Solid-State Polarization-Transfer Experiments Involving Quadrupolar Nuclei

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1 Introduction

Historically, cross-polarization experiments [1,2] have been used to transfer spin coherence from abundant spins to a dilute spin system. Protons (^{1}H) have been used almost exclusively as the source of strong nuclear polarization for cross-polarization experiments, although there have been some examples where other abundant nuclei have been used. Coupled with magic-angle spinning (MAS) NMR [3], cross-polarization techniques have proven extremely powerful for the study of organic solids.

Inorganic systems such as zeolites, gels, and ceramics are of great technological importance and interest and contain many quadrupolar nuclei but very few protons. For quadrupolar nuclei with non-integral spins such as ^{11}B, ^{17}O, and ^{27}Al, the second-order quadrupolar broadening of the readily observed central ($+1/2 \leftrightarrow -1/2$) transition is not completely averaged by MAS, and the NMR lines from quadrupolar spins are shifted and distorted in single-axis spinning experiments [4,5]. Very few examples exist of cross-polarization experiments involving quadrupolar nuclei, and they all involve magnetization transfer from protons *to* quadrupolar nuclei. We have undertaken a study to determine the feasibility of polarization transfer and dipolar dephasing experiments between spin pairs in these systems, particularly between ^{31}P ($I = 1/2$) and ^{27}Al ($I = 5/2$). Our preliminary results show that these experiments are indeed possible [6].

The attainment of cross-polarization *from* quadrupolar spin systems is particularly important in materials chemistry as these nuclei usually have very short T_1 relaxation times. Spin-1/2 nuclei in dense inorganic systems may have T_1 values ranging from many seconds to hours, effectively precluding their observation in many instances. By using cross-polarization from the quickly relaxing quadrupolar spins, spectra of the spin-1/2 nuclei could be obtained in a relatively short time. Additional information regarding the local structure and bonding in these systems might also be obtained through the distance dependence of the cross-polarization process.

Similarly, dipolar-dephasing NMR experiments such as rotational-echo double-resonance (REDOR) and transferred-echo double-resonance (TEDOR) have been demonstrated to be useful for demonstrating connectivities and determining internuclear distances [7,8] in heteronuclear spin systems with dipolar couplings. Experimental verification of these experiments with the same heteronuclear spin pair (^{31}P and ^{27}Al) demonstrates the feasability of applying these techniques to systems containing quadrupolar nuclei.

2 Experimental

The sample chosen for study was the very large pore molecular sieve VPI-5, an aluminophosphate dihydrate containing 18-membered-rings [9]. NMR experiments were performed under MAS conditions in a 9.4 T superconducting magnet where the resonance frequencies for ^{31}P and ^{27}Al are 161.98 MHz and 104.26 MHz respectively. The rotational frequencies in all experiments were approximately 3.1 kHz, and 90° pulse times for the nuclei studied ranged from 9 to 12 μsec.

3 Results

The spectra in Figure 1 demonstrate the transfer of magnetization using cross-polarization in both directions between the ^{27}Al and ^{31}P spins in the Al-O-P bonding units in VPI-5. The cross-polarization is accomplished with an appropriate spin-locking pulse sequence [2] after a preparation pulse creates spin coherence for the nuclei used as the polarization source. With MAS the ^{31}P chemical shift anisotropies are averaged to their isotropic values for the three crystallographically inequivalent ^{31}P sites in the unit cell. For the ^{27}Al nuclei, MAS partially averages the second-order quadrupolar interaction and two resonances are seen: One from the

