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Structure of Crystalline Phosphates from ^{31}P Double-Quantum NMR Spectroscopy

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Abstract: ^{31}P multiple-quantum solid-state NMR spectroscopy is introduced as a new approach for elucidating internuclear distances between phosphorus nuclei in phosphates. The typical shorter distance between chemically bound groups allows the determination of the chemical network. The method is superior to ^{31}P exchange experiments, which, in principle, provide similar information. Separation of two crystalline $Mg_2P_2O_7$ phases is observed by both methods, but the double-quantum experiment gives further information of couplings between sites with equal isotropic chemical shifts. In $Ca_2P_6O_{17}$, which contains Q^2 and Q^3 groups with large chemical shift anisotropies, the connectivities can be deduced from the double-quantum experiment due to different cross-peak intensities. Our results are in good agreement with X-ray diffraction measurements and suggest applications to other, more complicated phosphates.

Introduction

High-resolution solid-state NMR has emerged as a complementary method to diffraction techniques for the investigation of crystal structures. The former is most sensitive to local properties, as the fundamental NMR interactions are short range in character, whereas the latter provides information about the long-range order. Therefore, the combination of both methods offers substantial advantages for the understanding of the structure of solids. Furthermore, amorphous systems are accessible to NMR, where X-ray diffraction suffers from liquid-like broad reflection peaks.

One of the earliest experiments to establish crystalline structures in solids with NMR was the detection of internuclear distances in small molecules[1] like water by exploiting the homonuclear $^1H-^1H$ dipolar coupling. The development of multiple pulse line narrowing[2] has opened the opportunity to investigate chemical shift tensor orientations for various nuclei like ^{19}F and ^1H that usually exhibit strong dipolar couplings.[3,4] Also, rotation patterns of ^{13}C chemical shift tensors have been reported.[5,6] Last, but not least, high resolution in powdered solids is achieved by combining these methods with magic angle spinning (MAS).[3]

Two-dimensional (2D) NMR experiments[7,8] of powdered samples were applied to zeolites[9] to investigate their structure. *J*-coupling was used in these experiments, to provide information about the connectivity scheme. However, the *J*-coupling in solids is usually weak and long evolution times are required to produce the necessary magnetization that can be transferred in the mixing part of the 2D experiment. Therefore, the signal-to-noise ratio is poor due to relaxation of transverse magnetization in these evolution periods.[9] Furthermore, pure absorptive spectra may be difficult to achieve.

Different 2D NMR variants are based on the dipolar coupling. In 2D exchange spectra the coupling strength between spin pairs manifests itself in the intensities of the corresponding cross peaks.[10] Since the dipolar coupling constant $d \sim 1/r^3$ is very sensitive against the distance between the nuclei of interest, an experiment using these couplings should provide results analogous to those from X-ray diffraction techniques. In the presence of magic angle spinning and large chemical shift interactions the flip−flop part of the dipole−dipole coupling is reduced.[11] Therefore, recoupling schemes, such as radio frequency dipolar recoupling (RFDR)[11] have to be used to observe cross peaks in 2D exchange experiments.

In a previous publication,[12] we introduced 2D-^{31}P RFDR-NMR to study the local structure of sodium phosphate glasses. This method proved to be robust with a high signal-to-noise ratio. However, the simple exchange of magnetization exploited there has several disadvantages. The magnetization transfer from connectivities between spins with exactly equal isotropic chemical shifts and magnetization that has not taken part in the exchange process during the mixing period lead to overlapping signals on the diagonal. Also, the 2D RFDR-NMR spectrum cannot distinguish direct magnetization transfer from that via a third or more spins.[8]

A new approach that provides a selective route to probe dipolar connectivities is high-resolution homonuclear multiple-quantum NMR spectroscopy of solids[13] which has successfully been applied to determine connectivities between protons in

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[1] Pake, G. E. *J. Chem. Phys.* **1948**, *16*, 327.

[2] Waugh, J. S.; Huber, L. M.; Haeberlen, U. *Phys. Rev. Lett.* **1968**, *20*, 180.

