Theory of multipulse spin-locking in nuclear quadrupole resonance

B. N. Provotorov and A. K. Khitrin
Institute of Chemical Physics, Academy of Sciences of the USSR

(Submitted 12 May 1981)

Pis'ma Zh. Eksp. Teor. Fiz. **34**, No. 4, 165–168 (20 August 1981)

A theoretical explanation of multipulse spectra, which were observed for the first time [R. A. Marino and S. M. Klainer, J. Chem. Phys. **67**, 3388 (1977); D. Ya. Osokin, Phys. Stat. Sol. (b) **102**, 681 (1981)] in a nuclear quadrupole resonance, is given.

PACS numbers: 76.60.Gv

Multipulse NMR methods have been developed extensively in recent years. These methods have been highly successful in obtaining high-resolution spectra in solids and in studying molecular motion. The multipulse spin-locking method[3] was used in Refs. 1 and 2 to observe the quadrupole resonance of ^{14}N nuclei. An echo sequence, which attenuates after ~1 sec, i.e., in a time much greater than the characteristic time T_2 of dipole-dipole interactions, has been detected. This made it possible to increase substantially the effective sensitivity of the experiment.[1]

The mechanism for the formation of an echo was explained in terms of a simple model with two spins.[4] This approach, however, cannot describe the behavior of a macroscopic spin system for large times, in which the many-spin processes play an important role.[5]

In this letter we analyze theoretically the dynamics of a spin system with a strong quadrupole interaction under the conditions of multipulse spin locking at a time $t \gg T_2$, using the canonical-transformation method.[5]

We shall analyze a crystal sample containing nuclei with spin 1, in which the electric-field gradients are identical in all the nuclei. The quadrupole-interaction Hamiltonian

$$\hat{\mathcal{H}}_Q = \frac{1}{3}\omega_Q[3\hat{I}_z^2 - \hat{I}^2 + \eta(\hat{I}_x^2 - \hat{I}_y^2)] \qquad (1)$$

with use of the operators[6]

$$\hat{I}_{p,1} = \frac{1}{2}\hat{I}_p,\ \hat{I}_{p,2} = \frac{1}{2}(\hat{I}_q\hat{I}_r + \hat{I}_r\hat{I}_q),\ \hat{I}_{p,3} = \frac{1}{2}(\hat{I}_r^2 - \hat{I}_q^2), \qquad (2)$$

where $p, q, r = x, y, z$, or their cyclic permutation, can be written in the form[4]

$$\hat{\mathcal{H}}_Q = -\omega_Q(1-\eta/3)\hat{I}_{y,3} - \frac{1}{3}\omega_Q(1+\eta)(\hat{I}_{z,3} - \hat{I}_{x,3}). \qquad (3)$$

Suppose that the system is irradiated by pulses at a frequency $\omega_y = -\omega_Q(1-\eta/3)$. The interaction with an rf field has the form

$$\hat{\mathcal{H}}_1 = \hat{\mathbf{I}}\mathbf{n}\, f(t) \sin \omega_y t, \qquad (4)$$

where $\mathbf{n}$ is the direction of the axis of the rf coil, and $f(t)$ is the impulse function.[7] Using Eq. (3) and the relation $[\hat{I}_{p,i}, \hat{I}_{q,3} - I_{r,3}] = 0$, we can easily obtain the secular part of $\hat{\mathcal{H}}_1$ with respect to $\hat{\mathcal{H}}_Q$ (Ref. 4),

$$\hat{\mathcal{H}}_1^{\text{sec}} = \hat{I}_{y,2}\, f(t) \cos\theta \qquad (5)$$

Here θ is the angle between the direction $\mathbf{n}$ and the axis y. The secular part of the dipole-dipole interaction with respect to $\hat{\mathcal{H}}_Q$ can be represented in the form

$$\hat{\mathcal{H}}_d^{\text{sec}} = \sum_{i \neq j} \frac{\gamma^2\hbar^2}{r_{ij}^3} \sum_{p=x,y,z} a_{ij}^p (I_{p,1}^i I_{p,1}^j + I_{p,2}^i I_{p,2}^j). \qquad (6)$$

Here $a_{ij}^p = 1 - 3\cos^2\gamma_{ij}^p$, and γ_{ij}^p is the angle between $\mathbf{r}_{ij}$ and the p axis. In the interaction representation with respect to $\hat{\mathcal{H}}_Q$ the Hamiltonians of the problem have the form

$$\hat{\mathcal{H}}(t) = \hat{\mathcal{H}}_1^{\text{sec}} + \hat{\mathcal{H}}_d^{\text{sec}} \qquad (7)$$

(here the rapidly oscillating nonsecular terms have been dropped).

