



HAL
open science

1D to 3D NMR study of microporous alumino-phosphate AlPO₄-40

C. Morais, V. Montouillout, M. Deschamps, D. Iuga, F. Fayon, F.A.A. Paz, J.
Rocha, C. Fernandez, D. Massiot

► **To cite this version:**

C. Morais, V. Montouillout, M. Deschamps, D. Iuga, F. Fayon, et al.. 1D to 3D NMR study of microporous alumino-phosphate AlPO₄-40. *Magnetic Resonance in Chemistry*, 2009, 47 (11), pp.942-947. 10.1002/mrc.2492 . hal-00116245

HAL Id: hal-00116245

<https://hal.science/hal-00116245>

Submitted on 24 Nov 2006

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1D to 3D NMR study of microporous alumino-phosphate AlPO₄-40

*Cláudia Morais^{a,b}, Valérie Montouillout^a, Michael Deschamps^a, Dinu Iuga^{a†},
Franck Fayon^a, Filipe A.A. Paz^c, João Rocha^c, Christian Fernandez^d and
Dominique Massiot^{‡,*a}*

- a) CRMHT-CNRS (UPR4212 & FR2950), 1D Ave Recherche Scientifique, 45071 Orléans cedex 2, France. Fax: +33 238 63 81 03; Tel: +33 238 25 55 18; E-mail: massiot@cnrs-orleans.fr
- b) IREM (UMR8637) Université de Versailles Saint-Quentin-en-Yvelines, 45 Ave des Etats-Unis, 78 035 Versailles France
- c) Department of Chemistry, CICECO, University of Aveiro, 3810-192 Aveiro, Portugal.
- d) LCS (UMR6506), ENSICAEN, 14050 Caen, France

Short abstract (<200 characters)

We describe a new 3D ²⁷Al-³¹P MQ-HMQC experiment and make use of one- to two- and three-dimensional MAS NMR solid state experiments to describe the complex structure of microporous alumino-phosphate AlPO₄-40

Abstract (<300 words)

From one- to two- and three-dimensional MAS NMR solid state experiments involving ³¹P and ²⁷Al we show that the structure of microporous alumino-phosphate AlPO₄-40 contains at least four times more sites than expected and we attribute two types of Al_{IV} sites. The newly described ²⁷Al-³¹P MQ-HMQC opens new possibilities in describing details of three dimensional bounded networks.

Keywords: NMR, ³¹P, ²⁷Al, aluminophosphate, microporous materials

Introduction

Alumino-phosphate zeolitic or porous materials raise considerable interest for their properties as catalysts or molecular sieves. Because they involve abundant and sensitive nuclei (²⁷Al, ³¹P) high resolution solid state NMR is a tool of choice for characterizing their local structure. Information obtained from high resolution solid state NMR can often be combined with diffraction results to examine complex structures with large unit cells and reach a comprehensive interpretation [1, 2]. High resolution solid state NMR provides different types of information. First, the spectral resolution provides a direct way for enumerating the non equivalent crystallographic sites occupied by the observed nuclei. Second, homo- or hetero-nuclear correlation experiments established using through space (dipolar) or through bond (indirect J-coupling) interactions, characterize the polyatomic structural motifs. In this contribution we examine the case of the microporous alumino-

[†] Now at Lethbridge University, Canada

[‡] To whom correspondence should be addressed massiot@cnrs-orleans.fr

phosphate compound $\text{AlPO}_4\text{-40}$ whose structure remains a matter of debate. We show that with NMR experiments conducted at high magnetic field (750 MHz – 17.6 T), it is possible to obtain improved spectral resolution by applying heteronuclear ^{31}P or ^{27}Al decoupling. These high resolution heteronuclear correlation experiments between ^{31}P and ^{27}Al or ^{27}Al and ^{27}Al , show more than twenty different sites for each nucleus and provide their respective connectivity. From these results we show that the actual structure contains at least four times more sites than the proposed structure and, based on Al-Al correlation, we can also ascribe the two different types of Al_{IV} environments to two of the sites of the proposed structure.

The $\text{AlPO}_4\text{-40}$ sample is a microporous aluminophosphate synthesized under hydrothermal conditions, using by tetrapropyl- and tetramethyl-ammonium templating cations [3]. The sample was kindly provided by Profs J. Lourenço & M.F. Ribeiro (Portugal). Its structure was established from high resolution X-Ray diffraction [4] and involves eight distinct four fold $\text{P}(\text{OAl})_4$ phosphorous sites and eight distinct aluminium sites (6 four fold Al_{IV} - $\text{Al}(\text{OP})_4$ sites and 2 five fold Al_{V} - $\text{Al}(\text{OP})_4\text{OH}$ sites). However, as already demonstrated by several NMR studies, its structure appears to be much more complex, involving more than eight non-equivalent sites [5, 6].

Experimental

The high resolution solid state NMR experiments have been acquired on Bruker Avance 400 and 750MHz spectrometers using triple resonance MAS probeheads (4mm and 2.5mm). Each radiofrequency channel was equipped with band-pass filters. ^{31}P and ^{27}Al chemical shifts are reported in ppm relative to 85% H_3PO_4 and $\text{Al}(\text{NO}_3)_3$ 1M solutions.

