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# COMMUNICATIONS

# New Line-Narrowing Effect in Triple-Quantum Resonance in a Two-Level NMR System

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**We report a new line-narrowing effect associated with triple-quantum resonance in a two-level NMR system. The experiment was carried out in the rotating frame on $^{19}$F nuclei in Teflon; namely, the magnetization is spin-locked along the RF field and the triple-quantum resonance is induced by the oscillating field perpendicular to the RF field. We observed that the decay time of the triple-quantum nutation becomes extraordinarily long at a particular intensity and frequency of the oscillating field. The decay time is about seven times as long as that of the single-quantum nutation and also much longer than that of the magic angle nutation. The mechanism is not interpreted by straightforward analogy to the theory of the current magic angle narrowing.** 

*Key Words*: **multiple-quantum NMR; line narrowing; double resonance; magic angle nutation; $^{19}$F resonance in Teflon.**

Various novel effects have been observed in the field of multiple-quantum NMR (*1*). In this paper, we report for the first time, to our knowledge, a new line-narrowing effect in the triple-quantum (TQ) resonance in a two-level NMR system. The experiment was carried out on $^{19}$F nuclei in Teflon in the rotating frame; namely, the magnetization is first aligned along the resonant RF field with intensity $\omega_1/\gamma$ ($\gamma$; gyromagnetic ratio) by a standard spin-locking technique (*2*) and the TQ resonance in the rotating frame is induced by a low-frequency (LF) oscillating field perpendicular to the RF field. Experimentally, the LF field is effectively produced by a phase modulation (PM) of the RF field. As is well known a sinusoidal PM at an angular frequency $\omega_2$ with modulation index $2\phi_{\mathrm{m}}$ produces a virtual oscillating magnetic field at $\omega_2$ with amplitude $2\phi_{\mathrm{m}}\omega_2/\gamma$ perpendicular to the RF field in the phase-modulated rotating frame.

What we observed is as follows. When $\omega_2/2\pi = 26.45$ kHz (which is slightly higher than the TQ resonance frequency $\frac{1}{3}\omega_1/2\pi$) and $2\phi_{\mathrm{m}} = 0.764\pi$ rad ($\phi_{\mathrm{m}}\omega_2$ is not so small compared to $\omega_1$), the decay of the TQ transient nutation becomes extraordinarily long as shown by the dotted curve in Fig. 1. The line narrowing is most remarkable at these values of $\phi_{\mathrm{m}}$ and $\omega_2$. The solid line in Fig. 1 is a single-quantum (SQ) nutation signal obtained when $\omega_2/2\pi = 66$ kHz ($\cong\omega_1/2\pi$), and the dashed line is a spin–lattice relaxation curve in the rotating frame observed with the same RF intensity. The decay time of the TQ nutation ($\cong$1.8 ms) is about seven times as long as that of the SQ nutation ($\cong$260 $\mu$s), and is compared with the spin–lattice relaxation time in the rotating frame ($\cong$6.5 ms). It is noteworthy that the decay time of the TQ nutation is also much longer than that of the magic angle rotary echo envelope observed in Teflon (*3*).

As will be shown below, the long decay results from the disappearance of the secular dipole Hamiltonian in the TQ resonance and also the considerable decrease of the effects of the nonsecular part. This effect is not interpreted by straightforward analogy to that of the current magic angle nutation (*4, 5*).

