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Communication

Chemical bonding differences evidenced from J -coupling in solid state NMR experiments involving quadrupolar nuclei

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Abstract

Small scalar J -coupling between quadrupolar nuclei and spin 1/2 can be measured in inorganic solids using J -Resolved experiments and further used to acquire 2D J -HMQC heteronuclear correlation, giving detailed insight into the chemical bonding scheme. © 2003 Elsevier Science (USA). All rights reserved.

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1. Introduction

Indirect spin–spin coupling constants, J , are known to provide detailed information about the chemical bonding and molecular structure, even in solid state materials [1]. Typical isotropic values of spin–spin coupling constants between light nuclei and across oxygen bonds are in the range of a few tens of Hertz, while dipolar couplings are in the range of kHz, chemical shift anisotropy in the range of several or tens of kHz, and quadrupolar couplings in the range of MHz [2]. It has been known for several years that weak unresolved J -couplings of ~ 20 Hz or less, involving quadrupolar nuclei, can be used to promote magnetization transfer in INEPT-based sequences [3–5]. Recent results on spin 1/2 nuclei in solid state materials have shown that the through-bond approach can lead to spectral simplification and enhanced resolution, as well as J -coupling measurements by transposing liquid sequences based on scalar coupling like J -Resolved [6–10], J -HMQC [11], or J -HSQC [12] experiments.

The aim of this contribution is to show that, when considering inorganic compounds involving quadrupolar nuclei bonded to $I = 1/2$ nuclei (^{27}Al and ^{31}P in our

case), and providing long enough coherence life time, it is possible to accurately measure J -couplings, using J -Resolved experiments [6–10,13], and to transpose the J -HMQC heteronuclear correlation experiment [14,11] to obtain new ways of characterizing the chemical bonds. This approach makes use of the isotropic part of the J -coupling tensor, which does not vanish with MAS, leading to improved efficiency at the high spinning rates that are required to obtain high resolution spectra for quadrupolar nuclei. We shall first consider the relatively simple case of berlinite (AlPO_4) that involves only one aluminum and one phosphorus crystallographic sites, and then show that this approach can be used to characterize chemical bonding in hydrated AlPO_4 VPI-5 molecular sieve with three different aluminum and three different phosphorus sites.

All experiments were conducted on a Bruker Avance DSX 400 spectrometer (9.4 T) equipped with a 4 mm triple resonance MAS probe (spinning rate ν_R up to 13 kHz). Radio-frequency fields were kept low for ^{27}Al (~ 5 kHz) to obtain a selective excitation of the central transition (20 kHz for ^{31}P). The experimental 1D and 2D datasets were modeled using a modified version of the dmfit program [15].

The structure of berlinite AlPO_4 (Space group $P3_1 2 1$) involves one Al, one P, and two O (O_1 and O_2) inequivalent crystallographic sites [16]. Aluminum and

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phosphorus occupy tetrahedrally coordinated positions, Al-(OP)₄ and P-(OAl)₄, crosslinked by μ_2 bridging oxygen atoms, O₁ and O₂. The ³¹P MAS NMR signal consists in a single gaussian line ($\delta_{\text{iso}} = -24.6$ ppm, FWHM = 1.6 ppm). The ²⁷Al MAS NMR signal shows a typical second order quadrupolar lineshape ($\delta_{\text{iso}} = 42.9$ ppm, $C_Q = 4.07$ MHz, and $\eta_Q = 0.34$). Usually, in this type of compounds, the scalar J -couplings are too weak to alter significantly the ²⁷Al second order quadrupolar lineshape, and to resolve the complex multiplet in the ³¹P spectrum [3,5,17]. Considering that it is possible to excite selectively the central transition of a quadrupolar nucleus as a fictitious spin 1/2 using low rf fields, that the coupling of ³¹P with 4 multi level quadrupolar nuclei is much more complex than that of the central transition of ²⁷Al coupled to 4 spin 1/2 (³¹P), and finally that T_1 for ³¹P and ²⁷Al is greater than 700 and 27s, respectively, we chose to examine scalar $^2J_{\text{Al-O-P}}$ couplings starting with ²⁷Al excitation.