[3] Mehring, M. *Principles of High Resolution NMR in Solids*; Springer-Verlag: Berlin, 1983).

[4] Haeberlen, U. *High Resolution NMR of Solids, Advances in Magnetic Resonance*; Academic Press: San Diego, 1976; Suppl. 1.

[5] Pines, A.; Chang, J. J.; Griffin, R. G. *J. Chem. Phys.* **1974**, *61*, 1021.

[6] Chirlian, L. E.; Opela, S. J. *Adv. Magn. Reson.* **1990**, *14*, 183.

[7] Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Magnetic Resonance in One and Two Dimensions*; Clarendon: London, 1990.

[8] Schmidt-Rohr, K.; Spiess, H. W. *Multidimensional solid state NMR and polymers*; Academic Press: New York, 1994.

[9] Fyfe, C. A.; Feng, Y.; Grondey, H.; Kokotailo, G. T.; Gies, H. *Chem. Rev.* **1991**, *91*, 1525.

[10] Meier, B. H. *Adv. Magn. Opt. Reson.* **1994**, *18*, 1.

[11] Benett, A. E.; Ok, J. H.; Griffin, R. G.; Vega, S. *J. Chem. Phys.* **1992**, *96*, 8624.

[12] Jäger, C.; Feike, M.; Born, R.; Spiess, H. W. *J. Non.-Cryst. Solids* **1994**, *180*, 91.

[13] Geen, H.; Titman, J. J.; Gottwald, J.; Spiess, H. W. *Chem. Phys. Lett.* **1994**, *227*, 79.

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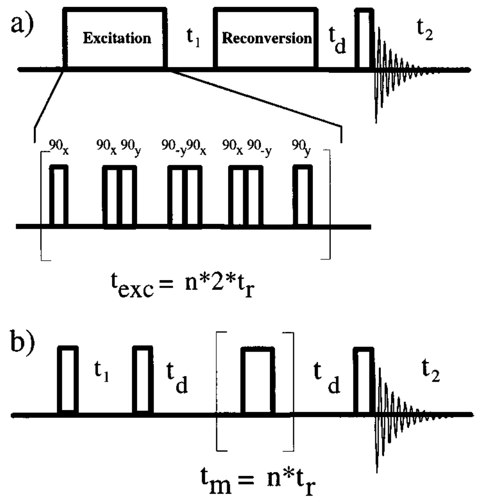

Figure 1. Pulse sequences and experimental parameters used in the experiments. The double-quantum excitation (a) is built of four suitable phase cycled 90° pulses which provide a pure double-quantum Hamiltonian with compensation for chemical shifts. Four rotor cycles have been used in the excitation and reconversion period. The sign of the pulse phases was inverted for the third and fourth rotor period. For the RFDR experiment the 180° pulse length was 4.0 ms. The mixing time consisted of 80 rotor cycles of pulse irradiation at a spinning frequency of 12.5 kHz. The t_1 dwell time was set to the rotor period time interval, so that no spinning sidebands appear in the ω_1 dimension.

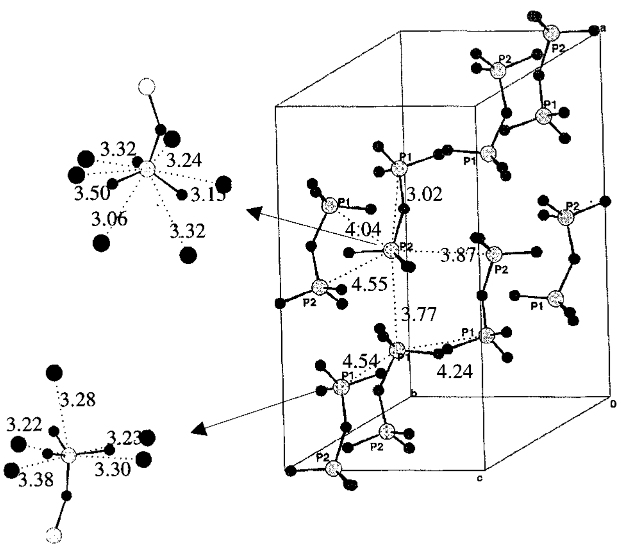

Figure 2. Section out of the crystal structure of α-$Mg_2P_2O_7$.[15] The two different phosphate sites are cut out of the anionic network and displayed at the left to characterize the structural difference.

