Q-shear transformation for MQMAS and STMAS NMR spectra

Ivan Hung [a], Julien Trébosc [b], Gina L. Hoatson [c], Robert L. Vold [d], Jean-Paul Amoureux [b], Zhehong Gan [a],*

[a] Center of Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, 1800 East Paul Dirac Drive, Tallahassee, FL 32310, USA
[b] Unité de Catalyse et Chimie du Solide, UMR-CNRS 8181, Université de Lille 1, 59652 Villeneuve d'Ascq cedex, France
[c] Department of Physics, College of William and Mary, P.O. Box 8795, Williamsburg, VA 23187-8795, USA
[d] Department of Applied Science, College of William and Mary, P.O. Box 8795, Williamsburg, VA 23187-8795, USA

ARTICLE INFO

ABSTRACT

The multiple-quantum magic-angle spinning (MQMAS) and satellite-transition magic-angle spinning (STMAS) experiments refocus second-order quadrupolar broadening of half-integer quadrupolar spins in the form of two-dimensional experiments. Isotropic shearing is usually applied along the indirect dimension of the 2D spectra such that an isotropic projection free of anisotropic quadrupolar broadening can be obtained. An alternative shear transformation by a factor equal to the coherence level (quantum number) selected during the evolution period is proposed. Such a transformation eliminates chemical shift along the indirect dimension leaving only the second-order quadrupolar-induced shift and anisotropic broadening, and is expected to be particularly useful for disordered systems. This transformation, dubbed Q-shearing, can help avoid aliasing problems due to large chemical shift ranges and spinning sidebands. It can also be used as an intermediate step to the isotropic representation for expanding the spectral window of rotor-synchronized experiments.

1. Introduction

The multiple-quantum magic-angle spinning (MQMAS) [1] and later satellite-transition magic-angle spinning (STMAS) [2] experiments have been developed to refocus the second-order quadrupolar broadening in the form of two-dimensional spectroscopy. The correlation of multiple-quantum or satellite transitions with the central transition of half-integer spins yields tilted ridge-shaped peaks in the 2D spectra. Isotropic spectra free of anisotropic broadening can be obtained by a shear transformation along the indirect dimension of the 2D spectra.

Since the introduction of these experiments, many schemes for improving the efficiency [3–9] and various methods for acquiring absorptive 2D spectra [10,11] have been developed. This contribution addresses a few remaining issues of possible concern. First, rotor synchronization of the evolution period (t_1) is a must for STMAS [12] and is strongly desired for MQMAS [13] in order to enhance peak intensities by overlaying/aliasing spinning sidebands. Rotor synchronization of t_1 limits the indirect spectral window to the spinning frequency, which is often insufficient to cover the chemical shift range especially at high magnetic fields. Peaks outside the window are aliased or folded back hindering spectral interpretation. The second issue concerns spinning sidebands associated with large chemical shift anisotropy and quadrupolar coupling.

With a rotor-synchronized t_1 evolution, spinning sidebands indeed appear only along the direct dimension (F_2). However, isotropic shearing with non-integer factors shifts spinning sidebands so that they appear in the indirect dimension (F_{iso}) as well. These numerous sidebands alias back into the small F_{iso} window complicating the isotropic projection and spectral interpretation.

In this paper, an alternative shear transformation by a factor equal to the coherence level selected during the t_1 period is proposed [14], for example, 3 for triple-quantum (3Q) MAS, 1 for (1Q) STMAS and 2 for double-quantum (2Q) STMAS [15]. This transformation is dubbed Q-shearing because it eliminates the chemical shift, leaving only the second-order quadrupolar-induced shift and anisotropic broadening along the indirect dimension (F_Q) of the Q-sheared spectrum. In some aspects this method bears similarities to recent reports on shearing of multiple-quantum spectra acquired under conditions of 70.12° spinning [16] and double rotation [17]. It will be shown that chemical shift elimination can solve the aforementioned problems effectively. The Q-shear transformation gives a simple and unified representation for MQMAS and STMAS spectra, especially for disordered samples for which isotropic shearing does not necessarily yield high spectral resolution. In the case where isotropic spectra of crystalline samples free of aliasing are desirable, zero-filling in the frequency-domain of Q-sheared spectra is proposed as an intermediate step to the isotropic representation. In this way, the spectral window can be expanded at will such that spinning sidebands appear in an orderly fashion without aliasing/folding. It should be noted that *all shear*

transformations are only changes of representation for the convenience of spectral interpretation; the information content of the spectra (including resolution and signal-to-noise ratio) remains unchanged from its original representation.

