



Some triple resonance experiments in solid-state CP MAS NMR: $^{51}\text{V}/^{29}\text{Si}$, $^{31}\text{P}/^{13}\text{C}$, and $^{29}\text{Si}/^{13}\text{C}$

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Abstract

It is shown that the phenylphosphinic acid $\text{C}_6\text{H}_5\text{PH}(\text{O})(\text{OH})$ and the octavinylsilsesquioxane $[\text{SiO}_{1.5}(\text{C}_2\text{H}_5)]_8$ act as good candidates for the set-up of the Hartmann–Hahn condition under MAS condition for $^{31}\text{P} \rightarrow ^{13}\text{C}$ and $^{29}\text{Si} \rightarrow ^{13}\text{C}$ CP transfer, respectively. The study of the polyoxometalate derivative $[\text{AsW}_9\text{O}_{33}(\text{BuSiO})_3(\text{VO})](\text{Bu}_4\text{N})_3$ allowed us to clearly demonstrate the effect of $\{^{51}\text{V}\}$ decoupling during ^{29}Si acquisition for this type of compounds. These examples open new possibilities for the detailed study of inorganic compounds and hybrid materials, by triple resonance solid-state NMR experiments. **To cite this article:** C. Bonhomme et al., C. R. Chimie 9 (2006).

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Résumé

Nous montrons que l'acide phénylphosphinique $\text{C}_6\text{H}_5\text{PH}(\text{O})(\text{OH})$ et l'octavinylsilsesquioxane $[\text{SiO}_{1.5}(\text{C}_2\text{H}_5)]_8$ peuvent servir de standards pour le réglage des conditions de Hartmann–Hahn suivantes (sous rotation à l'angle magique MAS) : $^{31}\text{P} \rightarrow ^{13}\text{C}$ et $^{29}\text{Si} \rightarrow ^{13}\text{C}$. L'étude du polyoxométallate $[\text{AsW}_9\text{O}_{33}(\text{BuSiO})_3(\text{VO})](\text{Bu}_4\text{N})_3$ permet de mettre clairement en évidence l'effet du découplage $\{^{51}\text{V}\}$ sur l'acquisition ^{29}Si dans ce type de composés. Ces exemples montrent que les expériences de triple résonances à l'état solide offrent d'excellentes perspectives pour l'étude de composés inorganiques et de matériaux hybrides. **Pour citer cet article :** C. Bonhomme et al., C. R. Chimie 9 (2006).

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1. Introduction

Since the pioneering work of Fyfe [1] and Eckert [2] in the 90 s, ^1H - X - Y triple resonance solid-state NMR probes are now used in the frame of inorganic materials, as invaluable tools of structural investigation. Various $\{\text{X}-\text{Y}\}$ pairs have been considered, including the most frequently used, $\{^{27}\text{Al}, ^{31}\text{P}\}$, $\{^{27}\text{Al}, ^{29}\text{Si}\}$ and $\{^{19}\text{F}, ^{29}\text{Si}\}$. Demonstration of the use of more ‘exotic’ $\{\text{X}, \text{Y}\}$ pairs has been also proposed in the literature, including: $\{^{31}\text{P}, ^{113}\text{Cd}\}$ [2b], $\{^{27}\text{Al}, ^{13}\text{C}\}$ [3], $\{^{31}\text{P}, ^{77}\text{Se}\}$ [4], $\{^{31}\text{P}, ^{29}\text{Si}\}$ [5]. The NMR techniques used so far can be roughly divided in three categories:

- (i) CP MAS [6,7] experiments (cross polarization magic angle spinning), involving either a single $\text{X} \rightarrow \text{Y}$ transfer or a double $^1\text{H} \rightarrow \text{X} \rightarrow \text{Y}$ transfer (with Y detection in both cases). In the latter case, ^1H irradiation is mainly used for T_1 purposes;
- (ii) REDOR [8] (rotational-echo double resonance) and TEDOR [9] (transferred-echo double resonance) experiments;
- (iii) J -mediated techniques, like J -resolved and HMQC [10] (heteronuclear multiple quantum coherence) experiments.

