

High-Resolution Solid-State Heteronuclear Correlation NMR for Quadrupolar and Spin- $1/2$ Nuclei

T. P. Jarvie, R. M. Wenslow, and K. T. Mueller*

Department of Chemistry, 152 Davey Laboratory
The Pennsylvania State University
University Park, Pennsylvania 16802-6300

Received October 17, 1994

Heteronuclear correlation nuclear magnetic resonance (NMR) experiments provide useful chemical and structural information such as local geometry and the proximity of atoms to one another.¹ In this paper, we introduce a new solid-state NMR technique that provides true high-resolution correlations between quadrupolar and spin- $1/2$ nuclei. This high resolution is achieved by correlating the dynamic angle spinning (DAS) spectrum^{2,3} of half-integer spin quadrupolar nuclei in one dimension to the magic angle spinning (MAS) spectrum of nearby spin- $1/2$ nuclei in the second dimension. Demonstration of internuclear connectivities or proximity of spin- $1/2$ and quadrupolar nuclei with NMR will prove useful in studies of complex noncrystalline or microcrystalline systems such as glasses and framework solids containing quadrupolar nuclei, especially if diffraction techniques are ineffective or inconclusive.⁴

Two-dimensional correlation techniques are well documented for pairs of spin- $1/2$ nuclei in solution⁵ and solid-state⁶ NMR. A two-dimensional solid-state NMR correlation experiment, performed between two spin- $1/2$ nuclei X and Y, is usually carried out under MAS conditions, and the spectrum, therefore, has high resolution in both dimensions. Limits to the observed resolution arise principally from local disorder in the sample or inefficient averaging of more complicated spin interactions. In a general heteronuclear correlation experiment, the evolution of X-spin coherences for a time t_1 is followed by a mixing period in which polarization or coherence is transferred from the X nuclei to the Y nuclei by any of a number of schemes, including Hartmann–Hahn cross polarization (CP),^{7–10} isotropic mixing,^{11,12} or pulsed coherence transfer.^{13,14} At the proper point after mixing, signal is detected on the Y channel for a time t_2 . Fourier transformation of the time domain signals in both dimensions yields a two-dimensional frequency spectrum with nuclear connectivities displayed as cross peaks.

Similar two-dimensional MAS correlation experiments have been performed on systems with quadrupolar and spin- $1/2$

nuclei.^{15–18} In these experiments, polarization was transferred from noninteger spin quadrupolar nuclei to spin- $1/2$ nuclei using either cross polarization^{19,20} or transferred-echo double-resonance (TEDOR)¹³ mixing schemes, taking advantage of the fast longitudinal relaxation rates ($1/T_1$) of the quadrupolar spins in many materials. The two-dimensional correlation spectrum from these experiments reveals nuclear connectivities but, due to incomplete averaging of the resonances from the quadrupolar nuclei under MAS conditions, lacks high resolution in the quadrupolar dimension.

One way to achieve high resolution for half-integer spin quadrupolar nuclei is dynamic angle spinning NMR. In DAS, the sample rotor is mechanically hopped between two complementary angles.^{3,21} When a properly incremented time period is spent at each angle, anisotropic broadening of the resonances is removed and spectral lines appear at their isotropic frequencies. These total isotropic shifts are a combination of the field-independent chemical shift and a field-dependent quadrupolar shift of the resonance. DAS has been used to separate overlapping and crowded resonances in the NMR spectra of a variety of quadrupolar nuclei, including ^{11}B , ^{17}O , ^{23}Na , and ^{87}Rb .^{22–25} Field-dependent studies of the ^{17}O DAS spectra of minerals has allowed determination of true isotropic chemical shifts and parameters describing the quadrupolar coupling ($C_Q = e^2qQ/h$ and η) in a number of different oxygen environments.²⁶ In studies of potassium and potassium–magnesium network-modified silicate glasses, ^{17}O DAS was used as a truly local probe to quantify disorder in amorphous systems through the variation of Si–O–Si bond angles.²⁷

Our new two-dimensional NMR correlation experiment, shown in Figure 1, employs DAS to obtain a high-resolution spectrum of the quadrupolar nuclei. This spectrum is correlated to a high-resolution MAS spectrum of the spin- $1/2$ nuclei via a cross polarization mixing period. The quadrupolar nucleus studied was ^{23}Na , while the spin- $1/2$ nucleus was ^{31}P . The experiment begins by performing a DAS experiment on the ^{23}Na nuclei with a hop of the rotor axis from 79.19° to 37.38° . The evolution periods at the first and second angles are of equal times.² A spin echo forms at the end of the t_1 evolution, due to refocusing of the anisotropic quadrupolar frequencies. Following a hop to 0.00° , magnetization is transferred to the ^{31}P nuclei with a Hartmann–Hahn spin-lock. Cross polarization from ^{23}Na to ^{31}P was performed at 0.00° for maximum efficiency.^{20,28–30} Finally, the ^{31}P magnetization, derived only from the original

* Author to whom correspondence should be addressed.