solids.[14] It enables the investigation of crystallographic sites with both equal and unequal isotropic chemical shifts. As a first application to inorganic materials, we have chosen two phosphates, $Mg_2P_2O_7$ and $Ca_2P_6O_{17}$. The topologies of the ^{31}P spin systems are known from published X-ray diffraction experiments[15−17] and were confirmed by IR investigations.[18] Two different crystalline forms of $Mg_2P_2O_7$ have been identified.[15,16] Both are present in our particular sample and the question arises, whether these phases are linked on an atomic scale. The second sample, $Ca_2P_6O_{17}$,[17,18] consists of two different Q^2 and one Q^3 unit and provides a test for the sensitivity of double-quantum NMR for probing the connectivities between these groups. A comparison between RFDR and double-quantum NMR is also performed on both samples.

Experimental Section

All experiments were performed on a Bruker ASX 500 spectrometer at a ^{31}P Larmor frequency of 202 MHz. As described before[13] DQ-NMR spectra are recorded employing a pulse sequence of the type depicted in Figure 1a. There DQ coherence is excited, then evolves during t_1, and is subsequently reconverted to detectable magnetization. For phosphates particular care has to be taken to achieve broadband excitation and reconversion, because of the large ^{31}P chemical shift. In our experiments we used a rotor synchronized back-to-back (BABA) excitation sequence, depicted in Figure la and described in detail elsewhere.[19] For comparison, a 2D RFDR spectrum was also recorded for $Mg_2P_2O_7$ with the pulse sequence in Figure lb.

As shown in a previous paper,[14] the rotor phase dependence of the produced double-quantum Hamiltonian leads to spinning sidebands in the ω_1 dimension, if the t_1 dwell time is not synchronized with the rotor period. Hence, the t_1 dwell time of the double-quantum experiments was set to the rotor period time interval of 70 ($Mg_2P_2O_7$) and 77 μs ($Ca_2P_6O_{17}$). The repetition time was 10s. A saturation sequence was applied prior to each sequence to ensure equivalent conditions for each experiment. Sixty-four slices have been recorded for $Ca_2P_6O_{17}$ and 128 for $Mg_2P_2O_7$ with 8 experiments for every t_1 increment (double-quantum 2D experiment). The phase cycling is adjusted to select ±2 coherence for the double-quantum and ±1 coherence for the RFDR 2D experiments in the t_1 period. This is necessary to obtain amplitude modulated time domain data. In addition, a time proportional phase increment (TPPI) with a 45° phase increment for the double-quantum experiment and a 90° phase increment for the RFDR experiment was applied.

The combination of these methods allows pure absorptive and phase sensitive 2D spectra[7,8,19] to be obtained. The quality of the double-quantum experiment strongly depends on the efficiency of the applied phase cycling, therefore, a digital phase shifter is recommended.

To reduce the spin−lattice relaxation time, the $Mg_2P_2O_7$ sample contains Fe^{3+} at a concentration of 2000 ppm and $Ca_2P_6O_{17}$ contains Co^{2+} at 1000 ppm.

The powdery $Mg_2P_2O_7$ sample was obtained by thermal decomposition of $MgNH_4PO_4$.[15] Two phases of magnesium diphosphate, called α and β, had been found by X-ray diffraction.[15,16] Both phases are present at room temperature which was determined by the NMR measurements, although the β-phase is known as a high-temperature (>60 °C) modification. This effect is possibly due to the addition of Fe^{3+}.

