Through-bond phosphorus–phosphorus connectivities in crystalline and disordered phosphates by solid-state NMR

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2D ^{31}P refocused INADEQUATE NMR experiments have been used to determine through-bond P–O–P connectivities in crystalline and disordered phosphates.

The determination of P–O–P connectivities in crystalline and disordered inorganic phosphates is essential for a proper understanding of their atomic structures. Over the last few years, a series of solid-state magic angle spinning NMR experiments have been proposed to determine the atomic connectivities in solids. Most of these methods use pulse sequences which reintroduce the through-space dipolar interaction under magic angle spinning (MAS) which leads to the observation of nearest-neighbour spatial proximities in different structural units.[1,2] These dipolar recoupling techniques have been applied to crystalline and glassy phosphates for the determination of phosphorus *through-space* connectivities in two-dimensional (2D) ^{31}P homonuclear correlation spectra.[3,4] A more convenient approach would be to determine directly the P–O–P *through-bond* connectivities using the through-bond scalar *J* coupling, as is routinely done in liquid-state NMR spectroscopy. In rigid solids the isotropic *J* coupling is usually much smaller than the dipolar interactions or the chemical shift anisotropy. Nevertheless, homonuclear ^{31}P or ^{13}C through-bond 2D correlation spectra have been obtained previously in solids from TOBSY[5]-type experiments.[6–9] These 2D correlation methods use a multiple pulse sequence to suppress resonance offsets and promote polarization transfer driven only by the *J* coupling, while simultaneously avoiding the recoupling of dipolar interactions. A much less demanding alternative possibility to determine through-bond connectivities in the solid-state is provided by the INADEQUATE[10–12] and refocused INADEQUATE pulse sequences.[13,14] This was recently demonstrated for ^{13}C in ordered[11,14] and disordered samples.[13] In this work, we show that the refocused INADEQUATE experiment applies very efficiently to inorganic crystalline and glassy phosphates, and that it allows an unambiguous determination of the P–O–P connectivity scheme.

The determination of through-bond P–O–P connectivities in solids using the refocused INADEQUATE experiment is first demonstrated for the simple crystalline pyrophosphate $Zn_2P_2O_7$. Its structure can be described as a network of corner-sharing ZnO_6 octahedra and P_2O_7 units. It contains two distinct P_2O_7 groups in the ratio of 2:1, one in which the two P sites are crystallographically non-equivalent (P_1–O–P_2) and one in which the two P sites are equivalent (P_3–O–P_3).[15] The ^{31}P though-bond correlation spectrum of this sample, obtained using the refocused INADEQUATE pulse sequence[13] is shown in Fig. 1a. In this 2D spectrum, the resonances of two coupled phosphorous atoms occur at a common double quantum frequency in the ω_1 indirect dimension, correlated with the single-quantum frequency of each peak in the ω_2 dimension. For example, the P_1–O–P_2 intra-P_2O_7 connectivity is clearly indicated by two intense correlation peaks. In contrast, the P_3–O–P_3 connectivity gives rise only to a very weak-intensity correlation peak, as expected in the case of *J*-mediated coherence transfer involving two equivalent phosphorous

