JOURNAL OF MAGNETIC RESONANCE, Series A 103, 171–174 (1993)

78

Reduction and Suppression of the Nuclear Quadrupole Interaction in Solids by NMR Strong Nutation Spectroscopy

DONGHUI WU* AND B. C. SANCTUARY†

*Wuhan Institute of Physics, The Chinese Academy of Sciences, P.O. Box 71010, 430071, Wuhan, Hubei, People's Republic of China; and †Department of Chemistry, McGill University, 801 Sherbrooke Street West, Montreal, Canada H3A 2K6

Received June 19, 1992; revised October 9, 1992

It is shown theoretically and experimentally that the magnitude of the quadrupole-coupling constant can be changed by varying the resonance offset frequency in nutation spectroscopy. In particular, while the RF pulse is being applied at resonance, the effective quadrupole changes sign and is reduced by a factor of 2. When the offset is applied at the value $\Delta\omega/\omega_1 = 1/\sqrt{2}$, the effective quadrupole is 0. Good agreement is found between theory and experiment.

INTRODUCTION

One of the major problems in the NMR studies of solids containing spins of greater than $\frac{1}{2}$ is the broadening of the lines by the electric nuclear quadrupole interaction. The usual method used to narrow these lines is sample rotation techniques (MAS). Pulse sequences have not been widely used although calculations have shown that the WAHUHA sequence also works for quadrupole systems (*1*).

In this paper, it is shown that the quadrupole-coupling constant, ω_q, is modified during the time that an RF pulse is being applied (*2*). This is a type of nutation experiment, but the nutation pulse is strong. That is, the RF amplitude $|\omega_1|$ is greater than the quadrupole-coupling strength $|\omega_q|$. This is in contrast to the common nutation experiments where the pulses are usually weak (*3*). Although more physical systems fit into the criterion of the usual weak nutation experiment, the emphasis here is on the ability to modify the quadrupole-coupling strength by applying an RF field at various off-resonance values.

Under many different conditions, it is possible to vary the effective quadrupole-coupling strength. The examples chosen here are the cases where the strong nutation pulse varies from on resonance, $\Delta\omega = 0$, to $\Delta\omega/\omega_1 = 1/\sqrt{2}$. Under these conditions, the effective quadrupole varies from $(-\frac{1}{2})$ its value, to 0. Applied to dipole–dipole interactions, Lee and Goldburg have found similar effects for spin-$\frac{1}{2}$ systems (*4–6*). The Lee–Goldburg results focus on line narrowing in solids, ideas taken up in the WAHUHA experiment (*5*).

Although we confirm the results only for $I = 1$, for the cases described in the above paragraph, many other results of modifying the quadrupole-coupling constant by varying the effective field direction occur. Since these effects result from modifying the path of precession, they appear to be manifestations of the geometric phase (*7*) [Berry's phase (*8*) in the adiabatic limit]. Consequently, this effect is not limited to the quadrupole interaction alone. Apart from the dipole–dipole interaction in Lee–Goldburg-type experiments, selective excitations cause the RF amplitude to be modified by a geometric factor giving (*9, 10*)

$$\omega_{1,\text{eff}} = \sqrt{(I+M)(I-M+1)}\,\omega_1. \qquad [1]$$

For a spin-$\frac{3}{2}$ system, a selective excitation from the $+\frac{1}{2}$ level to the $-\frac{1}{2}$ level has an effective RF amplitude of $2\omega_1$. These effects have been observed often and are manifested in nutation spectroscopy both theoretically (*11*) and experimentally (*3*).

What is less well known (*2*) is that, for selective excitation between a pair of adjacent levels, a system has an effective quadrupole constant of 0 (when nonsecular terms are dropped). This is because such two-level systems act as a fictitious spin-$\frac{1}{2}$ and, as such, have no quadrupole. In the same level of approximation, for double-quantum selective excitation, we find

$$\omega_q^{\text{eff}} = \frac{2\omega_q}{I(2I-1)}, \qquad [2]$$

and for triple-quantum selective excitation,

$$\omega_q^{\text{eff}} = \frac{75}{16I(2I-1)}\,\omega_q, \qquad [3]$$

where ω_q is the quadrupole-coupling constant. For nonselective pulses, the modification of the quadrupole-coupling constant is similar (*2*). In this case, the pulse is soft enough that nuclear quadrupole nutation can take place. The application of an RF pulse changes the magnetic field from the z axis to the effective magnetic field direction. When an ax-

