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Three-dimensional through-bond homonuclear–heteronuclear correlation experiments for quadrupolar nuclei in solid-state NMR applied to ^{27}Al–O–^{31}P–O–^{27}Al networks

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Abstract

We present here the first 3D homonuclear/heteronuclear correlation experiment applied to quadrupolar nuclei and making use of the sole scalar *J*-coupling. This experiment, based on the 2D-Homonuclear–Heteronuclear Single Quantum Correlation (H–HSQC) experiment, uses a relayed transfer from the ^{27}Al central transition to neighbouring ^{31}P spins and to the central transition of a second ^{27}Al. It confirms the correlation map characterizing the two ^{27}Al and the ^{31}P NMR signatures of ^{27}Al–O–^{31}P–O–^{27}Al chemically bonded molecular motifs.

Keywords: 3D; *J*-coupling; Quadrupolar nuclei; Aluminium; Phosphate

1. Introduction

3D *J*-mediated correlation experiments have been introduced a long time ago in liquid-state NMR experiments [1]. They enable characterization of triplets of atoms which are connected together, and, as such, are very powerful to characterize the network of chemical bonds in a solution or in a solid-state sample as well. High resolution solid-state experiments can make efficient use of the scalar part of the *J*-coupling in MAS experiments on organic and inorganic solids [2,3], despite the heterogeneous line broadening mechanisms that usually mask the direct spectral expression of the *J*-couplings, taking directly benefits from the increased sensitivity and resolution obtained at high fields and high MAS spinning rates [4]. Aluminophosphates materials ($AlPO_4$) attracted much interest over the last two decades, as a credible alternative to other sorbents and catalysts [5]. Among mesoporous materials made from $AlPO_4$, $AlPO_4$-14 has already been studied by X-ray crystallography [6,7] and NMR [7–9] and will be taken as a demonstration example. Its structure is well known and similar to those of zeolithes, but the framework is entirely built up with AlO_x and PO_4 polyhedrons. Four, five and sixfold coordination states are observed for the Al atoms and Al are connected together by either bridging oxygen atoms or O–P–O chains. Four different sites can be distinguished for Al and also for P atoms [7]. Al_1 is fivefold coordinated trigonal–bipyramidal (bonded to 4 –O–P–$(O–Al)_4$ and 1 –O–Al), Al_2 and Al_3 are fourfold coordinated tetrahedra (bonded to 4 –O–P–$(O–Al)_4$) and Al_4 is a sixfold coordinated octahedra (bonded to 4 –O–P–$(O–Al)_4$ and 2 –O–Al).

In contrast with liquid-state experiments in which short relaxation times of quadrupolar nuclei often precludes the proper manipulation of quadrupolar spins, several 2D dipolar mediated or *J*-mediated homonuclear and heteronuclear correlation methods have been introduced for

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solid-state experiments involving one or two quadrupolar nuclei like ^{27}Al ($S = 5/2$) [7,9–13], ^{71}Ga ($S = 3/2$) [14] or ^{27}Al and ^{17}O ($S = 5/2$) [15]. The efficiency of ^{27}Al/ ^{31}P ($S = 1/2$) experiments benefits from their 100% natural abundance and their good receptivity, with increased sensitivity at high field by diminishing the second order quadrupolar broadening of ^{27}Al dimensions [16]. Moreover, the magnetization of the ^{27}Al central transition (which is only affected by the second-order quadrupolar broadening) can be efficiently enhanced by populating the central transition from the outer satellites using methods like DFS or RAPT [17,18]. In this contribution we show that it is possible, in solid-state, to characterize structural motifs involving three different spins (2 ^{27}Al and 1 ^{31}P in a Al–O–P–O–Al linkage) in a three-dimensional experiment that correlates the 1D spectra of the three bonded cation nuclei ($2\times{}^{27}$Al and $1\times{}^{31}$P). Because we use the scalar coupling J_2(X–O–Y), the 3D H–HSQC spectrum allows an identification of molecular entities extending over 4 chemical bonds and typically over 0.4 to 0.5 nm in size. Despite its low sensitivity, this experiment provides a new and unique way for obtaining unambiguously this type of information.

2. Results and discussion

The new 3D homonuclear/heteronuclear correlation experiment (3D H–HSQC) that we developed makes use of the sole scalar J-coupling to transfer the magnetization. This results in a robust and rather simple pulse sequence that only involves manipulation of the spin system with soft $\pi/2$ and π pulses, which ensures manipulation of the ^{27}Al central transition as a fictitious spin 1/2. The transfer occurs from the first aluminium atom to the neighbouring phosphorus and then to a second aluminium through the isotropic scalar part J_2(Al–O–P) of the J-coupling in an Al–O–P–O–Al group. This pulse sequence is the extension of the 2D-Homonuclear–Heteronuclear Single Quantum Correlation (H–HSQC) experiment that we recently described [13], obtained by introducing an additional evolution time t_2 encoding the ^{31}P isotropic dimension (Fig. 1). It provides experimental evidence for through-bond correlations between X_1, Y and X_2 nuclei in X_1–O–Y–O-X_2 motives with spectral identification of the resonances of these three nuclei in the different projections. Because the experiment uses the scalar coupling it does not require any reintroduction of interaction averaged out by MAS and it undergoes no limitation with the spinning rate which is usually required to achieve better resolution. It only requires long enough transverse relaxation times T_2' (typically 15 ms in our case) and a sufficient sensitivity for the acquisition of the 3D dataset within a reasonable experimental time.

