

Communication

Indirectly detected through-bond chemical shift correlation NMR spectroscopy in solids under fast MAS: Studies of organic–inorganic hybrid materials

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ABSTRACT

Indirectly detected, through-bond NMR correlation spectra between ¹³C and ¹H nuclei are reported for the first time in solid state. The capabilities of the new method are demonstrated using naturally abundant organic–inorganic mesoporous hybrid materials. The time performance is significantly better, almost by a factor of 10, than in the corresponding ¹³C detected experiment. The proposed scheme represents a new analytical tool for studying other solid-state systems and the basis for the development of more advanced 2D and 3D correlation methods.

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1. Introduction

The usefulness of solid-state NMR spectroscopy in structural analysis hinges on the availability of high-resolution spectra and good sensitivity. Remarkable advances are currently being made in both these areas due to the development of fast magic angle spinning (MAS) [1,2]. Recent reports have shown the major advantages of using fast MAS in the study of organic–inorganic mesoporous materials [3,4]. Most importantly, MAS at 40 kHz provided a simple and artifact-free way of achieving high ¹H resolution in these materials without the use of multiple-pulse radiofrequency (RF) irradiation and stroboscopic observation (CRAMPS [5]) [3]. Excellent sensitivity per spin, lack of spinning sidebands and the possibility of using low-power decoupling schemes [6] have enabled convenient acquisition of highly resolved 2D ¹³C{¹H} and ²⁹Si{¹H} heteronuclear correlation (HETCOR) NMR spectra. Another consequence of achieving CRAMPS-quality resolution without stroboscopic sampling is the opportunity for sensitivity enhancement by detecting the low- γ (X) nuclei indirectly via high- γ ¹H nuclei. Although the maximum gain of $(\gamma_H/\gamma_X)^{3/2}$ is unrealistic in solids, we found the time performance of indirect detection to be better than the standard ¹³C{¹H} HETCOR experiment by a factor of more than ten. Remarkably, the indirectly detected ¹³C–¹H HETCOR spectra of samples containing a few μ mole of covalently bound functional groups (in the absence of templating molecules) were

obtained within minutes or hours without using isotope enrichment [4].

The fast MAS-based HETCOR spectra reported thus far are based on cross-polarization (CP), providing through-space correlations via the dipolar interaction. Due to the strength of dipolar coupling (which is on the order of 20 kHz for closely spaced C–H pairs), the CP transfers are fast and efficient. However, they can be affected by molecular motions and are poorly suited for differentiating between short- and long-range correlations. Although the through-bond scalar (*J*) couplings are much weaker (in directly bonded C–H pairs the ¹J_{CH} values are on the order of 100 Hz), their utilization in solids has become increasingly practical following the progress in MAS technology and RF decoupling methods. The *J* couplings have been successfully exploited in various 1D and 2D experiments, including measurement of *J* coupling constants [7–9], spectral editing [10–12], and acquisition of homo- and heteronuclear correlation spectra in organic and inorganic materials [13–16].

The heteronuclear *J* correlation sequences reported for solids are based on mixing schemes developed for solution NMR, of which refocused INEPT is the most common. The key to achieving high efficiency in this experiment is to prevent the decoherence of transverse magnetization due to interactions that are non-refocusable by the rotor-synchronized spin-echo sequence under fast MAS. Since transverse relaxation is dominated by the dipolar couplings, the corresponding *T*₂' values and the efficiency of INEPT are expected to increase with increasing MAS rate ν_R . In addition to fast MAS, the use of proton homonuclear decoupling can be used to extend the ¹H coherence lifetimes [17].

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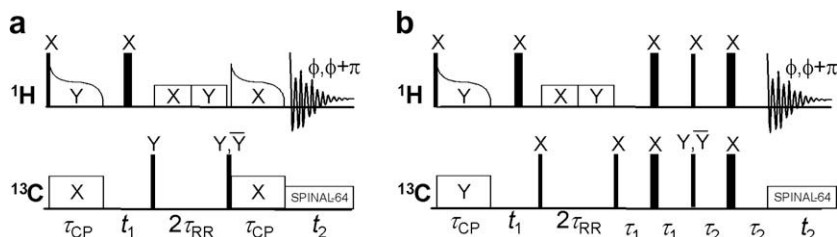


Fig. 1. Pulse sequences for CP-based (a) and INEPT-based (b) ^1H detected HETCOR experiments under fast MAS. Solid rectangles represent $\pi/2$ and π pulses. Phase cycling was simplified by the use of direct digital receiver. States-TPII detection was implemented through appropriate phase switching of the first $\pi/2$ pulse in the ^{13}C channel.

