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Dipolar Relaxation by Rotation in Spin Space

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The influence of rotating the quantization axis on dipolar relaxation is studied. Rotation with variable frequency ω_r is simulated by a pulsed rf field of amplitude large compared to the local frequency ω_l. For $\omega_r \ll \omega_l$ the dipolar relaxation rate increases with increasing ω_r, reaches a maximum for $\omega_r \simeq \omega_l$, and diminishes to that in the unperturbed system for $\omega_r \gg \omega_l$, as predicted.

INTRODUCTION AND STATEMENT OF THE PROBLEM

Sample rotation has been shown to speed up considerably dipolar relaxation (*1–5*). For angular rotation frequencies Ω_r much smaller than the local dipolar frequency ω_l, the total relaxation rate for a rotating sample can be written (*1*, *2*)

$$\left(\frac{1}{T_{1D}}\right)_{\rm tot} = \left(\frac{1}{T_{1D}}\right)_{\rm st} + \left(\frac{1}{T_{1D}}\right)_{\rm rot},$$

$$\left(\frac{1}{T_{1D}}\right)_{\rm rot} = \frac{3\Omega_r^2}{\omega_l} \qquad (\Omega_r^2 \ll \omega_l^2), \qquad [1]$$

where $(1/T_{1D})_{\rm st}$ is the relaxation rate the sample would already have when not rotated and $(1/T_{1D})_{\rm rot}$ is the enhancement attributable to the sample rotation. It was argued in (*1*) that $(1/T_{1D})_{\rm rot}$ will reach an upper limit of the order of ω_l when Ω_r becomes of the order of ω_l or greater. We note, however, that the approach in (*1*) is not valid for $\Omega_r \gg \omega_l$. In this case Pines (*6*) predicted that the relaxation of the average dipolar energy would be equal again to that of the static sample. In the present paper the emphasis is on the latter case, where the rotation frequency is fast compared to ω_l.

There is a close analogy between relaxation by sample rotation and relaxation by natural motion. In particular, there is a close analogy between slow sample rotation (*1–5*) and slow motion (*7*, *8*). Both cases fall into the category of changing the initial dipolar interaction $\mathcal{H}_{Di}$ into a final interaction $\mathcal{H}_{Df}$, and $(T_{1D})_{\rm rot}$ of slow

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sample rotation is closely related to the T_{1D} of slow motion. In the case of natural motion it is known that the relaxation rate increases with increasing frequency of motion (ω_m) in the slow motion regime $\omega_m < \omega_l$; the relaxation rate becomes a maximum for $\omega_m \simeq \omega_l$ and decreases when the motion becomes rapid, $\omega_m > \omega_l$. In case of sample rotation, when $\Omega_r \gg \omega_l$ one can decompose the original static dipolar interaction $\mathscr{H}_D$ into a new static part $\bar{\mathscr{H}}_D$ and a time-dependent part $\tilde{\mathscr{H}}_D(t)$

$$\mathscr{H}_D = \bar{\mathscr{H}}_D + \tilde{\mathscr{H}}_D(t) \qquad [2]$$

as in the case of natural motion when the motion is rapid. The relaxation rate of $\langle \bar{\mathscr{H}}_D \rangle$ should be equal to $(1/T_{1D})_{st}$ of Eq. [1]. $\tilde{\mathscr{H}}_D(t)$ does not contribute to relaxation because it does not contain the proper resonance frequencies of the spin system. An experiment should test whether the above prediction is correct, but since proton linewidths δ of typical dipolar solids are of the order of $2\pi \times 30$ kHz ($\delta = 4.08\omega_l$ for a Gaussian lineshape (*9*)), it would require $\Omega_r > 2\pi \times 100$ kHz to satisfy the condition $\Omega_r \gg \omega_l$, whereas in practice $\Omega \lesssim 2\pi \times 4$ kHz. Therefore such an experiment will not be easy. By dilution or deuteration, one can reduce the linewidth, say, to 5% of the original proton contents. But then signal-to-noise ratio will be poor.

