Two-dimensional Nutation Echo Nuclear Quadrupole Resonance Spectroscopy *

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Z. Naturforsch. **45a**, 575–580 (1990); received August 25, 1989

We discuss two new two-dimensional nuclear quadrupole resonance experiments, both based on the principle of nutation spectroscopy, which can be used to determine the asymmetry parameter, and thus the full quadrupolar tensor, of spin-3/2 nuclei at zero applied magnetic field. The first experiment is a simple nutation pulse sequence in which the first time period (t_1) is the duration of the radiofrequency exciting pulse; and the second (t_2) is the normal free-precession of a quadrupolar nucleus at zero-field. After double Fourier-transformation, the result is a 2 D spectrum in which the first frequency dimension is the nutation spectrum for the quadrupolar nucleus at zero-field. For polycrystalline samples this sequence generates powder lineshapes; the position of the singularities, in these lineshapes can be used to determine the asymmetry parameters η in a very straightforward manner. η has previously only been obtainable using Zeeman perturbed NQR methods. The second sequence is the same nutation experiment with a spin-echo pulse added. The virtue of this refocussing pulse is that it allows acquisition of nutation spectra from samples with arbitrary inhomogeneous linewidth; thus, asymmetry parameters can be determined even where the quadrupolar resonance is wider than the bandwidth of the spectrometer. Experimental examples of ^{35}Cl, ^{81}Br and ^{63}Cu nutation and nutation-echo spectra are presented.

Introduction

The problem of determining the complete set of principal values of the electric quadrupole tensor of spin-3/2 nuclei is a long-standing one in magnetic resonance. Because the quadrupolar frequency observed in pure or zero-field NQR is a function of two free-parameters, often expressed as the quadrupole coupling constant ($QCC = e^2 q Q_{zz} h^{-1}$) and the asymmetry parameter of the electric field gradient produced at resonant nuclei. The latter tensor principal values cannot be determined, except in cases where local symmetry requires the asymmetry parameter to be zero. Accordingly, a variety of other methods has been used to determine η; these include Zeeman-perturbed NQR of single crystals [1, 2] or powders [3, 4], and high-field NMR [5]. All of these methods have severe drawbacks: single crystals of requisite size for NQR are frequently unobtainable, and the methods for determining the quadrupole interaction from the Zeeman-perturbed spectra are laborious. Additionally, Zeeman-perturbed NQR powder spectra are convolved with the full inhomogeneous NQR linewidth, which may be 100 kHz or greater, and therefore large Zeeman fields are necessary to obtain accurate values for the asymmetry parameter, with consequent problems associated with large bandwidths and loss of sensitivity. NMR spectra of nuclei with large QCC's are spread over many megahertz; if QCC is comparable to the Zeeman frequency, even the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition, which is unaffected by the quadrupolar interaction to first order in the perturbation expansion, will be greatly broadened by higher order perturbation terms.

It was to avoid these difficulties that we recently introduced a new two-dimensional nutation NQR experiment which allows measurement of η at zero field without Zeeman perturbation [6]. The method exploits the fact that the precession of a quadrupolar spin at zero field depends both on the relative orientation of the quadrupolar tensor and rotating frame field axis [7], and on η [8]. It has been shown theoretically that in powders the NQR signal intensity as a function of r.f. pulse length depends on η [8, 9]; however, for small flip angles the dependence is rather weak, and it is questionable whether it is experimentally feasible to directly use this fact to obtain η; our

* Presented at the Xth International Symposium on Nuclear Quadrupole Resonance Spectroscopy, Takayama, Japan, August 22–26, 1989.

