Dynamic-angle spinning without sidebands

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By means of rotor-synchronized π-pulses, it is possible to eliminate the spinning sidebands (while retaining their full intensity in the isotropic centerband) that usually arise in dynamic-angle spinning (DAS) NMR. The theory of this approach, dynamic-angle hopping (DAH-180), is described and illustrated with experimental results on quadrupolar nuclei. A magic-angle hopping (MAH-180) version of magic-angle spinning is also possible and can be used in a two-dimensional NMR experiment to produce sideband-free isotropic–anisotropic correlation spectra for spin-1/2 nuclei.

1. Introduction

For spin-1/2 nuclei, the technique of magic-angle hopping (MAH) [1] has been shown to average the chemical shift anisotropy of spin-1/2 nuclei in powdered solids, yielding high-resolution spectra in a manner similar to magic-angle spinning (MAS) but without the presence of spinning sidebands. In MAH, the sample can be reoriented in 120° steps around an axis oriented at the magic angle (54.74°) with respect to the magnetic field. These angles correspond to the vertices of an octahedron and they can also be implemented by combinations of orthogonal 90° steps. A technically simple implementation [2] involves spinning the sample slowly at the magic angle in order to approximate hopping between discrete angles during evolution. In both of these methods, $\pi/2$ pulses are required in order to store the magnetization along the magnetic field while the sample is being reoriented to the next angle. Since only half of the transverse magnetization can be stored by a pair of $\pi/2$ pulses, there is a decrease by a factor of $\sqrt{2}$ in the signal-to-noise ratio for every pair of storage pulses used. In the extension of such hopping techniques to the sample orientations of dynamic-angle spinning (DAS) [3] used for quadrupolar nuclei, the loss of signal-to-noise would be substantial.

In this Letter, we show that by using synchronized π pulses, sideband-free spectra can be obtained in spinning experiments without the loss of intensity caused by storage pulses and without the loss of intensity caused by suppression techniques such as TOSS [4]. For the case of MAS, our approach forms an alternative to the TOSS–deTOSS approach of Kolbert and Griffin [5], recently exploited by Geen and Bodenhausen [6]. Related MAS experiments have recently been performed by Grant and co-workers [7]. For quadrupolar nuclei, the analog to MAH is dynamic-angle hopping (DAH), in which a sample is reoriented rapidly in five 72° steps about an axis oriented at 63.43° with respect to the magnetic field followed by a reorientation of the rotor axis to 0°. These are the orientations defining the vertices of an icosahedron [8]; of course, other orientations could be used (with a minimum of six necessary), consistent with DAS averaging [3]. One way to implement such an experiment is to combine sample spinning with either $\pi/2$ storage pulses (DAH-90) or refocusing π pulses (DAH-180). The latter method is expected to be preferable as to the signal-to-noise ratio, since all components of the evolving magnetization are preserved. A similar method might be useful in removing sidebands arising from the slowly spinning outer rotor in double rotation (DOR) experiments [9].

2. Theory

In a static sample, the secular part of the spin Hamiltonian for the chemical shift anisotropy (CSA) and quadrupolar interaction may be written

$$H = \sum_l \sum_m A_{lm} D_{m0}^{(l)}(\Omega) I_z , \qquad (1)$$

where Ω are the Euler angles which describe the orientation of the magnetic field with respect to the sample, A_{lm} are the spatial tensors which relate the principal axes of a given crystallite to the sample frame, and $D^{(l)}$ is a Wigner rotation matrix of rank $l=0$, 2 or 4. It is well known that sample spinning experiments, such as MAS, DAS, and DOR, can produce high-resolution NMR spectra of powder samples by averaging to zero all relevant $D^{(l)}$ of rank greater than zero. However, such techniques also introduce spinning sidebands in the spectra due to the time dependence of the Hamiltonian under sample rotation [10]. Although these sidebands can be suppressed [4], it would be preferable to eliminate the spinning rate dependence of the Hamiltonian altogether, thereby preserving the full spectral intensity in the isotropic centerband.

