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A Novel Multipulse Sequence to Suppress Quadrupolar Interaction in NMR Experiments

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A novel multipulse sequence to suppress quadrupolar interaction is suggested. This pulse sequence is based on the fact that quadrupolar interaction will be scaled and change sign when a RF field is applied to the system. This is demonstrated by obtaining high-resolution spectrum of deuterated 1,4-dimethoxybenzene. © 1993 Academic Press, Inc.

INTRODUCTION

In the NMR study of quadrupolar nuclei, the resonance line of a powder sample is broadened by the quadrupolar interaction to 10^4–10^7 Hz. It is therefore important that the quadrupolar interaction be suppressed to reveal the high-resolution spectrum. The commonly used method is sample rotation in real space, that is, the magic-angle-spinning method (*1*). Another way to eliminate the quadrupolar broadening in solids is by use of multipulse experiments, such as WAHUHA (*2*), the Carr–Purcell (*3*), or the Lee–Goldburg (*4*). Although these pulse sequences are aimed at removing dipole–dipole broadening contributions in solids containing spins of $\frac{1}{2}$, they can also be applied to solids which are broadened by quadrupolar interactions (*5*). For example, the WAHUHA sequence has been shown to successfully narrow the spectrum of a spin-$\frac{3}{2}$ system (*6*). The basic reason for these successes is that both dipole–dipole and quadrupolar interactions are second-rank tensor interactions and respond in a similar way to these pulse sequences. Both MAS and pulse sequences can eliminate the first-order quadrupolar interactions, although new techniques have been developed in recent years to suppress the second-order interactions (*7*).

Although the theoretical calculations show that multipulse sequences can be used to suppress quadrupolar interaction, these have not been widely used in the investigation of quadrupolar systems. The main reason for this is the difficulty in realizing the stringent conditions required by multipulse experiments. Such experiments require carefully calibrated pulse widths and RF phases and a well-tuned probe. All these practical problems hinder application of multipulse techniques to quadrupolar systems. In this paper, we suggest a novel multipulse sequence which can be used to suppress the quadrupolar interaction with less stringent conditions. That is, other line-narrowing sequences require powerful RF pulses which dominate the quadrupolar interactions. For strong quadrupolar interactions, this is a difficult condition to achieve. The sequence which we propose here does not require strong dominating pulses. Rather, we need relatively weak RF pulses so that evolution under the quadrupolar interaction occurs while the RF pulses are on. The method is based on the theory that the quadrupolar interaction will be replaced by an effective one when a RF field is applied to the spin systems (*8*, *10*). In particular, for axially symmetric quadrupolar interactions, while a RF pulse is being applied, the effective quadrupolar coupling constant actually changes sign over a range of offsets, $\Delta\omega$, from resonance (i.e., $\Delta\omega = 0$) to the magic angle ($\Delta\omega/\omega_1 = 1/\sqrt{2}$). Here, ω_1 is the RF amplitude. Those polarizations which change sign when the quadrupolar constant is reversed evolve "backward" while the pulse is on. It is therefore possible to construct a multipulse sequence to average out the quadrupolar interaction. In the paper, a brief theoretical discussion is given and an example is presented confirming that the quadrupolar interaction of deuterium is dramatically suppressed by this method.

THEORY

With a RF field on, the spin Hamiltonian can be expressed by the following equation in the rotating frame:

$$\mathscr{H} = \Delta\omega I_z + \frac{\hbar\omega_q}{3}[3I_z^2 - I(I-1)] + \omega_1 I_x. \qquad [1]$$

It has been shown before (*8*) that, under this interaction, the quadrupolar coupling constant ω_q is modified to an effective value ω_q^{eff} (*8*), where

$$\omega_q^{\text{eff}} = \chi\omega_q, \qquad [2]$$

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with

$$\chi = -\frac{1}{2}\left(\frac{1 - 2\Delta\omega^2/\omega_1^2}{1 + \Delta\omega^2/\omega_1^2}\right) = d^2_{00}(\theta). \qquad [3]$$

Here $d^2_{00}(\theta)$ is a reduced rotation-matrix element (*9*) and $\cos(\theta) = \Delta\omega/\sqrt{\Delta\omega^2 + \omega_1^2}$. This scaling has been confirmed by numerical simulation and experimental results (*10*).