Under magic angle spinning it is possible to measure the *spin-echo decay time* T_2' of the selectively irradiated central transition of ²⁷Al ($\pi/2 - \tau - \pi - \tau$ -acquire Fig. 1a), which corresponds to a *non-refocusable linewidth* under the current experimental conditions. Although this value is currently referred to as “ T_2 relaxation time,” we prefer to name it T_2' which clearly states its experimental nature and makes no hypothesis on its underlying mechanism [10,18,19]. Fig. 1b1 and c1 show the spin-echo decay (b1) and its Fourier transform. They can be modeled with a close to perfect mono-

exponential decay, in time domain or a lorentzian line, in frequency domain, leading to $T_2' = 14.1 \pm 0.5$ ms. The application of a π pulse on the ³¹P channel simultaneously with the ²⁷Al π pulse of the echo sequence (Fig. 1a) introduces a modulation of the obtained signal by the heteronuclear Al-O-P J -coupling [8,10,13], which can be modeled as:

$$S(\tau) = \prod_n \cos(2\pi J_n \tau) \exp(-2\tau/T_2'),$$

where n are the different coupled nuclei with their coupling J_n , and T_2' corresponds to the non-refocusable linewidth under this experiment. This signal can be analyzed in time domain, or frequency domain after Fourier transformation. A good fit of experimental data (not shown) is already obtained using the simplest model of 4 equal J -couplings of 22.7 ± 2 Hz. However, this yields a T_2' value of 13 ms, significantly lower than that of the spin-echo experiment. This difference may be due to a small recoupling effect due to the additional π pulse, but we obtain a significant improvement of the model (Figs. 1b and c) when considering two different J -couplings $J_a = J_{\text{Al-Oa-P}} = 26.0 \pm 1$ Hz ($n = 2$), $J_b = J_{\text{Al-Ob-P}} = 19.5 \pm 1$ Hz ($n = 2$), and $T_2' = \text{spin-echo } T_2'$ (Figs. 1b2 and c2). This second model is more consistent with the berlinite structure that involves two slightly different O sites (O₁ and O₂) and thus two different Al-O-P bonds [16]. We cannot yet ascribe the two different values of J -coupling (a and b) to the two different oxygen bridges (O₁ and O₂), but it is remarkable to notice that the

