

Communications to the Editor

Determination of Molecular Reorientation Rates and Electron–Nuclear Coupling in Paramagnetic Materials by Deuterium Solid Echo NMR Spectroscopy

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Deuterium NMR spectroscopy is widely recognized as a valuable technique for characterizing molecular motion in liquid crystalline, semisolid, and solid samples,^{1–4} and the effect of nearby paramagnetic ions on deuterium NMR spectra of single crystals of hydrated salts was recognized early by Soda and Chiba.^{5,6} It was surprising to us, therefore, to discover that deuterium line shape analysis and relaxation measurements have not been used to probe molecular motion in paramagnetic materials. The effects of rapidly relaxing, unpaired electrons on deuterium NMR spectra of both randomly and macroscopically oriented samples^{7–14} have been observed and simulated^{9–11} as an orientation-dependent shift arising from dipolar coupling to an effective electron magnetic moment,^{15,16} but the information obtained in these studies about molecular motion was as best semiquantitative. We have now developed programs for calculating deuterium solid echo spectra of such materials and report the first quantitative NMR line shape simulations and rate determination for molecular reorientation in a paramagnetic complex.

In the current version of our line shape simulation program PMXQET, it is assumed (a) that the electron–deuteron interaction is purely dipolar, (b) that the electronic magnetic moment is localized, and (c) that the electron spin–lattice relaxation rate is much higher than the electron Larmor frequency. The electron–nuclear coupling then manifests itself as an anisotropic hyperfine shift^{15,16} which can be introduced readily into standard line shape simulation programs such as MXQET.¹⁷ Examples of deuterium powder line shapes generated with this program for a D₂O molecule flipping 180° about the DOD bisector were presented recently.¹⁸

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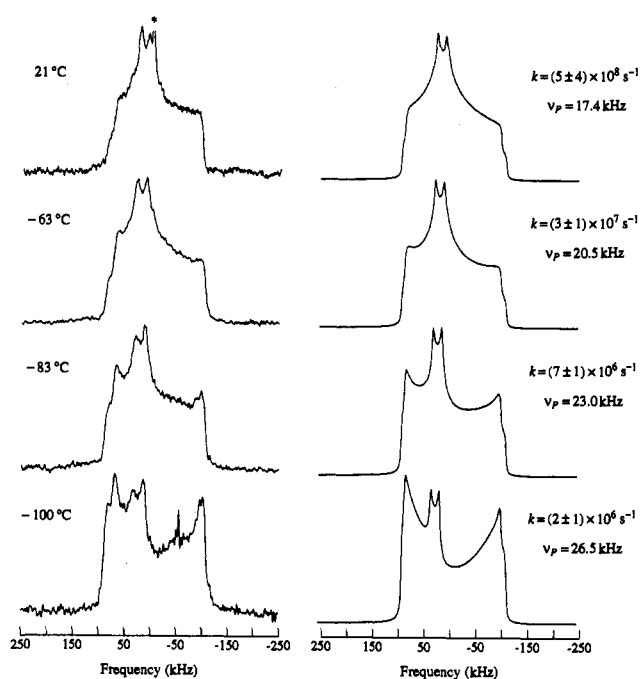


Figure 1. Deuterium NMR spectra (left column) of NdCl₃·6D₂O recorded as a function of temperature at 38.4 MHz (5.9 T) using a shift-compensated quadrupole echo pulse sequence⁹ (see text) with pulse spacings $\tau/2 = 20 \mu\text{s}$, a $\pi/2$ pulse length of 1.8 μs , and recycle delay of 400 ms. 512 transients were collected, zero-filled, and apodized with exponential filter functions (2 kHz) before Fourier transformation. The theoretical spectra (right column) were calculated with the following input parameters: $e^2qQ/h = 237 \text{ kHz}$ and $\eta = 0.14$, angles $\beta_{mp} = 54.7^\circ$, $\gamma_{mp} = 0^\circ$, and $\beta_{mp'} = 15^\circ$, all independent of temperature, and dipolar interaction constants ν_p and 180° flip rates, k , as shown in the figure. A Lorentzian line broadening of 3 kHz was applied before Fourier transformation. The sharp, cutoff feature marked with an asterisk in the top spectrum arises from residual free D₂O.

A hydrated lanthanide salt, NdCl₃·6D₂O, was chosen as a test sample because (a) electron relaxation times are known to be very short (10⁻¹²–10⁻¹³ s) at “normal” temperatures, thus ensuring minimal effect on ²H relaxation times; (b) the structure of a series of lanthanide chloride hydrates has been reasonably well established by X-ray crystallography;^{19,20} (c) Nd³⁺ ($S = 3/2$) has a moderately large magnetic moment, $\mu = 3.6 \mu_B$; and (d) in contrast to the d-electrons of transition-metal complexes, the f-electrons are localized quite well on the metal ion, so the paramagnetic shift of the deuterons is strongly dominated by the electron–nuclear dipole–dipole interactions. Actually, the Nd³⁺ ion in neodymium trichloride hydrate is 8-coordinate, and the structure of the complex ion Ln[Cl₂(D₂O)₆]⁺ shows¹⁹ the water molecules to be slightly different.