1064-1858/93 $5.00

ially symmetric quadrupole interaction for a spin 1 is transformed to this effective (tilted) field direction, the axially symmetric quadrupole tensor is modified and has nonaxial terms. At the same time, the axial component is dressed with a term, a reduced Wigner rotation matrix element $d^2_{00}(\theta)$, that is responsible for the transformation to give

$$\omega_q^{\text{eff}} = d^2_{00}(\theta)\omega_q = -\frac{1}{2}\left[\frac{1 - 2\Delta\omega^2/\omega_1^2}{1 + \Delta\omega^2/\omega_1^2}\right]\omega_q. \quad [4]$$

The nonaxial terms all oscillate with other nutation frequencies, but the intensities of these are small for strong nutation pulses and dropped in a perturbation treatment (*2*). Hence the final result is a quadrupole interaction for which the quadrupole-coupling constant is replaced by the effective value given in Eq. [4]. This is valid for all spin magnitudes and is manifested in spin dynamics as well as relaxation or line-narrowing experiments (*4–6*).

In order to test these predictions, experiments have been performed on a fully deuterated sample of 1,4-dimethoxybenzene, and the spin-1 of the deuterium has been studied. The results confirm that the calculations are correct.

THEORY

In this treatment, relaxation is not included. During the nutation pulse, the system is described by the Hamiltonian

$$\mathcal{H}(t) = \hbar\Delta\omega I_z + \frac{\hbar\omega_q}{3}[3I_z^2 - I(I+1)] - \hbar\gamma H_1 I_x, \quad [5]$$

where all symbols have their usual meaning. The z component of the Zeeman interaction has been removed by transforming to the rotating frame. Assuming that the RF component dominates, it is possible to transform to a tilted frame by rotating the system to a frame directed along the effective field direction at angle θ from the z axis such that

$$\tan\theta = \frac{\omega_1}{\Delta\omega}. \quad [6]$$

This transformation diagonalizes the RF term, but introduces nonaxial components for the quadrupole that depend on θ.

In the tilted frame, the effective Larmour frequency $\Omega = \sqrt{\Delta\omega^2 + \omega_1^2}$ can be removed by transforming to a second rotating frame about the effective field direction. This leads to nonsecular terms in the nonaxial components of the quadrupole interaction which are dropped in degenerate perturbation theory, leaving only the time-independent axial component with the quadrupole-coupling constant modified according to Eq. [4].

These equations can be solved exactly (*2*) and the results transformed back from the tilted frame to the rotating frame. Specializing this result for a spin-1 with initial z magnetization, the system evolves giving rise to a doublet separated by $2\omega_q$. For powders, a Pake doublet, characteristic of spin-1 systems, is expected (*12*).

Before averaging over orientations, the magnetization $M(t_1 + t_2)$, after a nutation pulse of length t_1 and an acquisition time of length t_2, is given by

$$(\tilde{M}_x + i\tilde{M}_y)(t_1 + t_2) = \exp[i\Delta\omega t_2]\sin^2\theta\{\cos\omega_q t_2 \times [(\cos\theta\cos\Omega t_1 + i\sin\Omega t_1)\cos\omega_q^{\text{eff}} t_1 - \cos\theta] - \sin\omega_q t_2 \sin\omega_q^{\text{eff}} t_1[\cos\theta\cos\Omega t_1 + i(2\cos^2\theta - 1)\sin\Omega t_1]\}. \quad [7]$$

The ~ indicates that the expression is in the rotating frame of the Larmour frequency ω_0.

On resonance $\Delta\omega = 0$ and $\omega_q^{\text{eff}} = -\omega_q/2$, $\theta = \pi/2$ and $\Omega = \omega_1$. For powder samples, two Pake doublets are expected to be centered about $\pm\omega_1$ in the F_1 domain. The splitting of these Pake doublets is $\omega_q/2$, which is half the usual value expected in the F_2 acquisition domain.