The pulse sequences described in (i) and (ii) rely on the dipolar interaction between X and Y nuclei and allow to establish *spatial connectivities* by 1D (CP, REDOR, TEDOR) or 2D (CP HETCOR, heteronuclear correlation) [1,11] experiments. In some cases, distances between nuclei were even accurately measured by studying carefully the dipolar oscillations of the variable contact time CP curves or by REDOR experiments [1f,12–14]. The spectroscopic approach cited in (iii) establishes connectivities between X and Y nuclei through the isotropic J coupling, and allows the direct proof of *chemical bonding* between X and Y [15].

The main goal of this article is to highlight double X/Y and triple $^1\text{H}/\text{X}/\text{Y}$ CP MAS experiments, involving ‘exotic’ spin pairs such as $\text{X}/\text{Y} = ^{51}\text{V}/^{29}\text{Si}$; $^{31}\text{P}/^{13}\text{C}$; $^{29}\text{Si}/^{13}\text{C}$. One notes that in all cases, at least one resonant nucleus presents a low natural abundance (^{29}Si : 4.7%; ^{13}C : 1.1%). In the $^1\text{H}/^{29}\text{Si}/^{13}\text{C}$ CP MAS experiments, both target nuclei can be considered as low abundant nuclei. The results presented here are definitely encouraging for the set-up of 2D correlation experiments (such as HETCOR CP MAS experiments). Moreover, three compounds were found to act as good candidates for the set-up of the Hartmann–Hahn condition

under MAS, namely: $\text{C}_6\text{H}_5\text{PH}(\text{O})(\text{OH})$ for the $^{31}\text{P}/^{13}\text{C}$ transfer $[\text{SiO}_{1.5}(\text{C}_2\text{H}_3)]_8$ for the $^{29}\text{Si}/^{13}\text{C}$ transfer and $[\text{AsW}_9\text{O}_{33}(\text{tBuSiO})_3(\text{VO})]^{3-}$ for the $^{51}\text{V}/^{29}\text{Si}$ transfer. Such experiments seem interesting for the fine description of polyoxometalate derivatives and silica/phosphate based hybrid materials [16–19].

2. Experimental

A typical triple resonance MAS experiment used in this work is presented in Fig. 1. The acquisition of the Y spectra is performed under ^1H CW or TPPM decoupling and with/or without X high-power CW decoupling.

$^1\text{H}/^{51}\text{V}/^{29}\text{Si}$ experiments were performed on a Bruker AVANCE 400 spectrometer (^{51}V : 105.40 MHz; ^{29}Si : 79.48 MHz). Zirconia rotors (4 mm) were spun at the magic angle at 2 and 5 kHz (^{51}V coupled and ^{51}V decoupled, respectively). The polyoxometalate (POM) derivative $[\text{AsW}_9\text{O}_{33}(\text{tBuSiO})_3(\text{VO})]^{3-}$ ($(\text{tBu}_4\text{N})^+$ salt) (Fig. 2) was used as a standard. The multistep synthesis of this hybrid compound proceeds as follows: (i) synthesis of the trivacant anion $[\text{AsW}_9\text{O}_{33}]^{9-}$ by co-condensation of WO_4^{2-} and AsO_2^- under aqueous acidic conditions, (ii) reaction with tertiotbutyltrichlorosilane tBuSiCl_3 to afford the organosilyl open-structure hybrid $[\text{AsW}_9\text{O}_{33}(\text{tBuSiOH})_3]^{3-}$ as $(\text{tBu}_4\text{N})^+$ salt [24], and (iii) reaction with vanadyltrichloride VOCl_3 leading to closing-up of the structure by the capping group VO^{3+} [25]. Standard $^1\text{H}/^{29}\text{Si}$ CP MAS experiment (including ^1H CW high-power decoupling) was combined with CW ^{51}V decoupling. As ^{51}V is a quadrupolar nucleus, the CW power level on the ^{51}V channel was carefully adjusted, in order to obtain the best resolution on the

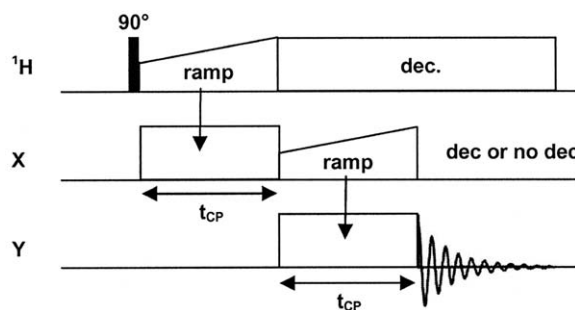


Fig. 1. Typical triple resonance experiment used in this work (under MAS). $\text{X} = ^{31}\text{P}, ^{29}\text{Si}$; $\text{Y} = ^{13}\text{C}, ^{29}\text{Si}$. CW decoupling on the X channel ($^{29}\text{Si}, ^{31}\text{P}, ^{51}\text{V}$) is optional (see text for details).

