Effects of pulse strength, width, and sample spinning speed on the spectral spin diffusion of multiquantum coherences of spin-\(\frac{3}{2}\) quadrupolar nuclei

Zhihong Liu and Feng Deng

Wuhan Institute of Physics and Mathematics, The Chinese Academy of Sciences, Wuhan 430071, China

Shangwu Ding

Department of Chemistry and Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, 70 Lien-Hai Road, Kaohsiung, Taiwan 80424, Republic of China

(Received 21 July 2003; accepted 10 October 2003)

The effects of radio-frequency pulse strength, width, and sample spinning speed on the spin-diffusion spectrum of half-integer quadrupolar spins in solids have been studied by theoretical, numerical, and experimental investigations. It is revealed that the line shape of the cross peaks changes nonmonotonically with respect to the change of pulse strength, pulse width, or sample spinning speed. It is also found that the sample spinning speed has much more pronounced influence on the spin-diffusion spectral line shape. In many cases of practical importance, the effect of sample spinning must be included in spectral analysis, in contrast to the practice of previous studies. Moreover, this effect can be exploited to further improve the precision in the determination of relative orientation of the electric-field gradient tensors of the exchange partners. © 2004 American Institute of Physics. [DOI: 10.1063/1.1630569]

I. INTRODUCTION

The invention of multiquantum magic-angle-spinning (MQMAS) technique have brought the area of solid state NMR spectroscopy of half integer quadrupolar nuclei (the majority of NMR sensitive nuclei in the periodic table) to a new stage. This technique, by correlating the multiquantum coherences in one dimension with single-quantum coherences in the second dimension, provides a relatively simple method to obtain a high-resolution spectrum of half integer quadrupolar nuclei with satisfactory sensitivity. The prowess and accessibility of this technique rapidly led to applications to various types of systems from minerals and artificially manufactured materials to biological systems. The quadrupolar coupling constant (QCC) and asymmetry parameter (\(\eta\)), i.e., the principal values of the electric-field gradient (EFG) tensor or quadrupolar tensor, can be extracted from an MQMAS spectrum with simple numerical simulation. While these values offer important information on the electronic and geometric structure of a compound under study, the orientation of the EFG tensor, normally described by three Euler angles relative to a molecule-fixed frame (such as a coordinate system defined by certain essential chemical bonds), is not accessible from such a spectrum. From the perspective of structure studies, the orientation of an EFG tensor is equally important as other principal values, QCC and \(\eta\). It is therefore extremely desirable if the orientation of an EFG tensor can also be obtained. Unfortunately, in a typical solid-state NMR experiment with quadrupolar nuclei where a powder sample is normally used, it is impossible to determine the absolute orientation of an EFG tensor because the crystallites of all orientations contribute to the resultant spectrum. If there are two or more quadrupolar nuclei which are dipolar coupled to each other (or via a common “bath” such as protons), however, it is possible for one to determine the relative orientation of two EFG tensors. This can be realized by spin-diffusion or exchange experiment. The orientation information is “encoded” in the characteristic line shape of the cross peaks of the two coupled nuclei. This phenomenon has been studied in spin-\(\frac{3}{2}\) systems for decades (see, e.g., Refs. 43–49 and references therein), but for half integer quadrupolar nuclei there have been very few publications. As demonstrated recently by Wimperis and co-workers, the relative orientation of two coupled sodium nuclei (spin-\(\frac{3}{2}\)) can be uniquely determined by systematically simulating the line shape of the cross peaks. This method has been recently extended to three-dimensional spectra.

However, there are a number of important questions that have not been addressed regarding the spin-diffusion/exchange spectrum of half integer quadrupolar nuclei. The previous studies assumed infinite rf pulses (without considering the finite strength and width of the pulses used). In addition, the effects of sample spinning on the line shape of cross peaks have not been discussed. The purpose of this paper therefore is to study the effects of sample spinning speed, the rf pulse strength, and pulse width on the line shape of a spin-diffusion cross peak. We believe the conclusions drawn here are valuable to further improvement and extension of this method and instructive to its practical applications.
II. THEORETICAL

A. General

In this section, a general treatment of the spin-diffusion spectrum is presented so that the effect of sample spinning and rf pulse strength/width can be considered. Throughout the paper a generic three-pulse spin-diffusion pulse sequence is used, \( P_1-t_1-P_2-t_2-P_3 \) where \( P_1 \), \( P_2 \), and \( P_3 \) are three pulses. We include this effect by explicitly computing the excitation efficiency (\( QC \rightarrow QC \)) of the first pulse (\( QC \rightarrow QC \) creation), the conversion efficiency (\( QC \rightarrow QC \rightarrow QC \)) of the mixing pulse, and the conversion efficiency (\( QC \rightarrow QC \rightarrow QC \)) of the last read pulse. Note that the derivation is closely similar to the treatment of MQMAS spectrum, but the difference is appreciable as shown below.

