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A Dip in Powder Deuterium NMR Lineshapes

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An analysis of powder ^{2}H NMR lineshapes based on the Redfield theory reveal an interesting dip at the center of the powder spectra, that is, at the magic angle $\beta = 54.7$. This extra feature, which has completely been ignored in the literature, has interesting dynamic implications. From its presence or absence it is possible to tell whether the dominant dynamic process causing relaxation is fast or slow relative to the inverse of the Larmor frequency, $1/\omega_0$. The angle-dependent lineshape function is derived in closed form and the powder spectra are displayed for two typical cases. © 2000 Academic Press

In textbooks (*1*), powder deuterium ($I = 1$) lineshapes in solid state NMR are usually described as sums of two orientation-dependent transitions. For D_2O, a typical powder lineshape of a hydrated "solid particle" such as a liquid crystalline lamellar phase is displayed in Fig. 1A. Generally, one illustrates the ^{2}H NMR powder spectra by displaying the separate contributions from the two "independent" transitions described by the spin density matrix elements $\rho(\omega)_{1,0}$ and $\rho(\omega)_{0,-1}$. These transitions are taking place between Zeeman eigenstates $|I, m\rangle$, namely $|1, 1\rangle \rightarrow |1, 0\rangle$ and $|1, 0\rangle \rightarrow |1, -1\rangle$. However, this is an oversimplification. Such a powder lineshape is an approximation if one also considers the effect of the Redfield relaxation supermatrix. It is usually not stated that the powder lineshape of Fig. 1A is only valid under *nonextreme narrowing* conditions. A ^{2}H powder lineshape derived using the Bloch–Wangsness–Redfield theory (BWR) (*2*) may have an interesting extra feature, namely a *dip* at the center of the spectra, i.e., at the *magic angle* $\beta_{LD} = 54.7°$, as illustrated in Fig. 1B. The dip has been observed for D_2O/detergent systems (*3*) and also for solid polycrystalline *tert*-butyl alcohol and when absorbed on zeolite (*4*), but without recognizing it. The presence or absence of this dip is due to the relative size of nondiagonal Redfield relaxation matrix elements and contains important dynamic information. For instance, for a simple dynamic model it is possible to tell just by visual inspection whether the dominant dynamic process causing relaxation, described by a correlation time τ_c, is short or long compared with $1/\omega_0$. In terms of the Redfield matrix elements, the presence of a dip

requires that the spectral density $J_0(0)$ is comparable with $J_1(\omega_0)$ and $J_2(2\omega)$. In this communication the ^{2}H powder lineshape function is derived using the BWR theory and thus the origin of this dip is explained.

Consider the orientation-dependent resonance frequencies which are given by

$$\omega_1(\alpha_{LM}, \beta_{LM}) = \omega_0 + \omega_Q(\alpha_{LM}, \beta_{LM}) \qquad [1]$$

and

$$\omega_2(\alpha_{LM}, \beta_{LM}) = \omega_0 - \omega_Q(\alpha_{LM}, \beta_{LM}). \qquad [2]$$

There are a Zeeman resonance frequency ω_0 and an angle-dependent quadrupolar term ω_Q. The latter term is half the quadrupole splitting observed in NMR spectra and is given by

$$\omega_Q = \frac{3\chi(2\pi)}{2} |S_{D_2O}S_0|(d_{00}^2(\beta_{LM}) + \eta \cos(\alpha_{LM})d_{02}^2(\beta_{LM})), \qquad [3]$$