We consider like spins $I$ $(=\Sigma I_j)$ which are spin-locked by the exactly resonant RF field at the angular frequency $\omega_0$ and affected by the magnetic dipole interaction described by the Hamiltonian $\hbar\mathscr{H}_{\mathrm{d}}^{(0)} = \Sigma D_{jk}(3I_{jz}I_{kz} - I_j I_k)$, where $D_{jk}$ is a geometrical factor of a well-known form (*6*). The total Hamiltonians $\mathscr{H}_j(t)$ ($j = 0 \sim 7$) and a series of unitary transformations necessary for the explanation are shown in Table 1. The magnitude $\phi_{\mathrm{m}}\omega_2$ is not sufficiently weak compared to $\omega_1$. We first transform the Hamiltonian $\mathscr{H}_0(t)$ to $\mathscr{H}_2(t)$ in the phase-modulated and tilted rotating frame with the unitary operators $U_1$ and $U_2$. For the TQ resonance in the two-level system to occur, the existence of the counterrotating field contained in the LF field is necessary (*7*) because of the angular momentum conservation. The counterrotating field also induces level shifts; the resonance frequency increases as $\phi_{\mathrm{m}}\omega_2$ increases (*7, 8*). In order to take into account the contribution of the counterrotating field, we transform the Hamiltonian $\mathscr{H}_2(t)$ to that in the reference frame rotating at $\omega_2$ around the RF field in the reverse sense to the nuclear precession (*9, 10*). Then, the transformed Hamiltonian $\mathscr{H}_3(t)$ is furthermore transformed to $\mathscr{H}_5(t)$ in the reference frame rotating at $2\omega_2$ in



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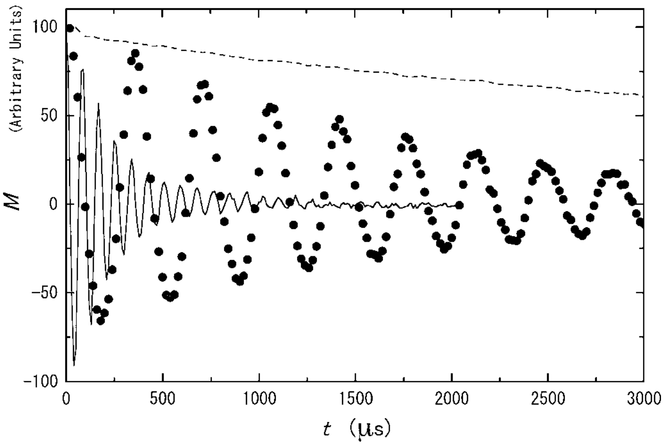


**FIG. 1.** TQ nutation signal almost at $K = 0$ (dots). The experimental condition is that $\omega_2/2\pi = \omega_{20}/2\pi = 26.45$ kHz, $2\phi_m = 0.764\pi$ rad, $\omega_1/2\pi = 65$ kHz, and $\omega_0/2\pi = 27$ MHz. The solid line shows the SQ nutation signal observed at $\omega_2/2\pi = 66$ kHz and with $2\phi_m = 0.0940\pi$ rad, where the difference $(\omega_2 - \omega_1)/2\pi = 1$ kHz corresponds to a Bloch–Siegert shift (*8*). The dashed line is the decay curve of the magnetization spin-locked by the RF field without the PM, showing a spin–lattice relaxation in the rotating frame. All curves are obtained by plotting the intensity of the free induction decay signal just after the spin-locking RF pulse as a function of the duration $t$ of the PM (dotted and solid lines) or of the RF pulse (dashed line).

the same sense to the nuclear precession around the resultant effective field $\omega_e/\gamma = [(\omega_1 + \omega_2)^2 + (\phi_m\omega_2)^2]^{1/2}/\gamma$, where the effective field $\omega_e/\gamma$ is at an angle $\theta = \arccos[(\omega_1+\omega_2)/\omega_e]$ with the RF field. In the reference frame rotating simultaneously at $\omega_2$ and $2\omega_2$, there exists a field of the amplitude $\phi_m\omega_2 \sin\theta/\gamma$ oscillating at $2\omega_2$ along the effective field $\omega_e/\gamma$ together with the static field $\omega_e^*/\gamma = \{(\omega_e - 2\omega_2)^2 + [\frac{1}{2}\phi_m\omega_2(1 + \cos\theta)]^2\}^{1/2}/\gamma$, which is at an angle $\alpha = \arccos[(\omega_e - 2\omega_2)/\omega_e^*]$ with the effective field $\omega_e/\gamma$.

