Dynamic-Angle Spinning Without Sidebands

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Abstract

By means of rotor synchronized π-pulses, it is possible to eliminate the spinning sidebands that usually arise in dynamic-angle spinning (DAS). The theory of this approach, dynamic-angle hopping (DAH) is described and illustrated by means of experimental results. A magic-angle hopping (MAH) version of the experiment is also possible and can be used in a two-dimensional experiment with a hop of the spinner axis 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) [1,2] has been shown to average the chemical shift anisotropy of spin-1/2 nuclei in powdered solids yielding high-resolution spectra in manner similar to magic-angle spinning (MAS) but without the presence of spinning sidebands. In MAH, the sample is reoriented quickly 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. A technically simple implementation [3] involves spinning the sample slowly at the magic angle in order to approximate hopping between discrete angles during evolution. In both of these methods, $\pi/2$ storage pulses are needed 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 $\sqrt{2}$ signal-to-noise for every pair of storage pulses used.

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]. In the extension of hopping to the icosohedral orientations of dynamic-angle spinning (DAS) used for quadrupolar nuclei, the loss of signal-to-noise can be substantial.

The experiment for quadrupolar nuclei analogous to MAH, which we might term dynamic-angle hopping (DAH), is one where 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 $0°$, which are the orientations defining the vertices of an icosahedron; of course, other orientations

could be used (with a minimum of six necessary), consistent with DAS averaging. 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 superior in signal-to-noise, since all components of the evolving magnetization are preserved.

2. Theory

It is well known that sample spinning, as in magic-angle spinning (MAS)[5], dynamic-angle spinning (DAS)[6,7] or double rotation (DOR)[8], can be used to produce high resolution NMR spectra of powder samples. However, all of these techniques introduce artifacts called spinning sidebands in the spectra due to the time dependence of the net Hamiltonian under sample rotation[9]. The behavior of these sidebands is well understood in all of these cases[9-11]. There already exist a number of techniques which can suppress sidebands to some degree[4,12]. However, the best solution is to eliminate the spinning rate dependence of the Hamiltonian all together. In a static sample, the overall Hamiltonian may be written below.

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

In this expression, Ω are the Euler angles which describe the orientation of the magnetic field to the sample and A_{lm} are the spatial tensors which relate the principal axes of a given crystallite to the sample frame. Suppose, instead of using sample spinning to obtain high resolution spectra, a sample were to be instantaneously reoriented between the vertices of an octahedron (for chemical-shift anisotropy (CSA) interactions) or an icosohedron (for both CSA and second-order quadrupolar (2Q) interactions) and allowed to evolve for equal time at each vertice. The effective Hamiltonian governing this experiment may be written as the sum of static Hamiltonians at each orientation and is completely isotropic and time independent.

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

Here, $\left\langle D_{m0}^{(l)}(\Omega) \right\rangle$ has been averaged over the vertices of either an octahedron (averaging $l = 1$-2) or an icosohedron ($l = 1$-4)[11,13]. Of course, it is impossible to hop instantaneously between orientations in this fashion and a possible implementation is to store the magnetization with $\pi/2$ pulses during the reorientation period. The sample is then allowed to evolve for equal times at each orientation, however, now the NMR experiment has become two-dimensional, in that data must be taken in a point by point fashion where a point is acquired after evolving at each of the three (octahedral) or six (icosohedral) orientations. For octahedral symmetry, this experiment (MAH)

has been performed by Maciel et. al. [1,2] to average the chemical shift anisotropy by rotating a powder sample by 120° hops about an axis inclined at the magic-angle (54.74°) with respect to the magnetic field while storing the magnetization between hops with $\pi/2$ pulses.

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 to interrupt evolution as the rotor effectively "hops" between 120° orientations[3]. The Hamiltonian under this interaction is completely equivalent to the one given above since every point in the evolution is related by symmetry to two other points 120° and 240° rotated about the magic-angle at all times. The basic problem with both of these experiments is that the overall signal-to-noise ratio is reduced by a factor of 2 due to the two sets of $\pi/2$ storage pulses. An improvement can be achieved by replacing the $\pi/2$ pulses with π pulses and creating an overall Hamiltonian which is isotropic. Consider the following two-dimensional experiment performed over N rotor periods of length τ_r, where N is an even integer, $(t_1/6)$ and Δ are delays with $\Delta = (N\tau_r/6) - (t_1/6)$, and π and $\pi/2$ are pulses and t_2 is acquisition.