where the Euler angles α_{LM} and β_{LM} describe the orientation of the director (M) of the solid "particle" (lamellar phase) and the direction of the magnetic field (L) (*5*). χ is the quadrupole coupling constant (for D_2O: $\chi = eQ/h\ V_{zz} \approx 220$ kHz); η is the asymmetry parameter. The order parameters, S_{D_2O} and S_0, describe the partial averaged field gradient due to fast local anisotropic reorientation of water molecules outside the interface (*6*). The second order parameter describe the averaged order of a bound water site at the water–lipid interface of a lamellar liquid crystalline phase (*6*). The powder lineshape $L(\omega)$ is obtained from an average over the angle-dependent lineshapes $L_{1,0}(\Delta\omega_1) + L_{0,-1}(\Delta\omega_2)$, given by the Fourier–Laplace transform of the reduced spin density matrix elements $\rho(\Delta\omega_1)_{1,0} + \rho(\Delta\omega_2)_{0,-1}$, where $\Delta\omega_i \equiv \omega_i(\alpha_{LM}, \beta_{LM}) - \omega$ (*7*);
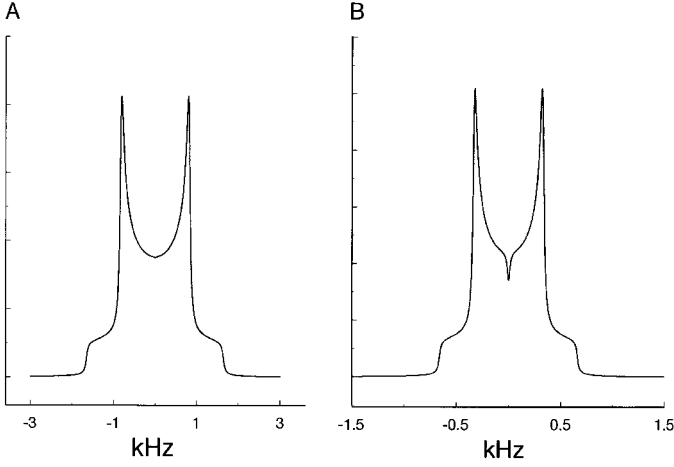
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FIG. 1. The powder NMR ^{2}H lineshape in a magnetic field $B_0 = 2.36$ T (100 MHz), $\chi = 220$ kHz, $\eta = 0$ and at two correlation times: (A) $\tau_c = 60$ ns, $S_{\mathrm{D_2O}} = 0.1$, $S_0 = 0.1$ and (B) $\tau_c = 1$ ns, $S_{\mathrm{D_2O}} = 0.4$, $S_0 = 0.1$, and ω_q been reduced by a factor of 10 compared with (A). The dip disappears under *nonextreme narrowing* conditions.

$$L(\omega) = \int_0^\pi \mathrm{Re}(\rho_{1,0}(\Delta\omega_1) + \rho_{0,-1}(\Delta\omega_2))$$
$$\times\, P(\alpha_{\mathrm{LM}}, \beta_{\mathrm{LM}})\sin(\beta_{\mathrm{LM}})\mathrm{d}\beta_{\mathrm{LM}}\mathrm{d}\alpha_{\mathrm{LM}}, \qquad [4]$$

where $P(\alpha_{\mathrm{LM}}, \beta_{\mathrm{LM}})$ is a distribution density function of the orientations. In the BWR relaxation theory the lineshape function of one site is readily derived. This derivation is here made in the Zeeman representation in order to more clearly illustrate the effect of the Redfield relaxation matrix for powder lineshapes. The equation of motion for the reduced spin density operator is given by

$$\frac{d\rho(\mathrm{t})}{dt} = -\frac{i}{\hbar} L_0\rho(t) - R_2\rho(t). \qquad [5]$$

However, it is more convenient to derive the lineshape function in the frequency domain. We therefore introduce the Fourier–Laplace transform of the density operator $\rho(\omega) = \int_0^\infty \rho(t)e^{i\omega t}dt$. The equation of motion is transformed to

$$\rho(0) = \left(\frac{i}{\hbar} L_0 - i\omega + R_2\right)\rho(\omega). \qquad [6]$$

The nondiagonal spin–spin Redfield relaxation matrix reads

$$\mathbf{R}_2 = \begin{pmatrix} R_{1010} & R_{100-1} \\ R_{0-110} & R_{0-10-1} \end{pmatrix}. \qquad [7]$$

The Redfield supermatrix elements of R_2 are defined in terms of spectral densities as

$$R_{100-1} = R_{0-110} = \frac{3}{10}\,(\chi\pi)^2(J_1(\omega_0)) \qquad [8]$$

and

$$R_{1010} = R_{0-10-1}$$
$$= \frac{3}{20}\,(\chi\pi)^2(3J_0(0) + 3J_1(\omega_0) + 2J_2(2\omega_0)). \qquad [9]$$

The spectral densities used in this work are quite simple. For instance, angular dependence is ignored, as well as a detailed dynamic model for the field gradient time correlation function. We focus on the slow dynamics. However, for illustrating the origin of the dip this is not a serious approximation. The model spectral density, ignoring the contribution due to fast local water reorientation $((1 - S^2_{\mathrm{H_2O}})\tau_f$, where $(\tau_f \approx 5\text{–}50$ ps), is given by

$$J_n(n\omega) = (S_{\mathrm{H_2O}})^2(1 - (S_0)^2)\frac{\tau_c}{(1 + (n\omega\tau_c)^2)}, \qquad [10]$$

which is reduced by two order parameters reflecting the restricted motions of water molecules and the order of the "bound" water sites at the interface. τ_c is a correlation time which characterizes the slowest active dynamic process. Combining the Redfield relaxation matrix with the diagonal frequency matrix $\mathbf{L}_0$, which includes the Zeeman matrix and the static quadrupole interaction matrix, we obtain the matrix