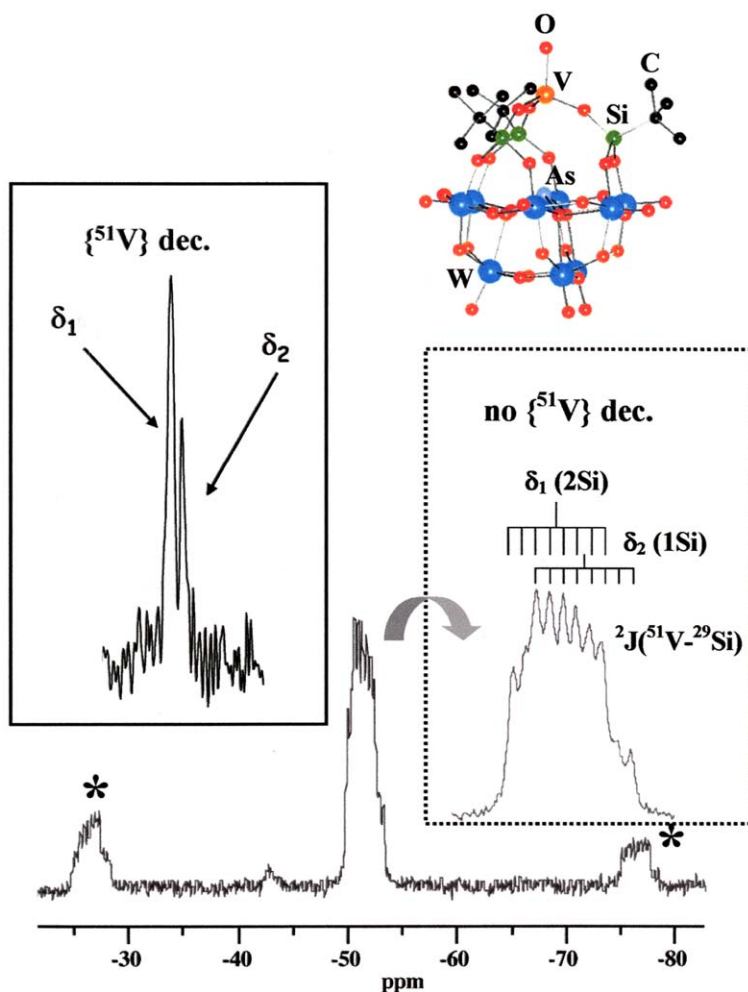


Fig. 2. ^{29}Si CP MAS spectrum (2 kHz) of $[\text{AsW}_9\text{O}_{33}(\text{BuSiO})_3(\text{VO})]^{3-}$ and the corresponding ORTEP view (orange: V, gray: As, blue: W, red: O, black: C, green: Si). Dashed inset: isotropic lines without $\{^{51}\text{V}\}$ decoupling. Full line inset: isotropic lines with CW $\{^{51}\text{V}\}$ decoupling (MAS at 5 kHz, ★ spinning sidebands).

^{29}Si spectra. Indeed, it is now well known [11] that efficient decoupling from quadrupolar nuclei is best obtained at rather low power levels (here 30 kHz on the ^{51}V channel). Other decoupling schemes (such as TPPM) were not used in this case. Chemical shifts are referenced towards TMS (0 ppm). Typical parameters were: recycle delay: 5 s, contact time ($^1\text{H}\rightarrow^{29}\text{Si}$): 5 ms; number of scans (NS) = 4380 for the fully coupled ^{29}Si spectrum (7-mm CP MAS Bruker probe: standard ^{29}Si CP MAS spectrum; 4-mm triple resonance CP MAS Bruker probe: ^{51}V decoupled ^{29}Si CP MAS spectrum).

