A TWO-FREQUENCY METHOD FOR CONTROLLING QUADRUPOLE RELAXATION

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Submitted October 9, 1969

Zh. Eksp. Teor. Fiz. 58, 1543–1548 (May, 1970)

A number of novel physical effects that appear on excitation of nuclear quadrupole energy levels at two frequencies are described. It is shown that by introducing a saturating power at the adjacent transition one can control spin-lattice relaxation. The method can be employed to determine the ratio of the relaxation probabilities and the magnitude of the radio-frequency field in a saturating pulse.

1. INTRODUCTION

IF the spin of a nucleus is a half-integer larger than 3/2, then several levels of nuclear quadrupole energy can arise in a crystal[1,2]. A study of quadrupole relaxation of such a many-level system is a complicated problem, since the time variation of the vector of nuclear magnetization is described by a sum of several exponentials[3,4]. The separation of these exponentials is possible only at very low temperatures.

One can attempt to eliminate this ambiguity by saturating one of the transitions with a strong radio frequency field, and observing the behavior of the difference in the populations of the levels at the neighboring transition. If we confine ourselves to the case of the spin 5/2, then two transitions are possible in the spectrum of nuclear quadrupole resonance: $\pm 1/2 \rightarrow 3/2(\nu_1)$ and $\pm 3/2 \rightarrow \pm 5/2(\nu_2)$. We can therefore consider two cases:

I. Saturation of the transition of the frequency ν_2 and observation of the population difference at the frequency ν_1.

II. Saturation of the transition at the frequency ν_1 and observation of the population difference at the frequency ν_2.

As shown below, these two cases differ from each other not only quantitatively but also qualitatively.

2. THEORY

Let us assume that the saturating radio frequency field in the case of spin 5/2 (three quadrupole energy levels), acts on the frequency ν_2. Then it is necessary to introduce into the kinetic equations[3] the probability P of transitions under the influence of the radio-frequency field.

In case I, the system of kinetic equations is written in the form

$$\begin{gathered}\dot{n}_1 - {}^1/_5 n_2(2W_1 - W_2) + {}^1/_{25}(8W_1 + 23W_2)n_1 - Pn_2 \\ = -{}^3/_{25}n_0(4W_1 - 11W_2),\end{gathered} \tag{1}$$

$$\dot{n}_2 + {}^1/_5 n_2(4W_1 + W_2) - {}^4/_{25}(W_1 + W_2)n_1 + 2Pn_2 = {}^6/_{25}n_0(6W_1 + W_2),$$

where $n_1 = N_{\pm 1/2} - N_{\pm 3/2}$, $n_2 = N_{\pm 3/2} - N_{\pm 5/2}$; $N_{\pm i}$ is the population of the level $\pm i$; W_1 is the probability of the single-quantum mechanism of quadrupole relaxation, W_Z is the probability of the two-quantum relaxation mechanism; $n_0 = (\hbar\omega_1/3kT)N$, and N is the total number of spins. The solution of the system of differential equations (1) is written in the form of a sum of two exponentials

$$\frac{n_1}{n_0} = C_1 e^{-x_1 t} - C_2 e^{-x_2 t} + \left(1 + \frac{2p\gamma}{A}\right), \tag{2a}$$

$$\frac{n_2}{n_0} = B_1 e^{-x_1 t} - B_2 e^{-x_2 t} + \left(2 - \frac{{}^4/_5 p(2 + 7\gamma)}{A}\right) \tag{2b}$$

where

$$C_{1,2} = \frac{2p}{x_1 - x_2}\left(\frac{\gamma x_{2,1}}{A} - 1\right), \quad B_{1,2} = \frac{4p}{x_1 - x_2}\left(-\frac{{}^1/_5(2 + 7\gamma)x_{2,1}}{A} + 1\right),$$

$$A = {}^1/_{25}(8 + 32\gamma + 9\gamma^2) + {}^2/_5 p(2 + 7\gamma),$$

$$x_{1,2} = {}^{14}/_{25}(1 + \gamma) + p \pm [{}^1/_{625}(76 - 88\gamma + 61\gamma^2) + {}^2/_{25}(8 - 7\gamma) + p^2]^{1/2},$$

$$p = P / W_1, \quad \gamma = W_2 / W_1.$$

The solution (2) has been obtained under initial conditions corresponding to a Boltzmann equilibrium. Thus, in separating the saturating radio-frequency field, both the quantities $x_{1,2}$ (the reciprocal spin-lattice relaxation times) and the coefficients of the exponentials will be functions of the probability p, which is proportional to the pump-generation power. This leads to a possibility of not only greatly decreasing the coefficient of one

