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Proton relaxation by tunnelling in ammonium salts at low temperature

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Abstract. Proton spin–lattice relaxation times T_1 and $T_{1\rho}$ have been measured in partly deuterated NH_4ClO_4, $(NH_4)_2SnCl_6$, cubic and trigonal $(NH_4)_2SiF_6$ and $(NH_4)_2Ce(NO_3)_6$ at several frequencies 4 to 30 MHz and from 1·5 to 4.2 K. T_1 depends upon the deuterium content in all cases, but $T_{1\rho}$ is very short also in some of the undeuterated salts. The true relaxation is a direct process proportional to T but T_1 is diffusion-limited in some of the more deuterated salts. We discuss the relaxation rates in terms of transition probabilities between tunnel-split energy states slightly mixed by the dipolar interaction. First-order mixing gives relaxation of asymmetric NH_3D^+, but second-order mixing is required for relaxation of symmetric NH_4^+. The relaxation is rapid where the unperturbed levels cross, and we derive $T_1 \propto \omega_0^2$ for salts with small tunnel frequencies $\omega_t \ll \omega_0$. This behaviour is seen in cubic $(NH_4)_2SiF_6$. The observed behaviour $T_{1\rho} \propto \omega_t^{-2}$ cannot be explained by dipolar mixing and we suggest spin–rotational interaction.

1. Introduction

Some time ago we demonstrated that proton spin–lattice relaxation in NH_4ClO_4 and $(NH_4)_2SnCl_6$ at liquid helium temperatures depend upon the deuterium content in these salts (Svare and Tunstall 1975). We interpreted this as a consequence of reorientation tunnelling which causes relaxation in NH_3D^+ but not in symmetric NH_4^+ ions. The possibility that the natural deuterium content is the cause of the relaxation in solid methane also has been discussed by Zweers and Brom (1977).

We have now studied several other partly deuterated low-barrier ammonium salts where we expect tunnelling, with pulse and cw methods at various frequencies, and we always find the proton T_1 at liquid helium temperature to be determined by the deuterium content. The relaxation rate of NH_3D^+ is here proportional to T and the transitions must be direct one-phonon processes involving energies much smaller than kT. But temperature independent spin diffusion from the NH_4^+ ions towards the NH_3D^+ impurities is in some cases the bottleneck for energy transfer.

In our previous letter (Svare and Tunstall 1975) we suggested a two-step energy transfer in NH_3D^+ made possible by tunnelling: From spins to tunnel states with time

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constant T_{1tm} due to dipolar interaction, and from tunnel states to phonons with T_{1pt} due to lattice vibration. The slower of these times would then dominate the spin–lattice relaxation time $T_1 = T_{1tm} + T_{1pt}$. The energy levels were assumed to be lifetime broadened by T_{1pt} (Haupt 1971). However, we now think that tunnel-assisted relaxation can be better discussed as transitions between tunnel states slightly mixed by the dipolar interaction (Zweers and Brom 1977). This permits conclusions about the expected temperature and frequency dependence of T_1, and we will for example show that the observed dependence $T_1 \propto \omega_0^2$ is reasonable in partly deuterated $(NH_4)_2SiF_6$ where the tunnel frequencies ω_t are much smaller than the Zeeman frequency ω_0. But we will not attempt numerical calculations for relaxation in the complicated ammonium ions.

We have also measured the relaxation times $T_{1\rho}$ in the rotating frame, which are mostly short and not dependent upon deuteration. We will show that it is necessary to involve a spin–rotational NH_4^+ relaxation mechanism proportional to ω_t to explain the observed dependence $T_{1\rho}^{-1} \propto \omega_t^2 T$ in most of the ammonium salts studied.

2. Theory

2.1. Lineshape and spin–lattice relaxation T_1

The eigenstates Ψ_{nsm} with energy E_{nsm} of a tunnelling NH_4^+ ion are specified by the torsional or rotational quantum number $n = \sum_x n_x$ around the x possible axes, by the symmetry state s of the spatial wavefunction associated with the protons and by the magnetic quantum number m. At low temperature only $n = 0$ is populated and we will leave out this index in most of the following expressions. The Pauli principle couples spin and space parts of the states since the total wavefunction must by symmetric in a tunnelling reorientation which interchanges two pairs of identical fermions. The symmetry states are: One A state with nuclear spin $I = 2$, three T states with $I = 1$ and two E states with $I = 0$. Tunnelling around the three-fold axes in NH_4^+ gives the main tunnel splitting, but tunnelling around the two-fold axes is also possible with one to three order-of-magnitude smaller splitting (Svare 1977). Two-fold tunnelling thus removes the degeneracy of the T states in a tetrahedral field.

Intra-ion dipolar interaction H_D broadens the NMR resonance induced within each T state, but not the A resonance. Thus the observed spectrum has a sharp A line broadened only by inter-ion coupling and long wings on the line from T resonance (Tomita 1953). Since energy is not exactly conserved in spin flips between neighbouring ions in T and A states, spin diffusion is somewhat restricted in salts with tunnelling (Emid and Wind 1974, 1975).