The relevant Hamiltonian is given by
\[
H = H_{CSA} + H_Q + H_{rf},
\]
where the chemical shift anisotropy interaction for the two exchanging sites is
\[
H_{CSA} = \delta_{1,0}I_1 + \delta_{2,0}I_2
\]
and the rf interaction (only when a pulse is applied) is
\[
H_{rf} = \omega_t (I_1, I_2, \phi, \gamma), \quad \phi = x, y, \quad \text{etc.}
\]
The quadrupolar interaction up to second order is
\[
H_Q = H_Q^{(0)} + H_Q^{(1)} + H_Q^{(2)} + H_Q^{(1)}
\]
which can be written explicitly as

\[
H_Q^{(0)} = \sqrt{\frac{2}{3}} V_{1,0}^Q [3I_{1,2}^Q - I_1(I_1 + I_1)]
\]
\[
H_Q^{(1)} = -\frac{2}{\omega_L} I_{1,2}^Q (4I_{1,2}^Q - 8I_{1,2}^Q - 1)V_{1,2}^Q [V_{1,2}^Q + 2I_{1,2}^Q - 2I_{1,2}^Q - 1)V_{1,2}^Q V_{1,2}^Q],
\]
\[
V_{1,2}^Q = \sum_{m,n=-2}^2 D_m^2 (\omega_{pl}, \theta_M) D_{nm}^2 (\alpha_i, \beta_i, \gamma_i) \rho_{i,2n}^Q, \quad j = 0, \pm 1, \pm 2,
\]
\[
\rho_{i,2n}^Q = \sqrt{6} \omega_i Q_i = \sqrt{6} \frac{e^2 Q_i}{8I_i(2I_i - 1)} \hbar, \quad \rho_{i,2n}^Q = \rho_{i,2n}^Q = \eta_i \omega_i Q_i, \quad i = 1, 2,
\]

where \( D \) is Wigner matrix and the quadrupolar coupling constant is denoted as \( Q_i = eQ V_i / 2I_i(2I_i - 1) \hbar \). where \( V_i \) is the \( z \) component of the \( k \)th (\( k = 1, 2 \)) EFG tensor. We use Euler angles \( \Omega_x(\alpha_1, \beta_1, \gamma_1) \) and \( \Omega_z(\alpha_2, \beta_2, \gamma_2) \) to describe the relative orientation between the principal axis systems (PAS) of two EFG tensors, respectively.

B. Ideal case

Just for completeness, we first summarize the calculation of line shape without considering the pulse or spinning effect (i.e., both are set to infinite). Consider a pair of quadrupolar nuclei (1, 2) in a powder sample of a compound with multiple magnetically nonequivalent quadrupolar nuclei. The relative orientation of the EFG tensors is described by Euler angles \( (\alpha', \beta', \gamma') \). The general expression of the powder line shape of a spin-diffusion spectrum of a pair of quadrupolar nuclei with spin \( S \) is given by

\[
S(\omega_1, \omega_2) = \int d\Omega S(\omega_1 - \omega_{m_1}^{(2)} - \omega_{m_2}^{(2)} - \omega_{m_2}^{(2)} - \omega_{m_2}^{(2)}). \quad (6)
\]

For single-quantum spin-diffusion experiments, \( m_1 = m_2 = 1/2 \) whereas for multiquantum–single-quantum spin-diffusion experiment, \( m_1 > 1/2 \) and \( m_2 = 1/2 \). In Eq. (6), the second-order quadrupolar frequencies are given by

\[
\omega_{m_1}^{(2)} \approx \frac{3C_i}{4I_i(2I_i - 1)}, \quad (8)
\]

\[
A_1 = I(I + 1) - 3m_1^2, \quad (9)
\]

\[
A_2 = 8I(I + 1) - 12m_1^2 - 3, \quad (10)
\]

\[
A_4 = 18I(I + 1) - 34m_1^2 - 5, \quad (11)
\]

and asymmetry factor \( \eta \) and \( Q^i(i = 0, 2, 4) \):

\[
Q^0(\eta) = \left( 1 + \frac{\eta^2}{3} \right), \quad (12)
\]

\[
Q^2(\xi, \theta, \phi, \eta) = \left( 1 - \frac{\eta^2}{3} \right) [D^2_{0,0}(\xi, \theta, \phi) - \frac{\sqrt{2}}{\sqrt{3}} \eta D^2_{0,-2}(\xi, \theta, \phi)].
\]