The TQ resonance is induced by the component of this oscillating field perpendicular to the static field $\omega_e^*/\gamma$ in this rotating frame, when $2\omega_2 \cong \omega_e^*$ (see $\mathcal{H}_6$). We limit ourselves to the case

$$\omega_2 = \frac{1}{2}\omega_e^*. \qquad [1]$$

The frequency $\omega_2$ that satisfies Eq. [1] is the exact TQ resonance frequency including level shifts, which is denoted by $\omega_{20}$ hereafter. Although the explicit expression of $\omega_{20}$ is complicated because $\omega_e^*$ is a function of $\omega_2$, Eq. [1] shows that for $\phi_m = 0, \omega_{20} = \frac{1}{3}\omega_1$, and for $\phi_m \neq 0, \omega_{20} > \frac{1}{3}\omega_1$, and $\omega_{20}$ increases as $\phi_m\omega_2$ increases. The amplitude of the resonant component $(\phi_m\omega_2 \sin\theta \sin\alpha)/\gamma$ in $\mathcal{H}_6(t)$ is so small that its counterrotating field can be neglected. The TQ nutation at $\omega_2 = \omega_{20}$ is described by the Hamiltonian $\mathcal{H}_7$, neglecting the time-dependent part of $\mathcal{H}_d^{(7)}(t)$. The time-independent part of $\mathcal{H}_d^{(7)}(t)$ is denoted by $\bar{\mathcal{H}}_d$. The TQ nutation decay is predominantly governed by the secular part $\mathcal{H}_d^\dagger$ which is the part of $\bar{\mathcal{H}}_d$ that commutes with $I_x$. The explicit expression of $\mathcal{H}_d^\dagger$ is

$$\mathcal{H}_d^\dagger = \sum_{j,k} D_{jk}\sqrt{6} \sum_{\ell=-2,}^{2} \sum_{m=-2,}^{2} \sum_{n=-2,}^{2} \sum_{s=-2}^{2} T_{2s}^{(jk)} d_{s0}^2\left(\frac{\pi}{2}\right) d_{0n}^2\left(-\frac{\pi}{2}\right)$$
$$(\ell-2m-2n=0)$$
$$\times\, d_{nm}^2(-\alpha) d_{m\ell}^2(-\theta) d_{\ell 0}^2\left(-\frac{\pi}{2}\right)$$
$$= K\sum_{j,k} D_{jk}(3I_{jx}I_{kx} - I_j I_k), \qquad [2]$$

**TABLE 1**
**Total Hamiltonians and the Transformation Process**

$\mathcal{H}_0(t) = -\omega_1 e^{2i\phi_m I_z \sin\omega_2 t} I_x e^{-2i\phi_m I_z \sin\omega_2 t} + \mathcal{H}_d^{(0)}$ (The $x$ axis is along the RF field.),
$U_1 = e^{-2i\phi_m I_z \sin\omega_2 t}$,
$\mathcal{H}_1(t) = -\omega_1 I_x + 2\phi_m\omega_2 I_z \cos\omega_2 t + \mathcal{H}_d^{(1)}$,
$U_2 = e^{i\frac{\pi}{2}I_y}$,
$\mathcal{H}_2(t) = -\omega_1 I_z - 2\phi_m\omega_2 I_x \cos\omega_2 t + \mathcal{H}_d^{(2)}$,
$U_3 = e^{i\omega_2 I_z t}$,
$\mathcal{H}_3(t) = -(\omega_1 + \omega_2)I_z - \phi_m\omega_2 I_x - \phi_m\omega_2 I_x \cos 2\omega_2 t + \phi_m\omega_2 I_y \sin 2\omega_2 t + \mathcal{H}_d^{(3)}(t)$,
$U_4 = e^{i\theta I_y}$,
$\mathcal{H}_4(t) = -\omega_e I_z - \phi_m\omega_2 I_x \cos\theta \cos 2\omega_2 t - \phi_m\omega_2 I_z \sin\theta \cos 2\omega_2 t + \phi_m\omega_2 I_y \sin 2\omega_2 t + \mathcal{H}_d^{(4)}(t)$,
$U_5 = e^{-2i\omega_2 I_z t}$,
$\mathcal{H}_5(t) = -(\omega_e - 2\omega_2)I_z - \frac{1}{2}\phi_m\omega_2(1 + \cos\theta)I_x - \phi_m\omega_2 I_z \sin\theta \cos 2\omega_2 t$
$\quad - \frac{1}{2}\phi_m\omega_2(\cos\theta - 1)e^{-4i\omega_2 I_z t} I_x e^{4i\omega_2 I_z t} + \mathcal{H}_d^{(5)}(t)$ (the fourth term neglected),
$U_6 = e^{i\alpha I_y}$,
$\mathcal{H}_6(t) = -\omega_e^* I_z + \phi_m\omega_2 I_x \sin\theta \sin\alpha \cos 2\omega_2 t$
$\quad - \phi_m\omega_2 I_z \sin\theta \cos\alpha \cos 2\omega_2 t + \mathcal{H}_d^{(6)}(t)$ (the third term neglected),
$U_7 = e^{-2i\omega_2 I_z t}$,
$\mathcal{H}_7(t) = \frac{1}{2}\phi_m\omega_2 \sin\theta \sin\alpha I_x + \mathcal{H}_d^{(7)}(t)$.

