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Spin-Locking, Spin-Locked Echo and Rotary Saturation Associated
with a Two-Quantum Transition in a Multilevel NMR system

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We have observed a two-quantum analog of spin-locking and spin-locked echo, and single and multiple quantum rotary saturation in the two-quantum spin-locked state in a multilevel NMR system, ^{27}Al in Al_2O_3 .

In a series of papers we have reported the observation of several coherent phenomena associated with two-quantum (or two-photon) transition in a multi-level NMR system [1,2]. This paper is concerned with the study of a two-quantum analog of spin-locking [3] and spin-locked echo [4], and rotary saturation [5] in the two-quantum spin-locked state. The experiment was carried out on the same NMR system (at 77 K) as in the previous papers [1,2] i.e., ^{27}Al ($I=5/2$) nuclei in Al_2O_3 subjected to the static magnetic field H_0 parallel to the symmetry axis (z-axis) of the efg tensor, where energy level spacings are unequal and no level mixing exists. We used the two-quantum transition between levels a ($I_z = -3/2$) and c ($I_z = +1/2$).

The operation used to obtain two-quantum (TQ) spin-locking [6] is schematically shown in the lower part in Fig. 1 together with a relevant energy level diagram. An rf field $2H_1 \cos \frac{1}{2} \omega_3 t$ which is exactly at resonance for the TQ transition between levels a and c is applied at $t=0$ to the spin system in thermal equilibrium, and then its rf phase is suddenly shifted by 45° at $t = \pi / 2 \beta$, where β is the TQ nutation frequency $2 \gamma^2 H_1^2 \langle a | I_x^2 | c \rangle / \Delta \omega$ given by eq.(2) in ref.[2]. This method is a TQ analog of the well known 90° pulse – 90° phase shift technique [4] used to obtain a single quantum spin-locked state. Because of the characteristics of the TQ coherence [1,2], the amount of phase shift necessary for the spin-locking is 45° instead of 90° . The achievement of TQ spin-locking can easily be seen from eq.(1) in ref.[2], the rf field from $t=0$ to $t = \pi / 2 \beta$, which is a TQ 90° pulse,

creates the coherence $\nu(\text{ac})$ (we choose $\phi = 0$ at $t=0$), and the coherence is no longer changed by the rf field after the phase shift. In terms of the vector model, the effective field in a frame rotating at the frequency ω_3 around H_0 (TQ rotating frame) is made to be parallel to $\nu(\text{ac})$. A probe pulse (a 180° pulse with frequency ω_3) is used to detect the coherence $\nu(\text{ac})$ [7].

The experimental results are shown in Fig. 1. Open circles show the magnitude of $\nu(\text{ac})$ as a function of the length τ of the rf field after the phase shift, or the relaxation of the TQ spin-locked state. As in the case of the single quantum spin-locking, no oscillation appears and the relaxation time is considerably prolonged compared with the decay time of the TQ free decay. The relaxation was almost exponential for H_1 larger than about 20Oe. As H_1 was decreased, the relaxation deviated from the exponential type and the relaxation time became shorter. Closed circles show the relaxation of the single quantum spin-locked state for comparison, which were taken for the transition between levels a and b in the same sample and at the same temperature.

In connection with TQ spin-locking, we observed TQ spin-locked echoes by using the operation in Fig. 2. An artificial field inhomogeneity was introduced to H_0 . The echo is due to the phase memory along the effective field in the TQ rotating frame. The echo is observed by plotting the amplitude of the free induction decay signal at ω_1 as a function of the time τ' . The echo peak was at $\tau' = \tau_0$ and the

echo width was about one half of that of ordinary spin echo reflecting the nature of the TQ coherence reported previously [1].

We observed rotary saturation in the TQ spin-locked state. After the TQ spin-locking was achieved with an rf field $2H_1 \cos(\Omega t)$, where $\Omega \approx \frac{1}{2} \omega_3$, an af field $H_z \cos \omega_z t$ ($H_z \ll H_1$) was applied along the z-axis. The time development of the system is governed by the following Bloch-like equations

$$\begin{aligned}\dot{u}(ac) &= -2\delta v(ac) + 2\gamma H_z v(ac) \cos \omega_z t + \beta w(ac), \\ \dot{v}(ac) &= 2\delta u(ac) - 2\gamma H_z u(ac) \cos \omega_z t, \\ \dot{w}(ac) &= -\beta u(ac),\end{aligned}\tag{1}$$

where $\delta = \Omega - \frac{1}{2} \omega_3$ ($|\delta| \ll \beta$) is the amount of TQ off resonance. In the derivation of eq.(1), a three-level system consisting of the levels a, b and c is assumed and the small level shift terms are neglected.