In this paper we use a much more convenient alternative, based on the analogy between sample rotation (*10, 11*) and rotation in spin space (*12–14*). Thus instead of rotating the sample we rotate the quantization axis by applying an rf field. The rotation frequency ω_r can be varied from a value well below ω_l to a value well above ω_l simply by pulsing the rf field at the required rate. The method is described in the following section.

ROTATING QUANTIZATION AXIS

We consider dipolar coupled spins in solids, subject to a high static magnetic field along the z axis of the reference frame. The Hamiltonian of the spin system can be written

$$\mathscr{H} = -\omega_0 I_z + \mathscr{H}_D, \qquad [3]$$

where $\omega_0 I_z$ is the Zeeman interaction and $\mathscr{H}_D$ is the secular part of the dipolar interaction, i.e., $[\mathscr{H}_D, I_z] = 0$.

In the absence of any rf field the z axis is the quantization axis. One can change the quantization axis by changing the direction of the effective field H_e. Applying an rf field with (angular) frequency $\omega = \omega_0 + \gamma\Delta$ and amplitude γH_1, along the x axis of the frame rotating with frequency ω, one changes the quantization axis into the z direction of the rotating tilted frame, Fig. 1, where $\theta = \mathrm{arctg}\ (H_1/\Delta)$ and the effective field $H_e = \{\Delta^2 + H_1^2\}^{1/2}$. It is assumed that $H_e \gg \omega_l$ to have good quantization along H_e; $\omega_l^2 = \mathrm{Tr}\, H_D^2/\mathrm{Tr}\, I_z^2$.

By letting H_1 and/or Δ be time dependent in a proper way, it would in principle be possible to change θ in a continuous fashion, as in real rotation. However, for practical simplicity we shall consider only the case that the rf field is pulsed on and off and for $\Delta = 0$, so θ will take on only two values, namely, $\theta = 0°$ when the rf field is off and $\theta = 90°$ when the rf field is on.

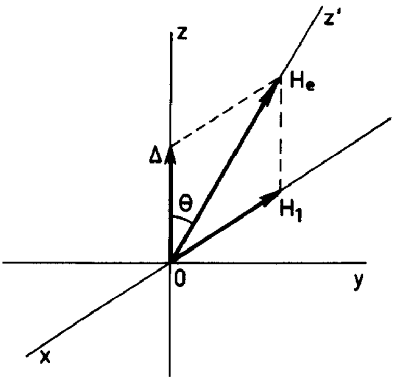

FIG. 1. Rotating quantization axis. The z axis $\parallel$ to the static magnetic field is the quantization axis in the absence of an rf field. The z' axis of the rotating tilted frame becomes the quantization axis with an rf field of amplitude in frequency units large compared to local dipolar frequency. The rf field is along the x-axis of the rotating frame, Δ is the offset, and H_e is the effective field $\parallel$ z' axis.

ANALOGY BETWEEN SAMPLE ROTATION AND ROTATING QUANTIZATION AXIS

We consider successively the influence of sample rotation and of rotating quantization axis on the dipolar interaction. This interaction can be written

$$\mathcal{H}_{\mathrm{D}} = \sum_{i<j} \mathcal{H}_{\mathrm{D}ij}(\phi, I),$$

$$\mathcal{H}_{\mathrm{D}ij}(\phi, I) = \frac{\gamma^2\hbar}{r_{ij}^3}(1 - 3\cos^2\phi_{ij})(3I_{iz}I_{jz} - \mathbf{I}_i\cdot\mathbf{I}_j), \qquad [4]$$

where the subscripts i and j denote the spins i and j, r_{ij} is their internuclear distance, and ϕ_{ij} is the angle between r_{ij} and the magnetic field. When a sample is rotated with angular frequency Ω_r around an axis perpendicular to the static magnetic field the ϕ_{ij} becomes time dependent and $\cos\phi_{ij}$ can be written (*10*, *11*, *15*)