Here, we demonstrate that the benefits of fast MAS and polarization transfer via INEPT can be mutually utilized to measure, for the first time, the indirectly detected 2D $^1\text{H}\{^{13}\text{C}\}$ through-bond correlation spectra in solids. The new method is used to study mesoporous silica nanoparticles (MSN's) containing the templating molecules or covalently bound surface functional groups under natural abundance.

2. Experimental

2.1. NMR measurements

The pulse sequence for the 2D $^1\text{H}\{^{13}\text{C}\}$ INEPT experiment, shown in Fig. 1b, draws from the previously described CP-based schemes (Fig. 1a) [4,18]. The experiment uses the tangentially ramped $^{13}\text{C}\{^1\text{H}\}$ CP (or $^{13}\text{C}\{^1\text{H}\}$ INEPT, not shown) to create the initial ^{13}C magnetization, which then evolves during t_1 under the isotropic chemical shift in the presence of low-power decoupling (SPINAL-64 or, as shown in the figure, a single π pulse [4]). Following the t_1 period, ^{13}C magnetization is stored along the B_0 field, while the residual ^1H coherence is purged using two long pulses ($\tau_{\text{RR}} = 40$ ms for CTAB and 25 ms for PFP) with orthogonal phases, where the magnitude of RF field at the ^1H frequency satisfies the rotary resonance recoupling condition $\nu_{\text{RF}}^{\text{H}} = 0.5\nu_{\text{R}}$ [19,20]. Subsequently, the INEPT sequence is applied to transfer ^{13}C polarization back to ^1H nuclei. The SPINAL-64 ^{13}C decoupling is used during the detection period (t_2), to eliminate the residual dipolar broadening and the J splitting of ^1H lines in the ν_2 dimension. The so-called steady duty cycle compensation is implemented (if needed, i.e., when SPINAL-64 ^1H decoupling is used during t_1) [21], along with

other previously described measures [4], to minimize the t_1 -noise. All measurements were performed on a Varian NMR System 600 spectrometer, equipped with a 1.6-mm triple resonance FastMASTM probe, using $\nu_{\text{R}} = 40$ kHz.

2.2. Sample preparation

Two samples were synthesized according to the procedures described in our previous papers: (1) a non-functionalized sample of mesoporous silica containing the surfactant (CTAB), referred to as CTAB-MSN [22], and (2) a sample functionalized via co-condensation with covalently bound pentafluorobenzene groups ($-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}_6\text{F}_5$), and referred to as PFP-MSN [23]. CTAB was removed from PFP-MSN by acid extraction. Based on the deconvolution of ^{29}Si MAS spectra, we estimated that $13 \pm 2\%$ of silicon atoms in this sample are bound to carbon, which corresponds to the functional group concentration of 1.2 mmol/g. The samples were packed in MAS rotors after exposure to ambient conditions in the laboratory. The static ^1H linewidths were 6 kHz in CTAB-MSN and 12 kHz in PFP-MSN.

3. Results and discussion

The 2D $^1\text{H}\{^{13}\text{C}\}$ INEPT spectrum of CTAB-MSN is shown in Fig. 2a, where the peak assignments are made based on the NMR spectrum of CTAB in solution. Acquisition of 4 scans per row yielded a signal to noise ratio of ≈ 200 for ^{13}C resonance at 30.5 ppm. As demonstrated in Fig. 2b and c, the sensitivity is better by a factor of 3 than in the corresponding ^{13}C detected spectrum, and as good as in the indirectly detected CP-based spectrum (not

