Through-bond homonuclear correlation experiments in solid-state NMR applied to quadrupolar nuclei in Al–O–P–O–Al chains†

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Through-bond homonuclear correlation experiments can be realised in solids between spins of type X, separated by four chemical bonds, in X–O–Y–O–X motifs, provided a *J* coupling between X and Y exists: central transitions of quadrupolar ^{27}Al spins can be correlated *via* the J^2 scalar coupling between ^{27}Al (X) and ^{31}P (Y) in materials featuring Al–O–P–O–Al motifs.

Solid-state NMR is widely recognized as an extremely powerful tool for the structural characterization of a large variety of solid materials (inorganic materials like zeolites or glasses and organic materials like proteins or hybrid organic–inorganic…). The power of this method relies on the ability to characterize the local environment (chemical shift), the spatial proximity (through-space dipolar interaction) or the chemical bonding (through-bond scalar coupling). Quadrupolar nuclei (spin > ½) are actually difficult to deal with, as they exhibit fast relaxation in liquid phase and strong first and second order broadenings in solid state. A 2D NMR HMQC experiment has been recently introduced to characterize through-bond *heteronuclear* correlations between adjacent quadrupolar nuclei (in ^{27}Al–^{17}O systems) under MAS (Magic Angle Spinning) in solids.[1] Homonuclear through-space correlations methods have also been introduced, using dipolar interactions between neighbouring quadrupolar nuclei.[2–4]

We present here the first homonuclear correlation experiment applied to quadrupolar nuclei making use of the sole scalar *J*-coupling. This experiment uses a relayed transfer from ^{27}Al to neighboring ^{31}P and to a second ^{27}Al and is based on an Heteronuclear Single Quantum Correlation (HSQC) experiment.[5] This experiment, shown in Fig. 1, and further referred to as an Homonuclear–Heteronuclear Single Quantum Correlation experiment (H-HSQC), provides experimental evidence for through-bond homonuclear correlations between quadrupolar nuclei separated by *four* chemical bonds.

Weak pulses have been used on the ^{27}Al central transition (further described as a fictitious spin-½), which is prepared by enhancement from the satellite transitions by DFS[6] or RAPT[7] transfer. The first INEPT transfer allows for the creation of a density operator proportional to $2\mathrm{Al}^1_{z,\mathrm{CT}}\mathrm{P}_y$ after an evolution under the scalar coupling during a delay 2τ. The transfer efficiency from the central transition of ^{27}Al to ^{31}P is equal to $\sin(2\pi J\tau)\cos^{n-1}(2\pi J\tau)$, where n is the number of ^{31}P atoms *J*-coupled to the central transition of the ^{27}Al spin. The optimum transfers for $n = \{1, 2,3,4\}$ are obtained when $\tau \approx \{(4J)^{-1},(8J)^{-1},(10J)^{-1},(12J)^{-1}\}$ respectively, provided the dephasing of the magnetization can be neglected, and assuming equal *J* values. The second echo period ($2\ \tau_2$) allows for the conversion of $\mathrm{Al}^1_{z,\mathrm{CT}}\mathrm{P}_y$ into $\mathrm{Al}^2_{z,\mathrm{CT}}\mathrm{P}_y$. The diagonal signal corresponds to the remaining $\mathrm{Al}^1_{z,\mathrm{CT}}\mathrm{P}_y$ term. This transfer depends upon n', the number of ^{27}Al spins coupled to the ^{31}P nucleus. The functions describing the intensities of the diagonal signal ($\mathrm{Al}^1_{z,\mathrm{CT}}\mathrm{P}_y$) and of the cross-peaks (stemming from the conversion of $\mathrm{Al}^1_{z,\mathrm{CT}}\mathrm{P}_y$ into $\mathrm{Al}^2_{z,\mathrm{CT}}\mathrm{P}_y$) are given below. Eqn (1), (2) and (3) correspond to $n' = 2$, 3 and 4, respectively, with an initial density operator $\sigma(\tau_2 = 0) = 2\mathrm{Al}^1_{z,\mathrm{CT}}\mathrm{P}_y$.

