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HRMAS NMR Diffusometry of Liquid Mixtures in Porous Materials

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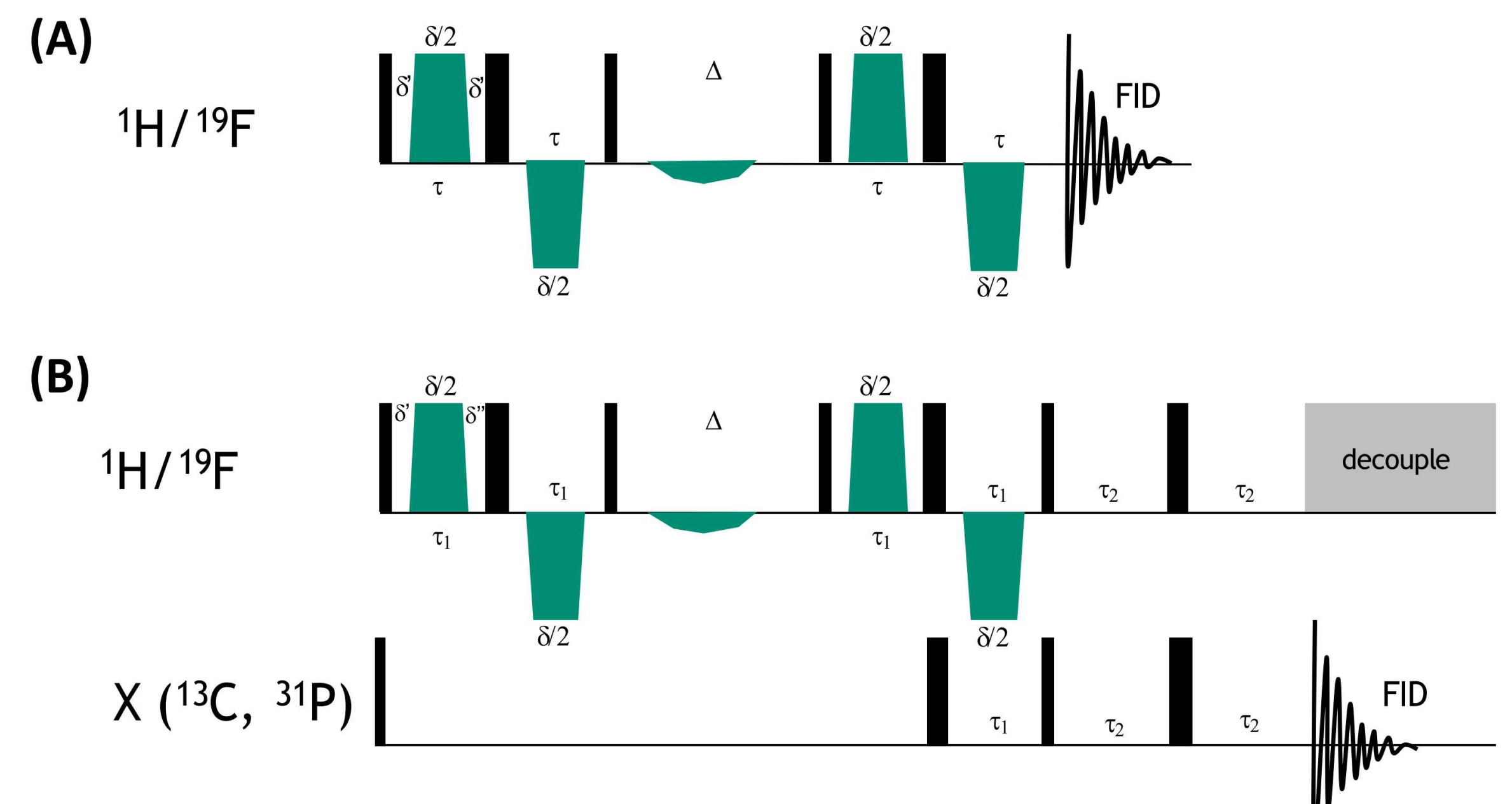
INTRODUCTION

Measuring the self-diffusion for different chemical species in complex multi-component (MC) mixtures adsorbed within porous materials is critical for developing and optimization of applications ranging from separation membranes in batteries and fuel cells, to coatings and barriers. Here we describe the development of high-resolution magic angle spinning (HRMAS) NMR diffusometry techniques to probe MC mixture diffusion in different porous materials. Introducing MAS reduces the magnetic susceptibility heterogeneity of the fluid-filled materials resulting in significantly improved chemical shift resolution. The diffusion rates for individual species in MC mixtures can now be directly measured without the need for selective isotopic labeling. Experiments reveal differential surface adsorption and are used to highlight the benefits and limitations of HRMAS NMR diffusometry in porous materials.