$^1\text{H}/^{31}\text{P}/^{13}\text{C}$ and standard $^1\text{H}/^{13}\text{C}$ CP MAS experiments were performed on a Bruker AVANCE 300 spec-

trometer (4-mm triple resonance CP MAS Bruker probe) (^{13}C : 75.43 MHz; ^{31}P : 121.44 MHz). Zirconia rotors (4 mm) were spun at the magic angle at 5 kHz. The phenylphosphinic acid $\text{C}_6\text{H}_5\text{PH}(\text{O})(\text{OH})$ (purchased from Fluka) was used as a standard compound (see Fig. 3). For the $^1\text{H}/^{13}\text{C}$ CP MAS experiment: recycle delay: 20 s; contact time ($^1\text{H}\rightarrow^{13}\text{C}$): 2 ms; NS: 832. For the $^1\text{H}/^{31}\text{P}/^{13}\text{C}$ CP MAS experiment: recycle delay: 20 s; contact time ($^1\text{H}\rightarrow^{31}\text{P}$): 2 ms; contact time ($^{31}\text{P}\rightarrow^{13}\text{C}$): 5 ms; NS = 2500. In both cases, variable-amplitude cross-polarization (VACP) pulse schemes were used [20]. In particular, a VACP scheme is absolutely necessary for the second CP transfer ($^{31}\text{P}\rightarrow^{13}\text{C}$),

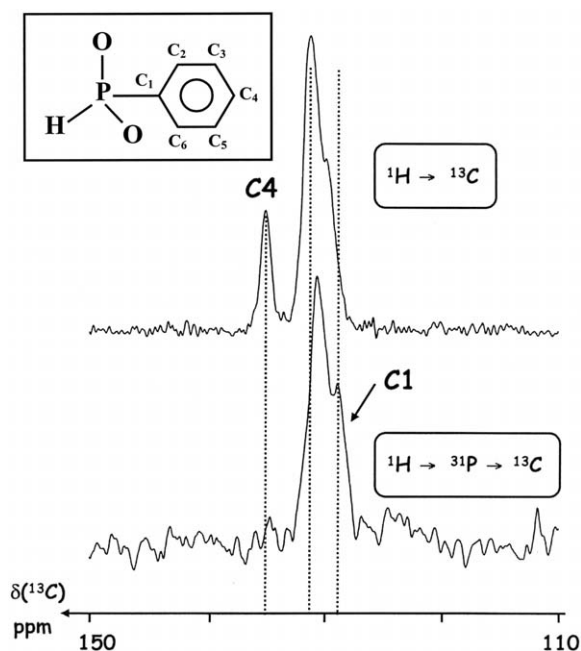


Fig. 3. $^1\text{H}/^{13}\text{C}$ and $^1\text{H}/^{31}\text{P}/^{13}\text{C}$ CP MAS spectra of the phenylphosphinic acid $\text{C}_6\text{H}_5\text{PO}(\text{OH})\text{H}$ (see the inset for the C atoms labeling scheme).

as the rather weak $^{31}\text{P}-^{13}\text{C}$ heteronuclear dipolar coupling is strongly modulated by the MAS process. The second contact time ($^{31}\text{P}\rightarrow^{13}\text{C}$) is adapted for the detection of close neighbors of the ^{31}P nuclei. This parameter can be used for spectral editing purposes. The ^{13}C acquisition was performed under ^1H TPPM decoupling, but without ^{31}P decoupling (the TPPM parameters – phase and pulse duration – were adjusted by using the phenylphosphinic acid). Chemical shifts were referenced towards TMS (0 ppm) via solid adamantane.

The $^1\text{H}/^{29}\text{Si}/^{13}\text{C}$ experiments were performed on a Bruker AVANCE 400 spectrometer (4-mm triple resonance CP MAS Bruker probe) (^{13}C : 100.56 MHz; ^{29}Si : 79.48 MHz). Zirconia rotors (4 mm) were spun at the magic angle at 5 kHz. The octavinylsilsesquioxane $[\text{SiO}_{1.5}(\text{C}_2\text{H}_5)]_8$ derivative (Fig. 4) (purchased from Hybrid Plastics) was used as a standard for the set-up of the experiment. The following parameters were used: recycle delay: 15 s; contact time ($^1\text{H}\rightarrow^{29}\text{Si}$): 10 ms; contact time ($^{29}\text{Si}\rightarrow^{13}\text{C}$): 5 ms, NS = 15000. TPPM decoupling on the ^1H channel was used during the ^{13}C acquisition but ^{29}Si decoupling was not performed.

