# $NH_4^+$ Ion Motions in Some Ammonium Salts

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Z. Naturforsch. **36a**, 205–209 (1981); received December 4, 1980

Spin-lattice relaxation times of protons in polycrystalline $(NH_4)_2SO_4$, $(NH_3OH)_2SO_4$, $(NH_4)_2HPO_4$, $NH_4VO_3$, $(NH_4)_2CrO_4$, $(NH_4)_2C_2O_4 \cdot H_2O$ and $NH_4HF_2$ salts were measured over the temperature range 100–430 K. The double minima in $T_1$ for the first three compounds were attributed to the nonequivalent $NH_4^+$ ions in the unit cells. In $NH_4VO_3$, the double minima were attributed to the reorientations about two and three fold axes. However only one minimum in $T_1$ was observed for $(NH_4)_2CrO_4$, $(NH_4)_2C_2O_4 \cdot H_2O$ and $NH_4HF_2$ and the relaxation mechanisms for the first three compounds were attributed to random reorientations of $NH_4^+$ ions. The experimental results are in good agreement with the calculated values by using the existing theoretical expressions. The discrepancies between experimental and calculated values for $(NH_4)_2HPO_4$ and $NH_4HF_2$ at low temperatures were attributed to the tightness of the hydrogen bonding at those temperatures.

## 1. Introduction

During the last years ammonium salts have been under investigation by pulsed and wide-line nmr techniques over a wide temperature range [1–6]. $(NH_4)_2SO_4$, $NH_4VO_3$ and $(NH_4)_2HPO_4$ were studied early by some authors [7–12]. It is the purpose of this paper to investigate the $NH_4^+$ motions in some more ammonium salts together with the above mentioned three compounds to make more careful measurements and test the agreement between the existing theoretical expressions and experimental results not only at limited points but over wide temperature intervals as well. It is hoped that a standard commercial apparatus would make the experimental data comparable with the theoretical expressions when the standard parameters of the compounds are used.

## 2. Experimental

The spin-lattice relaxation times were measured with an SXP type Bruker pulse spectrometer at 60 MHz using $\pi - \tau - \pi/2$ pulse sequence. The pure compounds used in this study were obtained from commercial sources and the samples were filled in glass tubes $9 \times 10^{-3}$ m in diameter and $5 \times 10^{-3}$ m in hight. The samples were left under $1.33 \times 10^{-2}$ Nm$^{-2}$ vacuum for several hours and then sealed off to erase any trace of water. The temperature control system used was a Bruker B-ST 100/700 temperature controller and approximately fifteen minutes were waited after each setting of the temperature to allow the sample to reach the desired temperatures.

## 3. Results

The experimental results of spin-lattice relaxation times have been plotted on a semi-logarithmic scale as a function of $10^3/T$ in Figures 1–4. The $T_1$ results for $(NH_4)_2SO_4$, $(NH_3OH)_2SO_4$, $(NH_4)_2HPO_4$ and $NH_4VO_3$ exhibit well defined double minima as shown in Figures 1–2. Furthermore the minima are exactly equal and 23 ms for $(NH_4)_2SO_4$, 25 ms for $(NH_4)_2HPO_4$ and 56 ms for $(NH_3OH)_2SO_4$. However the $T_1$ minima for $NH_4VO_3$ are not equal and the left minimum is 35 ms whereas the right is 15.4 ms. On the other hand, for $(NH_4)_2CrO_4$, $(NH_4)_2C_2O_4 \cdot H_2O$ and $NH_4HF_2$ the spin-lattice relaxation time passes through only one minimum. The minima are 12.5 ms, 12.5 ms, 11.5 ms, respectively, for the above order of the compounds. The results are very well reproducible over the whole temperature ranges in which the experiments were performed.

