounts to  $\approx 1.8 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  at 400 K. The corresponding mean molecular reorientational rate  $\tau_r^{-1} = 2 \tau_d^{-1} \approx 2.8 \times 10^9 \text{ s}^{-1}$  is much slower than the jump rate between the two potential minima of the H-bond ( $\approx 8 \times 10^{10} \text{ s}^{-1}$  at 400 K) and thus is the limiting process of the proton diffusion. Let us note that this diffusion has been recently observed by incoherent neutron scattering on a very high resolution spectrometer [30].

The two-dimensional character of the diffusion is shown both by the  $^2\text{H}$  NMR spectrum and by the frequency dependence of the spin-lattice relaxation rate. On the high temperature side of the  $T_1$  minimum, the logarithmic frequency dependence, typical for 2-d diffusion is observed. On the low temperature side,  $T_1$  is well fitted by the Fries's model for plane fluids undergoing fast chemical exchange between molecular species, here  $\text{H}_2\text{O}$  and  $\text{OH}^-$ .

Below the hexagonal-monoclinic phase transition (229 K), the translational diffusion process persists down to about 160 K. Simultaneously the free induction decay starts to exhibit a solid-like Gaussian component showing the disappearance of the dynamic character of the proton disorder in the monoclinic phase. Besides, other studies down to 80 K indicate that in this phase there is no real proton ordering but that the disorder may be frozen in, thus leading to a 2-d proton glass. Further NMR and other experiments are being pursued in order to conform this result.

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