Sample spinning experiments are in general an implementation of the following idealized experiment. Suppose the sample were to be instantaneously reoriented between the vertices of an octahedron or an icosahedron and allowed to evolve for equal times at each vertex. The effective Hamiltonian governing this experiment may be written as the sum of static Hamiltonians at each orientation,

$$\langle H \rangle = \sum_l \sum_m A_{lm} \langle D_{m0}^{(l)}(\Omega) \rangle I_z = A_{00} I_z . \qquad (2)$$

Under octahedral reorientations, $D^{(l)}$ with $l=2$ (as in CSA) are averaged to zero, while under icosahedral reorientations, $D^{(l)}$ with $l=2$ and $l=4$ (as in both CSA and the second-order quadrupolar interaction) are averaged to zero [8].

Of course, it is not feasible to hop instantaneously between orientations in this fashion. One possible implementation is the magic-angle hopping (MAH) experiment performed by Szeverenyi et al. [1] which has been used to average chemical shift anisotropy. A powder sample is rotated by 120° hops about an axis inclined at the magic angle (54.74°) with respect to the magnetic field while storing the magnetization along the direction of the magnetic field with $\pi/2$ pulses during the reorientation. A second method for implementing MAH is to spin the sample slowly about an axis oriented at the magic angle and again use $\pi/2$ storage pulses (see fig. 1a) to interrupt evolution so that the rotor effectively "hops" between 120° orientations [2]. Both of these experiments involve two-dimensional spectroscopy since a separate experiment is required for each evolution time.

As an alternative, consider the use of π pulses in the following two-dimensional experiment to average CSA performed over N rotor periods of length τ_r, where N is an even integer, $(t_1/6)$ and Δ are delays with $\Delta = (N\tau_r/6) - (t_1/6)$, π and $\pi/2$ are pulses, and t_2 is the acquisition period,

$$\frac{\pi}{2} - \frac{N\tau_r}{2} - \left(\frac{t_1}{6} - \pi - \Delta - \pi \right)_2 - \frac{t_1}{6} - \pi - \Delta - t_2 . \qquad (3)$$

Under this pulse sequence, the Hamiltonian effectively changes sign each time a π pulse is applied. Therefore, the evolution during the Δ periods will directly cancel the complementary evolution in the first $N\tau_r/2$ period and is thereby refocused. The remaining evolution periods will consist of two sets of evolutions with relative phases of 0°, 120° and 240°. As before, these will cancel and yield and isotropic Hamiltonian. In contrast to using $\pi/2$ storage pulses, the only loss in signal-to-noise is due to π pulse imperfections.