\[
Q^4(\xi, \theta, \phi, \eta) = \left( 1 - \frac{\eta^2}{3} \right) [D^2_{0,0}(\xi, \theta, \phi) + D^2_{0,-2}(\xi, \theta, \phi)], \quad (13)
\]
\[ Q^4(\xi, \theta, \phi, \eta) = \left( 1 + \frac{\eta^2}{18} \right) D^4_{0,0}(\xi, \theta, \phi) \]
\[ + \frac{\sqrt{10}}{6} \eta [D^4_{0,2}(\xi, \theta, \phi) + D^4_{0,-2}(\xi, \theta, \phi)] \]
\[ + \frac{35}{18 \sqrt{70}} \eta^2 \{ D^4_{0,4}(\xi, \theta, \phi) \}
\]
\[ + D^4_{0,-4}(\xi, \theta, \phi), \]  
\[ (14) \]

where the \( l \)th degree Wigner matrix \( D^l_{p',p}(\alpha, \beta, \gamma) = e^{-i(p \cdot p' + \gamma)} d^l_{p',p}(\beta) \). Under MAS, \( Q^2(\xi, \theta, \phi, \eta) \) would be averaged out and Eq. (7) is rewritten as

\[ \langle \omega^{(2)}_{m_1, -m_1} \rangle = \frac{\alpha^2}{\alpha_L} \{ A^0(1, 1) \} Q^0(\eta) + A^4(1, 1) \]
\[ \times \langle Q^4(\xi, \theta, \phi, \eta) \rangle, \]  
\[ (15) \]

where

\[ \langle Q^4(\xi, \theta, \phi, \eta) \rangle \]
\[ = \left( 1 + \frac{\eta^2}{18} \right) (D^4_{0,0}(\xi, \theta, \phi) + \frac{\sqrt{10}}{6} \eta [D^4_{0,2}(\xi, \theta, \phi) + D^4_{0,-2}(\xi, \theta, \phi)]) \]
\[ + \frac{35}{18 \sqrt{70}} \eta^2 \{ D^4_{0,4}(\xi, \theta, \phi) \}
\]
\[ + D^4_{0,-4}(\xi, \theta, \phi), \]  
\[ (16) \]

where \( \langle \rangle \) stands for powder average.

Sample spinning can be taken into account by two successive rotations, first from PAS to rotor frame and then from rotor to laboratory frame:

\[ D^4_{p, p}(\xi, \theta, \phi) = \sum_m D^4_{0,m}(0, \theta_m, \omega, t) D^4_{m, p}(\alpha, \beta, \gamma). \]  
\[ (17) \]

The average over one spinning period is then carried out in computing a spin-diffusion spectrum:

\[ \langle D^4_{0,p}(\xi, \theta, \phi) \rangle = d^4_{0,0}(\theta_m) \sum_n d^4_{0, p}(\beta) e^{i(n \alpha + p \gamma)}. \]  
\[ (18) \]

Magic angle spinning corresponds to the case where \( \theta = \theta_m(54.736^\circ) \). For the second quadrupolar tensor \( Q_2 \), an extra rotation from the PAS of \( Q_2 \) to that of \( Q_1 \) is needed. Therefore we have

\[ D^4_{0,p}(\xi, \theta, \phi) = \sum_m \sum_n D^4_{0,m}(0, \theta_m, \omega, t) D^4_{m, n} \]
\[ \times (\alpha, \beta, \gamma) D^4_{n, p}(\alpha', \beta', \gamma'). \]  
\[ (19) \]

Average over a spinning period is given by

\[ \langle D^4_{0,p}(\xi', \theta', \phi') \rangle = d^4_{0,0}(\theta_m) \sum_n D^4_{0,p}(0, \beta, \gamma) D^4_{n, p}(\alpha', \beta', \gamma') \]
\[ \times \sum_n D^4_{0, p}(0, \beta, \gamma) D^4_{n, p}(\alpha', \beta', \gamma') \]
\[ = d^4_{0,0}(\theta_m) \sum_n d^4_{0, p}(\beta) d^4_{n, p}(\beta') \]
\[ \times e^{-i(n \alpha + \gamma + p \gamma)}. \]  
\[ (20) \]

