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Suppression of sidebands in two-dimensional exchange and MQMAS spectroscopies in solids by variable-speed magic-angle sample spinning

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Abstract

The variable-speed magic-angle sample spinning (VSMAS) technique has been extended to two-dimensional spectroscopy in solids yielding two-dimensional spectra free of spinning sidebands.

Magic -angle sample spinning (MAS) is an important tool in high-resolution solid-state NMR [1,2]. If the spinning speed is less than the inhomogeneous anisotropy tensors, the spectrum splits up into centerbands and sidebands. Sidebands are located on either side of respective centerbands at integral multiples of the spinning speed. Sidebands contain information about the anisotropic tensor values. However, in many cases, only information on the centerbands is required and sidebands are not needed. In such cases, and especially when multiple centerbands are present, sidebands can become a nuisance. The most direct way of avoiding sidebands is fast spinning. As the spinning speed is increased, the sidebands move away from the centerbands and decrease in intensity and, when the spinning speed becomes greater than the anisotropy tensor values, the sidebands disappear, yielding spectra containing only the centerbands. However, this is technically demanding if the anisotropy is very large. Also at very high spinning speeds, cross-polarization becomes less efficient in certain cases [3–5].

Many alternative techniques have been developed for the suppression of sidebands [6–14]. The two most commonly used ones are total suppression of sidebands (TOSS) [7] and sideband elimination by temporary interruption of chemical shift (SELTICS) [12]. These methods cause destructive interference between the Fourier components of the magnetization, which normally give rise to sidebands by suit-

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ably aligning sideband magnetization trajectories of single crystallites [12,15,16]. TOSS uses a series of π pulses [7] while SELTICS uses pairs of RF pulses of equal intensity and opposite phase that suppress the evolution of magnetization during that period [12]. These techniques require precise calibration of pulse widths and delays. Also, they are sensitive to RF inhomogeneity and to the ratio of the size of the tensor to the spinning speed. Depending on this ratio, the centerband intensity can become very small or even negative under certain circumstances [12,15,16]. In TOSS, the delays between the pulses are definite fractions of the rotation period. Therefore, at high spinning speeds, the pulse widths are no longer negligible compared to the delays and hence TOSS becomes less efficient. Although at high spinning speeds, SELTICS is claimed to have a higher efficiency compared to other techniques, the intensity of the centerband compared to normal MAS experiments is attenuated when the anisotropy becomes comparable to the spinning speed [12]. Because of these difficulties, many people prefer to keep sidebands and identify them with asterisks in their spectra [17,18].

Recently a simple method was proposed to disperse sidebands in one-dimensional NMR by varying the spinning speed of the sample during the course of signal averaging [19]. This technique, called variable-speed magic-angle sample spinning (VSMAS), is based on the fact that when the sample spinning speed is changed, the centerbands remain at the same frequencies while the sidebands move. Averaging of signals acquired at different spinning speeds leads to coaddition of centerbands without coadding sidebands. By acquiring enough scans at different speeds, sidebands can be dispersed to noise level. This method, which involves no extra RF pulses, is straightforward, universally applicable and is independent of the widths of the tensors. Also the method can easily be implemented in spectrometers with computer controlled MAS units by using automation programs.

Until now, VSMAS has been applied only to one-dimensional spectra in solids. This method may not be feasible for two-dimensional experiments which involve suppression of sidebands in one dimension and not in the other dimension. Indeed, the time that would be required for changing the spinning speed between the evolution period t_1 and the detection period t_2 is greater than T_1 and T_2 in most cases. However, if sidebands are to be removed from both dimensions of the two-dimensional experiment, then the VSMAS technique can be applied in a straightforward manner. In this Letter, we apply VSMAS to two different two-dimensional methods in solids, namely, two-dimensional chemical exchange spectroscopy and multiple-quantum magic-angle sample spinning (MQMAS) spectroscopy.