$$\cos\phi_{ij}(t) = \sin\phi'_{ij}\cos(\Omega_r t + \alpha_{ij}), \qquad [5]$$

where ϕ'_{ij} is the angle between r_{ij} and the rotation axis and α_{ij} is the azimuth angle of r_{ij} at $t = 0$, on a plane perpendicular to the rotation axis. From Eqs. [4] and [5] it follows that $\mathcal{H}_{\mathrm{D}}$ becomes time dependent. Denoting the static parts by $\mathcal{H}_{\mathrm{D}}^{\mathrm{st}}$ and $\mathcal{H}_{\mathrm{D}ij}^{\mathrm{st}}$ and the fluctuating parts by $\tilde{\mathcal{H}}_{\mathrm{D}}(t)$ and $\tilde{\mathcal{H}}_{\mathrm{D}ij}(t)$ one can write

$$\mathcal{H}_{\mathrm{D}}(t) = \mathcal{H}_{\mathrm{D}}^{\mathrm{st}} + \tilde{\mathcal{H}}_{\mathrm{D}}(t),$$

$$\mathcal{H}_{\mathrm{D}}^{\mathrm{st}} = \sum_{i<j} \mathcal{H}_{\mathrm{D}ij}^{\mathrm{st}}(\phi'_{ij}, I),$$

$$\tilde{\mathcal{H}}_{\mathrm{D}}(t) = \sum_{i<j} \tilde{\mathcal{H}}^{\mathrm{D}}{}_{ij}(\phi'_{ij}, I, t), \qquad [6]$$

with

$$\mathcal{H}_{\mathrm{D}ij}^{\mathrm{st}}(\phi'_{ij}, I) = -(1/2)\mathcal{H}_{\mathrm{D}ij}(\phi'_{ij}, I), \qquad [7]$$

where the right-hand side of Eq. [7] is given by Eq. [4] with ϕ'_{ij} instead of ϕ_{ij}, and

$$\tilde{\mathcal{H}}_{\mathrm{D}ij}(\phi'_{ij}, I, t) = -3/2 \sin^2 \phi'_{ij} \cos 2(\Omega_r t + \alpha_{ij})\frac{\gamma^2\hbar}{r^3_{ij}}(3I_{iz}I_{jz} - \mathbf{I}_i\cdot\mathbf{I}_j). \qquad [8]$$

For $\Omega_r \lesssim \omega_1$ it is not possible to define a time-average dipolar interaction in an unambiguous way (i.e., averaged over a period of order ω_1^{-1}). It is also obvious that the dipolar interaction, being explicitly time dependent, is no longer a constant of the motion. However, when $\Omega_r \gg \omega_1$ one can unambiguously define a time-average dipolar interaction $\overline{\mathcal{H}_{\mathrm{D}}(t)}$:

$$\overline{\mathcal{H}_{\mathrm{D}}(t)} = \mathcal{H}_{\mathrm{D}}^{\mathrm{st}}. \qquad [9]$$

The effect of $\tilde{\mathcal{H}}_{\mathrm{D}}(t)$ can be neglected. It contributes neither to the dipolar energy, nor to the observable main NMR spectrum. It also does not contribute to relaxation when $2\Omega_r$ is not a proper resonance frequency of the spin system. For a powder sample one has

$$\overline{\mathcal{H}_{\mathrm{D}}(t)} = -(1/2)\mathcal{H}_{\mathrm{D}} \qquad [10]$$

with $\mathcal{H}_{\mathrm{D}}$ given by Eq. [4].

Now we consider the influence of a rotating quantization axis on the dipolar interaction. As mentioned in the previous section, for practical simplicity we let the quantization axis jump periodically with period ω_r^{-1}, between the z and x axes of the rotating frame. With a jumping quantization axis the angle θ, Fig. 1, becomes time dependent. The part of the dipolar interaction that is still secular in the rotating tilted frame is (*12–14*)

$$\mathcal{H}'_{\mathrm{D}}(t) = -(1/2)\{1 - 3\cos^2\theta(t)\}\mathcal{H}_{\mathrm{D}}. \qquad [11]$$

We can rewrite Eq. [11] as

$$\mathcal{H}'_{\mathrm{D}}(t) = (1/4)\mathcal{H}_{\mathrm{D}} + (3/4)\{\cos 2\theta(t)\}\mathcal{H}_{\mathrm{D}}. \qquad [12]$$