Essentially the same equations are obtained even when the effects of all six levels in the system are taken into account. In this case the level shift terms vanish because of the special feature of the present NMR system. Equation (1) involves the feasibility of the rotary saturation when $\omega_z \approx \beta$, which can easily be seen in a manner similar to the case of ordinary rotary saturation.

Figure 3 shows the experimental results in the case of TQ exact resonance ($\delta = 0$) together with the operation. The af field was applied not suddenly but in a time of about 1 ms in order to avoid the destruction of the spin-locked state caused by the Fourier components produced by sudden switching. The dip centered at 20kHz shows the

rotary saturation mentioned above. The frequency at which the dip appears is in good agreement with the TQ nutation frequency β for $H_1=26\text{Oe}$. The small dip at about $\beta/2$ is due to double-quantum rotary saturation (DQRS) in the TQ spin-locked state. The analysis based on a perturbation calculation (the details of which will be published later) shows that the DQRS in the TQ spin-locked state can only be expected in the case of TQ off resonance ($\delta \neq 0$), which may be qualitatively understood from angular momentum conservation. Actually in the case of slightly TQ off resonance ($\delta \neq 0$, $|\delta| < \beta$) the dip at the lower frequency side was greatly enhanced relative to the main dip for the same values of H_z and τ as in Fig. 4(A). The appearance of the dip due to DQRS in Fig. 3 ($\delta = 0$) is considered to be the result of the relatively large linewidth (about 12kHz) of the TQ transition concerned. The increase of H_z or τ caused further enhancement of the dip due to DQRS and, in addition, the appearance of the dip due to triple-quantum rotary saturation near $\beta/3$ as in Fig. 4(B). It was carefully checked that the dips near $\beta/2$ and $\beta/3$ were not due to the harmonics in the applied rf field. Multiple quantum rotary saturation in the single quantum spin-locked state was already observed in NMR [8] and recently in quantum optics [9].

We examined the shift of the DQRS in the TQ spin-locked state due to H_z . Our theory shows that the shift is towards the higher frequency side and the shift from $\beta/2$ is given by $2\beta^2\gamma^2H_z^2/3\{\beta^2+4\delta^2\}^{3/2}$ depending of H_z^2 . The observed shift as a function of H_z is shown in Fig. 5. The experiment is in good agreement with the theory

within experimental error. Similar shift is also expected for the main dip. However, the theory predicts that the shift is much smaller than that of DQRS. We observed a shift of about 0.5kHz for $H_z=6\text{Oe}$ consistent with the theory.

We also performed an experiment on the TQ analog of adiabatic demagnetization in the rotating frame. The detailed study is now under way.

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Figure Captions

Fig. 1. Open circles show prolonged relaxation of TQ spin-locked state obtained by the operation below. The relaxation time is much longer (about 30 ms for $H_1=26\text{Oe}$ or $\beta=2\pi\times 20\text{kHz}$) than that of TQ free decay ($\approx 30\mu\text{s}$). We used a sample whose T_1 was artificially shorten by the impurities Cr^{3+} (0.01%) to reduce the repetition period of the experiment. T_1 between levels a and b was about 4.3s. Closed circles show the relaxation of the single quantum spin-locked state. $\omega_1/2\pi=10.00\text{MHz}$, $\omega_2/2\pi=9.64\text{MHz}$ and $\frac{1}{2}\omega_3/2\pi=9.82\text{MHz}$.

Fig. 2. Experimental operation used to obtain TQ spin-locked echoes.

Fig. 3. Rotary saturation in the TQ spin-locked state in the case of TQ exact resonance ($\delta=0$), $H_z=2\text{Oe}$ ($\beta/2\pi=20\text{kHz}$) and $\tau=6\text{ms}$.

Fig. 4. Rotary saturation in the TQ spin-locked state in the case of TQ off resonance ($\delta/2\pi=3.7\text{kHz}$ and $H_z=2\text{Oe}$). Dips at about 11 kHz and 7 kHz represent the double and triple-quantum rotary saturation in the TQ spin-locked state, respectively. $\tau=6\text{ms}$ for (A), and 18ms for (B).

Fig. 5. Shift of double-quantum rotary saturation in TQ spin-locked state. The shift is towards the higher frequency side. Solid curve is theoretical. $\beta/2\pi=20\text{kHz}$, $\delta/2\pi\approx 1\text{kHz}$.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5