Multi-photon resonances in pure multiple-pulse NQR

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Abstract

We have observed multi-photon resonances in a system with a spin 3/2 irradiated simultaneously by a multiple pulse radiofrequency sequence and a low frequency field swept in the range 0-80 kHz. The used excitation scheme allowed us to measure the effective field of the radiofrequency sequence. A peculiarity of this scheme is that the intensity of the resonance lines decreases slowly with the mode number. The theoretical description of the effect is presented using both the rotating frame approximation and the Floquet theory. Both approaches give identical results at the calculation of the resonance frequencies, transition probabilities and shifts of resonance frequency. The calculated magnetization vs. the frequency of the low-frequency field agrees well with the obtained experimental data. The multi-frequency spectra give a way for studying slow atomic motion in solids.

Introduction

One of the most effective and promising high-resolution nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) techniques for the study of solids is a multiple-pulse radiofrequency (RF) action \cite{1,2}. The multiple-pulse methods allow one to remove dipolar broadening from a resonance line in solids thus increasing by several orders the sensitivity of the NMR and NQR spectroscopy in the study of weak interaction. These methods are very effective in the study of the spin lattice relaxation processes due to a slow atomic motion. Usually the theoretical description of multiple-pulse experiments both in NMR \cite{3} and NQR \cite{4} is based on the construction of the effective time-independent Hamiltonian by using the conditions for periodicity and cyclicity of the pulsed action. Then the dynamics of a spin system subjected by pulsed RF fields is presented in an equivalent form as the motion of nuclear spins in a constant effective field $H_e$ \cite{5}. The magnitude and direction of this effective field are determined by parameters of the multiple-pulse sequence. An experimental measurement of the value of the effective field is important for the confirmation
of this theoretical model.

It is reasonable to suggest that an additional field with an angular frequency $\Omega$ close to $\omega_e = \gamma H_e$ should cause resonance absorption of energy ($\gamma$ is the gyromagnetic ratio of nuclei). Spin-echo signals observed between RF pulse sequence would allow us to determine $H_e$ as well as to obtain the information on slow atomic motion that is not available from the traditional methods.

With this in mind, we have studied experimentally resonance transitions in the nuclear spin system subjected by a simultaneous action of a multiple–pulse RF sequence and an additional low frequency (LF) field with an angular frequency $\Omega$. The results of our experiments described in the next section have shown that resonance transitions were observed not only at the frequency close to $\Omega_0 = \omega_e$, but also at frequencies close to $\Omega_n$ given by the expression:

$$\Omega_n = |\omega_e \pm 2\pi n/t_c|, \quad n = \pm 1, \pm 2... \quad (1)$$

where $t_c$ is the period of the multiple pulse RF sequence.

Multiple resonance modes of higher orders have been detected by microwave spectroscopy [6], molecular beam technique [7], optical pumping [8] and observed previously in NMR experiments [9–13]. However the amplitude of these resonances decreased abruptly with the mode order of the resonance. As distinct from this, the amplitude of the resonances observed in our experiments decreased slowly and the resonances of higher orders were well observable.

Because the nuclear spin system possesses a set of the resonance frequencies, the relaxation measurements performed on one resonance frequency $\Omega_n$ can give the information on oscillations of atoms on all the frequencies from the spectrum determined by (1). It moves us to comprehensive experimental and theoretical study of this system.

The theoretical treatment of NMR phenomena is usually based on three approaches: i) a semi-classical mathematical approach [14]; ii) a second quantization method [15]; and iii) the Floquet theory [17].
The semi-classical mathematical approach [14], where the field is considered as a classical system and the atomic system as a quantum one, has allowed one to explain a series of experimentally observed phenomena. This approach is quite natural if to take into account, that the average number of photons in a mode of the periodic field is extremely great. The main method used in the framework of the semi-classical approach is the so-called "rotating frame approximation", keeping exactly just the terms that are resonant. The remaining non-resonant terms are considered as a perturbation.