The ^{31}P $\{^{27}\text{Al}$ decoupled $\}$ MAS spectra of $\text{AlPO}_4\text{-40}$ (Figure 1) were recorded on 400 and 750 MHz spectrometers with MAS at $\nu_r=14\text{kHz}$. Due to large T_1 relaxation times ($>100\text{s}$), ^{31}P MAS spectra have been acquired with pre-saturation (20 pulses of alternating phase x-y spaced by a delay of 30ms) and recycle delays of 40s. Optimal resolution in the ^{31}P MAS spectrum was achieved using a ^{27}Al decoupling field of 12 kHz, however, no further resolution enhancement was obtained when using double resonance $^1\text{H}/^{27}\text{Al}$ decoupling.

Results and discussion

^{31}P MAS NMR spectra of $\text{AlPO}_4\text{-40}$ are shown in Figure 1. Application of ^{27}Al decoupling during acquisition of the ^{31}P signal [6] leads to an important gain in resolution which is further enhanced by acquisition at higher field (750 MHz). Because the 14 kHz MAS spinning rate used is much larger than the heteronuclear dipolar couplings, the resolution enhancement obtained with heteronuclear decoupling is a direct evidence of the presence of an unresolved but significant isotropic J-coupling between ^{31}P and ^{27}Al . The extra resolution obtained at high field (750 MHz) further shows that the line broadening is not dominated by chemical shift distribution, as is often the case in inorganic solids. It is important to notice that even if the ^{31}P - ^{27}Al J-couplings remain small (in the order of 10 to 20 Hz) each P is linked to 4 different $I=5/2$ Al sites which give rise to a significant broadening (quadruplet of quintuplets with a $J_{\text{Al-O-P}}$ splitting) [6]. A good decomposition of the highest resolution spectrum involves a minimum of 21 different ^{31}P lines (Table 1).

The single-pulse ^{27}Al spectrum already shows some resolution at high field with a complete separation of Al_{IV} and Al_{V} domains and a partial resolution of two groups of Al_{IV} resonances which was not observed at lower field due to the dominant second order quadrupolar broadening. The three Al_{IV} -I Al_{IV} -II and Al_{V} groups are in a 2:1:1 intensity ratio. Because second order quadrupolar effect is the dominant broadening mechanism, resolution enhancement is only observed in the isotropic dimension of the ^{31}P decoupled MQMAS experiment [12] (Figure 1) where second order broadening is cancelled out. The effect of

heteronuclear decoupling is also of lesser importance for ^{27}Al nuclei because ^{31}P nuclei are $I=1/2$ spins and thus the coupling of the observed ^{27}Al linked to four different P sites only give rise to quartet splitting, five times narrower than the J-broadening effect due to ^{27}Al in the ^{31}P spectrum. A crude first modeling of the MQMAS spectrum (Figure 2) would require more than 15 different ^{27}Al lines characterized by their isotropic chemical shifts and quadrupolar parameters. The high resolution MQMAS spectrum confirms the separation of the Al_{IV} resonances in two groups with isotropic chemical shifts ranging from 44 to 46 ppm for $\text{Al}_{\text{IV-I}}$ and 37 to 41 ppm for $\text{Al}_{\text{IV-II}}$ (while Al_{V} are located between 19 and 23 ppm).

Enhanced resolution can be obtained by spreading the resonance lines in homo- or hetero-nuclear two dimensional correlation experiments. This proved to be very efficient in the study of SnP_2O_7 where $^{31}\text{P}/^{31}\text{P}$ correlation enabled to spectrally differentiate 49 different P_2O_7 groups (98 resolved non-equivalent P sites) in a $3\times 3\times 3$ superstructure [2]. We have shown recently that the small but significant scalar J-coupling between ^{31}P and ^{27}Al can be used to efficiently generate $\{^{31}\text{P}\}^{27}\text{Al}$ correlation using an HMQC experiment [7]. The $\{^{31}\text{P}\}^{27}\text{Al}$ HMQC spectrum of $\text{AlPO}_4\text{-40}$ is shown in Figure 3, where each cross peak evidences the presence of a chemical bond between Al and P sites. This spectrum can be modeled from the isotropic positions of ^{31}P and ^{27}Al obtained from the analysis of the 1D ^{31}P and MQMAS ^{27}Al experiments but does not allow a complete resolution because of the significant second order broadening of the ^{27}Al resonances (along the horizontal axis) already observed in the 1D and MQMAS experiments.

