Spin diffusion of methyl protons in sodium and lithium acetates

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Abstract. The transfer of nuclear magnetisation between the spectral components of CH_3 protons is studied in single crystals of $CH_3COONa \cdot 3D_2O$ and $CH_3COOLi \cdot 2D_2O$ from 4.2 K to 300 K. The results support a model derived for the methyl-proton spin diffusion (also called spectral diffusion) by time-independent dipolar transitions. Two independent processes are predicted and verified in sodium acetate under conditions that hold above 20 K. At 10 K the lattice-dependent processes dominate but at still lower temperatures the magnetisation transfer is again independent of motion. The influence of rotational tunnelling on spin diffusion is demonstrated in lithium acetate at 4.2 K.

1. Introduction

The diffusion of the nuclear Zeeman energy in solids is usually a fast process caused by time-independent dipolar flip-flop transitions [1]. In molecular crystals the process (called spectral or spin diffusion) is limited by the non-equidistance of the Zeeman levels and the motional narrowing of the line width. Spin diffusion between protons in two fast reorienting methyl groups, for example, is effected only by that part of the intergroup dipole–dipole interaction which is symmetric with respect to permutations of the protons in both of the groups [2]. The consequences of this so-called symmetry-restricted spin diffusion for the methyl-proton NMR have been extensively studied (for a review, see [3]). The spin diffusion itself has not, according to our knowledge, been measured in any methyl compound so far.

In the theoretical section we derive rate equations for the energy-level populations under the restricted spin diffusion and explain how to measure the rates by the pulse sequence $\theta_x - t_1 - \theta_{-x} - t_2 - \theta'$ discussed recently [4, 5]. Experiments are made on single crystals of two methyl compounds, sodium and lithium acetates, with deuterated crystal water.

2. Theory

The rotor-spin eigenfunctions ψ_{X_m} of the three methyl protons (or other nuclear $\frac{1}{2}$-spins) forming an equilateral triangle) reorienting about the threefold axis in a high external
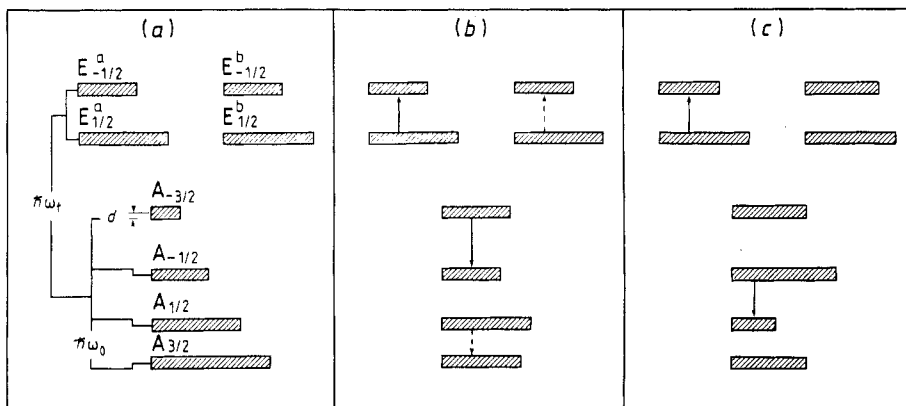
Figure 1. Energy levels of methyl protons. The level populations correspond to (a) thermal equilibrium and the situation after the pulse pair (b) 55°_x–$\pi\hbar/2d$–55°_{-x} or (c) 90°_x–$\pi\hbar/2d$–90°_x. Some flip-flop transitions, whose rate is not averaged to zero by fast reorientation, are shown.

magnetic field B_0 can be labelled by $X_m = A_{\pm 3/2}$, $A_{\pm 1/2}$, $E^a_{\pm 1/2}$ and $E^b_{\pm 1/2}$ according to the C_3 symmetry and the z component of the total nuclear spin [6]. The proton tunnelling raises the E levels and lowers the A levels in the rotational ground state [7]. The dipole–dipole interaction between the three protons mixes the A and E levels unless the angle ϕ, made by the threefold axis of the methyl group with B_0, vanishes. ψ_{X_m} are good starting functions also for other crystal orientations, if the reorientation is fast or the tunnelling frequency ω_t large. The energy levels corresponding to various X_m are [8, 9]

$$E_{E^a \pm 1/2} = E_{E^b \pm 1/2} = \mp\tfrac{1}{2}\hbar\omega_0 + \tfrac{1}{3}\hbar\omega_t$$

$$E_{A \pm 3/2} = \mp\tfrac{3}{2}\hbar\omega_0 - \tfrac{2}{3}\hbar\omega_t + d$$

$$E_{A \pm 1/2} = \mp\tfrac{1}{2}\hbar\omega_0 - \tfrac{2}{3}\hbar\omega_t - d.$$

Here

$$d = (\mu_0/4\pi)(3\gamma^2\hbar^2/8r^3)(3\cos^2\phi - 1) \tag{1}$$

is the intragroup dipolar shift with the magnetogyric ratio $\gamma = 0.2675$ rad GHz T^{-1} and the proton–proton distance $r = 0.18$ nm in the CH_3 group. The levels are shown in figure 1(a). The NMR spectrum consists of the central resonance at $\omega_0 = \gamma B_0$ and two satellites at $\omega_0 \pm 2d/\hbar$ with the intensity ratio of $1:2:1$ when all the CH_3 groups of the sample are identically oriented [10].