Intrinsic inconsistency of the semi-classical approach is obviated in the framework of the secondary quantization method [15,16]. Treating the RF field as photons, the evolution of the united system ”atom +field" (so called ”dressed” atom) is described by the Hamiltonian which is independent of time, and its investigation turns out simpler than solving the Schrödinger equation with the time-dependent Hamiltonian. With the time-independent Hamiltonian, one can define energy levels of the physical system. Each of these levels corresponds to a stationary state of the system: atom dressed by photons. The dependence of the energy of the united system on the field frequency allows one to construct the diagram of levels. The coupling between RF photons and an atom perturbs the energy levels and allows one to interpret all resonances as ”crossings” and ”anticrossings” of the conforming levels [18].

The Floquet theory [17] is a powerful method widely used in NMR spectroscopy for solving time-dependent problems [10,19]. On the one hand, this approach uses the advantages of the secondary quantization method resulting in the time-independent Hamiltonian. On the other hand, it simplifies calculations as the terms related to the system of free RF photons are not included in the Hamiltonian. The last is justified because an RF field applied in the NMR method contains abundant photons and changes in the state of the photon system may be neglected. In the framework of the Floquet theory, the interaction of the spin system with RF field is considered as completely quantum-mechanical. Therefore, the Floquet theory can be considered to be a bridge between the semi-classical and the quantum methods.

To calculate the transition probabilities and the shift of the center of the resonance line,
two theoretical methods are used: the semi-classical approach and the Floquet theory. We extend the theory of the multiphoton resonances [14,15,17] to the case of the pure multiple-pulse NQR. The results given by both theoretical approaches are compared with each other and with the experiment.

**Experiments**

The experiments were performed using an automated multiple-pulse NQR spectrometer. Mutually perpendicular continuous LF and pulse RF magnetic fields were generated by crossed coils. Resonances were observed in the effective field of a multiple-pulse RF sequence \((\pi/2)_y - (t_c/2 - \varphi - t_c/2)^N\), where \(\varphi\) denotes the pulse that rotates the nuclear magnetization about direction of RF field in the rotating frame by an angle \(\varphi\), and \(N\) is the number of pulses in the sequence. This sequence consisted of \(N = 256\) pulses and spin locking signal was sampled in the interval between them. The period of the pulse sequence was \(t_c = 100\) ms.

The NQR of \(^{35}\)Cl nuclei was observed in polycrystalline \(KClO_3\) at 77 K. Without action of the LF field, we recorded the sequence of echo signals in the interval between pulses at 28.9539 MHz with practically constant amplitude (height of the spin echo signals) during the observation time (Fig. 1). This amplitude corresponds to a quasi-equilibrium state of the spin system with magnetization \(M_0\).

LF field with the amplitude 2.5 G, nonsynchronized with RF pulses, was swept in the range 1 ÷ 80 KHz. The resonance reduction of the magnetization amplitude was observed (Fig.1) at several different frequencies \(\Omega\). The transient process with the spin-spin relaxation time \(T_2\) was followed by establishment of a new quasi-equilibrium state of the spin system with the reduced amplitude of the magnetization. Our measurements give the value \(T_2 = 455\) ms.

Fig. 2 shows the dependence of the relative magnetization \(M/M_0\) on the frequency \(\Omega\) of the LF field for the \(\varphi = \pi/2\) RF pulse (corresponding to the pulse duration \(t_w = 15\) \(\mu\)s ). The effective frequency of the RF field is determined by \(\omega_e = \frac{\varphi}{t_c}\). For example, \(\omega_e = 2.5\) kHz.
for $\varphi = \frac{\pi}{2}$.

As follows from Fig. 2, the amplitude of the resonances decreases slowly with increasing the mode number $n$.

**Theory**

1. **Semi-classical approximation: rotating frame approximation**

Let us consider a system of nuclear spins $I = 3/2$ placed in an inhomogenous electric field gradient (EFG) and subjected to a joint action of two time-dependent magnetic fields: a multiple–pulse RF sequence with the angular frequency $\omega$ equaled to the resonance frequency $\omega_0$ and a continuous low frequency (LF) field with the angular frequency $\Omega$.