If the pulse duration is ignored, then the impulse function can be represented as follows:

$$f(t) = \phi_0 \delta(t) + \phi \sum_{k=0}^{\infty} \delta(\tau + 2k\tau - t). \qquad (8)$$

It is convenient to represent $\hat{\mathcal{H}}_d^{\text{sec}}$ in the form

$$\hat{\mathcal{H}}_d^{\text{sec}} = \sum_{n=-2}^{2} \hat{\mathcal{H}}_d^n, \qquad [\hat{I}_{y,2}, \hat{\mathcal{H}}_d^n] = n\hat{\mathcal{H}}_d^n . \tag{9}$$

The initial density matrix $1-\alpha_0 \hat{\mathcal{H}}_Q$ becomes[4]

$$\rho_+ = 1 + \alpha_0 \omega_Q (1 - \eta/3) \{ \hat{I}_{y,3} \cos(\phi_0 \cos\theta) - \hat{I}_{y,2} \sin(\phi_0 \cos\theta) \}$$

$$+ \alpha_0 \frac{\omega_Q}{3} (1 + \eta)(\hat{I}_{z,3} - \hat{I}_{x,3}) \tag{10}$$

after the first preparatory pulse. Further evolution of the density matrix is determined by the Hamiltonian

$$\hat{\mathcal{H}}(t) = \hat{I}_{y,2}\, \phi \cos\theta \sum_{k=0}^{\infty} \delta(\tau + 2k\tau - t) + \sum_{n=-2}^{2} \hat{\mathcal{H}}_d^n . \tag{11}$$

It can be seen[7] from Eq. (11) that a quasiequilibrium

$$\rho_{\text{st}} = 1 - \alpha_{\text{st}} \hat{I}_{y,2} - \beta_{\text{st}} \hat{\mathcal{H}}_d^0 - \gamma_{\text{st}} (\hat{I}_{z,3} - \hat{I}_{x,3}),$$

$$\alpha_{\text{st}} = \alpha_0 \omega_Q (1 - \eta/3) \sin(\phi_0 \cos\theta), \quad \beta_{\text{st}} = 0, \quad \gamma_{\text{st}} = \alpha_0 \frac{\omega_Q}{3}(1+\eta) \tag{12}$$

is established in the system during the time of the order of T_2. We can easily see, taking Eq. 5 into account, that the amplitude of the observed signal at times of $\sim T_2$ is proportional to $\cos\theta \sin(\phi_0 \cos\theta)$. At times $t \gg T_2$ $y = \text{const}$, and α and β vary slowly under the influence of the dipole-dipole interaction modulated by rf pulses.

To determine the rate of this variation, we must perform a canonical transformation of the equation for the density matrix.[5] In the transformations for our problem, which were used in Ref. 5, we must substitute only the operators (2) for the spin-projection operators $\hat{I}_p$ ($p = $ x, y, z). Switching to the coordinate system with an effective field[7] $\omega_e = \phi\cos\theta/2\tau$, and after canonical transformations, we can see that the evolution of the density matrix is determined by the equation

$$\frac{d\rho}{dt} = -i[-\omega_e \hat{I}_{y,2} + \hat{\mathcal{H}}_d^0 + \sum_{n,m} (e^{im\pi t/\tau} \hat{R}_m^n + e^{-im\pi t/\tau} \hat{R}_m^{-n}), \rho] \tag{13}$$

$$[\hat{I}_{y,2}, \hat{R}_m^n] = n\hat{R}_m^n,$$

where the sum over n and m must take into account the nearest resonance processes which are determined by the condition

$$n\omega_e = m\pi/\tau , \tag{14}$$

and the resonance term $\hat{R}_m^n$ causes a spin reversal n, which is accompanied by a quantum absorption m of frequency π/τ.

The envelope of the attenuating echo sequence is determined by the decrease of the value $\alpha(t)$ with time, and its temporal variation can be calculated with the help of kinetic equations for $\alpha(t)$ and $\beta(t)$, which were used in Ref. 7 and which take into account the effect of all the essential resonances. For a single crystal the envelope depends exponentially on time, and the damping factor is equal to $\sim\tau^4$ for $\phi\cos\theta=\pi/2$ and τ^6 for $\phi\cos\theta=2\pi/5$ and $\pi/3$.

An approximate calculation for a powder showed that the characteristic time of the envelope depends on τ as τ^{-4}. These conclusions are in satisfactory agreement with the experimental data for an $NaNO_2$ powder, given in Ref. 1 (the experiment and calculation were performed for $\phi=\pi/2$).

The authors thank G. E. Karnaukh and V. L. Turovets for their help with our work.

1. R. A. Marino and S. M. Klainer, J. Chem. Phys. 67, 3388 (1977).
2. D. Ya. Osokin, Phys. Stat. Sol. (b) **102**, 681 (1981).
3. E. D. Ostroff and J. S. Waugh, Phys. Rev. Lett. **16**, 1097 (1966).
4. R. S. Cantor and J. S. Waugh, J. Chem. Phys. 73, 1054 (1980).
5. B. N. Provotorov and É. B. Fel'dman, Zh. Eksp. Teor. Fiz. 79, 2206 (1980) [Sov. Phys. JETP **52**, 1116 (1980)].
6. S. Vega and A. Pines, J. Chem. Phys. 66, 5624 (1977).
7. Yu. N. Ivanov, B. N. Provorotov, and É. B. Fel'dman, Zh. Eksp. Teor. Fiz. 75, 1847 (1978) [Sov. Phys. JETP **48**, 930 (1978)].

Translated by S. J. Amoretty
Edited by Robert T. Beyer