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Elucidation of Central Line Refocusing in Quadrupolar Echo Formation

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Abstract: Quadrupolar interaction is a strong line broadening agent for nuclei of half-integer spin except the central line. The two-pulse quadrupolar echo technique is widely used, which refocuses the quadrupolar broadening. Echo formation is due to the cancellation of quadrupolar broadening effect by the applied two pulses. Since the central line is not quadrupolar broadened, it should not be involved in the echo formation. However, the central line peak always appears in experiments. This is explained qualitatively here by close examination on the time development of individual coherence. This explanation is used to predict the number of echoes that will be formed with 2 pulse sequence for nuclei of $I = 3/2, 5/2, 7/2, 9/2$ with ease.

INTRODUCTION

There are many nuclei whose spin is greater than 1/2. Such nuclei possess quadrupole moments, which can interact with the electric field gradient around the nucleus. Usually the quadrupolar interaction is stronger than any other internal interactions such as magnetic dipole-dipole interaction or chemical shift anisotropy in solid samples. For pulsed NMR, it poses two major practical problems in obtaining information from a single pulse FID. First, the quadrupolar interaction, in many cases, is so strong that its strength can exceed that of rf-pulse which supposedly rotates the longitudinal magnetization to transverse plane. In this case we cannot neglect the effect of quadrupolar interaction even during pulsing time, and the spin system is subjected to the combining effect of the rf-pulse and the quadrupolar interaction. The rf-pulse cannot act as a simple rotation of spin coherences. The simple rotation is possible only if internal interactions can be neglected during the pulse, which is so called the *hard pulse* condition. In the presence of strong quadrupolar interaction, however, nutation NMR technique has been developed and applied successfully.

The second problem is the receiver deadtime during which FID cannot be acquired.

Deadtime problem becomes more serious for wider spectral width. The resonance lines broadened by the quadrupolar interaction, typically a few 100 kHz, decay in about 10 μs which is an order of the receiver deadtime. Therefore, quadrupolar echo technique is indispensable in observing undistorted quadrupolar broadened lines in this case. In this paper, the procedures to set up for quadrupolar echo experiment will be reviewed carefully and several points hitherto misunderstood will be clarified. Exact understanding for experimental parameter is vital for correct data acquisition and their further processing.

THEORETICAL BACKGROUND

Solomon has demonstrated experimentally that the quadrupolar broadened lines for nuclei of spin 5/2 can be refocused so that zero-time resolution can be achieved just like the famous Hahn echo for inhomogeneously broadened lines with two pulses. He has also provided theoretical explanation for this refocussing on the basis of density operator formalism.[1] His theory was later applied for many other general cases with success.[2-5] We present here the result of his theory when applied for spin 3/2. Ih general, signal in transverse plane can be calculated as

$$S_+(t) = \mathrm{Tr}\left\{I_+ \exp\left(-iH_Q t\right)\rho(0)\exp\left(iH_Q t\right)\right\} \tag{1}$$

where $I_+ = I_x + iI_y$,

$$\begin{aligned} H_Q &= \frac{1}{4}\omega_Q a_0(\theta,\phi)\left(I_z^2 - \frac{I(I+1)}{3}\right) \propto I_z^2 \equiv QI_z^2, \\ \omega_Q &= \frac{3e^2qQ}{2I(2I-1)}, \end{aligned} \tag{2}$$

and

$$a_0(\theta,\phi) = 3\cos^2\theta - 1 + \eta\sin^2\theta\cos 2\phi$$

Only the secular part of the quadrupolar interaction is considered for line broadening. After a 90(x)-degree pulse, the signal will be given as,

$$S(t) = \mathrm{Tr}\left\{I_y \exp\left(-iQI_z^2 t\right)I_y \exp\left(iQI_z^2 t\right)\right\} = \mathrm{Im}\left\{S_+(t)\right\}$$

$$
\begin{aligned}
&= \mathrm{Im}\sum_{m} < m \left|\exp\left(-iQI_z^2t\right)I_y \exp\left(iQI_z^2t\right)I_+\right| m > \\
&= \tfrac{1}{2}\left\{3\exp(-2iQt)+4+3\exp(2iQt)\right\}
\end{aligned} \tag{3}
$$

According to this result, there are three peaks located at $-2Q$, 0, $2Q$ with relative intensities of 3, 4, 3, respectively. Since the central peak is not broadened by the secular part of quadrupolar interaction, it appears as time-independent term. The central transition is broadened by the non-secular part of quadrupolar interaction, though, which is not considered here.[6]