In the rotating frame the equation for the density matrix of the system takes the form:

$$i \frac{d\rho(t)}{dt} = [\mathcal{H}(t), \rho(t)],$$

where the Hamiltonian of the system is

$$\mathcal{H}(t) = 2\omega_2 S_z \cos \Omega t + S_x \varphi \sum_{k=1}^{\infty} \delta (t - kt_c - t_c/2),$$

$S_x$ and $S_z$ are $X$- and $Z$-components of the effective spin operator [4]; the pulse angle $\varphi = \gamma H_1 t_w$ and $0 < \varphi < 2\pi$; $\omega_2 = \gamma H_2$; $H_1$ and $H_2$ are the amplitudes of the RF pulse and LF fields, respectively. The initial phase of LF field is chosen equal zero.

To solve Eq.(2), we apply the unitary transformation

$$\tilde{\rho}(t) = e^{-iS_x t} P^+(t) \rho(t) P(t) e^{iS_x t},$$

where the unitary operator $P(t)$ is given by the solution of the equation

$$i \frac{dP(t)}{dt} = S_x \varphi \sum_{k=1}^{\infty} \delta (t - kt_c - t_c/2) P(t) - P(t) \mathcal{H}_e$$

with the initial condition

$$P(0) = 1$$

and the effective time-independent Hamiltonian
\[ \mathcal{H}_e = \omega e S_x. \] (7)

After performing the unitary transformation (4) we obtain the following equation for the transformed density matrix $\tilde{\rho}(t)$

\[ \frac{d\tilde{\rho}(t)}{dt} = [\mathcal{H}^{tr}(t), \tilde{\rho}(t)] \] (8)

with

\[ \mathcal{H}^{tr}(t) = (\omega_e - \Omega) S_x + \tilde{S}_z(t), \] (9)

where $\tilde{S}_z(t) = P^+(t) S_z P(t)$ is the periodic function of time and can be expanded into the Fourier series

\[ \tilde{S}_z(t) = S_+ \sum_{n=-\infty}^{\infty} b_n e^{-in\omega_c t} + S_- \sum_{n=-\infty}^{\infty} b_n e^{in\omega_c t} \] (10)

where $S_\pm = S_z \pm iS_y$, $b_n = \omega_2 \frac{(-1)^n \sin \frac{n\phi}{2}}{\varphi + 2\pi n}$ are the Fourier coefficients, and $\omega_c = \frac{2\pi}{\tau_c}$.

The resonance terms in the solution of Eq. (8) are determined by the lowest values of the differences $\xi = |\omega_e - \Omega \pm n\omega_c|$. At $\xi = 0$ we obtain the expression (1) for resonance conditions. The rest non-resonant terms determine a frequency shift $\Delta$ for the position of the resonance dips shown in Figs 1 and 2. Let us estimate this shift as a function of the frequency $\Omega$ using the average Hamiltonian theory [24,21]. We will consider three various cases depending on the value of the frequency $\Omega$.

The first case, $\Omega = 0$, corresponds to the appearance of an additional constant magnetic field along $Z$-axes resulting in the difference between $\omega$ and $\omega_0$.

To determine the influence of all the non-resonant terms, we will perform the unitary transformation under Eq.(8),

\[ \rho'(t) = e^{i\varphi S_z \frac{t}{\tau_c}} \tilde{\rho}(t) e^{-i\varphi S_z \frac{t}{\tau_c}}, \] (11)

which leads to

\[ \frac{d\rho'(t)}{dt} = [\mathcal{H}'(t), \rho'(t)] = \left[ S_+ \sum_{n=-\infty}^{\infty} b_n e^{-i(2\pi n + \varphi) \frac{t}{\tau_c}} + S_- \sum_{n=-\infty}^{\infty} b_n e^{i(2\pi n + \varphi) \frac{t}{\tau_c}}, \rho'(t) \right]. \] (12)
Let us replace $H'(t)$ by the average Hamiltonian up to second order of the expansion in $\omega_2/\omega_e$:

$$
\mathcal{H}^{av} = t_c \sum_{n=-\infty}^{\infty} \frac{b_n^2}{2(2\pi n + \varphi)} [S_-, S_+],
$$

(13)

Note that in the case of non-zero initial phase of the LF field $\bar{H}$ includes $|b_n|^2$. Therefore the initial phase of the LF field does not influence the result. Performing the summation in Eq.(13) we obtain

$$
\Delta_1 = \frac{\omega_2^2 t_c}{8} \cot \frac{1}{2} \varphi \text{ with } \varphi \neq -2\pi n.
$$

(14)