## 4. Analysis and Discussion

The spin-lattice relaxation results of the compounds studied can be analyzed by assuming reorientational motions of the $NH_4^+$ ion. When the

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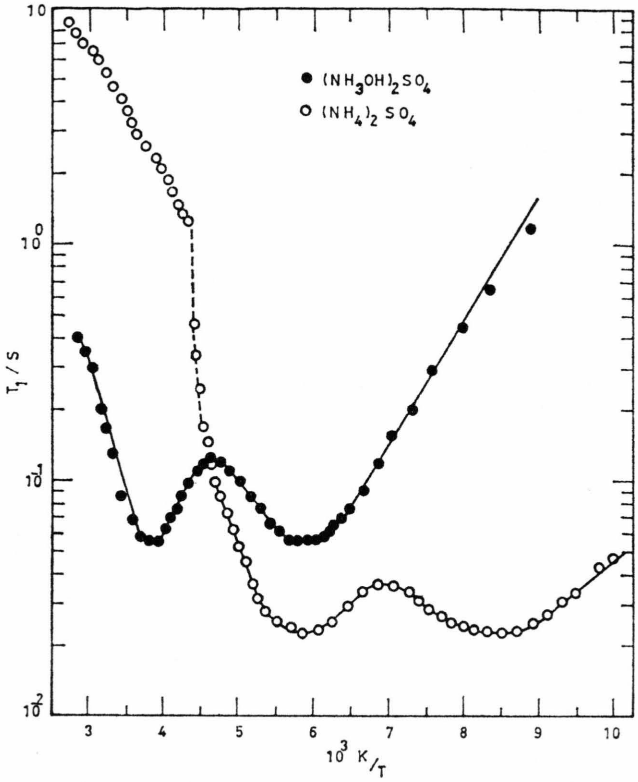

Fig. 1. Spin-lattice relaxation times of $(NH_4)_2SO_4$ (○) and $(NH_3OH)_2SO_4$ (●) against $10^3$ K/T.

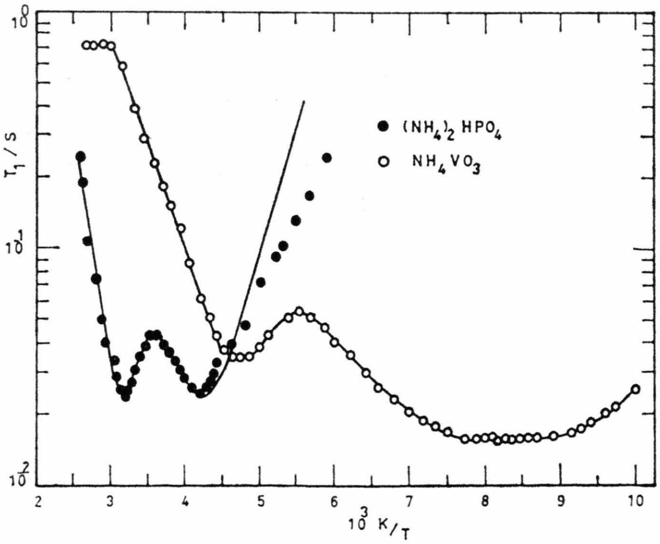

Fig. 2. Spin-lattice relaxation times of $(NH_4)_2HPO_4$ (●) and $NH_4VO_3$ (○) against $10^3$ K/T.

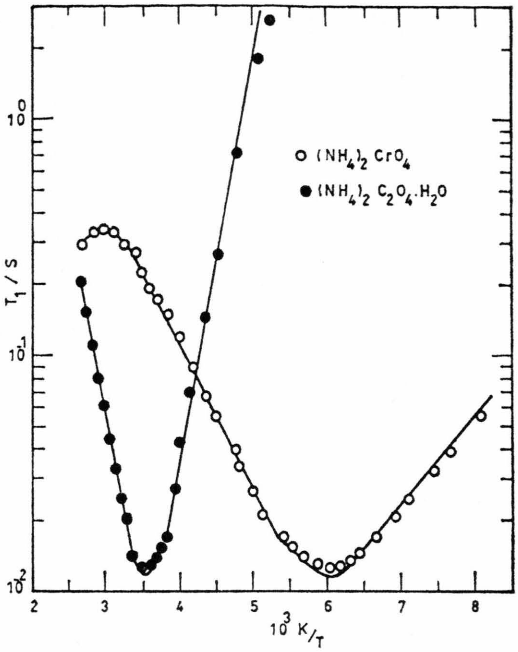

Fig. 3. Spin-lattice relaxation times of $(NH_4)_2CrO_4$ (○) and $(NH_4)_2C_2O_4 \cdot H_2O$ (●) against $10^3$ K/T.