*Note*. Hamiltonians $\mathcal{H}_j(t)$ ($j = 0 \sim 7$) are expressed in units of $\hbar$. Explicit forms of the dipole Hamiltonians $\mathcal{H}_d^{(j)}(t)$ are given in Table 2.

**TABLE 2**
**Dipole Hamiltonians**

$$\hbar\mathcal{H}_{\mathrm{d}}^{(p)}=\sum_{j,k}D_{jk}H_{p}^{(jk)}\quad(p=1\sim 7),$$
$$H_1^{(jk)}=3I_{jz}I_{kz}-I_jI_k=\sqrt{6}T_{20}^{(jk)}$$
$$H_2^{(jk)}=\sqrt{6}\sum_{\ell=-2}^{2}T_{2\ell}^{(jk)}d_{\ell 0}^{2}(-\tfrac{\pi}{2}),$$
$$H_3^{(jk)}(t)=\sqrt{6}\sum_{\ell=-2}^{2}T_{2\ell}^{(jk)}d_{\ell 0}^{2}(-\tfrac{\pi}{2})e^{i\ell\omega_2 t},$$
$$H_4^{(jk)}(t)=\sqrt{6}\sum_{\ell=-2,}^{2}\sum_{m=-2}^{2}T_{2m}^{(jk)}d_{m\ell}^{2}(-\theta)d_{\ell 0}^{2}(-\tfrac{\pi}{2})e^{i\ell\omega_2 t},$$
$$H_5^{(jk)}(t)=\sqrt{6}\sum_{\ell=-2,}^{2}\sum_{m=-2}^{2}T_{2m}^{(jk)}d_{m\ell}^{2}(-\theta)d_{\ell 0}^{2}(-\tfrac{\pi}{2})e^{i(\ell-2m)\omega_2 t},$$
$$H_6^{(jk)}(t)=\sqrt{6}\sum_{\ell=-2,}^{2}\sum_{m=-2,}^{2}\sum_{n=-2}^{2}T_{2n}^{(jk)}d_{nm}^{2}(-\alpha)d_{m\ell}^{2}(-\theta)d_{\ell 0}^{2}(-\tfrac{\pi}{2})e^{i(\ell-2m)\omega_2 t},$$
$$H_7^{(jk)}(t)=\sqrt{6}\sum_{\ell=-2,}^{2}\sum_{m=-2,}^{2}\sum_{n=-2}^{2}T_{2n}^{(jk)}d_{nm}^{2}(-\alpha)d_{m\ell}^{2}(-\theta)d_{\ell 0}^{2}(-\tfrac{\pi}{2})e^{i(\ell-2m-2n)\omega_2 t},$$
$$\hbar\bar{\mathcal{H}}_{\mathrm{d}}=\sum_{j,k}D_{jk}\sqrt{6}\sum_{\substack{\ell=-2,\; m=-2,\; n=-2\\(\ell-2m-2n=0)}}^{2}\sum^{2}\sum^{2}T_{2n}^{(jk)}d_{nm}^{2}(-\alpha)d_{m\ell}^{2}(-\theta)d_{\ell 0}^{2}(-\tfrac{\pi}{2}).$$