Results and Discussion

$Mg_2P_2O_7$. The structure of the α-phase is outlined in Figure 2. It contains two crystallographically inequivalent $Q^{(1)}$ units linked together to a $[P_2O_7]^{4-}$ anion. In the left section of Figure 2 all Mg^{2+} cations up to a maximum distance of 0.33 nm from the central phosphorus nucleus are shown. In the lD MAS spectrum (Figure 3a) the two phosphate sites lead to separated resonances at −14.0 and −20.3 ppm,[21] labeled A and B, respectively. The β-phase is a high-temperature modification where the P−O−P bonding angle in the $[P_2O_7]^{4-}$ anion is 180°. The phosphate sites are symmetric and cannot be distinguished by NMR. This is reflected by a single resonance at −19.2 ppm[22] labeled C (Figure 3a). Thus in our sample both modifications are present.

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(14) Gottwald, J.; Demco, D. E.; Graf, R.; Spiess, H. W. *Chem. Phys. Lett.* **1995**, *243*, 314.

(15) Calvo, C. *Acta Cryst.* **1967**, *23*, 289.

(16) Calvo, C. *Can. J. Chem.* **1965**, *43*, 1139.

(17) Stachel, D.; Paulus, H.; Svoboda, I.; Fuess, H. *Z. Kristallogr.* **1992**, *202*, 117.

(18) Meyer, K.; Hobert, H.; Barz, A.; Stachel, D. *Vib. Spectrosc.* **1994**, *6*, 323.

(19) Feike, M.; Demco, D. E.; Graf, R.; Gottwald, J.; Hafner, S.; Spiess, H. W. *J. Magn. Reson. A* In press.

(20) Marion, D.; Wüthrich, K. *Biochem. Biophys. Res. Commun.* **1983**, *113*, 967.

(21) Haubenreisser, U. Dissertation B, FSU Jena, 1986.

(22) Jäger, C.; Ehrt, D. *Z. Phys. Chem.: Neue Folge* **1988**, *159*, 103.

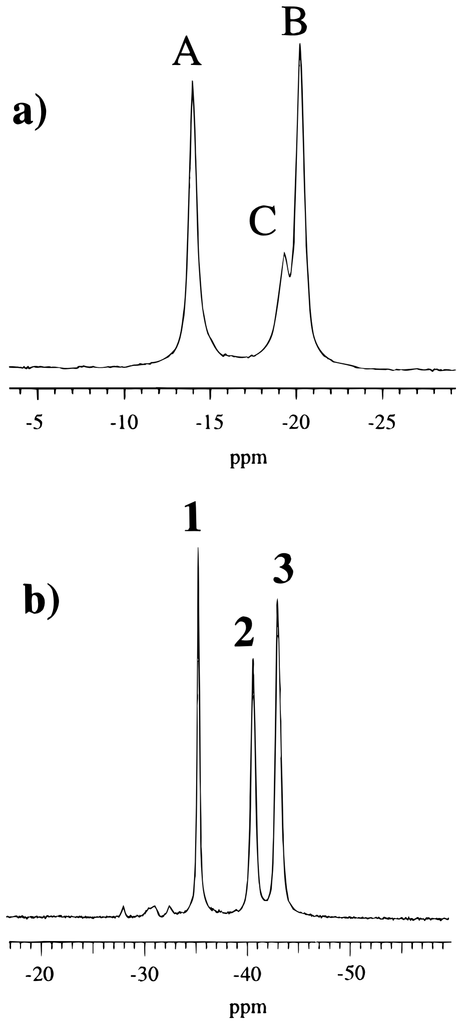

Figure 3. (a) ^{31}P-lD MAS-NMR spectrum of $Mg_2P_2O_7$ at 202 MHz. The NMR signals at −14.0 (A) and −20.3 ppm (B) are assigned to the α-phase, the signal at −19.2 ppm (C) to the β-phase.[21,22] (b) ^{31}P-lD MAS-NMR spectrum of $Ca_2P_6O_{17}$ at 202 MHz. The resonance lines are at −35.3, −40.6, and −43.2 ppm. The assignment to the structure is discussed in Figure 5. The small peaks on the left site of the three large signals belong to β-Ca(PO$_3$)$_2$.