Classically we think of NH_4^+ as having a definite orientation, and this can be described with a given combination of eigenfunctions Ψ_{nsm}. Such a combination will change periodically with time with tunnel frequencies in the groundstate $\omega_{s's} = (E_{0s'm} - E_{0sm})/\hbar$, and a complete description of the tunnel motion is given by the complete set of linear combinations. Spin–lattice relaxation can then be described as resulting from modulation of the dipolar interaction by the tunnel motion randomly interrupted by phonon-induced transitions (Punkkinen 1975, Svare 1977). Provided there is thermal equilibrium over the A, T and E states, the relaxation rate is:

$$T_1^{-1} = \sum_{\substack{s,s' \\ a=1,2}} A_{as's}\tau_{s's}[1 + (\omega_{s's} - a\omega_0)^2\tau_{s's}^2]^{-1}. \tag{1}$$

Each component of motion with tunnel frequency $\omega_{s's}$ and coherence time $\tau_{s's}$ has a relaxing power $A_{as's}$ given by the corresponding fraction of the dipolar interaction. Equation (1) demonstrates the relation with the classical BPP theory of relaxation since it reduces to this if all $\omega_{s's} \ll \omega_0$ or all $(\omega_{s's}\tau_{s's}) \ll 1$. But it is not easy to visualise the tunnel motion of a complex system like NH_4^+ or to calculate the coefficients $A_{as's}$ with proper regard to the Pauli principle. It is also difficult to give any relations between the magnitudes of different $\tau_{s's}$. Moreover, information about the exact energy of the phonons involved in the relaxation is lost in this approach.

We prefer to discuss relaxation in tunnelling systems in terms of phonon-induced transitions between energy states where m changes, as has been done by Haupt (1971) and Zweers and Broom (1977). Since the interaction $H_C(\omega t)$ with the phonons through the crystal field cannot change m, relaxation is only possible through the slight mixing of the states Ψ_{nsm} by the small dipolar interaction H_D. This approach must of course lead to the same result as a proper description in terms of the spectral fluctuation densities (1), since a physically observable like relaxation cannot depend upon our choice of wavefunction basis. In another paper (Svare, to be published) we discuss relaxation of NH_4^+ by excitations from the mixed groundstate to the excited states Ψ_{nsm} and how this leads to the classical BPP behaviour at high temperature or small tunnel splittings. Such processes are the equivalent of the Orbach relaxation in electron spin relaxation (Orbach 1961). Here we will discuss only direct one-phonon transitions within the groundstate multiplets of NH_4^+ and NH_3D^+. Raman two-phonon transitions can be treated by similar perturbation expressions. Raman processes may be important in low-temperature relaxation experiments to avoid hot phonons, but we have not observed their higher power of T dependence in T_1^{-1} from 1·5 to 4·2 K.

We give a semiclassical treatment of the direct process transition and write out symbolically only the ion part of the matrix elements. We do not attempt to calculate the magnitude of T_1, but we hope to find its frequency dependence in limiting cases. The approximation $(E_{s'm'} - E_{sm}) \ll kT$ is good at 1 K for all ammonium salts investigated by us, and then the transition probability between states sm and $s'm'$ is:

$$\tau^{-1}_{ss'mm'} = (2\pi/\hbar)|M_{ss'mm'}|^2\rho(E_{s'm'} - E_{sm})kT/(E_{s'm'} - E_{sm}). \qquad (2)$$

Here $M_{ss'mm'}$ is the net matrix element of $H_C(\omega) + H_D$ in the lowest perturbation that connects states sm and $s'm'$. The density of states ρ of phonons with proper energy is proportional to $(E_{s'm'} - E_{sm})^2$ in the long wavelength limit, and the last factor in (2) gives the probability that these phonons are excited. Transitions are caused by the lattice strain set up by the phonons. Therefore $|M_{ss'mm'}|^2$ implicitly contains the phonon frequency to the first power, and the net frequency dependence of (2) will be the explicit frequency of $|M_{ss'mm'}|^2$ that we will write out, multiplied with the frequency dependence of ρ.

The sum of the rates (2) where m changes, taken according to the Hebel–Slichter (1959) relation, gives the spin–lattice relaxation rate T_1^{-1}, provided a uniform spin temperature exists over all states. But, symmetry conversion transitions, where s changes, are necessary to establish thermal equilibrium over the symmetry species. Since the symmetry conversion rate may be comparable to, or slower than, the spin–lattice relaxation rate, neither process can necessarily be described with a single time constant, and a system of coupled rate equations should be considered.

In asymmetric NH_3D^+ the spatial wavefunction of the protons can still be characterised by a symmetry s, but there is no Pauli principle coupling to the magnetic quantum number m in tunnelling where D takes part. Low symmetry interactions with the lattice are also possible since the lattice can to some extent 'feel' the orientation of D. Hence:

$$\langle sm|H_{\mathrm{C}}|s'm\rangle \neq 0$$

and relaxation transitions are possible in first-order perturbation of H_{D} since:

$$M_{ss'mm'} \propto \sum_{s''}\left[\frac{|\langle s'm'|H_{\mathrm{D}}|s''m\rangle}{(E_{s'm'}-E_{s''m})}\langle s''m|H_{\mathrm{C}}|sm\rangle + \langle s'm'|H_{\mathrm{C}}|s''m'\rangle\frac{\langle s''m'|H_{\mathrm{D}}|sm\rangle}{(E_{sm}-E_{s''m'})}\right], \tag{3}$$

is finite unless all groundstate tunnel splittings of NH_3D^+ vanish as they do in high-barrier salts. We have assumed that the levels have long lifetimes and are sharp at low temperatures.