In the limit that $t_c \to 0$, a one long pulse, we obtain from Eq. (14) a simple expression for the shift $\Delta_1 = \frac{\omega_2^2}{4\omega_e}$, which is similar to the Bloch-Siegert results [22]. However, in contrast to the Bloch-Siegert shift which is produced by the RF field and has the value of the order of $(\frac{\omega_1}{\omega_0})^2 \sim 10^{-6}$, the obtained shift is sufficiently higher because it is determined by the ratio of two weak fields with the amplitudes $H_2$ and $H_e$. For example, for the angle $\varphi = \frac{\pi}{2}$, the shift $\Delta_1$ is of the order of $10^{-2}$. The shift $\Delta_1$ is caused by a deviation of the frequency of the applied RF field from the Larmor frequency and should be taken into account when the results of multiple-pulse experiments are analyzed.

The second case: $\Omega = \omega_e$. The average Hamiltonian $\bar{H}$ is

$$
\mathcal{H}^{av} = 2b_0 S_x + \sum_{n=-\infty; n\neq 0}^{\infty} \frac{b_n^2}{2n\omega_c} [S_-, S_+]
$$

(15)

After the summation in Eq.(15) we obtain the shift due to common action of the non-resonant terms

$$
\Delta_2 = \frac{\omega_2^2 t_c}{\varphi^3} \left[ \sin^2 \frac{1}{2} \varphi - \frac{\varphi}{8} (\varphi + \sin \varphi) \right].
$$

(16)

Thus, the resonance frequency differs from $\omega_e$. A shift appears also when we consider $\Omega = \omega_e + n\omega_c$.

In order to determine correctly the resonance conditions, let us consider the third case: $\Omega \neq \omega_e + n\omega_c$. Using the transformation
\[ \rho''(t) = e^{i(\varphi - \Phi)S_x \frac{1}{tc}} \rho(t) e^{-i(\varphi - \Phi)S_x \frac{1}{tc}}, \tag{17} \]

where \( \Phi = \Omega t_c \), we obtain

\[ \frac{d\rho''(t)}{dt} = \left[ S_+ \sum_{n=-\infty}^{\infty} b_n e^{-i(\varphi - \Phi + 2\pi n) \frac{t}{tc}} + S_- \sum_{n=-\infty}^{\infty} b_n e^{i(\varphi - \Phi + 2\pi n) \frac{t}{tc}}, \rho''(t) \right]. \tag{18} \]

Let us exclude from the sums in (18) the terms with \( n = -\frac{\varphi - \Phi}{2\pi} \):

\[ \frac{d\rho''(t)}{dt} = \left[ (-1)^{\frac{\varphi - \Phi}{2\pi}} \frac{\omega_2}{\Phi} \sin \frac{\varphi}{2} S_x + S_+ \sum_{n=-\infty, n \neq -\frac{\varphi - \Phi}{2\pi}}^{\infty} b_n e^{-i(\varphi - \Phi + 2\pi n) \frac{t}{tc}} + S_- \sum_{n=-\infty, n \neq -\frac{\varphi - \Phi}{2\pi}}^{\infty} b_n e^{i(\varphi - \Phi + 2\pi n) \frac{t}{tc}}, \rho''(t) \right]. \tag{19} \]

The average Hamiltonian up to second order of the expansion in \( \omega_e/\omega_c \)

\[ \mathcal{H}_{av} = (-1)^{\frac{\varphi - \Phi}{2\pi}} \frac{\omega_2}{\Phi} \sin \frac{\varphi}{2} S_x + \omega_2^2 t_c \sin^2 \frac{\varphi}{2} \sum_{n=-\infty, n \neq -\frac{\varphi - \Phi}{2\pi}}^{\infty} \frac{1}{(\varphi + 2\pi n)^2 (\varphi - \Phi + 2\pi n)} [S_-, S_+]. \tag{20} \]

Because in the considered case \( \varphi - \Phi \neq -2\pi n \), the first term in (20) disappears and the summation over all \( n \) gives the following equation for the frequency shift:

\[ \Delta_3 = \omega_2^2 t_c \left( 1 - \frac{2 \sin \frac{\varphi}{2} \sin \frac{\Phi}{2}}{\Phi \sin \frac{\varphi - \Phi}{2}} \right). \tag{21} \]

Emphasize that \( \Phi \) is a function of \( \Delta_3 \) and Eq. (21) has infinite number of roots. Resonance transitions are realized at \( \Omega = \tilde{\Omega}_n \), where

\[ \tilde{\Omega}_n = \omega_c + \Delta_3 n + n \omega_c, \; n = 0, \pm 1, \pm 2, \ldots \tag{22} \]

Resonance frequencies calculated according (22) using numerical solutions of (21) for the shift are presented in Table 1 and 2 along with the experimental data. The shift is caused by off-resonant component of the LF field.