C. Exact treatment

To include the possible effects of sample spinning, rf pulse strength, and other factors that might influence the line shape of a spin-diffusion spectrum, it would be best to compute the spectrum exactly using a time-dependent Hamiltonian. In this case, the evolution of a density matrix driven by Hamiltonian \( H(t) \) is usually calculated according to the following approach:

\[ \rho(t + \Delta t_p) = U(t + \Delta t_p) \rho(t) U^{-1}(t + \Delta t_p), \]
\[ U(t + \Delta t_p) = e^{-iH(t)\Delta t_p}D^{-1}(t) e^{-i\Lambda(t)\Delta t_p}D(t), \]  
\[ (21) \]

\[ \Lambda(t) = D(t)H(t)D^{-1}(t), \]

i.e., \( H(t) \) is diagonalized by \( D(t) \). The first pulse is divided into \( J_1 \) steps: \( t_{1,p} = J_1 \Delta t_p \) and the density matrix is calculated according to

\[ \rho\left[(k + 1)\Delta t_p\right] = U\left(k\Delta t_p\right) \rho\left(k\Delta t_p\right) U^{-1}\left(k\Delta t_p\right), \]  
\[ (22) \]

\[ U\left[(k + 1)\Delta t_p\right] = e^{-iH\left(k\Delta t_p\right)\Delta t_p} \]
\[ = D^{-1}\left(k\Delta t_p\right) e^{-i\Lambda\left(k\Delta t_p\right)\Delta t_p} D\left(k\Delta t_p\right), \]

where

\[ \Lambda\left(k\Delta t_p\right) = D\left(k\Delta t_p\right)H\left(k\Delta t_p\right)D^{-1}\left(k\Delta t_p\right), \]  
\[ (23) \]

\[ k = 0, 1, 2, ..., J_1. \]

With appropriate phase cycling, MQC of a given order of \( m \) is chosen which evolves as follows:

\[ \rho_{1,m_1}(t_1) e^{i\omega^\prime_{1,m_1}t_1} + \rho_{2,m_1}(t_1) e^{i\omega_{2,m_1}t_1}. \]  
\[ (24) \]

The second pulse is divided into \( J_2 \) steps: \( t_{2,p} = J_2 \Delta t_p \) and the density matrix evolves according to
\[
\rho(t_{1p} + t_1 + (l + 1)\Delta t_p) = U(t_{1p} + t_1 + l\Delta t_p)\rho(t_{1p} + t_1 + l\Delta t_p)U^{-1}(t_{1p} + t_1 + l\Delta t_p),
\]

\[
U[t_{1p} + t_1 + (l + 1)\Delta t_p] = e^{-iH(t_{1p} + t_1 + k\Delta t_p)\Delta t_p} = D^{-1}(t_{1p} + t_1 + l\Delta t_p)e^{-i\Lambda(t_{1p} + t_1 + k\Delta t_p)\Delta t_p}D(t_{1p} + t_1 + l\Delta t_p),
\]

where

\[
\Lambda(t_{1p} + t_1 + l\Delta t_p) = D(t_{1p} + t_1 + l\Delta t_p)H(t_{1p} + t_1 + l\Delta t_p)D^{-1}(t_{1p} + t_1 + l\Delta t_p),
\]

\[
l = 1, 2, 3, ..., J_2.
\]

The mixing time is divided into \(J_D\) steps with \(\tau_m = J_D\tau_m\). Only the zero-quantum coherences are kept after a sufficiently long mixing period. Following the mixing, the third pulse is applied and the density matrix is changed to

\[
\rho(t_{1p} + t_1 + \tau_m + (n + 1)\Delta t_p) = U(t_{1p} + t_1 + \tau_m + n\Delta t_p)\rho(t_{1p} + t_1 + \tau_m + n\Delta t_p)U^{-1}(t_{1p} + t_1 + \tau_m + n\Delta t_p),
\]

\[
U[t_{1p} + t_1 + \tau_m + (n + 1)\Delta t_p] = e^{-iH(t_{1p} + t_1 + \tau_m + n\Delta t_p)\Delta t_p} = D^{-1}(t_{1p} + t_1 + \tau_m + n\Delta t_p)e^{-i\Lambda(t_{1p} + t_1 + \tau_m + n\Delta t_p)\Delta t_p}D(t_{1p} + t_1 + \tau_m + n\Delta t_p),
\]

where

\[
\Lambda(t_{1p} + t_1 + \tau_m + n\Delta t_p) = D(t_{1p} + t_1 + \tau_m + n\Delta t_p)H(t_{1p} + t_1 + \tau_m + n\Delta t_p)D^{-1}(t_{1p} + t_1 + \tau_m + n\Delta t_p),
\]

\[
n = 0, 1, 2, ..., J_3.
\]

After the third pulse, the calculation is trivial by just retaining the single-quantum coherences. The spectrum is obtained by two-dimensional Fourier transform.