Off resonance, in addition to the splitting of ω_q^{eff}, a peak arises centered in the middle of the F_1 domain (see Eq. [7]). Under the special condition that (see [4])

$$\frac{\Delta\omega}{\omega_1} = \frac{1}{\sqrt{2}}, \quad [8]$$

the effective quadrupole vanishes, giving a 2D nutation signal

$$(\tilde{M}_x + i\tilde{M}_y)(t_1 + t_2) = \frac{\sqrt{2}}{3}\exp[i\Delta\omega(t_1 + t_2)]\cos\omega_q t_2 \times \left[\cos\sqrt{\frac{3}{2}}\omega_1 t_1 + i\sqrt{3}\sin\sqrt{\frac{3}{2}}\omega_1 t_1 - 1\right]M_z(0). \quad [9]$$

Under this special condition, with quadrature detection in the F_1 domain, three peaks are expected centered at $\omega_1/\sqrt{2}$ at $(+\sqrt{(3/2)}\,\omega_1, 0, -\sqrt{(3/2)}\,\omega_1)$ with intensities of $((1 + \sqrt{3})/2, -1, (1 - \sqrt{3})/2)$, respectively.

EXPERIMENTAL

A powder sample of 1,4-dimethoxybenzene (DMB) deuterated by 97 to 98% was used. The quadrupole-coupling constant of ^{2}D of benzene is 130 kHz, and that of $-OCD_3$ is 33.3 kHz. The spin–lattice relaxation time T_1 of $-OCD_3$ is several seconds while that of the ^{2}D on benzene is several minutes (*8*). For short recycle times of several seconds, the deuterium signal is entirely due to the $-OCD_3$.

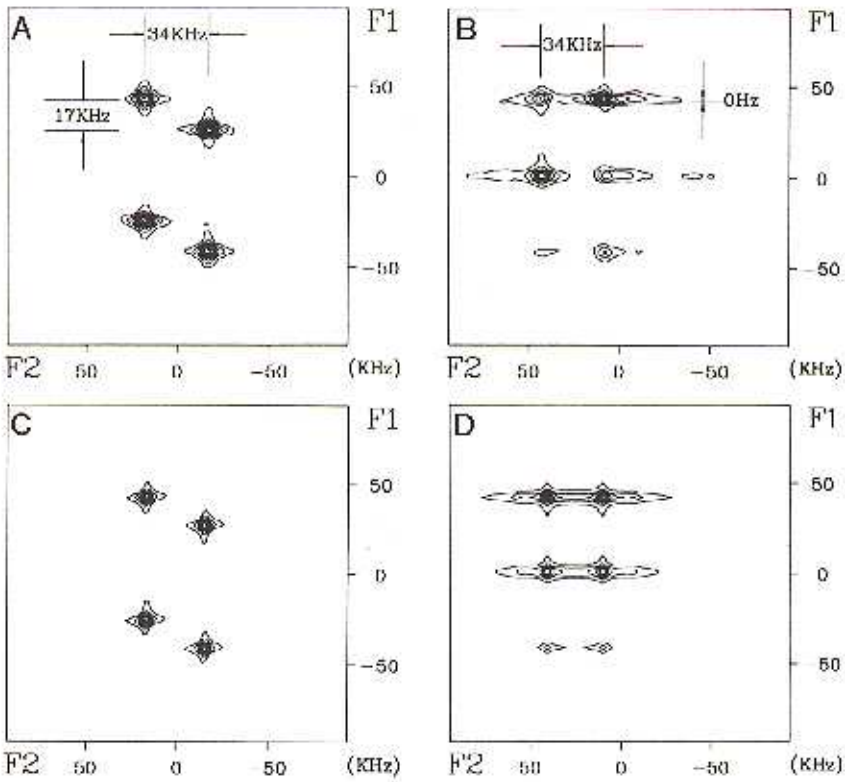

FIG. 1. The nutation spectra of DMB at different offsets. A is the on-resonance spectrum, and the offset for spectrum B is $\omega_1/\sqrt{2}$. The RF field strength $\omega_1/2\pi$ is 36 kHz. The spectrum widths are 250 and 200 kHz for F_2 and F_1 domains, respectively. Sixty-four FIDs were recorded for a 2D spectrum and the 2D FFT data size was 256 × 128 words. Gaussian window functions were used for both dimensions and the line-broadening factors for two domains were both 2500 Hz. The splittings due to quadrupole interaction in F_1 and F_2 are indicated. C and D are the numerical simulations of A and B using [7]. The data set was 64 × 64 words for each 2D spectrum, zero filled to 128 × 128 words for the 2D FFT. The quadrupole-coupling constant was set to 33.3 kHz, and $\Delta\omega$ 0 for C and $\omega_1/\sqrt{2}$ for D.