The experiment consists in two INEPT transfers separated by a constant time period achieving the magnetization transfer and containing the ^{31}P encoding time t_2. The first INEPT transfer leads to the creation of a density operator proportional to $2\mathrm{Al}^1_{z,\mathrm{CT}}\mathrm{P}_y$ (where the aluminium

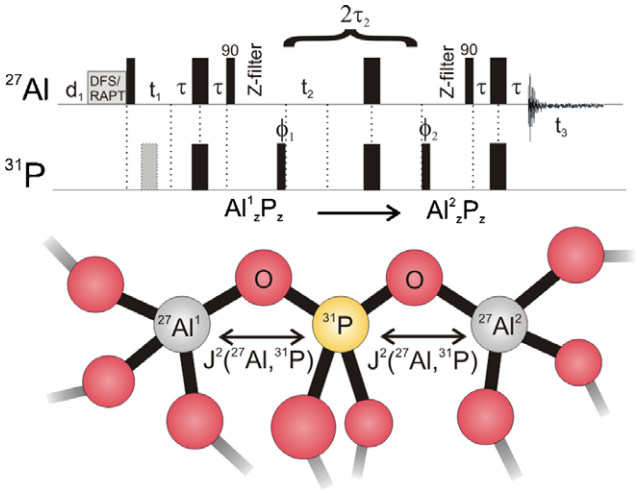

Fig. 1. Pulse sequence for the 3D (t_1 and t_2 incremented) H–HSQC experiment. A scheme of the atoms and the scalar couplings involved is shown below in the ^{27}Al/^{31}P case. The $2\tau_2$ delay is a constant time period allowing for the magnetization transfer from the Al_1 spin to the Al_2 spin. $^{27}\mathrm{Al}_1$ and ^{31}P chemical shift evolutions occur during the t_1 and t_2 delays respectively. Two Z-filters (300 rotor periods or 21 ms) have been used to suppress unwanted contributions. τ and τ_2 were set to 40 rotor periods (2.86 ms) and 120 rotor periods (8.57 ms), respectively, with a MAS speed of 14 kHz and $B_0 = 17.63$ T (750 MHz ^{1}H Larmor frequency). $\Phi_1 = \{0°, 180°\}$, $\Phi_2 = \{0°, 0°, 180°, 180°\}$ and $\Phi_{\mathrm{rec}} = \{0°, 180°, 180°, 0°\}$.

central transition is described as a fictitious spin 1/2) after an evolution under the scalar coupling during a delay 2τ ($1/4J$). The second constant time echo period ($2\ \tau_2$) allows for the conversion of $\mathrm{Al}^1_{z,\mathrm{CT}}\mathrm{P}_y$ into $\mathrm{Al}^2_{z,\mathrm{CT}}\mathrm{P}_y$, which gives rise to a negative cross-peak in the 2D H–HSQC spectrum. The positive diagonal signal corresponds to the remaining $\mathrm{Al}^1_{z,\mathrm{CT}}\mathrm{P}_y$ term. When each Al atom is bound to four O–P–O–Al groups, the evolution of the density operator during τ_2 is described by [13]:

$$\begin{aligned}\sigma(\tau_2 = 0) &= 2\mathrm{Al}^1_{z,\mathrm{CT}}\mathrm{P}_y \\ \sigma(\tau_2) &= \frac{1}{8}[3 + 4\cos(4\pi J\tau_2) + \cos(8\pi J\tau_2)](2\mathrm{Al}^1_{z,\mathrm{CT}}\mathrm{P}_y)_{diagonal} \\ &\quad + \frac{1}{8}[\cos(8\pi J\tau_2) - 1](2\mathrm{Al}^2_{z,\mathrm{CT}}\mathrm{P}_y)_{\text{cross-peak}}\end{aligned} \tag{1}$$

These equations are plotted in Fig. 2 as a function of τ_2 in $1/J$ units. The ^{31}P chemical shift evolves during the delay t_2, and the ^{31}P scalar couplings to the neighbouring ^{27}Al spins evolve in a constant time manner during $2\tau_2$.

The resulting three-dimensional hypercomplex dataset is Fourier transformed against the three evolution times and Figs. 3B–D shows one ^{27}Al/^{27}Al plane (with the x and y axis corresponding to the direct and indirect ^{27}Al dimensions) extracted from the 3D matrix (as shown in Fig. 3A) and corresponding to the phosphorus chemical shift of the P_2 site $\delta(^{31}\mathrm{P}) = -8.03$ ppm. Hence, this 2D spectrum will feature the negative diagonal peaks of any Al_x–O–P_2 group and the positive cross-peaks of any Al_x–O–P_2–O–Al_y groups. Three different strips along the ^{31}P axis, perpendicular to the ^{27}Al/^{27}Al plane and intersecting