We note the resemblance of Eq. [12] to Eq. [6], in particular, the time-dependent part of Eq. [12] to Eq. [8]. When θ takes on the values 0° and 90° with equal duration τ the time-dependent part of Eq. [12] is a block function and can be written as

$$\cos 2\theta(t) = \sum_{n=0} \frac{1}{2n+1} \cos 2\omega_r(2n+1)t, \qquad [13]$$

where $\omega_r = \pi/\tau$. Since the higher harmonics have diminishing amplitudes, the effect of Eq. [13] will be mainly determined by the lowest harmonics. So for $\omega_r \lesssim \omega_1$ we have a situation analogous to that for sample rotation with $\Omega_r \lesssim \omega_1$ and for $\omega_r \gg \omega_1$ a situation analogous to that for $\Omega_r \gg \omega_1$. When $\omega_r \gg \omega_1$ we can define a time-average dipolar interaction

$$\mathcal{H}'_{\mathrm{D}}(t) = (1/4)\mathcal{H}_{\mathrm{D}}, \qquad [14]$$

which is the analog of Eq. [10]. The different numerical factors in the two cases are of no importance for their relaxation behavior which is the point of our main concern. (One could get a factor of 1/2 instead of 1/4 in Eq. [14] by choosing $\theta = 54°44'$ instead of $\theta = 90°$. The sign difference is irrelevant since the dipolar energy is proportional to Tr $\mathcal{H}_{\mathrm{D}}^2$.)

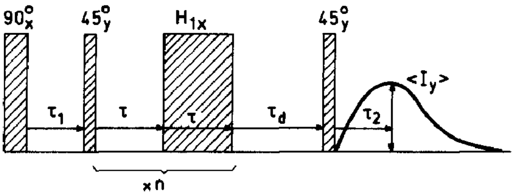

FIG. 2. Pulse sequence for the measurement of the dipolar relaxation by rotation of the quantization axis. Dipolar order is created by the 90°_x–τ_1–45°_y pulse sequence. Then the quantization axis jumps periodically between the z and x axis for a time $t = 2n\tau$ by pulsing the rf field of amplitude H_1 along the x axis of the rotating frame. After waiting for a time τ_d the remaining dipolar order is measured with the 45°_y readout pulse.

Equation [14] could also be obtained using multiple-pulse coherent averaging theory. For multiple 90°_x pulses (*16*) the multiple pulse–average dipolar interaction is $\bar{\mathcal{H}}_D = (1/2)(\mathcal{H}_D + \mathcal{H}_{yy}) = -(1/2)\mathcal{H}_{xx}$ and its secular part is $\bar{\mathcal{H}}'_D = (1/4)\mathcal{H}_D$; cf. Eq. [14]. $\mathcal{H}_{xx}$ and $\mathcal{H}_{yy}$ are given by the expression for $\mathcal{H}_D$, Eq. [14], with z replaced by x and y, respectively.

EXPERIMENTAL RESULTS

We now study the relaxation behavior of the dipolar energy under the influence of a rotating quantization axis. The rotation is done in the manner explained in the previous section. The experimental procedure is depicted in Fig. 2. First, dipolar order is created with the Jeener–Broekaert program (90°_x–τ_1–45°_y) (*17*). After the first 45°_y pulse in Fig. 2 the dipolar order can be described by a density matrix

$$\rho = \beta\mathcal{H}_D, \qquad [15]$$

where β is a measure of the dipolar order. Then we introduce a pulsed rf field of amplitude H_1, for example, along the x axis in the rotating frame, for a period $t = n \times (2\tau)$, where we call $\nu_r = (2\tau)^{-1}$ the rotation ground frequency of the quantization axis and $\omega_r = 2\pi\nu_r$. After that period we wait for a time τ_d allowing multiple-quantum (*18*, *19*) coherences to decay to zero. Then we measure the remaining dipolar order, which is proportional to $\langle I_y \rangle$ at a fixed time τ_2 after the 45°_y readout pulse (*17*). (In fact, one should also wait long enough before applying the first pulse after creating the dipolar order, but it turned out experimentally that this time can be as short as 5 μsec.) $\langle I_y \rangle$ is measured as a function of $t = n\nu_r^{-1}$ for several values of ν_r.