The frequency behaviour of T_1^{-1} resulting from (3) is complicated, but we see that relaxation is especially rapid wherever the unperturbed levels cross and the energy denominators vanish. For small tunnel splittings we can contract (3) to:

$$(\hbar\omega_{m'm})^{-1}\left[\left(1-\frac{\omega_{s's}+\omega_{ss''}}{\omega_{m'm}}\right)\langle s'm'|H_{\mathrm{D}}H_{\mathrm{C}}|sm\rangle - \left(1+\frac{\omega_{ss''}}{\omega_{m'm}}\right)\langle s'm'|H_{\mathrm{C}}H_{\mathrm{D}}|sm\rangle\right], \tag{4}$$

which has the explicit frequency dependence ω_t/ω_0^2 where we write ω_t for the 'average' tunnel frequency. The phonon frequencies involved in this transition are $(\omega_{m'm} \pm \omega_t) \approx (m'-m)\omega_0$, and we therefore have for NH_3D^+:

$$T_1^{-1} \propto \omega_t^2/\omega_0^2 \qquad \text{for } \omega_t \ll \omega_0 \tag{5}$$

In symmetric NH_4^+ spin and space parts of the wavefunctions are coupled and the phonon excitations can only be of A symmetry. Then:

$$\langle sm|H_{\mathrm{C}}|s'm\rangle = 0 \quad \text{for } s \neq s', \tag{6}$$

and

$$\langle sm|H_{\mathrm{C}}|sm\rangle = \langle s'm'|H_{\mathrm{C}}|s'm'\rangle, \tag{7}$$

for normalised states. Transitions with $m' \neq m$ now vanish to first orders in H_{C} and H_{D} since:

$$M_{ss'mm'} \propto \left[\frac{\langle s'm'|H_{\mathrm{D}}|sm\rangle}{(E_{s'm'}-E_{sm})}\langle sm|H_{\mathrm{C}}|sm\rangle + \langle s'm'|H_{\mathrm{C}}|s'm'\rangle\frac{\langle s'm'|H_{\mathrm{D}}|sm\rangle}{(E_{sm}-E_{s'm'})}\right] = 0. \tag{8}$$

using (7).

Mixing the symmetrised states of NH_4^+ to second order in H_{D}, we find that most of the possible terms in the transition matrix element cancel using (6) and (7), and we are left with only:

$$M_{ss'mm'} \propto \left\{\langle sm|H_{\mathrm{C}}|sm\rangle\frac{\langle sm|H_{\mathrm{D}}|s'm'\rangle}{(E_{sm}-E_{s'm'})^2}\left[\langle sm|H_{\mathrm{D}}|sm\rangle + \langle s'm'|H_{\mathrm{D}}|s'm'\rangle\right]\right\}. \tag{9}$$

Thus the transition probability for this process is:

$$\tau_{ss'mm'}^{-1} \propto (E_{sm}-E_{s'm'})^{-2}, \tag{10}$$

and we have for the second-order dipolar relaxation rate in NH_4^+,

$$T_1^{-1} \propto \begin{cases} \omega_0^{-2} & \text{for } \omega_0 \gg \omega_t \gg \omega_d \qquad (11a) \\ \omega_t^{-2} & \text{for } \omega_t \gg \omega_0. \qquad (11b) \end{cases}$$

The tunnel energies must be larger than the dipolar energy $\hbar\omega_d$ for the perturbation calculation to be valid.

We have also tried to use components of H_C to mix excited states n into the groundstate before we apply H_D once. But again most terms cancel and we are left with matrix elements of order $H_C[H_C H_D/(E_n - E_0)^2]$, which are probably even smaller than (9).

Comparing (9) with (3) we see that except in fields B_0 exactly where some of the NH_4^+ unperturbed levels cross, the proton relaxation is much slower in NH_4^+ than in NH_3D^+ by a factor or order of magnitude:

$$\omega_d^2/(\omega_t - \omega_0)^2. \tag{12}$$

The factor may well be less than 10^{-4} which is the natural isotope ratio D/H. Then the protons relax by spin diffusion to the rapidly relaxing NH_3D^+ impurities. Since T_1 of a given NH_3D^+ ion varies greatly with tunnel splittings which depend somewhat on crystal strain, the diffusion may go primarily to those NH_3D^+ ions which happen to have the right tunnel splitting for a level crossing.

While the pure NH_4^+ relaxation should be relatively fast at a level crossing, we are unlikely to observe such very sharp maxima in T_1^{-1} for $\omega_t = \omega_0$. This is because the crystal field barrier and the tunnel frequencies of NH_4^+ also depend upon crystal strain, and ω_t in actual salts is likely to be distributed over a range much larger than ω_d.

Spin diffusion through the dipolar interaction $I_i^+ I_j^- (3\cos^2\theta_{ij} - 1) r_{ij}^{-3}$ between protons in different ammonium ions i and j is a temperature independent process in contrast to the direct relaxation process discussed so far, which involves a phonon and is proportional to temperature. Spin diffusion may be the limiting process for energy transfer, and diffusion-limited relaxation can be recognised from its temperature independence. This case is more likely to occur at high concentrations C of NH_3D^+ since the random walk diffusion time is proportional to $L^2 \propto C^{-2/3}$, while the relaxation time in the rapid diffusion case is proportional to C^{-1}. Here L is the average distance between efficient NH_3D^+ impurities.