When the dynamical details of spin diffusion are not pursued, there is a time-saving approach to calculate the cross peaks. The two sites can be treated separately. In the period \(P_1-P_2\), each site is treated separately as an ordinary MQMAS spectrum and we have the difference between two density matrices at the end of the second pulse, \((t_{1p} + t_1 + t_{2p})\): \(\Delta\rho_{m_1, QC}(t_{1p} + t_1 + t_{2p}) = \rho_{m_1, 1, -m_1}(t_{1p} + t_1 + t_{2p}) - \rho_{m_1, 2, -m_1}(t_{1p} + t_1 + t_{2p})\)

which is the initial difference of the MQC coherences of the two sites. After the spin diffusion is sufficiently done, we have

\[
\Delta\rho_{m_1, QC}(t_{1p} + t_1 + \tau_m) = 0,
\]

\[
\rho_{m_1, 1, -m_1}(t_{1p} + t_1 + t_{2p} + \tau_m) = \rho_{m_1, 2, -m_1}(t_{1p} + t_1 + t_{2p} + \tau_m) - 0.5\Delta\rho_{m_1, QC}(t_{1p} + t_1 + t_{2p}),
\]

\[
\rho_{m_1, 1, -m_1}(t_{1p} + t_1 + t_{2p} + \tau_m) = \rho_{m_1, 2, -m_1}(t_{1p} + t_1 + t_{2p} + \tau_m) + 0.5\Delta\rho_{m_1, QC}(t_{1p} + t_1 + t_{2p}).
\]

“Mixing” (diffusion/exchange) is clearly seen in the above equation. Then we continue to use the third pulse and \(t_2\) dimension evolution, the same as \(t_1\) evolution:

\[
\rho_{1, -1, QC}(t_{2p})e^{i\omega(21, -1, 21) + \rho_{2, -1, QC}(t_{2p})}e^{i\omega(21, -1, 21)}.
\]

This second approach surely saves much time and therefore should be adopted in current programming. However, the general approach is certainly more precise and more flexible for extension to, e.g., the case of explicit inclusion of dipolar interactions in the first dimension and the mixing period, which is under study at this lab.

### III. EXPERIMENT

Three compounds were chosen for present study:
- \(\text{Na}_2\text{B}_4\text{O}_{7}\cdot\text{2H}_2\text{O}\) (borax) \((\delta_{\text{CS}_1} = 11.4\ \text{ppm}, \ \delta_{\text{CS}_2} = -1.6\ \text{ppm}, \ C_1 = 0.541\ \text{MHz}, \ \eta_1 = 0.449, \ C_2 = 0.849\ \text{MHz}, \ \eta_2 = 0.143)\),
- \(\text{Na}_2\text{SiO}_3\cdot5\text{H}_2\text{O}\) \((\delta_{\text{CS}_1} = 9.0\ \text{ppm}, \ \delta_{\text{CS}_2} = 9.5\ \text{ppm}, \ C_1 = 1.8\ \text{MHz}, \ \eta_1 = 0.75, \ C_2 = 2.8\ \text{MHz}, \ \eta_2 = 0.17)\),
- \(\text{Na}_2\text{MoO}_4\cdot2\text{H}_2\text{O}\) \((\delta_{\text{CS}_1} = -0.9\ \text{ppm}, \ \delta_{\text{CS}_2} = 6.3\ \text{ppm}, \ C_1 = 0.88\ \text{MHz}, \ \eta_1 = 0.23, \ C_2 = 2.68\ \text{MHz}, \ \eta_2 = 0.08)\).

All compounds have two distinct \(^{23}\text{Na}\) sites and the two sites are resolved in ordinary MAS spectrum for borax. For borax, the QCC value is relatively small for both sites; for \(\text{Na}_2\text{MoO}_4\cdot2\text{H}_2\text{O}\), one site has smaller QCC while the other larger; for \(\text{Na}_2\text{SO}_3\cdot2\text{H}_2\text{O}\), both QCC’s are moderately large. With these samples with different quadrupolar coupling constants, the conclusion on the effects of sample spinning and pulse strength on cross peaks is valid for a relatively large range of compounds. The samples were purchased from Aldrich and used without further purification. Similar results for these compounds were observed in both numerical and experimental studies. Therefore only the experimental result of \(\text{Na}_2\text{MoO}_4\cdot2\text{H}_2\text{O}\) is presented in the following section.