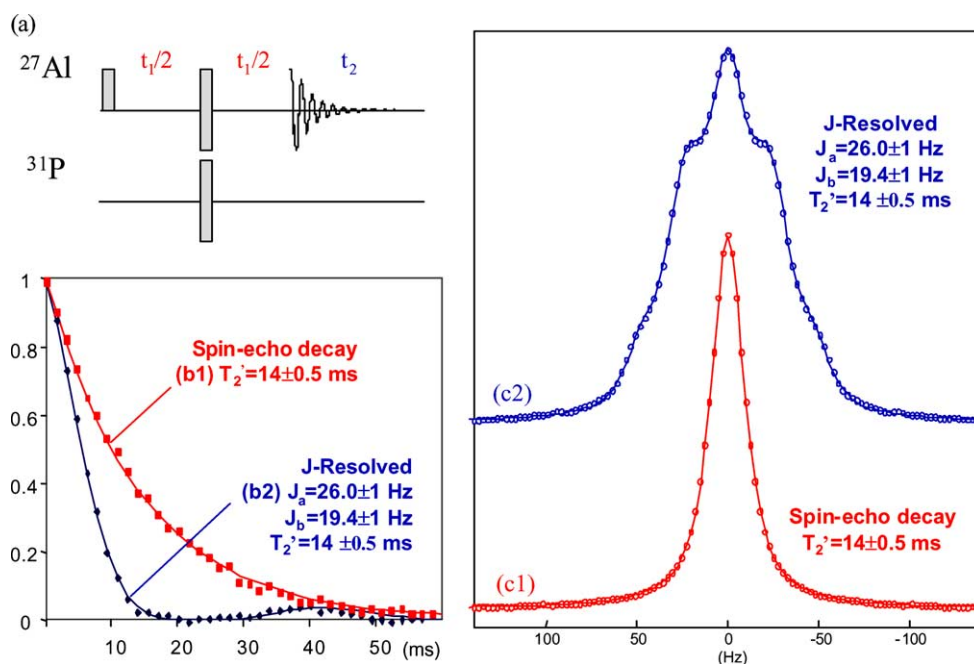


Fig. 1. $\{^{31}\text{P}\}^{27}\text{Al}$ J -Resolved experiment on AlPO_4 berlinite, acquired with $\nu_R = 13$ kHz: (a) Pulse sequence of the J -Resolved experiment, (b1, c1) time and frequency domains of the ²⁷Al spin-echo spectra (no ³¹P pulse); (b2, c2) time and frequency domains of the $\{^{31}\text{P}\}^{27}\text{Al}$ J -Resolved spectra (symbols) with their modeling (continuous line).

$\{^{31}\text{P}\}^{27}\text{Al}$ J -Resolved experiment allows us to experimentally evidence the presence of the two non-equivalent O sites translating into their different scalar J -couplings.

The Al–O–P J -coupling can be further used to generate an heteronuclear J -HMQC correlation experiment (Fig. 2a) [14,11]. J -HMQC directly derives from the J -Resolved experiment, by splitting the ^{31}P π pulse into two $\pi/2$ pulses placed on both parts of the central ^{27}Al π pulse and separated by an incremented $t_1/2$ evolution encoding the indirect dimension of the two-dimensional spectrum. The phase cycling is designed to build up the difference signal arising from double quantum heteronuclear coherence, which evolves under ^{31}P isotropic chemical shift during t_1 . The ^{27}Al projection of the 2D experiment superimposes with the 1D spectrum and the modeled lineshape (Figs. 2c1–c3). This can be understood, since the transfer involves the isotropic part of the J -coupling, independent of crystallite orientation. It thus appears that MAS J -HMQC can be an efficient way for obtaining through-bond heteronuclear correlation between quadrupolar and dipolar nuclei.

The structure of hydrated VPI-5 molecular sieve [20,21] contains three inequivalent aluminum sites: two Al–(OP) $_4$ tetrahedra (Al $_2$ and Al $_3$), and one octahedron Al–(OP) $_4$ (O–H $_2$ O) $_2$ (Al $_1$); and three different tetrahedral phosphorus sites. This compound has already been studied by solid state NMR using different methods, including $\{^{27}\text{Al}\}^{31}\text{P}$ cross-polarization [22–26], TEDOR

[23], MQ-MAS [26], or combination of these experiments. At usual magnetic fields, the ^{31}P MAS NMR spectrum shows three resolved lines, while the ^{27}Al spectra show one well-resolved AlO $_6$ resonance and two overlapping AlO $_4$ resonances (Al $_2$ and Al $_3$). The Al $_2$ and Al $_3$ lines can be resolved with MQ-MAS [25] or MQ-HETCOR [26] experiments allowing to assign the resonances to the different structural sites [20,21].

The T'_2 spin-echo decay times of the different Al sites of VPI5 are significantly shorter than that of berlinite. Therefore, it is not possible to resolve their multiplets in a J -Resolved experiment. T'_2 values for Al $_2$ (4.5 ms) and Al $_3$ (7.5 ms) sites remain independent from the spinning rate, but are significantly different, while for the Al $_1$ octahedral site T'_2 increases from 6.2 to 8.4 ms when increasing the spinning frequency from 10 to 13 kHz. Application of continuous wave ^1H decoupling during evolution and acquisition does not modify the observed lineshape, but slightly increases T'_2 for Al $_1$ site up to ~ 9 ms. This clearly shows that residual dipolar couplings between the octahedron and its neighboring ^1H are still not perfectly averaged out. Fig. 3 presents the $\{^{31}\text{P}\}^{27}\text{Al}$ MAS J -HMQC spectrum of hydrated VPI5 obtained for $\tau = 5.4$ ms. As in the previous case, we remark that the quadrupolar lineshape of site Al $_1$ is close to ideal. Intensity of cross-peaks in the 2D J -HMQC spectra will depend upon T'_2 of the different sites and individual Al–O–P J -couplings. Signal of sites