(1) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon Press: Oxford, 1990; Vol. 14, p 610.
(2) Mueller, K. T.; Sun, B. Q.; Chingas, G. C.; Zwanziger, J. W.; Terao, T.; Pines, A. *J. Magn. Reson.* **1990**, *86*, 470–487.
(3) Wooten, E. W.; Mueller, K. T.; Pines, A. *Acc. Chem. Res.* **1992**, *25*, 209–215.
(4) Eckert, H. *Prog. Nucl. Magn. Reson. Spectros.* **1992**, *24*, 159–293.
(5) Maudsley, A. A.; Ernst, R. R. *Chem. Phys. Lett.* **1977**, *50*, 368–372.
(6) Caravatti, P.; Bodenhausen, G.; Ernst, R. R. *Chem. Phys. Lett.* **1982**, *89*, 363–367.
(7) Hartmann, S. R.; Hahn, E. *Phys. Rev.* **1962**, *128*, 2042–2053.
(8) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569–590.
(9) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031–1032.
(10) Hagaman, E. W.; Ho, P. C.; Brown, L. L.; Schell, F. M.; Woody, M. C. *J. Am. Chem. Soc.* **1990**, *112*, 7445–7450.
(11) Weitekamp, D. P.; Garbow, J. R.; Pines, A. *J. Chem. Phys.* **1982**, *77*, 2870–2883.
(12) Caravatti, P.; Braunschweiler, L.; Ernst, R. R. *Chem. Phys. Lett.* **1983**, *100*, 305–310.
(13) Hing, A. W.; Vega, S.; Schaefer, J. *J. Magn. Reson.* **1992**, *96*, 205–209.
(14) Franke, D.; Hudalla, C.; Eckert, H. *Solid State Nucl. Magn. Reson.* **1992**, *1*, 33–40.

(15) Fyfe, C. A.; Grondey, H.; Mueller, K. T.; Wong-Moon, K. C.; Markus, T. *J. Am. Chem. Soc.* **1992**, *114*, 5876–5878.

(16) Fyfe, C. A.; Mueller, K. T.; Grondey, H.; Wong-Moon, K. C. *Chem. Phys. Lett.* **1992**, *199*, 198–204.

(17) Fyfe, C. A.; Mueller, K. T.; Grondey, H.; Wong-Moon, K. C. *J. Phys. Chem.* **1993**, *97*, 13484.

(18) Fyfe, C. A.; Wong-Moon, K. C.; Huang, Y.; Grondey, H.; Mueller, K. T., submitted to *J. Phys. Chem.*

(19) Vega, A. J. *J. Magn. Reson.* **1992**, *96*, 50–68.

(20) Vega, A. J. *Solid State Nucl. Magn. Reson.* **1992**, *1*, 17–32.

(21) Mueller, K. T.; Chingas, G. C.; Pines, A. *Rev. Sci. Instrum.* **1991**, *62*, 1445–1452.

(22) Chmelka, B. F.; Mueller, K. T.; Pines, A.; Stebbins, J.; Wu, Y.; Zwanziger, J. W. *Nature (London)* **1989**, *339*, 42–43.

(23) Mueller, K. T.; Wu, Y.; Chmelka, B. F.; Stebbins, J.; Pines, A. *J. Am. Chem. Soc.* **1991**, *113*, 32–38.

(24) Mueller, K. T.; Wooten, E. W.; Pines, A. *J. Magn. Reson.* **1991**, *92*, 620–627.

(25) Baltisberger, J. H.; Gann, S. L.; Wooten, E. W.; Chang, T. H.; Mueller, K. T.; Pines, A. *J. Am. Chem. Soc.* **1992**, *114*, 7489–7493.

(26) Mueller, K. T.; Baltisberger, J. H.; Wooten, E. W.; Pines, A. *J. Phys. Chem.* **1992**, *96*, 7001–7004.

(27) Farman, I.; Grandinetti, P. J.; Baltisberger, J. H.; Stebbins, J. F.; Werner, U.; Eastman, M. A.; Pines, A. *Nature (London)* **1992**, *358*, 31–35.

(28) Fyfe, C. A.; Wong-Moon, K. C.; Grondey, H.; Mueller, K. T. *J. Phys. Chem.* **1994**, *98*, 2139–2142.

(29) Stejskal, E. O.; Schaefer, J.; Waugh, J. S. *J. Magn. Reson.* **1977**, *28*, 105–112.

