2672 *J. Am. Chem. Soc.* **1998,** *120,* 2672−2673

Measurement of Heteronuclear Dipolar Interactions between Quadrupolar and Spin-1/2 Nuclei in Solids by Multiple-Quantum REDOR NMR

C. Fernandez,[†] D. P. Lang,[‡] J. P. Amoureux,[†] and M. Pruski*,[‡]

Laboratoire de Dynamique et Structure des Matériaux
Moléculaires, CNRS URA 801, Université des Sciences et
Technologies de Lille, F-59655 Villeneuve
d'Ascq Cedex, France
Ames Laboratory, 230 Spedding Hall, Ames, Iowa 50011

Received September 22, 1997
Revised Manuscript Received December 15, 1997

During the past decade, significant progress has been made in developing methods to observe high-resolution solid-state NMR for half-integer quadrupolar spins (S) and to measure the interactions between these nuclei and their spin-1/2 neighbors (I). The complete averaging of second-order broadening in half-integer quadrupolar nuclei can be achieved using double rotation (DOR),[1] dynamic angle spinning (DAS),[2] or multiple-quantum magic angle spinning (MQMAS).[3] The increasingly powerful, MAS-based techniques for studies of I−S interactions include rotational echo double resonance (REDOR),[4,5] transferred echo double resonance (TEDOR),[5,6] transfer of populations in double resonance (TRAPDOR),[7,8] rotational echo, adiabatic passage, double resonance (REAPDOR),[9] and dipolar exchange-assisted recoupling (DEAR).[10] These techniques use rotor-synchronized rf pulses to reintroduce the heteronuclear dipolar dephasing between the I spins and the observed S spins.

A natural consequence of these efforts are the most recent experiments that measure the I−S connectivities using the isotropic spectra of quadrupolar nuclei, i.e., without the limitations in resolution imposed by MAS. These methods utilize indirect excitation of quadrupolar spins via cross-polarization (CP) for spectral editing of the DOR[11] and MQMAS[12,13] spectra or for the DAS-[14] and MQMAS-based heteronuclear[15] correlation (HETCOR) experiments. Although these techniques provide a new means of analyzing the intermediate range ordering in various inorganic solids, they suffer from the severe quantitative uncertainties that are associated with the polarization transfer from spins-1/2 to the central transition coherence of the quadrupolar nuclei.[16,17] In this Communication, we present a method that combines MQMAS with S-observe, I-dephase REDOR. This technique, referred to as MQ-REDOR, was applied to ^{19}F−^{27}Al spin pairs in a fluorinated aluminophosphate sample. It proved to be a promising new tool for spectral editing and, additionally, for studying the internuclear distances in complex systems involving quadrupolar spins under high-resolution conditions.

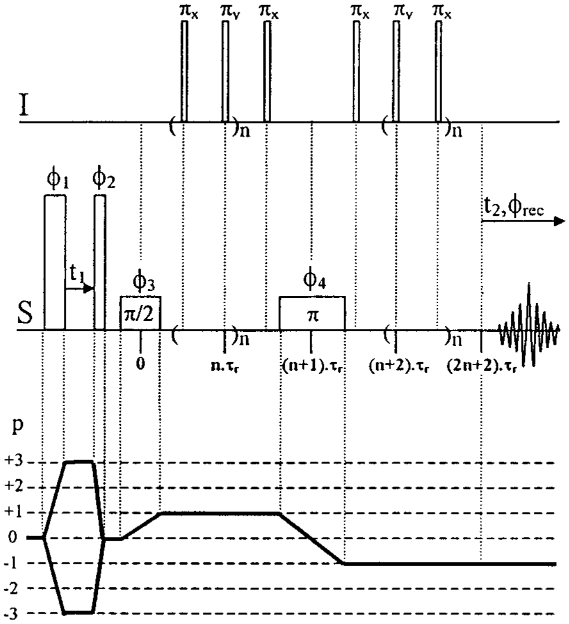

Figure 1. Pulse sequence used in the 3Q-REDOR experiment. The phase cycling was as follows: $\phi_1 = (0°)_{96}$; $\phi_2 = (0°,60°,120°,180°,240°,300°)_{16}$; $\phi_3 = (0°)_{24}, (90°)_{24}, (180°)_{24}, (270°)_{24}$; $\phi_4 = [(0°)_6,(90°)_6,(180°)_6,(270°)_6]_4$, $\phi_{rec} = [(0°,180°)_3,(180°,0°)_3]_2,[(270°,90°)_3,(90°,270°)_3]_2,[(180°,0°)_3,(0°,-180°)_3]_2,[(90°,270°)_3,(270°,90°)_3]_2$. A hypercomplex dataset was obtained by collecting, for each t_1, a complementary set of 96 FID's with $\phi_1 = 30°$. To increase the signal-to-noise and reduce the acquisition time, t_1 was advanced in rotor-synchronized fashion using increments τ_r.[21]