Exchange spectroscopy has previously been used to study the tautomeric hydrogen shift in tropolone in the fast spinning regime [20] as well as in the slow spinning regime [21]. In the latter case, sidebands have been suppressed in the t_1 dimension by TOSS, brought back by a time-reversed TOSS and again suppressed in the t_2 dimension by a second TOSS [21]. Even though this experiment works quite well at suppressing sidebands in both dimensions, it has not been widely utilized presumably because TOSS experiments require careful tuning. Fig. 1 shows the exchange spectra of tropolone obtained (a) using low speed (3.5 kHz) MAS and (b) using VSMAS (2–5 kHz). The spinning speed in VSMAS was incremented in 256 regular steps of about 12 Hz during the recycle delay, after each t_1 increment. In this manner, the sidebands are dispersed in the ω_1 domain. A total number of 256 t_1 increments, each with eight scans, were acquired for both experiments. In the MAS spectrum the appearance of a large number of sidebands makes it difficult to distinguish exchange cross-peaks from centerband–sideband cross-peaks while in the VSMAS spectrum the sidebands are suppressed and exchange peaks are clearly observed. Cross-sections (Fig. 2) taken parallel to ω_1 and ω_2 dimensions of the VSMAS spectrum compare favorably with those obtained earlier using the TOSS technique [21], except that the signal to noise ratio is lower in Fig. 2 due to four-fold reduction in experimental time (half the number of scans and half the recycle delay). It may be noted that the VSMAS experiment requires only a 4-step phase cycle for TPPI while the TOSS experiment requires a 16-step phase cycle.

Multiple-quantum magic-angle sample spinning (MQMAS) for obtaining resolved spectra of half-integral quadrupolar nuclei having $I \geqslant 3/2$ has become a powerful and popular technique for studying

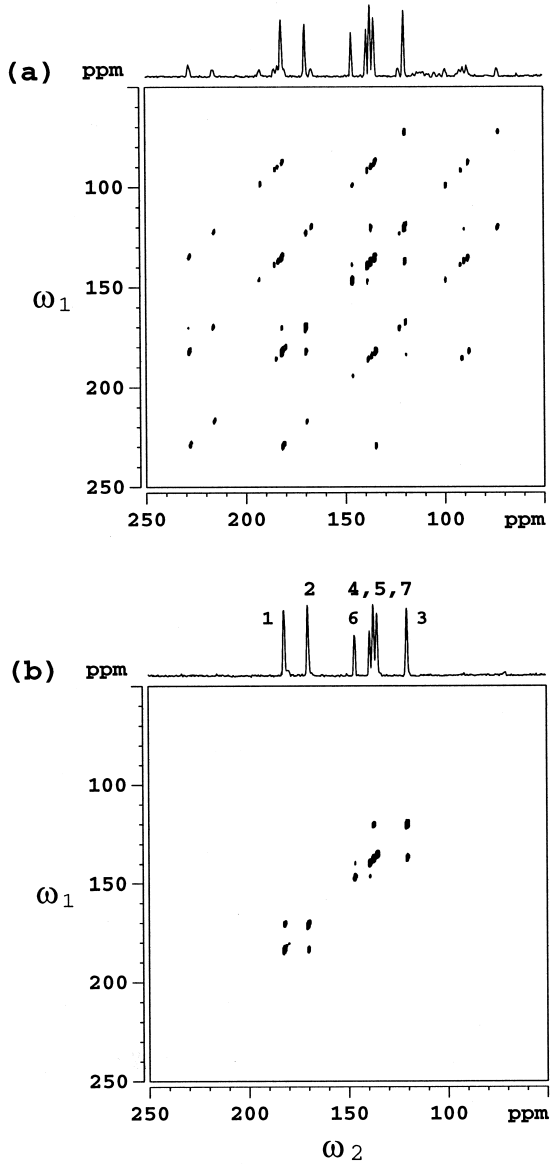

Fig. 1. ^{13}C exchange spectrum of tropolone using (a) MAS at a constant spinning speed of 3.5 kHz and (b) VSMAS. In (b), the spinning speed was varied from 2 to 5 kHz in 256 regular steps of about 12 Hz after every t_1 increment. Both the experiments were carried out at 315 K and use the pulse scheme CP–t_1(^{1}H-decoupled)–$90_{-y}-\tau-90_y-t_2$(^{1}H-decoupled) with recycle delay 30 s, mixing time (τ) 1s and TPPI phase cycle for CP.

