The Effect of Spin-$\frac{1}{2}$ Dipolar Coupling on the ^{2}H Quadrupolar Echo

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The effects of dipolar coupling between a deuteron and a spin-$\frac{1}{2}$ nucleus on the deuterium quadrupolar echo is calculated. Due to the dipolar coupling the quadrupolar echo amplitude is shown to decay to 1/2 times its initial value for $t \to \infty$.

Key words: Quadrupolar echo, Dipolar coupling

Deuterium, spin-1, quadrupolar echo spectroscopy has become an important tool in the study of dynamic processes in solids and anisotropic liquids [1, 2]. Longitudinal (T_1) relaxation of deuterium nuclei is completely dominated by the quadrupolar mechanism [3]. However, apart from the quadrupole interaction, the transverse (T_2) relaxation can also contain contributions from dipolar couplings [4]. As a consequence, quadrupolar echo line shapes obtained as a function of the interpulse spacing should be interpreted with care [5].

Because of the small gyromagnetic ratio γ of the deuteron, dipolar coupling with nearby spins is commonly ignored. However, in systems with fast anisotropic motion, dipolar dephasing of the quadrupolar echo due to residual dipolar interactions will cause the echo to decay faster than determined by the motion. Homonuclear dipolar interactions between deuterons have been studied by Boden et al. [6]. Recently, Heaton et al. [7] discussed the effects of $^2\mathrm{H}-^{14}\mathrm{N}$ dipolar interactions on the deuterium quadrupolar echo. In both studies dipolar coupling between two three-level systems was considered. Here the dipolar interaction of deuterons with spin-$\frac{1}{2}$ nuclei will be discussed.

The Hamiltonian for the ^{2}H spins is, at exact resonance in the rotating frame, given by

$$H = \frac{1}{3}\,\omega_\mathrm{Q}[3I_z^2 - I^2] - \omega_\mathrm{D} I_z S_z\,, \tag{1}$$

$$\omega_\mathrm{Q} = \frac{3}{4}\,2\pi\,\chi\,P_2(\cos\alpha)\,, \tag{2}$$

$$\omega_\mathrm{D} = 2\,\frac{\gamma_\mathrm{S}\,\gamma_\mathrm{Z}\,\hbar}{r^3}\,P_2(\cos\beta)\,. \tag{3}$$

χ is the nuclear quadrupolar coupling constant which amounts to approximately 170 kHz for most deuterium nuclei. The internuclear distance between the spin-$\frac{1}{2}$ and the spin-1 nucleus is given by r. Note that the asymmetry parameter of the electric field gradient is assumed to be zero. If no hydrogen bonds are involved, this is an excellent approximation for most deuterium bonds [3]. For the dipolar Hamiltonian in (1), all terms containing transverse spin operators have been excluded. The orientation dependence of both the quadrupolar and dipolar coupling can be expressed by the second rank Legendre polynomial. However, each coupling can in principle have a different orientation dependence as expressed in (2) and (3).

The quadrupolar echo pulse sequence is given by

$$\frac{\pi}{2}\bigg|_y - \tau - \frac{\pi}{2}\bigg|_x - t \qquad \mathrm{QE}.$$

In the absence of dipolar coupling, thus only taking the first term on the righthand side of (1), the well-known result for the time dependence of the quadrupolar echo, $F_\mathrm{Q}(t)$, is given by

$$F_\mathrm{Q}(t) = \langle \cos\omega_\mathrm{Q}(t-\tau)\rangle\,. \tag{4}$$

The obtained signal is a powder average over all orientations as indicated by the brackets. Recently, Bayerl and Bloom [8] discussed the effects of dipolar fields as produced by glass beads on the deuterium quadrupolar echo. Dipolar coupling of deuterium with spin-$\frac{1}{2}$ nuclei can be treated in an analogous manner. Using the full Hamiltonian as given by (1), the time dependence of the nmr signal after the second pulse in the QE sequence can thus be written as

$$F_\mathrm{QD}(t) = \mathrm{Re}\,\langle \tfrac{1}{2}\,[1 + e^{i\,\omega_\mathrm{D}\tau}]\cos\omega_\mathrm{Q}(t-\tau)\rangle\,. \tag{5}$$

In (5) it is assumed that $|\omega_\mathrm{D}| \ll |\omega_\mathrm{Q}|$. Thus, due to the dipolar coupling only part of the signal is refocussed at $t = \tau$.

Now the powder average of the signal can be calculated at the top of the echo, $t = \tau$. The dipolar coupling is orientation dependent as described by (3) and can be written as $\omega_\mathrm{D}(\beta) = \omega_\mathrm{D}(0)\,P_2(\cos\beta)$. By means of the

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transformation properties of second-rank tensors, $P_2(\cos\beta)$ can be made to coincide with the deuterium electric field gradient tensor. Uniaxial motion can also be included through the addition theorem of spherical harmonics [9]. After these transformations one can write the dipolar coupling in terms of the powder angle θ which describes the orientation of the symmetry axis of molecular motions with respect to the static magnetic field. Thus one obtains

$$\omega_D(\beta) = \omega_D(0)\, S P_2(\cos\theta)\,, \tag{6}$$

where S resembles an order parameter. For the real part of the powder average in (5) one thus obtains

$$F_{QD}(t) = \tfrac{1}{2} \int_{-1}^{1} d\xi\, [1 + \cos(\tau\, \omega_D(0)\, S P_2(\xi))]\,. \tag{7}$$

The integral in (5) can easily be rewritten in terms of Fresnel integrals [10]

$$F_{QD}(t) = \frac{1}{2}\left[1 + \sqrt{\frac{\pi}{6}}\left[\frac{\cos p\tau}{\sqrt{p\tau}}\, C\left(\sqrt{\frac{6p\tau}{\pi}}\right) + \frac{\sin p\tau}{\sqrt{p\tau}}\, S\left(\sqrt{\frac{6p\tau}{\pi}}\right)\right]\right]. \tag{8}$$

$p = \frac{1}{2}\omega_D(0) \cdot S$ is the effective dipolar coupling constant in rad/s and $C(x)$ and $S(x)$ are, respectively, the real and imaginary parts of the Fresnel integrals. Equation (8) shows that for $\tau \to \infty$ the echo top amplitude will decay to 1/2 times its initial value at $\tau = 0$. This behaviour is different from that of two dipolar coupled spin-1 particles. In that case the echo top amplitude decays to 2/3 times its initial value at $\tau = 0$ [6, 7].

It should be pointed out here that another, equivalent, way of describing the dipolar interaction is given in Abragam's book [11]. The model describes the effect of the dipolar couplings on the free induction decay through an expansion

$$F(t) = F(0)\left[1 - \frac{A_2}{2!}\, t^2 + \frac{A_4}{4!}\, t^4 + \cdots\right], \tag{9}$$

where $t = 2\tau$ for the QE sequence. Note that the coefficients A_i are not the conventional moments of the dipolar spectrum. The expansion can be used for hetro- and homonuclear dipolar coupling, however, the extraction of coupling constants is not as straightforward as through (8).

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