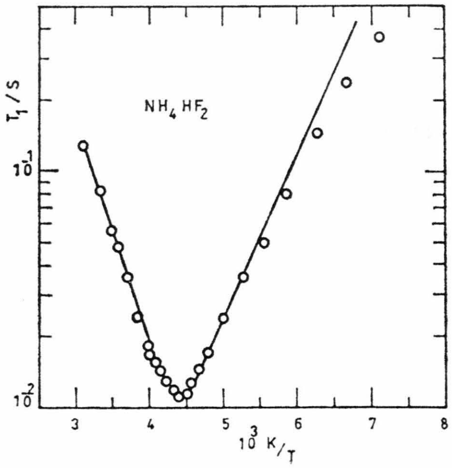

Fig. 4. Spin-lattice relaxation times of $NH_4HF_2$ against $10^3$ K/T.

reorientational motion of $NH_4^+$ ion is random the spin-lattice relaxation rate is expressed as [7],

$$T_1^{-1} = \frac{9}{10} \frac{\gamma^4 \hbar^2}{r^6} \left( \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{4 \tau_c}{1 + 4 \omega_0^2 \tau_c^2} \right), \quad (1)$$

where $\tau_c$ is the correlation time of random reorientational motion of $NH_4^+$ ion and the other symbols have their conventional meanings [13]. This equation has a minimum when $\omega_0 \tau_c = 0.6158$ and

$$T_{1\,\min}^{-1} = \frac{9}{10} \frac{\gamma^4 \hbar^2}{r^6} \frac{1.43}{\omega_0}. \quad (2)$$

On the other hand, when the reorientational motion is about the three-fold axis, then the spin-lattice relaxation rate becomes [14]

$$(T_1^{-1})_3 = \frac{27}{40} \frac{\gamma^4 \hbar^2}{r^6} \left( \frac{\tau_{c3}}{1 + \omega_0^2 \tau_{c3}^2} + \frac{4 \tau_{c3}}{1 + 4 \omega_0^2 \tau_c^2} \right), \quad (3)$$

where $\tau_{c3}$ is the correlation time or reorientational motion of the $NH_4^+$ ion around the three-fold axis. Furthermore, when the reorientational motion of the $NH_4^+$ ion is about the two-fold axis, then the spin-lattice relaxation rate turns out to be [14],

$$(T_1^{-1})_2 = \frac{9}{20} \frac{\gamma^4 \hbar^2}{r^6} \cdot \left( \frac{\tau_{c2}}{1 + \omega_0^2 \tau_{c2}^2} + \frac{4 \tau_{c2}}{1 + 4 \omega_0^2 \tau_{c2}^2} \right), \quad (4)$$

where $\tau_{c2}$ is the correlation time of the reorientational motion of $NH_4^+$ ion about the two-fold axis. On the other hand, it has been shown that in the presence of reorientational motion about three and two-fold axes when $\tau_{c3} \ll \tau_{c2}$) the spin-lattice relaxation rate becomes [14].

$$T_{1\,\mathrm{obs}}^{-1} = \tfrac{1}{3} (T_1^{-1})_2 + (T_1^{-1})_3 . \quad (5)$$

Furthermore, when there are two nonequivalent types of equal numbers of $NH_4^+$ ions in the unit cell of the compound, then due to the spin exchange process the observed spin-lattice relaxation rate becomes [7]

$$2\, T_{1\,\mathrm{obs}}^{-1} = T_{1,\mathrm{I}}^{-1} + T_{1,\mathrm{II}}^{-1}, \quad (6)$$

where $T_{1,\mathrm{I}}$ and $T_{1,\mathrm{II}}$ are the spin-lattice relaxation times of type I and type II ammonium ions.