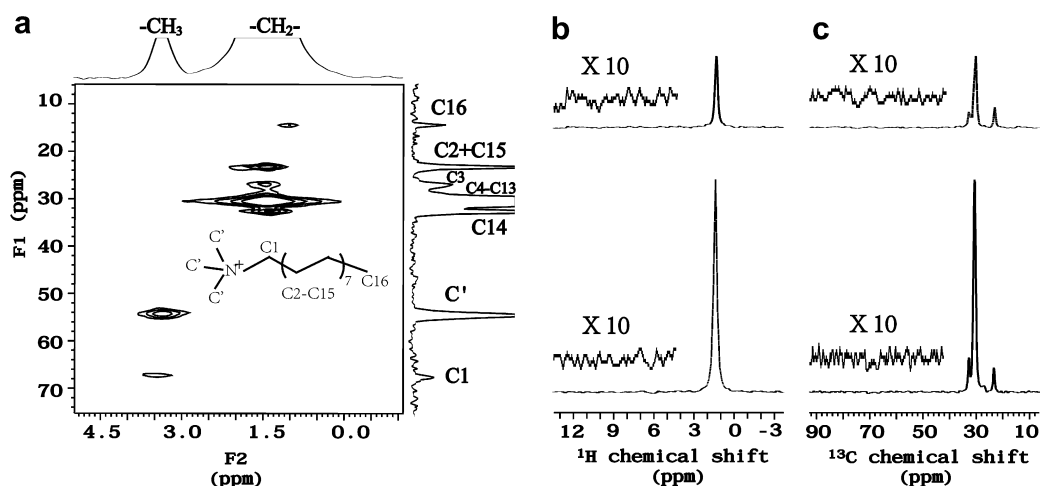


Fig. 2. (a) 2D indirectly detected $^1\text{H}\{^{13}\text{C}\}$ spectrum of CTAB-MSN with INEPT mixing recorded at 14.1 T, using $\nu_{\text{R}} = 40$ kHz, $\nu_{\text{RF}}^{\text{H}} = 110$ kHz during short pulses, $\nu_{\text{RF}}^{\text{H}} = 60$ kHz (with tangent ramp) during CP, $\nu_{\text{RF}}^{\text{C}} = 100$ kHz during short pulses and CP, $\nu_{\text{RF}}^{\text{C}} = 10$ kHz during SPINAL-64 decoupling. The spectrum was acquired in 240 rows, 4 scans per row with t_1 increments of 50 μs , $\tau_{\text{CP}} = 2.0$ ms, $\tau_1 = 1.1$ ms, $\tau_2 = 1.2$ ms, and recycling delay of 1.5 s. Total acquisition time was 50 min. (b,c) Selected cross-sections along ^1H (b) and ^{13}C (c) dimensions of spectrum (a) (bottom traces), and of the corresponding ^{13}C -detected spectrum acquired under the same experimental conditions (top traces).

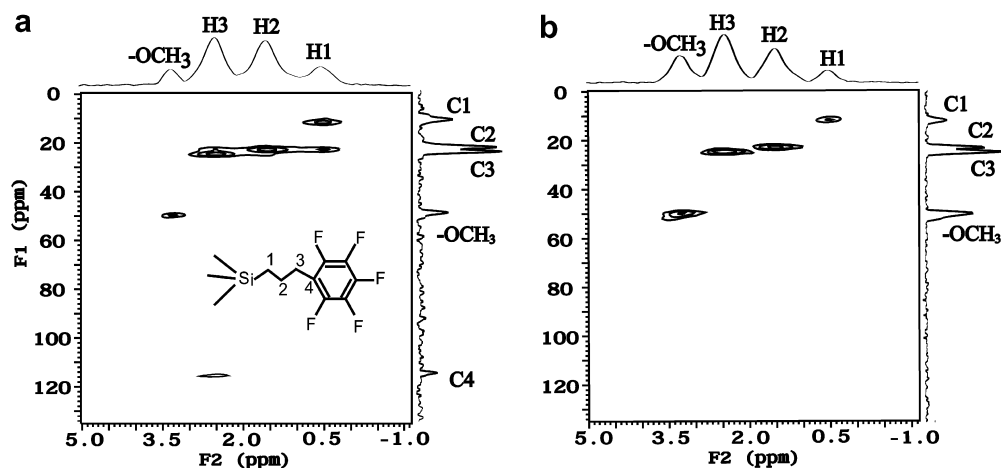


Fig. 3. 2D indirectly detected $^1\text{H}\{^{13}\text{C}\}$ spectra of PFP-MSN with CP (a) and INEPT (b) mixing. The spectra were acquired in 160 rows, with t_1 increments of 25 μs , $\tau_{\text{CP}} = 4.5$ ms, recycling delay of 1 s, 48 (a) and 128 (b) scans per row, $\tau_1 = 0.6$ ms, and $\tau_2 = 0.8$ ms (c). Acquisition times were 4.5 h (a), and 12.5 h (b). Other experimental details are provided in caption to Fig. 2

