New Method to Study Spin Conversion of a Nuclear-Spin Rotor with Low Tunnel Splitting

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A new method is developed to measure the spin-conversion time $\tau_{\rm con}$ in low–tunnel-frequency systems. The experiment uses field cycling and consists of three steps: saturation of the tunnel reservoir by Zeeman-tunnel resonance; waiting, away from resonance, during a variable time interval t_w; and measurement of the decreased tunnel temperature T_T, by use of a saturated Zeeman reservoir. A plot of T_T vs t_w yields $\tau_{\rm con}$. $\tau_{\rm con}$ of CH_3 rotors in copper acetate is measured at 15, 12.5, and 6 K and turns out to be extremely long, at least $20T_1$. This discrepancy is discussed and compared with the one found in lithium acetate.

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When the free rotation of a methyl group is hindered by its surroundings, it librates in a potential well while reorienting itself, because of its threefold symmetry. At low temperatures, these reorientations occur largely by rotational tunneling. The corresponding tunnel splitting $h\nu_t$ gives rise to the existence of two nuclear-spin isomers, A and E, the latter representing the degenerate E^a and E^b spin species. If the reorientation rate or frequency is sufficiently high, the molecular total nuclear spin becomes the good quantum number: $I_A=\frac{3}{2}$ and $I_E=\frac{1}{2}$. Transitions between the tunnel levels, due to interactions with the "lattice," modify I by one unit and bring about *nuclear-spin conversion.*

Nuclear-spin conversion of methyl and other groups has been extensively studied for high–tunnel-splitting cases: $h\nu_t \gtrsim kT$.[1-6] After a quick temperature jump (for experimental reasons chosen as from 77 to 4.2 K) one follows, using NMR, the evolution of the proton Curie constant C or the evolution of the dipolar proton spin temperature T_D (Haupt effect[7]). The rates of change of C and T_D are mostly very low, because spin-conversion transitions are in first order forbidden. Moreover, the mechanisms in the lattice, leading to spin conversion, are complicated and not always well understood. The nuclear-spin-conversion time $\tau_{\rm con}$ is often of the order of hours. However, if $h\nu_t \gtrsim kT$ and the temperature jump is large enough, the variations of C and T_D, because of the depopulation of the E levels to the A level, are quite large and easily detectable by NMR techniques.[5,6] In lithium acetate, e.g., where $h\nu_t/k = 2.9$ K at 4 K, the relative variation of C is about 20% and T_D increases drastically from 1 mK to 4.2 K.[4]

These methods however, are not applicable for low tunnel splittings, when $h\nu_t \ll kT$, as is the case for many methyl compounds, e.g., copper acetate, where $h\nu_t/k = 3.26$ mK. After a jump from 77 to 4.2 K, C would change only by 0.02%. As a consequence, to our knowledge, nuclear-spin conversion has never been detected in substances with ν_t in the megahertz range and no spin-conversion rates have been measured in this region. We developed a new method, based on the application of Zeeman-tunnel resonance and using field cycling, which enables us to study nuclear-spin conversion at very low tunnel splittings.

Before describing the method, let us remind the reader that rotational tunneling—like all reorientational motions—is a powerful (proton) spin-lattice relaxation mechanism, even a resonant relaxation mechanism when the proton Larmor frequency ν_0 equals ν_t or $\nu_t/2$.[8,9] Under these so-called *Zeeman-tunnel resonance conditions,* one would think the flow of energy from the Zeeman reservoir to the lattice reservoir, and hence the spin-lattice relaxation rate T_1^{-1}, is enhanced resonantly (NMR relaxation resonance). It is, however, not that simple: Because $\tau_{\rm con}$ is in many cases very long, much longer than the "pure" spin-lattice relaxation time τ_1, a *tunnel reservoir* should be introduced in the thermodynamical picture of the system, a new and separate reservoir, not always isothermal with the lattice (Fig. 1).

The idea and the method.—The method we developed to determine $\tau_{\rm con}$ is very similar to the *saturation recovery technique,* used for measuring spin-lattice relaxation times τ_1.[10] Instead of saturating the Zeeman reservoir and measuring the decrease of T_Z as

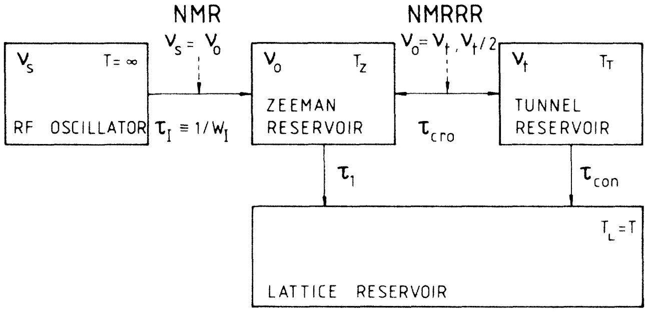

FIG. 1. The energy reservoirs and interaction times of a tunneling nuclear-spin rotor.