$$\frac{i}{\hbar}\,(\mathbf{L}_Z^0 + \mathbf{L}_Q^0)) - i\omega\mathbf{E} + \mathbf{R}_2$$
$$= \begin{pmatrix} i\omega_0 + i\omega_Q - i\omega + R_{1010} & R_{100-1} \\ R_{0-110} & i\omega_0 - i\omega_Q - i\omega + R_{0-10-1} \end{pmatrix} \qquad [11]$$

and the matrix equation from which we derived the lineshape function is the obtain from Eq. [6] after a matrix inversion

$$\begin{pmatrix} \rho_{10}(\Delta\omega_1) \\ \rho_{0-1}(\Delta\omega_2) \end{pmatrix}$$
$$= \begin{pmatrix} i\omega_0 + i\omega_Q - i\omega + R_{1010} & R_{100-1} \\ R_{0-110} & i\omega_0 - i\omega_Q - i\omega + R_{0-10-1} \end{pmatrix}^{-1}$$
$$\times \begin{pmatrix} \rho_{10}(0) \\ \rho_{0-1}(0) \end{pmatrix}. \qquad [12]$$

The angle-dependent deuterium lineshape function is $L(\omega, \beta_{\mathrm{LM}}) = \mathrm{Re}[\rho_{1,0}(\Delta\omega_1) + \rho_{0,-1}(\Delta\omega_2)]$, which gives the ^{2}H NMR spectrum obtained after an ordinary 90_y° or 90_x°–τ–90_y° pulse experiment. This lineshape function of one orientation is

readily obtained in closed form, Eq. [12], with the initial conditions $\rho_{1,0}(0) = \frac{1}{2}$ and $\rho_{0,-1}(0) = \frac{1}{2}$,

$$
\begin{aligned}
&\rho_{1,0}(\Delta\omega_1) + \rho_{0,-1})(\Delta\omega_2) \\
&= \frac{(R_{1010} - R_{100-1} + i(\omega_0 - \omega))}{\omega_Q^2 + R_{1010}^2 - R_{100-1}^2 \\ + 2i(\omega_0 - \omega)R_{1010} - (\omega_0 - \omega)^2}, \quad [13]
\end{aligned}
$$

where ω_Q is given in Eq. [3].

The powder ^2H lineshape is obtained by inserting the angle dependent lineshape function, Eq. [13], into Eq. [4]. Note that the density operators $\rho_{10}(\omega)$ and $\rho_{0-1}(\omega)$ are not generally eigenoperators of total Liouville superoperator $L_Z^0 + L_Q^0 - R$ of Eq. [11]. In the extreme narrowing regime, the off-diagonal element R_{100-1} is $\frac{1}{4}$ of the diagonal Redfield matrix element R_{1010}. The relaxation effect is maximum at the magic angle, where the quadrupole splitting term vanishes. In the nonextreme narrowing regime, when $J_0(0) \gg J_1(\omega_0)$, $J_2(2\omega_0)$, the Redfield relaxation matrix is also approximately diagonal at the magic angle and thus the powder lineshape does not show the dip.

Calculations based on the derived powder lineshape function (cf. Eq. [13]) reveal the lineshape dip at relatively fast dynamics, $\tau_c < 1/\omega_0$, and its disappearance as the dynamics is slowed down. In Fig. 1 the ^2H-powder NMR lineshapes are displayed for two correlation times: in Fig. 1A $\tau_c = 60$ ns, $S_{D_2O} = 0.1$, $S_0 = 0.1$ compared with Fig. 1B, where $\tau_c = 1$ ns, $S_{D_2O} = 0.4$, $S_0 = 0.1$ and ω_q has been reduced by a factor of 10 compared with Fig. 1A. In Fig. 1B extreme narrowing conditions prevails and the dip is present. When the dynamics is slower than approximately $\tau_c = 60$ (for a 100 MHz spectrometer) the dip

disappears. The presence of the dip can also be explained by the fact that the satellites of a quadrupole split spectra is slightly narrow compared with the isotropic case. The T_2 of the two satellites is given by $\frac{3}{20}(\chi\pi)^2(3J_0(0) + 3J_1(\omega_0) + 2J_2(2\omega_0))$ of Eq. [9], whereas for an isotropic spectra (or at the magic angle), the T_2 is given by the spectral combination $\frac{3}{20}(\chi\pi)^2(3J_0(0) + 5J_1(\omega_0) + 2J_2(2\omega_0))$.

We believe that these new findings may be important when ^2H_2O-powder NMR lineshapes of liquid crystals phases, polymer solutions, and polycrystalline systems are analyzed. The presence of a dip gives a simple visible indication of the dynamics present in the system.

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