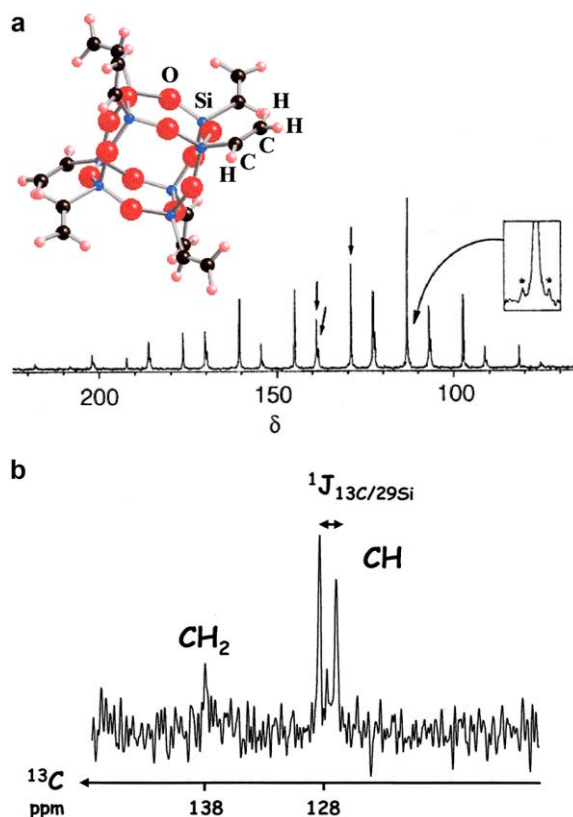


Fig. 4. (a) Standard $^1\text{H}/^{13}\text{C}$ CP MAS spectrum of $[\text{SiO}_{1.5}(\text{C}_2\text{H}_5)]_8$ at low spinning rate and the corresponding ORTEP view (blue: Si, red: O, black: C, white: H). Isotropic lines are shown by arrows. Inset: *satellites related to the ^{13}CH resonance due to $^1J(^{13}\text{C}-^{29}\text{Si})$ coupling. (CH_2 : $\delta \approx 138$ ppm, CH : $\delta = 128$ ppm). (b) $^1\text{H}/^{29}\text{Si}/^{13}\text{C}$ spectrum. The splitting due to $^1J(^{13}\text{C}-^{29}\text{Si})$ is clearly observable.

3. Results and discussion

3.1. $^1\text{H}/^{29}\text{Si}$ experiments with and without $\{^1\text{V}\}$ decoupling

The $^1\text{H}\rightarrow^{29}\text{Si}$ CP MAS spectrum (at 2 kHz) of $[\text{AsW}_9\text{O}_{33}(\text{tBuSiO})_3(\text{VO})](\text{tBu}_4\text{N})_3$ is presented in Fig. 2. This compound is one member of the large polyoxometalate family [16]. The polyoxometalate core ' $\text{AsW}_9\text{O}_{33}$ ' is capped by a vanadium atom linked through three tBuSiO groups (see the ORTEP representation in Fig. 2). This entity can be considered as intermediate between organic and inorganic moieties and acts, therefore, as a hybrid nanocluster [18]. The ORTEP view shows that at most three ^{29}Si isotropic resonances are expected. The ^{29}Si CP MAS spectrum

(without $\{^{51}\text{V}\}$ decoupling) exhibits a complex isotropic line, involving at least 10 resonances. Such a line can be decomposed into two isotropic contributions ($\delta_1 - 52.3$ ppm, 2Si; $\delta_2 - 53.0$ ppm, 1Si) subjected to the isotropic J coupling interaction ($^2J_{^{51}\text{V}-^{29}\text{Si}} = 28$ Hz). As $I = 7/2$ for ^{51}V , eight lines are expected for each ^{29}Si resonance. Whereas the three Si atoms are equivalent in solution, leading to a unique ^{29}Si resonance, this is no longer the case in the solid state, where the three Si atoms are crystallographically independent. The differences in the electronic surrounding of these three nuclei appear not sufficient to resolve three resonances.