2.1. Spin diffusion

The secular part of the dipole–dipole interaction between two protons i and j is $B_{ij}S_{ij} = B_{ij}S'_{ij} + B_{ij}S''_{ij}$ where

$$B_{ij} = (\mu_0/4\pi)\gamma^2\hbar^2(r_{ij})^{-3}[1 - 3(r_{ij} \cdot B_0/r_{ij}B_0)^2]$$

$$S'_{ij} = I_{iz}I_{jz}$$

$$S''_{ij} = -\tfrac{1}{4}(I_{i+}I_{j-} + I_{-}I_{j+}).$$

We consider two indentically oriented methyl groups k and l; the first with protons

r, s and t, and the second with u, v and w. The hamiltonian of the intergroup interaction can be symmetrised to the form

$$\sum_{i=r,s,t} \sum_{j=u,v,w} B_{ij} S_{ij} = \tfrac{1}{9}(B_{AA}S_{AA} + B_{AE^a}S_{AE^b} + B_{AE^b}S_{AE^a}$$

$$+ B_{E^aA}S_{E^bA} + B_{E^aE^a}S_{E^bE^b} + B_{E^aE^b}S_{E^bE^a}$$

$$+ B_{E^bA}S_{E^aA} + B_{E^bE^a}S_{E^aE^b} + B_{E^bE^b}S_{E^aE^a}). \tag{2}$$

Here the space operators $B_{XY}(kl)$ are given by the matrix equation ($\lambda = \exp(i2\pi/3)$)

$$
\begin{bmatrix} B_{AA} \\ B_{AE^a} \\ B_{AE^b} \\ B_{E^aA} \\ B_{E^aE^a} \\ B_{E^aE^b} \\ B_{E^bA} \\ B_{E^bE^a} \\ B_{E^bE^b} \end{bmatrix}
=
\begin{bmatrix}
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
1 & \lambda^* & \lambda & 1 & \lambda^* & \lambda & 1 & \lambda^* & \lambda \\
1 & \lambda & \lambda^* & 1 & \lambda & \lambda^* & 1 & \lambda & \lambda^* \\
1 & 1 & 1 & \lambda^* & \lambda^* & \lambda^* & \lambda & \lambda & \lambda \\
1 & \lambda^* & \lambda & \lambda^* & \lambda & 1 & \lambda & 1 & \lambda^* \\
1 & \lambda & \lambda^* & \lambda^* & 1 & \lambda & \lambda & \lambda^* & 1 \\
1 & 1 & 1 & \lambda & \lambda & \lambda & \lambda^* & \lambda^* & \lambda^* \\
1 & \lambda^* & \lambda & \lambda & 1 & \lambda^* & \lambda^* & \lambda & 1 \\
1 & 1 & \lambda & \lambda^* & \lambda & \lambda^* & \lambda^* & 1 & \lambda
\end{bmatrix}
\begin{bmatrix} B_{ru} \\ B_{rv} \\ B_{rw} \\ B_{su} \\ B_{sv} \\ B_{sw} \\ B_{tu} \\ B_{tv} \\ B_{tw} \end{bmatrix} .
$$

The spin operators $S_{XY}(kl)$ are obtained from a similar equation.

In a crystal of a methyl compound the spin diffusion of the proton magnetisation is caused by the time-independent intergroup flip-flop transitions. Fast CH_3 reorientation leaves in (2) time-independent the term with the subscript AA, which is symmetric with respect to all the permutations of the protons r, s and t and also to those of the protons u, v and w. In that case the relevant hamiltonian for spin diffusion is $\tfrac{1}{9}B_{AA}(kl)S''_{AA}(kl)$. The rate for a flip-flop transition $(X_m(k) \rightarrow X_{m+1}(k))$ and $(Y_n(l) \rightarrow Y_{n-1}(l))$ is [11]

$$W_{X_m Y_n} = \hbar^{-2}(\pi/\langle\Delta\omega^2\rangle_M)^{1/2} \exp[-(E_{X_m} + E_{Y_n} - E_{X_{m+1}} - E_{Y_{n-1}})^2/4\hbar^2\langle\Delta\omega^2\rangle_M]$$

$$\times \sum_{l} |\langle\psi_{X_{m+1}}(k)\psi_{Y_{n-1}}(l)| \tfrac{1}{9}B_{AA}(kl)S''_{AA}(kl) |\psi_{X_m}(k)\psi_{Y_n}(l)\rangle|^2. \tag{3}$$

The summation over l takes into account that the flip in the group k can take place simultaneously with a flop in any other group in the crystal. The quantity $\langle\Delta\omega^2\rangle_M$ is the second moment of a CH_3 proton without its intragroup contribution. If the methyl protons are the only magnetic nuclei in the sample, $\langle\Delta\omega^2\rangle_M$ is approximately equal to

$$\langle\Delta\omega^2\rangle_{MM} = \tfrac{27}{16}(\mu_0/4\pi)^2\gamma^4\hbar^2 \sum_{l} (r_{kl})^{-6}[1 - 3(r_{kl} \cdot B_0/r_{kl}B_0)^2]^2. \tag{4}$$

This is calculated from the Van Vleck formula [12, 13] by placing the protons at the centers of the fast reorienting triangles the centre-point separations being r_{kl}. Usually

Table 1. The rates $W_{X_m Y_n}$ of the time-independent proton transitions $(X_m \to X_{m+1})$ combined with $(Y_n \to Y_{n-1})$ in a crystal of fast-reorienting identically oriented CH_3 groups.

