

# Influence of Proton Chemical-Shift Anisotropy on Magic-Angle Spinning Spectra of Hydrate Crystals

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**It is shown that the proton chemical-shift anisotropy of hydrate crystals affect dipolar powder pattern at 7.0 T. This may be clearly observed via an asymmetric envelope of dipolar spinning sidebands in magic-angle spinning proton spectra. © 1997**

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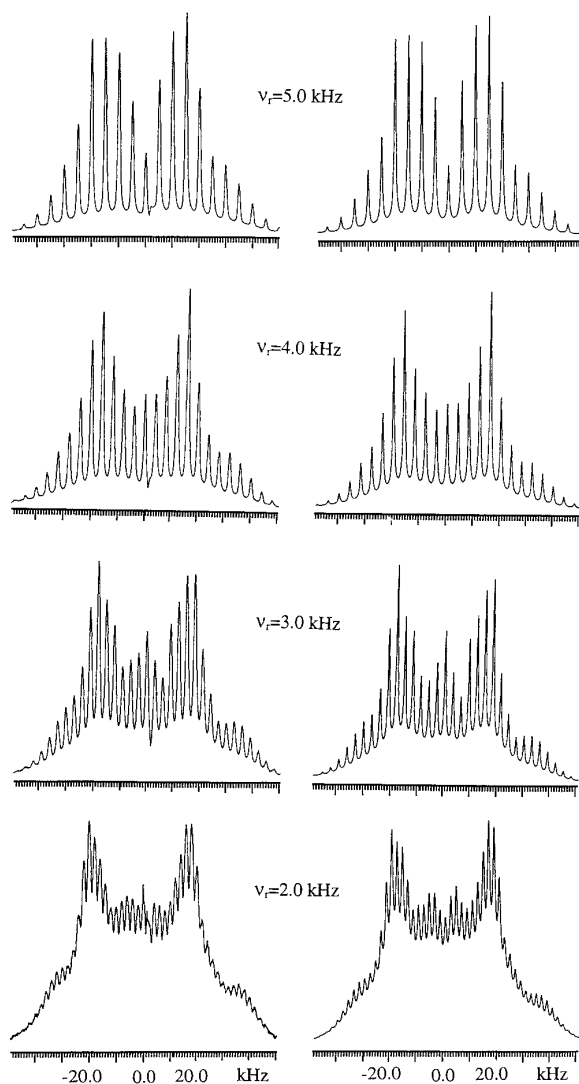
**Key Words:** proton chemical-shift anisotropy; dipolar spinning sidebands.

The development in the 1970s of multiple-pulse techniques designed to suppress dipolar interactions has opened the possibility of determining experimentally the shielding tensor of protons (1). The complete chemical-shift tensor provides information about the local symmetry of the electron distribution around the nucleus and the nature of molecular motions (2). Although the principal elements of the proton chemical-shift tensor can be determined from powder spectra recorded under homonuclear decoupling, the direction of the principal axes can be determined only from experiments on single crystals (3). On the other hand, the earlier technique for measuring proton shielding anisotropies, i.e., the liquid-crystal method, has been found to be generally unreliable due to large uncertainties and to the small range of proton shifts (4).

In the following, it is shown that information on the chemical-shift anisotropy (CSA) and the mutual orientation of shielding and dipolar tensors may be available from magic-angle spinning proton powder spectra of hydrate crystals.

Proton powder spectrum of barium chlorate monohydrate,  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ , when recorded under magic-angle spinning of a few kilohertz, shows a family of strong, well-separated dipolar spinning sidebands. This is due to the pronounced inhomogeneous character of the proton spectrum resulting from the relative isolation and flipping of water molecules in the crystal lattice.

Previous proton magnetic resonance studies of barium chlorate monohydrate have shown that there is only one



**FIG. 1.** Experimental (left) and calculated (right) 300.13-MHz  $^1\text{H}$  magic-angle spinning spectra of  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$  at different spinning frequencies. Spectra were simulated with linewidth parameters ( $1/T_2$ ) of 500 and 50,000  $\text{s}^{-1}$  for the narrow and broad components, respectively. For other simulation details, see text.