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

Under this pulse sequence, the Hamiltonian will effectively change sign each time a π pulse is applied. Therefore, the evolution during the Δ periods will directly cancel a complimentary evolution in the first $N\tau_r/2$ period. 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 an isotropic Hamiltonian for the chemical shift anisotropy. This same pulse sequence may be expanded to average evolution under a quadrupolar Hamiltonian. In this case, evolution at the six vertices of an icosohedron 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 a reorientation of the spinning axis to 0° relative to the magnetic field. This may be done with either π refocusing and slow rotation or $\pi/2$ storage pulses and slow rotation or hops. The former is preferable, as there will be no loss of signal-to-noise ratio due to storage pulses. A pulse sequence which implements this is given below, with $\Delta = (N\tau_r/10) - (t_1/12)$, which we will call dynamic-angle hopping (DAH-180).

$$\frac{\pi}{2} - \frac{N\tau_r}{2} - \left(\frac{t_1}{12} - \pi - \Delta - \pi \right)_4 - \frac{t_1}{12} - \pi - \Delta - \frac{\pi}{2} - t_{hop} - \frac{\pi}{2} - \frac{t_1}{6} - t_2 \qquad (4)$$

As in the previous sequence, the Hamiltonian changes sign with each π pulse and therefore again the evolution during the Δ periods will directly cancel a complimentary evolution in the first

$N\tau_r/2$ period. The remaining evolution will consist of two sets of t_1 evolution 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. Both the DAH-180 and the $\pi/2$ pulse version of DAH-180 called DAH-90 are shown in figure 2 where $n = 5$. These sequences can both be applied to spin 1/2 systems, in which case n is trivially 3. In the DAH-180 experiment above, the maximum value for $t_1/12$ is $N\tau_r/10$; therefore, the maximum acquisition length in the t_1 dimension is $12N\tau_r/10$.

3. Experimental

Rubidium sulfate and lead nitrate were obtained from standard commercial sources. 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. [14]. The details of the DAS experiment including pulse sequences and phase cycles have been described previously [15,16]. 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, also obtained from standard commercial sources. 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. Recycle delays of 2 s were used to allow for relaxation and to allow the spinning speed to stabilize after the hop to the initial angle. We have found that this delay is crucial 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 were acquired in t_1, and for the DAS experiment, 68 were acquired in t_1. The dwell time in t_2 was 16 μs and in t_1 was 33.6 μs. 512 transients were acquired for each t_1 point. Whole-echo acquisition was used to obtain pure-absorption mode 2D spectra [16,17]. The rotor period for the DAH-180 experiment was 199.6 μs (5.0 kHz). For the DAS experiment, the spinning frequency was 1.8 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 ($N = 8$).

^{207}Pb MAH-180 with a hop to 0° was performed on $PbNO_3$. Lead $\pi/2$ pulse widths were 11 μs. A recycle delay of 10.2 s was used. The hop time was 75 ms. 256 complex points were acquired in t_2 and 64 were acquired in t_1. Dwell time was 40 μs in t_1 and 50 μs in t_2. 128 transients were acquired. Whole-echo acquisition was used to obtain pure-absorption mode 2D

spectra. The rotor period was 1326.67 μs. The experiment was performed over two rotor cycles ($N = 2$).

4. Results and Discussion

The 2D-spectrum of rubidium sulfate taken with the DAH-180 sequence shown in fig. (1b) is shown in fig. (2). The projection of the isotropic dimension is shown in fig. (3a). The two sites occur at -25 ppm and 28 ppm in agreement with previous studies at 9.4 T [15]. Truncation artifacts are present since the maximum allowed value for t_1 was not sufficient to collect the full FID in the t_1 dimension. As expected, a sideband-free isotropic dimension is observed, correlated with an anisotropic dimension consisting of the separated static powder patterns for the individual sites. Since detection occurs under static conditions no sidebands are observed in the second dimension. The projection of the isotropic dimension of the standard DAS experiment is shown in fig. (3b). The site at -25 ppm has a large number of sidebands reducing the intensity of the isotropic position by a significant amount. In contrast, the same peak in the DAH spectrum is clearly resolved, and, in fact, the two sites show the expected 1:1 intensity [18].