Spin-diffusion experiments were performed on a Varian Infinityplus-400 NMR spectrometer with proton operating frequency of 400.12 MHz. The resonance frequency of \(^{23}\text{Na}\) is 105.8 MHz. The pulse sequence used was a typical spin-diffusion pulse sequence consisting of three pulses: \(P_1\) (MQC evolution)-\(P_2\) (mixing)-\(P_3\) (acquisition with coherence pathway \(\pm 3\rightarrow 0 \rightarrow -1\) through proper phase cycling). The hypercomplex acquisition scheme was used to ensure pure absorptive two-dimensional (2D) line shape. The mixing times used were tens or hundreds of milliseconds.
For a typical diffusion spectrum, 80 or more increments were used for the first dimension and 96 or more transients were collected with recycle delay of 1 s for normal MQMAS spectra and 5 s for spin-diffusion spectra. The heteronuclear ($^1$H/$^{23}$Na) decoupling power was set to 90 kHz during evolution and acquisition periods. The strengths of the three pulses were the same and varied from 50 to 100 kHz. The sample spinning speeds were set to 5, 6, 7, 8, 9, 10 kHz, respectively. All experiments were carried out at room temperature.

The simulation was performed on an IBM PC with CPU operating frequency of 400 MHz. The computing programs were based on GAMMA\textsuperscript{50} and SIMPLSON\textsuperscript{51} incorporated in MATLAB. The simulation time for a typical ideal MQMAS or spin-diffusion spectrum was several minutes while that for a typical exact spin-diffusion spectrum was tens of hours. The divisions of Euler angles in powder average were 36, 18, 36, 18, 36, respectively. The symmetrical properties of quadrupolar interaction were fully exploited so that the computing time was significantly saved. The time step used in calculating density evolution during pulses was set to 0.1 $\mu$s. The division of Euler angles and time step length used were verified to ensure sufficient precision in simulated spectra.

IV. RESULTS AND DISCUSSION

The above theoretical procedure was used for investigating the effects of pulse strength, pulse width, and spinning speeds on the line shape of cross peaks. We present the results for two situations in this work: larger (3.05) and lower (1.56) QCC ratios of two spins, for Na$_2$SO$_3$·5H$_2$O and Na$_2$MoO$_4$·2H$_2$O, respectively.

The effect of pulse strength is shown in Fig. 1. The most noteworthy feature of Fig. 1 is that the intensity of each cross peak is not a monotonic function of pulse strength as one would commonly assume at first. It is usually supposed that the larger the pulse strength, the stronger the multiquantum coherences after the first pulse hence stronger cross peaks in a spin-diffusion peak. Bearing in mind that the intensities of the cross peaks depend on the intensity difference of the two exchanging spins at the initial stage of mixing period, we believe that the reasonable physical picture of this phenomenon is that although larger pulse strength creates stronger multiquantum coherences, it does not necessarily creates a larger difference of the intensities of the multiquantum coherence of the two exchanging spins.

The other phenomenon deserving mention in Fig. 1 is that the relative intensities of the two cross peaks also depend rather strongly upon the pulse strength. For instance, the intensity ratio of the two cross peaks changes from about 4.5 at pulse strength of 50 kHz to about 11.2 at 200 kHz (taking volumes of the two peaks as their respective intensity). Again, the ratio is not a monotonic function of pulse strength.

The pulse width has obvious effect on the line shape of cross peaks, as shown in Fig. 2. The width ratio of the first two pulses was fixed to 3 while the last pulse has a fixed width of 20 $\mu$s and pulse strength of 20 kHz. Except for very short pulses, both the overall spectral feature and the intensity ratio of the two cross peaks show significantly weaker dependence on the width than on strength. This should be a good relief for experiments.

Figure 3 clearly shows the effect of spinning speed. Interestingly, not only does the line shape change with the
spinning speed, but also “new peaks” appear under certain spinning speeds. For instance, at speeds 5, 8, 10, 12, 15, 16, and 20 kHz, the cross peaks and their sidebands are “clean” while for other speeds, noiselike, new peaks occur, crowding the contour spectrum. This phenomenon is caused by the overlap of the folded sidebands and the central and unfolded sidebands when the spectral width is not sufficiently large. We show this because in practice, the spectral width cannot be arbitrarily large in order to retain a certain level of resolution and at the same time keep the total experimental time within an acceptable range. Changing the spinning speed lower or higher may help improve the overall feature of the cross-peak line shape.

Although pulse strength, width, and sample spinning speed can have significant influence on the spin-diffusion spectrum, the difference between an ideal spectrum and an exact spectrum can be minimized by proper selection of the these adjustable parameters. Figure 4 shows that with optimal parameters, the exact line shape can be made very analogous to the ideal line shape no matter what the relative orientation of the EFG tensors is. This means that ideal line shape can be used for simulating the relative orientation of EFG tensors if (and only if) optimized experimental parameters are used.

