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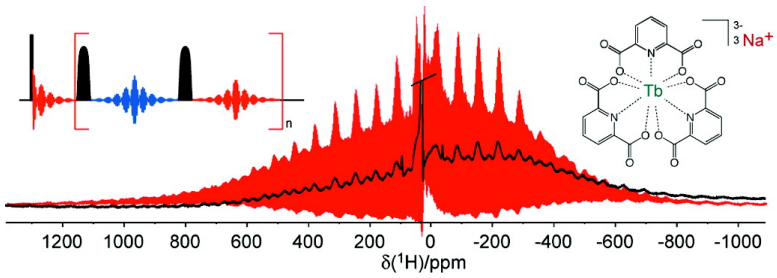

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Absence of Curie Relaxation in Paramagnetic Solids Yields Long ^{1}H Coherence Lifetimes

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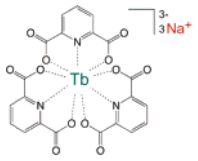
The detailed characterization of paramagnetic molecular and biomolecular materials is one of the key remaining challenges for NMR spectroscopy. Indeed, enhanced transverse relaxation (line broadening) of the nuclear spins surrounding a paramagnetic center presents one of the most prominent manifestations of paramagnetism. This relaxation enhancement strongly depends on the distance between the nuclear and the electron spin. On one hand, it potentially provides a source of long-range distance restraints for structure determination, but on the other hand, it prevents the observation of nuclear spins close to the paramagnetic center by inducing very short transverse coherence lifetimes;[1] this is often a limiting factor in studying paramagnetic systems. Increasing transverse relaxation times would therefore be of great importance.

Most studies of paramagnetic molecular systems have so far been carried out in solution, and this has become a well-developed field.[1] In solution, nuclear spins are relaxed by two principle mechanisms: (i) the stochastic interaction with the electron spin ("Solomon-Bloembergen" dipolar and contact mechanisms),[2] and (ii) by interaction with the net magnetic moment (Curie spin) in thermal equilibrium created by the very short electronic relaxation time (Curie mechanism).[3] In the case of small complexes that contain a paramagnetic ion with fast electronic relaxation and large μ_{eff} (a large "Curie spin"), as in the case of **1**, these effects account for 30 and 70%, respectively, of the observed T_2 in solution (see Supporting Information). Importantly, the Curie mechanism depends on molecular tumbling, and relaxation gets faster as tumbling gets slower.

As observed for the case of diamagnetic CSA relaxation, in the solid-state limit of no tumbling, Curie relaxation should be absent.[4] If true, this would have many important consequences since coherence lifetimes in solids could be longer than in liquids if competing solid-state effects can be removed, thus providing a new tool to study difficult paramagnetic systems, including proteins.[5,6] This has not been explored in the past, principally because no methods existed to access intrinsic line widths in paramagnetic solids.

Here, we present an easy method to access paramagnetic line widths in microcrystalline samples under MAS, and we show that the Curie relaxation mechanism is absent in the lanthanide complex **1**, and that proton coherence lifetimes are longer in solids than in liquids. Complexes like **1** are widely used as models for luminescence studies and have been extensively investigated in recent years by solution NMR.[7]

Experimental determination of paramagnetic line broadening mechanisms in the solid state is a complex task since the line width observed during a NMR experiment under MAS is determined by several factors, including field heterogeneity, magnetic susceptibility, structural disorder, and residual dipolar couplings left by the decoupling sequence used for acquisition. The apparent line width is therefore an insincere reporter of the real nuclear T_2 relaxation rates.[8]



(1)

The spectra of microcrystalline **1** acquired with 20 and 33 kHz MAS are shown in Figure 1a,b. Two key effects explain the main features of the spectrum. First, there are the large paramagnetic shifts and the very large shift anisotropy produced by the strong dipolar interaction between the electronic magnetic moment and the nuclei.[9] In the case of a paramagnetic center with high electron moment ($J = 6$, $\mu_{\text{eff}} = 9.1\ \mu_B$ for Tb^{3+}), the second rank orientation dependence of the shift, which looks formally the same as a very large chemical shift anisotropy, spans almost 1 MHz, a value larger than the practicable RF amplitudes. Consequently, standard irradiation schemes are not applicable for homonuclear dipolar decoupling, with consequently broad signals (i.e., short coherence lifetimes T_2').[10] Second, Tb^{3+} possesses a highly anisotropic magnetic susceptibility tensor, χ, which generates large bulk broadening. A molecular susceptibility anisotropy, $\Delta\chi = 1.6 \times 10^{-32}$ m^3,[7] is expected to produce an additional broadening of about 30 ppm in a microcrystalline sample.[11] Notably, the broadening directly due to paramagnetic relaxation enhancements (PRE) is expected to be much smaller than either of the broadening mechanisms above.

However, as shown recently, very fast MAS alleviates the first effect and has led to groundbreaking new applications of solid-state NMR to paramagnetic molecular complexes.[9,10,12] The large instantaneous paramagnetic shifts actually truncate the flip-flop interaction between protons, rendering the interaction inhomogeneous and allowing very fast MAS to efficiently refocus the homonuclear coupling, with a consequent increase in resolution, in sensitivity, and in T_2'. The phenomenon is illustrated by the spectra acquired with 33 and 66 kHz MAS in Figure 1.

