

# Multiquantum NMR of quadrupole nuclei with strong pulses

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## Abstract

A three-pulse sequence readily generates detectable 3 quantum coherences in  $I = 3/2$ , and 3 and 5 quantum coherences in  $I = 5/2$  spin systems.

The energy differences between the levels  $|m\rangle$  and  $| -m\rangle$  of half-integer spin  $I = 3/2, 5/2, \dots$  quadrupole nuclei in a strong magnetic field are shifted by electric quadrupole interactions only to second order [1]. In many practical cases the second-order modulations are relatively small and can be averaged by various mechanical sample reorientation methods [2]. The averaged energy levels (in rotating coordinates), however, still depend on two unrelated interactions: on the isotropic value of chemical shielding  $\sigma$  (with carrier offset  $\sigma_0$ )

$$E_m = (\sigma + \sigma_{\text{reference}})m = \sigma_0 m, \quad (1)$$

and on the isotropic second-order quadrupole shift

$$E_m = \frac{3}{40} \frac{e^2 Qq/h}{H(2I-1)^2 \nu_L} \left(1 + \frac{1}{3} \eta^2\right) \times [3m^2 - I(I+1)]m \quad (2)$$

where the quadrupole coupling constants are given by  $e^2 Qq/h$  and  $\eta$  and the Larmor frequency  $\nu_L$ . As the two contributions depend differently on transition quantum numbers, the deconvolution of interactions is, in principle, possible from the observation of different transitions.

Several schemes for the generation and detection of multiquantum coherences have been published.

They generally depend on both the interaction parameters as well as the excitation pulse length and amplitude [3]. For universal applications it is preferable to minimize the dependence on the experimental conditions. We demonstrate how a robust three-pulse sequence generates all multiquantum  $^{27}\text{Al}$  spectra of a common NaA zeolite.

A basic pulse sequence is shown in Fig. 1. The multiquantum coherence is generated by two  $\pi/2$  phase shifted pulses, separated by a quadrupole evolution time  $\tau$ . The third pulse converts multiquantum coherence after an evolution period  $t_1$  to the detectable single quantum coherence, proportional to

$$I_\phi = (\cos \Phi I_x + \sin \Phi I_y) \exp(i\omega_{3/2,-3/2} t_2) \quad (3)$$

in the rotating frame.

In a symbolic evaluation<sup>1</sup> we discard any quadrupole nutation [4] and finite spectral coverage effects, assuming the whole spin system, initially described by a density matrix  $I_z$ , receives an ideal  $\pi/2$  flip with each pulse. Neglecting the coherences

<sup>1</sup> Mathematica, Wolfram Research Inc. P.O. Box 6059, Champaign, IL.

depending on first-order quadrupole interactions either during the evolution time  $t_1$  or during acquisition time  $t_2$ , the signal intensity is described by simple expressions such as

$$I_{\phi}(t_1) = \frac{1}{16} \left[ \sin(\omega_{1/2,-1/2} t_1 - \Phi)(1 + 3 \cos \phi) - 9 \sin(\omega_{3/2,-3/2} t_1 - 3\Phi)(1 - \cos \phi) \right] \quad (4)$$

for spin  $I = 3/2$  and

$$I_{\phi}(t_1) = \frac{3}{32} \left[ \sin(\omega_{1/2,-1/2} t_1 - \Phi) \times \left( 1 + \frac{4}{3} \cos \phi + \frac{5}{3} \cos 2\phi \right) - \frac{1}{4} \sin(\omega_{3/2,-3/2} t_1 - 3\Phi) \times \left( 1 + 4 \cos \phi - 5 \cos 2\phi \right) + \frac{25}{4} \sin(\omega_{5/2,-5/2} t_1 - 5\Phi) \times \left( 1 - \frac{4}{3} \cos \phi + \frac{1}{3} \cos 2\phi \right) \right] \quad (5)$$

for spin  $I = 5/2$ . The expressions are invariant with respect to inversion of the second pulse.

The quadrupole mixing angle  $\phi$  is a function of the magnetic field orientation  $\alpha$ ,  $\beta$

$$\phi = 2\pi \frac{3eQ/h \sum_{n=-2}^2 \rho_{2n} D_{n0}^{(2)}(\alpha, \beta)}{2I(2I-1)} \tau \quad (6)$$

(with the usual definitions [5]) and renders multi-quantum excitation generally as a powder function. If the registered signals are narrow in both dimensions, the intensities are determined only by a powder average of coefficients depending on the mixing angle. For a sufficiently long  $\tau \gg h/e^2 Qq$ , the  $\overline{\cos \phi}$  and  $\overline{\cos 2\phi}$  terms thus effectively approach zero and the line intensities from a powder or amorphous sample will be given by constant ratios independent of actual mixing time  $\tau$ , i.e. the line intensity is invariant of the quadrupole coupling parameters (Fig.