### *a) Ammonium Sulfate*

The spin-lattice relaxation time of $(NH_4)_2SO_4$ passes through double minima of equal value below the ferroelectric phase transition at 223 K. These are in agreement in principle with the results reported in Ref. [7], however our $T_1$ results above and around the ferroelectric phase transition agree with the results reported in Ref. [8], therefore our measurements at high temperatures stay only for comparison. The dashed line in Fig. 1 shows the first-order ferroelectric phase transition which has also been observed previously [7, 8]. However for $T_1$ minima at low temperatures, $T_{1\,\min} = 23$ ms was obtained using the standard value of $r = 16.8$ nm and the Equations (2) and (6). At the left minimum ($10^3/T = 5.80$), $T_{1,\mathrm{II}}$ becomes too long and from (6) $T_{1\,\mathrm{obs}} = 2\, T_{1,\mathrm{I}}$, similarly at the right minimum ($10^3/T = 8.70$) $T_{1,\mathrm{I}}$ becomes too long and $T_{1\,\mathrm{obs}} = 2\, T_{1,\mathrm{II}}$. From the straight line portion of the experimental results above the left minimum an activation energy of $E_a = 16.6 \pm 0.3$ kJ mol$^{-1}$ was obtained. Using this activation energy and the Arrhenius equation

$$\tau_c = \tau_c^0 \exp(E_a / R\,T) \quad (7)$$

in (1) and (6), the line on the experimental points in Fig. 1 was obtained. The pre-exponential factor found from the $\omega_0 \tau_c = 0.6158$ condition was $\tau_c^0 = 1.52 \times 10^{-14}$ s. Similarly, from the high temperature side of the right minimum $E_a = 7.1 \pm 0.3$ kJ mol$^{-1}$ and $\tau_c^0 = 9.60 \times 10^{-13}$ s were obtained. Using these values in (7), (1) and (6), the line on the experimental points was obtained.

The experimental results obtained at 42 MHz [7] are somewhat longer ($T_{1\,\min} = 20$ ms) than ours when the proportion of the Larmor frequencies is considered. If the standard distance between the protons in the ammonium group $r = 16.8$ nm used in [7], then the calculation would give our experimental minimum with the multiplication factor of the ratio of the Larmor frequencies. Another point is that in [7] the right minimum (~ 24 ms) is somewhat longer than the left one (20 ms), while our observed minima are equal.

### *b) Hydroxylammonium Sulfate*

The same interpretation can be made for $(NH_3OH)_2SO_4$, but the $T_1$ minima (56 ms) are significantly longer than for $(NH_4)_2SO_4$. One reason for this is that the distant proton in the OH group does not contribute significantly to the spin-lattice relaxation and there comes a factor of 2/3 to Equation (1). But this does not account for the longness in $T_1$. Due to the presence of OH group the $NH_4$ tetrahedron is distorted and therefore, if we use $r = 18.1$ nm together with the factor 2/3 in (1), (2) and (6), then in the same way for $(NH_4)_2SO_4$ the line on the experimental points in Fig. 1 was obtained. Above the left minimum ($10^3/T = 3.94$) the activation energy was found to be $E_a = 23.0 \pm 0.3$ kJ mol$^{-1}$ and $\tau_c^0 = 3.0 \times 10^{-14}$ s. However from the high temperature side of the right minimum ($10^3/T = 5.90$) $E_a = 12.6 \pm 0.3$ kJ mol$^{-1}$ and from the $\omega_0 \tau_c = 0.6158$ condition $\tau_c^0 = 2.1 \times 10^{-13}$ s were obtained. The agreement between the experimental and the calculated values is good. There is a factor of ~ 2 between the activation energies of the first type and the second type ammonium ions.