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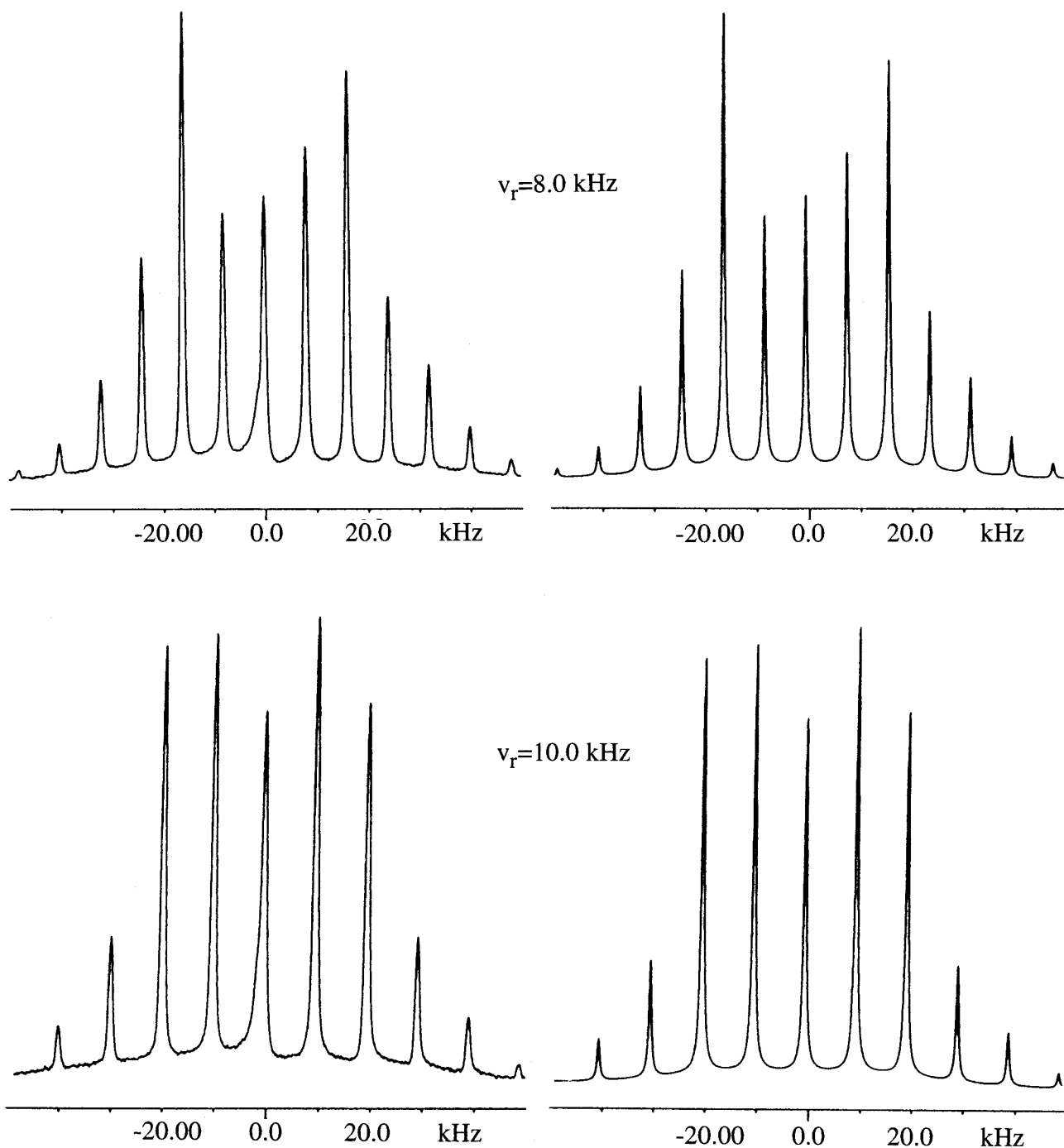


