DIPOLAR SPIN–LATTICE RELAXATION RATES OF QUADRUPOLE INTERACTING SPIN SYSTEMS

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This study is concerned with the dipolar spin–lattice relaxation of the quadrupole interacting spin system. Although the influence of the spin–lattice coupling to the dipolar relaxation has been a subject of many investigations [1–3] are still enough obscurities about the dipolar relaxation of less simple spin systems. The aim of this study is to find the dipolar spin–lattice relaxation rates of spins with equally and unequally spaced energy levels. The consideration is limited to the nuclear spins in the solid, which are subjected to a high magnetic field and perturbed by interactions with the electric field gradient tensor at their sites. Besides, it is supposed that the quadrupole interaction is stronger than the mutual spin–spin coupling and that the dominant process of the spin–lattice relaxation is the coupling with the efg tensor fluctuations.

The quadrupole interaction causes the line splitting in the NMR spectra, but if the external magnetic field is strong enough, we can always find such position of the efg tensor at spin site, with respect to magnetic field, that the line splitting is smaller than the line broadening due to the spin–spin interaction. Hence, with changing of the crystal orientation in the magnetic field, the unequally spaced energy levels can become nearly equidistant. We expect that this will be reflected in the dipolar spin–lattice relaxation because the spin–spin energy is sensitive to the level arrangement.

The hamiltonian which describes nuclear spins in the solid is

$$H = H_Z + H_Q + H_D + H'_Q(t). \tag{1}$$

The first term is due to the spin interaction with the external magnetic field, H_Q is the quadrupole hamiltonian, H_D describes the magnetic spin–spin interaction and $H'_Q(t)$ is the spin– lattice coupling due to spin interactions with the fluctuations of electric field gradient tensor.

In above mentioned approximation, all parts of the quadrupole hamiltonian can be neglected, except $H_Q^{(0)}$ which commutes with the Zeeman hamil-

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tonian and only that part of the dipolar hamiltonian is retained which commutes with $H_Z + H_Q^{(0)}$. The truncated hamiltonian has the form

$$H = H_Z + H_Q^{(0)} + H_D^{(s)} + H'_Q(t). \tag{2}$$

If the external magnetic field is strong enough, it is always possible to find the crystal position in the magnetic field where the quadrupole splitting vanishes or is smaller than the line dipolar broadening. Spin-energy levels become nearly equidistant and the new hamiltonian can be taken as

$$H = H_Z + H_D^{(0)} + H'_Q(t). \tag{3}$$

Here $H_D^{(0)}$ commutes only with H_Z and it differs from $H_D^{(s)}$.

In the following step, the dipolar spin–lattice relaxation rates can be calculated. The perturbation $H'_Q(t)$ can be devided into $H'_Q(t) = \Sigma_{\alpha=-2}^{2} H_Q^{(\alpha)}(t)$, where $[H_Z, H_Q^{(\alpha)}(t)] = h\omega_0\alpha H_Q^{(\alpha)}(t)$ is valid and if the spin-temperature approximation is taken into account the dipolar spin–lattice relaxation time is given by

$$T_{1D}^{-1} = \frac{1}{\mathrm{Tr}[H_D^{(0,s)}]^2} \left\{ \sum_{\alpha=1}^{2} \int_{-\infty}^{\infty} \mathrm{d}t \, \mathrm{Tr}\, \mathrm{e}^{\mathrm{i}H_0 t} [H_D^{(0,s)}, H_Q^{(\alpha)}(t)] \right.$$

$$\times \, \mathrm{e}^{-\mathrm{i}H_0 t} [H_Q^{(-\alpha)}(0), H_D^{(0,s)}]$$

$$\left. + \int_0^{\infty} \mathrm{d}t \, \mathrm{Tr}\, \mathrm{e}^{\mathrm{i}H_0 t} [H_D^{(0,s)}, H_Q^{(0)}(t)] \, \mathrm{e}^{-\mathrm{i}H_0 t} [H_Q^{(0)'}(0), H_D^{(0,s)}] \right\}. \tag{4}$$

The Zeeman hamiltonian and the quadrupole part $H_Q^{(0)}$ are mutually independent and if $H_D^{(s)}$ commutes with $H_Q^{(0)} + H_Z$ it also commutes with $H_Q^{(0)}$ and H_Z separately. In addition, the parts of the hamiltonian (2) which describe the quadrupole interactions, i.e., $H_Q^{(0)}$ and $H_Q^{(0)'}(t)$, are the sum of terms acting on only one spin and they have the same spin operators. Then $H_D^{(s)}$ must commute also with $H_Q^{(0)'}(t)$.

Hence, the expression for the dipolar spin–lattice relaxation time of the quadrupole interacting spin system with unequally spaced energy levels is

$$T_{1D}^{-1} = \sum_m \int_{-\infty}^{\infty} \mathrm{d}\omega \, \omega^2 \, [J^{(1)}(\omega + \omega_{m-1}^{m}) \, G_\omega^{(1m)} + J^{(2)}(\omega + \omega_{m-2}^{m}) \, G_\omega^{(2m)}]. \tag{5}$$

$G_\omega^{(\alpha m)}$ is determined by the dipolar spin–spin interaction [4], $\omega_{m'}^{m}$, is the frequency difference between the m th and m' th level and $J_{(\omega)}^{(\alpha)}$ is the auto correlation spectral density of the efg tensor fluctuations. Supposing that the quadrupole shifts of levels are much smaller than the Larmor frequency, then expression (5) can be written as

$$T_{1D}^{-1} = I^{(1)}(\omega_0) + I^{(2)}(2\omega_0). \tag{5a}$$

Similar calculations can be done for the spins with equally spaced levels which are described with the hamiltonian (3). Here, the dipolar hamiltonian does not commute with $H'^{(0)}_{Q}(t)$ and dipolar spin–lattice relaxation rate is

$$T_{1D}^{-1} = \int_{-\infty}^{\infty} d\omega\, \omega^2 \left[\tfrac{1}{2} J^{(0)}_{(\omega)} G^{(0)}_{\omega} + \sum_{\alpha=1}^{2} J^{(\alpha)}(\omega + \alpha\omega)\, G^{(\alpha)}_{\omega}\right]. \tag{6}$$

or shorter

$$T_{1D}^{-1} = I'^{(0)}(0) + I'^{(1)}(\omega_0) + I'^{(2)}(2\omega_0). \tag{6a}$$

In contrast to the expression (5a) here is the term which describes the spin interaction with the very slow efg tensor fluctuations.

This study shows that the experimental observation of the dipolar spin–lattice times of the quadrupole interacted spin system makes possible to get more information about motions in the crystals. With a suitable choice of a crystal position in the magnetic field we can measure the dipolar relaxation of the spins with equally and unequally spaced levels in the same sample and information about slow and "fast" motions can be extracted from the obtained data.

References

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