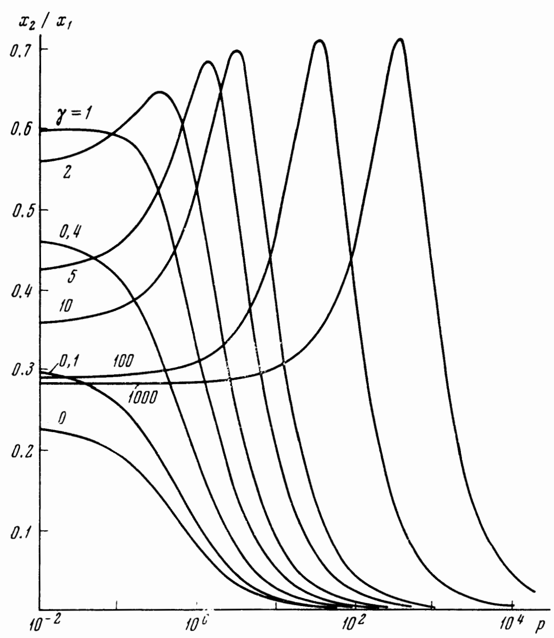

FIG. 1. Dependence of the ratio of the relaxation constants for the lower transition on the quantity $p = P/W_1$ for different $\gamma = W_2/W_1$. Saturation of the upper transition.

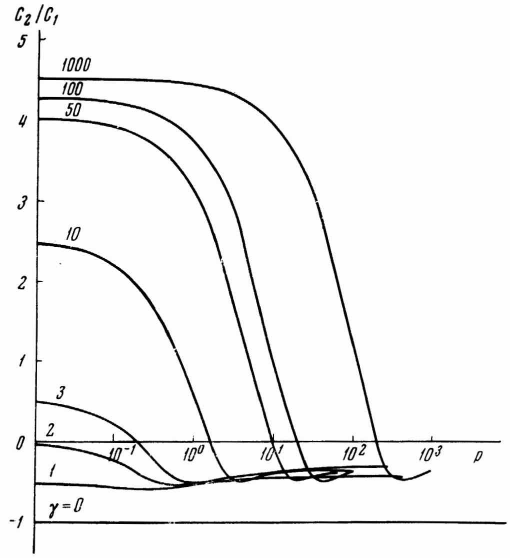

FIG. 2. Dependence of the ratio of the pre-exponential factors in the time dependence of the population difference of the lower transition on p = P/W_1 in the case of different γ. Saturation of the upper transition.

of the exponentials, but of radically altering the system relaxation behavior itself.

Figure 1 shows the dependence of the ratio of the relaxation constants of the system on the quantity p for different γ. It is seen from the figure that when $\gamma > 10$, considerable pump powers are necessary in order to control the relaxation behavior of the system. On the other hand, if $\gamma < 10$, then it is possible to detect changes in the relaxation time at powers that can be readily obtained in experiment.

Figure 2 shows the dependence of the ratio of the pre-exponential factors C_2/C_1 on p in the case of different γ. We see that for each γ, at a definite p, the coefficient C_2 vanishes, i.e., the relaxation is described by a single exponential. This, to be sure, can be realized only when $\gamma > 2$, since the condition for the vanishing of C_p is

$$p = {}^1/_5(\gamma - 2). \tag{3}$$

Analogously, for case II (saturation of the transition at the frequency ν_1) we obtain a system of kinetic equations in the form

$$\begin{aligned} \dot{n}_1 + {}^1/_{25}(8W_1 + 23W_2)n_1 + 2Pn_1 - {}^1/_5(2W_1 - W_2)n_2 \\ = -{}^3/_{25}n_0(4W_1 - 11W_2), \end{aligned} \tag{4}$$
$$\dot{n}_2 + {}^1/_5(4W_1 + W_2)n_2 - {}^4/_{25}(W_1 + W_2)n_1 - Pn_1 = {}^6/_{25}n_0(6W_1 + W_2).$$