a function of time t, we should try to saturate the tunnel reservoir and to measure $T_T(t)$: The tunnel reservoir replaces the Zeeman reservoir and the Zeeman reservoir replaces the rf oscillator (Fig. 1). Though the Zeeman and tunnel reservoirs are normally uncoupled, effective exchange of energy is possible whenever the Zeeman-tunnel resonance conditions are fulfilled. Thermal equilibrium between the two reservoirs is effected in a time $\tau_{\rm cro}$, the Zeeman-tunnel interaction time, which is fortunately much shorter than τ_1 and $\tau_{\rm con}$.[11] As the tunnel reservoir has a limited heat capacity, one is able to manipulate its temperature by performing sequential multiple contacts with a saturated Zeeman reservoir.

To perform the experiment, the NMR pulse spectrometer is tuned to a fixed frequency $\nu_s (=\gamma B_m/2\pi)$, which is far away from the tunnel frequency $\nu_t (=\gamma B_t/2\pi)$, or half the tunnel frequency $\nu_t/2$. A field cycling technique[8] is used, varying the steady magnetic field B_0 in time as shown in Fig. 2. All $\pi/2$ pulses and $\pi/2$-pulse trains are given at the fixed measuring field B_m, tuned to the spectrometer frequency ν_s.

In one run of the experiment, one can distinguish three time intervals.

Step 1 (saturation): The tunnel reservoir is saturated by a so-called general tunnel saturation sequence (GTSS).[8,9,11] This sequence consists of N subsequences in which the Zeeman magnetization M_0 is destroyed by a $\pi/2$-pulse train at $B_0 = B_m$; a slow sweep of B_0 through Zeeman-tunnel resonance establishes resonant contact between the Zeeman and the tunnel reservoirs during a time long enough compared to $\tau_{\rm cro}$; B_0 is brought back to B_m. We apply twenty subsequences for resonant passage through $B_0 = B_t/2$. For the $B_0 = B_t$ passage, we need only ten subsequences, because the heat capacity of the (heating) Zeeman reservoir is larger at high fields.

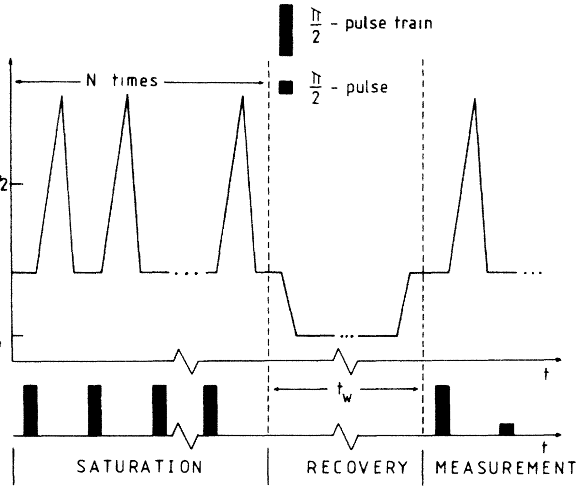

FIG. 2. The field cycling sequence. $B_t = 2\pi\nu_t/\gamma$, $B_m = 2\pi\nu_s/\gamma$, and $B_0 = 2\pi\nu_0/\gamma$.

Step 2 (recovery): The magnetic field B_0 remains fixed at a "wait" value B_w, far away from $B_t/2$ or B_t, and hence from Zeeman-tunnel resonance. Now, we let the tunnel reservoir, which was heated to $T_T = \infty$, recover during a time t_w, which is variable from run to run. The recovery towards $T_T = T_L$ is solely due to spin conversion, i.e., tunnel-lattice relaxation, since the contact with the Zeeman reservoir is negligible. Indeed, (1) measurements of the Zeeman reservoir recovery rate T_1^{-1} (not necessarily equal to τ_1^{-1}), which have been performed as a function of B_0,[12] indicate that T_1^{-1} in copper acetate peaks—due to Zeeman-tunnel resonance—in a rather narrow range (about 0.07 T at 35 K) around $B_t/2$; (2) if the Zeeman-tunnel contact were nonnegligible, it would be almost impossible to measure $\tau_{\rm con}$ times as long as 20 (and more) times τ_1 (see below).