(30) Sardashti, M.; Maciel, G. E. *J. Magn. Reson.* **1987**, *72*, 467–474.

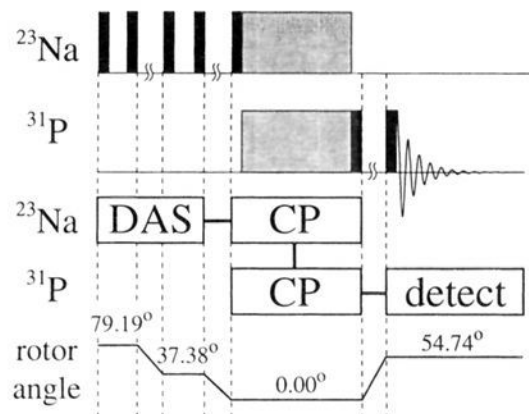


Figure 1. Pulse sequence and rotor angles used in the DAS/CP/MAS experiment. Hop times from 79.19° to 37.38° , 37.38° to 0.00° , and 0.00° to 54.74° were 40, 40, and 60 ms, respectively. Cross polarization contact time was 5 ms, and the ^{23}Na and ^{31}P $\pi/2$ pulses (small rectangles) were $20\ \mu\text{s}$ in length. TPPI phase cycling of the first pulse provided pure-phase spectra in both dimensions. Additional phase cycling ensured a reversal of spin-temperature in the rotating frame and a suppression of axial peaks which may arise due to relaxation during the hops.

^{23}Na DAS signal, was stored along the magnetic field, and the rotor axis was moved to the magic angle for high-resolution NMR detection of the ^{31}P signal. All spectra were recorded on a home-built NMR spectrometer using a DAS setup designed by Mueller *et al.*²¹ The probe was dual tuned to ^{23}Na and ^{31}P with resonance frequencies of 105.804 and 161.918 MHz, respectively. Time-proportional phase incrementation (TPPI) was used to obtain pure phase spectra in both dimensions.^{31,32}

As a demonstration of the experiment, we chose polycrystalline sodium trimetaphosphate, $\text{Na}_3\text{P}_3\text{O}_9$, as a test compound. This sample contains two crystallographically inequivalent ^{23}Na sites and two crystallographically inequivalent ^{31}P sites.³³ For both nuclei, the general site has a population twice that of the mirror site. The $\text{Na}_3\text{P}_3\text{O}_9$ sample was prepared by heating NaH_2PO_4 (Aldrich) to 550°C for 2 h and then slow cooling ($2^\circ\text{C}/\text{min}$) to room temperature. We experimentally determined the isotropic chemical shifts of the two ^{31}P sites, referenced to 85% H_3PO_4 (0.0 ppm), as -18.7 and -15.5 ppm for the general and mirror sites, respectively. A Herzfeld-Berger fit³⁴ to the ^{31}P MAS spectrum yielded chemical shift anisotropy ($\Delta\sigma$) and asymmetry parameter (η_σ) values of $\Delta\sigma = 256$ ppm, $\eta_\sigma = 0.47$ for the general site and $\Delta\sigma = 261$ ppm, $\eta_\sigma = 0.45$ for the mirror site. Quadrupolar coupling constants (C_Q) and asymmetry parameters for the two ^{23}Na sites were previously determined by Koller *et al.*³⁵ They reported $C_Q = 1.57$ MHz, $\eta_Q = 0.56$ for the general site and $C_Q = 2.20$ MHz, $\eta_Q = 0.70$ for the mirror site. The experimentally determined DAS total isotropic shifts of the two ^{23}Na sites in a 9.4 T magnetic field, referenced against 0.1 M NaCl (0.0 ppm), are -2.5 ppm for the general and -18.9 ppm for the mirror site.

The results of the two-dimensional DAS/CP/MAS experiment on $\text{Na}_3\text{P}_3\text{O}_9$ are presented in Figure 2. At the top is the MAS spectrum of ^{23}Na , revealing the presence of the two sodium environments. The resonance lines are broadened by quadrupolar interactions which result in spectral overlap. Below the MAS spectrum is the projection of the DAS dimension from the two-dimensional spectrum, showing the increased resolution possible with the DAS technique. The two-dimensional spectrum itself clearly shows the resolution of four distinct cross peaks between the two ^{31}P and two ^{23}Na resonances. Similar MAS correlation experiments (not shown) revealed only broad