The solution of the system (4) at Boltzmann initial conditions ($n_1(0) = n_0$, $n_2(0) = 2n_0$) are obtained in the form

$$\frac{n_1}{n_0} = C_1' e^{-x_1 t} - C_2' e^{-x_2 t} + \left(1 - \frac{p(\gamma + 2)}{D}\right), \tag{5a}$$

$$\frac{n_2}{n_0} = B_1' e^{-x_1 t} - B_2' e^{-x_2 t} + \left(2 + \frac{p\gamma}{D}\right), \tag{5b}$$

where

$$C_{1,2}' = \frac{p}{x_1 - x_2}\left(-\frac{(\gamma + 2)x_{2,1}}{D} + 2\right), \quad B_{1,2}' = \frac{p}{x_1 - x_2}\left(\frac{\gamma x_{2,1}}{D} - 1\right)$$

$$D = {}^1/_{25}(8 + 32\gamma + 9\gamma^2) + p(2 + \gamma),$$

$$x_{1,2} = {}^{14}/_{25}(1 + \gamma) + p \pm [{}^1/_{625}(76 - 88\gamma + 61\gamma^2) + {}^1/_{25}p(-2 + 13\gamma) + p^2]^{1/2}.$$

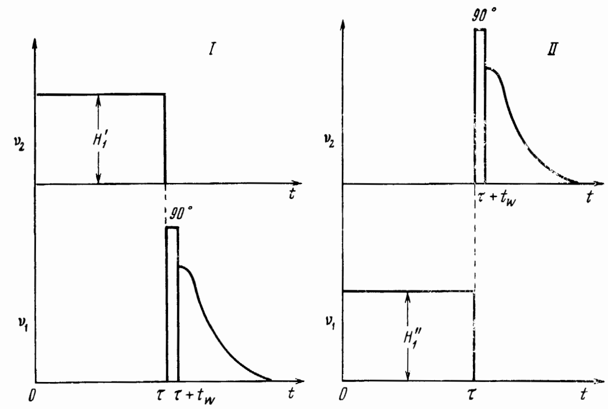

FIG. 3. I) Saturating pulse of amplitude H_1' and duration τ acts on the transition ±3/2 → ±5/2. Counting 90° pulse with carrier frequency ν_1 (transition ±1/2 → ±3/2). II) Saturating pulse of amplitude H_1'' and duration τ acts on the transition ±1/2 → ± 3/2 (ν_1). Counting 90° pulse with carrier frequency ν_2 (transition ±3/2 → 5/2).

Case II differs from case I primarily because it is no longer possible here to make the ratio of the pre-exponential factors equal to zero. The coefficient B_2' of the second exponential in (5b) can only be decreased appreciably compared with B_1'. On the other hand, the dependence of the relaxation time on the saturation power remains in force.

3. EXPERIMENT

To perform the experiments we used the programs shown in Fig. 3.

In case I, the saturating pulse of amplitude H_1' and duration τ acts on the transition ± 3/2 → ± 5/2 (carrier frequency ν_2). The trailing edge of this pulse is used to trigger the generator of a counting pulse with carrier frequency ν_1, after which an induction signal is observed. The receiver is tuned in this case to the frequency ν_1. Usually $\tau \gg t_W$ (t_W—duration of the RF pulse). The pulses act on a system of crossed coils, in which the investigated specimen is placed.

In case II, the saturating pulse of amplitude H_1'' and duration τ acts on the transition ± 1/2 → ± 5/2 (frequency ν_1). The counting 90° pulse acts at the frequency ν_2. During the course of the experiment, τ changes and t_W remains constant.

The object of the investigation was chosen to be an $SbCl_3$ crystal. Resonance of the nuclei Sb^{121} (I = 5/2) was observed at 77 and 292°K. The transition frequencies in this specimen at 292°K are ν_1 = 58.1 MHz and ν_2 = 112.5 MHz.

The amplitude of the saturating pulses changed by changing the anode voltage of the pump generator. It turned out simpler experimentally to obtain a larger pump power in case II (the saturating coil could be made with a large number of turns). Since the amplitude of nuclear induction following a 90° pulse[1)] is proportional to the difference of the populations between the levels,

1)We have in mind an initial amplitude of the induction signal (at t ≈ 0 with allowance for the insensitivity time of the receiver), which is proportional to the magnetization of the suitably "prepared" spin system at the given instant of time [5].

the proposed method makes it possible to follow directly the relaxation behavior of the system. The procedure for calculating the induction signals and the spin echo was described by us earlier[6].