For $\omega_r \ll \omega_l$, which is analogous to slow motion ($\omega_m \ll \omega_l$) or slow sample rotation ($\Omega_r \ll \omega_l$), one expects increasing relaxation rates with increasing ω_r. Relaxation rate will be maximum for $\omega_r \simeq \omega_l$, although relaxation behavior may not be simple, because then the dipolar energy is not a quasi constant of the motion and ω_l is changing.

For $\omega_r \gg \omega_l$, the case of our main concern, there is a unique average dipolar interaction; cf. Eq. [14]. The time-dependent part of the interaction (cf. Eqs. [12] and [13]) will not affect the relaxation behavior of the dipolar energy $\langle \mathcal{H}'_D \rangle$ when none of the relevant frequencies $2\omega_r(2n + 1)$ coincides with a resonance frequency

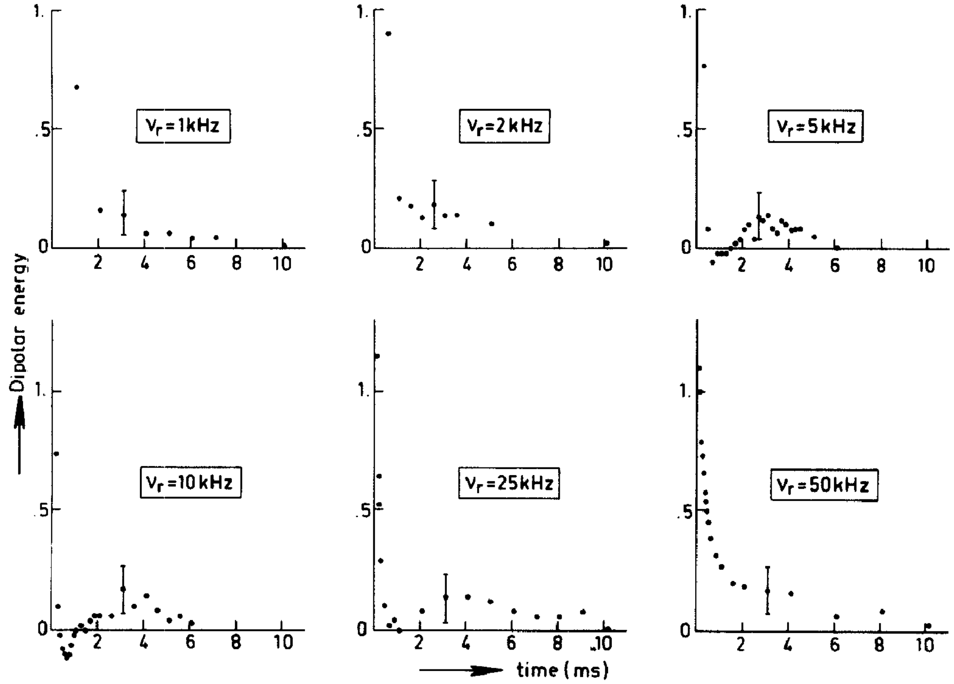

FIG. 3. Relaxation of the dipolar energy for different values of the rotation frequency ν_r of the quantization axis. Relaxation rate increases with increasing ν_r for $2\pi\nu_r < \omega_l$ and becomes maximum for $2\pi\nu_r \simeq \omega_l$.

of the spin system. Therefore the relaxation of $\langle \overline{\mathcal{H}'_D} \rangle$ will be governed by the same mechanism as $\langle \mathcal{H}_D \rangle$ in the static case and without the pulsed rf field.