X_m	Y_n	$E^a_{1/2}$	$A_{-1/2}$	$A_{1/2}$	$A_{3/2}$	$E^b_{1/2}$
$E^a_{-1/2}$		W	$3W\varepsilon$	$4W$	$3W\varepsilon$	W
$A_{-3/2}$		$3W\varepsilon$	$9W$	$12W\varepsilon$	$9W\varepsilon^4$	$3E\varepsilon$
$A_{-1/2}$		$4W$	$12W\varepsilon$	$16W$	$12W\varepsilon$	$4W$
$A_{1/2}$		$3W\varepsilon$	$9W\varepsilon^4$	$12W\varepsilon$	$9W$	$3W\varepsilon$
$E^b_{-1/2}$		W	$3W\varepsilon$	$4W$	$3W\varepsilon$	W

$\langle \Delta\omega^2 \rangle_M$ exceeds $\langle \Delta\omega^2 \rangle_{MM}$ due to the presence of other nuclei. The rates (3) are given in table 1 and they depend on the quantities

$$W = \tfrac{1}{27}\langle \Delta\omega^2 \rangle_{MM} (\pi/\langle \Delta\omega^2 \rangle_M)^{1/2} \qquad \varepsilon = \exp(-d^2/\hbar^2 \langle \Delta\omega^2 \rangle_M). \qquad (5)$$

A few examples of the allowed flip-flop transitions are shown in figures 1(b) and 1(c).

From the eight level populations N_{X_m} or the excess populations $n_{X_m} = N_{X_m}/N - \tfrac{1}{8}$ ($N = \Sigma_{X_m} N_{X_m}$) one can form seven independent combinations. We define

$$u \equiv \sum_m n_{A_m} - \sum_m (n_{E^a_m} + n_{E^b_m}) \qquad v \equiv \sum_m (n_{E^a_m} - n_{E^b_m}) \qquad z \equiv \sum_{X_m} m n_{X_m}$$

$$e \equiv n_{E^a_{1/2}} - n_{E^a_{-1/2}} - n_{E^b_{1/2}} + n_{E^b_{-1/2}} \qquad y \equiv n_{A_{1/2}} - n_{A_{3/2}} + n_{A_{-1/2}} - n_{A_{-3/2}} \qquad (6)$$

$$f \equiv n_{E^a_{1/2}} - n_{E^a_{-1/2}} + n_{E^b_{1/2}} - n_{E^b_{-1/2}} - 2n_{A_{1/2}} + 2n_{A_{-1/2}}$$

$$s \equiv n_{E^a_{1/2}} - n_{E^a_{-1/2}} + n_{E^b_{1/2}} - n_{E^b_{-1/2}} - n_{A_{3/2}} + n_{A_{1/2}} - n_{A_{-1/2}} + n_{A_{-3/2}}.$$

Here u and v are proportional to the population differences between the three symmetry species, z to the Zeeman energy and y to the intragroup dipolar energy. The combinations e, f and s are related to the inverse-spin-temperature differences between the E^a and E^b levels, between the E and the central A levels, and between the E and the outermost pairs of the A levels, respectively. In thermal equilibrium at the lattice temperature T the populations are $N_{E^a_m} = N_{E^b_m} = cN_{A_m} = cN(1 + m\hbar\omega_0/kT)/4(1 + c)$ where $c = \exp(-\hbar\omega_t/kT)$. This holds quite accurately for $d \ll \hbar\omega_0 \ll kT$. The substitution of the corresponding excess populations into (6) gives

$$\begin{aligned} u &= (1 - c)/(1 + c) & z &= (\hbar\omega_0/4kT)(c + 5)/(1 + c) \\ v &= e = y = 0 & f &= s = (\hbar\omega_0/2kT)(c - 1)/(1 + c). \end{aligned} \qquad (7)$$

If $\hbar\omega_t \ll kT$, all of them vanish except z.

The time-dependent flip-flop transitions allowed in the case of the fast reorientation (table 1) do not change u, v and z. The time dependence of the four other combinations are obtained from the rate equations formed for the five population differences related

to the five level pairs involved. (The calculation is made easier by the employment of the product populations $N_{X_m} N_{Y_n}$ as in [14].) The solution is

$$e(t) = e(0) \exp(-t/\tau_e) \qquad y(t) = y(0) \exp(-t/\tau_y)$$

$$f(t) = \delta + f_+ \exp(-t/\tau_s) + f_- \exp(-t/\tau_f) \qquad (8)$$

$$s(t) = \delta + s_+ \exp(-t/\tau_s) + s_- \exp(-t/\tau_f)$$

where

$$\tau_e = (1 + c)/W(2 + c + 3\varepsilon) \qquad \qquad \tau_f = (1 + c)/W(\alpha + \beta)$$

$$\tau_y = (1 + c)/W[(6 + 3c)\varepsilon + 9\varepsilon^4] \qquad \tau_s = (1 + c)/W(\alpha - \beta) \qquad (9)$$

$$\alpha = \tfrac{1}{2}[2 + 4c + 3(11 + c)\varepsilon]$$

$$\beta = \tfrac{1}{2}[(2 + 4c)^2 + 108(c - 1)\varepsilon + 9(81 + 14c + c^2)\varepsilon^2]^{1/2}$$

$$\delta = z(0)(2c - 2)/(5 + c) \qquad (10)$$

$$f_\pm = \pm\{(\alpha \pm \beta - 2 - 4c - 18\varepsilon)[f(0) - \delta] + (15 + 3c)\varepsilon[s(0) - \delta]\}/2\beta$$

$$s_\pm = (-\alpha \pm \beta + 2 + 4c + 18\varepsilon)f_\pm/(15 + 3c)\varepsilon.$$

The transitions which change the *intra*group dipolar energy take place at the expense of the *inter*group dipolar energy. Therefore spin diffusion actually cannot relax y to zero, if a nonzero state of y has been created, but can only lead to internal equilibrium of the total dipolar energy. Non-adiabatic processes are needed for the complete relaxation of y. The relaxation of e, f and s conserves the dipolar energy and these quantities reach adiabatically their equilibrium values (7). (The individual flip-flops sometimes increase, sometimes decrease the intragroup dipolar energy but the net change vanishes (cf figure 1(*b*)). The entropy of the intragroup dipolar reservoir oscillates staying constant on average while the entropy of the Zeeman reservoir increases continuously driving the process forward.)