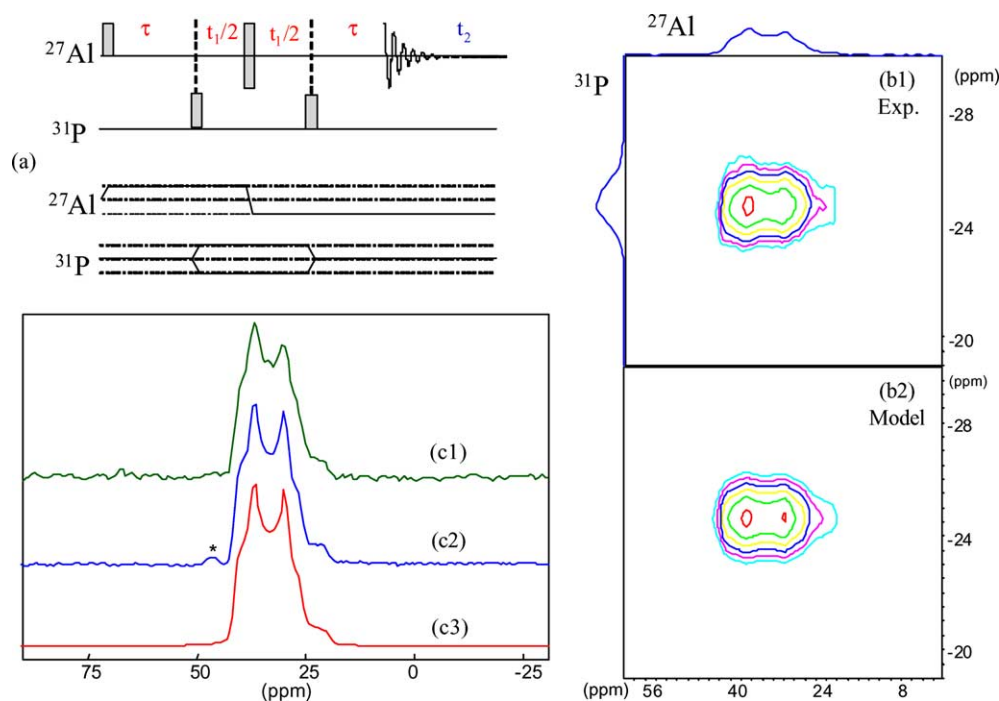


Fig. 2. MAS J -HMQC $\{^{31}\text{P}\}^{27}\text{Al}$ spectrum of AlPO_4 berlinite $\nu_R = 13$ kHz. (a) J -HMQC pulse sequence; (b1, b2) experimental ($\tau = 5.5$ ms) and modeled 2D J -HMQC experiments showing an ^{27}Al second order lineshape ($\delta_{\text{iso}} = 42.9$ ppm, $C_Q = 4.07$ MHz, $\eta_Q = 0.34$) in F2, and a ^{31}P gaussian line ($\delta_{\text{iso}} = -24.6$ ppm, FWHM = 1.6 ppm) in F1; (c1) the ^{27}Al projection of the J -HMQC, (c2) the ^{27}Al 1D MAS spectrum (* is the $n = 0$ spinning sideband of the satellite transitions), and (c3) the model ideal lineshape.