The time-average transition probability, \( \bar{P} \) can be determined using the method developed in [23] :

\[ \bar{P} = \frac{1}{2} \sum_n \frac{b_n^2}{(\omega_e - \Omega - n \omega_c + \Delta_3)^2 + b_n^2}. \tag{23} \]
Since \((\omega_e^2)^2 \ll 1\) (for example, \((\omega_e^2)^2 = 6.5 \times 10^{-2}\) for \(\varphi = \pi/2\)), the transition probabilities become significant only in the vicinity of the resonance frequency determined by the condition (22). The expression for the nuclear magnetization \(M\), the quantity needed to compare with experiment, can be found using Eq. (23):

\[
\frac{M}{M_0} = 1 - \sum_n \frac{b_n^2}{(\omega_e - \Omega - n\omega_e + \Delta_3)^2 + b_n^2}.
\] (24)

Expressions (23) and (24), obtained in the framework of the semi-classical approach, determine a multi-line resonance spectrum of the two-energy level system with spin 1/2 irradiated by multiple pulse RF and LF fields. As follows from (24) the amplitudes of the resonances decreases slightly with the number \(n\). There is disparity between a two-level energy model of the spin system and the multi-line resonance spectrum. In order to make a physical interpretation clear, the energy spectrum and transition probabilities will be calculated in the next section by using the Floquet theory [17].

2. Floquet theory

The Floquet theory provides a quite natural description of the multi-line resonance spectrum of the two-energy level spin system. Let us introduce the time-dependent operator

\[
U(t, t_0) = F(t) F^+(t_0),
\] (25)

where the unitary operator \(F(t)\) obeys to the evolution equation

\[
\frac{dF(t)}{dt} = \mathcal{H}^{tr}(t) F(t)
\] (26)

with the periodic time-dependent Hamiltonian (9). The general form of the solution of Eq.(26) is given by the Floquet theorem [17] is

\[
F(t) = \Psi(t) e^{-i\mathcal{H}^F t},
\] (27)

where \(\Psi(t)\) is a periodic function of time with the frequency \(\omega_c\), and \(\mathcal{H}^F\) is the time-independent effective Hamiltonian. Using the periodic character of the Hamiltonian \(\tilde{H}(t)\)
and function Ψ (t), the time-dependent Eq. (26) can be rewritten as an infinite set of the coupled equations [17]

\[ \sum_{\mu k} \left( \mathcal{H}_{\alpha\mu}^{n-k} + n\omega_c \delta_{nk} \delta_{\alpha\mu} \right) F_{\mu\beta}^k = h_{\beta} F_{\alpha\beta}^n, \]  

(28)

where \( h_{\beta} \) are diagonal elements of the effective Hamiltonian \( \mathcal{H}_F \), \( \mathcal{H}_{\alpha\mu}^{n-k} \) and \( F_{\alpha\beta}^n \) are the Fourier components of the matrix elements of \( \mathcal{H}_t (t) \) and \( F (t) \):

\[ F_{\alpha\beta}(t) = \sum_{n} F_{\alpha\beta}^n e^{i\omega_c t} e^{-ih_{\beta}}, \]  

(29)

\[ \mathcal{H}_t^{\alpha\beta}(t) = \sum_{n} \mathcal{H}_{\alpha\beta}^n e^{i\omega_c t}. \]  

(30)

Here \( \alpha = \pm 1/2, \beta = \mp 1/2 \) characterize various spin states. Using the orthogonal basis \(|\alpha n\rangle\), where \( n \) denotes the Fourier component, the term in the brackets of the Eq. (28) can be presented as the Floquet Hamiltonian [17]

\[ \langle \alpha n | \mathcal{H}_F | \beta k \rangle = \mathcal{H}_{\alpha\beta}^{n-k} + n\omega_c \delta_{nk} \delta_{\alpha\beta}. \]  