Our main interest is in f and s. According to (8) they are generally coupled together. However, if the ratio $d/\hbar(\langle \Delta\omega^2\rangle_M)^{1/2}$ is large enough to make $\varepsilon \ll 1$ and the tunnel splitting is relatively small ($c = 0.99$ at 4 K for $\omega_t/2\pi = 1$ GHz), f and s relax to zero independently of each other. In that case the time constants and weights are

$$\tau_f \simeq 1/3W \qquad \delta \simeq f_+ \simeq s_- \simeq 0$$

$$\tau_s \simeq 1/9W\varepsilon \qquad f_- \simeq f(0) \qquad s_+ \simeq s(0). \qquad (11)$$

The s-relaxation can be many orders of magnitude slower than the f-relaxation, if the distance $2d/\hbar$ of the spectral satellites from the central resonance is large as compared to the width (FWHM) of $2(2 \ln 2\langle \Delta\omega^2\rangle_M)^{1/2}$ for the Gaussian-broadened line. The reduction of the satellite separation couples f and s and shortens the time constants. Tunnelling shortens τ_s, the maximum reduction being by the factor 3/10, but may lengthen (by a factor 3/2) or shorten (by 18/30) τ_f depending on the value of ε.

The model derived here requires that the reorientation rate is large as compared to the line width. In the case of a slow reorientation none of the terms in (2) is averaged to zero. This makes the number of time-independent flip-flops ninefold for no tunnelling and about threefold for a tunnelling frequency which exceeds the line width. Without detailed calculations we can just propose that spin diffusion should be clearly faster at the lowest temperatures due to those additional transitions. In the intermediate region
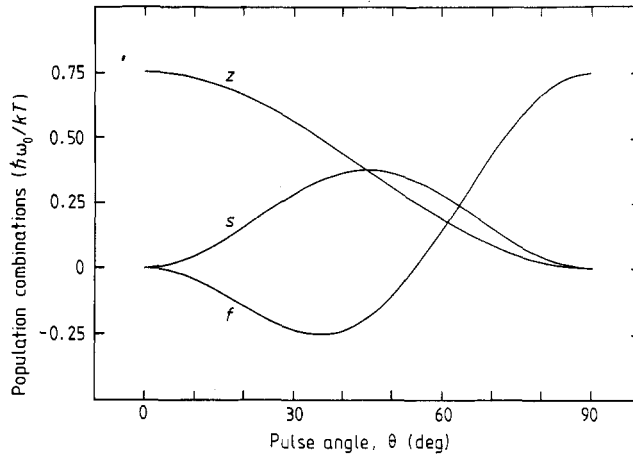
Figure 2. Population combinations z, s and f after the application of the pulse pair θ_x–$\pi\hbar/2d$–θ_{-x} on a sample at equilibrium as a function of the pulse angle θ (obtained from the equation (13) with $c \equiv \exp(-\hbar\omega_t/kT) = 1$).

where the reorientation rate is of the order of the line width we expect time-dependent or non-adiabatic processes to dominate the relaxation of e, f and s. Time-dependent processes are observed to dominate the cross relaxation in tunnelling ammonium compounds below the line-width transition temperature [14–17].

2.2. Pulse sequences

The effect of the resonant pulse pair θ_x–t_1–θ_{-x} on the level populations of the system of three $\frac{1}{2}$-spins was calculated in our earlier studies [4, 5]. Similar calculations show that immediately after this pulse pair the population combinations (6) have the values

$$u = u_0 \qquad v = v_0 \qquad e = e_0 \qquad y = (1 - 2a - 2b)y_0$$
$$z = (1 - a/3 - 4b/3)z_0 + (2b/3 - a/3)f_0 + (a/2)s_0$$
$$f = (4b/3 - 2a/3)z_0 + (1 - 2a/3 - 2b/3)f_0 + as_0 \tag{12}$$
$$s = (2a/3)z_0 + (2a/3)f_0 + (1 - a)s_0$$

where

$$a = 3 \sin^2(dt_1/\hbar) \sin^2 \theta \cos^2 \theta \qquad b = (3/4) \sin^2(dt_1/\hbar) \sin^4 \theta$$

and the subscripts '0' refer to the values before the pulse pair. If u_0, v_0, etc are equal to their values at thermal equilibrium (7) the modified values are

$$u = (1 - c)/(1 + c) \qquad v = e = y = 0$$
$$z = (\hbar\omega_0/4kT)(c + 5 - 2a - 8b)/(1 + c)$$
$$f = (\hbar\omega_0/2kT)(c - 1 - 2a + 4b)/(1 + c) \tag{13}$$
$$s = (\hbar\omega_0/2kT)(c - 1 + 2a)/(1 + c)$$

Figure 2 shows z, f and s as a function of the pulse angle θ for $c = 1$ or $\hbar\omega_t \ll kT$.

In the beginning of a spin-diffusion measurement the studied quantity (for example s) should be as large as possible while the other quantity (f) should vanish. According to (13) the two appropriate pulse pairs when $c \simeq 1$ are (1) $55^\circ_x{-}\pi\hbar/2d{-}55^\circ_{-x}$ which makes $f = 0$ and $s = (4/9)z_0$, and (2) $90^\circ_x{-}\pi\hbar/2d{-}90^\circ_{-x}$ producing (besides $z = 0$) $s = 0$ and $f = z_0$. The energy-level populations for these two cases are shown in figures 1(b) and 1(c).