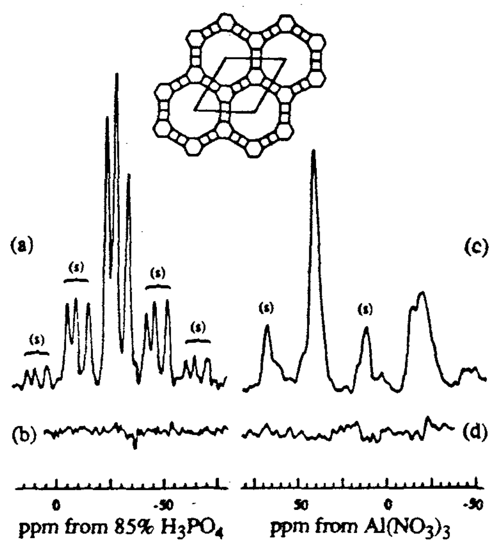

Figure 1. Demonstration of $^{27}Al \rightarrow {}^{31}P$ and $^{31}P \rightarrow {}^{27}Al$ cross-polarization in VPI-5 (projection of unit cell shown at top). Spinning sidebands are marked with an (s).

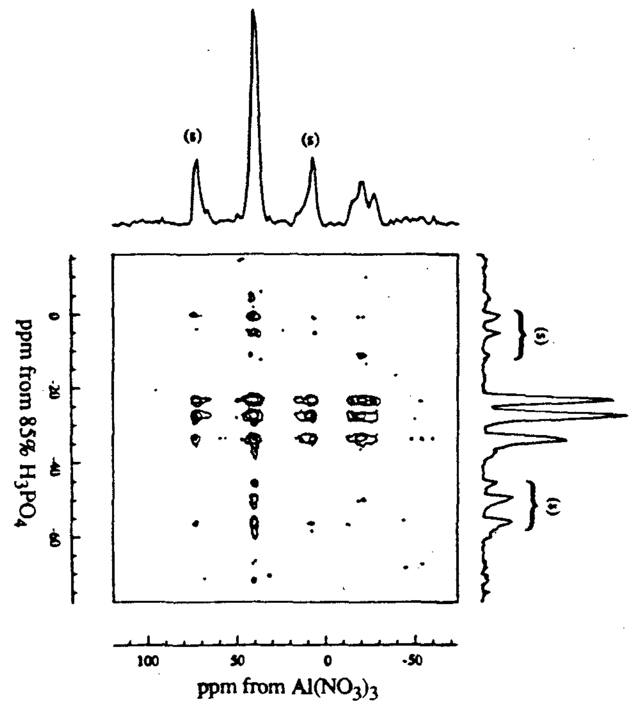

Figure 2. Two-dimensional heteronuclear correlation spectrum of ^{27}Al and ^{31}P in VPI-5.

tetrahedrally coordinated aluminum sites (41 ppm) and a second from the octahedrally coordinated aluminum (approximately -18 ppm). The observed signals are solely due to cross-polarization and not caused by direct irradiation during the spin-lock as proven by a series of cross-check experiments, of which spectra (b) and (d) of Figure 1 are representative.

A two-dimensional heteronuclear correlation experiment [10] using cross-polarization can be performed by preparing the aluminum spins with a 90° pulse, and then encoding their evolution frequencies in an initial time period. The aluminum polarization is subsequently transferred to the phosphorus spins with a spin-lock, and a phosphorus free induction decay is accumulated after each of a set of aluminum evolution times. Two-dimensional Fourier transformation provides the correlation spectrum of Figure 2. From the two-dimensional spectrum it is evident that each of the three ^{31}P resonances is connected to both tetrahedral and octahedral ^{27}Al resonances, in agreement with the proposed crystal structure of VPI-5 [11].

The REDOR experiment [7] was carried out in both directions between ^{27}Al and ^{31}P nuclei in VPI-5, and the results are shown in Figure 3. In both directions, negative cross-check experiments (not shown) were undertaken to ensure that the observed signal came from the dipolar dephasing phenomenon and not from timing missets or experimental artifacts.

The TEDOR experiment [8] was also accomplished with initial evolution of ^{27}Al spins and subsequent transfer to the ^{31}P after two rotor periods of preparative dephasing. The signal in Figure 3(c) was obtained after one additional period of dipolar evolution in order to create observable spin coherence from the antiphase signal which was transferred at the time of the ^{27}Al spin echo. As before, negative cross-check experiments were performed and gave null signals.