Step 3 (measurement): After a time t_w, the temperature T_T is measured, with a saturated Zeeman reservoir as a probe. This is done by making one single resonant contact between the tunnel reservoir and the Zeeman reservoir, saturated at $B_0 = B_m$. The recovered magnetization M_r, measured in B_m after returning the field B_0 to B_m, is a measure for the amount of tunnel energy relaxed via spin conversion.

The run is repeated several times for different values of t_w. If we assume an exponential spin-conversion process, this process is described by

$$[M_\infty - M_r(t_w)]/M_\infty = \exp(-t_w/\tau_{\rm con}), \qquad (1)$$

where $M_\infty = M_r(t_w = \infty)$. Hence $\tau_{\rm con}$ can be deduced from the slope of a semilogarithmic plot of $[M_\infty - M_r(t_w)]/M_\infty$ as a function of t_w.

Results. Discussion.—We measured at three temperatures (15, 12.5, and 6 K) the spin-conversion time of the methyl group in copper acetate, which has, below 10 K, a tunnel splitting $h\nu_t/k$ of 3.26 mK ($\nu_t = 68$ MHz).[12] In our first experiments, reported in this paper, we did not search for a dependence on the waiting field B_w. We should not forget that such measurements last extremely long. So in all experiments B_w is taken equal to $B_m = 0.468$ T ($\nu_s = 20$ MHz), in order to avoid as much as possible supplementary switching of the field.

We choose the $B_0 = B_t/2 = 0.799$ T resonance to make contact between the Zeeman and the tunnel reservoirs. The disadvantage of a long GTSS ($N = 20$) is amply compensated by having a sensitive probe to measure the tunnel temperature.

One experimental problem is the measurement of M_∞. Conversion times in copper acetate are so long that it is unrealistic to wait, after a GTSS, for a time of $5\tau_{\rm con}$, the time necessary for the tunnel reservoir to return to thermal equilibrium with the lattice. Therefore, after the GTSS we change the temperature to a higher value, where spin conversion is faster, and cool down again to measure M_∞. After stabilization of the temperature, we wait for another hour in order to be sure that the tunnel temperature equals the lattice temperature.

Figure 3(a) shows the semilogarithmic plot of the results we obtained at $T = 15$ K. Let us point out that the assumption of an exponential spin-conversion process, i.e., a process with kinetics of order one, is not self-evident. The evolution of spin conversion depends on the mechanisms driving the spin-conversion transitions. It is well known, e.g., that spin conversion in methane follows a linear time dependence,[6] probably because other parameters, like the presence of paramagnetic impurities, catalyze the spin conversion. An exponential time dependence as in Eq. (1) is typical for processes whereby the rate towards equilibrium is proportional to the deviation from equilibrium. Nevertheless, in our case, the assumption of exponential behavior seems to be justified, as we can fit the data points rather well with a straight line. From the value of the slope we deduce a spin-conversion time of 13 900 ± 1000 s at 15 K. The spin-lattice relaxation time, measured at the same temperature and the same field $B_m = 0.468$ T, is 680 ± 50 s.