X-Detected HRMAS NMR Diffusion



(A) Pulsed field gradient (PFG) NMR using the stimulated echo bipolar pulse (STEBP) diffusion sequence (13-interval sequence [1] for ^{1}H (or ^{19}F). B) STEBP NMR diffusion sequence with X-detection (^{13}C or ^{31}P on our 4mm HRMAS probe) using a ^{1}H-X INEPT transfer [X]. Experiments utilized trapezoid shaped pulses of variable strength with $\delta/2$ duration, a diffusion period Δ (containing a spoiler gradient pulse), and τ_1 and τ_2 delays optimized for INEPT coherence transfer and filtering based on the ^{1}H-X *J* coupling.

- The echo intensity following the STEBP portion was reported by Cotts *et al.* (Condition I, 13-interval sequence) [1].
- Imposed symmetry δ'-δ'' eliminates the cross-terms between gradients.
- As a side note, the standard STEBP sequence in the Bruker library does not maintain the symmetry in δ', δ'' or in τ_1

$$\ln\left[\frac{S(g_a,\Delta+2\tau)}{S(0,\Delta+2\tau)}\right]=-\gamma^2 D\left[4\Delta+6\tau-\frac{2}{3}\delta\right]g_a^2+2\tau\delta\overbrace{(\delta'-\delta'')}^{=0}g_a g_0+\frac{4}{3}\tau^3 g_0^3$$

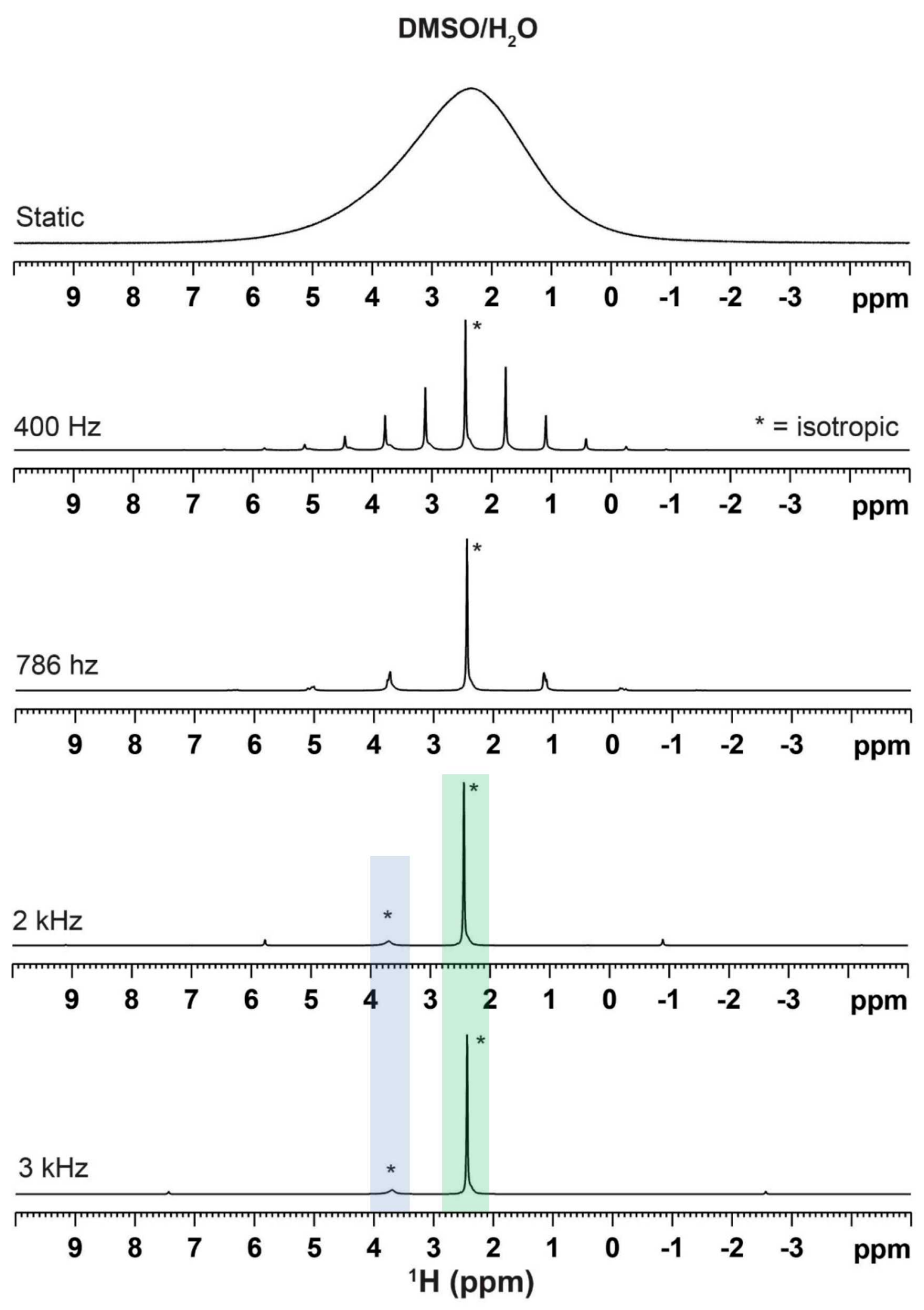
$g_0 =$ background gradient, $g_a =$ applied gradient

