

## “Shining Light” on NMR and MRI in porous materials

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Over the past decades, novel NMR and MRI developments including cross-polarization, multiple-pulse sequences, multiple-quantum coherence, multidimensional spectroscopy, sample reorientation and correlation, zero-field magnetic resonance spectroscopy and imaging, and optical pumping and detection, have made it possible to study with high resolution the molecular structure and dynamics of such systems as zeolites, catalysts, semiconductors, nanocrystals, nanotubes, liquid crystals, polymers, and proteins. This lecture will attempt to shine some light on the subject of how laser-polarized NMR and MRI are further contributing to these investigations. An overview of some developments and applications of polarized noble gases and liquids in the study of molecules, organisms, and materials (MOM) will be presented. Hyperpolarized xenon NMR and MRI allow the characterization of structure, distribution and flow inside porous samples from the nano-scale to the macro-scale. Detailed images have been obtained of polarized

fluids flowing and diffusing inside porous materials, including the observation of effects such as turbulence and single-file diffusion that are relevant to transport and processing. Xenon has been used as an atomic probe to investigate the hydrophobic surfaces and interiors of porous macrocyclic molecules and proteins; recent results show evidence for binding of xenon to the outside of a protein, a proposed basis for the anesthetic mechanism of xenon. Indeed, localized injection of polarized xenon solutions into human blood has provided observations of the real-time process of xenon penetrating red blood cells. Polarization transfer from xenon to hydrogen and carbon nuclei has also been observed and exploited for the study of surfaces and interfaces. Furthermore, the use of laser-polarized xenon also opens an exciting new frontier in the approach to “Zero-Field MRI.” A novel ultralow-field MRI instrument based on novel superconducting quantum interference device (SQUID) detectors has made it possible to obtain high-resolution images in environments similar to the earth’s natural magnetic field, without the need for high field magnets normally required for imaging and microscopy.

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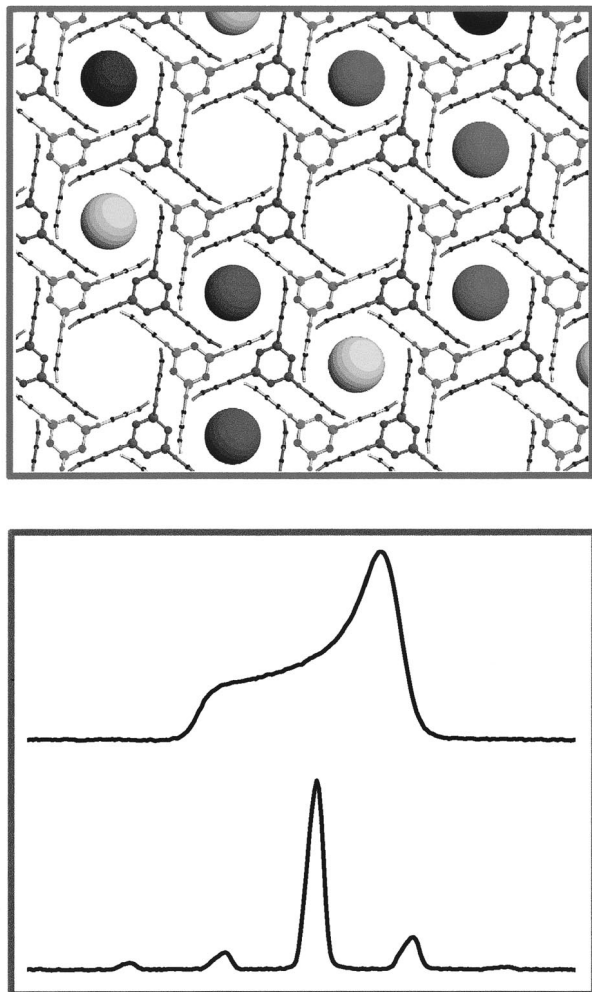


Fig. 1. Penetration and diffusion of xenon gas, effectively a one dimensional system, inside the benzene-walled nanochannels of TPP. The mechanism and dynamics of single-file diffusion, over tens of seconds, are elucidated through time-dependent NMR spectroscopy of laser-polarized  $^{129}\text{Xe}$ . Top: Schematic cross-section of xenon atoms at various depths inside the nanochannels of TPP. Bottom: Static (upper) and magic angle spinning (lower) NMR spectra showing the axially symmetric chemical shift tensor associated with the average distortion of dilute xenon atoms. Authors: Thomas Meersmann<sup>a,†</sup>, John W. Logan<sup>a</sup>, Roberto Simonutti<sup>a,b</sup>, Stefano Caldarelli<sup>c</sup>, Angiolina Comotti<sup>b</sup>, Piero Sozzani<sup>b</sup>, Lana Kasier<sup>a</sup>, and Alexander Pines<sup>a,\*</sup>