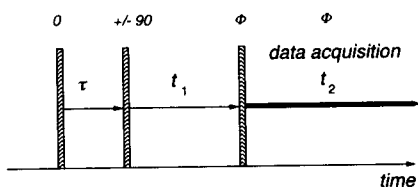


Fig. 1. Principal pulse sequence for generation of multi-quantum spectra.

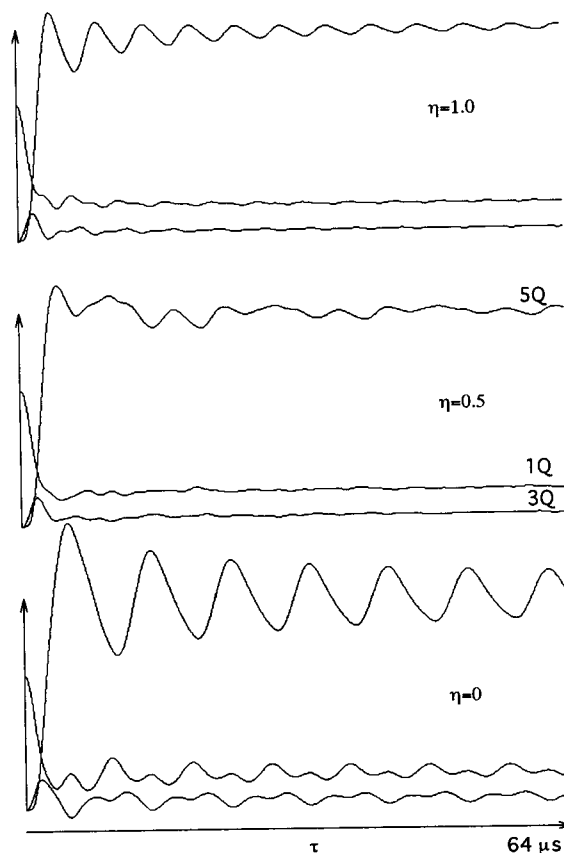


Fig. 2. Dependence of powder averaged relative intensities of 1, 3 and 5 quantum lines for  $\sqrt{1 + \eta^2/3} e^2 Qq/h = 1.424$  MHz,  $I = 5/2$ , on quadrupole evolution time  $\tau$ .

2). All lines assume a well-defined phase if  $\Phi$  is a multiple of  $\pi/2$ , and two-dimensional spectra can be analysed in a pure adsorption mode.

We tested the practical applicability of the above results on several powder samples. Magic angle sample spinning was used so that the residual second-order quadrupole line-broadening was obscured by other line-broadening mechanisms. Experiments were performed on a Bruker AMX-500 spectrometer, equipped with a narrow bore magnet and a standard 300 W power amplifier. A homebuilt MAS probe with rotor diameter 2.75 mm was used. An effective  $\pi/2$  pulse length on the central transition was about 2.5  $\mu$ s on both observed  $^{23}\text{Na}$  ( $\nu_L = 132$  MHz) and  $^{27}\text{Al}$  ( $\nu_L = 130$  MHz). Simulations give for the actual rf field amplitude  $\approx 80$  kHz. The data were col-

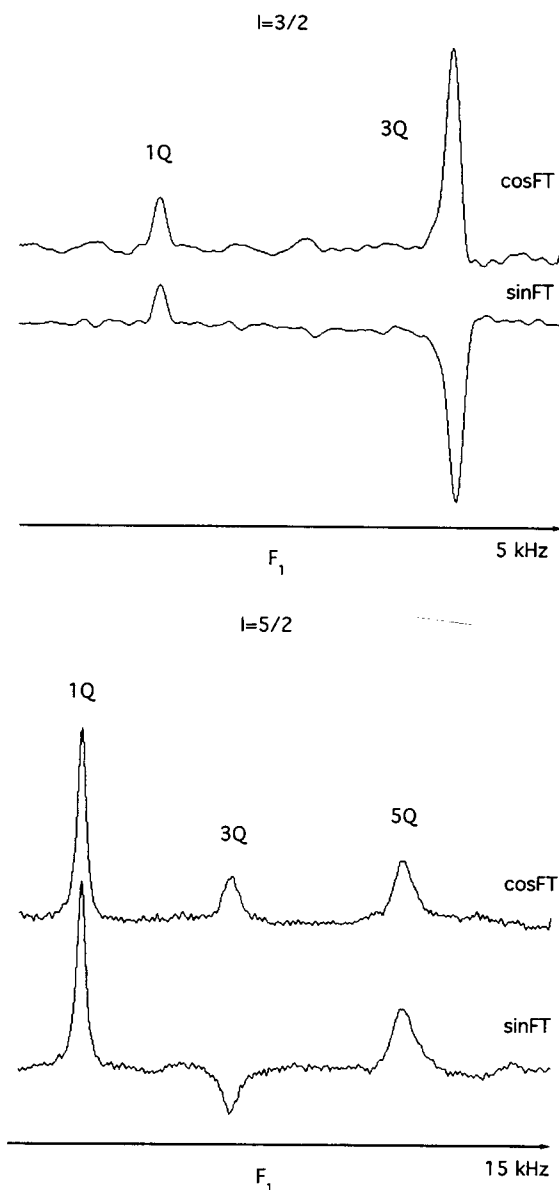


Fig. 3. Cos and sin phase multi-quantum spectra of  $^{23}\text{Na}$  in  $\text{NaNO}_3$ , line offset from carrier  $\sigma_0 = 1290$  Hz, and  $^{27}\text{Al}$  in NaA zeolite, offset from carrier  $\sigma_0 = 1970$  Hz. Only a projection of the  $F_1$  axis is shown.