A condition for fast relaxation by NH_3D^+ is that the ion is really tunnelling and not locked in the lattice with D in a fixed direction in a low-symmetry site due to its ability to 'feel' the surrounding crystal field. The energy difference between different directions of D must be less than the tunnel splitting for NH_3D^+ to be a relaxation centre, and this condition is most easily fulfilled in low-barrier cubic salts.

The symmetry conversion time $T_{S\text{-}C}$ in NH_4^+ can in principle be calculated by adding all transition rates (10) where s change. The dominant terms give approximately:

$$T_{S\text{-}C} \propto \omega_t^2 \qquad \text{for both } \omega_t \gg \omega_0 \text{ and } \omega_t \ll \omega_0. \tag{13}$$

If $\omega_t \approx \omega_0$, many of the same transitions contribute both to T_1 and $T_{S\text{-}C}$ and the other contributions are of about the same magnitude, so generally we expect $T_1 \approx T_{S\text{-}C}$ in this case. $T_{S\text{-}C}$ can influence a relaxation experiment, and T_1 and $T_{S\text{-}C}$ are probably the two relaxation times differing by a factor of order of magnitude five usually seen in non-deuterated salts with tunnelling (Güttler and von Schütz 1973, Punkkinen and Clough 1974).

But symmetry conversion by diffusion of symmetry energy from NH_4^+ to NH_3D^+ is not possible, and the single fast relaxation time we see in most of the partly deuterated ammonium salts must be spin–lattice relaxation via NH_3D^+. To observe $T_{S\text{-}C}$ we would have to saturate the sample with RF power for a time comparable with T_1 of the pure NH_4^+ salt and then wait for a similar time afterwards for signal recovery.

2.2. *Spin–lattice relaxation $T_{1\rho}$ in the rotating frame*

Classical reorientation motion of NH_4^+ with correlation time τ give the relaxation rate in powders:

$$T_{1\rho}^{-1} = A\left(\frac{5}{2}\frac{\tau}{1+\omega_0^2\tau^2} + \frac{\tau}{1+4\omega_0^2\tau^2} + \frac{3}{2}\frac{\tau}{1+4\omega_1^2\tau^2}\right).$$

Thinking in terms of spectral densities and taking the analogue of equation (1) for T_1, we believe that $T_{1\rho}$ in the tunnelling case should be given by:

$$T_{1\rho}^{-1} = \sum_{\substack{s,s'\\ a=1,2}} \{A'_{as's}\tau_{s's}[1 + (\omega_{s's} - a\omega_0)^2\tau_{s's}^2]^{-1} + B_{s's}\tau_{s's}[1 + (\omega_{s's} - 2\omega_1)^2\tau_{s's}^2]^{-1}\}. \tag{14}$$

The coefficients $A'_{as's}$ and $B_{s's}$ are given by the intra-ion dipolar coupling of the $s's$ component of tunnel motion. They have similar magnitudes, and $T_{1\rho}^{-1}$ must have maxima for $\omega_{s's} = 2\omega_1, \omega_0$ or $2\omega_0$. $T_{1\rho}$ is much different from T_1 only if the system has fluctuations at the very low frequency $2\omega_1$.

We believe that the same physics can also be formulated in terms of transitions between energy eigenstates, as we have done for T_1. Then $T_{1\rho}^{-1} \approx T_1$ plus some terms from transitions (9) in the very low effective field $B_1 = \omega_1/\gamma$. The latter terms may well dominate in $T_{1\rho}^{-1}$, and we use the limiting case (11) for $T_{1\rho}^{-1}$ as well and write:

$$T_{1\rho}^{-1} \propto \omega_t^{-2} \qquad \text{for } \omega_t \gg \omega_1 \tag{15}$$

which will be valid for most cases where we expect tunnel effects. For $T_{1\rho}^{-1}$ in NH_3D^+ we use (3) and (5) in the same way. Thus we expect short $T_{1\rho}$ for salts with small, but finite, tunnel frequencies, both for NH_3D^+ impurities and pure NH_4^+, and spin diffusion may not be necessary. Since the spread in ω_t due to crystal strain is likely to be proportional to ω_t, we expect a much greater fraction of the ions to have small denominators $(\omega_1 - \omega_t)^2$ in the transition rates in salts where $\omega_1 \approx \omega_t$, than have small $(\omega_0 - \omega_t)^2$ in salts where $\omega_0 \approx \omega_t$. Thus $T_{1\rho}$ is likely to be very short in some salts compared to the shortest T_1 found in any ammonium salt at 4.2 K.

3. Experiments

The ammonium salts studied were mostly in powder form, either as purchased or partly deuterated by dissolving in D_2O/H_2O mixtures and recrystallising. Only for trigonal $(NH_4)_2SiF_6$ did we use single crystals, grown below 5°C to get this crystal modification. The temperatures were measured from the He pressure. The magnet was a Fieldial controlled Varian 12″.