- Using combinations of the delays and gradient pulse lengths, and ignoring the remaining background gradient term, allows the decay to be modeled using the standard Stejskal-Tanner equation for diffusion [3].
- Using the ^{1}H (or ^{19}F) during the diffusion period maintains the larger *q* of the high frequency nuclei and improved intensity decay
- Other methods have demonstrated the heteronuclear transfer prior to the STE diffusion to take advantage of longer T_1 and T_2 of the X nuclei [4].

$$\Delta^*=\Delta+\frac{3}{2}\tau+\delta/2,\quad \delta^*=2\delta,\quad q=\gamma\delta^* g_a$$

$$\ln\left[\frac{S(g_a,\Delta+2\tau)}{S(0,\Delta+2\tau)}\right]=-\gamma^2 D\delta^{*2}g_a^2\left[\Delta^*-\frac{1}{3}\delta^*\right]=-Dq^2\left[\Delta^*-\frac{1}{3}\delta^*\right]$$

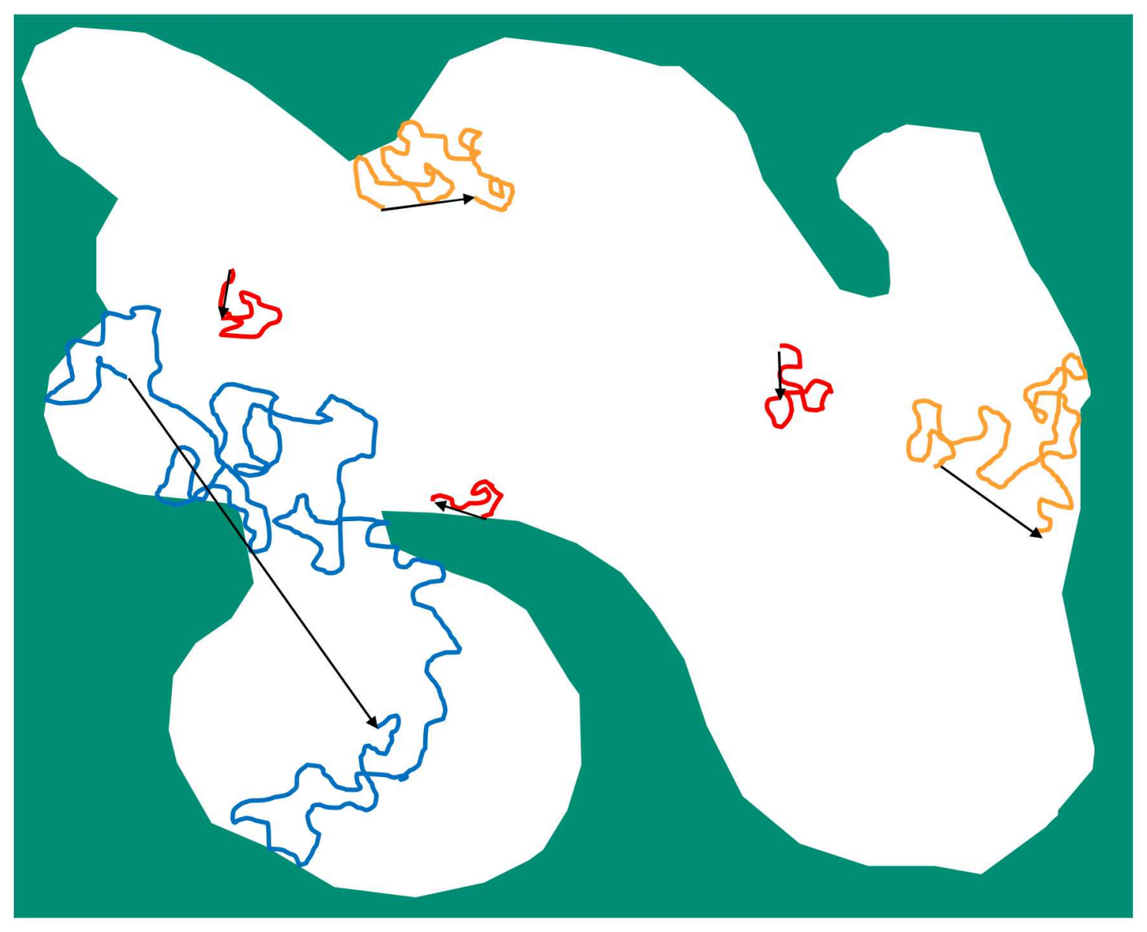
Improved Spectral Resolution under HRMAS NMR



