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Communication

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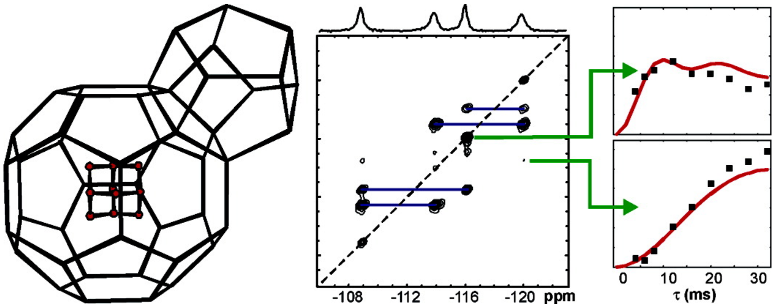

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Symmetry-Based ^{29}Si Dipolar Recoupling Magic Angle Spinning NMR Spectroscopy: A New Method for Investigating Three-Dimensional Structures of Zeolite Frameworks

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Many of the important properties and applications of zeolites are intimately related to their three-dimensional (3D) framework structures. However, structure determination of these materials by diffraction techniques is difficult since single crystals of adequate dimensions are usually not available. Powder X-ray diffraction (XRD) experiments can provide unit cell parameters and identify possible space groups. However, solving zeolite structures from powder XRD data alone is not straightforward.

Solid-state NMR can provide structural information that is complementary to diffraction, particularly with the development of dipolar recoupling magic angle spinning (MAS) NMR pulse sequences by which internuclear distances can be probed. In this communication, it is demonstrated that through-space dipolar interactions between naturally abundant ^{29}Si nuclei in pure silica zeolites can be exploited to provide information about the 3D structures of zeolite frameworks, including bonding connectivities as well as long-range distance information between Si sites.

Solid-state NMR experiments were carried out on the clathrasil Sigma-2,[1] whose structure is illustrated in Figure 1a. This material is an ideal test compound since the ^{29}Si spectrum (Figure 1b) consists of four resolved peaks corresponding to the four unique Si sites in the structure. In addition, the rapidly rotating 1-aminoadamantane template molecules provide a source of ^{1}H magnetization with a convenient T_1 relaxation time which can be used for signal enhancement by $^{1}\mathrm{H} \rightarrow {}^{29}\mathrm{Si}$ cross polarization, while the ^{1}H−^{29}Si dipolar interactions are weak enough such that ^{1}H decoupling is not necessary.

^{29}Si has a natural abundance of 4.7%, leading to a significant number of relatively isolated ^{29}Si−^{29}Si spin pairs distributed throughout the zeolite structure. To probe the Si−Si distances within these spin pairs, the recently developed $\mathrm{SR26}_4^{11}$ homonuclear dipolar recoupling sequence[2] has been incorporated into a two-dimensional (2D) double-quantum (DQ) correlation experiment, as described in Figure 2. The $\mathrm{SR26}_4^{11}$ sequence, designed using NMR symmetry principles,[3] is a very robust method for recoupling weak homonuclear dipolar interactions, while decoupling weak heteronuclear dipolar interactions.

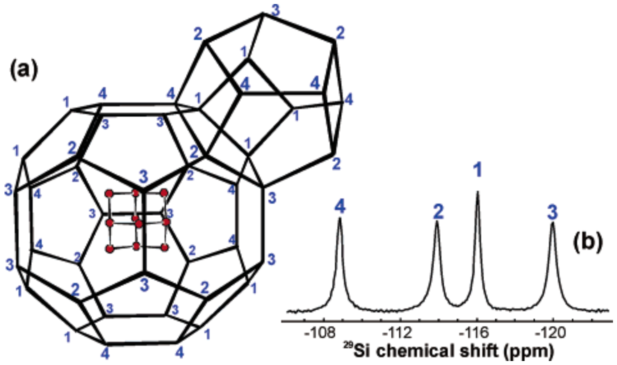

Figure 1. (a) Framework structure of the clathrasil Sigma-2[1] hosting 1-aminoadamantane template molecules. (b) ^{29}Si CP MAS NMR spectrum of Sigma-2.