Analogously we obtain for the program I

$$T_{\mathrm{I}} = T_{01}\left[1 + \frac{\omega_2}{\omega_1}\sin^2(a_1 H_1'\tau)\right] \cdot \sin\omega_1(t-\tau), \qquad (6)$$

where T_{01} is the initial amplitude of the induction at the frequency ν_1 in the absence of saturation at frequency ν_2,

$$a_1 = \frac{\gamma_0}{2}\sqrt{5}\left(1 + \frac{2}{9}\eta - \frac{8}{81}\eta^2\right)$$

γ_0 is the gyromagnetic ratio of the nucleus, η is the asymmetry parameter of the electric field gradient ($\eta \leq 0.3$). For the program II we have

$$T_{\mathrm{II}} = T_{02}\left[1 + \frac{\omega_1}{\omega_2}\sin^2(a_2 H_1''\tau)\right] \sin\omega_2(t-\tau), \qquad (7)$$

where T_{02} is the initial amplitude of the induction at the frequency ν_2 in the absence of saturation at the frequency ν_1;

$$a_2 = \frac{\gamma_0\sqrt{8}}{2}\left(1 + \frac{11}{18}\eta - \frac{329}{324}\eta^2\right).$$

Thus, when τ changes and H_1' is sufficiently strong it is possible to observe beats in the induction following a 90° pulse.

The results of the experiment are shown in Fig. 4. With increasing power of the saturating pulse in program I (Fig. 4a), the maximum of the induction becomes sharper and shifts towards the start of the sweep. This result also follows from Eq. (2a). With increasing power, the contribution of the second exponential decreases, and the equilibrium state is reached more rapidly. If we put $\gamma \sim 10$, then the experimental curves of Fig. 4a are well described by Eq. (2a). The saturating pulse acted in this case strictly at the resonant frequency.

Figure 4b shows the action of detuning of the saturating pulse. If the detuning is within the limits of the line width at the frequency ν_2, then its increase is equivalent to a lowering of the power. At larger detuning, the saturating pulse has no influence whatever.

Finally, inasmuch as in program II we were successful in obtaining large H_1'', Fig. 4c shows the beat occurring when the duration of the saturating pulse is varied. With increasing H_1'', the beat frequency increases in accordance with Eqs. (6). Observation of these beats makes it possible to estimate H_1'' in a saturating pulse. At a constant voltage U = 600 V on the generator tube, the beat period is 60 μsec, hence H_1'' = 11 Oe; at

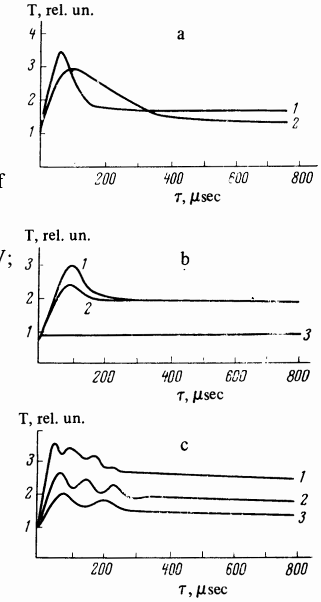

FIG. 4. Amplitude of induction of the nuclei Sb^{121} in $SbCl_3$ at 292°K: a—saturation of upper transition, $\Delta\nu$ = 0, curve 1—B = 700 V, 2—U = 500 V; b—saturation of upper transition, U = 600 V, curve 1— $\Delta\nu$ = 0, 2—$\Delta\nu$ = 3 kHz, 3—$\Delta\nu$ = 200 kHz; c—saturation of upper transition, induction from lower transition, curve 1—U = 600 V, 2—U = 500 V, 3—U = 400 V.

U = 400 V we have H_1'' = 4 Oe. On the other hand, the envelope of these beats is described by Eqs. (4), the validity of which follows from the fact that the values of the time T_1 in the investigated specimens exceed by one or two orders of magnitude the values of T_2.

We have thus shown that the two-frequency method makes it possible to control the quadrupole relaxation in a many-level system consisting of Kramer's doublets. It is possible in this case to determine the value $\gamma = W_2/W_1$ for different crystals, and also the amplitude of the radio-frequency field in a saturating pulse.

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Translated by J. G. Adashko
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