The degree of spin diffusion reached in a time t_2 can be measured by a third RF pulse. In our earlier studies [4, 5] we calculated the resonance spectrum after a pulse with an arbitrary angle θ' for an arbitrary set of excess populations n_{X_m}. The phase of the θ' pulse is immaterial as far as t_2 ($\gg t_1$) is longer than the phase memory of the system. The spectrum consists of three lines with amplitudes $M_\pm$ and M_c at $\omega_0 \pm 2d/\hbar$ and ω_0, respectively. These amplitudes can be expressed in terms of z, y, f and s instead of n_{X_m}

$$M_\pm = (1/32)[(8z - f - 3s)\sin\theta' \pm 12y\sin2\theta' + 3(f - s)\sin3\theta']$$

$$M_c = (1/32)[(16z + 2f + 6s)\sin\theta' + 6(s - f)\sin3\theta'].$$

(Note that $M_+ + M_- + M_c = z\sin\theta'$.) A relevant parameter indicating the disorder of the system in our case is

$$P \equiv M_+ + M_- - M_c = -\tfrac{1}{8}(f + 3s)\sin\theta' + \tfrac{3}{8}(f - s)\sin3\theta'. \tag{14}$$

According to (14), $P = -s/\sqrt{6}$ for $\theta' = \cos^{-1}(1/\sqrt{3}) \simeq 55^\circ$ and $P = -f/2$ for $\theta' = 90^\circ$ making it possible to determine f and s separately. Thus the s- and f-relaxation can be measured by the three-pulse sequences

$$s(t_2) = -\sqrt{6}\, P(55^\circ_x - \hbar/2d - 55^\circ_{-x} - t_2 - 55^\circ)$$
$$f(t_2) = -2P(90^\circ_x - \pi\hbar/2d - 90^\circ_{-x} - t_2 - 90^\circ) \tag{15}$$

to be referred in the following PS55 and PS90, respectively. Because $f(0) = 0$ in PS55 independently of the third pulse, a smaller θ' than 55° can be used to produce a larger value of P ($\theta' = 35^\circ$ optimal).

Numerical results for P are obtained experimentally by subtracting from the spectral area of the central resonance the area of the satellites. The borderlines between the satellites and the central line are defined to make $P = 0$ at equilibrium.

3. Experiments and discussion

A single crystal with identically oriented CH_3 groups is needed for the intragroup dipolar shift d to be unique. Our samples, $CH_3COONa \cdot 3D_2O$ and $CH_3COOLi \cdot 2D_2O$ belong to the rare compounds fulfilling this condition. However, in both crystals the methyl groups are arranged in proximate pairs which causes a relatively large dipolar interaction not included in our model. The additional interaction manifests itself by splitting the central resonance of the methyl-proton spectrum into a doublet [18]. Sodium acetate is the only known compound where this difficulty can be avoided by a proper orientation of the crystal.

The experiments were carried out at the proton resonance frequency 32.5 MHz by the apparatus explained before [5].

3.1. Sodium acetate

The single crystal of $CH_3COONa \cdot 3D_2O$ was the same as used in our earlier study [5]. Its orientation was determined by comparing the orientations of the growth faces with the monoclinic $C2/c$ structure given in [19].

The eight methyl groups in the unit cell of sodium acetate trihydrate have two different orientations. The two nearest neighbouring groups are situated almost antiparallel to each other the proton planes being separated by 0.29 nm [20]. Because the line joining the center points of the two proton triangles makes an angle of about 18° with the CH_3 axes, the secular part of the dipolar interaction between the two groups can be eliminated, without completely destroying the intragroup dipolar shift d, by orienting the magnetic field B_0 to the 'magic' angle of 55° relative to the line joining the center points. One such orientation is $B_0 \| [001]$, for which we observed the satellite separation $4d/h = 38$ kHz corresponding to $\phi = 30°$ in equation (1). For comparison, some experiments were made for $B_0 \| [1\bar{1}3]$ where the central line is split by 9 kHz but $4d/h$ is practically the same (figure 3).

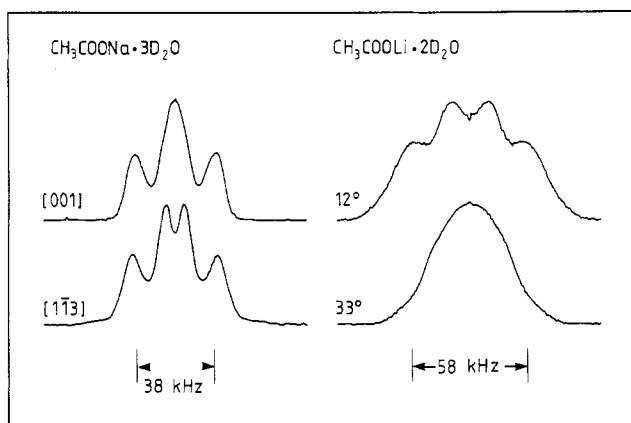**Figure 3.** Equilibrium spectra of $CH_3COONa \cdot 3D_2O$ at 30 K and $CH_3COOLi \cdot 2D_2O$ at 4.2 K for two crystal orientations. The width of the spectral window is 125 kHz.

Averaging (4) over all directions and assuming (to make the calculation easier) that the CH_3 groups in $CH_3COONa \cdot 3D_2O$ form a simple cubic lattice one obtains $\langle \Delta\omega^2 \rangle_{MM} = 268$ rad² kHz². A similar assumption for the D_2O groups and the Na nuclei gives the total intergroup second moment $\langle \Delta\omega^2 \rangle_M = 394$ rad² kHz², which means the width (FWHM) of 7.44 kHz for the Gaussian curve. The central line of the experimental spectrum for $B_0 \| [001]$ has the width of 12.5 kHz. The discrepancy could be, in principle, due to the crude approximation but more probably the centre-line splitting does not completely vanish under our experimental conditions. The satellites, on the other hand, should be only slightly broadened due to the angle of 4.4° between the axes of the nearly antiparallel proximate CH_3 groups [20].