quadrupolar nuclei [22]. In this experiment, multiple-quantum coherence is allowed to evolve during the t_1 period, is converted into single-quantum coherence and detected during the t_2 period. An echo is formed during the t_2 period giving rise to a sharp resonance in the ω_1 dimension. Many developments are taking place to improve the sensitivity and resolution of MQMAS experiments. These include the use of higher RF power, higher spinning speed, zero-quantum filtering and modulated RF pulses [23–25]. Multiple spinning sidebands are frequently observed in both dimensions in the 2D MQMAS spectra at multiples of spinning speed. Their number is usually much greater along the multiple-quantum (ω_1) than along the single-quantum (ω_2) dimension. Furthermore, the overall width of the sideband pattern along the ω_1 dimension often exceeds the spectral range expected from direct rotational modulation of the interaction anisotropies during t_1, which is the classical origin of the spinning sidebands in solid-state NMR. It has been shown that these sidebands in the ω_1 dimension arise mainly from rotor-driven reorientations of the first-order quadrupolar tensors of the crystallites during the evolution period resulting in a modulation of the conversion of the multiple- to single-quantum coherence by the second RF pulse [26]. No pulse technique has been developed for removal of sidebands in MQMAS. High spinning speed or rotor synchronization with t_1 incrementation can suppress the sidebands in MQMAS. However, since the spectral width in the t_1 dimension of MQMAS is usually very large, rotor synchronization

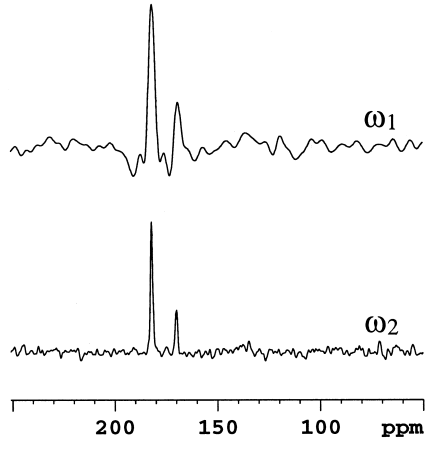

Fig. 2. ω_1 and ω_2 cross-sections at site 1 (181.7 ppm) of Fig. 1b.

also requires a high spinning speed [27]. Fig. 3 shows MQMAS spectra of sodium oxalate with zero-quantum filter obtained (a) using a constant spinning speed of 5 kHz and (b) using VSMAS (MQVSMAS) with a spinning speed varied between 3.5 and 6.5 kHz during the recycle delay after each t_1 increment in 256 regular steps of about 12 Hz. A total number of 256 t_1 points, each with 72 scans, were acquired. The MQVSMAS spectrum (Fig. 3b) is practically free of spinning sidebands. One aim of MQMAS spectroscopy is to identify chemically distinct sites of the same quadrupolar nuclei in a polycrystalline powder. For example, the normal one-dimensional single-quantum spectrum of trisodium-citrate dihydrate yields only a single broad line. The MQMAS at an intermediate speed of 5 kHz has many sidebands (Fig. 3c) making the identification of individual sites difficult. The sidebands are removed by VSMAS (Fig. 3d) yielding clear identification of three sites.