In order to test the theoretical predictions, the 2D nutation spectra of ^{2}D were recorded in both the F_1 and the F_2 domains using quadrature detection. The offset values used span a frequency range of 80 kHz about the on-resonance position. The RF field strength was 36 kHz, and the nutation pulses were nonselective. The experiments were performed on a Bruker MSL-400 spectrometer and two different probes were used to confirm the results (one is a broad-line probe from Bruker, and the other is a MAS probe from Doty Scientific, Inc.) The sample was not spun in the nutation experiments.

The numerical simulations were performed on a VAX-11/785. The theoretical FID signals for the 2D nutation spectra for a spin-1 were calculated according to [7]. The 2D FIDs were processed by a normal 2D FFT program to produce the simulated spectra shown in Figs. 1C and 1D.

RESULTS AND DISCUSSION

The nutation experiments of DMB were used to test the theory presented above (*2*), which shows that the quadrupole-coupling constant is modified to an effective value while the nutation pulse is applied to the system. In the 2D nutation experiments, the F_1 domain displays the behavior of quadrupole nuclei under the nutation pulses. The chemical-shift interaction does not affect this domain, thereby revealing the pure quadrupole spectra. This assumes also that the dipole–dipole interaction is negligible.

According to Eq. [4] of the theory, the quadrupole-coupling constant will be changed to an effective value under the RF field, not only for a single crystal, but also for powder samples. Figure 1A is the 2D nutation spectrum of DMB recorded on resonance. This shows that the splitting of the Pake doublets in the F_1 domain is 17 kHz, or half of the original value, in agreement with the theory. Figure 1B is the off-resonance 2D nutation spectrum recorded at a value of $\Delta\omega = \omega_1/\sqrt{2}$ and $\omega_1/2\pi = 36$ kHz. This spectrum shows that the effective quadrupole-coupling constant reveals no splitting due to the quadrupole interaction in the F_1 domain. We therefore conclude that the effective quadrupole is zero, again in agreement with the theoretical predictions showing that the quadrupole interaction can be suppressed under this special condition. From Fig. 1B, it is found that there are three resonance lines in the F_1 domain, and their offsets are −44, 0, and 44 kHz, respectively. Their offsets are consistent

with the theoretical prediction, which gives the result that the offsets are $(3/2)^{1/2}\omega_1$, 0, $(3/2)^{1/2}\omega_1$, while $\omega_1 = 36$ kHz. The relative intensities of three resonance lines in the F_1 domain are listed in Table 1. From the data in Table 1, the intensities of the lines are consistent with theoretical calculation. This experimental agreement also justifies the approximation of dropping the nonsecular nutation frequencies in the case of strong nutation pulses.

The numerical simulation results of the 2D nutation spectra are shown in Figs. 1C and 1D for $\Delta\omega = 0$ and $\Delta\omega = \omega_1/\sqrt{2}$, respectively. The agreement is convincing evidence that the theory is correct.

Experiments were also done at different offsets and the splittings of the Pake doublets measured. These results show that [4] is also satisfied at different values of resonance offsets. The experimental points and the theoretical line from [4] are shown in Fig. 2. For $\Delta\omega/\omega_1$ greater than about 2, deviations occur. This is likely because the RF pulses no longer dominate and are becoming weak. The region of agreement, however, justifies the dropping of the nonsecular terms of the quadrupole interaction for strong nutation pulses.

CONCLUSION

Suppression of quadrupole coupling in powders and single crystals can be accomplished by pulsing the system at a resonance offset of $\Delta\omega/\omega_1 = 1/\sqrt{2}$. This value of offset will suppress the effective quadrupole evolution for spins of any magnitude and has been shown here to be experimentally valid for a spin-1 system.