$$\begin{gathered} I(\mathrm{Al}^1_z\mathrm{P}_y) = -1/2[1 + \cos 4\pi J\tau_2] \text{ and} \\ I(\mathrm{Al}^2_z\mathrm{P}_y) = -1/2[-1 + \cos 4\pi J\tau_2] \end{gathered} \tag{1}$$

$$\begin{gathered} I(\mathrm{Al}^1_z\mathrm{P}_y) = 1/4[\cos 6\pi J\tau_2 + 3\cos 2\pi J\tau_2] \text{ and} \\ I(\mathrm{Al}^2_z\mathrm{P}_y) = 1/4[\cos 6\pi J\tau_2 - \cos 2\pi J\tau_2] \end{gathered} \tag{2}$$

$$\begin{gathered} I(\mathrm{Al}^1_z\mathrm{P}_y) = 1/8[3 + 4\cos 4\pi J\tau_2 + \cos 8\pi J\tau_2] \text{ and} \\ I(\mathrm{Al}^2_z\mathrm{P}_y) = 1/8[-1 + \cos 8\pi J\tau_2] \end{gathered} \tag{3}$$

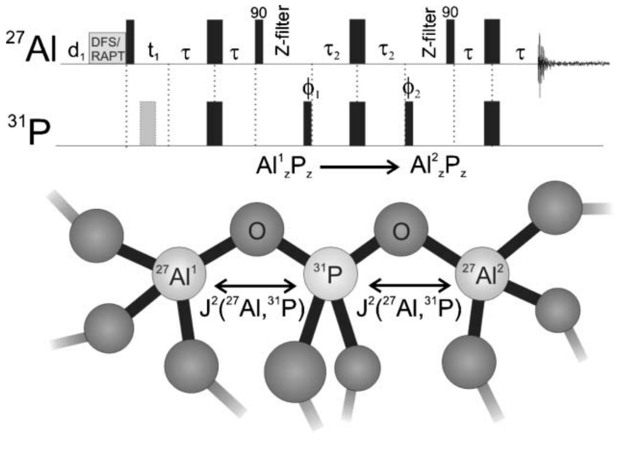

Fig. 1 The H-HSQC experiment is presented, featuring the magnetization transfer from the Al^1 spin to the Al^2 spin. A scheme of the atoms and the scalar couplings involved is shown below in the ^{27}Al/^{31}P case. The DFS or RAPT (signal enhancement for the Central Transition of the quadrupolar nucleus) and ^{31}P 180° pulses (to prevent the evolution under the scalar coupling of ^{27}Al magnetization during the t_1 delay) in grey are optional. The Bruker pulse sequence is given in the supplementary material.† The States method was used to achieve quadrature detection in the indirect dimension. Two Z-filters (300 rotor periods) have been used to suppress unwanted contributions; these can actually be suppressed for amorphous materials.[8]

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If the ^{31}P spin is only coupled to $^{27}Al^1$ and $^{27}Al^2$ ($n' = 2$), the transfer, which is proportional to $-1 + \cos(4\pi\ J\tau_2)$, will be complete when $\tau_2 = (4J)^{-1}$. Hence, the diagonal signal, which is proportional to $1 + \cos(4\pi\ J\tau_2)$, vanishes, and no diagonal will be observed in the 2D spectrum. The diagonal peak and the cross peak are of opposite signs, and this allows one to discriminate the cross peak contribution from the residual diagonal signal. This is especially useful whenever the refocalization is not complete, as some residual diagonal signals will be observed.

When $n' = 3$ or 4, the diagonal signal cannot be suppressed, but an optimum value for τ_2 can be determined experimentally by optimizing τ_2 to get the maximum negative signal (which characterizes the cross peak). These optimum values are found to be $\tau_2 \approx (5J)^{-1}$ and $(6J)^{-1}$ when $n' = 3$ or 4, respectively, provided all the scalar couplings are equal and relaxation or broadening phenomena can be neglected.