Similarly, the signal resulting from $90(x)$-t_1-$\theta(y)$-t_2 is given as,

$$
\begin{aligned}
S(t_1,t_2) &= \mathrm{Tr}\left\{I_+ \exp(-iQI_z^2t_2)\exp(-i\theta I_y)\exp(-iQI_z^2t_1)\, I_y + (\text{herm.conj.})\right\} \\
&= \sum_{m,m',m''}\sqrt{I(I+1)-m(m+1)}\left\langle m\middle|\exp(-i\theta I_y)\middle|m''\right\rangle\left\langle m''\middle|I_y\middle|m'\right\rangle\left\langle m'\middle|\exp(i\theta I_y)\middle|m+1\right\rangle \\
&\qquad \times \exp\left[-iQ(m''^2-m'^2)\left\{t_1-\frac{2m+1}{m''^2-m'^2}t_2\right\}\right]
\end{aligned} \tag{4}
$$

which shows five different kinds of terms are involved. Terms having no time-dependence correspond to the coherence restricted to central transition throughout the pulse sequence. This will result in the central peak signal when FT is applied. Terms having t_1 dependence correspond to the coherence which were excited to the sideband transition after the first pulse but transferred to the central transition by the second pulse. Terms with t_2 dependence is opposite to those with t_1. Terms with (t_1+t_2) dependence correspond to the sideband coherences generated by the first pulse and then not affected by the subsequent second pulse, so that they contribute to the same sideband transitions. Terms having (t_1-t_2) dependence are the echo coherence terms which were first on one sideband after the first pulse and then transferred to the other opposite sideband by the second pulse. Therefore, it is obvious there would be only one echo at $t_1 = t_2$, noting that $H_Q = QI_z^2$. This arguments can easily be extended to the spin 5/2 case to show there are 3 echoes at $t_2 = 1/2\ t_1$, t_1, $2\ t_1$. For spin 7/2, it predicts peaks at $t_2 = 1/3\ t_1$, $1/2\ t_1$, $2/3\ t_1$, t_1, $3/2\ t_1$, $2\ t_1$, $3\ t_1$. For spin 9/2, there should be 11 allowed echoes at $t_2 = 1/4\ t_1$, $1/3\ t_1$, $1/2\ t_1$, $2/3\ t_1$, $3/4\ t_1$, t_1, $4/3\ t_1$, $3/2\ t_1$, $2\ t_1$, $3\ t_1$, $4\ t_1$.

The echo intensity is given as

$$
S_{\text{echo}}(t_1,t_2) = \frac{9}{8}\sin^2\theta \times \left\{\exp[2iQ(t_1-t_2)] + \exp[-2iQ(t_1-t_2)]\right\}, \tag{5}
$$

whereas the time independent term is

$$S_0 = 2 - \frac{3}{2}\sin^2\theta \tag{6}$$

From this result, we can expect that the maximum echo will be formed with 90(y) pulse and the time independent term would last long enough to give the central line peak. In other words, the appearance of central peak may be ascribed not to refocusing of the quadrupolar interaction but to its long decay time.

EXPERIMENTAL

Material

$NaNO_3$ is chosen to test the theoretical arguments. NaCl solution is used to measure solution 90 degree pulse.

NMR measurements

Experiment is done with Varian Unity Inova model of 4.7T. High power amplifier is capable of delivering 1kW. The sample coil has 5 mm diameter. Probe is from Chemagnetics. Deadtime was about 15 μs at 52.9 MHz with digitizing spectral width of 500 kHz, which found to be related to the deadtime. Magnetic field inhomogeneity is measured with solution sample. FWHM in frequency is about 27 Hz. All spectra are taken around 52.9 MHz.

RESULTS AND DISCUSSIONS

Fig. 1 shows a collection of FID's obtained for a $NaNO_3$ powder sample taken with 0.1 μs increment of the pulsing time starting from 0.1 μs each in a single pulse experiment. The width of a 90-degree pulse was about 0.6 μs which corresponds to 420 kHz of *rf*-field strength $\gamma B_1 / 2\pi$. The same experiment on a NaCl solution gave very similar result, which indicates that the *rf* strength satisfy the hard pulse condition. Fig. 2 is the corresponding frequency spectrum obtained from the FID's shown in Fig. 1. The spectrum shows a typical powder pattern with η close to 0 and quadrupolar coupling constant ω_Q being about $2\cdot 835$ kHz. There are two features that need to be mentioned. First. sideband singularities are not equal. Second, except at those singularities, powder signal from sidebands is almost lost under baseline. The first feature is due to the fact that the center of power transfer does not necessarily coincide with carrier frequency for observation. To fix this problem, change in tuning is required. The optimal point can be found only by trial and error. The second arises from large loss of the initial part of the signal as is clearly illustrated in Fig. 3 showing several lost data points. Total time elapse is about 100 μs. It is apparent that 15 μs of deadtime setting is not short enough. First 7 data points were omitted before FT is applied. Therefore, total 15 + 2 × 7 = 29 μs of the signal is lost. When the first part of FID is lost, it pulls the center region of spectrum downward to the baseline which explains our spectrum where the center region moves close to baseline. The author has observed on occasions this effect can generate 2 split peaks out of one true peak, which is of course an artifact. So, in order to get correct spectral pattern for broad lines quadrupolar echo sequence should be used.