atoms.[16] This very weak auto-correlation peak reflects a small ^{31}P chemical shift distribution and thus the high degree of crystallinity of the sample. The excitation efficiency of double quantum coherence as a function of the preparation time in a 1D refocused INADEQUATE spectrum is shown in Fig. 1b (15 kHz MAS spinning frequency). The damped oscillatory build-up of double quantum coherence indicates that the polarization transfer is only driven by through-bond *J*-coupling and that the contribution of residual dipolar interactions is negligible. From the zero-crossing of the experimental build-up curve at $2\tau = 1/J$, the $^2J(^{31}P$–O–$^{31}P)$ coupling constant is estimated to be 21 Hz. This value is in good agreement with those previously determined in TiP_2O_7,[6] SiP_2O_7[7] and $Cd_2P_2O_7$[8] using the TOBSY experiment. This $^2J(^{31}P$–O–$^{31}P)$ scalar coupling constant is significantly smaller than the line widths ($\sim$ 80 Hz) and is not resolved as a doublet in the ^{31}P spectrum. It should be noted that the experimental efficiency of the refocused INADEQUATE sequence reaches approximately 18% (at a 15 kHz MAS spinning frequency) allowing the collection of a 2D through-bond correlation spectrum with a good signal to noise ratio in a few hours. As pointed out previously,[13] this efficiency
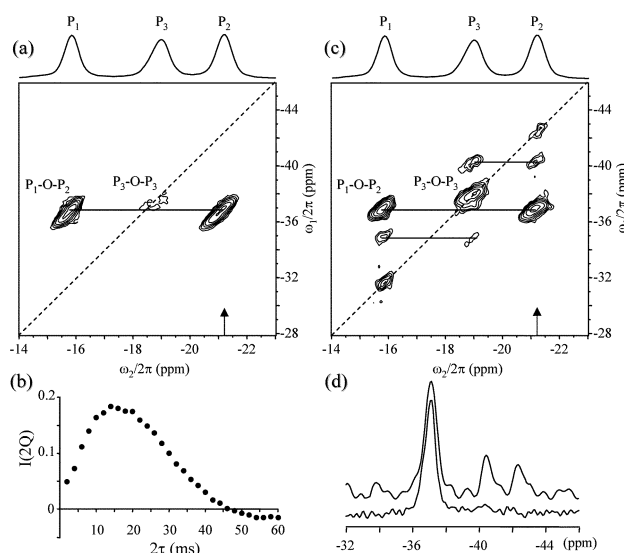

Fig. 1 (a) Through-bond double quantum MAS correlation spectrum of $Zn_2P_2O_7$ obtained using the refocused INADEQUATE sequence.[13] The ^{31}P 1D MAS spectrum is shown above the 2D spectrum. (b) Efficiency of the double quantum excitation as a function of the excitation time (2τ) in a 1D refocused INADEQUATE experiment (the reconversion time was fixed to 4 ms). (c) Through-space double quantum MAS correlation spectrum of $Zn_2P_2O_7$ obtained using the POSTC7[2] sequence. (d) Cross section of the through-bond (bottom) and through-space (top) correlation spectra at the position indicated by an arrow. All experiments were carried out at 121 MHz on a Bruker DSX300 spectrometer using a 2.5 mm MAS probe. The spinning frequency was 15 kHz. For the 2D spectra, 128 t_1 increments with 32 transients each were collected using the hypercomplex method.[17] The recycle delay was 10 s. The excitation and reconversion periods were set to 8 ms and 267 μs for the through-bond and through-space correlation experiments, respectively.

should be improved at higher spinning rates, and indeed experimentally it increases to 20% at a spinning frequency of 25 kHz.

To illustrate the higher selectivity of the refocused IN-ADEQUATE experiment in inorganic phosphates relative to dipolar through-space correlation methods, the dipolar double-quantum MAS correlation spectrum of $Zn_2P_2O_7$ (obtained under the same experimental conditions using the POSTC7[2] sequence) is depicted in Fig. 1c. This spectrum was recorded using very short excitation and reconversion periods of 267 μs each to mainly probe the short range spatial proximities between nearest neighbour ^{31}P sites.[3] Even with a limited excitation time (and at the expense of low signal to noise ratio in the resulting spectrum), we observe both intense *intra*-P_2O_7 correlation peaks and weaker intensity *inter*-P_2O_7 correlation peaks. These low-intensity peaks are due to longer range dipolar interactions and reflect the spatial proximities between the different P_2O_7 groups in the structure. It should be noted that correlations between equivalent ^{31}P sites (with the same chemical shift) are directly detected in the dipolar double quantum experiment in contrast to the refocused INADE-QUATE spectrum. Fig. 1d presents the comparison between the cross sections of the 2D spectra for the P_2 resonance showing the single correlation for the through-bond experiment (bottom) and the multiple correlations for the through-space experiment (top). In the case of broad overlapping resonances, the presence of these longer range correlation peaks can make the determination of the P–O–P connectivity pattern more difficult.