These pulse sequences of fig. 1 may also be utilized to average the evolution under a quadrupolar Hamiltonian. In this case, evolution at the six vertices of an icosahedron are required. Experimentally, this may be achieved by rotating a sample in 72° steps about an axis oriented 63.43° relative to the magnetic field, followed by reorientation of the spinning axis to 0°, using either $\pi/2$ storage pulses (fig. 1a) or preferably π pulses (fig. 1b) during the reorientation. A pulse sequence which implements the latter, which we term dynamic-angle hopping (DAH-180), is given below, with $\Delta = (N\tau_r/10) - (t_1/12)$ and t_{hop} is the time needed to reorient the sample spinning axis from 63.43° to 0°. This particular set of DAS angles requires that 5/6 of the evolution time be spent at 63.43°,
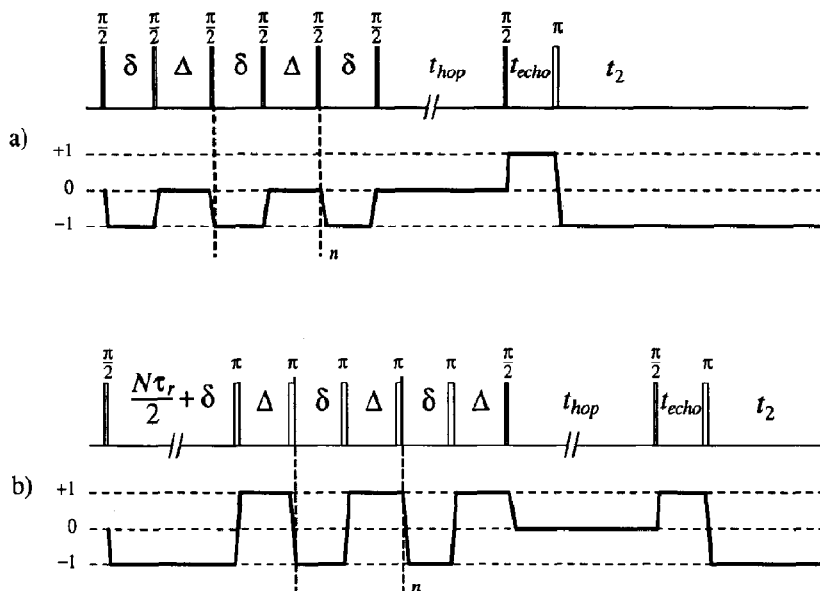
Fig. 1. Pulse sequences for producing sideband-free magic-angle and dynamic-angle spinning spectra. t_{hop} is the time required to hop the rotor axis between angles, and t_{echo} is the spin echo time. The sequences between the dashed lines are repeated n times. The experiment is performed over N rotor cycles with a rotor period of τ_r. (a) DAH-90 ($n=3$, $\delta=t_1/12$, $\Delta=(N\tau_r/10)-(t_1/12)$) or MAH-90 ($n=1$, $\delta=t_1/6$, $\Delta=(N\tau_r/6)-(t_1/6)$) pulse sequence and coherence transfer pathway. (b) DAH-180 ($n=3$, $\delta=t_1/12$, $\Delta=(N\tau_r/10)-(t_1/12)$) or MAH-180 ($n=1$, $\delta=t_1/6$, $\Delta=(N\tau_r/6)-(t_1/6)$) pulse sequence and coherence transfer pathway.

$$\frac{\pi}{2}-\frac{N\tau_r}{2}-\left(\frac{t_1}{12}-\pi-\Delta-\pi\right)_4-\frac{t_1}{12}-$$

$$\pi-\Delta-\frac{\pi}{2}-t_{hop}-\frac{\pi}{2}-\frac{t_1}{6}-t_2. \qquad (4)$$

As with the corresponding MAH sequence (3), the Hamiltonian changes sign with each π pulse and, therefore, the evolution during the Δ periods will be refocused by a complementary evolution in the first $N\tau_r/2$ period. The remaining (uncancelled) evolution consists of two sets of $t_1/12$ periods with relative rotor phases of $0°$, $72°$, $144°$, $216°$ and $288°$. When these rotations about the $63.43°$ axis are combined with the evolution about the $0°$ axis following t_{hop}, the net Hamiltonian is again isotropic. Again, the total evolution time will be t_1 and a two-dimensional Fourier transform with respect to t_1 and t_2 will give a sideband-free high-resolution spectrum in the ω_1 dimension. In the DAH-180 experiment, the maximum value for $t_1/12$ is $N\tau_r/10$; therefore, the maximum acquisition length in the t_1 dimension is $6N\tau_r/5$.

3. Experimental

The ^{87}Rb experiments were performed at 9.4 T (130.89 MHz) and the ^{207}Pb experiments were performed at 11.7 T (104.25 MHz) using a home-built DAS probe described in ref. [11]. The details of the DAS experiment including pulse sequences and phase cycles have been described previously [12,13]. The pulse sequences used for the DAH and MAH experiments are shown in fig. 1 along with the corresponding coherence transfer pathways. In fig. 1a only the first $\pi/2$ pulse along with the first storage pulse of every pair is phase cycled. In fig. 1b all $\pi/2$ pulses are phase cycled. The π pulses were not phase cycled.

