

# Distributions of the Quadrupolar and Isotropic Chemical Shift Interactions in Two-Dimensional Multiple-Quantum MAS NMR Spectra

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**The distributions of both the quadrupolar and the isotropic chemical shift interactions are shown to give multiple-quantum MAS spectra that remain tilted after shearing. For both types of distribution, the theoretical slopes, formed by the resulting distribution of the centers of gravity of the signals, are calculated.** © 1998 Academic Press

**Key Words:** multiple-quantum MAS; distributions; shearing.

The recently described multiple-quantum magic-angle spinning (MQMAS) NMR experiment provides a way of obtaining two-dimensional high-resolution spectra for quadrupolar nuclei of half-integer spin ( $I$ ). The MQMAS technique, by selecting the  $2m$ - and 1-quantum transitions, exploits the dependence of the second-order quadrupolar shift on the angular momentum quantum number  $m$ . The projections of the two-dimensional MQMAS spectrum onto its two axes give the one-dimensional 1- and  $2m$ -quantum spectra, and an isotropic spectrum can be obtained by a projection of the sheared spectrum. The aim of this communication is to demonstrate that a distribution of the quadrupolar interaction (or of the isotropic chemical shift) gives rise to a two-dimensional spectrum that remains tilted after shearing. Such effects have already been observed in MQMAS spectra of glass or amorphous containing materials (2, 3) but have not been explained.

Amoureux (4) has described the resonance frequencies ( $\nu_{\pm m}$ ) of symmetrical transitions ( $-m, +m$ ) for a quadrupolar nucleus with an infinite rotation speed around an axis  $\theta$  tilted from the static magnetic field. Assuming that  $\theta$  is the magic angle, the resonance frequencies  $\nu_{\pm m}$  can be written (in units of hertz) as

$$\nu_{\pm m} = -\frac{\lambda^2}{\nu_0} \{A_{I,m} + P \times B_{I,m}\} \quad [1]$$

with

$$A_{I,m} = \frac{3}{20} m \frac{I(I+1) - 3m^2}{I^2(2I-1)^2},$$

$$B_{I,m} = m \frac{18I(I+1) - 34m^2 - 5}{4I^2(2I-1)^2} \quad [2]$$

and

$$\lambda^2 = \left(\frac{e^2qQ}{h}\right)^2 \left(1 + \frac{\eta^2}{3}\right). \quad [3]$$

$P$  is a function of the Euler angles expressing the rotor frame with respect to the quadrupolar principal axis system and of the asymmetry parameter  $\eta$ ; it gives rise to the infinite-speed MAS powder pattern. Equation [1], calculated for the  $2m$ - and 1-quantum transitions and combined with the frequencies derived from the Zeeman Hamiltonian, gives

$$\begin{cases} \nu_{\pm 1/2} = \nu_{iso} - \frac{\lambda^2}{\nu_0} \{A_{I,1/2} + P \times B_{I,1/2}\} & [4a] \\ \nu_{\pm m} = 2m\nu_{iso} - \frac{\lambda^2}{\nu_0} \{A_{I,m} + P \times B_{I,m}\} & [4b] \end{cases}$$

The system of Eq. [4] describes the two correlated spectra (the summations of the two-dimensional spectrum projected onto the two axes) obtained in a multiple-quantum experiment; it is a representation of the two-dimensional spectrum. In the  $2q$  quantum dimension ( $q = 1/2$  or  $m$ ), the signal is described by the classical infinite-speed MAS powder pattern ( $P$ ) scaled by a factor  $B_{I,q}$ , and the center of gravity of the signal is at  $2q\nu_{iso} - A_{I,q}\lambda^2/\nu_0$ . The term  $A_{I,q}\lambda^2/\nu_0$  is the second-order shift in the  $2q$ -quantum dimension. The system [4] can be expressed in the following form:

$$\begin{cases} \nu_{\pm 1/2} = \nu_{iso} - \frac{\lambda^2}{\nu_0} \{A_{I,1/2} + P \times B_{I,1/2}\} & [5a] \\ \nu_{id} = \nu_{\pm m} - \frac{B_{I,m}}{B_{I,1/2}} \nu_{\pm 1/2} = C_{I,m}\nu_{iso} + \frac{\lambda^2}{\nu_0} D_{I,m} & [5b] \end{cases}$$

with

$$C_{I,m} = 2m - \frac{B_{I,m}}{B_{I,1/2}} \quad \text{and} \quad D_{I,m} = \frac{B_{I,m}}{B_{I,1/2}} A_{I,1/2} - A_{I,m}. \quad [6]$$

Since the second equation [5b] of the system [5] is independent

TABLE 1

Slopes  $S_{I,m}^Q$  of the Distribution of the Center of Gravity in Sheared MQMAS Spectra in Which the Quadrupolar Interaction Is Distributed

$I$	$m$				
	1/2	3/2	5/2	7/2	9/2
3/2	0	-20/9			
5/2	0	-5/6	-25/6		
7/2	0	-4/9	-20/9	-56/9	
9/2	0	-5/18	-25/18	-35/9	-25/3

of  $P$ , a spectrum independent of the orientation of the crystallites is obtained, so Eq. [5b] defines an isotropic dimension. The signals in the two-dimensional spectrum associated with the system [5] are parallel to the 1-quantum dimension. The passage of the system [4] to the system [5] is known as shearing and the factor  $B_{I,m}/B_{I,1/2}$  is the shearing factor often referred in the literature as  $k$ . We note that the isotropic dimension is not scaled by a factor  $1/(k+1)$ , as some authors indicate, in reference to the DAS experiments (5). Now consider the center of gravity ( $\nu_{\pm 1/2}^G$ ;  $\nu_{id}^G$ ) of the signal in the sheared spectrum:

$$\left\{ \begin{array}{l} \nu_{\pm 1/2}^G = \nu_{iso} - \frac{\lambda^2}{\nu_0} A_{I,1/2} \\ \nu_{id}^G = C_{I,m} \nu_{iso} + \frac{\lambda^2}{\nu_0} D_{I,m} \end{array} \right. \quad [7a]$$

$$\left\{ \begin{array}{l} \nu_{\pm 1/2}^G = \nu_{iso} - \frac{\lambda^2}{\nu_0} A_{I,1/2} \\ \nu_{id}^G = C_{I,m} \nu_{iso} + \frac{\lambda^2}{\nu_0} D_{I,m} \end{array} \right. \quad [7b]$$