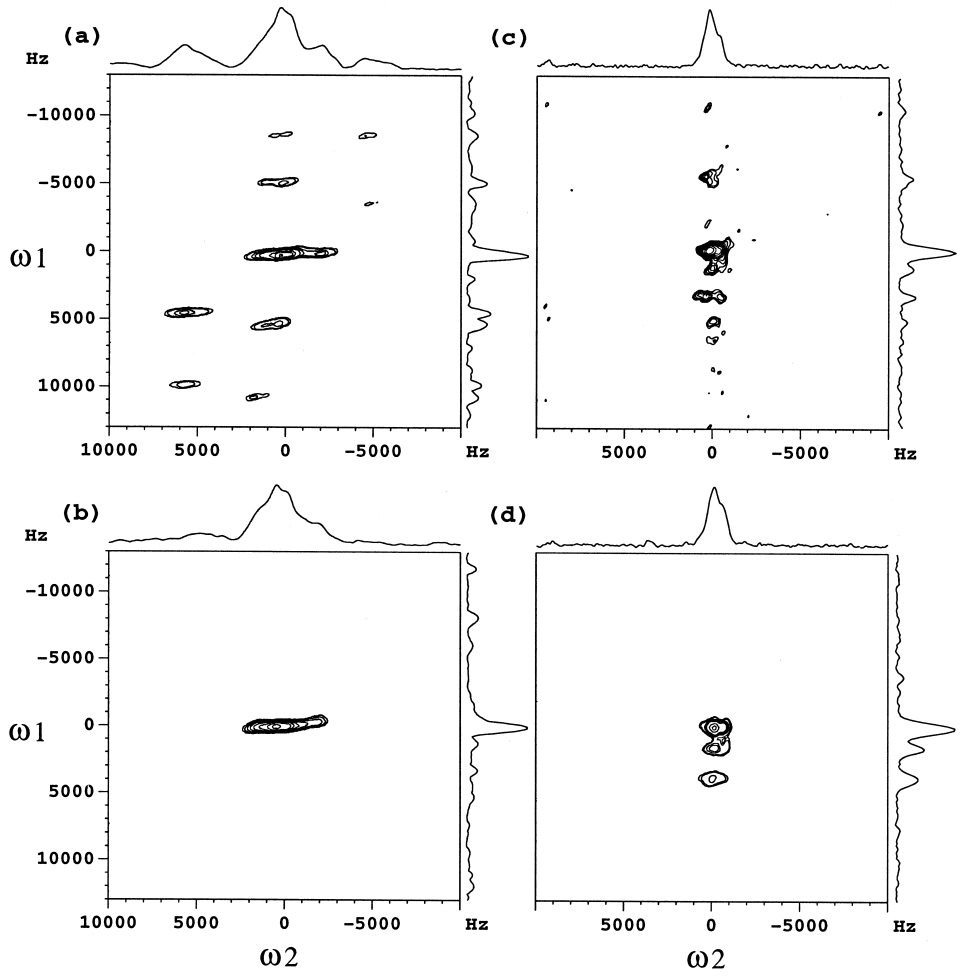

Fig. 3. ^{23}Na MQMAS spectra of sodium oxalate (a) at a constant spinning speed of 5 kHz and (b) with VSMAS. ^{23}Na MQMAS spectra of trisodium-citrate dihydrate (c) at a constant spinning speed of 5 kHz and (d) with VSMAS. In (b) and (d), the spinning speed was varied from 3.5 to 6.5 kHz in 256 regular steps of about 12 Hz. The spectra were obtained using the sequence p_1–t_1–p_2–τ–p_3–t_2. In (a) and (b), the three pulse widths were 8, 2.5 and 25 μs with RF powers 55, 55 and 24 kHz, respectively. In (c) and (d), the pulse widths were 7.5, 2.4 and 28 μs with RF powers 62.5, 62.5 and 28 kHz, respectively. In all the experiments, zero-quantum filtering was utilized during the τ period with $\tau = 10$ μs.

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