From Eq. [3] we can find that when $\Delta\omega < \omega_1/\sqrt{2}$, the scaling factor χ is negative; that is, $-0.5 < \chi < 0$. This means that the quadrupolar interaction changes sign as the pulses are turned on and off. If we use a pulse sequence shown in Fig. 1 and do strobe data acquisition at the points marked in the figure, this sign change can be exploited by making odd terms in the spin dynamics reverse. Over the course of the total sequence, the quadrupolar interaction averages out, giving a spectrum with the quadrupolar interactions suppressed.

The above discussion is based on the condition that the sample is a single crystal. From Eq. [3], however, the scaling factor χ is the function of $\Delta\omega$ and ω_1 only and does not depend upon the quadrupolar coupling constant ω_Q. For the randomly oriented powder samples, although the different Euler angles of individual nuclei will cause different ω_q, their scaling factors χ due to the RF field will be the same. Therefore, Eqs. [2] and [3] are also valid for powder samples. This has also been confirmed by nutation experiments on a powder sample (*10*), indicating that the pulse sequence shown in Fig. 1 can be used to obtain a high-resolution powder spectrum if the ratio of pulse duration to time delay between pulses is chosen to be 2. This analysis is quite different from other multipulse sequences in that the pulses are not treated as hard delta function rotations. Rather, the pulse must be soft enough to allow the quadrupole evolution that occurs between pulses to be time reversed during the pulse. We also note that as long as $|\Delta\omega/\omega_1| < 1$, the above description is still valid, indicating that the pulses need not necessarily be applied close to resonance. This insensitivity to offset has distinct advantages for powder systems with large widths.

EXPERIMENTAL

Experiments were performed on a powder sample of 1,4-dimethoxybenzene (DMB) which had been deuterated to 97–98%. The signal of the quadrupolar nuclei in $-OCD_3$ was observed. A Bruker MSL-400 spectrometer equipped with a MAS probe from Doty Scientific, Inc., was used. The sample was not spun during the experiment. A short recycle time (2 s) was used, so that the signal observed was entirely due to the $-OCD_3$ because of the relatively long spin–lattice relaxation time T_1 of ^{2}D in benzene. The pulse sequence employed in the experiment is shown in Fig. 1, and the phases of RF pulses were not cycled. The strength of RF pulses was 69.5 kHz, which was calibrated by a nutation experiment. The resonance offset $\Delta\omega$ was 1456 Hz. According to the theory, τ_1 and τ_2 in Fig. 1 were chosen to be 40.05 and 20 μs, respectively, giving a dwell time of 60.05 μs. The spectrum width was 8333 Hz, and 512 data points were acquired. The data-acquisition points were set at the end of windows without pulses to avoid a ringdown effect.

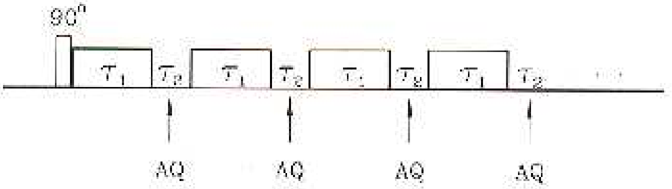

FIG. 1. The multipulse sequence used in the experiment to suppress quadrupolar interaction. The ratio of τ_1/τ_2 is determined by Eq. [3] in the text.

RESULTS AND DISCUSSION

According to Eq. [3], the scaling factor χ is negative when $\Delta\omega < \omega_1/\sqrt{2}$. This enables us to design a pulse sequence to eliminate the quadrupolar interaction in order to reveal the high-resolution spectrum, as described under Theory. As shown by Fig. 1, in the pulse sequence, a hard 90° pulse first turns the Zeeman polarization to the xy plane. A series of pulses whose length is τ_1 then follows, with each separated by a free evolution period τ_2. To show the effect of this pulse sequence, consider one pulse and one delay discussed in Ref. (*10*), Eq. [7], under the on-resonance condition, $\Delta\omega = 0$, $\theta = \pi/2$. Equation [7] of Ref. (*10*) reduces to

$$M_y(\tau_1 + \tau_2) = (\cos \omega_q\tau_2 \cos \omega_q^{\mathrm{eff}}\tau_1 - \sin \omega_q\tau_2 \sin \omega_q^{\mathrm{eff}}\tau_1) \sin \omega_1\tau_1. \qquad [4]$$

Since $\omega_q^{\mathrm{eff}} = -\omega_q/2$ at resonance, the quadrupolar interaction has no effect on the spin system if $\tau_1 = 2\tau_2$. As the resonance condition is relaxed, this refocusing is not perfect. The quadrupole, however, continues to evolve the polarizations in opposite senses as the pulses are switched on and off. In addition, the effective quadrupolar coupling constant decreases as $|\Delta\omega/\omega_1|$ increases and it remains negative until $|\Delta\omega/\omega_1| = 1/\sqrt{2}$. Hence the condition of exact resonance for this pulse sequence to suppress the quadrupolar interaction is not stringent.

