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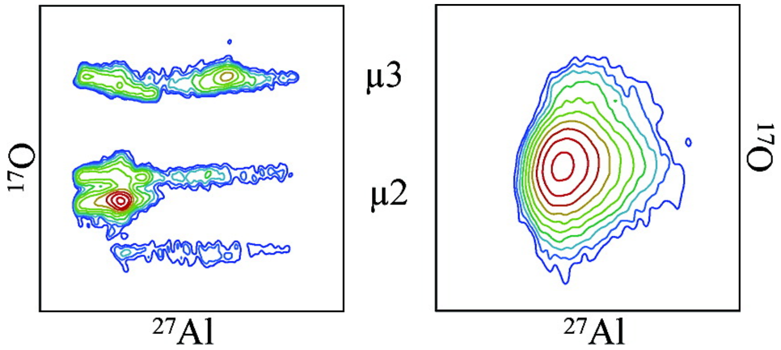

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NMR Heteronuclear Correlation between Quadrupolar Nuclei in Solids

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High-resolution solid-state NMR has become an extremely useful tool for the structural characterization of a large variety of materials ranging from inorganic to porous materials, zeolites, hybrid organic−inorganic, organic, and bioinvolved materials. This is due to the ability of NMR not only to characterize ordered crystalline structures but also to give detailed insight to the structure of partly disorganized, amorphous or glassy materials.[1,2] An important part of the power of solid-state NMR methods comes from their ability to produce homonuclear or heteronuclear correlation charts that can evidence spatial proximity (from dipolar interaction)[3,4] or chemical bonding (from *J*-couplings),[1,3] as used to derive protein structures in liquid-state NMR experiments. Nevertheless, a major difficulty arises with quadrupolar nuclei (nuclear spin $I > {}^{1}/_{2}$) because the quadrupolar interaction induces quick relaxation in the liquid state and broadening at first and second order in solids. The quadrupolar nuclei are the most abundant nuclei in inorganic materials and are of crucial importance in many biological structures.[5] The question of efficiently generating a correlation between quadrupolar nuclei under high-resolution conditions (fast magic angle spinning—MAS and high-magnetic fields) remained an open question. In this contribution, we show that such a correlation experiment can be generated with a simple and robust pulse sequence, using an isotropic (or scalar) interaction that does not necessitate reintroduction by sophisticated spin manipulation. We demonstrate the experiment with a $\{^{17}O\}^{27}Al$ (both $I = {}^{5}/_{2}$ nuclei) experiment carried out on a crystalline test sample and show that the technique is reliable and sensitive enough to unambiguously evidence the presence of an unusual "tricluster" μ_3 oxygen coordination in a glass of $CaAl_2O_4$ composition, with specific ^{17}O and ^{27}Al signatures.

Two possible ways exist for building up heteronuclear high-resolution solid-state NMR experiments. The first, and most commonly used, method is to restore the through-space dipolar interaction. This interaction vanishes under magic angle spinning (MAS) and has to be reintroduced using continuous wave or modulated radio frequency (rf) pulses in cross polarization (CP-MAS) experiments. This is very efficient for pairs of $I = {}^{1}/_{2}$ nuclei but suffers large limitations when involving a quadrupolar nucleus because spin locking requires very small rf fields.[6,7] This leads to difficulties in obtaining homogeneous irradiation of the whole spectral domain, which extends over typically tens of kilohertz (offset dependence). The CPMAS becomes even more complex, difficult and insensitive, when dealing with pairs of quadrupolar nuclei.[8] The second method makes use of the nonvanishing isotropic terms, namely, the scalar (or isotropic) part of the indirect *J*-coupling.[9] This interaction is directly characteristic of the existence of a chemical bond and can provide very detailed insight to the structure of crystalline or glassy materials.[1,3,10−13] Although small to very small (expected tens of hertz in our materials) as compared to the other interactions (kilohertz to megahertz), the isotropic *J*-coupling terms do not vanish upon MAS and, thus, do not necessitate reintroduction. However, it requires long evolution times to develop and, consequently, could only be used for spin systems exhibiting long enough spin−spin relaxation times (T_2' or coherence lifetime).[14] Finally, it is important to remark that there exist, to our knowledge, few (if any) measurements of *J*-coupling between quadrupoles. In liquid-state experiment, the rapid reorientation induces quick relaxation that precludes their observation; while in solid state, the dominant quadrupolar broadenings (~kilohertz) masks these small effects (hertz). This interaction thus remains largely unknown for the case of two quadrupoles, but we think that we demonstrate that it is present and usable.

