

Absence of Curie Relaxation in Paramagnetic Solids Yields Long ^1H Coherence Lifetimes

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Supporting Information

1. Predicted paramagnetic relaxation enhancements

The expression for the paramagnetic enhancement of longitudinal and transverse relaxation of a nuclear spin in the presence of a paramagnetic center with a fast-relaxing electronic spin, according to the Solomon-Bloembergen mechanism (R_1^{SB} and R_2^{SB}) [1,2] and to the Curie mechanism (R_1^{C} and R_2^{C}) are the following [1,3]:

$$R_2^{\text{SB}} = \frac{1}{15} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma_I^2 g_J^2 \mu_B^2 J(J+1)}{r_{Ln-I}^6} \left(4\tau_c + \frac{\tau_c}{1+(\omega_I - \omega_S)^2 \tau_c^2} + \frac{3\tau_c}{1+\omega_I^2 \tau_c^2} + \frac{6\tau_c}{1+\omega_S^2 \tau_c^2} + \frac{6\tau_c}{1+(\omega_I + \omega_S)^2 \tau_c^2} \right) \\ + \frac{1}{3} J(J+1) \left(\frac{A}{\hbar} \right)^2 \left(\tau_e + \frac{\tau_e}{1+\omega_S^2 \tau_e^2} \right)$$

$$R_2^{\text{Curie}} = \frac{1}{5} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_I^2 B_0^2 \mu_B^4 g_e^4 J^2 (J+1)^2}{r_{Ln-I}^6 (3kT)^2} \left(4\tau_r + \frac{3\tau_r}{1+(\omega_I \tau_r)^2} \right)$$

$$R_1^{\text{SB}} = \frac{2}{15} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\hbar^2 \gamma_I^2 g_J^2 \mu_B^2 J(J+1)}{r_{Ln-I}^6} \left(\frac{\tau_c}{1+(\omega_I - \omega_S)^2 \tau_c^2} + \frac{3\tau_c}{1+\omega_I^2 \tau_c^2} + \frac{6\tau_c}{1+(\omega_I + \omega_S)^2 \tau_c^2} \right) \\ + \frac{2}{3} J(J+1) \left(\frac{A}{\hbar} \right)^2 \left(\frac{\tau_e}{1+\omega_S^2 \tau_e^2} \right)$$

$$R_1^{\text{Curie}} = \frac{2}{5} \left(\frac{\mu_0}{4\pi} \right)^2 \frac{\gamma_I^2 B_0^2 \mu_B^4 g_e^4 J^2 (J+1)^2}{r_{Ln-I}^6 (3kT)^2} \left(\frac{3\tau_r}{1+(\omega_I \tau_r)^2} \right)$$

where γ_I is the magnetogyric ratio of the nuclear spin I ; ω_I and ω_S are the nuclear and electronic Larmor frequencies. τ_r and τ_e are the rotational and electronic correlation times,

respectively, and $\frac{1}{\tau_c} = \frac{1}{\tau_e} + \frac{1}{\tau_r}$. \hbar is Planck's constant divided by 2π , A the Fermi hyperfine coupling constant, μ_0 the vacuum permeability, μ_B Bohr's magneton, B_0 the magnetic field strength, k the Boltzmann factor, T the temperature, g_J and J are the g -factor and spin of the lanthanide ion. Finally, r_{Ln-I} denotes the distance between the lanthanide ion and the nuclear spin I . Typical values of the relaxation enhancements are illustrated in Table S1.

R_1^{SB}	30-140 s ⁻¹
R_1^C	165 s ⁻¹
R_2^{SB}	30-150 s ⁻¹
R_2^C	200 s ⁻¹

Table S1. Paramagnetic relaxation enhancements experienced by a proton 5 Å from the metal center in a small molecule ($\tau_R=100$ ps) containing Tb³⁺ ($J=6$; $g_J=3/2$; $\tau_e=2\cdot 10\cdot 10^{-13}$ s) [1].

2. NMR measurements

All NMR experiments were recorded at a temperature of 30±0.5°C on a Bruker Avance-500 spectrometer operating at a proton frequency of 500 MHz, and equipped with a triple-resonance TXI probe (liquid-state spectra) or with double-resonance 1.3 mm or 2.5 mm CP-MAS probes (solid-state spectra).

A sample for liquid-state NMR spectroscopy was prepared by dissolving about 20 mg of compound (**1**) in 0.5 ml D₂O.

Samples for solid-state NMR spectroscopy were prepared by packing approximately 1 mg of powder into a 1.3 mm zirconia rotor (or approximately 5 mg of powder into a 2.5 mm

rotor). All solid-state NMR spectra were acquired with either a double-resonance 1.3 mm or 2.5 mm CP-MAS probe at 303 K.

As fast MAS efficiently removes a large part of ^1H - ^1H dipolar couplings, no heteronuclear nor homonuclear decoupling was applied during acquisition. In the ^1H spectra, the signals were recorded with 1 μs sampling for a total acquisition time of 1 ms. To avoid baseline distortions on the very large spectral width, a rotor-synchronous double spin-echo refocusing sequence employing tanh/tan SHAPs ($\tau_p=50\mu\text{s}$; $B_{1\text{max}}=200$ kHz; $\Delta\omega_{\text{max}}/(2\pi)=5\text{MHz}$) was always used before acquisition [4]. The RF nutation frequency used for all pulses was 200 kHz.