Fig. 4 shows FID's obtained with the pulse sequence 90(x)-delay-90(y)-Acquisition. Delay is varied as 100, 300, 500, 700, 900 μs. In case delay is longer than 500 μs, slowly varying part of the signal does not participate in echo formation. For shorter delay, echo shape can mislead us to believe central transition is refocused, which is not true. This is the central point the author would like emphasize in this writing.

Fig. 5 shows spectrum similar to theoretical prediction. But the relative intensity is not exact and only the overall shape is correct. So, one should be careful to use the echo for quantitative analysis. It should be used only for certain specific qualitative analysis.

Fig. 6 shows digitized data in time domain around an echo. Data points are 2 μs apart. To compare the result, 12 data points from the top of echo is omitted before FT was performed, producing Fig. 7 which is very similar to Fig. 2.

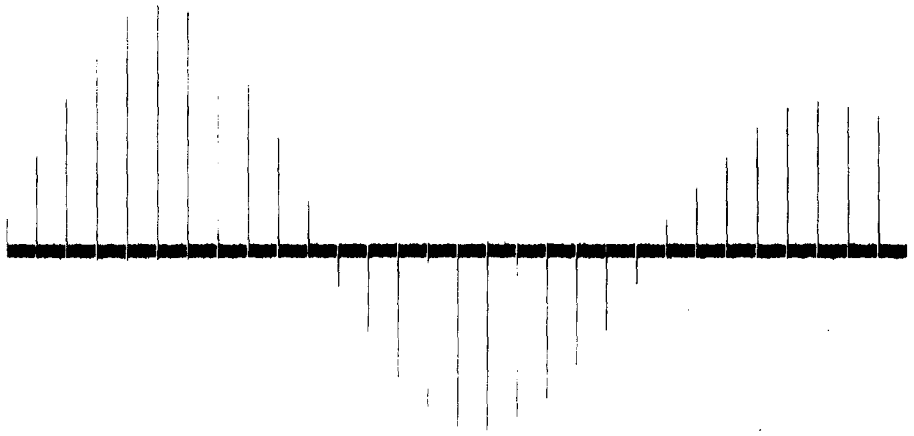

Fig. 1. FID taken with increasing pulsing time starting from 0.1 μs to 3 μs in step of 0.1 μs. The nice sinusoidal pattern implies rf-pulse is much stronger than quadrupolar broadening.

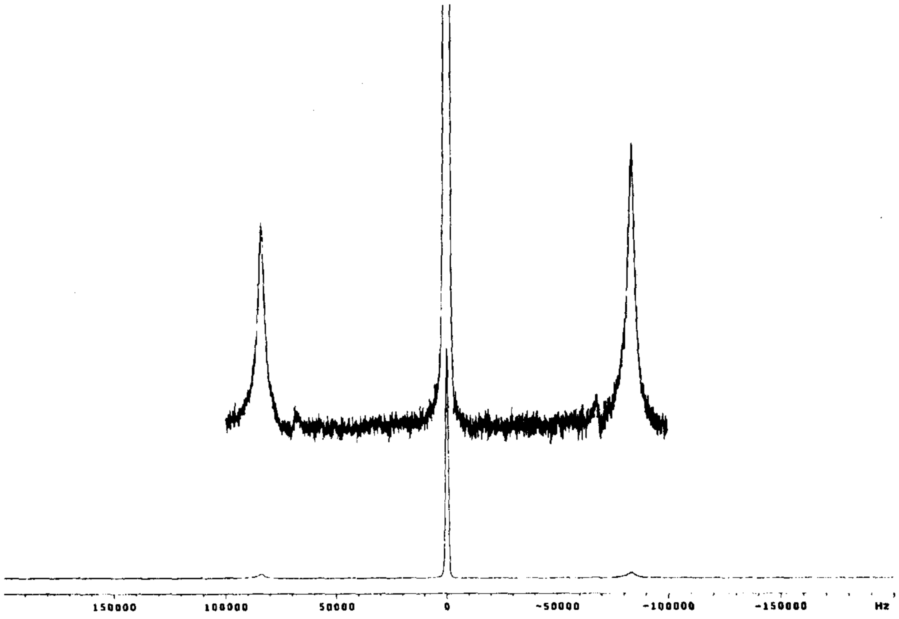

Fig. 2. Signal from a $NaNO_3$ powder sample.