In theory, the signal-to-noise of the DAH-180 spectrum should be identical to that of the standard DAS experiment in the limit of infinite speed. In contrast, a method such as TOSS [19] can result in a loss of signal-to-noise since the sideband intensity is not always folded into the isotropic peak. However, in practice, imperfections in the train of π pulses can lead to a loss of intensity. Incomplete inversion due to resonant offset effects of the π pulses can also lead to significant loss of intensity. For these reasons, the sequences given in either eq. (13) or eq. (15) should give slightly better results than the one in eq. (3). Indeed, we found that the sequence in eq. (13) in the DAH-180 experiment (ten π pulses instead of nine) gave a slightly worse signal-to-noise (spectrum not shown). The DAH-180 experiment is expected to be superior to the DAH-90 experiment (pulse sequence shown in fig. (1a) but spectrum not shown) where $\pi/2$ storage pulses are used to store the magnetization while the sample rotates to the next desired orientation, because half the magnetization is lost with every storage pulse. This corresponds to a reduction by a factor of 4 signal-to-noise in the DAH-90 experiment. However, in practice, we found that DAH-90 gives much worse signal-to-noise than predicted.

The 2D-spectrum of lead nitrate taken with the MAH-180 with a hop to 0° sequence is shown in fig. (4) along with the projections of both dimensions. As expected, an isotropic dimension is observed correlated to the static powder pattern. Truncation artifacts are again present. Slight distortions are present in the lineshape probably due to cumulative effects of imperfect π pulses.

Since these are constant-time experiments, the evolution at the end of the sequence in eq. (3) 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 at least as narrow as in a corresponding MAS or DAS experiment with the same acquisition time. Also, to improve resolution, more points in t_1 must be acquired, which would mean applying the π pulses over more rotor periods or reducing the spinning speed. This will result in an overall reduction in the signal-to-noise of the spectrum because of increased time for transverse relaxation. Effectively, there will always be a compromise between signal-to-noise and resolution in this type of experiment. However, this method should prove especially useful for samples with a continuos distribution of isotropic sites, such as a glass, where fewer t_1 points are required due to the rapid dephasing in t_1 [20].

5. Conclusions

Dynamic-angle hopping is a feasible method of obtaining sideband-free high resolution spectra of quadrupolar nuclei. This method would be particularly useful for nuclei which give large number of sidebands with normal DAS. In addition, it is superior to a method such as TOSS in that the signal-to-noise is usually greater. We also demonstrated how to obtain sideband-free isotropic-anisotropic spectra of spin-1/2 nuclei by combining MAH-180 with a hop to another angle for detection.

Acknowledgments

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Figure Captions

Fig. 1. In the above figure, $\delta = t_1/2n$, $\Delta = (N\tau_r/2n) - \delta$, t_{hop} is the hop time, and t_{echo} is the echo time. The sequences between the dashed lines are repeated $n-2$ times. The experiment is performed over N rotor cycles. a) DAH-90 ($n = 5$) or MAH-90 ($n = 3$) pulse sequence and coherence transfer pathway. b) DAH-180 or MAH-180 pulse sequence and coherence transfer pathway.

Fig. 2. ^{87}Rb DAH-180 2D-spectrum of Rb_2SO_4 taken at 9.4 T. Both contour and stacked plots are shown.

Fig. 3. Projections along the isotropic dimensions of a) the DAH-180 spectrum (fig. 2) and b) the ^{87}Rb DAS spectrum of Rb_2SO_4 taken at 9.4 T at a spinning frequency of 1.8 kHz. Isotropic peaks appear at -25 ppm and 29 ppm.

Fig. 4. ^{207}Pb MAH-180 2D-spectrum of $PbNO_3$ with a hop to $0°$ for detection taken at 11.7 T. Projections of both isotropic and anisotropic dimensions are shown.