^{87}Rb DAH-180 and DAS experiments were performed on Rb_2SO_4. The magic angle was set by detecting ^{81}Br present in a KBr internal standard. The spectra were referenced relative to a 1 M $RbNO_3$ solution. Rubidium $\pi/2$ pulse widths selective for the central transition were 4.7 μs. A recycle delay of 2 s was used after the hop back to the initial angle to allow for relaxation and to allow the spinning speed to

stabilize; this delay is important, since significant variations in spinning speed may lead to a loss of signal-to-noise and resolution. The hop time was 55 ms. For both DAH-180 and DAS experiments, 256 complex points were acquired in t_2. For the DAH-180 experiment, 49 points were acquired in t_1, and for the DAS experiment, 68 points were acquired in t_1. The dwell times were 16 µs in t_2 and 3.6 µs in t_1, with 512 transients acquired for each t_1 point. Whole-echo acquisition was used to obtain pure-absorption mode 2D spectra [13,14]. For the DAS experiment, the spinning frequency was 1.8 kHz while the rotor reorientation periods used for DAH-180 were 199.6 µs corresponding to a spinning frequency of 5.0 kHz. The rotor period was monitored during the DAH experiment by observing the piezoelectric signal from the vibrations of the spinner detected with a wire attached to the stator housing. The DAH-180 experiment was performed over eight rotor cycles ($N=8$).

MAH-180 experiments with a hop to 0° were performed on the [207]Pb resonance in PbNO$_3$, using $\pi/2$ pulse widths of 11 µs, a recycle delay of 10.2 s, a hop time of 75 ms, 256 complex points were acquired in t_2 and 64 points were acquired in t_1 with dwell times of 40 µs in t_1 and 50 µs in t_2. 128 transients were acquired with whole-echo acquisition to obtain pure-absorption mode 2D spectra. The rotor period was 1326.67 µs and the experiment was performed over two rotor cycles ($N=2$). The MAH-180 without a hop experiment was taken with pulse sequence (3) with a rotor period of 3360 µs.

4. Results and conclusions

The projection of the isotropic dimension of the standard DAS experiment is shown in fig. 3a. The two [87]Rb site resonances occur at −25 ppm and 28 ppm in agreement with previous studies at 9.4 T [12]. The site at −25 ppm has a large number of sidebands, reducing the intensity of the isotropic line. The 2D spectrum of rubidium sulfate taken with the DAH-180 sequence of fig. 1b is shown in fig. 2. The projection of the isotropic dimension is shown in fig. 3b. As expected, a sideband-free spectrum in the isotropic dimension is observed, correlated with an anisotropic dimension consisting of the separated static powder patterns for the individual sites. Since de-
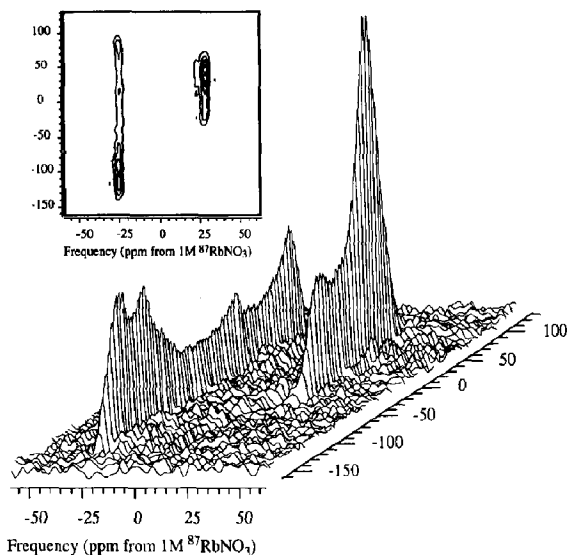

Fig. 2. DAH-180 spectra of [87]Rb in Rb$_2$SO$_4$ taken at 9.4 T using the sequence in fig. 1b. The spectra are free of spinning sidebands while retaining the full intensity of both sites. Both contour and stacked plots are shown.
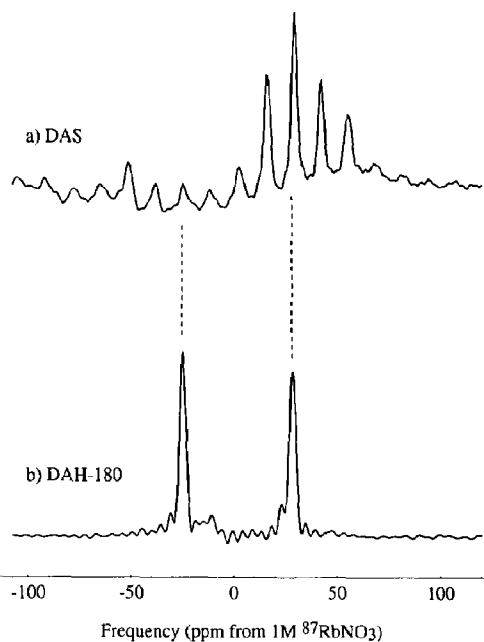