On resonance, it is noted that the effective quadrupole constant not only is reduced by a factor of 2, but also changes sign. This suggests that a possible way to suppress quadrupole line broadening might be to repeatedly pulse the system on resonance for a time $2t$ with times between pulses of t. Initial experiments confirm that this is true, although the present results contain an artifact which we cannot suppress and therefore do not present here. This suggestion is similar to

TABLE 1
The Relative Intensities of the Three Resonance Lines in the F_1 Nutation Domain with $\Delta\omega = \omega_1/\sqrt{2}$

Offset in F_1 (kHa)*	−44	0	44
a	25.0	198.0	100.0
b	25.0	33.4	100.0
c	24.2	81.3	100.0
d	26.8	73.2	100.0

* a, b correspond to the two peaks of the Pake doublet in the F_2 domain with offsets of $\Delta\omega$ + ($\omega_0/2$), respectively. c is the projection of the F_1 domain. d is the theoretical calculated results which are given under Theory.

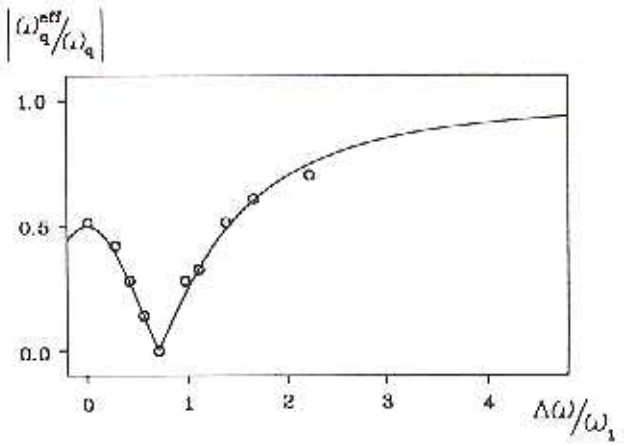

FIG. 2. The comparison of the theoretical predictions of Eq. [4] (solid line) and the experimental results (○). The offset dependence of the scaling factor for the quadrupole-coupling constant under a strong nonselective RF field is shown. The offsets vary from 0 to 80 kHz and the strength of the RF field is 36 kHz.

the use of "natural" pulses, or delays between pulses. Not all polarizations are odd with respect to ω^q_{0T}, and the sign change only effects such terms. In contrast, relaxation effects always occur with the geometrical term $d^2_{00}(\theta)$ squared, and so the sign has no consequences.

ACKNOWLEDGMENTS

This work is supported by a research grant from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Chinese Academy of Sciences of the People's Republic of China.

REFERENCES

1. B. C. Sanctuary and T. K. Halstead, private communication.
2. B. C. Sanctuary, *Mol. Phys.* **49,** 785 (1983); B. C. Sanctuary, T. K. Halstead, and P. A. Osment, *Mol. Phys.* **49,** 753 (1983).
3. W. S. Veeman, A. P. M. Kentgens, R. Janssen, and Z. Frosenius, *Anal. Chem.* **327,** 63 (1987).
4. M. Lee and W. Goldburg, *Phys. Rev. A* **140,** 1261 (1965).
5. M. Mehring, "High Resolution NMR in Solids," Springer-Verlag, New York/Berlin, 1983.
6. R. A. Wind, *in* "Modern NMR Techniques and Their Application in Chemistry" (A. I. Popov and K. Hallenger, Eds.), M. Dekker, New York, 1991.
7. C. A. Mead, *Rev. Mod. Phys.* **64,** 51 (1992).
8. M. Berry, *Proc. R. Soc. London Ser. A* **392,** 45 (1984).
9. A. Wokaun and R. R. Ernst, *J. Chem. Phys.* **67,** 1752 (1977).
10. S. Vega, *J. Chem. Phys.* **68,** 5518 (1978).
11. E. Lippmaa and A. Samoson, *J. Magn. Reson.* **79,** 255 (1988); B. C. Sanctuary, *J. Magn. Reson.* **85,** 573 (1989).
12. H. Spiess, "Rotation of Molecules and Nuclear Spin Relaxation in NMR: Basic Principles and Progress," Vol. 15, p. 55, Springer-Verlag, New York/Berlin, 1978.
13. R. R. Eckman, Ph.D. Thesis, Lawrence Berkeley Laboratory, University of California at Berkeley, 1982.