We have done measurements on the relaxation of the proton dipolar energy of L-alanine($NH_3^+CHCH_3COO^-$) powder at room temperature using a Bruker CXP pulse spectrometer at 60 MHz. The sample was chosen because of its short Zeeman relaxation time (88 msec). The 90° pulse width was 3 μsec, corresponding with an amplitude $\gamma H_1 \simeq 2\pi \times 83$ kHz; $\tau_1 = 16\cdot \mu$sec, $\tau_2 = 22$ μsec, and $\tau_d = 100$ μsec. The local frequency of L-alanine is $\omega_l \simeq 2\pi \times 8$ kHz. The experiment has been done on resonance ($\Delta = 0$). The amplitude of the x pulse is equal to γH_1, which is much greater than ω_l.

Figure 3 shows the experimental results for the dipolar energy $\langle \mathcal{H}'_D(t) \rangle$ (cf. Eq. [12]) as a function of $t = n\nu_r^{-1}$ for $\nu_r = 1, 2, 5, 10, 25$, and 50 kHz. The expected increase of the relaxation rate with increasing ν_r is evident for $\nu_r \lesssim 10$ kHz. The relaxation is maximum for $\nu_r \simeq 5$ to 10 kHz, as should be, and relaxation shows some significant oscillatory behavior for ν_r between 5 and 25 kHz. Such oscillatory behavior has also been observed in the rotating sample experiments (*20–22*). This oscillatory behavior reflects the time dependence of the dipolar interaction either by sample rotation or by rotating quantization axis, combined with the fact that the spin-diffusion rate (of the order ω_l) is not fast compared to rotation frequency, but as yet no theory exists for a good quantitative description for the case $\omega_r \simeq \omega_l$. Qualitatively, Fig. 3 shows the expected behavior for $\omega \lesssim \omega_l$. No

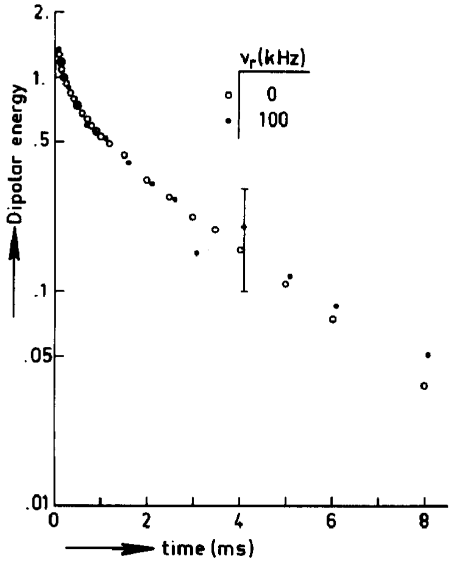

FIG. 4. Relaxation of the dipolar energy for rotation of the quantization axis, with a frequency much higher than the dipolar frequency, compared to that of a static sample without rotation of the quantization axis. Relaxations are quite similar for $2\pi\nu_r \gg \omega_l$ and for $\nu_r = 0$.

quantitative comparison with Eq. [1] has been attempted for $\omega_r \ll \omega_l$, but we note that this has already been done in Ref. (*1*).

Figure 4 shows the relaxation of the dipolar energy $\langle \tilde{\mathscr{H}}'_D \rangle$ (cf. Eq. [14]) as a function of $t = n\nu_r^{-1}$ for $\nu_r = 100$ kHz, compared to the case of $\nu_r = 0$. Figure 4 shows definitely that the relaxations for the two cases are indeed the same, confirming the expectation. The relaxation can be described by two exponentials, in accordance with the symmetry-restricted spin-diffusion model (*23–25*).

CONCLUSION

We have studied the influence of a rotating quantization axis on the relaxation of the dipolar energy. The rotation of the quantization axis is achieved by a pulsed rf field. The rf amplitude should be large compared to the local frequency ω_l to provide a good quantization axis along the effective field also on resonance. The rotation frequency ω_r of the quantization axis can be varied easily from a value well below to a value well above ω_l, just by changing the pulse rate of the rf field. In this way we extend the range of the rotation experiment to the limit of very high rotation frequencies, as yet inaccessible by sample rotation. For $\omega_r \ll \omega_l$ relaxation rates increase with increasing ω_r, reach a maximum for $\omega_r \simeq \omega_l$ and diminish to that in the unperturbed system for $\omega_r \gg \omega_l$, as expected from theoretical considerations.

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