Very fast MAS can also play a role in overcoming the second effect: as soon as the MAS rate exceeds the size of the anisotropic bulk magnetic susceptibility (ABMS) broadening, the families of sidebands do not melt into a broad envelope any longer, but appear separated, with a striking impact on the spectral resolution (particularly evident in the 66 kHz MAS spectrum of Figure 1c). MAS does not modify the extent of the ABMS broadening. However, its inhomogeneous nature suggests that the ABMS terms can be refocused by a RF pulse, provided the irradiation is able to manipulate correctly the whole anisotropic pattern under MAS. We have recently demonstrated the use of short, high-power adiabatic

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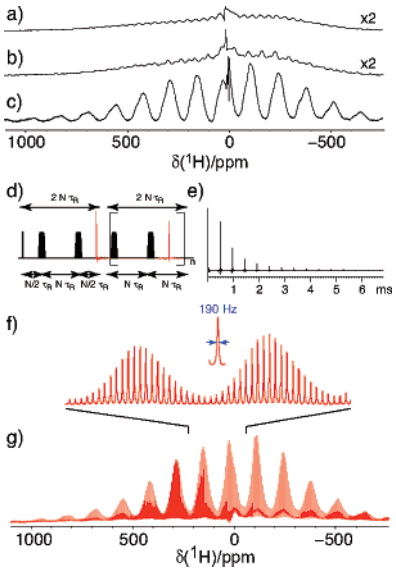

Figure 1. ¹H MAS spectra of **1** recorded at 20 kHz (a), 33 kHz (b), and 66 kHz (c); CPMG pulse sequence and timing (d); CPMG FIDs (e) and spectrum (f) at 66 kHz MAS. Spectra were recorded on a Bruker Avance 500 MHz spectrometer at 303 K (see Supporting Information for more details).

pulses (SHAPs) for population inversion in paramagnetic solids and shown their application in inversion and refocusing schemes on various systems with differing proton anisotropies, from 400 to more than 1000 ppm.[13]

Thus, in spite of the broadening mechanisms and even with anisotropies over 1000 ppm, the decay of an adiabatic spin−echo signal should yield a refocused coherence lifetime T_2' determined solely by the sum of the PRE and the non-refocusable residual dipolar terms. This should yield a measurable upper limit for the PRE in solids.

To measure the PRE in solids, we have implemented a CPMG experiment[14] with broadband adiabatic refocusing pulses. Figure 1d shows the timing diagram of such a sequence. The sequence is rotor synchronized to ensure coincidence of rotary and spin−echoes. To avoid phase problems when using adiabatic pulses for refocusing, the basic element is a pair of SHAP pulses,[13] repeated in n basic CPMG elements. The full spin−echo envelopes are appended to form the FID through interrupted sampling.

Figure 1e shows how, while the FID decays in less than 200 μs, sizable echoes could be acquired on compound **1** for up to 6 ms. In the Fourier-transformed spectra (Figure 1f), the MAS sideband profiles are now broken up into a second manifold of sidebands separated by the rate of CPMG pulsing. The result is twofold. First, the spectra obtained show significant sensitivity enhancements relative to standard MAS spectra. Concentration of the overall spectral intensity, initially distributed over the full dipolar anisotropy spinning sideband patterns, into a reduced number of spin−echo sidebands leads to a considerable increase in spectral sensitivity relative to experiments relying on MAS alone. This phenomenon bears a close resemblance to the sensitivity gain encountered by going from MAS to QCPMG-MAS NMR spectra in the case of quadrupolar interactions.[15]

More importantly, the width of each sideband line should now correspond to a T_2' dominated by the PRE. In the fast MAS experiments recorded here, *the CPMG echo tops decay with a time constant of 1.7 ms, which corresponds to a line width of 190 Hz, and which is now smaller than the solution counterpart, which we measured to be 228 Hz* (noting that no exchange broadening effects are present in these compounds, and that the para protons in compound **1** are not observed in the solid-state spectrum; see Supporting Information). This result is of paramount importance, as it provides the first experimental evidence that Curie relaxation is indeed abolished in the absence of molecular tumbling, and confirms that solid-state coherence lifetimes in paramagnetic solids can be longer than in solution. This is true despite the fact that the presence of several closely spaced paramagnetic centers in the crystal tends to amplify the paramagnetic effect, by producing an apparent shorter effective proton−electron distance: $r_{\mathrm{eff}} = (\Sigma_i(1/r_i^6))^{-6}$.

In conclusion, we have demonstrated that the CPMG technique may advantageously be combined with fast MAS of paramagnetic solids and suitable adiabatic pulses both to provide increased sensitivity and to allow experimental determination of the homogeneous coherence lifetimes T_2'. In this way, we have shown that the Curie contribution to PRE is absent and, therefore, that the lifetimes of nuclear coherences may be longer in solids than in liquids for paramagnetic systems, even for protons. As Curie relaxation increases with increasing molecular weight, this result implies that solid-state NMR may have an immense impact for the study of large, slowly tumbling molecules with fast-relaxing paramagnetic metals, such as cobalt-containing proteins[5] or lanthanide-substituted macromolecules.[16]

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Supporting Information Available: Additional experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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