The above observations have also been made by simulations with different QCC ratios (Na₂MoO₄·2H₂O and borax). We here choose, as an example, the sample of Na₂MoO₄·2H₂O; similar conclusions can be drawn for borax. Figure 5(a) shows its spin-diffusion spectra calculated with different pulse strengths and an optimized spinning speed of 10 kHz. Although the change of spectral line shape upon the change of pulse strength is observable, it is obvious that both the diagonal and cross peaks do not show strong dependence on pulse strengths. It implies that, under already optimized spinning speed and pulse width, the setting of pulse strength does not need high precision as long as it is not too weak, in agreement with above results. On the other hand, it means that the spectra obtained with different pulse strengths do not offer a new route to improving the accuracy of the relative orientation of quadrupolar tensors.

The effect of spinning speed on the spin-diffusion spec-
trum of Na$_2$MoO$_4$·2H$_2$O is shown in Fig. 5(b). Although the general spectral features are retained at different spinning speeds, the influence of sample spinning is much more appreciable than that of pulse strength. The most affected portion (the “tail”) is that related to those crystallites with larger effective quadrupolar couplings in a powder sample. It is therefore necessary to include this effect in the simulation because that part of the spectrum is crucial to precise determination of QCC.

The above findings have been confirmed by comparing theoretical and experimental results. As exemplified in Fig. 6, the contrast between the ideal spectrum, exact simulated spectrum, and experimental spectrum is illustrated. Comparing the ordinary MQMAS spectrum given in Fig. 6(a) with the spin-diffusion spectrum Fig. 6(b), the cross peaks are readily identifiable. The spectrum shown in Fig. 6(c) was calculated based on the ideal case [Eqs. (7)–(20)] which did not include the effect of finite pulse strength and spinning speed. The simulated spectra with and without considering the spinning effect show a significant difference and the exact spectrum has better agreement with the experimental spectrum. The relative orientation obtained from the simulation is given by Euler angles ($\alpha' = 90^\circ$, $\beta' = 24^\circ$, $\gamma' = 15^\circ$), in good agreement with previously reported values.

It is somewhat counterintuitive to find that the sample spinning has much more significant influence on cross peaks than pulse strength because at first sight, considering the MQC creation, conversions from MQC to 0QC and 0QC to 1QC are all affected, rather strongly, by rf pulse strength as demonstrated by previous simulations, although, as shown by Amoureux et al., the MQC creation does show dependence on spinning speed. The result of this work, however, quantitatively proves that the cross peaks of a spin-diffusion spectrum is only weakly affected by pulse strength (as long as the pulse strength is in the “reasonable” range, i.e., not too weak) and the line-shape variation is largely determined by spinning speed. To our best knowledge, this result has not been reported nor implied before.

This spinning-speed dependence of cross peaks suggest that the relative orientation of the EFG tensors may be determined with improved precision. Specifically, this phenomenon may be used for improving the accuracy in determining the relative orientation of EFG tensors by acquiring experi-

![FIG. 5](image_url)

**FIG. 5.** (a) The calculated $^2$Na MQMAS spin diffusion cross peaks of Na$_2$MoO$_4$·2H$_2$O at different pulse strengths for the first two pulses (a) 50 kHz, (b) 60 kHz, (c) 70 kHz, (d) 80 kHz, (e) 90 kHz, and (f) 100 kHz. The last pulse strength was fixed at 20 kHz. The pulse widths were 6, 2, and 10 $\mu$s, respectively. The sample spinning speed was 5 kHz. The time step used for calculating the density matrix during pulses was 0.1 $\mu$s. (b) The calculated $^2$Na MQMAS spin-diffusion cross peaks of Na$_2$MoO$_4$·2H$_2$O at different spinning speeds (a) 5 kHz, (b) 6 kHz, (c) 7 kHz, (d) 8 kHz, (e) 9 kHz, and (f) 10 kHz. The pulse strengths were 80, 80, and 20 kHz for the three pulses, respectively. The pulse widths were 6, 2, and 10 $\mu$s, respectively. The time step used for calculating the density matrix during pulses was 0.1 $\mu$s.