Only one x-ray diffraction study exists on $(NH_3OH)_2SO_4$ [15] and that does not report the distance between the protons, however four molecules in the unit cell was reported, and this study shows that they are in different sites of equal numbers (i.e. 2 and 2) in the unit cell. The proton-proton distance, we have used, is in the order of the earlier reported $r_{H-H}$ values for ammonium compounds and is reasonable.

### c) *Diammonium Hydrogen Phosphate*

The explanation of the experimental results for $(NH_4)_2HPO_4$ follows the same lines as for the above mentioned two compounds. The experimental $T_1$ minima are equal and 25 ms, which is somewhat longer than the calculated $T_{1\,\text{min}} = 23$ ms. But this does not invalidate our conclusion. The activation energy above the left minimum ($10^3/T = 3.20$) is $E_a = 37.6 \pm 0.3$ kJ mol$^{-1}$ and $\tau_c^0 = 8.3 \times 10^{-16}$ s. The straight line portion of the high temperature side of the right minimum ($10^3/T = 4.20$) gives $E_a = 23.0 \pm 0.3$ kJ mol$^{-1}$ and the $\omega_0 \tau_c = 0.6158$ condition at the minimum gives $\tau_c^0 = 1.47 \times 10^{-14}$ s. Using these values in (1), (6) and (7) as above, we obtain the solid curve on the experimental points in Figure 2. The agreement between the experimental and calculated values is good down to 210 K. Below 210 K the calculated values becomes longer than the experimental values. This compound has been studied by several authors [10—12]. The experimental $T_1$ minima in Ref. [10] (19 ms and 16 ms) do not agree with ours when the ratio of the Larmor frequencies ($60/30 = 2$) is considered, and no attempt was made to predict the relaxation times in that work. However the experimental $T_1$ minima in Ref. [11] agree with ours when the ratio of the Larmor frequencies (60/37) is considered. The activation energy reported $\approx 23$ kJ mol$^{-1}$ is exactly equal to the activation energy we obtained for the type II ammonium groups (i.e. high temperature side of the right minimum). But the experimental results above the left minimum in that work do not agree with ours, and no attempt was made to predict the relaxation times over the whole temperature interval by the authors. On the other hand, when the study (at 18 MHz) by Shimomura et al. is considered [12], their high $H_1$ field $T_1$ minima agree with ours when the ratio of the Larmor frequencies is taken into account, but they made no attempt to predict the relaxation times explicitly. The longness in $T_1$ that they have observed at low $H_1$ field ($4 \times 10^{-4}$ $T$) is probably worth of trying it with a commercial spectrometer. We did not observe the case, and this may be due to our strong $H_1$ field ($1.4 \times 10^{-3}$ $T$). However our results are in good agreement with the predictions, and the $T_1$ minima at 60, 37 [11] and 18 MHz [12] Larmor frequencies satisfy the frequency dependence of $T_{1\,\text{min}}$. But there remains the explanation of the discrepancies of the calculated values from the experimental results below 210 K. This should be due to the fact that the structure of $(NH_4)_2HPO_4$ is determined to a large extend by hydrogen bonds [16]. The structure consists of $PO_4$ and $NH_4$ tetrahedra held together by O—H..O and N—H...O bonds. Therefore we think that this hydrogen bonding becomes stronger at low temperatures and restricts the motions of the ammonium groups. This case happens in completely hydrogen bonded $NH_4HF_2$ as seen in Figure 4.