^{1}H HRMAS NMR of DMSO/H2O solution in controlled pore glass (CPG) as a function of spinning rate.

- Line broadening due to heterogeneity of magnetic susceptibility produced by the porous matrix can be removed at relatively slow spinning speeds.
- Spinning at 3 to 4 kHz places the spinning sidebands outside of typical ^{1}H chemical shift chemical shift window (not ^{19}F).
- Improved spectral resolution allows for diffusion measurement on species with small relative concentrations.
- Not possible with static PFG NMR.

Diffusion Length Scales and Tortuosity [5]



$$\xi=\frac{D_0}{D_\infty}$$

$D_0 =$ diffusion rate unrestricted liquid

$\xi =$ PFG interaction parameter

$\xi=\tau$ (nonviscous, no surface interaction)

$\xi>\tau$ (non-negligible surface interaction)

$\xi<\tau$ (hydrogen bond disruption)

$$D_\infty=\mathrm{f}_1\,D_1+\mathrm{f}_2\,D_2=\mathrm{f}_{pore}\,D_{pore}+\mathrm{f}_{surf}D_{surf}$$

$$D_\infty=\frac{(1-\mathrm{f}_{surf})D_0}{\tau}+\frac{\mathrm{f}_{surf}D_{0,surf}}{\tau_{surf}}$$

$\Theta=\frac{D_0\Delta}{l^2}$, $\Theta\ll 1$ (short diffusion time limit); $\Theta\approx 1$ (intermediate); $\Theta\gg 1$ (long)

$D_{eff}(\Delta\rightarrow\infty)\equiv D_\infty$ [what we are measuring]; $\tau=\frac{D_0}{D_\infty}$; $D_0 =$ diffusion rate unrestricted liquid; $\tau =$ tortuosity