*Note*. Definitions of $T_{2m}^{(jk)}$ and $d_{nm}^{2}(\alpha)$ are given in Ref. (*11*).

with

$$K=\frac{1}{16}(3\cos^2\alpha-1)(3\cos^2\theta-1)-\frac{3}{64}\sin 2\alpha(3\sin 2\theta+2\sin\theta)+\frac{3}{32}\sin\alpha(\sin 2\theta-2\sin\theta)-\frac{3}{32}(1-\cos\alpha)^2\sin^2\theta. \qquad [3]$$

Numerical evaluations of $K$ as a function of $\phi_{\mathrm{m}}\omega_2$ ($\omega_{20}$ is also a function of $\phi_{\mathrm{m}}\omega_2$) indicate that $K$ becomes 0 at $\cos\theta\cong 0.9476$ and $\cos\alpha\cong 0.8236$ independent of $\omega_1$. The value of $\omega_{20}$ for $K=0$ depends on $\omega_1$, and for $\omega_1/2\pi=65$ kHz, $\omega_{20}/2\pi$ becomes $\cong$26.46 kHz at $K=0$. Since the angles $\theta$ and $\alpha$ for $K\cong 0$ are not large, the TQ nutation can be fully observed through an oscillation of the magnetization $M$ along the RF field.

In the experiment, we searched TQ resonance including level shifts by varying $\omega_2$ and $\phi_{\mathrm{m}}$. The longest decay time was observed at $\omega_2/2\pi=26.45$ kHz and $2\phi_{\mathrm{m}}=0.764\pi$ rad as shown by the dotted curve in Fig. 1. The corresponding values of $\theta$ and $\alpha$ are almost equal to the theoretical values for $K=0$. The TQ nutation frequency $(\frac{1}{2}\phi_{\mathrm{m}}\omega_2\sin\theta\sin\alpha)/2\pi$ (2.99 kHz) calculated with the values of $\omega_2$ and $\phi_{\mathrm{m}}$ is in good agreement with the oscillation frequency (2.83 kHz) estimated from the dotted curve. Thus, the TQ nutation in Fig. 1 represents the behavior at the exact TQ resonance including level shifts almost at $K=0$.

As $\omega_{20}$ deviates from the value for $K=0$ the nutation decay time (at $\omega_2=\omega_{20}$) decreases as shown by the dots in Fig. 2, where an exponential decay ($e^{-t/T}$) is assumed. The solid line shows the theoretical dependence of the value of $|K|$ on $\omega_{20}$. The experimental result in Fig. 2 indicates that the decay is due mainly to the dipole interaction represented by Eq. [2]. The result that the decay time $T$ around $\omega_{20}/2\pi=26.46$ kHz is not as long as is expected from the theoretical curve may be due to the influences of the dipole interaction represented by the nonsecular part $\mathcal{H}_{\mathrm{d}}^{\ddagger}=\bar{\mathcal{H}}_{\mathrm{d}}-\mathcal{H}_{\mathrm{d}}^{\dagger}$ (*3*) and the spin–lattice relaxation in the rotating frame. (The effect of the inhomogeneity in $\phi_{\mathrm{m}}\omega_2$ can be neglected because a sample whose volume was about 1/80 of that of the sample coil was used.) The fact that the decay time near $K=0$ is much longer than that of the current magic angle nutation (*3*) may be explained by comparing the explicit forms of $\mathcal{H}_{\mathrm{d}}^{\ddagger}$ and the corresponding dipole Hamiltonian in the magic angle nutation. In both cases the nonsecular dipole Hamiltonians consist of two terms written as $A\Sigma D_{jk}(I_{jy}I_{ky}-I_{jz}I_{kz})$ and $B\Sigma D_{jk}(I_{jx}I_{kz}+I_{jz}I_{kx})$. The values of $|A|$ and $|B|$ in $\mathcal{H}_{\mathrm{d}}^{\ddagger}$, which are complicated functions of $\theta$ and $\alpha$, become $\cong 2.4\times 10^{-3}$ and $\cong$0.23 at $K=0$, respectively. On the other hand, the corresponding values in the magic angle nutation are 1 and $\sqrt{2}$, respectively.