With the 2D-RFDR experiment only cross peaks between the two lines of the α-phase, A and B, but none between either of them and the single line of the β-modification C on the diagonal are observed (Figure 4a). This proves that both modifications are not mixed on an atomic scale. It is inherent to exchange-type experiments that signal intensities along the diagonal do not provide information about connectivities. For instance, the C peak on the diagonal could also be caused by phosphorus nuclei which are not dipolar coupled to other ^{31}P spins. As mentioned earlier,[12] we note that this case is less important in amorphous materials if the inhomogeneous line width exceeds the homogeneous one. Thus, in inorganic glasses, the cross-peak intensities for similar groups are well separated from the very narrow resonance lines of the magnetization not transferred during the mixing period.[12] Hence, in such systems the connectivities of similar but not identical Q$^{(n)}$ units can be probed as well.

In contrast to the RFDR experiment, only dipolar coupled spins are displayed in the 2D DQ spectrum (Figure 4b). Since ^{31}P spins without dipolar couplings cannot create double-quantum coherences, their magnetization is filtered out by the phase cycling and hence cannot appear in the DQ spectrum. As explained in detail elsewhere,[13] auto-peaks resulting from DQ coherences between like spins occur on the diagonal. Off-diagonal cross peaks indicate DQ coherences between chemically different groups. Thus the single peak labeled C−C in the double-quantum spectrum for β-$Mg_2P_2O_7$ results from the two equivalent phosphate tetrahedra forming the $[P_2O_7]^{4-}$ anion. It should be noted that for the short excitation time used here the DQ peaks are always positive and their strength depends on the square of the dipolar coupling of the excited spin pairs.[14]