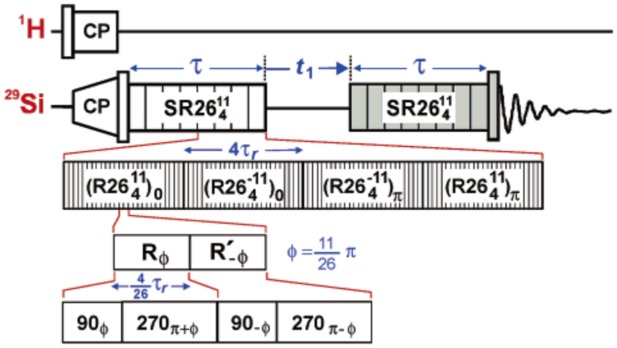

Figure 2. Pulse sequence diagram for 2D ^{29}Si DQ correlation spectroscopy using the $\mathrm{SR26}_4^{11}$ dipolar recoupling sequence.[2]

A 2D ^{29}Si $\mathrm{SR26}_4^{11}$ DQ correlation spectrum of Sigma-2 is presented in Figure 3a. Correlations between pairs of ^{29}Si resonances appear in the indirect dimension at the sum of their isotropic chemical shifts. The intensities of these correlations are related to the distribution of Si−Si distances. This spectrum was obtained with a short recoupling time for which the DQ signals arise primarily from ^{29}Si−^{29}Si spin pairs across the Si−O−Si linkages. Since the Si−O−Si distances fall within a narrow range (3.0−3.2 Å) and the ^{29}Si−^{29}Si dipolar interactions between nuclei separated by more than one Si−O−Si linkage are weak in comparison, there exists a correspondence between the intensities of the correlation peaks and the number of Si−O−Si connectivities, a relationship that can be used to probe the bonding network and assign the peaks in the ^{29}Si spectrum to the Si sites in the zeolite framework structure.[4]

This ^{29}Si dipolar recoupling experiment has a number of important advantages over the *J*-coupling-based INADEQUATE experiment[5] which has been used previously to investigate the bonding networks of zeolites.[6] A comparison of the correlation spectra obtained with the $\mathrm{SR26}_4^{11}$ sequence (Figure 3a) and those obtained with the refocused INADEQUATE sequence[7] (Figure 3b) reveals that the former contains all of the Si−O−Si connectivity information, whereas the latter is missing the correlations between symmetry-related Si sites that should appear along the DQ diagonal. These “auto-correlations” provide important information about the

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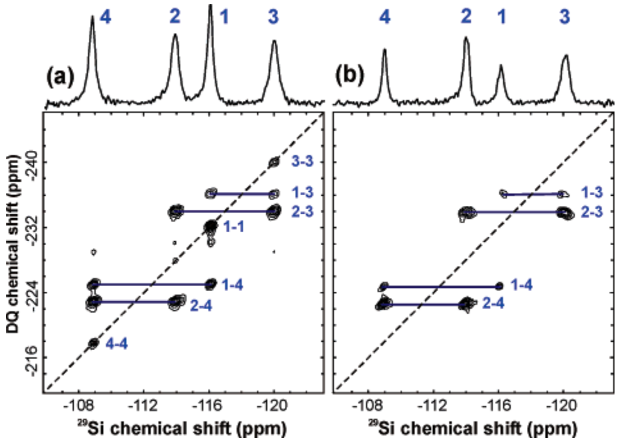

Figure 3. ^{29}Si DQ correlation spectra of Sigma-2 obtained with (a) the SR26_4^{11} dipolar recoupling sequence ($\tau = 6$ ms) and (b) the *J*-coupling-based refocused INADEQUATE experiment ($\tau = 24$ ms). The projections are 1D DQ-filtered spectra for each experiment.

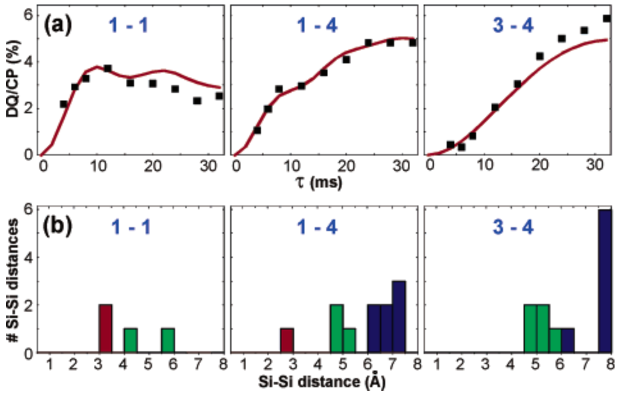

Figure 4. (a) Three of the ^{29}Si DQ build-up curves obtained by integrating the correlation peaks obtained in a series of 2D SR26_4^{11} DQ correlation spectra. The solid lines are simulations of DQ build-up curves taking into account ^{29}Si−^{29}Si spin pairs with distances less than 8 Å. The curves were fit to the experimental data by multiplying by $A \exp\{-k\tau\}$ where a scaling factor of $A = 3.94$ and a relaxation parameter of $k = 26.9$ s^{-1} were used for every curve. (b) Histograms of Si−Si distance distributions in Sigma-2.