The 38.4 MHz deuterium NMR spectra shown in Figure 1 were obtained using the “shift compensated” pulse sequence $(\pi/2)_x - \tau - (\pi)_y - \tau - (\pi/2)_y - \tau - (\pi)_x - \tau - \text{acq}$ originally proposed by Siminovitich et al.⁹ The π -pulses are inserted into the regular quadrupole echo pulse sequence²¹ to ensure refocusing of both the chemical shift and the quadrupolar precession, and although

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our 3.4- μ s π -pulses are far from ideal,²² simple pulses were used since a composite π -pulse for refocusing chemical shift anisotropy in the presence of quadrupolar coupling has yet to be developed.²³ Other experimental details are included in the caption to Figure 1.

The theoretical spectra shown in Figure 1 were calculated using the model of 2-site 180° flips of the water molecules about the DOD bisector. Besides the jump rate k and the regular site parameters for deuterium quadrupole echo spectra— e^2qQ/h , η , and the angles β_{mp} and γ_{mp} between the principal axis of the quadrupole coupling tensor (p) and the rotation axis (m)—PMXQET accepts as input an electron–nuclear dipolar coupling parameter ν_p , which actually is the principal component of a traceless, symmetric shift anisotropy tensor, and the angle $\beta_{mp'}$ between the rotation axis and the metal–deuteron vector (p'). Values of these input parameters are given in the caption to Figure 1. The locations of the deuterons relative to the Nd³⁺ ion are not known, and in the simulations shown in Figure 1, the rotation axis for the dipolar tensor is assumed to coincide with the metal–oxygen internuclear vector. There are small annoying differences between the experimental and theoretical spectra, in particular the minor shoulders appearing on opposite sides of the spectra. However, considering the fact that the six water molecules are not fully equivalent and that neither the exact position nor the quadrupole coupling parameters of the deuterons are known, the fits must be considered quite acceptable at this early stage.

The best fit 180° flip rates shown in Figure 1 correspond to an activation energy of 5 ± 1 kcal/mol, similar to what is observed for other hydrated salts.²⁴ Note that k is poorly determined at 21 °C, because the quadrupole echo line shape is insensitive to the rate in the fast motion limit. Measurements of the spin–lattice relaxation anisotropy are in progress to improve the accuracy in this range.

The paramagnetic shifts $\nu_p = 17$ –26 kHz observed to give the best fit to the experimental spectra in Figure 1 obey the Curie law within experimental error between +21 °C and –100 °C. It is interesting to compare these values of ν_p to those predicted from a pure dipolar shift ν_D originating with the magnetic moment

$\mu_{\text{eff}} = 3.5 \mu_B$ measured for the ⁴I_{9/2} Nd³⁺ ion²⁵ in several materials. The principal component of the dipolar shift tensor is given by

$$\nu_D = \frac{2\gamma_D B_0 \mu_{\text{eff}}^2 \beta^2}{3k_B T r^3} \quad (1)$$

Substitution of the following parameters into eq 1, $\mu_{\text{eff}} = (\mu_0/4\pi)^{1/2} \mu_{\text{eff}}$, $\beta = 9.2731 \times 10^{-24}$ JT⁻¹, $B_0 = 5.87$ T, $\gamma_D = 6.5357$ MHz/T, $k_B = 1.381 \times 10^{-23}$ J K⁻¹, $T = 294$ K, and $r = 3.15$ Å estimated from the X-ray structures,^{19,20} yields $\nu_D = 21.2$ kHz. This is not very different from $\nu_p = 17.4 \pm 0.5$ kHz found at 21 °C from the line shape simulations, suggesting that the major part of the hyperfine coupling is in fact dipolar.

Future adjustments of the structural parameters, obtained from low-temperature work and comparison with deuterium spectra of other lanthanide chloride hydrates, are expected to improve the quality of the fits and permit a better characterization of the anisotropy of the shift tensor and a more accurate determination of the rate of motion. Also, measurements of the T_1 anisotropy of several related compounds are in progress with the specific goal of determining when to expect paramagnetic interactions to contribute to the spin–lattice relaxation rate.

We are encouraged by these early results, since they suggest that we have a good method for characterizing molecular dynamics and electronic properties of transition metal and rare earth complexes at room temperature. In particular, we expect studies of this kind to be useful for characterizing the environment of paramagnetic centers in metalloenzymes and consequently to be of use in high-resolution NMR studies of protein structures.

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