The build up curves of the HMQC experiment are shown in Figure 4. Since very similar T_2' relaxation times (typically $\sim 15\text{ms}$) were measured for each Al sites ($\text{Al}_{\text{IV-I}}$, $\text{Al}_{\text{IV-II}}$ and Al_{V}) and since all the sites correspond to $\text{Al}(\text{OP})_4$ environments, these curves directly translate into differences in the isotropic scalar $J_2(\text{Al-O-P})$ couplings. We already know from experiment on simpler phases [7] or from selective excitation experiments [8] that these couplings may vary significantly from one Al-O-P bond to another. This is obviously bearing valuable information on the conformation of the Al-O-P bonds; however, an analysis of the dispersion of measured scalar coupling values is beyond the scope of this paper, given our current ignorance of the ins and outs of the scalar $J_2^{27}\text{Al-O-}^{31}\text{P}$ couplings due to the very limited number of published measurements. No measurement of such a coupling has been performed in liquid state due to the rapid quadrupolar relaxation of ^{27}Al and very few recent measurements in solids have actually been reported [7,8]. However, the current progress in the calculation of J-couplings (GAUSSIAN) from structural data will provide a tool for the interpretation of our measured scalar coupling values.

It has already been shown that isotropic MQMAS resolution can be combined with INEPT in an MQ-INEPT experiment [9]. This experiment allows ultimate resolution in a 2D experiment at the cost of the loss of the anisotropic quadrupolar broadening information that is part of the characterization of the ^{27}Al sites. We designed a new 3D experiment that combines all the powers of the MQMAS experiment, which correlates isotropic to anisotropic ^{27}Al signatures, and provides the correlation map to adjacent ^{31}P . The 3D MQMAS-HMQC pulse sequence consists in three different steps. The experiment starts with triple quantum coherence excitation of ^{27}Al , followed by t_1 evolution before conversion to single quantum coherence with a shifted echo evolution and full echo acquisition during t_2 , as proposed in the shifted echo MQMAS experiment [10]. The third dimension is obtained by implementing the HMQC scheme (Heteronuclear Multiple Quantum Correlation) with an evolution delay t_3 during the shifted-echo pulse of MQMAS-SE experiment.

The resulting spectrum is a three dimensional dataset correlating the $\{^{27}\text{Al-3Q}\}$, $\{^{31}\text{P}\}$, and $^{27}\text{Al-1Q}$ observed spectrum. This dataset is sheared in the $\{^{27}\text{Al-3Q}\}^{27}\text{Al-1Q}$ plane to build the isotropic dimension and provide a spectrum as presented in Figure 6. An optimal

signal to noise ratio is obtained by acquiring the full echo and synchronizing all the evolution times with multiple of the MAS rotation period [11].

The wealth of available data allows us to give a comprehensive interpretation of the ^{31}P and ^{27}Al spectra and discuss the number of non-equivalent sites in the structure. Our modeling of the different spectra, performed using a modified version of the “dmfit” software [13], requires at least 21 different P sites and 20 different Al sites to account for the isotropic/anisotropic dimensions of the 3D experiment, the $\{^{31}\text{P}\}^{27}\text{Al}$ HMQC, and the ^{27}Al MQMAS. Among the 21 resolved ^{31}P lines, 8 have multiple intensities (6-x2, 1-x3 and 1-x4) and show more than four correlation peaks with distinct ^{27}Al resonances. We suggest that the unit cell proposed from X-Ray diffraction should at least be quadrupled and could contain 32 different P (and Al) sites in a single phase or in an assembly of different phases.

As reported by McCusker et al. [1] from a high resolution X-Ray diffraction study, the anionic $[\text{Al}_{32}\text{P}_{32}\text{O}_{128}(\text{OH})_4]^{4-}$ framework of $\text{AlPO}_4\text{-40}$ can be understood as constructed from two distinct types of clusters, each containing four crystallographically independent Al sites. One cluster contains 4 Al and 4 P sites plus the hydroxyl O_{33} site bridging two Al_V sites. The second cluster only contains Al_{IV} sites. Simple considerations do not allow the direct identification of the Al_{IV-I} and Al_{IV-II} sites. $^{27}\text{Al}/^{27}\text{Al}$ correlation experiment obtained using through space dipolar interaction [14] (Figure 7) or through bond P relayed J-coupling [15] (not shown) must be deployed. In these two experiments the only absent Al/Al correlation is the $\text{Al}_{IV-II}/\text{Al}_{IV-II}$ correlation, which implies that no $\text{Al}_{IV-II}\text{-O-P-O-Al}_{IV-II}$ chemical bond can be observed. An analysis of the Al/P and P/Al bond tables (ICSD-88919 ref. 4) reveals that only Al_1 and Al_5 are not connected to a common P site and may thus be ascribed to the Al_{IV-II} group. These sites are also the inner most sites of the framework structure.

Conclusion

In conclusion, we show that the microporous alumino-phosphate $\text{AlPO}_4\text{-40}$ has NMR signatures globally compatible with the proposed X-Ray structure with a quadrupling of the unit cell. Thanks to the enhanced resolution obtained with common 2D experiments and a new 3D MQMAS-HMQC experiment we could measure the NMR parameters of 21 resolved ^{31}P sites and 20 resolved ^{27}Al sites, along with their respective multiplicities. Moreover, the two types of Al_{IV} , segregated by their chemical shifts and revealed by high field NMR spectra are attributed to the generic crystallographic sites Al_1 and Al_2 which are the only ones not connected together. The set of $^{31}\text{P}/^{27}\text{Al}$ 1D, 2D experiment along with the new 3D MQMAS-HMQC allow the direct analysis of binding schemes in the three dimensional building units.