The schematic diagram of the MQ-REDOR experiment is shown in Figure 1. The first part of the experiment employs two strong (∼300 kHz) rf pulses at the frequency of the observed quadrupolar spins S. The phase ϕ_2 of the second pulse is cycled through $N_2 = 2p$ steps[18] for the selection of the symmetrical coherence transfer pathway $0 \rightarrow \pm p \rightarrow 0$. In the standard z-filter MQMAS experiment this sequence is followed by a selective $\pi/2$ pulse to create $0 \rightarrow -1$ coherence transfer and produce a pure-phase observable signal.[19,20] Herein, we replace this pulse with two selective pulses, $\pi/2$ and π, with phases ϕ_3 and ϕ_4 that are cycled through $N_3 = N_4 =$ four steps to select the coherence transfer pathway $0 \rightarrow +1 \rightarrow -1$ (Figure 1).[18] With an rf power of ∼10 kHz used for selective excitation, any leakage of magnetization via other allowed coherence pathways ($0 \rightarrow -3 \rightarrow -1$ and, in case of ^{27}Al, $0 \rightarrow +5 \rightarrow -1$) is unlikely. When spaced by an integer number of rotor periods $(n + 1)\tau_r$, these pulses create two windows in which the dephasing pulse sequences can be applied to the spins-1/2. As shown in Figure 1, the method used in our experiment consisted of a $(\tau_r/2-\pi_X-\tau_r/2-\pi_Y)_n-\tau_r/2-\pi_X-\tau_r/2$ sequence and its mirror image applied to spins I before and after the selective π pulse is activated on spins S. Similar to the standard REDOR experiment, the role of the π pulses on spins I is to prevent MAS from refocusing the dephasing due to the dipolar interaction between spins I and S.

[†] Université des Sciences et Technologies de Lille.

[‡] Ames Laboratory.

(1) Samoson, A.; Lipmaa, E.; Pines, A. *Mol. Phys.* **1988**, *65*, 1013.

(2) Mueller, K. T.; Sun, B. Q.; Chingas, G. C.; Zwanziger, J. W.; Terao, T.; Pines, A. *J. Magn. Reson.* **1990**, *86*, 470.

(3) Frydman, L.; Harwood: J. S. *J. Am. Chem. Soc.* **1995**, *117*, 5367.

(4) Guillion, T.; Schaefer, J. *J. Magn. Reson.* **1989**, *81*, 196.

(5) Fyfe, C. A.; Mueller, K. T.; Grodney, H.; Wong-Moon, K. C. *Chem. Phys. Lett.* **1992**, *199*, 198.

(6) Hing, A. W.; Vega, S.; Schaefer, J. *J. Magn. Reson.* **1992**, *96*, 205.

(7) van Eck, E. R. H.; Jansen, R.; Maas, W. E. J. R.; Veeman, W. S. *Chem. Phys. Lett.* **1990**, *174*, 428.

(8) Grey, C. P.; Vega, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 8232.

(9) Guillion, T. *Chem. Phys. Lett.* **1995**, *246*, 325.

(10) Sachleben, J. R.; Frydman, V.; Frydman, L. *J. Am. Chem. Soc.* **1996**, *118*, 9786.

(11) Sun, W.; Stephen, J. T.; Porter, L. D.; Wu, Y. *J. Magn. Reson.* **1995**, *A 116*, 181.

(12) Pruski, M.; Lang, D. P.; Fernandez, C.; Amoureux, J.-P. *Solid State Nucl. Magn. Reson.* **1997**, *7*, 327.

(13) Fernandez, C.; Delevoye, L.; Amoureux, J.-P.; Lang, D. P.; Pruski, M. *J. Am. Chem. Soc.* **1997**, *119*, 6858.

(14) Jarvie, T. P.; Wenslow, R. M.; Mueller, K. T. *J. Am. Chem. Soc.* **1995**, *117*, 570.