lected with a few kilohertz carrier offset  $\sigma_0$  from the line, and a systematic increase of the  $t_1$  value. A phase correction for the Fourier transformation in the  $F_2$  dimension was determined by the spectrum with  $t_1 = 0$  and  $\Phi = -\pi/2$ . Instead of complex FT we

used either a sin or cos transform depending on the  $\Phi$  value to speed up data processing in the  $F_1$  dimension. Generally, quantum filtering can be performed with a suitable selection of  $\Phi$  values. This, however, leads to a reduction of the signal-to-noise ratio as the signal is linearly polarized in  $t_1$ . The triple-quantum lines can be inverted without any signal loss, however. All lines are simultaneously positive if  $\Phi = -\pi/2$ , and triple quantum transition lines turn negative if  $\Phi = 0$  (Fig. 3). This inversion of the triple quantum lines may be beneficial for spectral editing and a hypercomplex Fourier transform. We used eightfold phase cycling to average each acquisition (see Table 1).

In the case of spin  $I = 3/2$   $^{23}\text{Na}$  nuclei in  $\text{NaNO}_3$ , where a relatively small [6] quadrupole coupling gives a  $\pm 160$  kHz spectral span in  $F_2$ , relative single and triple quantum line intensities (4) of 1:9 reached a 1:5 ratio experimentally.

A dependence of the relative intensities of the multi-quantum lines on the mixing time  $\tau$  in the case  $I = 5/2$  is shown in Fig. 4. Here the quadrupole coupling 1.4 MHz means a  $\pm 400$  kHz shift for outermost transitions which is significantly more than the rf amplitude. Indeed, the intensity of the associated five-quantum line did not reach the maximum theoretical value but the general behaviour of all

Table 1  
Rf pulse phases (in deg) for eightfold averaged acquisition of multi-quantum spectra. 3rd pulse and receiver: upper row sin FT in  $F_1$  dimension, lower row cos FT in  $F_1$  dimension

1. pulse	2. pulse	3. pulse	Receiver
0	90	0	90
		90	0
0	90	180	90
		270	0
180	270	180	270
		270	180
180	270	0	270
		90	180
0	270	0	90
		90	0
0	270	180	90
		270	0
180	90	180	270
		270	180
180	90	0	270
		90	180

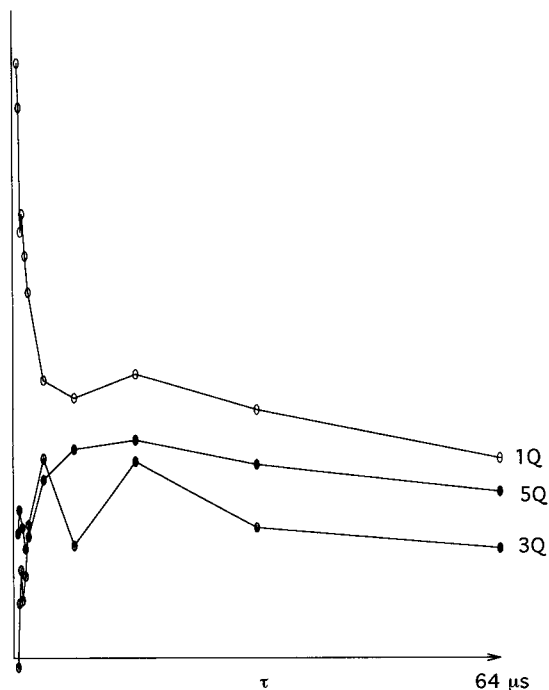


Fig. 4. Experimental relative intensities of multiquantum  $^{27}\text{Al}$  lines in NaA zeolite at various  $\tau$  values.

lines with increasing mixing time is still in qualitative agreement with predictions. The intensities depend marginally on mixing time  $\tau$  after an initial transient. The intensity of the multiquantum lines was possibly reduced further due to the sample spinning used, as generally a different collection of

spins receives the ideal third pulse due to rotor movement during  $t_1$ . The increase in the rf pulse amplitude decreases the difference between the measured and theoretical multiquantum line intensities. The particular value of coupling constant was evaluated self-consistently from 2D multiquantum spectra, using expressions (1) and (2).

This work illustrates a relatively general generation of multiquantum spectra with three strong pulses. Introducing additionally suitable sample reorientation for averaging of the second-order effects, a true 2D high-resolution NMR spectroscopy of quadrupole nuclei in solids can be realized. The correlated presentation of isotropic chemical and second-order quadrupole shifts may be applicable for analyses of non-rigid solid structures.

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