Acknowledgments

We acknowledge financial support for CNRS and Région Centre; CM & DI acknowledge fellowship support from CNRS and Le Studium.

Notes and references

- 1 N. Hedin, R. Graf, S.C. Christiansen, C. Gervais, R.C. Hayward, J. Eckert, B.F. Chmelka, *J. Am. Chem. Soc.* 2004, 124, 9425-9432; D.H. Brouwer, R.J. Darton, R.E. Morris, M.H. Levitt, *J. Am. Chem. Soc.* 2005; J. Dutour, N. Guillou, C. Huguenard, F. Taulelle, C. Mellot-Draznieks, G. Férey, *Solid State Sciences* 2004, 6, 1059-1067.
- 2 F. Fayon, I.J. King, R.K. Harris, R.B.K. Gover, J.S.O. Evans, D. Massiot, *Chem. Mater.* 2003, 15, 2234-2239
- 3 J.P. Lourenço, M.F. Ribeiro, F. Ramôa Ribeiro, J. Rocha, B. Onida, E. Garrone, Z. Gabelica, *Zeolites*, 1997, 18, 398-407; J.P. Lourenço, M.F. Ribeiro, C. Borges, J.

- Rocha, B. Onida, E. Garrone, Z. Gabelica, *Microporous and Mesoporous Materials*, 2000, 38, 267-278.
- 4 V. Ramaswamy, L.B. McCusker, C. Baerlocher, *Microporous Mesoporous Materials*, 1999, 31, 1-8; ICSD-88919
 - 5 J. Rocha, J.P. Lourenço, M.F. Ribeiro, C. Fernandez, J.P. Amoureux, *Zeolites*, 1997, 19, 156-160; C. Fernandez, C. Morais, J. Rocha, M. Pruski *Solid State NMR*, 2001, 21 61-70 ; C.M. Morais, C. Fernandez, V. Montouillout, F. Taulelle and J. Rocha, *Stud. Sci. Surf. Catal.*, 2002, 142, 1915-1918. Eds. R. Aiello, G. Giordano and F. Testa, Elsevier.
 - 6 L. Delevoye, C. Fernandez, C. M. Morais, J. P. Amoureux, V. Montouillout and J. Rocha, *Solid State Nucl. Magn. Reson.*, 2002, 22 501-512.
 - 7 D. Massiot, F. Fayon, B. Alonso, J. Trebosc and J.P. Amoureux, *J. Magn. Reson.*, 2003, 164, 165-170.
 - 8 J.P. Amoureux, J. Trebosc, J.W. Wiench, D. Massiot, M. Pruski, *Solid State NMR* 2005, 27, 228-232.
 - 9 J.W. Wiench and M. Pruski, *Solid State Nucl. Magn. Reson.*, 2004, 26, 51-55.
 - 10 D. Massiot, B. Touzo, D. Trumeau, J.P. Coutures, J. Virlet, P. Florian and P.J. Grandinetti, *Solid State Nucl. Magn. Reson.*, 1996, 6, 73-83.
 - 11 D. Massiot, *J. Magn. Reson. A*, 1996, 122, 240.
 - 12 V. Lacassagne, P. Florian, V. Montouillout, C. Gervais, F. Babonneau and D. Massiot, *Magn. Reson. Chem.*, 1998, 36, 956-959.
 - 13 D. Massiot, F. Fayon, M. Capron, I. King, S. Le Calvé, B. Alonso, J-O. Durand, B. Bujoli, Z. Gan, G. Hoatson, *Magn. Reson. Chem.*, 2002, 40, 70-76.
 - 14 G. Mali, F. Taulelle, *Chem. Commun.*, 2004, 868-869; G. Mali, G. Fink, F. Taulelle *J. Chem. Phys.* 2004, 120, 2835-2845
 - 15 M. Deschamps, F. Fayon, V. Montouillout, D. Massiot *Chem. Commun.*, 2006, 1924-1925

Tables

(a)			(b)				
	$\delta_{CS}(\text{ppm})$	Multiplicity		$\delta_{CS}(\text{ppm})$	C_Q (MHz)	η_Q	Multiplicity
P 1	-14.1	1	4-coordinated				
P 2	-14.7	2	Al 1	46.5	3.10	0.90	2
P 3	-15.7	2	Al 2	46.0	4.14	1.00	2
P 4	-16.5	1	Al 3	45.5	2.83	0.40	2
P 5	-17.4	1	Al 4	45.0	3.79	0.53	2
P 6	-18.2	1	Al 5	44.3	2.98	0.00	2
P 7	-18.5	1	Al 6	44.1	2.03	0.21	3
P 8	-19.1	1	Al 7	43.6	2.74	0.50	3
P 9	-20.6	1	Al 8	40.4	2.43	0.42	2
P 10	-21.1	1	Al 9	39.6	3.63	0.80	1
P 11	-21.5	2	Al 10	39.4	2.22	0.51	1
P 12	-22.8	2	Al 11	38.6	2.42	0.53	1
P 13	-24.8	1	Al 12	37.9	2.30	0.38	1
P 14	-25.2	3	Al 13	37.5	4.54	0.40	2
P 15	-26.7	2	5-coordinated				
P 16	-27.1	2	Al 14	22.7	1.98	0.78	1
P 17	-28.6	4	Al 15	22.5	2.72	1.00	1
P 18	-28.9	1	Al 16	21.7	2.87	0.30	2
P 19	-29.7	1	Al 17	20.8	4.85	0.55	1
P 20	-30.0	1	Al 18	20.4	2.38	0.58	1
P 21	-30.3	1	Al 19	19.8	1.44	1.00	1
		32	Al 20	19.4	4.36	0.67	1
							32