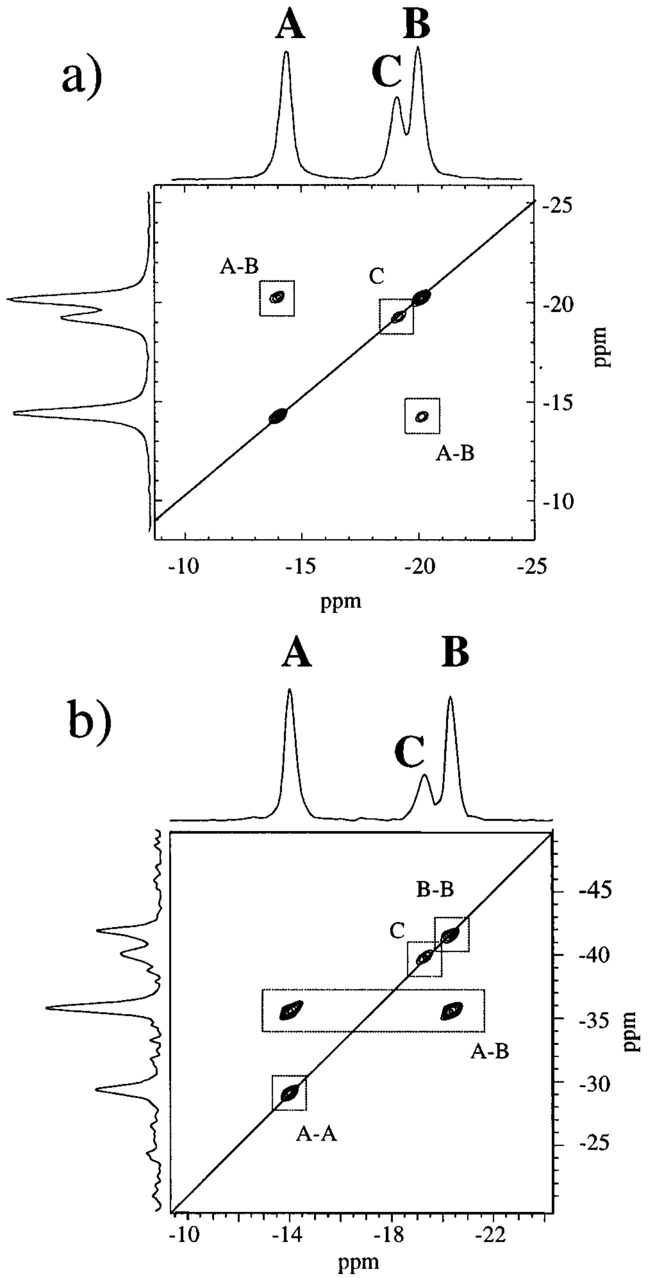

Figure 4. (a) 2D RFDR spectrum of $Mg_2P_2O_7$ for a mixing time of t_m = 6.4 ms obtained with the pulse sequence outlined in Figure lb. The two resonances of α-$Mg_2P_2O_7$ are labeled A and B and the signal that corresponds to β-$Mg_2P_2O_7$ is denoted as C. The ratio of the intensity between the peaks A−A, B−B to A−B is about 1:3. The contour levels were set to 18.2, 25.5, 35.7, 50.0, 70.0, and 97.9% of the maximal peak intensity. (b) DQ spectrum of the same sample, recorded with the pulse sequence 1, part a. A−B represents the connectivity within the anion in α-$Mg_2P_2O_7$ whereas A−A and B−B correspond to DQ coherences of like phosphate tetrahedra in adjacent $[P_2O_7]^{4-}$ units. C is the analogue for β-$Mg_2P_2O_7$.

The two resonances that belong to α-$Mg_2P_2O_7$ show the typical DQ spectrum of a system where all sites are connected among each other by dipole−dipole coupling.[21] It can be subdivided into peaks of sites with the same isotropic chemical

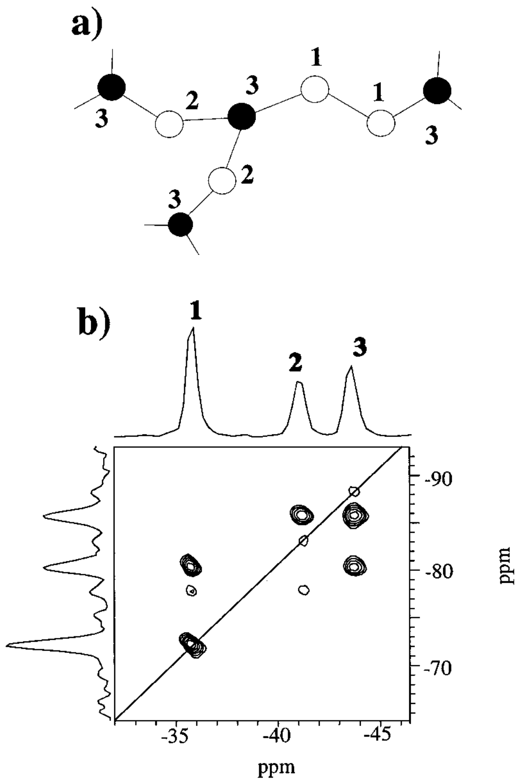

Figure 5. A section out of the $Ca_2P_6O_{17}$ structure is given in part a.[17] The full circles represent $Q^{(3)}$ and the open ones $Q^{(2)}$ units. In part b the 2D double-quantum spectrum is displayed. The biggest intensities marked in the spectrum indicate the direct connectivities of the $Q^{(n)}$ units. The peak assignment to the crystallographic sites is possible just by the detection of these intensities and confirms the structure determined by X-ray diffraction. The smaller signals 1−2, 2−2, and 3−3 show dipolar connectivities of not chemically bound nuclei with small distances. The contour levels were set to 15.2, 20.8, 28.5, 39.1, 53.3, and 73.3% of the maximal peak intensity.

Table 1. P−P Distances in nm up to 0.50 nm in $Ca_2P_6O_{17}$[a]

(n)-species	(1)	(2)	(3)
(1)	0.309	0.391, 0.447	0.285, 0.453
(2)	0.391, 0.448	0.460	0.293, 0.295, 0.469
(3)	0.285, 0.453	0.293, 0.295, 0.469	0.486

[a] The chemically bound species are on average 0.1 nm closer than the nearby but not linked $Q^{(n)}$ units. The assignment of the numbers to the structure scheme is given in Figure 5.