By using CW $\{^{51}\text{V}\}$ decoupling during the ^{29}Si acquisition (at an adequate RF power – see Section 2), the spectrum is clearly simplified. All splitting due to $^2J_{^{51}\text{V}-^{29}\text{Si}}$ couplings are efficiently suppressed and only two isotropic ^{29}Si resonances are observed (δ_1 , δ_2). These are in the ratio 2:1, as expected from the fully coupled spectrum. The high-frequency signal is, however, significantly broader, likely because the two crystallographically unequivalent silicon nuclei are not strictly isochronous. Therefore, it is shown that triple resonance experiments involving exotic pairs, such as $^{51}\text{V}/^{29}\text{Si}$, open new areas in the structural studies of polyoxometalate derivatives.

3.2. $^1\text{H}/^{31}\text{P}/^{13}\text{C}$ experiments on the phenylphosphinic acid: towards $^{31}\text{P}/^{13}\text{C}$ spectral editing

The phenylphosphinic acid $\text{C}_6\text{H}_5\text{PH}(\text{O})(\text{OH})$ (see Fig. 3) appears as a good candidate for the set-up of the $^{31}\text{P}/^{13}\text{C}$ Hartmann–Hahn condition under MAS. Indeed, such a compound is characterized by a direct P–H bond, leading to a very efficient $^1\text{H}/^{31}\text{P}$ CP transfer. Moreover, the attached phenyl group exhibits ^{13}C nuclei, which can be easily distinguished through their distances to the ^{31}P nucleus. The quaternary C_1 atom is directly related to P, whereas the C_4 (para) atom is characterized by the longest P...C distance. It is, therefore, expected that the CP experiment (based on the dipolar coupling) will allow a clear distinction between ^{13}C nuclei, based on the strong variation of $^{31}\text{P}-^{13}\text{C}$ distances. We note, however, that the $T_1(^1\text{H})$ relaxation processes at $\nu_0 = 300$ MHz ($B_0 = 7$ T) are rather long, leading to a relaxation delay of 20 s (see Section 2). To the best of our knowledge, spectral editing in the frame of $^{31}\text{P}/^{13}\text{C}$ NMR spectroscopy in *natural abundance*

was never proposed in the literature, though some data involving fully labeled $^{31}\text{P}/^{13}\text{C}$ spin pairs were published by Hagaman [21].

The standard $^1\text{H}/^{13}\text{C}$ CP MAS spectrum is presented in Fig. 3. It is characterized by strong resonances located at $\delta \approx 130$ ppm and related to the phenyl groups. One resonance ($\delta = 135.1$ ppm) is clearly deshielded and can be safely assigned to the C_4 atom [22].

By using the double CP transfer $^1\text{H}/^{31}\text{P}/^{13}\text{C}$, the $^{13}\text{C}\{^1\text{H}\}$ spectrum is strongly modified ($^{31}\text{P}/^{13}\text{C}$ contact time: 5 ms). The line centered at $\delta = 135.1$ ppm is no more observed, in agreement with the proposed assignment (C_4). Moreover, the part of the spectrum centered at $\delta = 129.2$ ppm is overestimated under the $^{31}\text{P}/^{13}\text{C}$ CP transfer. This line can be assigned to C_1 . However, the ^{13}C acquisition was performed under ^1H decoupling, but *without* ^{31}P high-power decoupling. It has been shown previously that $^1J_{^{31}\text{P}-^{13}\text{C}}$ in phenyl derivatives can be estimated to ~ 200 Hz [22]. We believe that the line at $\delta = 129.2$ ppm corresponds to one branch of the C_1 doublet, due to the isotropic $^1J_{^{31}\text{P}-^{13}\text{C}}$ splitting. The second branch of the doublet is surely located at $\delta \approx 130.9$ ppm, superimposed to (C_2, C_6) resonances.

Further experiments, involving $\{^{31}\text{P}\}$ high-power decoupling and variable $^{31}\text{P}/^{13}\text{C}$ contact time, will be necessary for the complete assignment of the ^{13}C spectrum. Such experiments are now in progress in the laboratory.