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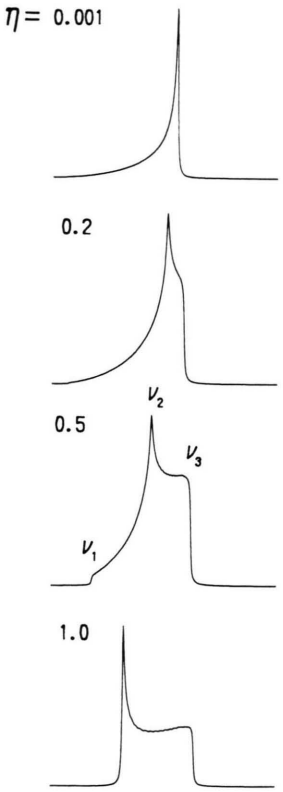

Fig. 1. Calculated nutation lineshapes (in the ω_1 dimension) for a spin-3/2 nucleus using the present pulse sequence as a function for various asymmetry parameters η. The lineshapes were obtained by numerical integration of (1), using 192 values of θ over an interval of 0 to π radians, and 384 values of ϕ over 0 to 2 π radians. 512 time points were taken before Fourier transformation.

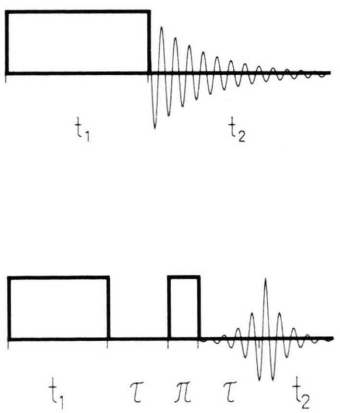

Fig. 2. Pulse sequences used in the present work. Top: The simple nutation sequence. Bottom: The nutation echo sequence. The pulse denoted π is a refocussing pulse which is effective only π radians for a single nutation frequency.

approach, rather, was to incorporate the r.f. pulse length as the first time variable in a two dimensional NQR experiment. After double Fourier transformation (FT), the spectrum in the ω_1 dimension is a powder pattern with three sharp singularities, whose frequencies can be used to obtain η in a very straightforward way. Calculated nutation spectra for samples with varying values of η are shown in Figure 1. We demonstrated the efficacy of the technique using the ^{35}Cl nucleus in a variety of organic and inorganic compounds and showed that it gave results in excellent agreement with previous studies.

The simple nutation sequence (Fig. 2, top) has, however, the major disadvantage that data acquisition can only begin after full ringdown of the long, hard nutation pulse; this ringdown time is typically 20 μs at frequencies of the order of 30 MHz. If the inhomogeneous linewidth is 10 kHz or greater, significant intensity losses will be encountered as a result of dephasing of the NQR signal before acquisition can commence. Since NQR linewidths of interesting samples are often greater than 100 kHz, the unmodified nutation sequence is of limited usefulness. We have therefore modified the sequence by introducing a refocussing pulse, as shown at the bottom of Figure 1. As before, the length of the exciting pulse is the first time variable in the 2D nutation experiment. However, after this pulse is over, we introduce a fixed delay τ, long enough for the pulse to ring down, followed by a refocussing pulse denoted by π in the figure, which produces a spin echo after a further period τ. Acquisition can then be commenced at the top of the spin echo, or alternately, if the quadrupolar signal is placed exactly on-resonance, the spin-echo can itself be transformed in the t_1 dimension without prior transformation in t_2.

One major difference between the 'π' pulse in the present experiment and a conventional NMR π pulse is that in the NQR experiment a single pulse cannot perfectly refocus all of the magnetization in a powder sample since the precession frequency depends on the crystallite orientation. Since it is this precession frequency which is mapped out in the first dimension of the nutation experiment, introduction of the refocussing pulse will tend to enhance one part of the powder pattern at the expense of the rest. However, the positions of the singularities in the pattern, which are features used to obtain η, are not affected, and therefore the simple extraction of η from the powder pattern, which is one of the virtues of the nutation experiment, is still possible.

Theory

The two dimensional nutation lineshape for a spin 3/2 nucleus in an isotropic powder has already been derived [6] and is given by

$$G(\omega_1,\omega_2)\propto\int_0^{2\pi}\int_0^{\pi}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\sin\theta\,\sin(\omega_R t_1 R(\theta,\phi)/2\sqrt{3}\varrho)\cdot\sin(\omega_Q t_2)\,e^{i\omega_1 t_1}\,e^{i\omega_2 t_2}\,dt_2\,dt_1\,d\theta\,d\phi \quad (1)$$