Deuterated 1,4-dimethoxybenzene was used to demonstrate this method. The experimental spectrum is shown in Fig. 2a. We find that there is a resonance signal at a frequency of 1456 Hz which has a linewidth of about 500 Hz, that is, the signal of deuterium of $-OCD_3$ as DMB. For comparison, the solid-echo spectrum of the same sample is shown in Fig. 2b, displaying a typical Pake doublet due to quadrupolar

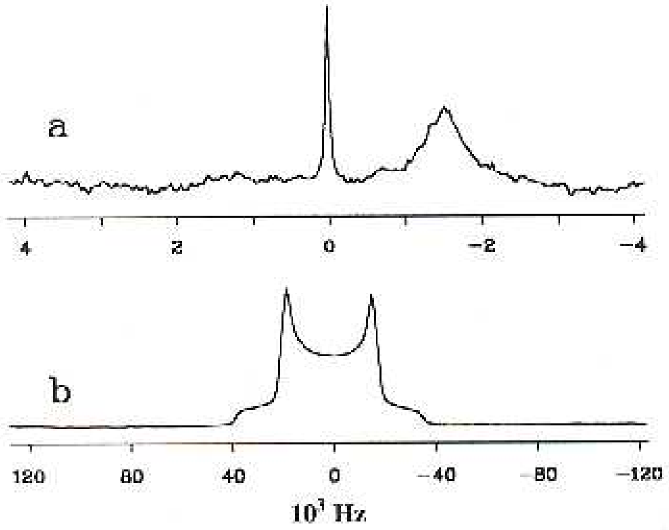

FIG. 2. (a) The multipulse spectrum of 1,4-dimethoxybenzene obtained by the method described in the text. The linewidth of the signal is about 500 Hz, and there is a sharp central peak in the middle of the spectrum. (b) For comparison, the solid-echo spectrum of 1,4-dimethoxybenzene is shown. The splitting of the Pake doublets shows that the quadrupolar coupling constant is about 33 kHz. One should note the different frequency scales in a and b.

interaction. Its splitting is about 33 kHz. Obviously, the quadrupolar interaction of deuterium has been successfully eliminated by the multipulse sequence shown in Fig. 1, since the linewidth of the deuterium signal in the multipulse spectrum has been reduced to about 1% of it original value. Compared to the linewidth of MAS spectrum for the same sample, the resonance line in our multipulse spectrum is relatively broad, and the lineshape of the multipulse spectrum fits a Gaussian function, not a scaled Pake doublet such as an off-MAS spectrum will give. This suggests that the residual linewidth is due to the effect of RF field inhomogeneity. The nonuniformity of the RF field gives slightly different ω_1 values, causing the scaling factors χ to differ at various places in the sample. Since the ratio τ_1/τ_2 is fixed in the experiment, the quadrupolar interaction cannot be entirely averaged out over the whole sample. This causes the residual line broadening of the multipulse spectrum. Use of a sample of small volume and improvement of the homogeneity of the RF coil should result in better resolution. Using a phase cycle, such as the positive–negative nutation experiments (*11*), will partially suppress the inhomogeneity of the RF field and further improve resolution.

In Fig. 2a, there is a sharp peak in the middle of the spectrum which we call the central peak. This arises naturally in our multipulse sequence analysis and is well known in spin-lock experiments. As discussed in our previous paper (*10*), there exists in the nutation experiments an axial peak located at the center of the F_1 domain of two-dimensional nutation spectra when the transmitter frequency is removed from the resonance condition. This phenomenon has been confirmed by numerical simulation and by experiments (*10*). Our multipulse experiment is similar to a nutation experiment. The first nutation experiment which was suggested by Yannoni *et al.* is also a multipulse experiment (*12*), and they also observed a central peak. We have not been able to suppress this peak.

In summary, we suggest a novel multipulse experiment that can be used to suppress the quadrupolar interaction. The experimental results show that it is successful for deuterium, and it should also be effective for other kinds of nuclei with $I > \frac{1}{2}$. One advantage of this method over other multipulse sequences is that it does not need exact 90° or 180° pulses, so it can be easily implemented.

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