(15) Wang, S. H.; De Paul, S. M.; Bull, L. M. *J. Magn. Reson.* **1997**, *125*, 364.

(16) Vega, A. J. *J. Magn. Reson.* **1992**, *96*, 50.

(17) Vega, A. J. *Solid State Nucl. Magn. Reson.* **1992**, *1*, 17.

(18) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Oxford University Press: New York, 1987.

(19) Amoureux, J.-P.; Fernandez, C.; Steuernagel, S. *J. Magn. Reson.* **1996**, *A 123*, 116.

(20) Brown, S. P.; Heyes, S. J.; Wimperis, S. *J. Magn. Reson.* **1996**, *A 119*, 280.

S0002-7863(97)03311-8 CCC: $15.00

The π pulses applied to the I-spins were phased according to the XY-4 scheme in order to eliminate the effects of resonance offset and pulse imperfections.[22]

By combining REDOR with MQMAS, the dephasing of spins S can be monitored under high-resolution conditions. Furthermore, by changing the number of rotor cycles $N_c = 2n + 2$, we were able to measure the REDOR curves[4] for the various Al species

$$\frac{\Delta S}{S_0} = 1 - \frac{S(DN_c\tau_r)}{S_0(N_c\tau_r)} \qquad (1)$$

where ΔS is the so-called REDOR difference which results from subtraction of the MQMAS spectra obtained without (S_0) and with (S) the dipolar dephasing pulses applied on spins I. We note that this curve reflects the evolution of signal which is solely due to I−S dipolar coupling D and which is free from the relaxation effects and other quantitative distortions normally associated with the MQMAS method.[23]

The ^{27}Al MQ-REDOR experiment is demonstrated on a sample of fluorinated triclinic chabazite-like AlPO$_4$−CHA aluminophosphate which was used in its as-synthesized form with trialuminum morpholinium fluoride tris(phosphate), $C_4H_{10}NO^+$-$Al_3(PO_4)_3F^-$, as a template.[24] The microcrystal structure of this compound, which was established using the synchrotron radiation method, contains three equally populated aluminum sites: an Al$_1$ site octahedrally coordinated to four oxygen and two fluorine atoms located at $r_{Al_1-F_1} = 1.88$ Å and $r_{Al_1-F_2} = 1.96$ Å, and two sites labeled Al$_2$ and Al$_3$ representing tetrahedral aluminum.[24] The nearest neighbor Al−F distances for the tetrahedral sites are $r_{Al_2-F} = 3.94$ Å and $r_{Al_3-F} = 5.72$ Å, respectively. The following values for the isotropic chemical shift σ_{iso} and the second-order quadrupolar effect (SOQE) parameter were measured in our earlier MQMAS and CPMQMAS studies of this sample: σ_{iso} of −4.5, 43.9, and 47.6 ppm and SOQE of 0.9, 2.0, and 2.6 MHz for sites Al$_1$, Al$_2$, and Al$_3$, respectively.[25]

In Figure 2, the ^{27}Al MAS spectrum of AlPO$_4$−CHA (trace 2a) is compared with the isotropic projections of sheared 3QMAS (2b) and 3Q-REDOR difference spectra taken with $N_C = 4$ (2c) and $N_C = 60$ (2d). The immediate advantage of the MQ-REDOR technique is that it provides direct evidence of the proximity of F and Al$_1$ (see spectrum 2c). This result is consistent with our previous work obtained using CPMQMAS.[12] Furthermore, by measuring the REDOR curve for Al$_1$ we estimated the strength of ^{27}Al$_1$−^{19}F dipolar coupling to be $D = 4.4$ (±0.1) kHz (see Figure 3), which corresponds to $r_{Al_1-F} = 1.88$ (±0.02) Å, in apparent agreement with the synchrotron radiation data. However, the estimate was made using the standard method for an isolated I−S spin pair[4] and thus neglected the presence of two F atoms around Al$_1$. We note that for the Al$_1$ site the resolution is sufficient to permit the REDOR measurement without including the MQMAS method. On the other hand, the tetrahedral aluminum sites are not resolved by MAS alone, and the standard 1Q-REDOR experiment yields only the combined REDOR curve for Al$_2$ and Al$_3$. However, the individual dipolar couplings for these two sites can be measured with MQ-REDOR. An example of the 3Q-REDOR difference spectrum taken for $N_C = 60$ is shown in Figure 2d. The integrated intensities of such spectra measured for $N_C = 12$, 16, 30, 40, and 60 show a clear distinction between the tetrahedral sites (see Figure 3). Analysis of these data yielded ^{19}F−^{27}Al dipolar couplings D of 0.42 (±0.02) and 0.28 (±0.02) kHz which correspond to r_{Al_2-F} and r_{Al_3-F} distances of 4.1 (±0.2) and 4.7 (±0.2) Å, respectively. While not in perfect agreement with the results of the synchrotron radiation study, the above data allow, for the first time, the assignment of resonances at 43.9 and 47.6 ppm to sites Al$_2$ and Al$_3$, respectively. It is not presently obvious to us whether the difference between the NMR and synchrotron radiation results for the Al$_3$ site is due to systematic experimental errors or due to the simplicity of our data treatment which neglects the presence of the fluorine neighbors located at a greater distance. A more detailed study of the spectral editing capabilities of MQ-REDOR, especially in the presence of multispin interactions is currently underway.