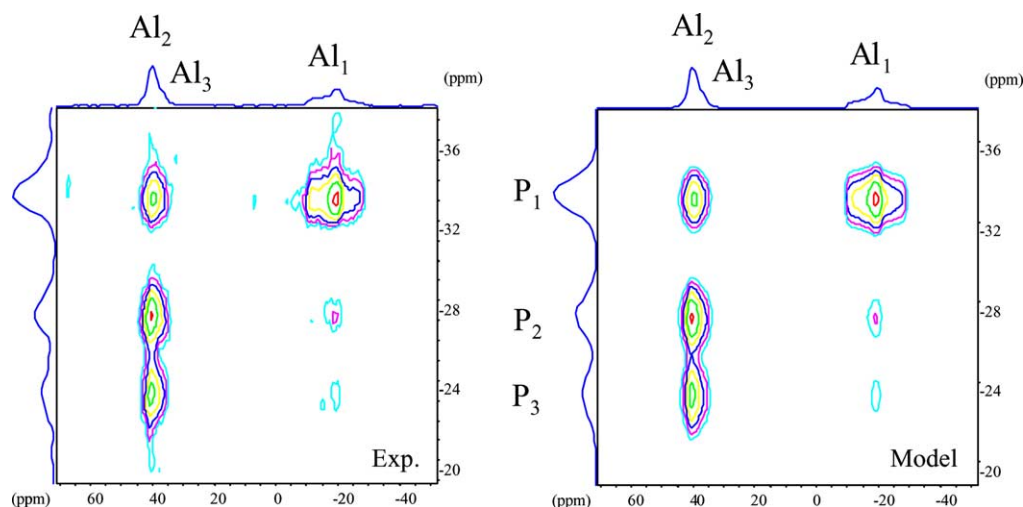


Fig. 3. MAS J -HMQC $\{^{31}\text{P}\}^{27}\text{Al}$ spectrum of VPI5 and its model assuming three different ^{31}P sites (P_1 -33.1 , P_2 -27.1 , and P_3 -23.3 ppm) and three different Al sites (Al_1 -10 ppm, $C_Q = 3.5$ MHz, $\eta_Q = 0.92$, Al_2 41 ppm, $P_Q = 1.3$ MHz, and Al_3 43 ppm, $C_Q = 2.2$ MHz $\eta_Q = 0.9$). $\nu_R = 13$ kHz, 256 scans, 1 s recycle delay (8 pre-saturation scans), $\tau = 5.4$ ms.

Al_2 and Al_1 will be minimized and maximized, respectively, due to their shorter and longer T_2' .

More interesting is to remark that, for each resolved aluminum resonance, the intensities of the cross-correlation peaks show very different behaviors. While overlapping $\text{Al}_{2,3}$ sites correlate with the three different phosphorus with close to equal intensity, the spectrally resolved Al_1 site correlates for 80% with P_1 site and for only 10% each with P_2 and P_3 sites. This cannot be only due to the coordination sphere of Al_1 ($2 \times P_1$, P_2 , P_3 , and water molecules). It clearly also implies that $^2J_{\text{Al-O-P}}$ scalar couplings between Al_1 and $P_{2,3}$ are much smaller than between Al_1 and P_1 . An examination of the HMQC build up curves yields $J_{\text{Al}_1-P_1} \sim 23$ Hz and $J_{\text{Al}_1-P_2} \sim J_{\text{Al}_1-P_3} \sim 14$ Hz. From crystal structure, we would expect four different $\text{Al}_1\text{-O-P}$ J -couplings (OP_2 , OP_3 , O_aP_1 , and O_bP_1) that we could not separate using this experiment. Nevertheless we remark that the P_1 sites, with $\text{Al}_1\text{-O-P}_1$ angles of 150 and 169°, are located in the walls of the zeolite structure, while the P_2 and P_3 sites, with nearly equal $\text{Al}_1\text{-O-P}_{2,3}$ angles of 139° connect Al_1 to its columns. This suggests that the J -coupling may be very sensitive to the Al-O-P bond angle for octahedral aluminum sites. The large contrast between J -coupling values may also open the possibility to establish a spectral edition based on chemical bond. It will be interesting to measure J -couplings involving fivefold coordinated aluminum sites that often arise during dehydration processes of zeolite structures and to compare with ab-initio quantum computation approaches.

Small scalar J -couplings of 15–25 Hz between quadrupolar and dipolar nuclei, directly characteristic of chemical entities, can be measured and used to establish through-bond correlation in J -HMQC experiment, providing long enough aluminum spin-echo decay time

T_2' . We evidence significant differences of Al-O-P scalar J -coupling between the two inequivalent Al-O-P bonds in the $\text{Al}(\text{OP})_4$ tetrahedron of berlinite, and between the different P sites bonded to the Al_1 octahedron of hydrated VPI-5 molecular sieve. These significant differences directly bear information on the individual Al-O-P chemical bonding and could be used to implement spectral edition methods directly based on the chemical bond characteristics. We anticipate that precise measurement of J -coupling constant could yield new sources of structural information. Works in progress involve application of selective excitation to individually measure J -coupling between the different types of sites [27], or combination with quadrupolar high resolution encoding [28,29], which could be implemented before or after the HMQC or INEPT sequences.

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