The tunnel frequency $\omega_t/2\pi$ in sodium acetate is 1.4 GHz at 4.2 K and decreases with increasing temperature being about 1.1 GHz at 30 K [21]. This makes $c =$
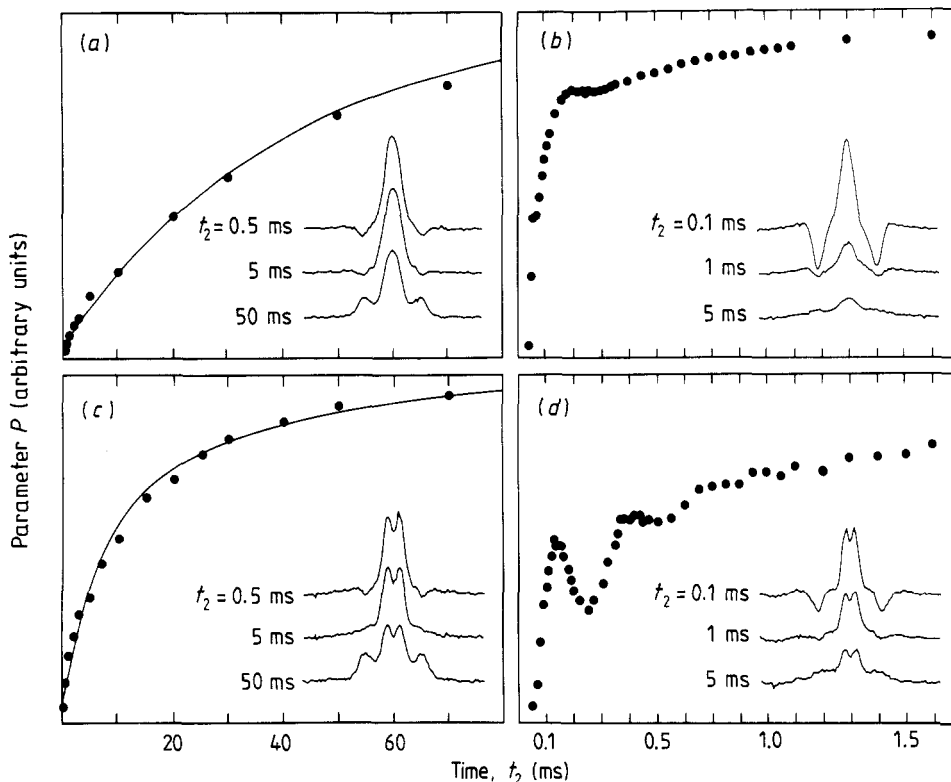
Figure 4. Spin diffusion in $CH_3COONa \cdot 3D_2O$ at 30 K. The points are values of P obtained from the spectra by the pulse sequence PS55 $((a), (c))$ and PS90 $((b), (d))$ for $B_0 \parallel [001]$ $((a), (b))$ and $B_0 \parallel [1\bar{1}3]$ $((c), (d))$. The upper horizontal frame of each figure corresponds to the equilibrium or $P = 0$. Only the beginning of the relaxation is shown. The curves are explained in the text. Spectra for some values of t_2 are also shown.

$\exp(-\hbar\omega_t/kT) = 0.98$ at 4.2 K and $c \simeq 1$ in the whole fast-motion region above 20 K.

The substitution of d, c and the second moments into (5), (9) and (10) gives $\tau_f = 0.4$ ms or 0.6 ms and $\tau_s = 1060$ ms or 6 ms depending on whether one uses the calculated $\langle\Delta\omega^2\rangle_M$ or the value corresponding to the observed centre-line width. The coupling between f and s is negligible or small in these cases, respectively.

Figure 4 shows the results of spin diffusion experiments at 30 K where the condition for the fast reorientation holds. For $B_0 \parallel [001]$ the relaxation of s or the dependence of the parameter P on the time t_2 in the spectra by PS55 (cf. equation (15)) is nearly exponential. The curve in figure 4(a) is the least-squares fit and it has the time constant $\tau_s = 41$ ms. The relaxation of f during PS90 in figure 4(b) bears some resemblance to a damped oscillator. After the shallow minimum at $t_2 = 0.25$ ms the evolution is exponential with $\tau_f = 0.82$ ms. Both time constants have the estimated order of magnitude. The value of τ_s is very sensitive to the spectral broadening, the measured τ_s corresponding to the line width of 9.5 kHz. In the fit for τ_f we ignored the first points and therefore the reported value is rather an upper limit for it. The substitution of the measured τ_s and τ_f into (9) gives $\tau_e = 1.7$ ms.
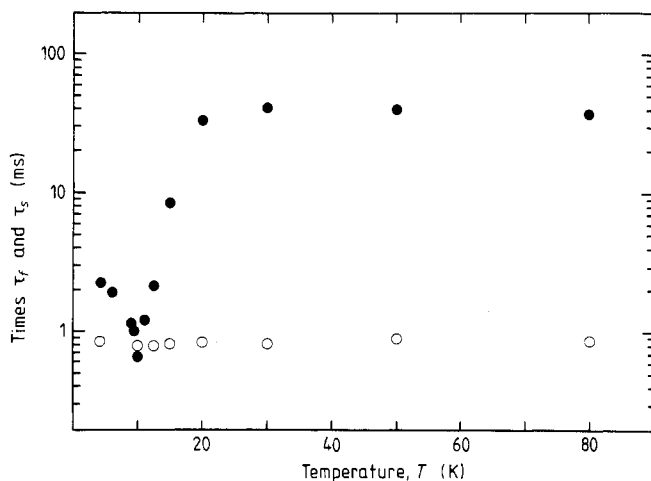
Figure 5. The temperature dependence of the times τ_s (●) and τ_f (○) in $CH_3COONa \cdot 3D_2O$ for $B_0 \| [001]$. The value $\tau_s = 37$ ms at 300 K is not shown.

