Modulation effects in multipulse NMR experiments

L. N. Erofeev, A. I. Sosikov, and A. K. Khitrin
Institute of Chemical Physics, Academy of Sciences of the USSR

(Submitted 23 December 1983; resubmitted 17 February 1984)
Pis'ma Zh. Eksp. Teor. Fiz. **39**, No. 8, 357–360 (25 April 1984)

The combined action of a multipulse sequence and modulation of the external field on a spin system is examined. A spin-locking signal in a doubly rotating coordinate system (DRCS) in multipulse NMR experiments is obtained experimentally for the first time.

It is convenient to describe a spin system irradiated with a strong rf field using a rotating coordinate system (RCS) in which an effective field is operating.[1] It is also possible to determine the corresponding effective field when a periodic sequence of rf pulses acts on the system.[2] If an additional alternating field with frequency close to the Larmor spin-precession frequency of the effective field is applied in this case perpendicularly to the latter, then a resonance appears in the effective field. This additional alternating field can be created, for example, by modulating the constant magnetic field.

Two cases can be distinguished. 1) If the amplitude of modulation is less than the effective dipole interactions, then the modulation will lead to a monotonic change of the projection of magnetization on the effective field. This case can be described with the help of the saturation theory.[3] 2) If the amplitude of modulation is greater than the effective dipole interactions, then the magnetization will precess in a coordinate system with double rotation (DRCS)[4] around the direction of the new effective field. Since the effective dipole interactions in such experiments can be much smaller than the starting dipole interaction,[5] the precession of magnetization can be observed in very weak effective fields.

 © 1984 American Institute of Physics

The NMR signal in the effective field created with the help of continuous irradiation was observed by Mefed,[6] the component of the magnetization aligned along the constant magnetic field with a relatively low frequency of the effective field was also studied. In multipulse experiments the magnetization is measured during the intervals between the pulses directly at the high frequency, which assures high sensitivity.

To create the additional alternating magnetic field varying with a frequency 1–30 kHz and with an amplitude up to 0.2 Oe, additional coils aligned along the direction of the constant magnetic field were placed in the sensor of the multipulse NMR spectrometer.[7] The sequence $90^0_y - (\tau - \phi^0_x - \tau)^n$ (multipulse spin-locking), where ϕ^0_x indicates the rf pulse, which rotates the spin by an angle ϕ^0 around the x axis of the rotating coordinate system, and 2τ is the interval between pulses, was selected as the multipulse sequence; the carrying frequency of the pulses can differ from the resonant frequency by an amount equal to the detuning Δ.

The behavior of the magnetization under the action of this sequence was studied in Refs. 8 and 9. The equation for the density matrix can be put into the following form with the help of a canonical transformation,[9]

$$\frac{\partial \rho}{\partial t} = -i\,[-\omega_e(\mathbf{n}\cdot\hat{\mathbf{S}}) + \hat{H}^0_d + R(t), \rho\,], \quad \rho(0) = 1 - \alpha\hat{S}_x; \tag{1}$$

where ω_e is the magnitude of the effective field

$$\cos(2\omega_e\tau) = \cos\phi\cos^2(\Delta\tau) - \sin^2(\Delta\tau); \tag{2}$$

$\mathbf{n}$ is a unit vector oriented along the effective field with components

$$n_x = \frac{\sin\phi\cos(\Delta\tau)}{\sin(2\omega_e\tau)}; \quad n_y = 0; \quad n_z = \frac{\sin(2\Delta\tau)\cos^2(\phi/2)}{\sin(2\omega_e\tau)}; \tag{3}$$