The experiment that we propose is a slightly modified version of the heteronuclear multiple quantum correlation (HMQC, Figure 1) experiment that we previously used for $^{27}Al/^{31}P$ correlation.[13] It leads a spectrum correlating the directly observed ^{27}Al central transition (CT) spectrum with the indirectly observed ^{17}O CT spectrum. The robustness of the sequence comes from the minimum number of pulses involved on both channels, all pulses selectively exciting the central transitions in the approximation of fictitious $I = {}^{1}/_{2}$ spins. This approach was previously used in several different experiments[13,15,16] and keeps providing a broadband excitation of the whole spectrum of the central transitions, even at high fields. The HMQC experiment is run synchronized with the MAS spinning rate so that possible spinning sidebands sum up in the indirect dimension.[17] Our experiments were acquired at high principal field (750 MHz − B_0 17.6 T), which reduces second-order quadrupolar broadenings and increases sensitivity,[5,18] with a gain proportional to $B_0{}^2$ for each dimension and to $B_0{}^4$ for the correlation experiment. The signal-to-noise of the whole experiment is optimized by several signal enhancement methods: double frequency sweep (DFS)[19] on the starting nucleus (gain >2.0), acquisition and processing of the full echo[13,15,16] (gain of $\sim\sqrt{2}$). If we assume that the scalar *J*-coupling is the active interaction, the double quantum filtered signal grows with $\sin^2(\pi J\tau)/(S + {}^{1}/_{2})$ and competes with the T_2' exponential decay. The T_2' of half integer quadrupolar nuclei can be significantly increased when spinning slightly off the magic angle.[20] For our test sample (CA2), Figure 2a shows that T_2' gets nearly twice as long, with a signal enhancement of ~3, when running the HMQC experiment off the magic angle by ~1°. Under these conditions, the dipolar interaction partially remains (off magic angle contribution) and may participate in the correlation. We can remark that this angle offset remains small enough to enhance the signal without broadening the line shapes of both nuclei. Moreover, because both nuclei undergo second-order broadening, the $\{^{17}O\}^{27}Al$ correlation chart contains the encoding of their relative spatial orientation.

The structure of Grossite ($CA2-CaAl_4O_7$) crystalline phase involves four different ^{17}O sites[22]: three with the usual μ_2

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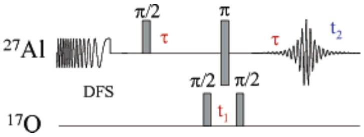

Figure 1. HMQC pulse sequences. All pulses are central transition CT-selective; τ and t_1 are synchronized with MAS spinning rate.

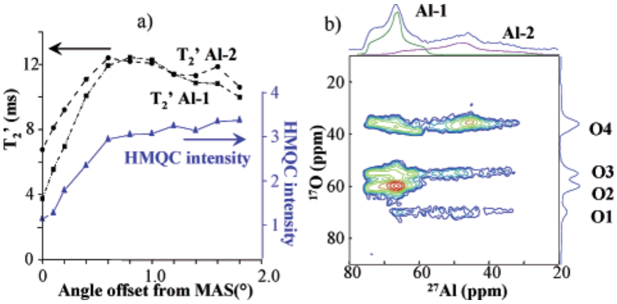

Figure 2. ^{17}O 30% enriched CA2$-$CaAl$_2$O$_7$ crystalline sample: (a) variation of T_2' for the two Al sites and HMQC intensity (normalized to *on angle*) versus angle offset from MAS. (b) $\{^{17}O\}^{27}Al$ HMQC spectrum (ν_R 15 kHz, τ 3ms, 17.6 T $-$ 750 MHz, 64 scans).