with the rotating frame frequency ω_R defined by

$$\omega_R=\gamma H_R. \quad (2)$$

Here H_R is the oscillating magnetic field strength of the radiofrequency irradiation. ω_Q is the quadrupolar frequency, given by

$$\omega_Q=\frac{e^2 q Q_{zz}\varrho}{2h} \quad (3)$$

with

$$\varrho=\left(1+\frac{1}{3}\eta^2\right)^{1/2}. \quad (4)$$

The orientation dependence of the nutation frequency in the t_1 dimension is contained in the factor $R(\theta,\phi)$, where θ,ϕ are the usual polar angles relating the coil axis to the quadrupolar reference frame, and

$$R(\theta,\phi)=(4\eta^2\cos^2\theta+(9+\eta^2+6\eta\cos(2\phi))\sin^2\theta)^{1/2}. \quad (5)$$

Equation (1) leads to a single line at the quadrupolar frequency in the ω_2 dimension and a powder pattern in the ω_1 dimension. The frequencies of the singularities in the powder pattern can be obtained by differentiating (1) with respect to θ and ϕ. They correspond to crystallite orientations of ($\theta=0°$), ($\theta=90°$, $\phi=0°$), and ($\theta=90°$, $\phi=90°$):

$$\nu_1=(1/2\pi)\frac{\eta\omega_R}{\sqrt{3}(1+\frac{1}{3}\eta^2)^{1/2}}, \quad (6a)$$

$$\nu_2=(1/2\pi)\frac{(3-\eta)\omega_R}{2\sqrt{3}(1+\frac{1}{3}\eta^2)^{1/2}}, \quad (6b)$$

$$\nu_3=(1/2\pi)\frac{(3+\eta)\omega_R}{2\sqrt{3}(1+\frac{1}{3}\eta^2)^{1/2}}. \quad (6c)$$

Usually only the two highest frequency singularities can be observed, but these (or any pair of singularities) are sufficient to determine η:

$$\eta=\frac{3(\nu_3-\nu_2)}{\nu_3+\nu_2}. \quad (7)$$

These equations give the lineshapes for the simple nutation experiment, and examples of such lineshapes calculated for various values of η are shown in Figure 1.

Introduction of a refocussing pulse of length τ_π causes the lineshape function to be modulated by an additional factor:

$$G(\omega_1,\omega_2)\propto\int_0^{2\pi}\int_0^{\pi}\int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty}\sin\theta\,\sin(\omega_R t_1 R(\theta,\phi)/2\sqrt{3}\varrho)\cdot\sin^2(\omega_R\tau_\pi R(\theta,\phi)/\sqrt{3}\varrho)\cdot\sin(\omega_Q t_2)\,e^{i\omega_1 t_1}\,e^{i\omega_2 t_2}\,dt_2\,dt_1\,d\theta\,d\phi. \quad (8)$$

This additional factor $\sin^2(\omega_R\tau_\pi R(\theta,\phi)/\sqrt{3}\varrho)$ does not affect the frequencies of the singularities in the ω_1 dimension. However, it enhances the intensity of one region of the nutation spectrum at the expense of others; specifically, that region where $\omega_1\tau_\pi\approx 180°$. However, as will be seen below, careful choice of τ_π will ensure hat the important features of the spectrum are still visible.

Methods

Nutation experiments were carried out using a home-built pulsed solid-state NMR spectrometer designed to operate at 7.04 T. For the experiments, a singly-series-tuned, parallel-inductively-matched NQR probe was used, sited at least 15 m away from the magnet; estimated stray magnetic fields at this distance were less than the field of the earth. The r.f. coil was typically a 3.4 cm long, 1.25 cm inner diameter (i. d.) 15 turn long-solenoid, evenly-wound with 16 gauge wire. The estimated inductance of this coil was 1.6 μH. For the chlorine work the Q-factor was approximately 120 and was unspoilt; for other nuclei, the Q-factor was reduced to 50 using high power carbon resistors in series with the sample coil. Samples were packed in a 9 mm i.d. glass tube, 9 mm long, and were placed as close as possible to the center of the solenoid. The root-mean-square variation in r.f. homogeneity over the sample volume, from all sources, was estimated at less than 5%. The transmitter was a ENI LPI-10 linear power amplifier, which can produce at least 2 kW power at most of the frequencies used; it was usually necessary to reduce this to 0.5–1 kW to prevent probe arcing towards the end of the nutation experiment, when pulse lengths are over 100 μs. A conventional quarter-wave duplexer was used, cut for a frequency of either 25 MHz (^{81}Br, ^{63}Cu)

or 46 MHz (^{35}Cl); the preamplifier was tuned before the experiment to the appropriate quadrupolar frequency.