For $B_0 \| [1\bar{1}3]$ the s-relaxation is non-exponential. The curve in figure 4(c) is proportional to the function $0.55 \exp(-t_2/6 \text{ ms}) + 0.45 \exp(-t_2/35 \text{ ms})$ which decreases to $1/e$ in 13 ms. The f-relaxation, described in figure 4(d), shows oscillations more clearly than for $B_0 \| [001]$ in figure 4(b). After the minima at $t_2 = 0.25$ ms and $t_2 = 0.50$ ms the relaxation goes on with the time constant of 1.6 ms. The extra splitting makes the situation for this orientation obviously different from our model. An increased relaxation rate of s is expected because the components of the split central lines are nearer to the satellites than the single line. The smaller number of equal energy-level spacings could slow down the f-relaxation.

The oscillations in the beginning of the f-relaxation are not expected in our model which predicts at most a slight non-exponentiality due to the coupling between f and s. The larger oscillation amplitude for the orientation with an apparent centre-line splitting suggests the interaction between the two nearest neighbouring groups to be responsible for it. The whole system of two CH_3 groups has 64 energy levels and the large number of processes with varying tendencies could cause minima in the evolution of P but unlikely with a definite period. The oscillations may indicate that the off-diagonal elements of the density matrix have not died out yet in 0.5 ms although the free induction signal decays in 0.08 ms (cf p 6 in [1]).

The temperature dependence of the s- and f-relaxation for $B_0 \| [001]$ was studied between 4.2 K and 300 K (figure 5). Near the T_1 minimum (0.6 s at 30 K) the pulse sequence was not repeated before thermal equilibrium was reached (we took 20–200 scans for each t_2). Below 10 K this was not possible because of $T_1 > 900$ s. At low temperatures the sample was heated to 30 K and cooled down (by a constant rate to produce a constant value of magnetisation) before each repetition (two coolings for each t_2). At room temperature the signal by PS90 for $t_2 > 1$ ms did not exceed noise preventing a reliable determination of τ_f.

The s-relaxation is nearly exponential at all temperatures. The time constant τ_s is about 40 ms from 300 K to 30 K, decreases with the lowering temperature to the minimum of 0.7 ms at 10 K and then increases to 2.3 ms at 4.2 K. The relaxation of f exhibits
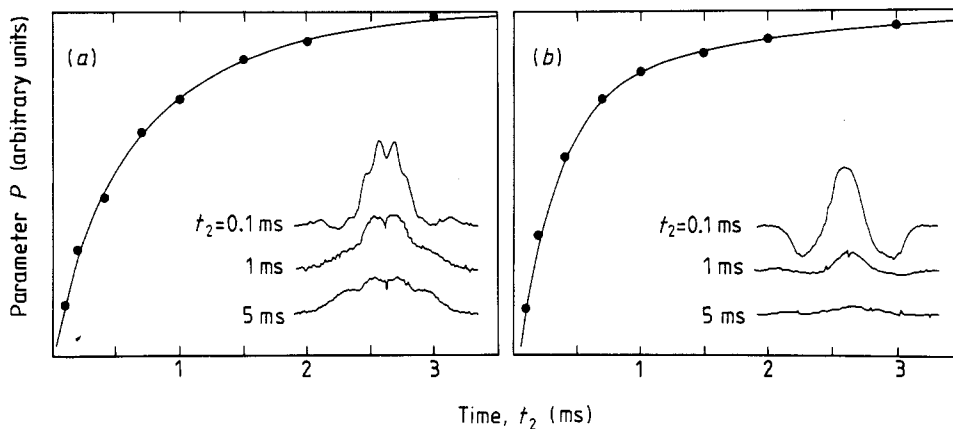
Figure 6. Spin diffusion in $CH_3COOLi \cdot 2D_2O$ at 4.2 K for $\varphi = 12°$. Experimental points for P by PS55 (*a*) and PS90 (*b*). The upper horizontal frame corresponds to the equilibrium. The curves are explained in the text. Some spectra are also shown.

oscillations in the beginning but continues then exponentially with $\tau_f \simeq 0.8$ ms at all temperatures in the range 4.2–80 K. Below 15 K, however, f slightly exceeds its equilibrium value, which is reached only by the spin–lattice relaxation.

The temperature dependence is in accordance with the ideas presented at the end of section 2.1. Below 20 K the methyl reorientations are not fast enough to average to zero those parts of the Hamiltonian (2) which are responsible for the flip-flop transitions with the energy change of $\pm 2d$. Thus those transitions are restricted just by the conservavation of the tunnel, Zeeman and dipolar energies. This speeds up the s-relaxation but has no effect on the f-relaxation dominated by the transitions with a much smaller energy change. Moreover, the lattice-dependent processes contribute by absorbing extra energy, maximally at 10 K where the reorientation rate equals $2d/\hbar$. Below 10 K the rate decreases further and the adiabatic processes are again left alone but with more possible pathways than in the fast-reorientation region.