Non-selective T_1 relaxation times of the ^1H resonances were measured by an inversion-recovery sequence. In the solid, inversion was performed by a 33 μs tanh/tan SHAP pulse with a $B_{1\text{max}}$ of 200 kHz and $\Delta\omega_{\text{max}}/(2\pi)=5\text{MHz}$ [4]. Ten experiments with relaxation delays in the range between 0.5 ms and 50 ms were recorded using an interscan recovery delay of 5 s. The measured echo peak intensities were fitted to a two-parameter exponential equation.

Paramagnetic enhancements of the R_2 relaxation rates of the ^1H resonances were measured in two ways, (i) in liquids, by evaluating the full line widths at half-height ($\Delta\nu^p$) in the ^1H spectrum, and disregarding the presence of scalar couplings ($R_2^p = \pi \Delta\nu^p$); (ii) in solids, by evaluating the exponential decay of the echo tops in a CPMG experiment [5], where the FID sampling (up to 10 ms) is interrupted by n basic elements of rotor-synchronized tanh/tan SHAP pulse pairs ($\tau_p=50\mu\text{s}$; $B_{1\text{max}}=200$ kHz; $\Delta\omega_{\text{max}}/(2\pi)=5\text{MHz}$).

3. Experimental determination of relaxation rates in solution and in the solid

The liquid-state spectrum of (**1**) (figure 1 SI) shows two lines, at 39 ppm (ortho protons [6]) and at 35 ppm (para proton). The two signals have longitudinal relaxation times of 3.5 and 8.1

ms, respectively, and transverse relaxation times of 1.4 and 1.96 ms, equivalent to a linewidth of 228 ± 0.5 Hz and 162 ± 0.5 Hz, respectively.

In the solid-state, the ortho and para proton sites are predicted to have largely different dipolar shift anisotropy. In particular, the dipolar anisotropy predicted following Nayeem and Yesinowski (*J. Chem. Phys.* **1988**, 89, 4600-4608) on the basis of the crystal structure (Cambridge database code: JEXWOY) is in the range 1000-2300 ppm for the para proton, which thus becomes unobservable under MAS, and is not refocused using the SHAP pulses here, tailored for a bandwidth of 1000 ppm. The MAS ^1H spectrum is thus representative of only the ortho protons, whose anisotropy is predicted in the range 500-1000 ppm. The longitudinal (T_1) and transverse (T_2') relaxation times of the ortho protons are measured to be $T_1 = 7.5$ ms and $T_2' = 1.7$ ms (figure 2 SI), respectively, the latter being equivalent to a refocussable linewidth of 187 Hz ($R_{\text{fit}}=0.93314$).

4. Bibliography

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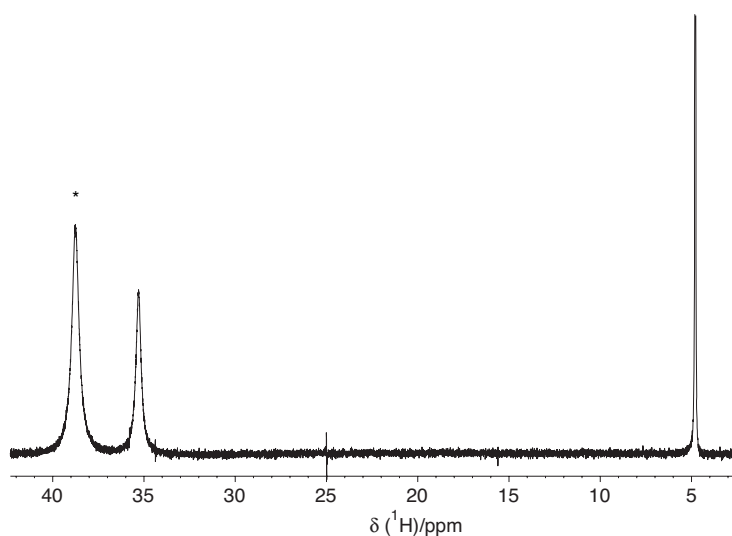


Figure 1 SI

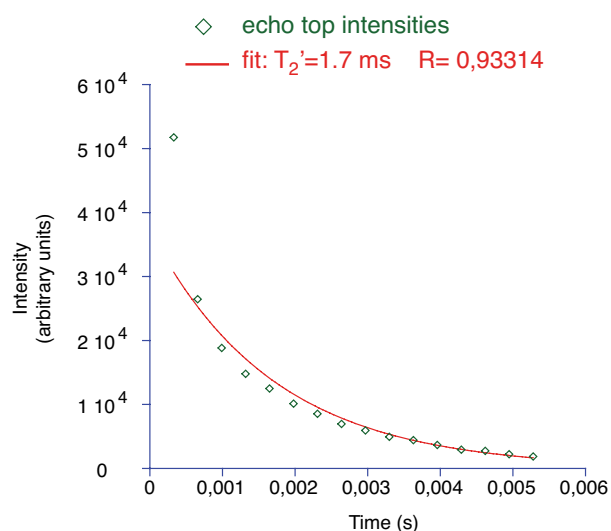


Figure 2 SI

Figure 1 SI:

Liquid state ^1H spectrum of compound (**1**) obtained on a 500 MHz spectrometer (Bruker Avance) at $T=30^\circ\text{C} \pm 0.5^\circ\text{C}$. The resonances at 35 and 39 ppm (*) correspond respectively to the para and ortho protons. The Bruker topspin utility gives a full linewidth at half height of 228 ± 0.5 Hz for the ortho resonance.

Figure 2 SI: Intensity of the echo tops of the adiabatic CPMG experiment obtained on compound (**1**) for protons at 500 MHz, $T=30 \pm 0.5^\circ\text{C}$. The decay is fitted by a mono exponential curve that gives a T_2' of 1.7 ms, which corresponds to a non-refocusable linewidth of 187 Hz.