3.1. Continuous-wave saturation and signal recovery

Lineshape and signal recovery after saturation were studied at very low CW power levels with a Robinson type marginal oscillator from 11 to 18 MHz. Only relaxation times longer than 50 s could be measured in this way and thus the method was restricted to natural salts and low deuterium contents, although we could get some qualitative information about the shorter times.

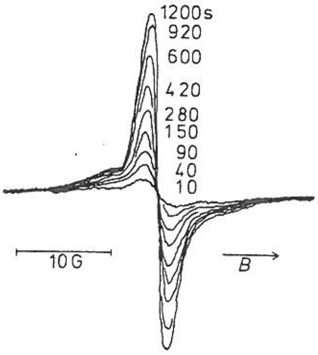

Figure 1. Proton resonance recovery after saturation in $(NH_4)_2Ce(NO_3)_6$ at 15·0 MHz and 2·2 K. $T_1 \gtrsim 700$ s.

An example of measurements on $(NH_4)_2Ce(NO_3)_6$ (Merck Z Anal) is shown in figure 1, from which we derive $T_1 \approx 700$ s at 2·2 K and 15·0 MHz. A shorter component of the signal recovery has a time constant of order 100 s. The noise level is relatively high since we used rapid sweep and the lowest possible RF level to avoid saturation. The line has a sharp A component and broad wings from T resonance. Most of the salts investigated gave proton lines of similar shape, but in $(NH_4)_2SiF_6$ the coupling to the ^{19}F spins broadened the line. In no case could we detect a difference in the long recovery times of the sharp peak and the wings. Hence we conclude that the short times seen are the symmetry conversion times $T_{S\text{-}C}$ and the long-times are the spin–lattice relaxation times T_1.

Other data for natural and slightly deuterated $(NH_4)_2Ce(NO_3)_6$, $(NH_4)_2SnCl_6$ (Schuchardt), and cubic and trigonal $(NH_4)_2SiF_6$ (Riedel de Haën) are included in figures 4 to 7 in § 3.2. The relaxation times in pure and 60 % D in NH_4ClO_4 (Fluka 99·5 %) were of order 1 s, but since the lineshape of 60 % D in NH_4ClO_4 narrowed slightly from 4·2 to 1·5 K, there must also be some time constant of order 10^{-3} to 10^{-4} s in this salt. This is most likely the allowed symmetry conversion rates in NH_3D^+ and $NH_2D_2^+$. Some samples of pure NH_4NO_3 showed the very long T_1 of order 2000 s expected for a medium high-barrier salt. In other samples we found $T_1 \approx 70$ s at 1·5 K and shorter at 4.2 K. NH_4VO_3 also had relatively short $T_1 \approx 50$ s, possibly due to paramagnetic impurities, but these salts were not investigated further.

In some experiments we changed the spin populations by changing the magnetic field to B_0'—for a while, instead of RF saturation. A minute at $B_0' \approx 100$ G gave a good saturation effect in cubic $(NH_4)_2SiF_6$ but not in $(NH_4)_2Ce(NO_3)_6$. High fields $B_0' \gg B_0$ increased the signals, but the relaxation times in high fields appeared to be very long. We tried unsuccessfully to find values of B_0' at level crossings where T_1 would be particularly short.

3.2. Measurements of T_1

The spin–lattice relaxation times T_1 of partly deuterated NH_4ClO_4, $(NH_4)_2SnCl_6$, $(NH_4)_2Ce(NO_3)_6$ and cubic and trigonal $(NH_4)_2SiF_6$ were measured at 4, 10 nd 30 MHz with a Spin–Lock pulse apparatus using the standard method of a 90° pulse at variable times after a 180° pulse or a saturating train of 90° pulses.

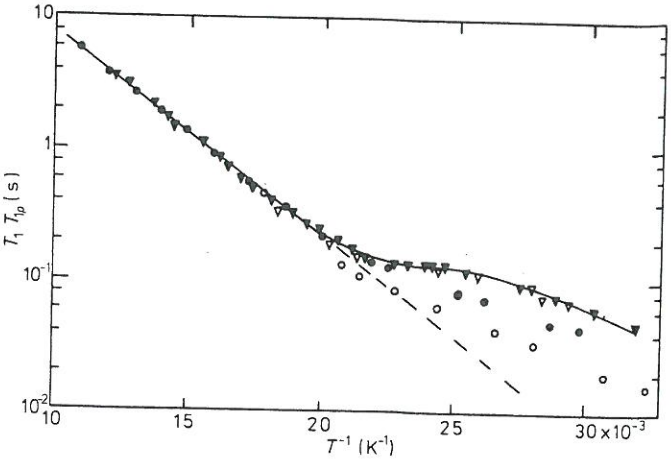

Figure 2. Measurements of proton T_1 (filled symbols) and $T_{1\rho}$ (open symbols) in natural NH_4ClO_4 (triangles) and in perchlorate with 25% D (circles) at 30 MHz as function of inverse temperature. Full curve shows 'Haupt maximum' in T_1 and $T_{1\rho}$; the dashed line is classical behaviour.