coordination, OAl$_2$ (O1, O2, O3) and one with a unique example, in a crystalline compound of that family, of a tricluster μ_3 coordination, OAl$_3$ (O4). Aluminum occupies two different Al$(\mu_2)_{4-x}(\mu_3)_x$ sites: Al$_1$ ($x = 1$) and Al$_2$ ($x = 2$) with different ^{27}Al chemical shifts and quadrupolar couplings.[21] The connectivity scheme is unambiguously established from the $\{^{17}O\}^{27}Al$ HMQC correlation spectrum (Figure 2b): Al-1 is connected with O4, O3, and 2xO2, whereas Al-2 is connected with 2xO4, O3, and O1. Summarizing the NMR parameters of the CA2 and CA(CaAl$_2$O$_4$) crystals (Supporting Information), we remark that the ^{27}Al isotropic chemical shift of Al$(\mu_2)_{4-x}(\mu_3)_x$ environment decreases by 5 ppm per x or μ_3, while ^{17}O μ_2 are found at ~70 ppm and μ_3 at ~40 ppm.

Given the robustness of the sequence and its remarkable sensitivity (only 64 transients for the CA2 experiment), it was possible to acquire a spectrum of a ground droplet of ~50 mg of a CA (CaO$-$Al$_2$O$_3$) glass sample obtained with a contactless laser-heated aerodynamic levitation device.[23] The ^{17}O and ^{27}Al individual MAS and MQMAS spectra of CA glass already provide information. The distribution of isotropic chemical shifts dominates the ^{17}O spectra with small second-order effects,[24] they show a main line extending from ~90 down to ~30 ppm, clearly suggesting two Gaussian components at 69 and 37 ppm. This 37 ppm component, absent in Ca-rich CA38 glass,[24] is located at the expected μ_3 position. The distributions of both isotropic chemical shifts and quadrupolar interaction dominate the ^{27}Al dimension, inducing typical asymmetric line shapes (with δ_{iso} in its rising left edge) that can be reliably modeled using a Gaussian isotropic model (GIM).[2] The $\{^{17}O\}^{27}Al$ HMQC correlation spectrum (Figure 3) confirms the presence of two bridging oxygen components (μ_2 and ~5% μ_3) with their relevant aluminum counterparts, Al$(\mu_2)_4$, and Al$(\mu_2)_3(\mu_3)_1$ unambiguously identified from their isotropic chemical shifts (79 and 74 ppm). This result is the first comprehensive experimental proof of the presence of μ_3 oxygen sites,[22,25−27] both from their O and Al signature.

In conclusion, we showed for the first time that it is possible to acquire efficiently heteronuclear correlation experiments in solid state between second-order-broadened half integer quadrupolar nuclei using isotropic mixing, presumably mediated by a scalar *J*-coupling that remains largely unknown. This experiment is possible thanks to the gain of sensitivity proportional to the fourth power of the principal field that turns a challenging experiment into a real efficient tool. This class of experiment could be extended to other pairs of nuclei. We believe that it may become very useful, providing detailed insight to the structure and properties of glasses, porous or mesoporous framework materials, zeolites, hybrid organic$-$inorganic, or even bioinvolved materials, addressing questions, such as the characterization of oxygen protonation state or activity of catalytic materials.

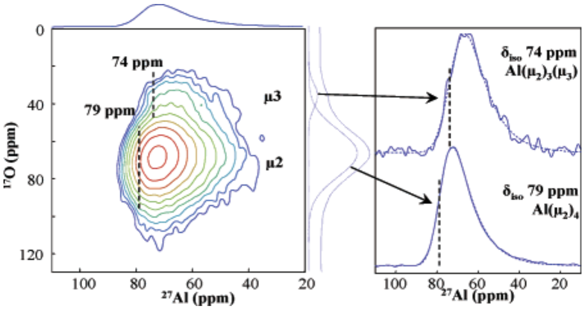

Figure 3. $\{^{17}O\}^{27}Al$ HMQC spectrum (ν_R 25 kHz, τ 7ms, 17.6 T, 480 scans) of CA glass (^{17}O 30% enriched) and ^{27}Al slices taken at μ_2 and μ_3 locations, exhibiting a 5 ppm difference in the isotropic chemical shift. The dotted lines are the modeled lines considering a GIM distribution.[2] The dashed lines indicate the position of ^{27}Al isotropic chemical shifts.