3.3. $^1\text{H}/^{29}\text{Si}/^{13}\text{C}$ experiments in natural abundance

The octavinylsilsesquioxane $[\text{SiO}_{1.5}(\text{C}_2\text{H}_3)]_8$ (Fig. 4) has been carefully studied by $^1\text{H}/^{29}\text{Si}$ and $^1\text{H}/^{13}\text{C}$ CP MAS experiments [23]. It can be considered as a starting building block for the synthesis of hybrid material exhibiting tailored porosity [19]. The standard CP $^1\text{H}/^{13}\text{C}$ experiment shows resonances assigned to $^{13}\text{CH}_2$ and ^{13}CH groups, in good agreement with crystallographic data [23]. The ^{13}CH resonance is characterized by satellites due to $^1J_{^{13}\text{C}-^{29}\text{Si}}$ splitting. This isotropic J coupling was estimated to $^1J_{^{13}\text{C}-^{29}\text{Si}} \approx 136$ Hz. The double CP ($^1\text{H}/^{29}\text{Si}/^{13}\text{C}$) experiment is presented in Fig. 4b. The signal-to-noise (S/N) ratio is rather poor (NS = 15000 – see Section 2), as ^{13}C and ^{29}Si are present in *natural abundance*. However, this spectrum is highly informative and proves that $^1\text{H}/^{29}\text{Si}/^{13}\text{C}$ experiments can be performed on hybrid silica materi-

als. The $^{13}\text{CH}_2$ resonances are strongly underestimated, as expected. Indeed, CH_2 groups are characterized by long Si...C distances (2.75 Å), when compared to the CH groups (1.81 Å). Moreover, the ^{13}CH resonance is splitted into a doublet, corresponding to $^1J_{^{13}\text{C}-^{29}\text{Si}}$ coupling, as no $\{^{29}\text{Si}\}$ high power decoupling was applied during ^{13}C acquisition. One notes that the intrinsic S/N ratio can be easily improved by using $\{^{29}\text{Si}\}$ high-power decoupling.

4. Conclusion

Three examples, involving rather ‘exotic’ spin pairs $^{51}\text{V}/^{29}\text{Si}$, $^{31}\text{P}/^{13}\text{C}$ and $^{29}\text{Si}/^{13}\text{C}$, have shown that triple resonance experiments are particularly adequate for the characterization of inorganic and hybrid molecules/materials. These examples were based on double CP transfer under MAS conditions in 1D version. 2D HETCOR versions and J -derivated experiments [15] can be surely performed as well. The phenylphosphinic acid $\text{C}_6\text{H}_5\text{PH}(\text{O})(\text{OH})$, the polyoxometalate derivative $[\text{AsW}_9\text{O}_{33}(\text{tBuSiO})_3(\text{VO})]^{3-}$ and the octavinylsilsesquioxane $[\text{SiO}_{1.5}(\text{C}_2\text{H}_5)]_8$ can act as potential standards for the set up of the Hartmann–Hahn condition in the frame of $^{31}\text{P}/^{13}\text{C}$, $^{51}\text{V}/^{29}\text{Si}$ and $^{29}\text{Si}/^{13}\text{C}$ CP MAS NMR, respectively.