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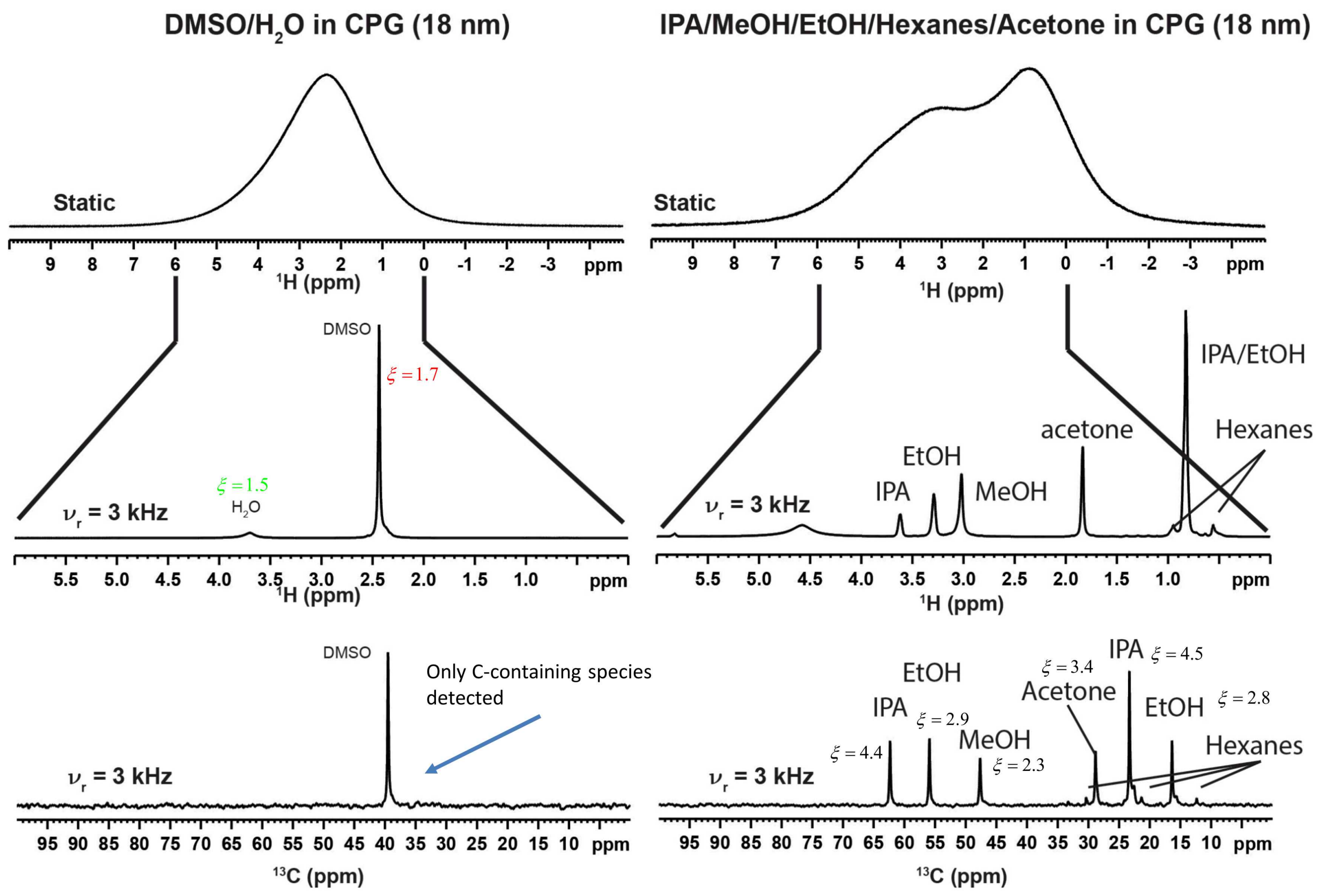
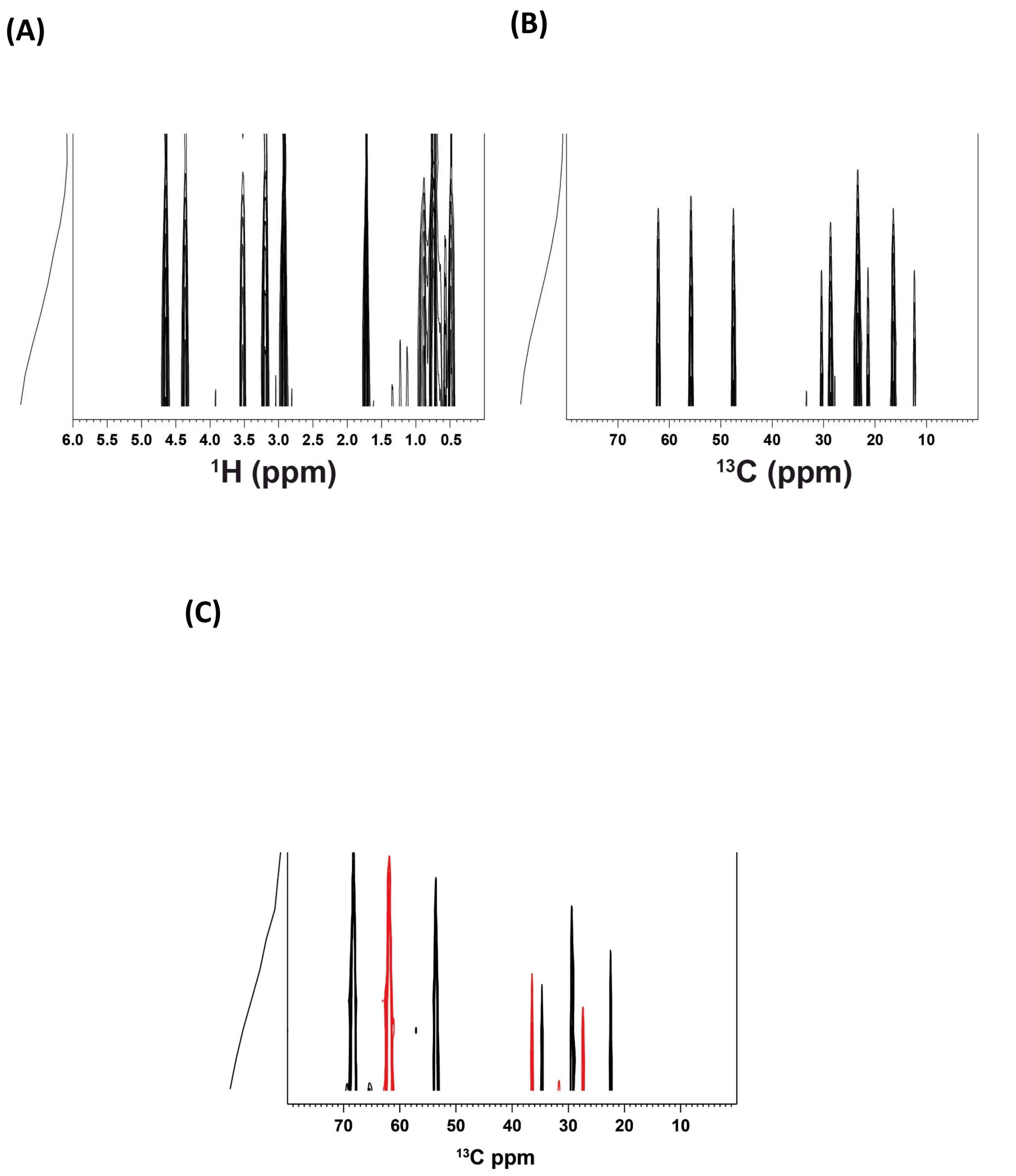
Improved Resolution and ^{13}C Detection