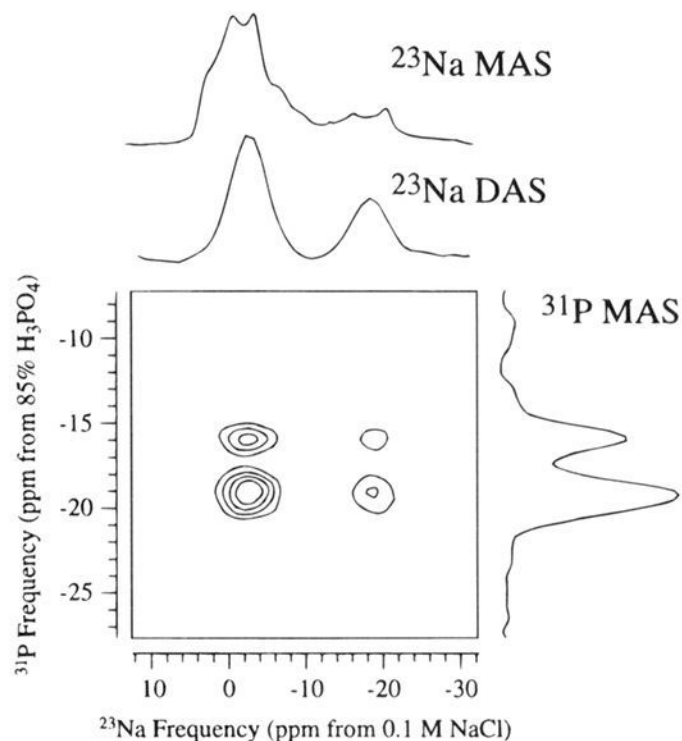


Figure 2. One-dimensional MAS spectrum (top) and the DAS narrowed spectrum (middle) of ^{23}Na in $\text{Na}_3\text{P}_3\text{O}_9$. The two-dimensional heteronuclear DAS/CP/MAS correlation spectrum of ^{23}Na and ^{31}P in $\text{Na}_3\text{P}_3\text{O}_9$ (bottom) was acquired with the pulse sequence shown in Figure 1. A total of 52 t_1 points with 800 run averages each were acquired using a recycle delay of 3 s. The two-dimensional spectrum was folded onto the ^{31}P isotropic peaks after transformation of the data to increase signal-to-noise and to fully quantify the cross peaks. The spectrum on the right is a projection of the ^{31}P dimension, showing the two resolved peaks under MAS conditions.

^{23}Na resonances connected to each of the ^{31}P sites. While the measured intensities in this new experiment qualitatively match the expected intensities, quantitative results will require a more complete characterization of the cross polarization dynamics, or possibly the use of an alternate mixing scheme such as TEDOR (refs 13, 16, and 17). A further important consideration in future experiments will be the T_1 relaxation time of the quadrupolar nuclei. In order for the DAS portion of the experiment to be successful, the hop time for changing rotor angles must be on the order of or less than the shortest T_1 in the system. This places a current lower limit on T_1 at approximately 50 ms if two hops are required.

In conclusion, a two-dimensional NMR correlation experiment has been successfully accomplished between the ^{23}Na and ^{31}P nuclei in polycrystalline $\text{Na}_3\text{P}_3\text{O}_9$. This technique has immediate application in the study of sodium phosphate glasses,³⁶ where characterization of the nuclear sites, as well as connectivity information between sites, is essential for understanding local ordering in the amorphous state. The separation of the ^{23}Na resonances by the local correlation to different phosphate species in the glasses will be necessary to quantify local disorder and will be possible with this new technique. The general nature of the experiment makes it capable of analyzing many noncrystalline and microcrystalline systems containing combinations of quadrupolar and spin- $1/2$ nuclei. These spin combinations are commonly found in glasses, ceramics, minerals, and framework solids. The new resolution and spectral editing capabilities now available will allow detailed inspection of local microstructure in these important classes of materials.

Acknowledgment. The authors wish to thank Professor Colin Fyfe for scientific advice and many worthwhile discussions. This work was supported in part by the Camille and Henry Dreyfus New Faculty Awards Program. This report is also based upon work supported by the National Science Foundation under Grant No. DMR-9458053.

JA943374Z

(31) Drobny, G.; Pines, A.; Sinton, S.; Weitekamp, D.; Wemmer, D. *Symp. Faraday Div. Chem. Soc.* **1979**, *13*, 49–55.

(32) Marion, D.; Wuthrich, K. *Biochem. Biophys. Res. Commun.* **1983**, *113*, 967–974.

(33) Ondik, H. M. *Acta Crystallogr.* **1965**, *18*, 226–232.

(34) Herzfeld, J.; Berger, A. E. *J. Chem. Phys.* **1980**, *73*, 6021–6030.

(35) Koller, H.; Engelhardt, G.; Kentgens, A. P. M.; Sauer, J. *J. Phys. Chem.* **1994**, *98*, 1544–1551.

(36) Brow, R.; Kirkpatrick, R.; Turner, G. *J. Noncryst. Solids* **1990**, *116*, 39–45.