![FIG. 6](image_url)

**FIG. 6.** (a) The experimental $^2$Na MQMAS spectrum of Na$_2$MoO$_4$·2H$_2$O. The number of $t_1$ increments was 128 with time step of 25.0 $\mu$s. The recycle delay was 1 s and the spinning speed 9 kHz. (b) The experimental $^2$Na MQMAS spin-diffusion spectrum of Na$_2$MoO$_4$·2H$_2$O with mixing time $\tau_M = 200.0$ ms. The number of $t_1$ increments was 80 with time step of 40.0 $\mu$s. The recycle delay was 5 s and the spinning speed 9 kHz. (c) The calculated $^2$Na MQMAS spin-diffusion spectrum of Na$_2$MoO$_4$·2H$_2$O without considering effects of finite rf pulse strength and sample spinning. (d) The calculated $^2$Na MQMAS spin-diffusion spectrum of Na$_2$MoO$_4$·2H$_2$O considering effects of finite rf pulse strength and sample spinning. The parameters used for spectra (c) and (d) were $\delta_{CS1} = -0.9$ ppm, $\delta_{CS1} = 6.3$ ppm, $\delta_{Q2} = 0.88$ MHz, $\eta_1 = 0.23$, $\delta_{Q1} = 2.68$ MHz, $\eta_2 = 0.08$, $\omega_2 / 2\pi = 105.8$ MHz. For spectrum (d), the rf pulse strengths and spinning speed were set to identical with corresponding experimental values. The time increment used for calculating the density matrix during pulses was 0.1 $\mu$s.
mental spin-diffusion spectra at different spinning speeds and then simulating these spectra.

We mention that in the above simulations, the final pulse was set to fixed values of 20 kHz and 10 $\mu$s for its strength and width, respectively. It is well known that this pulse is for creating single-quantum coherences of the central transition and a “soft” pulse is desired. In principle, it asserts influence on the overall 2D line shape, but as demonstrated in typical MQMAS experiments, the major effect is to change the intensity but not the overall line shape as long as the final pulse is sufficiently soft. Therefore this can be safely neglected in this work.

The fact that the relative orientation of two EFG tensors only depends on local chemical environment but does not depend on the orientation of the crystallites in a powder sample may imply interesting new applications of half integer quadrupolar nuclei. For instance, we may use it as a new probe for exploring the connection between the local structures, dynamics, and properties.

It should also be noted that, in this work, a number of dynamical complexities have been neglected particularly during the mixing time, for instance, the dipolar interactions between the quadrupolar nuclei and other nuclear species, the anisotropic relaxation effects on line shape, etc. These factors may have appreciable effects on the line shape and for certain systems, they even present peculiar experimental challenges. However, to account for these factors is beyond the scope of this work although we believe these questions are worthwhile and may be properly addressed in future work.

V. CONCLUSION

In summary, the theoretical procedure, numerical simulation, and experimental verification for analyzing the general spin-diffusion spectrum of half integer quadrupolar spins in solids are presented. A number of interesting findings have been made and the most significant results are: (i) The pulse strength, width, and spinning speed do have serious influence on the spin-diffusion line shape, implying that the precision can be improved, probably significantly, if these effects are considered in determination of relative orientation of two EFG tensors. (ii) Particularly relevant to practical application is that there are optimal parameters for pulse strength, width, and spinning speed for acquiring a satisfying spin-diffusion spectrum. (iii) The rf pulse width and strengths of the three rf pulses have a much less pronounced effect than spinning speed as long as the rf field is not too weak (e.g., $\approx \sim 10$ kHz) and the pulse widths are not too short [e.g., $\approx \sim (0.6$, $0.2 \mu$s) for the first two pulses, respectively], suggesting that the principal factor that affects the line shape of the cross peaks (hence the precision of relative orientation of the EFG tensors) is the sample spinning speed. It implies that the highest possible spinning speed is desired in this type of experiment. On the other hand, it is possible to use the spin-diffusion spectral line shapes at different spinning speeds to further improve the accuracy in the determination of the relative orientation of EFG tensors. This is under study at this laboratory. We believe that the theoretical framework presented herein and the results drawn from this work can be used for studying more complicated cases such as when more than two coupling partners are involved in spin exchange, 3D version of spin diffusion, and diffusion enhancement by recoupling techniques, etc. The theoretical treatment should be applicable to spin-$^5$$_{2}$, spin-$^7$$_{2}$, and spin-$^7$$_{2}$ systems where more orders of multiple-quantum coherences can be used to produce cross peaks.

ACKNOWLEDGMENTS

This work was supported by the Natural Science Foundation of China (Grant Nos. 20173072 and 20273082), the Hundred Talent Program of CAS, and the National Science Council of the Republic of China (Contract Nos. NSC-90-2113-M-110-010 and NSC-91-2113-M-110-018) as well as the Program for Promoting Academic Excellence of Universities funded by the Ministry of Education of ROC (Contract No. A-91-N-FA01-2-4-5).