$\hat{H}^0_d$ is an operator which commutes with $(\mathbf{n}\cdot\mathbf{S})$, whose leading term is

$$\hat{H}^0_d = \frac{1}{2}(3n_z^2 - 1)\hat{H}^n_d + \ldots\,. \tag{4}$$

In this expression the small terms of higher order in the parameter $\epsilon = \|\hat{H}_d\|\tau$ are dropped. (Here $\hat{H}^n_d$ is the secular, with respect to the $\mathbf{n}$ axis, part of the dipole-dipole interaction Hamiltonian). $R(t)$ contains the small nonsecular terms which describe the multispin resonance processes. Analysis of Eq. (1) shows that the evolution of the spin system passes through two stages. First, over a time $t \sim \|\hat{H}^0_d\|^{-1}$, a quasiequilibrium with $\rho_{st} = 1 + \alpha_{st}\omega_e(\mathbf{n}\cdot\mathbf{S}) - \beta_{st}\hat{H}^0_d$ and a corresponding value of the magnetization M_{st} are established. Then, the magnetization slowly decays under the action of the nonsecular term $R(t)$ over a time T_{2e}. If we are interested in times $t \ll T_{2e}$, then $R(t)$ in Eq. (1) can be dropped.

Thus, when modulation is activated at times $t \ll T_{2e}$, the evolution of the magnetization will proceed just as when an effective field with the same magnitude and orientation is created with the help of continuous irradiation[10] and will be deter-

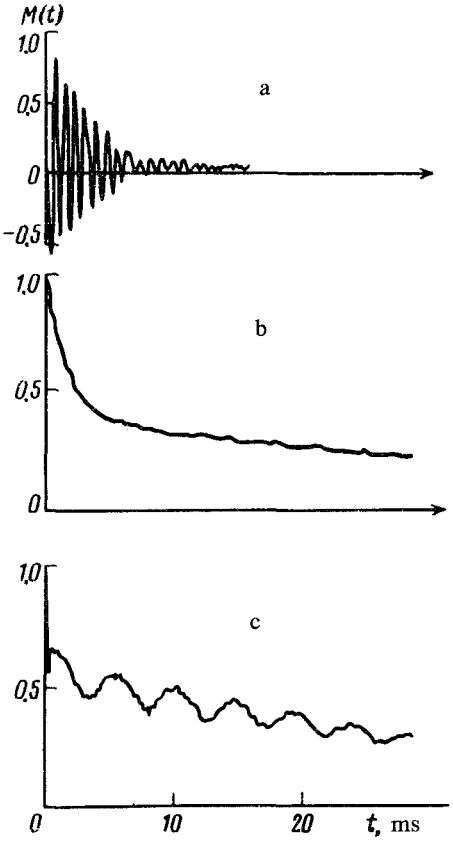

FIG. 1. NMR signals in the multipulse spin-locking regime with ϕ_x^0, $\tau = 8.86$ μs; a) water, $\omega_a/2\pi = 9.4$ kHz, $\Omega_a/\gamma = 0.125$ Oe, $\Delta = 0$; b) adamant, $\Delta = 0$, $\omega_a/2\pi = 8.0$ kHz, $\Omega_a/\gamma = 0.05$ Oe; c) adamant, $\Delta/2\pi = 10.0$ kHz, $\omega_a/2\pi = 14.0$ kHz, $\Omega_a/\gamma = 0.05$ Oe.

mined in the DRCS by the Hamiltonian[4]

$$\hat{H}_{\text{eff}} = \Delta' \hat{S}_z + \Omega_a \hat{S}_x + \hat{H}_d^0. \tag{5}$$

Here the z axis is oriented along the direction of $\mathbf{n}$, $\Delta' = \omega_e - \omega_a = -\gamma h'$, ω_a is the modulation frequency, and Ω_a is the modulation amplitude in DRCS which differs by a factor n_x from the modulation amplitude in the laboratory coordinate system.

For $\Omega_a \gg \|\hat{H}_d^0\|$ the magnetization in DRCS, according to (5), precesses around the new effective field Ω_e with components Δ' and Ω_a. Figure 1a shows the signal from protons at $\Delta' = 0$. The oscillation frequency here is Ω_a. This spectrum can be used to make a more accurate determination of the modulation amplitude. The damping of the oscillations is due primarily to the inhomogeneity of the modulation field.