For ^{35}Cl, where the simple nutation experiment was used, pulse increments of 2 μs were employed in the t_1 period, giving a sweep width of ± 250 kHz in the ω_1 dimension. 128 t_1 points were taken. 16 transients were accumulated per t_1 value; to avoid drifting of the quadrupolar frequency as a result of sample heating, recycle delays between transients were 8 s. No phase cycling was used. After conventional FT and phasing in the ω_2 dimension, a real FT was carried out in the ω_1 dimension, with zero-filling to 1024 points. Spectra were plotted only for positive frequencies, since the negative half of the spectrum is merely an antisymmetric mirror image of the positive half. The signal in the imaginary channel of the spectrometer after the first FT was usually less than 5% of the real channel signal.

For the copper and bromine spectra, where the nutation echo sequence was used, pulse increments of 1 μs were used in t_1. 256 transients were accumulated per t_1 value, with a delay of 200 ms between transients: 64 t_1 values were collected. The delay before the refocussing pulse (τ) was typically 20 μs. Data acquisition was commenced before the echo maximum; the spectrometer was set on-resonance, and therefore the echo could be phased entirely into a single channel of the spectrometer. In this experiment, both nutation and refocussing pulses were cycled independently through all four phases, as is routinely done in spin-1/2 echo experiments. Phase cycling of the echo pulse is necessary to remove signal arising from z-magnetization remaining after the nutation period which is excited by the second pulse; the remaining phase cycling greatly diminished experimental artifacts. However, if the nutation pulse itself is phase cycled, it is of crucial importance to adjust the power levels for the four phases to be exactly equal.

Data were processed either by shifting the start of the free-induction decay to the echo maximum, and thereafter processing the two-dimensional data set as described above; or by extracting and Fourier transforming t_1 slices through the echo maximum without prior FT in the t_2 dimension. In our hands, these two methods gave virtually identical results; their relative merits will be discussed below.

Sodium chlorite samples were prepared as already described [6]. Glycine hydrobromide was prepared by dissolving glycine (Fisher Chemical Company) in an excess hot concentrated hydrobromic acid, and cooling; the precipitated crystalline hydrobromide was filtered and dried in vacuo. Bis(thiourea)copper(I) chloride was prepared from thiourea and cuprous chloride by published methods [8].

Results

(i) Simple Nutation NQR Spectra

Figure 3 shows two typical nutation NQR spectra from powdered samples: anhydrous sodium chlorite and sodium chlorite trihydrate. These spectra were obtained at NQR frequencies of 51.82 MHz and 51.13 MHz, respectively. The lineshapes show the two high-frequency singularities (ν_2 and ν_3) quite clearly, with just a suggestion of the ν_1 singularity. The η values for these samples are both of the order of 0.5, and the spectra are quite similar in general lineshape to the calculated spectrum for this value of η shown in Figure 1. In this case, as with most ^{35}Cl spectra, we have observed that the simple nutation experiment performs quite adequately; linewidths for ^{35}Cl at room temperature are usually in the range of 2–5 kHz, and so minimal dephasing is experienced in the 20 μs ringdown time of the spectrometer.