Examples of the improved resolution using HRMAS NMR: (A) Spectra for a [DMSO]/[H$_2$O] =2.82 solution in a 18 nm SiO$_2$ controlled pore glass, ϕ_V= 0.85 and (B) Spectra for a complex multicomponent (MC) mixture in the 18 nm CPG. Both the ^{1}H and the INEPT detected $_{13}$C spectra are shown. The PFG interaction parameters obtained from the NMR diffusion experiments are shown next to the different resonances.

^{13}C-Detected HRMAS NMR Diffusion



(A) ^{1}H STEDP NMR diffusion spectra for MC mixture in CPG (18 nm) (B) ^{13}C INEPT STEDP diffusion spectra and (C) ^{13}C INEPT with J filtering with CH, CH$_3$ (positive) CH$_2$ (negative) .

CONCLUSIONS

- HRMAS NMR diffusometry proves useful for resolving susceptibility broadened spectra in porous materials.
- To maintain S/N required significant increase in the experimental time, and in many cases *would prove restrictive* for large number of samples! ^{1}H detection is still the best route to go.

CHALLENGES

- INEPT performance controlled by T_2 relaxation which becomes more dominant for low volume loading and high surface area porous materials.
- Higher spinning speeds could increase T_2 relaxation times, BUT runs the risk of irreversible spectral changes due to centrifugation forces of fluid into pores.
- Thermal convection at higher spinning speeds and low viscosity samples degrades diffusion measurements.
- Major issues with charged molecules - influence of varying magnetic field under MAS, magnetic convection?

References

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