Thus far, we have considered the case non-secular part of the quadrupolar interaction may be neglected. In this case strong pulse condition can be met and quadrupolar echo technique must be utilized to get correct spectrum. When the quadrupolar interaction becomes stronger, hard pulse condition cannot be met. If there is only one quadrupolar interaction environment to consider, second-order powder pattern for the central transition should be obtained. Second-order quadrupolar echo is the technique to be applied.[6] If there are more than one quadrupolar environment, nutation NMR technique should be applied, where only the central transition is observed.[7-8] Since the central transition is not refocused by the quadrupolar echo as explained here, we are forced to observe it right after long irradiation. If we are interested in chemical shift masked by the strong second-order quadrupolar interaction, we should apply DOR, DAS or triple quantum MAS technique that remove second-order quadrupolar broadening.[9] When the strong second-order broadening is observed, the sideband transitions are so broadened that they are beyond observation.

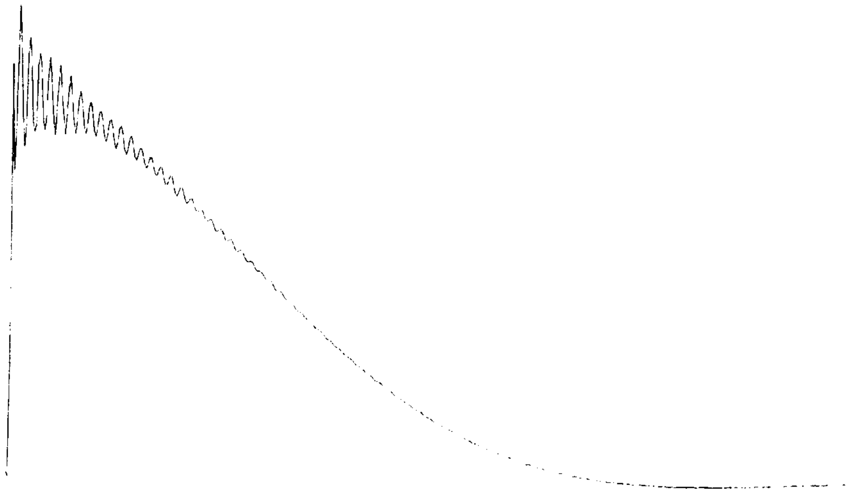

Fig. 3. FID after the single pulse. Deadtime was set to 15μs. (Inset) Digitized data in time domain. To perform an easier phase adjustment, 7 data points need to be omitted before sampling the first peak of signal

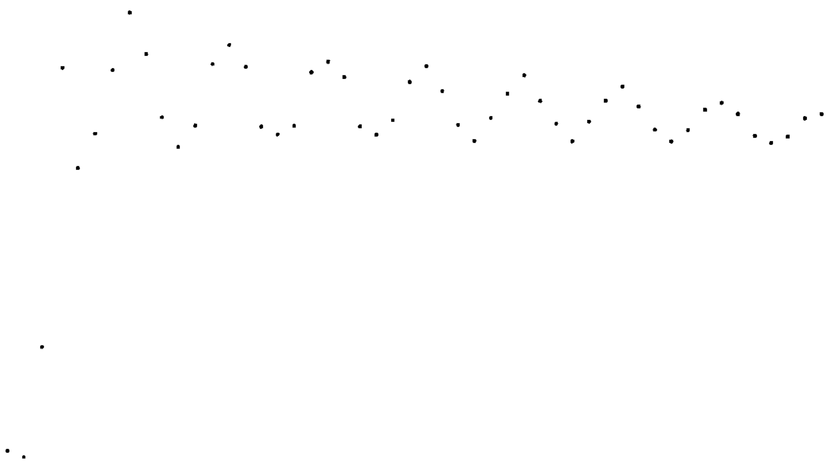

Fig. 4. Echoes were formed with delay of 100, 300, 500, 700, 900 μs. It is clear the central transition is not refocused. For shorter delay, though, central peak also seems to participate in echo formation.