2. Isotropic shear and Q-shear transformations

The MQMAS [18] and STMAS [12] experiments rely on the fact that for the different transitions involved in a MAS experiment the expansion coefficients of the second-order quadrupolar interaction are related to each other by certain constant ratios k_q^l [19], where q denotes the experiment type, i.e., the t_1-evolution coherence level. These can be derived from the ratio R_{S,m_S}^l between the expansion coefficients of any single-quantum transition $(m_S + 1/2 \Longleftrightarrow m_S - 1/2)$ and the central transition $(m_S = 0)$,

$$R_{S,m_S}^0 = 1 - \frac{36m_S^2}{4S(S+1)-3}, \qquad R_{S,m_S}^4 = 1 - \frac{68m_S^2}{3[4S(S+1)-3]} \tag{1}$$

where S is the spin quantum number. For example, for a 2Q satellite-transition the ratio is the sum of the central transition and one first-satellite transition $(k_2^l = R_{S,0}^l + R_{S,1}^l)$, for a 3Q transition the sum of the central transition and twice the first-satellite transition $(k_3^l = R_{S,0}^l + 2R_{S,1}^l)$, for 5Q transitions it is equal to the central transition plus twice the first- and second-satellite transitions $(k_5^l = R_{S,0}^l + 2R_{S,1}^l + 2R_{S,2}^l)$. The ratios k_q^l and multiple-quantum numbers selected during t_1 evolution (q) are listed in Table 1 for the MQMAS and STMAS experiments. Only the $l = 0$ and 4 rank terms are listed because the $l = 2$ term is averaged to zero by MAS. The $l = 0$ term only shifts the peak position whereas the $l = 4$ term is responsible for anisotropic broadening. In two-dimensional MQMAS and STMAS spectra, the correlation between two inhomogeneously broadened transitions yields a ridge tilted at slope k_q^4 and centered at $(q \cdot \upsilon_{CS} + k_q^0 \cdot \upsilon_{QIS}, \upsilon_{CS} + \upsilon_{QIS})$ in the (F_1, F_2) coordinates. Here υ_{CS} and $\upsilon_{QIS} = 3P_Q^2[3/4 - S(S+1)]/\{10\upsilon_0[2S(2S-1)]^2\}$ are the chemical and quadrupolar-induced shifts of the central transition in *hertz* along F_2, with $P_Q = C_Q\sqrt{1 + \eta_Q^2/3}$. The ratio of the chemical shift along the two frequencies F_1 and F_2 is equal to the quantum number q during t_1.

In their original representation, the MQMAS and STMAS experiments do not yield an isotropic projection along F_1 or F_2 directly. An isotropic projection can be obtained by two methods. The first and most commonly used method is by shearing 2D spectra along F_1 in the frequency-domain such that the tilted peaks become parallel to the F_2 axis [18,20]; this method is denoted herein as 'isotropic shearing'. Projection onto the new F_1 axis (henceforth called F_{iso}) becomes free of anisotropic broadening yielding an isotropic

spectrum. The other, so-called "split-t_1," method [21,22] is performed in the time domain by including a part of $t_2 = |k_q^4| \cdot t_1$ into the redefined evolution period, such that the echo from refocusing of the anisotropic broadening remains stationary in t_2 while t_1 is incremented. Fourier transformation of "split-t_1" 2D data yields isotropic spectra directly. In principle, the two methods are equivalent according to the similarity theorem of Fourier spectroscopy [23]. In fact, the conventional implementation of frequency-domain shearing is performed by t_1-dependent first-order phasing in the mixed time–frequency domain (t_1, F_2) [20], which translates into a redefinition of the evolution period in the same way as the "split-t_1" method. A detailed comparison of these methods can be found in Ref. [10]. The focus of the present work is on frequency-domain transformation, the time-domain equivalence of Q-shearing is not discussed further here.