(31)

Using the operator basis \( e_{\alpha n,\beta m} \) [24] with matrix elements \( \langle \mu p | e_{\alpha n,\beta m} | \eta q \rangle = \delta_{\alpha\mu} \delta_{\beta\eta} \delta_{pm} \delta_{mq} \)

the Floquet Hamiltonian can be expressed as

\[ \mathcal{H}_F = \sum_{\alpha,n} (\varepsilon_{\alpha} + n\omega_c) e_{\alpha,\alpha n} + \sum_{\alpha\neq\beta,n,m} \left( b_{m-n}^{\alpha\beta} e_{\alpha n,\beta m} + b_{m-n}^{\beta\alpha} e_{\beta n,\alpha m} \right) \]  

(32)

where \( \varepsilon_{\alpha} = \alpha (\omega_c - \Omega) \), \( b_{m-n}^{\alpha\beta} = b_{m-n} \) are the Fourier coefficients determined in (10). The first term in (32) is diagonal, while the second one is off-diagonal.

As follows from (32), nonzero off-diagonal matrix elements between \(|\alpha n\rangle\) and \(|\beta m\rangle\) for various \( n \) and \( m \) appear in first order of \( \omega_c / \omega_e \). Therefore all resonance transitions between different states of the Hamiltonian (32) can be excited in the straight way without involving intermediate states as it is used in the scheme of multiphoton excitation proposed in [10,19,25].

The intensity of a resonance transition can be estimated using the perturbation method [7] based on the approximation of the Floquet Hamiltonian \( H_F \) (32) by the \( 2 \times 2 \) matrix \((\alpha \neq \beta)\).
\[ H'_F = \epsilon_\alpha + m\omega_c + c_{am} b_{m-n} + d_{n-m}^{\alpha\beta}, \] (33)

with matrix elements corrected by taking into account the rest part of the Hamiltonian: the diagonal elements - by introducing the additional terms \( c_{an} \) which are up to second order to within \( \left( \frac{\omega}{\omega_c} \right)^2 \ll 1 \) is

\[ c_{an} = \sum_{\mu,k} \frac{\langle \alpha n | H_F | \mu k \rangle \langle \mu k | H_F | \alpha n \rangle}{E_{\alpha n} - E_{\mu k}}. \] (34)

and the off-diagonal ones - by adding the terms \( d_{n-m}^{\alpha\beta} \) of the same order

\[ d_{n-m}^{\alpha\beta} = 2 \sum_{\mu k} \frac{\langle \beta n | H_F | \mu k \rangle \langle \mu k | H_F | \alpha m \rangle}{E_{\beta n} - E_{\mu k}}. \] (35)

In (34) and (35) \( E_{\beta n} \) are eigenvalues of the Floquet Hamiltonian \( H_F \). Diagonalizing the matrix (33) gives the eigenvalues of the Hamiltonian \( H'_F \):

\[ 2E_{m,n}^{\pm(\alpha\beta)} = [\varepsilon_\alpha + \varepsilon_\beta + (m + n) \omega_c] \pm \\
\pm \left\{ [\varepsilon_\alpha + m\omega_c + c_{am}] - (\varepsilon_\beta + n\omega_c + c_{\beta n}) \right\}^2 + \left( b_{m-n} + b_{n-m}^{\alpha\beta} \right)^2 \right\}^{1/2}. \] (36)

Substituting the matrix elements (31) into (34) we obtain the expressions for the energy level shifts

\[ c_{an} = -c_{\beta n} = \sum_{k=-\infty}^{\infty} \frac{b_{k-n}^2}{(\varphi - \Phi + 2\pi (k - n))}. \] (37)

The summation in Eq.(37) gives the same equation for the frequency shift as above obtained using the rotating frame approximation (see Eq.(20)):

\[ \Delta_3 = c_{an} - c_{\beta n} = \frac{\omega_c^2 t_c}{2} \left( 1 - \frac{2 \sin \frac{\varphi}{2} \sin \frac{\Phi}{2}}{\Phi \sin \frac{\varphi - \Phi}{2}} \right). \] (38)