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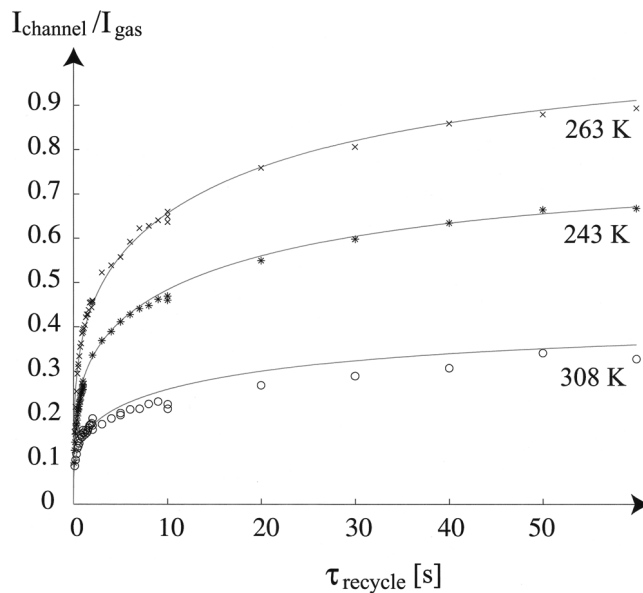


Fig. 2. Signal intensity from Xe inside the TPP channels (normalized to the gas phase peak area) vs buildup time for three different temperatures (308 K, circles; 243 K, stars; 263 K, crosses). The lines are fits of the experimental data points to a model using for single-file diffusion.

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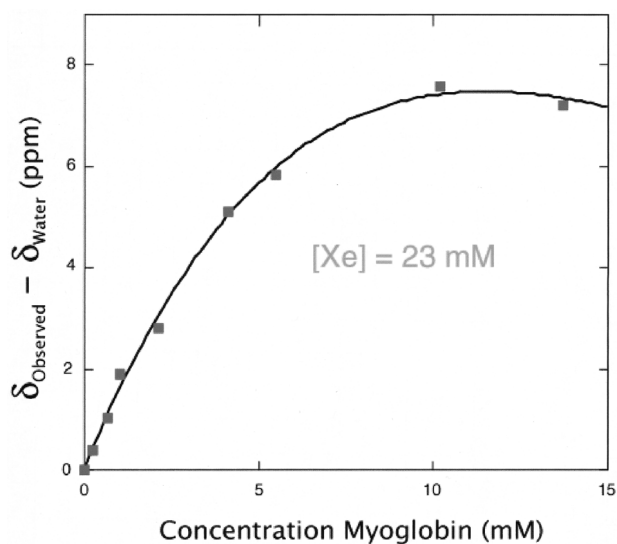


Fig. 3. Demonstration of both specific and non-specific binding of xenon to myoglobin. The variation of xenon chemical shift with myoglobin concentration is shown. An initial downfield shift is succeeded by a turn towards upfield at higher myoglobin concentrations. At low myoglobin concentrations, there is an excess of xenon, showing the downfield nature of non-specific, external binding sites. Once higher occupancy is reached, the intrinsic upfield shift of xenon in the internal, specific binding site is revealed.

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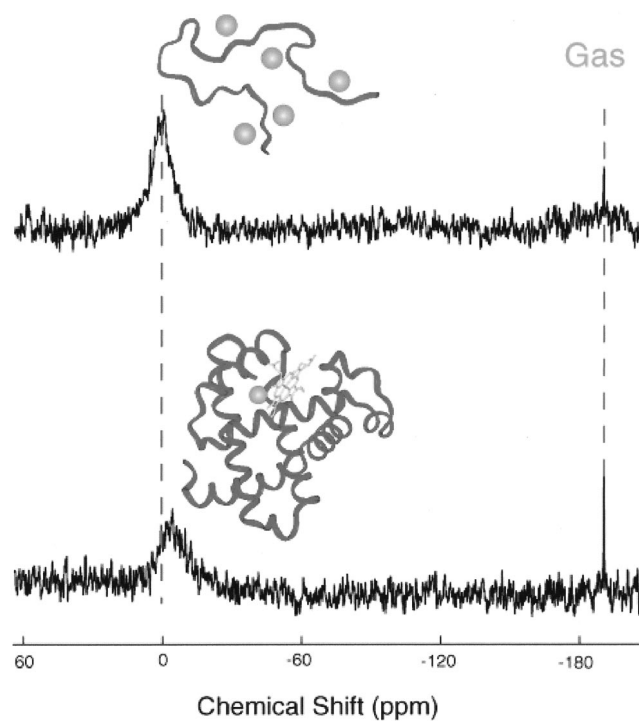


Fig. 4. Schematic of both specific and non-specific binding of xenon to myoglobin, with associated xenon-129 spectra non-specific binding dominates, leading to a downfield shift from the shift of xenon in water. The lower spectrum shows the xenon resonance actually shifting back towards the resonance in water, with an increase in the occupancy of the internal binding site. The peak to the right in both spectra is a high pressure xenon gas reference capillary, serving as a chemical shift reference in all experiments.

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