shift (A−A and B−B) and different ones (A−B). The (A−B) peaks indicate the connectivity between the two inequivalent phosphorus atoms within the $[P_2O_7]^{4-}$ anion whereas the peaks (A−A) and (B−B) reflect the spatial proximity of the like phosphate tetrahedra in adjacent $[P_2O_7]^{4-}$ anions. The larger intensities of the two A−B peaks compared to the A−A and B−B signals reflect the fact that the distance between A−B is much smaller than that between A−A and B−B. The results are in full agreement with the structure suggested from X-ray diffraction experiments.[15,16]

$Ca_2P_6O_{17}$. The structure of the ultraphosphate $Ca_2P_6O_{17}$ has recently been established using IR spectroscopy and X-ray diffraction.[17,18] It is composed of Q^2 and Q^3 units, forming corrugated sheets of linked rings with 14 phosphate tetrahedra. Figure 3b shows the 1D MAS-NMR spectrum and a simplified structural picture is displayed in Figure 5a. P−P distances deduced from X-ray diffraction are collected in Table 1.

In contrast to the case of $Mg_2P_2O_7$, the assignment of the peaks to the structure is possible just by the 2D DQ spectrum, displayed in Figure 5. Chemically linked $Q^{(n)}$ units exhibit the biggest intensities in analogy to $Mg_2P_2O_7$, i.e. 1−1, 1−3, and 2−3. The strength of the dipolar coupling and the statistical amount of the considered connectivity is reflected in the intensities of the respective peaks. Nearby but not chemically bound $Q^{(n)}$ units (1−2, 2−2, and 3−3) lead to much weaker DQ signal intensities, because the distances between them are larger compared with those of the directly connected groups (Table 1). The strong DQ signals reflect P−P distances of approximately 0.3 nm, whereas the weak DQ signals are due to P nuclei about 0.4 nm apart.

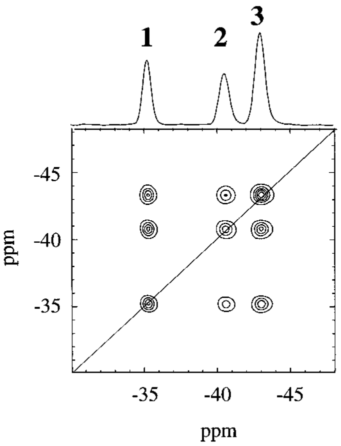

Figure 6. 2D RFDR magnetization exchange of $Ca_2P_6O_{17}$ for a mixing time of 3.84 ms. The cross-peak intensity of the 1−2 connectivity is of comparable size to the 1−3 and 2−3 connectivities. This demonstrates the improved sensitivity of double-quantum experiments.

The double-quantum NMR spectrum confirms the structure proposed from X-ray diffraction. In comparison to the RFDR-NMR experiment from the DQ spectrum it is usually easier to decide how the $Q^{(n)}$ sites are linked to each other. A representative RFDR 2D spectrum of $Ca_2P_6O_{17}$ with a mixing time of $t_m = 3.84$ ms is shown in Figure 6. The peak intensities are comparable for all types of connectivities and only a slight suppression of the cross peaks that belong to the not chemically bound sites is observed. The contrast in the double-quantum experiment is much bigger which demonstrates the higher selectivity of this advanced method.

Conclusions

Solid-state multiple-quantum NMR spectroscopy is a powerful new technique to elucidate structure in phosphate systems in addition to 2D exchange experiments, such as 2D RFDR-NMR. The intensities on the diagonal reflect dipolar connectivities of spin pairs with equal isotropic chemical shift. The magnetization of spins which are not dipolar coupled is filtered out by an appropriate phase cycle. Other important features of DQ NMR are the high sensitivity of the excitation efficiency to the coupling strength and, therefore, internuclear distances. Furthermore the method can be extended to higher multiple-quantum orders in 2D experiments. Hence, this approach can be used to confirm and complement X-ray data. Applications currently underway in our laboratory are quantitative measurements of $^{31}P-^{31}P$ distances, studies of phase separation and assignment of 1D MAS-NMR peaks in crystalline phosphates, and connectivities in phosphate glasses.

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