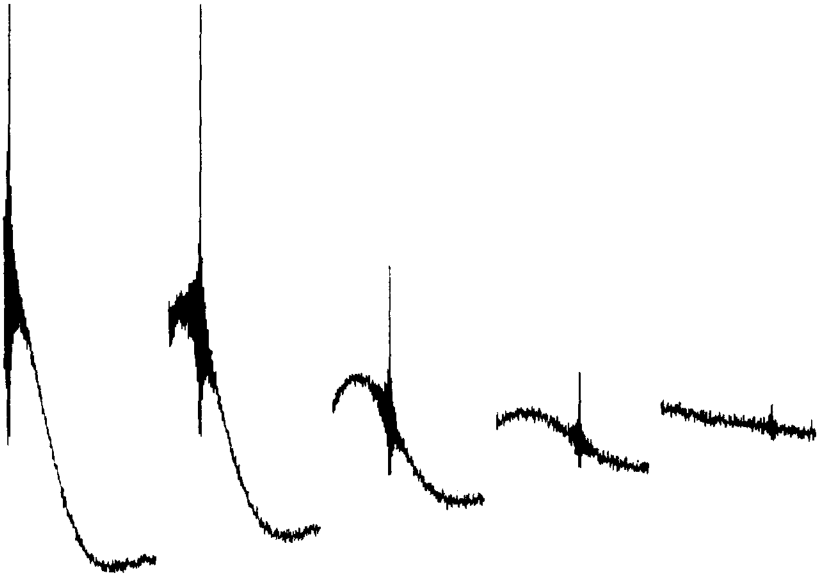

Fig. 5. Spectrum from 300 μs delay echo. The center region is clearly seen, which was missing in single pulse experiment.

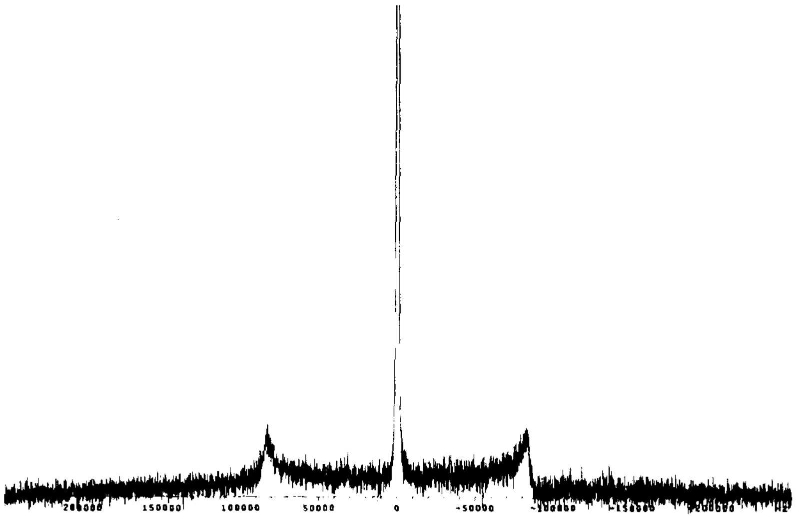

Fig. 6. Digitized signal in time domain. Since the spectral width was 500 kHz, digitizing time interval is 2 μs. We can see that first vital part of FID can be lost if the first data point is to start from 29 μs.

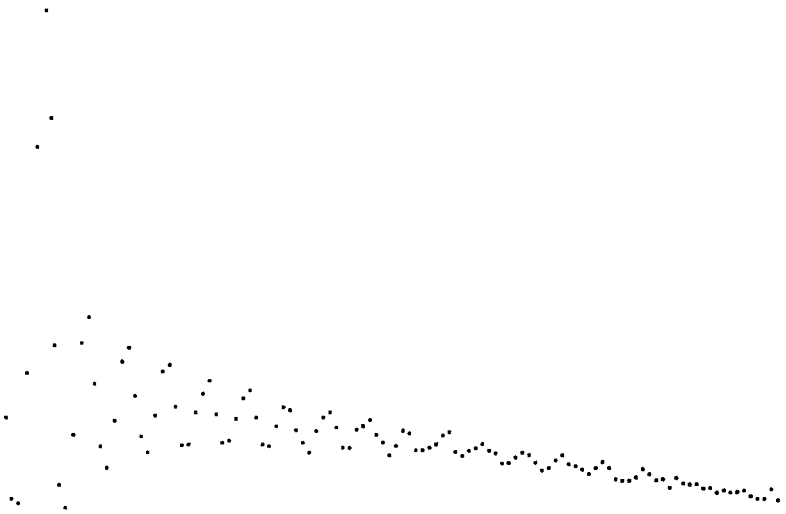

Fig. 7. Spectrum obtained from fig. 6 with moving from the peak of echo by 12 data points. It reproduces fig. 2.

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