A similar numerical calculation shows that line narrowing of this type can also be expected slightly at TQ off resonance.

The narrowing effect of this type may be useful for high-resolution NMR in solids and may occur for other multiple-quantum resonance. The details will be published later.

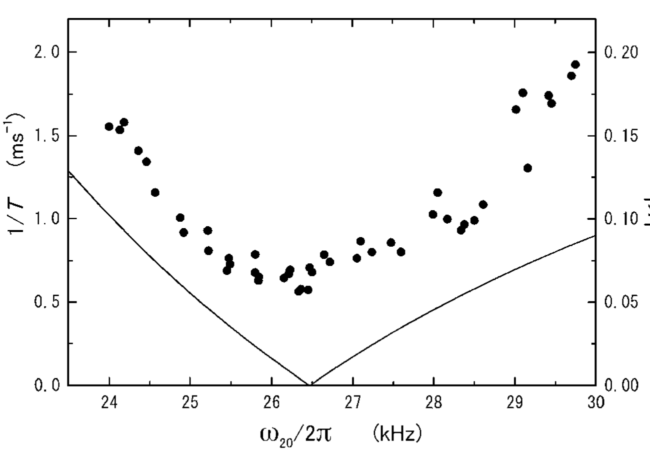


**FIG. 2.** Dependence of the experimental decay rate of the TQ nutation $T^{-1}$ (dots) and that of the theoretical value $|K|$ (solid line) on $\omega_{20}$. The decay rate $T^{-1}$ is measured by assuming an exponential decay.

## REFERENCES


1. See, for example, G. Bodenhausen, Multiple-quantum NMR, *Prog. Nucl. Magn. Reson. Spectrosc*. **14,** 137–173 (1981).
2. I. Solomon, Étude de la relaxation en résonance magnétique par la méthode de précession forcée transitoire, *Acad. Sci*. **248,** 92–94 (1959).
3. H. Kessemeier and W. Rhim, NMR line narrowing by means of rotary spin echoes, *Phys. Rev. B* **5,** 761–768 (1972).
4. W. I. Goldburg and M. Lee, Nuclear magnetic resonance line narrowing by a rotating rf field, *Phys. Rev. Lett*. **11,** 255–258 (1963).

*5*. M. Lee and W. I. Goldburg, Nuclear-magnetic-resonance line narrowing by a rotating rf field, *Phys. Rev. A* **140,** 1261–1271 (1965).

*6*. See, for example, C. P. Slichter, “Principles of Magnetic Resonance,” Springer-Verlag, Berlin/New York (1990).

*7*. J. Margerie and J. Brossel, Transitions à plusieurs quanta électromagnétiques, *Acad. Sci*. **241,** 373–375 (1955).

*8*. F. Bloch and A. Siegert, Magnetic resonance for nonrotating fields, *Phys. Rev*. **57,** 522–527 (1940).

*9*. A. Abragam, “The Principles of Nuclear Magnetism,” Oxford Univ. Press, Oxford (1961).

*10*. N. Tabuchi and H. Hatanaka, Rotating frame analog of spin-locking and spin–lattice relaxation in the doubly rotating frame, *J. Magn. Reson*. **148,** 121–125 (2001), doi:10.1006/jmre.2000.2217.

*11*. M. Mehring, “High Resolution NMR Spectroscopy in Solids,” Springer-Verlag, Berlin/New York (1976).