3.2. Lithium acetate

In lithium acetate dihydrate the methyl-group axes lie along the **b** axis of the orthorhombic crystal in coaxial pairs with their planes separated by 0.25 nm [18, 22]. The CH_3 groups are unusually free to rotate, about 2×10^8 rad s^{-1} at 5 K according to the minimum in T_1 [23, 24]. The tunnel splitting is very large, $\omega_t/2\pi \simeq 60$ GHz up to 10 K at least [25, 26].

The single crystal of $CH_3COOLi \cdot 2D_2O$ showing no clear growth faces was oriented to give the desired NMR spectrum at 80 K. The sample sealed in the probe could be rotated around one axis at a time. In experiments two orientations were used (figure 3). The satellite separation $4d/h = 58$ kHz corresponds to $\varphi = 12°$ and 35 kHz to the angle of 33° between $\boldsymbol{B}_0$ and the CH_3 axis. In lithium acetate the centre-line splitting cannot be removed without also destroying the satellite separation due to the coaxiality of the groups in the pair. Estimates similar to those in § 3.1 yield $\langle \Delta \omega^2 \rangle_{MM} = 433$ rad^2 kHz^2 and $\langle \Delta \omega^2 \rangle_M = 672$ rad^2 kHz^2. The latter value corresponds to the width (FWHM) of 9.7 kHz, which is apparently less than the width of the experimental lines.

Figure 6 shows the results by the pulse sequences PS55 and PS90 for the orientation

$\phi = 12°$ at 4.2 K. In both cases the evolution of the parameter P is non-exponential meaning that f and s are coupled. The curves plotted in figure 6 are proportional to (a) $0.28 \exp(-t_2/0.2 \text{ ms}) + 0.72 \exp(-t_2/0.9 \text{ ms})$ and (b) $0.77 \exp(-t_2/0.3 \text{ ms})$ $+ 0.23 \exp(-t_2/1.6 \text{ ms})$. According to equations (8) and (15) this would mean the value of 0.2–0.3 ms for τ_f and 0.9–1.6 ms for τ_s. The arithmetic means of the values by the two pulse sequences are shown in figure 7 for $\phi = 12°$ at several temperatures and for $\phi = 33°$ at 4.2 K. The room-temperature results contain the largest experimental error due to a poor signal to noise ratio. For $\phi = 33°$ the spin diffusion is faster consistent with the smaller value of d.

According to our model the tunnel splitting as large as in this crystal should affect the rate of spin diffusion ($c = 0.50$ at 4.2 K). The condition for the fast reorientation holds in the whole temperature range studied but the presence of the centre-line splitting makes the situation different from the model. To a first approximation one could consider the centre-line splitting as an increase of the line width and take it into account by adjusting $\langle \Delta \omega^2 \rangle_M$ to produce the observed values to the time constants. Such an estimate in equation (9) implies that τ_s should increase by the factor of 1.4 and τ_f be practically unchanged as $\hbar \Delta_t \ll kT$ at higher temperatures. The temperature dependence of ω_t in lithium acetate is not known. Usually the effective tunnel splitting stays
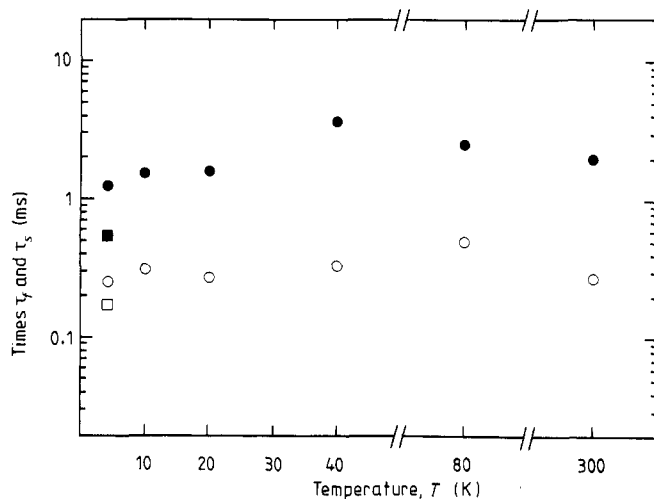

Figure 7. The temperature dependence of the times τ_s (filled) and τ_f (open) for $\phi = 12°$ (circles) and $\phi = 33°$ (squares) in $CH_3COOLi \cdot 2D_2O$.

about constant up to 20–40 K and then decreases fast [27]. Consequently τ_s should first grow steadily with rising temperature ($\omega_t \simeq$ constant) and then have an abrupt step (ω_t decreases). Figure 7 shows a tendency of that sort.

4. Summary

The populations of the eight methyl-proton energy levels can be combined into seven independent quantities. The combinations denoted by f and s are related to such deviations from a common spin temperature which do not couple to the tunnel and dipolar

energies. The relaxation of f and s can be observed separately by appropriate pulse sequences.

Experiments on two acetate crystals support the model derived for spin diffusion in the system of identically oriented CH_3 groups performing fast reorientation. In $CH_3COOLi \cdot 2D_2O$ the fast-reorientation region extends over the whole temperature range studied, 4.2–300 K, while in $CH_3COONa \cdot 3D_2O$ this condition is fulfilled above 20 K. If the separation of the satellites of the methyl-proton spectrum exceeds the width of the individual lines, then f and s relax independently of each other and f much faster than s. The reduction of the satellite separation by changing the orientation of the sample in the magnetic field couples f and s together and speeds up spin diffusion. The presence of a large tunnel splitting shortens the longer time constant in lithium acetate. The temperature dependence of the s-relaxation in sodium acetate shows that the slowing down of the methyl reorientation speeds up spin diffusion. Below 10 K, the temperature of the non-adiabatic peak, the rate of s-relaxation seems to approach a constant value which is an order of magnitude greater than its value in the fast-reorientation region.

Acknowledgments

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