Table 1: (a) Isotropic chemical shift (δ_{CS}) and relative intensities of the different phosphorous lines obtained from the simulation of the $^{31}\text{P}\{^{27}\text{Al decoupled}\}$ MAS spectrum acquired at 17.6 T (^1H Larmor frequency of 750 MHz). (b) Isotropic chemical shift (δ_{CS}), quadrupolar constant (C_Q) and asymmetry parameter (η_Q) obtained from the simulation of the $^{27}\text{Al}\{^{31}\text{P decoupled}\}$ 3Q MAS spectrum recorded at 17.6 T.

Figures

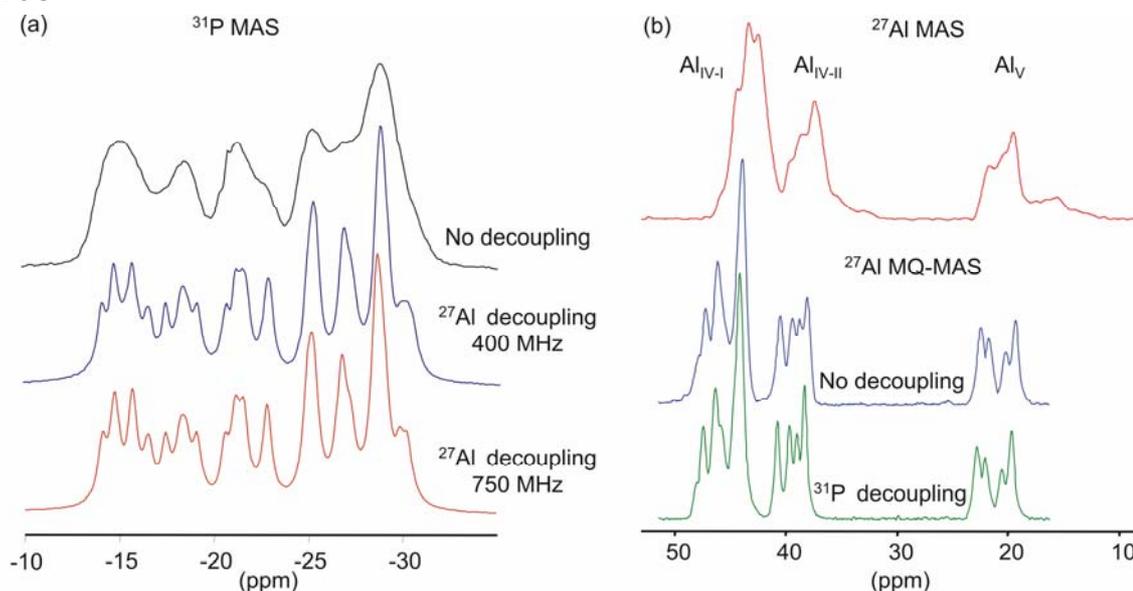


Figure 1 ^{31}P MAS spectra without and with ^{27}Al decoupling at 9.4 and 17.6 T (400 and 750 MHz for the ^1H Larmor frequency). (b) ^{27}Al MAS spectrum and MQMAS isotropic projections with and without ^{31}P decoupling.