As follows from Eq. (35), the terms \( d_{n-m}^{\alpha\beta} \) are proportional to \( \left( \frac{\omega}{\omega_c} \right)^2 \) and can be neglected in Eq. (36). Therefore the energy levels are given by

\[ E_{m,n}^{\pm(\alpha\beta)} = \frac{1}{2} \left\{ (m + n) \omega_c \pm \left[ (\omega_c - \Omega - (m - n) \omega_c + \Delta_3)^2 + b_{n-m}^2 \right]^{1/2} \right\}. \] (39)
The normalized energy $\frac{2E_{m,n}^{(\alpha,\beta)}}{\omega_c}$ is presented in Fig.3 as a function of $\frac{\Omega}{\omega_c}$ for $m - n = 0$.

The average probability [17] of the resonance transition is

$$\bar{P}_{\alpha \rightarrow \beta} = \frac{1}{2} \sum_{m,n} \frac{b_{m-n}^2}{(\omega_c - \Omega - (m - n)\omega_c + \Delta_3)^2 + b_{m-n}^2}. \tag{40}$$

The probability calculated according to Eq. (40) is presented in Fig.4 at $\phi = \frac{\pi}{2}$ as a function of $x = \frac{\Omega}{\omega_c}$ for the terms in the sum with $m - n = 0, \pm 1, \pm 2$.

Using (40) the expression for the nuclear magnetization $M$, is the quantity needed to compare with experiment, can be found:

$$\frac{M}{M_0} = 1 - \sum_{m,n} \frac{b_{m-n}^2}{(\omega_c - \Omega - (m - n)\omega_c + \Delta_3)^2 + b_{m-n}^2}. \tag{41}$$

Eqs. (40) and (41) coincide (by changing the summation index: $k = m - n$) with the equations obtained for the transition probability and the magnetization in the previous section (see Eqs. (23) and (24)). The magnetization calculated according to Eq. (41) is presented in Fig.5.

**Results and Discussion**

As follows clearly from the comparison of expressions (23), (24), (40), and (41), the calculations using both the semi-classical and Floquet methods give the identical results for the transition probability and nuclear magnetization. The results for the resonance conditions and for the shift $\Delta_3$ of the resonant frequency obtained within the framework of these methods are also identical. Moreover, the semi-classical approach allows one to obtain automatically the shift $\Delta_1$ under off-resonance conditions $\omega_0 \neq \omega (\Omega = 0)$ from RF excitation. However the interpretation of the multi-frequency resonance transitions for two-level energy system in the framework of the semi-classical approach involves difficulties.

The Floquet method gives clear physical description of observed phenomena. The time-independent Hamiltonian obtained using this method leads to the multi-level energy spectrum. Each of these levels corresponds to a stationary state of the system: spin dressed by photons. The coupling between photons and spin allows one to interpret the resonances as "anticrossing" of the levels [17,10].
Matching of the computed results for the nuclear magnetization with the experimental data displays series of essential differences. One of these differences consists in the fact that the observed NMR signal does not damp up to zero (Figs. 1 and 2), while the calculations predict zero magnetization at the resonant frequency (Eq.(41) and Fig.5). A possible reason of the observed finite value of $\frac{M}{M_0}$ is an inhomogeneity of the RF field in the bulk of the sample resulting in a distribution of angles $\varphi$ over the sample. To compare correctly the theoretical result for the nuclear magnetization with the experiment, we have to take into account the distribution of $\varphi$ over the real resonance line with nonzero line width averaging expression (41) over the line:

$$\langle \frac{M}{M_0} \rangle = \frac{1}{M_0} \int d\varpi M(\varpi)g(\varpi).$$

Let us consider the Lorentzian distribution of frequencies over a line having width $c$. It leads to the following distribution of angles $\varphi$

$$g(\varpi) = \frac{1}{\pi} \frac{c}{c^2 + \varpi^2},$$

where $\varpi = \varphi - \varphi_0$ and $\varphi_0 = \langle \varphi \rangle_V$ is an angle averaged over the sample. After the integration of (42) with the substitution of (43) we obtain

$$\langle \frac{M}{M_0} \rangle = 1 - \sum_n \frac{1 + a_n c}{a_n^2 \left(1 - x - \frac{2\pi n}{\varphi_0} + \frac{\Delta \omega}{\varphi_0}\right)^2 + (1 + a_n c)^2},$$

where

$$a_n = \frac{\varphi_0^4}{\left(\omega_0 t_c\right)^2 \sin^2 \frac{\varphi_0}{2}} \left(1 + \frac{2\pi n}{\varphi_0}\right)^2,$$