(ii) Nutation Echo NQR Spectra

In Fig. 4 we show a series of four nutation echo spectra of the ^{81}Br resonance in glycine hydrobromide. The ^{79}Br NQR frequency of this compound was first reported by Fleck and Weiss [9]; for experimental reasons at the time these experiments were carried out we found it easier to observe ^{81}Br, which incidentally has a higher gyromagnetic ratio and so gives higher nutation frequencies. The spectra were recorded at a quadrupolar frequency of 20.85 MHz. The figure illustrates the effect of the refocussing pulse length on the nutation spectra; short refocussing pulses affect primarily those crystallites with highest nutation frequencies, and so emphasise the ν_3 edge; longer refocussing pulses make the lower frequency part of the spectrum more intense, and thus make it easier to observe ν_2 and ν_1. It should be emphasised, however, that the positions of the singularities are not affected by the refocussing pulse length. From these spectra, we calculate an η of 0.689 ± 0.01 (mean ± 1 standard deviation for five measurements) for this substance. η has not previously been measured for amino acid hydrobromides; for hydroiodides, η values of between

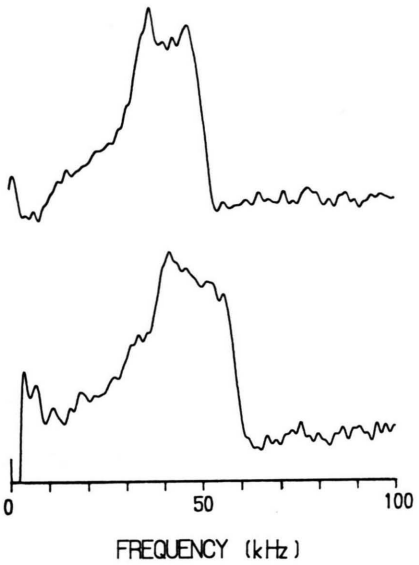

Fig. 3. Top: Nutation spectrum of a powdered sample of anhydrous sodium chlorite, obtained at $H_R = 12.7$ mT. Bottom: Nutation spectrum of powdered sodium chlorite trihydrate, $H_R = 14.4$ mT. The lineshape and the positions of the singularities in both cases indicate $\eta \approx 0.5$.

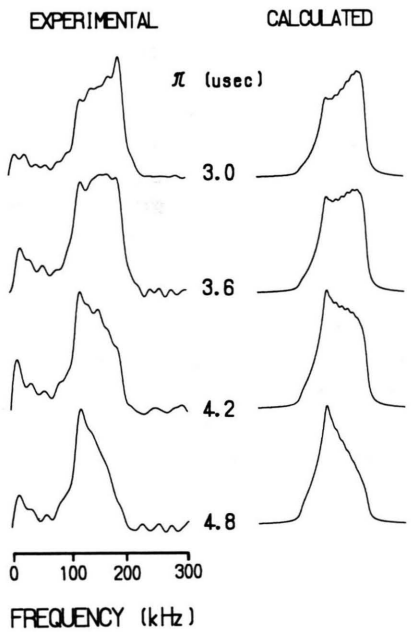

Fig. 4. ^{81}Br Nutation echo spectra of a powdered sample of glycine hydrobromide obtained at $H_R = 17.5$ mT and $\omega_2 = 20.85$ MHz, as a function of the length of the refocussing pulse. The experimental spectra are compared with theoretical lineshapes obtained by numerically integrating Equation (8).

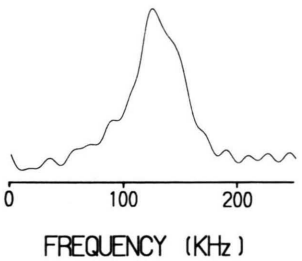

Fig. 5. ^{63}Cu Nutation echo spectra of a powdered sample of bis(thiourea)copper(I) chloride, obtained at $H_R = 14.7$ mT and $\omega_2 = 22.16$ MHz.

0.6 and 1.0 were reported by Fleck and Weiss [9], so the value observed here is reasonable. Similar experiments were carried out for the ^{79}Br resonance of *L*-leucine hydrobromide at 25.35 MHz, giving $\eta = 0.587 \pm 0.02$. This should be compared with η of the crystallographically isomorphous hydroiodide salt, which varies between 0.528 and 0.658 on going from 77 K to 300 K [9].