A two-dimensional TEDOR experiment [12] was performed with ^{27}Al spin frequency encoding before the initial dipolar dephasing period. After transfer of the coherence to the ^{31}P spins, an FID was accumulated and the t_1 value incremented. The two-dimensional correlation spectrum is shown in Figure 4, revealing cross-peaks between all three ^{31}P resonances and both the resonances from the tetrahedrally coordinated and octahedrally coordinated ^{27}Al sites, in agreement with the proposed crystal structure and the results of the two-dimensional CP experiment discussed above. These results are taken as demonstrating the general success of the experiments. A more detailed interpretation of the results in terms of the individual T-sites from the present data alone is not attempted.

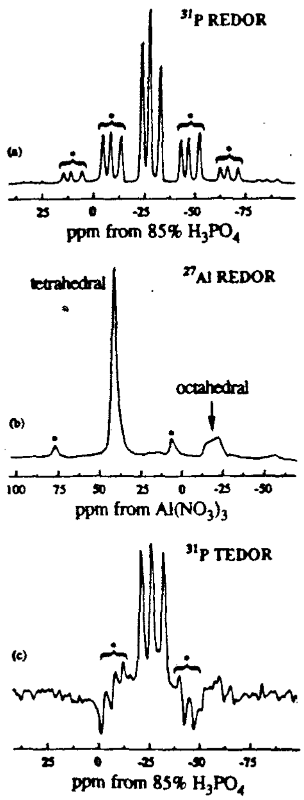

Figure 3. One-dimensional REDOR and TEDOR spectra of ^{27}Al and ^{31}P in VPI-5.

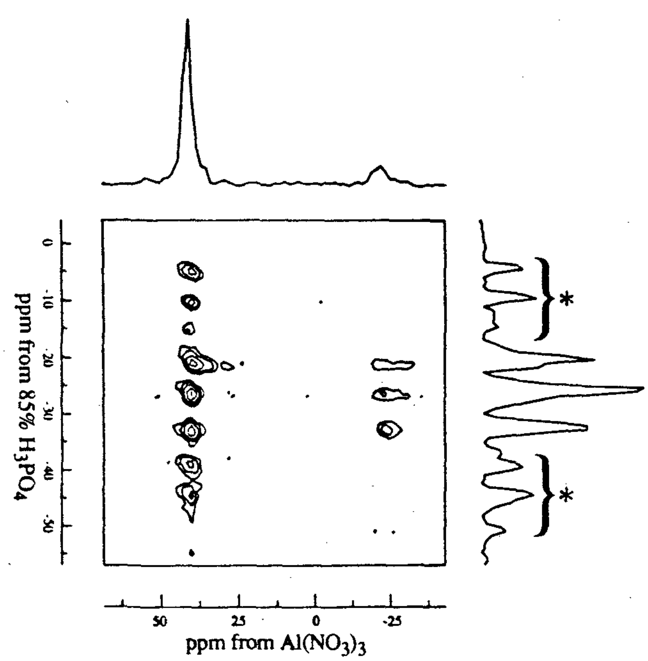

Figure 4. Two-dimensional TEDOR spectrum of ^{27}Al and ^{31}P in VPI-5.

4 Conclusions

In summary, cross-polarization *to* and *from* quadrupolar nuclei has been experimentally verified using the ^{31}P and ^{27}Al spin systems in an aluminophosphate molecular sieve. This bodes well for the use of heteronuclear correlations for further investigation of local microstructure in solids. Dipolar-dephasing experiments have also been accomplished, with both REDOR and TEDOR results confirming the connectivities detected by the cross-polarization studies. A two-dimensional TEDOR experiment has also been demonstrated that separates connectivities between distinct resonances.

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