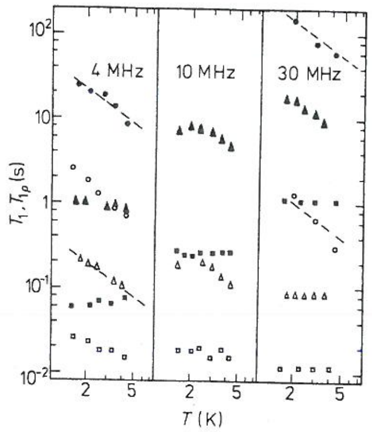

Figure 3. Measurements of proton T_1 (filled symbols) and $T_{1\rho}$ (open symbols) in $(NH_4)_2SnCl_6$ with 0·4% D (circles), 2% D (triangles) and 26% D (squares) at 4, 10 and 30 MHz as function of temperature. Dashed lines are direct process T^{-1} dependence.

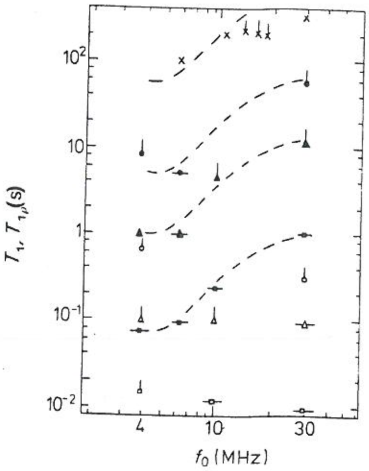

Figure 4. Proton T_1 (filled symbols) and $T_{1\rho}$ (open symbols) in $(NH_4)_2SnCl_6$ with 0·4% D (circles), 2% D (triangles) and 26% D (squares) at 4·2 K as function of measuring frequency. Crosses are from cw measurements of T_1 on natural $(NH_4)_2SnCl_6$. Symbols with vertical bars show direct process T^{-1} dependence, symbols with horizontal bars show temperature independence from 4.2 to 1.5 K. Dashed curves are drawn approximately through T_1 points and with vertical distance proportional to D percentage.

Some measurements were done at 40 to 200 K to check that the activation energy E_a for classical relaxation was the same in pure and partly deuterated salts. In no case could we find a difference in E_a, and figure 2 shows the results for pure and 25 % D in NH_4ClO_4. The relaxation times are the same in the classical region but the 'Haupt maximum' in T_1 and $T_{1\rho}$ due to tunnelling (Svare 1977) is reduced in the 25 % D salt. This is as expected since tunnelling that involves D is slower by an order of magnitude. However, the behaviour of NH_4ClO_4 with 25 % D is not completely classical since part of the signal still comes from NH_4^+ ions, and even in the NH_3D^+ ions there is tunnelling which does not involve D.

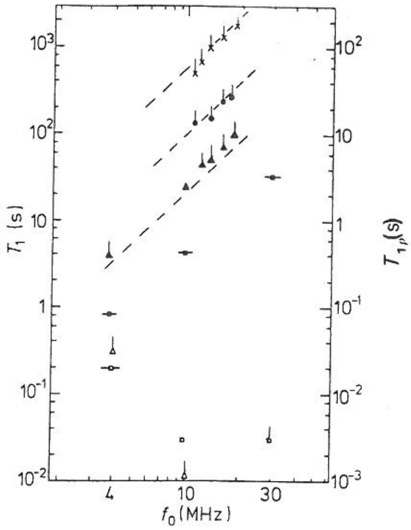

Figure 5. Proton T_1 (filled symbols) and $T_{1\rho}$ (open symbols) in cubic $(NH_4)_2SiF_6$ with 0·09 % D (circles), 0·47 % D (triangles) and 25 % D (squares) at 4·2 K. Crosses are T_1 in natural salt. Bars on symbols as in figure 4. Dashed lines show f_0^2 dependence of T_1 and are displaced in proportion to D percentage.

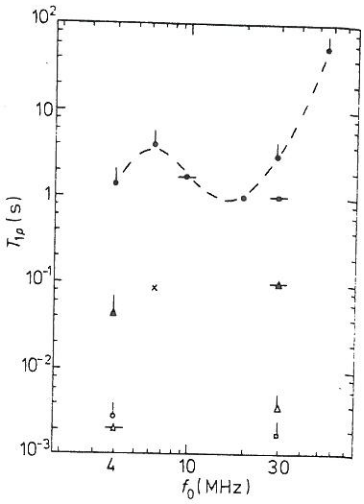

Figure 6. Proton T_1 (filled symbols) and $T_{1\rho}$ (open symbols) in natural NH_4ClO_4 (circles) and in salt with 10 % D (triangles) and in 60 % D (squares). Cross T_1 for 1 % D. Bars on symbols as in figure 4.

In the partly deuterated salts we usually found only one relaxation time at liquid helium temperatures. while we saw at least two recovery times for pure and heavily deuterated salts. In these cases we concentrated on the longest times. Examples of our measurements on $(NH_4)_2SnCl_6$ are given in figure 3. These data together with earlier pulse data (Svare and Tunstall 1975) plus our cw data are displayed in figure 4 as function of frequency and deuteration. T_1 is proportional to T^{-1} for low deuterium contents due to the direct relaxation process, and temperature independent for higher deuterium contents due to diffusion-limited relaxation. The experiments confirm that the relaxation is proportional to the D content up to 26 % D, as seen by the congruent dashed lines drawn approximately through the T_1 points and shifted vertically in proportion to the D content. The relaxation maximum for NH_3D^+ in $(NH_4)_2SnCl_6$ appears to be at about 5 MHz, which is reasonable from our previous estimate of $\omega_t/2\pi \approx 6$ MHz in this salt. But to determine ω_t with certainty from relaxation data we need a continuously variable frequency ω_0.