structure of the zeolite framework; thus, it is advantageous to observe them directly.

An important feature of the dipolar recoupling sequence is that the DQ coherences build up much faster than in the INADEQUATE experiment. The dipolar coupling constants for ^{29}Si−O−^{29}Si spin pairs are about −160 Hz, an order of magnitude larger than the ^{29}Si−O−^{29}Si *J*-couplings (approximately 10−15 Hz). Consequently, the excitation and reconversion of the DQ coherences require less time, meaning that the SR26_4^{11} experiment is affected less by relaxation. Although the DQ signals in the spectra presented in Figure 3 are similar, it is expected that, for zeolite samples with faster T_2 relaxation, the SR26_4^{11} sequence should give significantly stronger signals than the INADEQUATE sequence.

Another important feature of the SR26_4^{11} dipolar recoupling experiment is that long-range ^{29}Si−^{29}Si interactions can be probed. A series of 2D DQ correlation spectra were collected with the recoupling time τ incremented. The amplitudes of the correlation peaks in each 2D spectrum were extracted and plotted as functions of the recoupling time, yielding DQ build-up curves for each pair of Si−Si correlation peaks, three of which are presented in Figure 4a.

The experimental data are in excellent agreement with simulated[8] DQ build-up curves which consider all ^{29}Si−^{29}Si spin pairs with distances less than 8 Å. Each curve is the sum of a set of isolated two-spin simulations with the internuclear distances taken from the Sigma-2 structure.[1] Clusters of more than two spins were ignored. The summed curves were multiplied by the function $A \exp\{-k\tau\}$ to scale the data and to account for relaxation, using the same values of A and k for every curve. The quality of the fit improved as the cutoff distance was increased to 8 Å but did not improve beyond this value. The necessary inclusion of all Si−Si spin pairs within 8 Å indicates that the SR26_4^{11} sequence is capable of recoupling dipolar interactions as small as 10 Hz.

The shapes of the curves reflect the Si−Si distance distributions, while the maximum intensities of the curves reflect the number of Si−Si neighbors within the 8 Å sphere. These features can be seen by comparing the DQ build-up curves to the corresponding distance distribution plots presented in Figure 4b. For example, the 1−1 correlation peak contains contributions from Si1−Si1 spin pairs with internuclear distances of 3.16, 4.42, and 5.91 Å, with the 3.16 Å spin pairs being twice as abundant as the others. This is reflected in the DQ build-up curve which rises rapidly due to the contribution of the spin pairs across Si−O−Si linkages but reaches a plateau due to the fact that there are few other Si1−Si1 spin pairs with distances less than 8 Å. This behavior is remarkably different from the 3−4 curve which rises slowly but reaches a high intensity at long recoupling times, reflecting the fact that there are no Si3−Si4 spin pairs across Si−O−Si linkages but there are many Si3−Si4 spin pairs with distances between 4.5 and 8 Å.

^{29}Si dipolar recoupling experiments have recently been reported[9] for the study of a layered silicate material in which ^{29}Si was enriched to 50%. However, with such high enrichment, long-range interactions cannot be probed quantitatively due to the complexity of the spin dynamics arising from the high density of ^{29}Si spins.

We have shown that natural abundance ^{29}Si DQ build-up curves obtained in symmetry-based recoupling experiments are highly sensitive to Si−Si distance distributions and can be faithfully simulated. In a forthcoming publication, we demonstrate that it is even possible to *solve* the 3D structure of zeolite frameworks by combining these solid-state NMR data with the unit cell parameters and space group information easily obtained by powder XRD.

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Supporting Information Available: Details of solid-state NMR experiments and simulations, the full set of ^{29}Si DQ build-up curves, and Si−Si distance distributions. This material is available free of charge via the Internet at http://pubs.acs.org.

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