shown). 2D CP-based and INEPT-based $^1\text{H}\{^{13}\text{C}\}$ correlation spectra of PFP-MSN are shown in Fig. 3a and b. The observed cross-peaks indicated that the attached functional groups have the structure consistent with the PFP groups shown in Fig. 3a, thereby confirming that functionalization of the silica surface has indeed taken place as intended. Also present is a resonance representing the surface methoxy groups. The correlations due to long-range interactions (C2–H1, C2–H3, C3–H2 and C4–H3,) are only observed in Fig. 3a, which well demonstrates the through-bond filtering capabilities of $^1\text{H}\{^{13}\text{C}\}$ INEPT method. For the most prominent peaks, the CP-based and INEPT-based 2D spectra in Fig. 3 have similar intensities per scan. We note, however, that spectrum (a) has been acquired using $\tau_{\text{CP}} = 4.5$ ms in order to achieve substantial polarization between weakly coupled nuclei. This condition did not favor the strongly coupled pairs (C1–H1, C2–H2 and C3–H3) whose intensities would have been higher when using τ_{CP} in the 0.5 ms range. By shortening τ_{CP} to 50 μs , the correlations due to weakly coupled spins can be completely eliminated, yielding a spectrum similar to $^{13}\text{C}\{^1\text{H}\}$ INEPT, albeit much less intense.

While all expected resonances were detected in the MSNs, the relative intensities are influenced by a both CP and INEPT transfers. A detailed analysis of optimization strategies in this and other indirectly detected schemes will be presented separately. Here, we only report on the measurements of transverse relaxation in CTAB, which were made as a function of ν_{R} under conditions relevant to INEPT, i.e., using Hahn echo without heteronuclear decoupling. The measurement of ^{13}C relaxation (T_2^{C}), which in our experiment is operative during τ_1 , used $^{13}\text{C}\{^1\text{H}\}$ CP, whereas dephasing of ^1H (described by T_2^{H} and effective during τ_2) was studied following the $^1\text{H}\{^{13}\text{C}\}$ INEPT. As shown in Fig. 4a and b, a linear dependence on ν_{R} was found, both for T_2^{H} and T_2^{C} , in agreement with an earlier report [16]. This is critically important to our experiment. By reducing ν_{R} to 20 kHz, the sensitivity gain due to indirect detection would be essentially eliminated even if ^1H resolution remained constant.

4. Conclusions

We have demonstrated that refocused INEPT can be used with fast MAS to measure through-bond, ^1H detected HETCOR spectra of naturally abundant organic–inorganic mesoporous solids with excellent sensitivity and resolution. The time performance is significantly better, almost by an order of magnitude, than in the ^{13}C detected 2D $^{13}\text{C}\{^1\text{H}\}$ INEPT and matches that of through space,

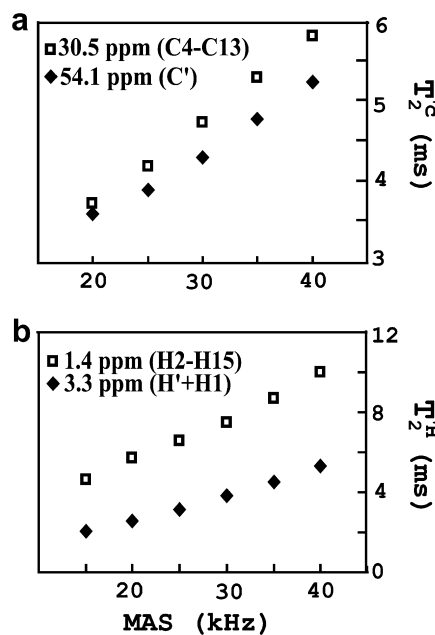


Fig. 4. Measurements of transverse relaxation times T_2^{C} (a) and T_2^{H} (b) during INEPT as a function of ν_{R} .

CP-based $^1\text{H}\{^{13}\text{C}\}$ method. The proposed scheme represents a new analytical tool for studying other solid-state systems and the basis for the development of more advanced 2D and 3D correlation methods. The development of more efficient homonuclear dipolar decoupling schemes can further improve the efficiency of this technique in strongly coupled spin systems.

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