The relaxation data on the other salts are displayed in figures 5 to 7 in the same way. The relaxation rate in cubic $(NH_4)_2SiF_6$ is direct and proportional to the deuterium content at least up to 0·47 % as seen by the dashed lines in figure 5. In fluorosilicate with 25 % D the diffusion-limited relaxation is relatively slower. The frequency dependence of T_1 is strikingly proportional to ω_0^2, as expected from equation (5).

Relaxation in NH_4ClO_4 shown in figure 6 is proportional to the D content only up to about 1 % D, and T_1 increases by an order of magnitude from 25 % D to 60 % D. This may be due to interaction between neighbouring NH_3D^+ or $NH_2D_2^+$ ions which will try to lock the ions with D in fixed and non-tunnelling directions in the non-cubic NH_4ClO_4 lattice. T_1^{-1} has a maximum at $\omega_0 \lesssim 4$ MHz in addition to the previously found maximum at 18 MHz.

The relaxation of natural and 25 % deuterated $(NH_4)_2Ce(NO_3)_6$ and natural trigonal $(NH_4)_2SiF_6$ are shown together in figure 7. Deuteration of the cerium nitrate is surprisingly ineffective in causing relaxation. The NH_3D^+ ions must be essentially locked and non-tunnelling in this non-cubic salt with relatively small tunnel splitting. On the other hand, the relaxation in natural trigonal $(NH_4)_2SiF_6$ is surprisingly fast, and there is possibly a level crossing of NH_4^+ in this salt at $\omega_0 \approx 30$ MHz. T_1 has not been checked in a partly deuterated single crystal of this salt.

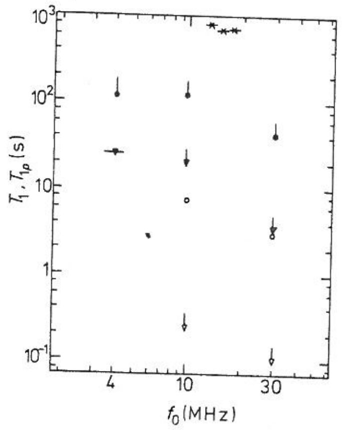

Figure 7. Proton T_1 (filled symbols) and $T_{1\rho}$ (open symbols) in $(NH_4)_2Ce(NO_3)_6$ with 25 % D (circles) and in natural trigonal $(NH_4)_2SiF_6$ (triangles) at 4·2 K. Crosses are T_1 in natural $(NH_4)_2Ce(NO_3)_6$. Bars on symbols as in figure 4.

3.3. *Measurements of $T_{1\rho}$*

The relaxation times $T_{1\rho}$ in the rotating frame of most of the partly deuterated salts were also measured. We observed the FID signal in the usual way after a locking pulse of variable length and 90° phase-shifted after a 90° pulse. The results are shown in figures 3 to 7 in the same way as the T_1 data.

We found $T_{1\rho}$ to be much shorter than T_1 and independent of deuteration except in $(NH_4)_2SnCl_6$. Thus NH_4^+ itself must relax fast in the rotating frame, and no spin diffusion to NH_3D^+ is necessary except in $(NH_4)_2SnCl_6$. Nevertheless, some of the measurements of $T_{1\rho}$ in NH_4ClO_4 and cubic $(NH_4)_2SiF_6$ appears to be independent of the temperature, which we do not understand, while most of the $T_{1\rho}$ data are proportional to T^{-1} as for the direct process.

Deuteration of $(NH_4)_2Ce(NO_3)_6$ is ineffective in causing relaxation $T_{1\rho}$ as it is for T_1. This confirms our belief that NH_3D^+ is permanently locked in this monoclinic salt.

When $T_{1\rho} \ll T_1$ we expect $T_{1\rho}$ from (14) to be independent of ω_0. This seems to be the case for $(NH_4)_2SnCl_6$ and NH_4ClO_4, but not for cubic $(NH_4)_2SiF_6$. The dependence of $T_{1\rho}$ on ω_1 for pure NH_4^+ salts is also puzzling and not in agreement with (15), as will be discussed.

4. Discussion

Our results for T_1 and $T_{1\rho}$ in these partly deuterated ammonium salts have to be correlated with the frequencies $\omega_t(3)$ and $\omega_t(2)$ for three-fold and two-fold tunnelling that we have estimated earlier from activation energies E_a and the 'Haupt maximum' in relaxation (Svare 1977). The calculated 'average' frequencies are given in table 1. The uncertainties are of course relatively large and greatest for $\omega_t(2)$. We should also remember that there are several frequencies, particularly for the non-cubic salts like NH_4ClO_4 where the T states are split (Prager *et al* 1976).

Table 1. Calculated tunnel frequencies in MHz. (Svare and Tunstall 1975, Svare 1977).