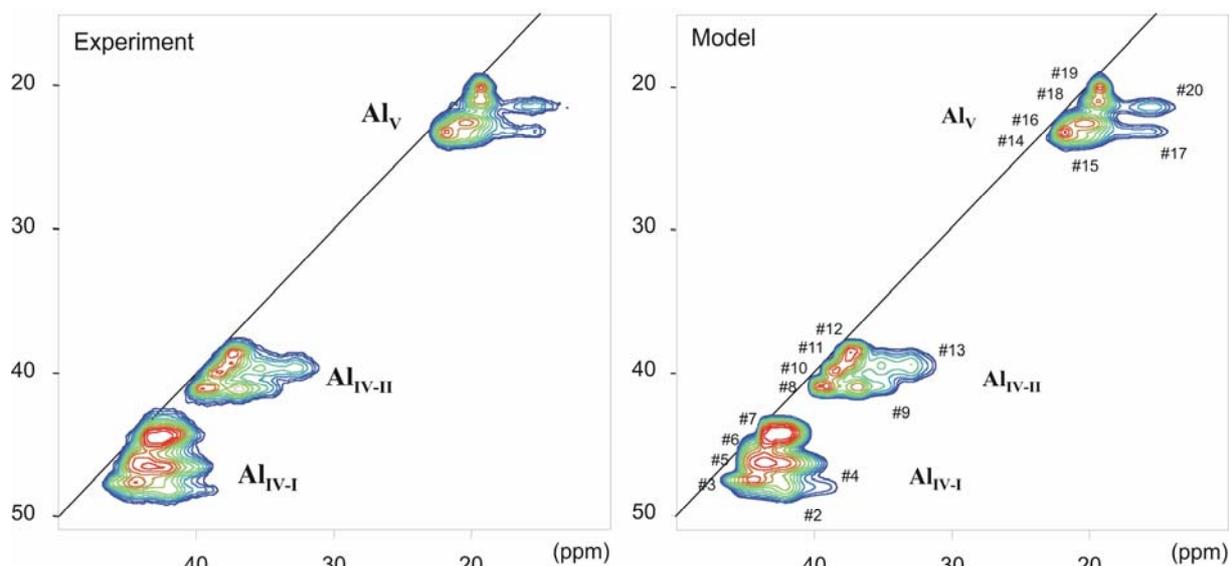


Figure 2 ^{27}Al MQMAS spectrum recorded at 17,6 T (1H Larmor frequency at 750 MHz) showing complete resolution of Al_{IV-I} , Al_{IV-II} and Al_V groups of lines (a) experimental spectrum and (b) modeled spectrum with 20 different lines according to Table 1. The MAS rate was $\nu_r = 14$ kHz spinning rate and the recycle delay was set to 1s. 192 points (24 scans per point) were acquired in the t_1 dimension, synchronously with the spinning rate (t_1 increments of $1/\nu_r$) [11].

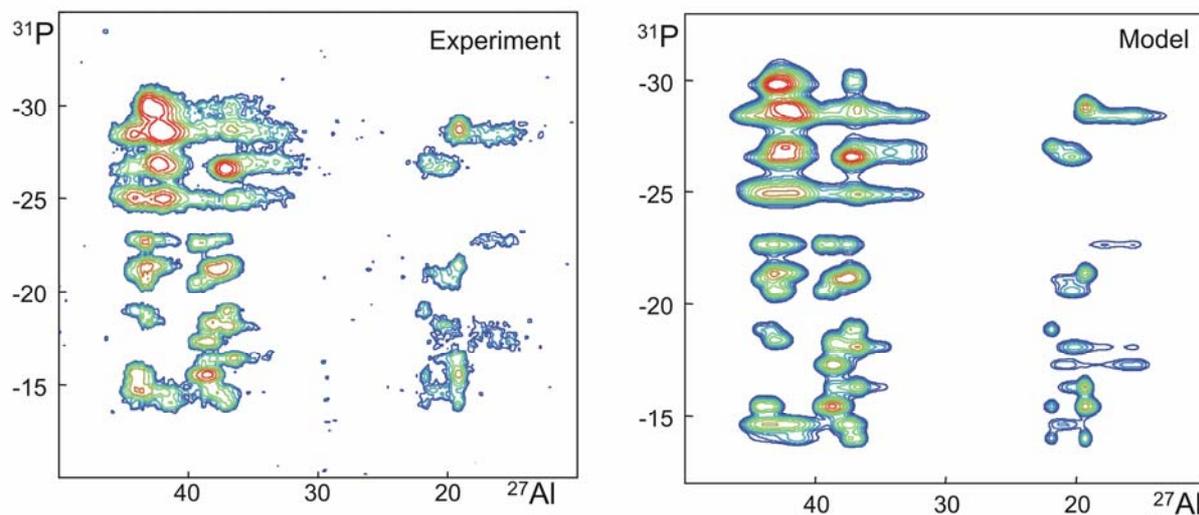


Figure 3. Left : $\{^{31}P\}^{27}Al$ HMQC correlation spectrum recorded at 17.6 T (750MHz) with a MAS rate of $\nu_r = 14$ kHz and a recycle delay of 1s. 256 points (32 scans per point) were acquired in the t_1 dimension synchronously with the spinning rate (i.e. using t_1 increments of $1/\nu_r$) [7]. Right: The corresponding modeled spectrum is displayed, using the parameters shown in Table 1.