For $\Omega_a \ll \|\hat{H}_d^0\|$ over a time $t \sim \|\hat{H}_d^0\|^{-1}$ a quasiequilibrium and a corresponding

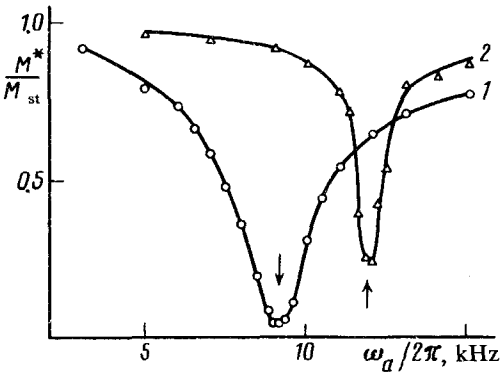

FIG. 2. Dependence of M^*/M_{st} on ω_a in adamant with $\tau = 8.86\,\mu s$, $\Omega_a/\gamma = 0.05$ Oe; 1 – $\Delta = 0$, $n_z = 0$; 2 – $\Delta/2\pi = 6.5$ kHz, $n_z = 0.52$.

magnetization M_{st} will be established in the system. Under the action of the modulation, as follows from (4) and (5), the magnetization will then decay exponentially (the short component in Fig. 1b) to the value[4]

$$M^* = M_{st} \frac{\Delta'^2}{\Delta'^2 + \Omega_a^2 + (3n_z^2 - 1)^2 \omega_{loc}^2 / 4}, \tag{6}$$

where $\omega_{loc}^2 = \mathrm{Sp}(\hat{H}_d^z)^2/\mathrm{Sp}\hat{S}_z^2$, followed by a slow decay of the magnetization to zero due to multispin resonances of the processes $R(t)$ (the long component in Fig. 1b). Figure 2 shows the dependence of M^* on the modulation frequency ω_a. The arrows mark the corresponding values of the effective field. In accordance with (6), the depression in this dependence narrows as the angle between the effective and the constant fields approaches a critical value ($n_z^2 = 1/3$). With the help of this method it is possible to pass "continuously" through the NMR line formed by the multipulse sequence.

For $\Omega_a \gtrsim \|\hat{H}_d^0\|$ the magnetization is "locked" by the field—spin-locking in DRCS ("second spin-locking"), and oscillations with frequency equal to the modulation frequency appear in the signal. Figure 1c shows the "second spin-locking" signal. The frequency of the oscillations observed here is equal to the difference between the magnetization sampling frequency for (14.1 kHz) and the modulation frequency (14.0 kHz). It was found that the decay time of the magnetization in the "second spin-locking" can greatly exceed T_{2e}. This opens up new possibilities for studying slow molecular motions by multipulse NMR methods.

The authors thank V. N. Provotorov for useful discussions.

[1]A. Abraham, Nuclear Magnetism, Inostr. Lit., Moscow, 1963.
[2]B. N. Provotorov and E. B. Fel'dman, Zh. Eksp. Teor. Fiz. **79**, 2206 (1980) [Sov. Phys. JETP **52**, 1116 (1980)].
[3]B. N. Provotorov, Zh. Eksp. Teor. Fiz. **41**, 1582 (1961) [Sov. Phys. JETP **14**, 1126 (1961)].
[4]M. Goldman, Spin Temperature and NMR in Solids, Mir, Moscow, 1972.
[5]J. S. Waugh, L. M. Huber, and U. Baeberlen, Phys. Rev. Lett. **20**, 180 (1968).

[6]A. E. Mefed, Zh. Eksp. Teor. Fiz. **86**, 302 (1984) [Sov. Phys. JETP, to be published].
[7]L. N. Erofeev, O. D. Vetrov, B. A. Shumm, M. Sh. Isaev, and G. B. Manelis, Prib. Tekh. Eksp. **2**, 145 (1977).
[8]L. N. Erofeev, B. A. Shumm, and G. B. Manelis, Zh. Eksp. Teor. Fiz. **75**, 1837 (1978) [Sov. Phys. JETP **48**, 925 (1978)].
[9]Yu. N. Ivanov, B. N. Provotorov, and E. B. Fel'dman, Zh. Eksp. Teor. Fiz. **75**, 1847 (1978) [Sov. Phys. JETP **48**, 930 (1978)].
[10]J. R. Franz and C. P. Slichter, Phys. Rev. **148**, 287 (1966).

Translated by M. E. Alferieff
Edited by S. J. Amoretty