FIG. 2. Experimental (left) and calculated (right) 300.13 MHz  $^1\text{H}$  magic-angle spinning spectra of  $\text{Ba}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$  at 8.0 and 10.0 kHz spinning frequencies. For simulation details, see text.

orientation of the water molecule in the hydrate (5) and that the proton-proton distance is  $1.61 \pm 0.01 \text{ \AA}$  (5-8). This distance includes the effect of vibrations of the water molecule in the hydrate crystal (7). The water hydrogen atoms form hydrogen bonds between the water oxygen

and the nearest chlorate oxygens (6). A deuteron magnetic resonance study has shown the presence of fast  $\pi$ -flipping motion of the water molecule at room temperature (9). No effect from  $\pi$ -flips upon the Pake splitting for protons would be expected (10).

During our recent work on barium chlorate monohydrate, we were puzzled by the asymmetric envelope of dipolar spinning sidebands. As shown in Fig. 1 and 2 (left), such an asymmetry may be clearly observed on magic-angle spinning proton spectra recorded at different spinning speeds. Instrumental effects such as finite pulse rise and fall times or finite transmitter, probe, and receiver bandwidth does not to be able to account for this lack of symmetry.

To simulate the observed deviations from symmetric dipolar spinning sideband family related to Pake-doublet powder pattern, we looked at possible effects arising from the residual proton chemical-shift anisotropy of water. In fact, if dipolar and CSA interactions are present simultaneously, we can expect that the evolution of nuclear magnetization during acquisition will depend on the magnitude of each interaction and on the mutual orientation of both tensors (11). Consequently, when calculating spectra, the correlation of orientation between the shielding and dipolar tensors must be specified by defining the proton-proton vector in the principal axis system of the shielding tensor. Furthermore, under conditions of magic-angle spinning, an additional two-step transformation from the CSA principal axis system to the laboratory frame via the rotor-fixed frame must be included.

The good agreement between experimental and calculated spectra (left and right parts of Fig. 1 and 2, respectively) assesses the effect of residual CSA effect in magic-angle spinning spectra dominated by dipolar proton-proton interaction in the water molecule. By using a dipolar coupling constant of 42.37 kHz corresponding to the proton-proton distance of 1.62 Å, the residual CSA derived from the spectrum recorded at  $\nu_r = 5.0$  kHz was found to be  $\Delta\sigma = 10.5 \pm 1.0$  ppm, whereas the principal axes of both tensors were found to coincide. This is the consequence of the rapid flipping motion of water molecules. These values have been used to simulate the spectra recorded at lower and higher spinning speeds. In the course of these simulations we noticed that spectra are sensitive to small changes of the polar coordinates of the dipolar vector in the CSA principal axis frame and to small changes of the proton-proton distance as well as to the value of the residual CSA.

Moreover, in order to reproduce a large hump on which the spinning sideband family is superposed, the presence of a second broad component must be assumed. Its relative proportion (with respect to the spinning sideband family) increases when decreasing the spinning speed and is respectively 0.5, 0.8, 1.2, and 1.8, for the spectra shown

in Fig. 1. This indicates a more important role played by intermolecular dipolar interactions and/or spin diffusion at lower spinning speeds.

Although the overall appearance of the spinning sidebands envelope is well reproduced in each case by using a unique set of parameters, small differences in the spinning sidebands intensities are still visible. This is related to the vibrationally induced asymmetry of the dipolar coupling tensor (12–14), which not only leads to the apparent increase of bond distance but also means that no single proton-proton distance yields a fully satisfactory result due to the nonuniform orientational dependence of spinning sidebands (15). The detailed analysis of the anisotropic vibration motion on dipolar-chemical-shift anisotropy proton spectra recorded under macroscopic rotation will be presented elsewhere.

Summing up, we have shown that the information on proton chemical-shift anisotropy tensors is available from magic-angle spinning powder spectra of crystalline water recorded with a magnetic field of 7.0 T. We anticipate that the effect of chemical-shift anisotropy on proton magic-angle spinning spectra recorded at higher spinning speeds ( $\nu_r > 15$  kHz) and at higher magnetic fields ( $B_0 > 14$  T) should be visible even for less isolated groups of protons in many typical organic solids.

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