Mathematically, isotropic shearing replaces F_1 with F_{iso},

$$F_{iso} = (F_1 - k_q^4 F_2)/(1 + |k_q^4|) \tag{2}$$

while Q-shearing, which replaces F_1 with F_Q, differs only by the slope q

$$F_Q = (F_1 - qF_2)/(1 + |q|) \tag{3}$$

It should be noted that shearing can in principle be carried out on either dimension. In this instance, the F_1 dimension has been chosen for shearing so that spectra along the un-sheared F_2 dimension can be readily compared with, and used to reconstruct, 1D MAS spectra.

3. Labeling and scaling of the sheared F_1 axis

Shear transformations change the appearance of 2D MQMAS and STMAS spectra for easier spectral interpretation. However, for quantitative analysis of the sheared spectra (e.g., using DMFIT [24]), it is important to label the new axis and define scaling factors for the chemical and quadrupolar shifts. These seemingly trivial tasks are complicated by the shear transformation. The scaling factors employed and their rationales are presented below (all discussions in the following are with respect to the F_1 dimension, as F_2 is not altered).

In the original representations, the F_1 spectral window in *hertz* is equal to $SW_1 = 1/dw_1$ where dw_1 is the t_1 dwell time. The first consequence of isotropic shearing is scaling of the spectral window in *hertz* (Eqs. (2) and (3)), which is necessary according to the Nyquist theorem,

$$SW_{iso}(Hz) = SW_1(Hz)/(1 + |k_q^4|) \tag{4}$$

The chemical and quadrupolar-induced shift frequencies (in *hertz*) along F_{iso} become

$$\upsilon_{CS}^{F_{iso}} = [(q - k_q^4)/(1 + |k_q^4|)] \cdot \upsilon_{CS} = \kappa_{iso}^{CS} \cdot \upsilon_{CS} \tag{5}$$

$$\upsilon_{QIS}^{F_{iso}} = [(k_q^0 - k_q^4)/(1 + |k_q^4|)] \cdot \upsilon_{QIS} = \kappa_{iso}^0 \cdot \upsilon_{QIS} \tag{6}$$

The chemical shift scale in *ppm* has been somewhat artificially defined in order to have the same chemical shift in *ppm* along both dimensions for any arbitrary spin value and t_1-evolution quantum number [25]. This is done by dividing $\upsilon_{CS}^{F_{iso}}$ with the apparent Larmor frequency $\upsilon_0 \cdot (q - k_q^4)/(1 + |k_q^4|)$. Such a scaling changes the spectral window in *ppm* to

$$SW_{iso}(ppm) = SW_{iso}(Hz) \cdot (1 + |k_q^4|)/[(q - k_q^4) \cdot \upsilon_0]$$
$$= SW_1(Hz)/[(q - k_q^4) \cdot \upsilon_0] \tag{7}$$

The chemical shift reference in *ppm* remains unchanged, i.e., the carrier/transmitter frequency has the same *ppm* shift in both F_{iso}

Table 1
Indirect dimension evolution quantum numbers (q) and ratios for the 0th- and 4th-rank second-order quadrupolar terms in various STMAS and MQMAS experiments with spin S up to 9/2.

q	1Q STMAS 1	2Q STMAS 2	3QMAS 3	5QMAS 5	7QMAS 7	9QMAS 9
$S = 3/2$ k_q^0	−2	−1	−3	—	—	—
k_q^4	−8/9	1/9	−7/9			
$S = 5/2$	−1/8	7/8	3/4	−25/4	—	—
	7/24	31/24	19/12	−25/12		
$S = 7/2$	2/5	7/5	9/5	−1	−49/5	—
	28/45	73/45	101/45	11/9	−161/45	
$S = 9/2$	5/8	13/8	9/4	5/4	−7/2	−27/2
	55/72	127/72	91/36	95/36	7/18	−31/6