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Supporting Information Available: Acquisition parameters, ^{27}Al and ^{17}O NMR parameters of the CA and CA2 crystals, and CA glass. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Cadars, S.; Lesage, A.; Emsley, L. *J. Am. Chem. Soc.* **2005**, *127*, 4466−4476.
(2) Neuville, D. R.; Cormier, L.; Massiot, D. *Geochim. Cosmochim. Acta* **2004**, *68*, 5071−5079.
(3) Hedin, N.; Graf, R.; Christiansen, S. C.; Gervais, C.; Hayward, R. C.; Eckert, J.; Chmelka, B. F. *J. Am. Chem. Soc.* **2004**, *126*, 9425−9432.
(4) Brouwer, D. H.; Kristiansen, P. E.; Fyfe, C. A.; Levitt, M. H. *J. Am. Chem. Soc.* **2005**, *127*, 542−543.
(5) Wu, G.; Wong, A.; Gan, Z.; Davis, J. T. *J. Am. Chem. Soc.* **2003**, *125*, 7182−7183.
(6) De Paul, S. M.; Ernst, M.; Shore, J. S.; Stebbins, J. F.; Pines, A. *J. Phys. Chem. B* **1997**, *101*, 3240−3249.
(7) Eden, M.; Grins, J.; Shen, Z.; Weng, Z. *J. Magn. Reson.* **2004**, *169*, 279−283.
(8) Eastman, M. *J. Magn. Reson.* **1999**, *139*, 98−108.
(9) Wasylishen, R. In *Encyclopedia of NMR*; Grant, D. M., Harris, R. K., Eds.; Wiley: New York, 2002; Vol. 9, pp 262−274.
(10) Fyfe, C. A.; Grondey, H.; Feng, Y.; Kokotailo, G. T. *J. Am. Chem. Soc.* **1990**, *112*, 8812−8820.
(11) Fayon, F.; Le Saout, G.; Emsley, L.; Massiot, D. *Chem. Commun*. **2002**, 1702−1703.
(12) Fayon, F.; King, I. J.; Harris, R. K.; Gover, R. B. K.; Evans, J. S. O.; Massiot, D. *Chem. Mater.* **2003**, *15*, 2234−2239.
(13) Massiot, D.; Fayon, F.; Alonso, B.; Trebosc, J.; Amoureux, J. P. *J. Magn. Reson.* **2003**, *164*, 165−170.
(14) De Paepe, G.; Hodgkinson, P.; Emsley, L. *Chem. Phys. Lett.* **2003**, *376*, 259−267.
(15) Grandinetti, P. J.; Baltisberger, J. H.; Llor, A.; Lee, Y. K.; Werner, U.; Eastman, M. A.; Pines, A. *J. Magn. Reson. A* **1993**, *103*, 72−81.
(16) Massiot, D.; Touzo, B.; Trumeau, D.; Coutures, J. P.; Virlet, J.; Florian, P.; Grandinetti, P. J. *Solid State NMR* **1996**, *6*, 73−83.
(17) Massiot, D. *J. Magn. Reson. A* **1996**, *122*, 240−244.
(18) Gan, Z.; Gor'kov, P.; Cross, T. A.; Samoson, A.; Massiot, D. *J. Am. Chem. Soc.* **2002**, *124*, 5634−5635.
(19) Iuga, D.; Kentgens, A. P. M. *J. Magn. Reson.* **2002**, *158*, 65−72.
(20) Kwak, H. T.; Srinivasan, P.; Quine, J.; Massiot, D.; Gan, Z. *Chem. Phys. Lett.* **2003**, *376*, 75−82.
(21) Skibsted, J.; Henderson, E.; Jakobsen, H. J. *Inorg. Chem.* **1993**, *32*, 1013−1027.
(22) Stebbins, J. F.; Oglesby, J. V.; Kroeker, S. *Am. Mineral.* **2001**, *86*, 1307−1311.
(23) Massiot, D.; Trumeau, D.; Touzo, B.; Farnan, I.; Rifflet, J. C.; Douy, A.; Coutures, J. P. *J. Phys. Chem.* **1995**, *99*, 16455−16459.
(24) Allwardt, J. R.; Keun Lee, S.; Stebbins, J. F. *Am. Mineral.* **2003**, *88*, 949−954.
(25) Lacy, E. D. *Phys. Chem. Glasses* **1963**, *4*, 234−238.
(26) Stebbins, J. F.; Xu, Z. *Nature* **1997**, *390*, 60−61.
(27) Toplis, M. J.; Dingwell, D. B.; Lenci, T. *Geochim. Cosmochim. Acta* **1997**, *61*, 2605−2612.

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