		NH_4^+		NH_3D^+
Salt	Structure	$f_t(3)$	$f_t(2)$	$f_t(3)$
NH_4ClO_4	orthorhombic	1300	7	100
$(NH_4)_2SnCl_6$	cubic	150	0·2	6
$(NH_4)_2SiF_6$	cubic	5	0·001	0·1
$(NH_4)_2SiF_6$	trigonal	250	0·4	8
$(NH_4)_2Ce(NO_3)_6$	monoclinic	30	0·02	1

We have confirmed that the ordinary spin–lattice relaxation T_1 of all salts is via spin diffusion to NH_3D^+ which relaxes $\gtrsim 10^4$ faster than symmetric NH_4^+. The observed maxima in T_1^{-1} for NH_3D^+ agree to order of magnitude with the calculated $\omega_t(3)$ for NH_4ClO_4 and $(NH_4)_2SnCl_6$. Cubic $(NH_4)_2SiF_6$ has $\omega_t(3) \ll \omega_0$, and we have here found slower relaxation $T_1 \propto \omega_0^2$ in agreement with (11). The NH_3D^+ tunnelling appears to be locked in $(NH_4)_2Ce(NO_3)_6$. Such locking is less likely to occur in the cubic salts $(NH_4)_2SiF_6$ and $(NH_4)_2SnCl_6$ or in the orthorhombic NH_4ClO_4 which has much higher tunnel frequencies.

The intrinsic relaxation rate of NH_4^+ in the undeuterated salts may not be much slower than the relaxation via the natural isotope fraction $4 \times 0{\cdot}016\,\%$ NH_3D^+, since we generally see two recovery times in them. They may be the coupled spin–lattice relaxation and symmetry conversion times for pure NH_4^+ salts.

The relaxation times $T_{1\rho}$ observed are mostly due to intrinsic NH_4^+ relaxation, and its variation is strange. From (15) we expected the very short $T_{1\rho}$ found in cubic $(NH_4)_2SiF_6$ where $\omega_t(2)$ is very small, and the observed $T_{1\rho} \approx 10$ ms is indeed what we find when we extrapolate $T_{1\rho}$ for undeuterated cubic $(NH_4)_2SiF_6$ to $f_1 \approx 30$ KHz for $B_1 \approx 8$ G. The other pure salts should have much longer times $T_{1\rho} \propto [\omega_t(2)]^2$ according to (15) and lie on the left dashed line in figure 8, which they do not, except perhaps $(NH_4)_2Ce(NO_3)_6$.

However, we see from figure 8 that clearly $T_{1\rho} \propto [\omega_t(3)]^{-2}$ for most of the salts, and we find it impossible to reconcile this with our theory of dipolar relaxation. Some other relaxation mechanism must be present for $T_{1\rho}$, and we suggest spin–rotational interaction.

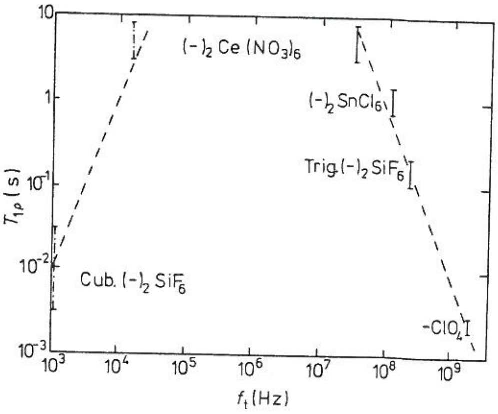

Figure 8. Proton $T_{1\rho}$ in natural salts at 4·2 K as function of calculated tunnel frequency $\omega_t(3)$ (solid bars) and $\omega_t(2)$ (chain bars). Dashed lines show $[\omega_t(2)]^2$ and $[\omega_t(3)]^{-2}$ dependences.

Spin–rotational relaxation has been discussed by for example Blicharski (1972) and Ikeda and McDowell (1972). The coupling H_{S-R} is caused by the magnetic moment of the reorienting charged protons interacting with the spin moments, and the interaction is proportional to $\omega_t(3)$. Interruptions of the tunnel motion due to transitions modulate the rotational field and cause relaxation in the spin system. Formally we can treat spin–rotational relaxation just by replacing H_D with H_{S-R} in the matrix elements $M_{ss'mm'}$, and this gives the required additional factor $[\omega_t(3)]^4$ in the transition rates (10). This factor partly cancels the denominator $[\omega_t(2)]^2$ in the dominating terms of (15) since $\omega_t(2)$ is approximately proportional to $\omega_t(3)$.

Spin–rotational interaction should also influence T_1 of pure NH_4^+ salts, but its relaxing power is distributed over a much greater frequency range around $\omega_0 \approx \omega_t$ and the effect is less likely to be seen.

We do not here attempt to calculate the magnitude of H_{S-R} to see whether it is sufficiently much greater than the dipolar coupling. The dependence of $T_{1\rho}$ on ω_0 in cubic $(NH_4)_2SiF_6$ remains unexplained. Perhaps it is significant that this salt has $\omega_t(3) \gtrsim 4$ MHz while NH_4ClO_4 and $(NH_4)_2SnCl_6$ have $\omega_t(3) > \omega_0(\max) = 30$ MHz. The possibility of hot phonons at ω_0 and phonon bottleneck phenomena in very low temperature relaxation will be investigated further both theoretically and experimentally.

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