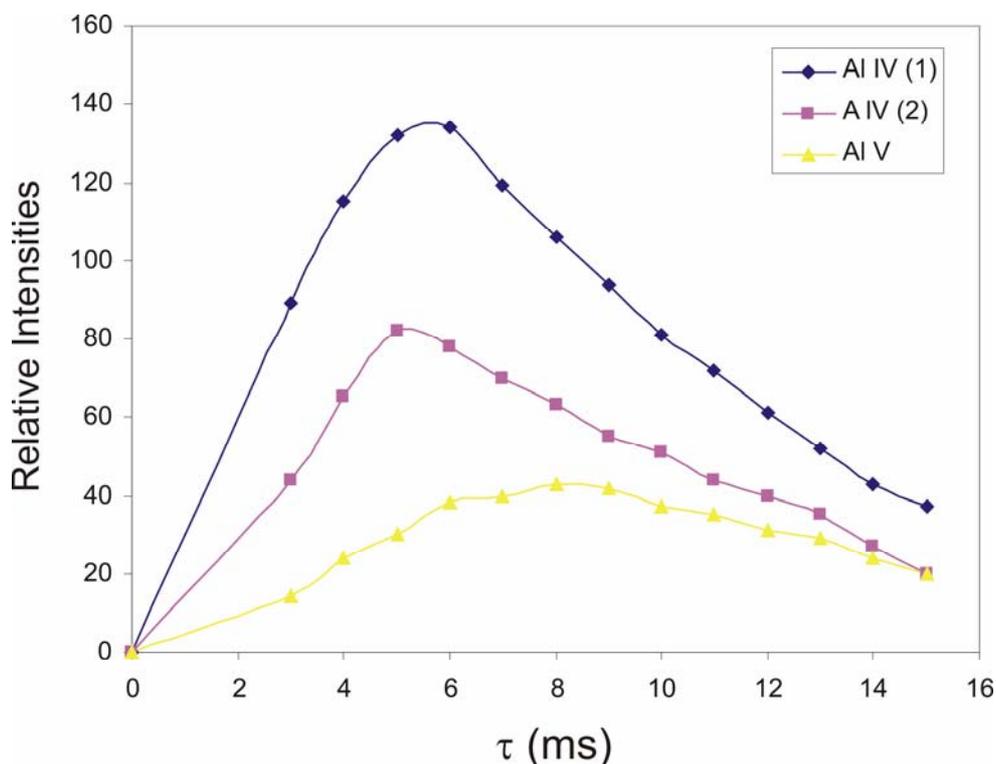


Figure 4. $\{^{31}\text{P}\}^{27}\text{Al}$ HMQC build up curves for $\text{Al}_{\text{IV-I}}$, $\text{Al}_{\text{IV-II}}$, and Al_{V} . The build up for Al_{V} component is slower, indicating weaker $J_{\text{Al-O-P}}^2$ scalar couplings for Al_{V} spins.

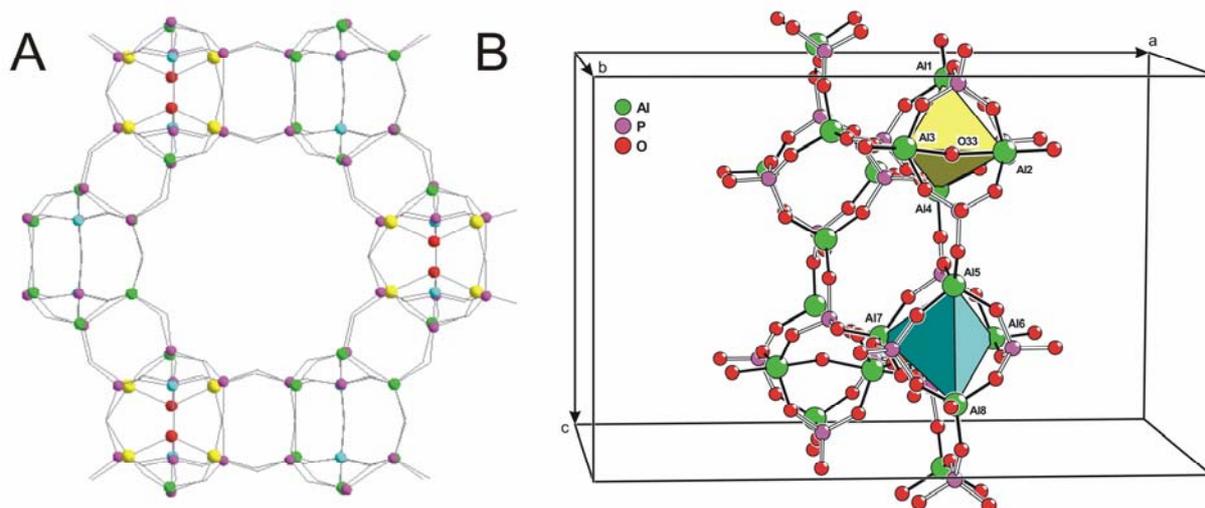


Figure 5. A. Structure (ICSD-88919) of $\text{AlPO}_4\text{-40}$ viewed along the c axis, featuring in red: O_{33} , in purple the phosphorus atoms, in green the $\text{Al}_{\text{IV-I}}$ atoms, in blue the $\text{Al}_{\text{IV-II}}$ (Al_1 and Al_5) and in yellow the Al_{V} atoms, as attributed in the discussion. B. Section of the anionic $[\text{Al}_{32}\text{P}_{32}\text{O}_{128}(\text{OH})_4]^{4-}$ framework of $\text{AlPO}_4\text{-40}$ viewed in perspective down the b -axis. The framework is constructed by the spatial repetition of two aluminium clusters (yellow and cyan tetrahedra).