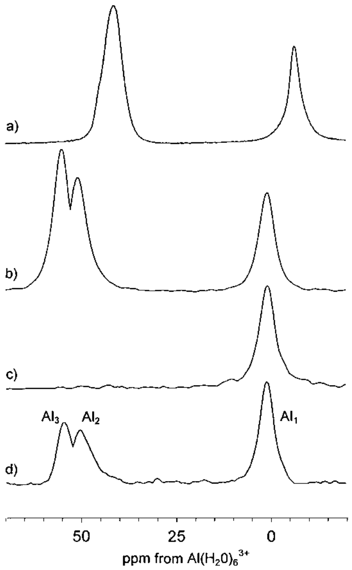

Figure 2. ^{27}Al NMR spectra of fluorinated AlPO$_4$−CHA aluminophosphate: (a) MAS; (b) 3QMAS; (c) 3Q-REDOR difference for $N_C = 4$; (d) 3Q-REDOR difference for $N_C = 60$. All spectra were acquired at 9.4 T on a Chemagnetics Infinity spectrometer using a 3.2 mm MAS probehead under a MAS speed of 20 kHz. The selective $\pi/2$ and π pulses for the S spins were obtained using an rf field of 10 kHz; the remaining pulses for both S (^{27}Al) and I (^{19}F) spins used an rf field of ~300 kHz.

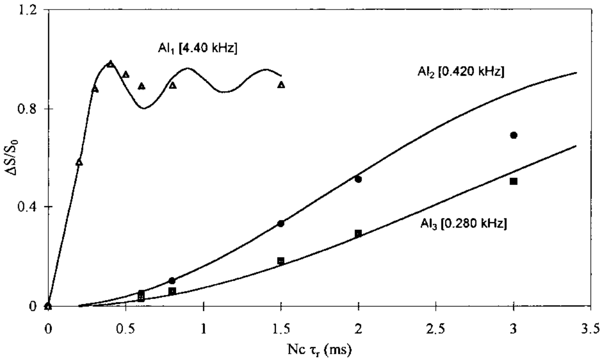

Figure 3. Measured and calculated REDOR curves for Al$_1$, Al$_2$, and Al$_3$ sites in AlPO$_4$−CHA. △ denote the datapoints obtained using 1Q-REDOR, ● and □ denote the datapoints obtained using 3Q-REDOR.

In conclusion, we have described a new experimental approach which allows one to study the connectivities between quadrupolar and spin-1/2 nuclei. Its main application should be in the spin systems where the MAS-based methods are ineffective in achieving good spectral resolution.

Acknowledgment. This research was supported at Ames Laboratory by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-7405-Eng-82. The authors thank Dr. S. Ganapathy and Dr. B. C. Gerstein for valuable discussions.

JA973311R

---

(21) Massiot, D. *J. Magn. Reson.* **1996**, *A 122*, 240.
(22) Guillion, T.; Schaefer, J. *J. Magn. Reson.* **1991**, *92*, 439.
(23) Wu, G.; Rovnyak, D.; Sun B.; Griffin, R. G. *Chem. Phys. Lett.* **1996**, *249*, 210.
(24) Harding, M. M.; Kariuki, B. M. *Acta Crystallogr.* **1994**, *C 50*, 852.
(25) Fernandez, C.; Amoureux, J.-P.; Delmotte, L.; Kessler, H. *Microporous Materials* **1996**, *6*, 125.