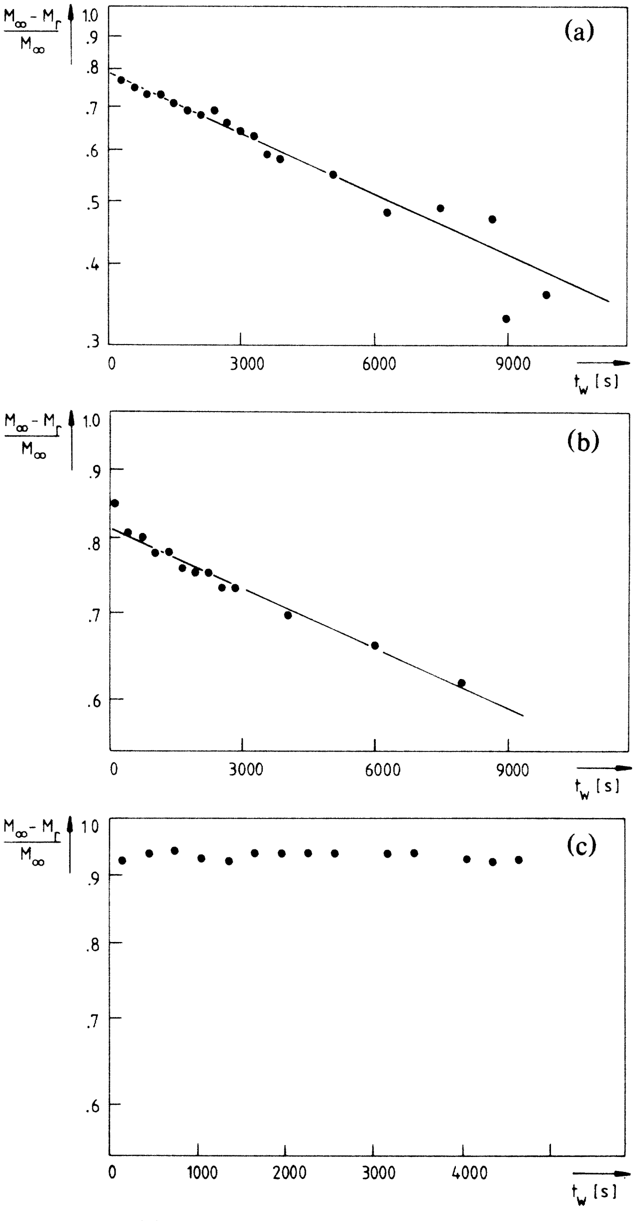

FIG. 3. (a) Spin-conversion-time measurement of the methyl group in copper acetate at $T = 15$ K. $\tau_{\rm con} = 13\,900 \pm 1000$ s. (b) Spin-conversion-time measurement of the methyl group in copper acetate at $T = 12.5$ K. $\tau_{\rm con} = 28\,000 \pm 3000$ s. (c) Spin-conversion-time measurement of the methyl group in copper acetate at $T = 6$ K. $\tau_{\rm con} = (\infty)$.

Figures 3(b) and 3(c) give the results obtained at 12.5 and 6 K. The values for $\tau_{\rm con}$ and τ_1 are listed in Table I. At 6 K, we were not able to obtain a realistic slope from the measurement. $\tau_{\rm con}$ is assumed to be infinite on the experimental scale.

It should be noted that none of the curves start at 1 for $t_w = 0$. This indicates insufficient saturation of the tunnel reservoir, which is probably due to relaxation of the Zeeman reservoir during the field switching in the GTSS and in the final measurement. The effect gets less important at lower temperatures, because τ_1 gets longer while the switching time remains the same.

Finally, we want to discuss in somewhat more detail the unexpected fact that in copper acetate the spin-conversion time is at least 20 times longer than the spin-lattice relaxation time at the same temperature. A similar discrepancy has been observed in lithium acetate, with the use of NMR dispersion spectroscopy: τ_1 is found to be 17 s, whereas $\tau_{\rm con}$ is 98 ± 2 min.[4] In both substances the methyl groups are close to each other, and so intermethyl proton-spin dipolar interactions can play a role, besides the intramethyl interactions: $A \leftrightarrow A$ and $E \leftrightarrow E$ transitions should be taken into account.

The discrepancy between τ_1 and $\tau_{\rm con}$ in lithium acetate, in which the tunnel frequency is 55 GHz, was attributed to the fact that this frequency is much larger than the Larmor frequency: $\omega_t \gg \omega_0$. Consequently,

TABLE I. The values of τ_1 and $\tau_{\rm con}$ as a function of temperature for the methyl group in copper acetate. The magnetic field is 0.468 T.

T (K)	$\tau_{\rm con}$ (s)	τ_1 (s)
15	13 900 ± 1000	680 ± 50
12.5	28 000 ± 3000	1200 ± 100
6	(∞)	3400 ± 400

the transition probabilities $A \leftrightarrow A$ and $E \leftrightarrow E$ (not containing ω_t in the denominator) not only play a role but become even more important than the transition probabilities $A \leftrightarrow E$ (containing ω_t in the denominator). In this way, τ_1^{-1}, which is determined by *all* transitions, gets much larger than τ_{con}^{-1}, which is determined by $A \leftrightarrow E$ transitions *only*.

As a matter of fact, these considerations cannot account for the discrepancy in copper acetate, since ω_t is here of the same order as ω_0. Neither can the interaction of the CH_3 rotor with the crystal water protons, for the same reason.

Our results indicate that the nuclear-spin-conversion process cannot be explained on the sole basis of "simple" proton-proton dipolar interactions. Some additional condition(s) should be fulfilled to initiate $A \leftrightarrow E$ relaxation transitions in tunnel reservoirs. One of them could be, e.g., the presence of a suitable *gradient* in the local field over a distance Δ, characteristic of the size of the rotor, as suggested by Beckmann.[13] This condition, written as a (small) probability *multiplying* τ_1^{-1}, would lead to a τ_{con}^{-1} smaller than τ_1^{-1}, as we have found experimentally.

Further measurements, in particular with varying magnetic fields and temperatures, are planned.

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