References

- [1] (a) C.A. Fyfe, H. Grondey, K.T. Mueller, K.C. Wong-Moon, T. Markus, *J. Am. Chem. Soc.* 114 (1992) 5876; (b) C.A. Fyfe, K.T. Mueller, H. Grondey, K.C. Wong-Moon, *Chem. Phys. Lett.* 199 (1992) 198; (c) C.A. Fyfe, K.T. Mueller, H. Grondey, K.C. Wong-Moon, *J. Phys. Chem.* 97 (1993) 13484; (d) C.A. Fyfe, K.C. Wong-Moon, Y. Huang, H. Grondey, K.T. Mueller, *J. Phys. Chem.* 99 (1995) 8707; (e) C.A. Fyfe, K.C. Wong-Moon, Y. Huang, H. Grondey, *Microporous Mat.* 5 (1995) 29; (f) C.A. Fyfe, D.H. Brouwer, A.R. Lewis, J.-M. Chézeau, *J. Am. Chem. Soc.* 123 (2001) 6882.
- [2] (a) D. Franke, C. Hudalla, H. Eckert, *Solid-State Nucl. Magn. Reson.* 1 (1992) 33; (b) D. Franke, C. Hudalla, R. Maxwell, H. Eckert, *J. Phys. Chem.* 96 (1992) 7506; (c) L. Zhang, J.C.C. Chan, H. Eckert, *Chem. Mater.* 15 (2003) 2702; (d) L. Zhang, H. Eckert, *Solid-State Nucl. Magn. Reson.* 26 (2004) 132.
- [3] L. Van Wüllen, *Solid-State Nucl. Magn. Reson.* 13 (1998) 123.
- [4] T. Pietrass, R. Seydoux, R.E. Roth, H. Eckert, A. Pines, *Solid-State Nucl. Magn. Reson.* 8 (1997) 265.
- [5] C. Lejeune, C. Coelho, L. Bonhomme-Coury, T. Azaïs, J. Maquet, C. Bonhomme, *Solid-State Nucl. Magn. Reson.* 27 (2005) 244.
- [6] S.R. Hartmann, E.L. Hahn, *Phys. Rev.* 128 (1962) 2042.
- [7] A. Pines, G. Gibby, J.S. Waugh, *J. Chem. Phys.* 59 (1973) 569.
- [8] T. Gullion, J. Schaefer, *J. Magn. Reson.* 81 (1989) 196.
- [9] A.W. Hing, S. Vega, J. Schaefer, *J. Magn. Reson.* 96 (1992) 205.
- [10] S. Braun, H.-O. Kalinowski, S. Berger, in: *150 and More Basic NMR Experiments*, Wiley-VCH, Weinheim, Germany, 1998, pp. 350 and 384.
- [11] L. Delevoye, C. Fernandez, C.M. Morais, J.-P. Amoureux, V. Montouillout, Rocha, *J. Solid-State Nucl. Magn. Reson.* 23 (2002) 501.
- [12] C.A. Fyfe, A.R. Lewis, J.-M. Chézeau, H. Grondey, *J. Am. Chem. Soc.* 119 (1997) 12210.
- [13] P. Bertani, J. Raya, P. Reinheimer, P. Gougeon, L. Delmotte, Hirschinger, *J. Solid-State Nucl. Magn. Reson.* 13 (1999) 219.
- [14] G. Mali, V. Kaucic, *J. Chem. Phys.* 117 (2002) 3327.
- [15] D. Massiot, F. Fayon, B. Alonso, J. Trebosc, J.-P. Amoureux, *J. Magn. Reson.* 164 (2003) 160.
- [16] Special Issue on Polyoxometalates, *Chem. Rev.* (1998) 98.
- [17] C.R. Mayer, V. Cabuil, T. Lalot, R. Thouvenot, *Adv. Mater.* 12 (2000) 417.
- [18] D. Agustin, C. Coelho, A. Mazeaud, P. Herson, A. Proust, R.Z. Thouvenot, *Anorg. Allg. Chem.* 630 (2004) 2049.
- [19] C. Zhang, F. Babonneau, C. Bonhomme, R.M. Laine, C.L. Soles, H.A. Hristov, A.F. Yee, *J. Am. Chem. Soc.* 120 (1998) 8380.
- [20] O.B. Peersen, X. Wu, I. Kustanovich, S.O. Smith, *J. Magn. Reson. A* 104 (1993) 334.
- [21] E. Hagaman, *J. Am. Chem. Soc.* 110 (1988) 5594.
- [22] C. Gervais, M. Profeta, V. Lafond, C. Bonhomme, T. Azaïs, H. Mutin, C.J. Pickard, F. Mauri, F. Babonneau, *Magn. Reson. Chem.* 42 (2004) 445.
- [23] C. Bonhomme, P. Toledano, J. Maquet, J. Livage, L. Bonhomme-Coury, *J. Chem. Soc., Dalton Trans.* (1997) 1617.
- [24] A. Mazeaud, N. Ammari, F. Robert, R. Thouvenot, *Angew. Chem.* 35 (1996) 1961.
- [25] (a) A. Mazeaud, PhD Thesis, Université Pierre-et-Marie-Curie, Paris-6, 1997; (b) Thouvenot et al., manuscript in preparation.