The possibility of determining the P–O–P through-bond connectivities in polymerised and disordered phosphate networks using the refocused INADEQUATE experiment is demonstrated for the crystalline tetrapolyphosphate $Pb_3P_4O_{13}$ and for the glass with the same composition. The structure of crystalline $Pb_3P_4O_{13}$ contains four crystallographic non-equivalent phosphorous sites forming a linear tetrameric $[P_4O_{13}]^{6-}$ anion with two Q_1 end-chain units and two Q_2 middle-chain groups.[18] The 2D refocused INADEQUATE spectrum of the crystalline $Pb_3P_4O_{13}$ sample is presented in Fig. 2a. First, it allows the distinction between the Q_1 end-chain groups and the Q_2 middle-chain groups since they exhibit one and two correlations respectively. This confirms the assignment made previously on the basis of the ^{31}P chemical shift range in phosphates. Moreover, we observe two Q_1–Q_2 and one Q_2–Q_2 correlation peak that confirm unambiguously the P–O–P connectivity pattern expected for the tetrameric $[P_4O_{13}]^{6-}$ anion.

The 2D correlation spectrum of the glass with the same composition is shown in Fig. 2b. In contrast to the spectrum of the cr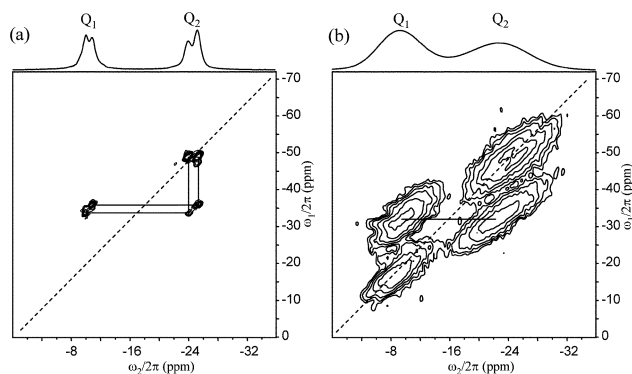ystalline sample that has narrow lines, this spectrum exhibits very broad correlation peaks. This inhomogeneous broadening comes from a large distribution of ^{31}P chemical shift that reflects the structural disorder in the glass (the line widths of the Q_1 and Q_2 resonances are 900 and 1200 Hz in the 1D MAS spectrum, respectively) *but does not affect the efficiency of the refocused INADEQUATE experiment.*[13] Consequently, Q_1–Q_1, Q_1–Q_2 and Q_2–Q_2 correlations peaks are clearly resolved in the 2D spectrum of the glass. The intense Q_1–Q_2 and Q_2–Q_2 correlations reveal the different P–O–P connectivites involved in phosphate chains of moderate length. The weaker intensity Q_1–Q_1 correlation peak evidences the through-bond connectivity between two Q_1 end-chain units and is characteristic of P_2O_7 groups. This spectrum thus indicates the presence of a chain length distribution in the $Pb_3P_4O_{13}$ glass network, in contrast to the $Pb_3P_4O_{13}$ crystalline structure that contains only tetrameric $[P_4O_{13}]^{6-}$ anions. This confirms the results previously obtained from interpretation of through-space dipolar correlation spectra.[4] It should be noted that using a dipolar correlation experiment, the correlations between nearby (but not bonded) Q_1 groups of different chains and the intra-P_2O_7 correlation peak overlap completely, leading to ambiguity in the interpretation of the 2D spectrum.

In conclusion, we have shown that the refocused INADEQUATE experiment allows a direct identification of the P–O–P through-bond connectivities in the solid-state and provides essential structural information in disordered phosphates.

Notes and references

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Fig. 2 Through-bond double quantum MAS correlation spectra of a crystalline $Pb_3P_4O_{13}$ sample (a) and a glass $Pb_3P_4O_{13}$ sample (b) obtained using the refocused INADEQUATE experiment. The 1D MAS spectra are shown above the 2D spectra. All experiments were carried out at 121 MHz on a Bruker DSX300 spectrometer using a 4 mm MAS probe. The spinning frequency was 14 kHz. The excitation (2τ) and reconversion (2τ) periods were set to 2.4 ms. 256 t_1 increments with 16 scans each and 64 t_1 increments with 128 scans each were collected using the hypercomplex method[17] for the crystalline and glass samples, respectively. The recycle delay was 10 s for the crystalline sample and 7 s for the glass sample.