It is clear from the system [7] that if the  $\lambda$  parameter, describing the quadrupolar interaction, is distributed, its distribution in the 1-quantum dimension is scaled by  $A_{I,1/2}$  and by  $D_{I,m}$  in the isotropic dimension. Consequently in the two-dimensional sheared spectrum, the center of gravity is distributed along a line of slope  $S_{I,m}^Q$  that is expressed as

$$S_{I,m}^Q = -\frac{D_{I,m}}{A_{I,1/2}} = \frac{20m(1-4m^2)}{36I(I+1)-27} \quad [8]$$

This slope  $S_{I,m}^Q$  is independent of the quadrupolar interaction and therefore cannot give information on the strength or on the type of the distribution. However, the signal in the isotropic dimension allows a measurement of the distribution of  $\lambda$  to be made. The different values of  $S_{I,m}^Q$  are reported in Table 1.

The same arguments are valid for distributions in the isotropic chemical shift. If the isotropic chemical shift is distributed, the center of gravity of the signal lies on a line of slope  $S_{I,m}^{ics}$  that can be expressed as

$$S_{I,m}^{ics} = C(I, m) = \frac{34m(4m^2-1)}{36I(I+1)-27} = -\frac{17}{10} S_{I,m}^Q \quad [9]$$

The slope  $S_{I,m}^{ics}$  is independent of the distribution parameters, but the isotropic spectrum gives information on these parameters.

Figure 1 shows the  $^{27}\text{Al}$  triple-quantum MAS spectrum of the crystalline 2:1-type mullite after shearing, recorded with the two-pulse sequence (6). The quadrupolar interactions of the aluminum atoms in this material are known to be strongly distributed (7). The sheared spectrum exhibits tilted signals that are close to the predicted line (dashed line) of the distribution of the center of gravity. We note that the tilt of the sidebands appears closer to the predicted line than the central peaks. This may be attributed to the fact that the sidebands, because of their low intensities, appear narrower, and therefore their tilt is more nearly equal to the tilt of the distribution of the center of gravity. The marked asymmetry in sideband intensities may be attributed to a rotational effect induced during radio-frequency pulses (8).

Numerous low-ordering systems such as clays, amorphous systems, glasses, or glass ceramics experience important distributions of the quadrupolar and isotropic chemical shift interactions. These materials are directly concerned by the phenomenon described here; we are currently working on the

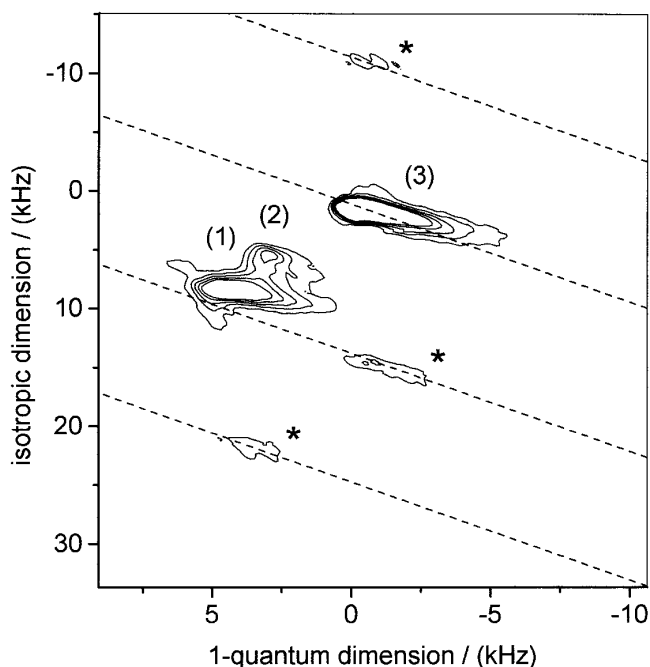


FIG. 1. Sheared 3QMAS  $^{27}\text{Al}$  spectrum of 2:1-type mullite of composition  $\text{Eu}_{0.02}\text{Al}_{4.78}\text{Si}_{1.2}\text{O}_{9.6}$  recorded on a Varian 300 Unity-plus spectrometer (7.04 T), with a radiofrequency field strength equivalent to 70 kHz. The sample was packed in a zirconia rotor and spun at the magic angle, at 12 kHz. Recycling time was 0.2 s and 576 transients were recorded for the  $211 \times 192$  hypercomplex ( $t_1 \times t_2$ ) points. Chemical shifts are reported with respect to a molar solution of  $\text{AlCl}_3$ . No broadening function has been applied. The sites (1) and (2) are assigned to  $[\text{AlO}_4]$  tetrahedra, the site (3) to  $[\text{AlO}_6]$  octahedra; spinning sidebands are labeled by an asterisk. Dashed lines report, in the case of a distribution of the quadrupolar interaction, the theoretical slope ( $-5/6$ ) predicted for the distribution of the center of gravity of the signal (see text for further elaboration). The contour lines are drawn from a level of 7.5% to a level of 27.5% with increments of 5%.

extraction of the distribution parameters from the isotropic projection.

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