This new H-HSQC pulse sequence has been tested on a powder sample of $AlPO_4$-14.[9–11] The ^{27}Al and ^{31}P spectra of $AlPO_4$-14 have been completely assigned[9] and its crystal structure is well known.[12] Each ^{31}P atom is connected to four ^{27}Al atoms *via* an oxygen atom and each ^{27}Al atom is connected to four ^{31}P atoms also *via* an oxygen atom. Four different Al sites and four different P sites can be distinguished. These are numbered according to ref. 9, from which the expected connectivities are also extracted. The HMQC[13] spectrum is shown as a reference in Fig. 2 and the H-HSQC spectrum featuring the expected connectivities is shown in Fig. 3. In the H-HSQC spectrum, negative cross peaks are observed for every pair of ^{27}Al atoms as expected, except for Al_1 which is never connected to another Al_1 atom. Hence the signal appearing at ($\delta(Al_1)$, $\delta(Al_1)$) is always positive and purely diagonal, whereas the signal at ($\delta(Al_4)$, $\delta(Al_4)$), stemming from the diagonal signal and from the Al_4–O–P_2–O–Al_4 motifs exhibits a negative sign for slightly longer delays ($130\tau_r$) and is observed in 1D mode using a larger number of scans. Signals stemming from Al_3 are actually stronger than the others, due to the fact that Al_3 is less affected by second-order quadrupolar broadenings (as seen in the projections of Fig. 2). The quadrupolar coupling constants and asymmetry parameters of $Al_{1,2,3,4}$ are equal to 5.58, 4.08, 1.74 and 2.57 MHz and 0.97, 0.82, 0.63 and 0.7, respectively.[10] Hence the cross peak ($\delta(Al_1)$, $\delta(Al_4)$) is not detectable, whereas the ($\delta(Al_4)$, $\delta(Al_1)$) cross peak is very weak.

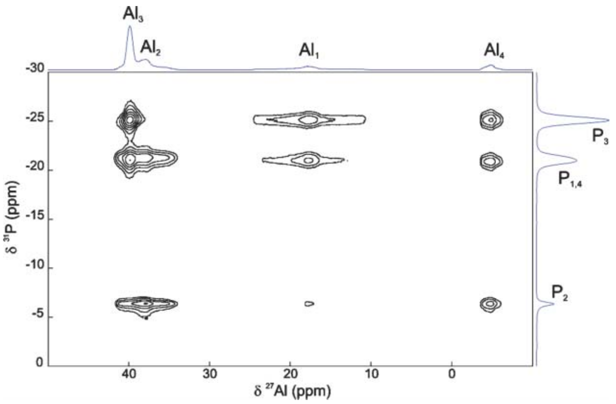

Fig. 2 $^{27}Al(CT)$-^{31}P HMQC spectrum of an $AlPO_4$-14 sample, performed at 17.6T (^1H Larmor frequency of 750 MHz), using MAS, in a 4 mm rotor (ν_r = 14 kHz). The corresponding projections are shown on the spectrum, as well as the peak assignments. Al_1 and Al_4 feature large second order quadrupolar broadenings.

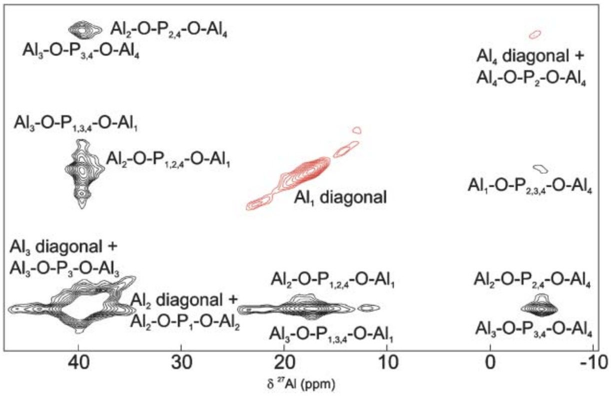

Fig. 3 H-HSQC spectrum of an $AlPO_4$-14 sample, featuring the Al–Al pairs giving rise to negative cross-peaks (in black) and the positive diagonal signals (in red). The spectrum was obtained in the experimental conditions mentioned in the Fig. 2 caption. The pulse sequence was run using the following parameters: the recycling delay d_1 was set to 250 ms, the τ period for the INEPT transfer was set to 40 rotor periods τ_r (optimized for the best overall signal-to-noise ratio, as the different ^{27}Al–^{31}P pairs feature distinct scalar couplings and dephasing times), the τ_2 period was set to $120\tau_r$ (in order to maximize the negative cross peaks intensities), and a Z-filter of $300\tau_r$ was used. 16 dummy scans and 1152 scans were acquired for each of the 128 t_1 increments and exponential broadening (LB = 100 Hz) was applied in both dimensions.

We show that small scalar couplings (J = 10–30 Hz), persisting in solids under MAS conditions, can be used to generate an Homonuclear H-HSQC correlation experiment that characterizes the through bond connectivity of quadrupolar nuclei in solids across four chemical bonds. This experiment has been tested and demonstrated on an $AlPO_4$-14 sample where it allows for a detailed characterization of the Al–O–P–O–Al motives in a complex three dimensional bonded network. This experiment opens new possibilities for the characterization of complex chemical bond networks in perfectly crystalline, disordered or amorphous solids.

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