Fig. 3. Comparison of DAS spectra exhibiting sidebands and DAH-180 spectra. Projections along the isotropic dimensions of (a) the [87]Rb DAS spectrum and (b) the DAH-180 spectrum (fig. 2) of Rb$_2$SO$_4$ taken at 9.4 T at a spinning frequency of 1.8 kHz. Isotropic peaks with full intensity appear at −25 ppm and 29 ppm.
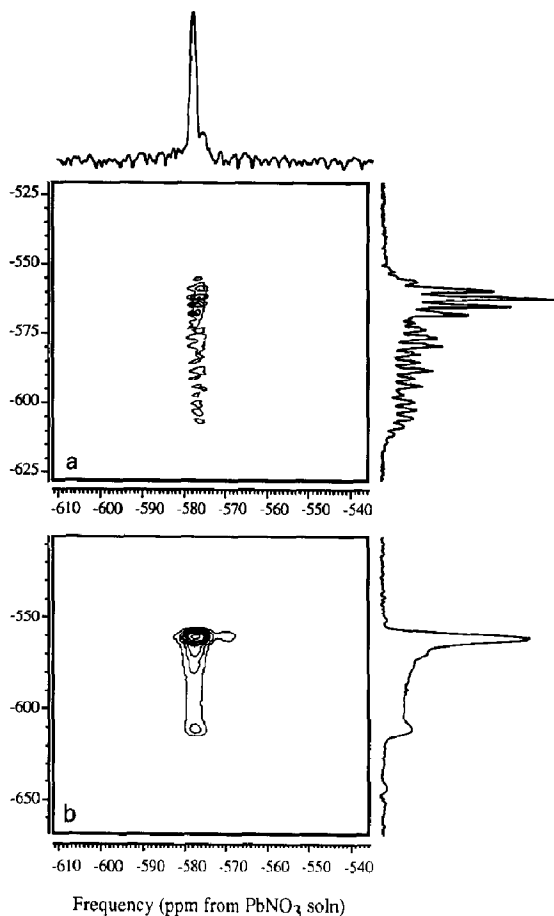
Fig. 4. ^{207}Pb MAH-180 2D spectrum at 11.7 T of PbNO$_3$ (a) performed at the magic angle and (b) with a hop to 0° for detection. In (a) the sideband-free isotropic spectrum is correlated with the spectrum corresponding to magic-angle spinning exhibiting sidebands. In (b) the sideband-free isotropic spectrum is correlated with the corresponding static powder spectrum.

tection occurs under static conditions no sidebands are observed in the second dimension. In contrast to DAS, the same peak in the DAH spectrum is clearly resolved, and, in fact, the two sites show the expected 1:1 intensity [15].

The 2D spectrum of lead nitrate taken with the MAH-180 with a hop to 0° is shown in fig. 4b along with the projections of both dimensions. As expected, an isotropic dimension is observed correlated to the static powder pattern. In fig. 4a is shown the 2D spectrum of lead nitrate without a hop taken with pulse sequence (3). The resulting spectrum has an sideband-free isotropic dimension correlated to

an isotropic dimension with sidebands.

Since these are constant-time experiments, the evolution at the end of the sequence (3) or (4) should be free of effects of transverse relaxation. However, there may be some dipolar contribution to the t_1 evolution. In any case, these lines should be of similar resolution as in a corresponding MAS or DAS experiment with the same acquisition time. In order to improve resolution, more points in t_1 should be acquired (our acquisitions were short enough to produce truncation effects), which would mean applying the π pulses over more rotor periods or reducing the spinning speed. This method should therefore prove especially useful for samples with a continuous distribution of isotropic sites, such as a glass, where fewer t_1 points are required due to the rapid dephasing in t_1 [16].

Acknowledgement

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