The average magnetization, calculated according Eq. (44) with $c = 0.018$, is presented in Fig.6 at $\varphi_0 = \frac{\pi}{2}$ as a function of $x = \left|\frac{\Omega}{\omega_c}\right|$ along with the experimental results. Using the relationship $c = \langle (\varphi - \varphi_0)/\varphi_0 \rangle$ the dispersion of angles can be estimated as $\langle (\varphi - \varphi_0) \rangle = 2.8274 \times 10^{-2}$ rad or 1.620. One can see the excellent agreement of the theoretical and experimental results.
The resonance transitions corresponding to negative frequencies $\Omega$ (see Fig. 5) can be interpreted as ones caused by the rotating in the opposite direction component of the linearly polarized LF field.

The multi-frequency resonances were observed in the experiments with other excitation schemes [10,19,25] and explained by multiphoton transitions between different states. Because the multiphoton transitions involves intermediate states and the transition probability decreases with number of photons [10,19,25], the intensity of the resonance signal diminishes quickly with number of the mode. A peculiarity of the excitation scheme proposed in the present paper is that, along with multiphoton transitions, there are direct transitions between dressed spin states with $(n - m) > 1$. Therefore, the transition probability is the same for all the differences $n - m$. As a result, the intensity of the resonance signal is slowly decreased with number of the mode (Figs. 1 and 2).

Conclusions

We have studied both experimentally and theoretically the dynamics of a spin system with the spin 3/2 under simultaneous influence of DC, multiple-pulse RF and LF fields. An important peculiarity of the applied excitation scheme is the possibility of the measurement of the effective field $H_e$ and observation of odd and even resonances with large mode numbers. It was shown that the intensity of the resonance lines decreases slowly.

Both used theoretical approaches, the semi-classical and the Floquet methods, give the identical results at the calculation of the resonant frequencies, magnetization amplitudes and shifts of resonance frequency. These results are in a good agreement with the experimental data for different angles and mode numbers equaled to $n = 0, \pm 1, \pm 2$. Some difference between the theoretical and experimental values of the signal intensity can be explained by the inhomogeneity of the RF field over the sample leading to the dispersion of the angle $\varphi$.

The proposed technique can be incorporated for the study of the slow atomic motion in systems involving spin-3/2 nuclei.

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Figure captions:

Fig. 1 Time dependence of relative magnetization $\frac{M}{M_0}$ in the absence of the LF field (open circle) and in the present of the LF field (solid circle) at $\varphi = \frac{\pi}{2}$ in hexamethylbenzene $C_6(CH_3)_6$.

Fig. 2 Dependence of relative magnetization $\frac{M}{M_0}$ on the LF field frequency $\Omega$ at $\varphi = \frac{\pi}{2}$ in hexamethylbenzene $C_6(CH_3)_6$.

Fig. 3 The normalized energy as a function of $x = \frac{\Omega}{\omega_e}$ for $m - n = 0$.

Fig. 4 The probabilities as functions of $x = \frac{\Omega}{\omega_e}$ for $\varphi = \frac{\pi}{2}$ and $m - n = 0, \pm 1, \pm 2$.

Fig. 5 Normalized magnetization $\frac{M}{M_0}$ as function of $x = |\Omega/\omega_e|$ calculated according Eq.(41) for $\varphi = \frac{\pi}{2}$ and $m - n = 0, \pm 1, \pm 2$.

Fig. 6 Dependence of averaged magnetization $\langle \frac{M}{M_0} \rangle$ of $x = |\Omega/\omega_e|$ at $\varphi_0 = \frac{\pi}{2}$ in hexamethylbenzene $C_6(CH_3)_6$: solid curve - theory (44), open circle - experiment.
The graph illustrates the function $M/M_0$ as a function of $x = |\Omega|/\omega_e$. The oscillatory behavior is evident with sharp drops at specific intervals along the $x$-axis.