The bromine NQR resonances of these amino acid salts are typically 10–30 kHz wide, which would be an unfavorable but not impossible case for the simple nutation experiment. Figure 5 shows the nutation echo experiment for ^{63}Cu in bis(thiourea)copper(I) chloride, obtained at 22.16 MHz. This compound has a pure NQR linewidth of the order of 75 kHz at room temperature. The spectrum was obtained with a relatively short refocussing pulse of 3.0 μs. The ν_2 and ν_3 singularities are quite apparent; their frequencies give $\eta = 0.332 \pm 0.025$. It should be noted that the resolution in the nutation dimension is entirely independent of the inhomogeneous linewidth – it depends on the inhomogeneity of r.f. and on the relaxation time of the nucleus in the rotating frame. In this case, as in several others we have observed that the apparent single-crystallite linewidth in the ω_1 dimension is considerably less than that in ω_2.

Discussion

Several different experimental approaches have been detailed here; we shall discuss briefly their relative merits. In the limit of narrow NQR linewidth, the echo version of the experiment gives somewhat less signal than the simple nutation experiment since the signal is only perfectly refocussed at one frequency in the nutation spectrum. This situation might be ame-

liorated by using a composite refocussing pulse; any pulse designed to refocus spin-1/2 nuclei and compensate for r.f. inhomogeneity should be applicable here. The trade-off is that such pulses are usually considerably longer than simple π pulses, and so rotating frame relaxation will tend to diminish the signal during the composite pulse itself.

For wider NQR lines the advantages of the echo sequence are clear. It is not obvious what, if any, are the bandwidth limits of the latter sequence; spin echoes can be obtained for NQR resonances which span many MHz, and the nutation echo sequence should be applicable wherever such echoes can be detected. The ultimate limitation on the sequence will be the homogeneous relaxation of the NQR signal, both during the nutation pulse and during the echo sequence. We have employed time delays (τ), during the echo sequence, of as little as 16 μs at 25 MHz; more attention to acoustic and electronic damping might shorten this to 10 μs or less. The effect of rotating frame relaxation during the nutation pulse can be ameliorated by increasing the rotating frame field strengths in the experiment; our field strengths of 10–20 mT are obtained using power levels of the order 0.5–1 kW and large sample coils. Smaller coils and higher power levels might make r.f. field strengths of as high as 50 mT attainable. Since the nutation frequencies are proportional to the rotating frame field, such high field strengths will increase the spectral width in ω_1 and allow equally well-resolved spectra to be obtained in shorter nutation times. If we incorporate the above improvements, nutation spectra can probably be obtained for samples with T_1's of less than 30 μs.

As discussed above, in processing the NQR echo data, one can either perform a conventional 2D-FT, or simply transform the echo maximum in the t_1 dimension. The latter approach requires less time and effort in data processing; it also has the advantage that broad NQR lines, which are highly spread-out in frequency space, give very narrow spin echoes, in which all the signal intensity is concentrated in one or a few data points. Thus, in order to get the same signal intensity obtained by transforming one or a few slices at the top of the spin-echo, one must add many slices through the broad NQR line in ω_2. Unless sufficiently broad apodization functions are used in ω_2, this will cause extra noise to be added to the signal. However, a cautionary note should be sounded here; if the NQR line is of comparable linewidth to the average nutation frequency, the flanks of the line will be significantly off resonance. Under these circumstances, the nutation frequencies contain an off-resonance term not included in (8) (this term is given by Pratt et al. [8]). The spin-echo will contain both on- and off-resonance contributions, and so a nutation spectrum obtained by transforming the echo maximum will contain a distorted component from the off-resonance signal. In these circumstances it will be safer to do the full 2D-transform and obtain the nutation spectrum only from the central part of the NQR line.

In conclusion, these new experiments appear to represent an easy and reliable way of obtaining the full quadrupolar tensors from spin-3/2 nuclei in powders. In some circumstances (broad NQR lines, and where only powders are available) they may in fact be the only practicable means of determining η. The availability of these methods should enhance the usefulness of NQR in several areas of chemistry and physics.

Acknowledgements

Acknowledgement is made to the Donors of the Petroleum Research Fund, grant number 19107G7, for partial support of this research. Support was also obtained from the National Institutes of Health (GM-39071) and the National Science Foundation Materials Research Initiative (DMR-8706432). We thank Dr. Thomas M. Barbara for ever-helpful discussions, and Professor M. Goldman for sending us a preprint of his paper prior to publication.

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