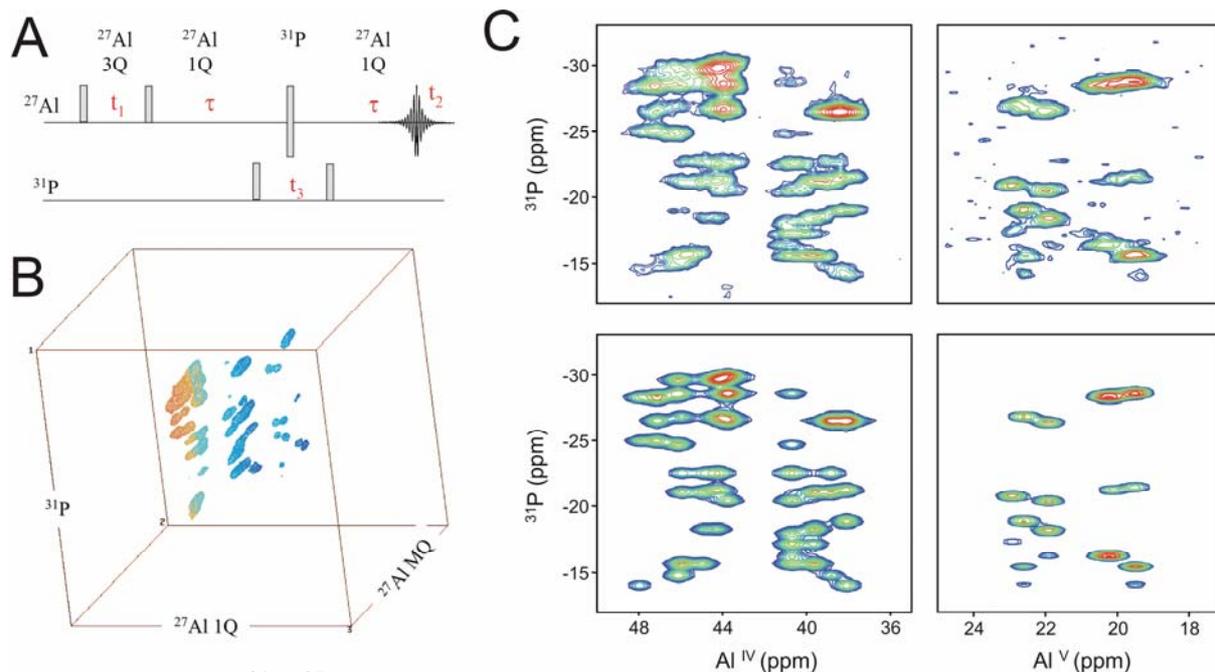


Figure 6. 3D $\{^{31}\text{P}\}^{27}\text{Al}$ MQMAS pulse sequence (A) and spectrum (B) providing isotropic/anisotropic and bonding characterization of the Al-O-P network. The spectrum was recorded at 17.6 T with a MAS spinning rate of 14 kHz. The t_2 increment for the indirect dimension of the ^{27}Al MQMAS was set to $2/v_r$ while the t_1 time increment for the HMQC ^{31}P dimension was set to $1/v_r$. In C, observed and modelled $\{^{31}\text{P}\}^{27}\text{Al}$ (isotropic dimension) 3D MQ-HMQC projections are displayed. The parameters used in the model are shown in Table 1.

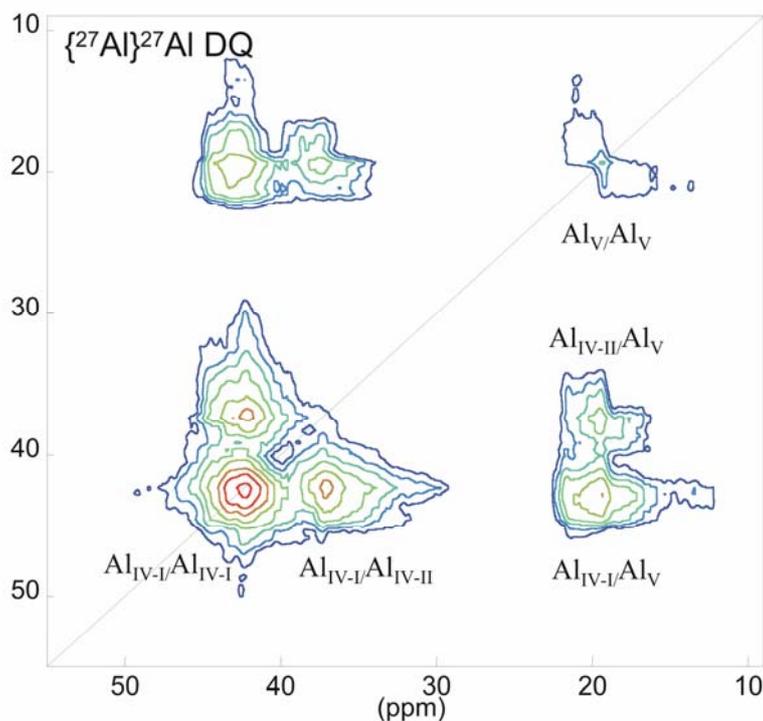


Figure 7 Double Quantum dipolar $^{27}\text{Al}/^{27}\text{Al}$ correlation spectrum featuring no intensity at the $\text{Al}_{\text{IV-II}}/\text{Al}_{\text{V}}$ position