### d) *Ammonium Metavanadate*

The $T_1$ minima for $NH_4VO_3$, 35 ms at $10^3/T = 4.60$ and 15.4 ms at $10^3/T = 8.40$, are different from the minima of the above mentioned compounds. The right minimum is due to the reorientational motions of $NH_4^+$ ions about the three-fold axis and the left minimum is due to the reorientational motions about the two-fold axis. The activation energies for the motions obtained from the experimental results in Fig. 2 are $15.8 \pm 0.3$ kJ mol$^{-1}$ and $5.8 \pm 0.3$ kJ mol$^{-1}$, respectively, for the two and three-fold reorientations. The $T_{1\,\text{min}}$ for the three-fold reorientations obtained from (3) using $\omega_0 \tau_{c3} = 0.6158$ gives 15.4 ms, which is exactly the experimental value. The calculated $T_1$ values for three-fold reorientations above and below the right minimum are in good agreement with the experimental results. Two-fold reorientations do not contribute to $T_1$ below the $T_1$ maximum between the two minima in Fig. 2. The pre-exponential factor for the Arrhenius equation was found to be $\tau_{c2}^0 = 4.40 \times 10^{-12}$ s. However the three-fold rotations contribute to $T_1$ until the left minimum, and therefore (5) was used. Above the left minimum from (5), the observed spin-lattice relaxation becomes $T_{1\,\mathrm{obs}} = 3(T_1)_2$. Using this, (7) and (4), the calculated results were found to be in good agreement with the experimental results shown as a line on the experimental points. The pre-exponential factor was found to be $\tau_{c2}^0 = 2.47 \times 10^{-13}$ s at the left minimum using $E_a = 15.8$ kJ mol$^{-1}$ and the condition $\omega_0 \tau_{c2} = 0.6158$.

A previous study (at 38.3 MHz) on $NH_4VO_3$ was limited on the $T_1$ minima [9]. Although the right minimum (11 ms) is in the same proportion of the Larmor frequencies, the activation energies and the value of the left $T_1$ minimum are quite different from ours.

### e) *Ammonium Cromate and Oxalate*

The experimental $T_1$ minima for $(NH_4)_2CrO_4$ and $(NH_4)_2C_2O_4 \cdot H_2O$ are 12.5 ms and these agree with the calculated $T_{1\,\mathrm{min}} = 11.5$ ms for random reorientational motions of $NH_4^+$ ions given by (1) and (2). The activation energies from the high temperature sides of the $T_1$ minima in Fig. 3 were obtained as $12.5 \pm 0.3$ kJ mol$^{-1}$ and $33.8 \pm 0.3$ kJ mol$^{-1}$, respectively to $(NH_4)_2CrO_4$ and $(NH_4)_2C_2O_4 \cdot H_2O$. The pre-exponential factors found for $(NH_4)_2CrO_4$ and $(NH_4)_2C_2O_4 \cdot H_2O$ from the $\omega_0 \tau_c = 0.6158$ condition (at $10^3/T = 6.0$ and $10^3/T = 3.55$) were $\tau_0^c = 1.89 \times 10^{-13}$ s and $\tau_c^0 = 8.48 \times 10^{-16}$ s, respectively to the above order of the compounds. Using these pre-exponential factors and the activation energies in (7) and (1), the relaxation times were calculated along the whole temperature ranges and found to be in good agreement with the experimental results as shown in Figure 3.

### f) *Ammonium Hydrogen Difluoride*

With the same lines as above the activation energy for $NH_4^+$ ion reorientations in $NH_4HF_2$ was found as $E_a = 17.9 \pm 0.3$ kJ mol$^{-1}$ from the high temperature side of the $T_1$ minimum in Figure 4. $\tau_c^0$ was found to be $8.7 \times 10^{-14}$ s at $10^3/T = 4.55$. Using these in (7) and (1), the calculated values were drawn as a curve on the experimental results. As seen in Fig. 4, the calculated values are in good agreement with the experimental results down to 180 K, but below 180 K the calculated values become longer than the experimental results. We suppose that this is due to the completely hydrogen bonded structure of the type N—H...F [17]. Above 180 K the hydrogen bonds become sufficiently weak to allow the reorientations of the ammonium groups, and therefore the experimental and calculated values agree. However below 180 K the bonds become stronger and the reorientations begin to cease.

This study was supported in part by the Magnetic Resonance Unit of TBTAK (Turkish Scientific and Technical Research Council).

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