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Hyperpolarized Xenon-Mediated Cross-Polarization to Material Surfaces Observed at Room Temperature and Above

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Hyperpolarized (HP) xenon has been proposed as a source of NMR sensitivity and selectivity enhancement for studying solid surfaces.^{1–10} By its nature, xenon gas probes only the sites of a material that are accessible by diffusion. HP xenon produced by optical pumping methods¹¹ can attain spin polarizations 10⁵ times larger than thermal polarizations, which can subsequently be used to produce surface-selective NMR spectra with enhanced sensitivity. A number of approaches have proven successful in transferring the high-spin polarization of optically pumped xenon to surface nuclei,^{1–4,12} although most require near cryogenic temperatures to work successfully. The largest overall signal enhancements of solid surfaces have been observed using the spin polarization-induced nuclear Overhauser effect (SPINOE)^{3,4} for transferring polarization from HP xenon to surface nuclei, which works over a moderate temperature range ($T < 200$ K). Detailed analysis of the transfer mechanism has revealed that SPINOE is only effective when surface nuclei have long T_1 's (> 10 s) and when there is a minimum number of cross-relaxation pathways,^{13,14} limiting the general applicability of SPINOE to a small subset of samples. An appealing alternative for HP Xe/surface polarization transfer is the use of high field cross-polarization (CP). Unlike SPINOE, CP can generate surface selective NMR spectra without the use of difference measurements, making it suitable for studying low-surface area materials. CP between surface ¹H's and an adsorbed layer of ¹²⁹Xe has been examined previously^{1,9,15–17} but was thought to be limited to microporous materials and colder temperatures where the mobility of the adsorbed xenon atoms is decreased.

In this communication we demonstrate the robust nature of the CP method for HP Xe/surface polarization transfer and assess

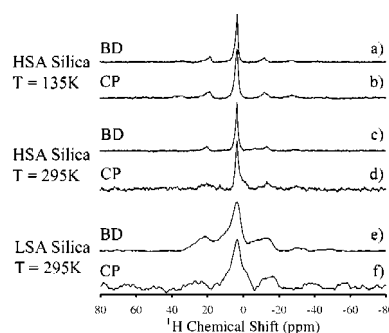


Figure 1. (a) ¹H Bloch decay (BD) and (b) ¹²⁹Xe–¹H cross-polarization (CP) spectra of 25 mg of silica (175 m²/g) acquired at 135 K. The CP spectrum had 104% of the intensity of the BD spectrum. (c) BD and (d) CP ¹H spectra of the same sample taken at 295 K. Room-temperature (e) BD and (f) CP ¹H spectra of 150 mg of a low-surface area (5 m²/g) silica sample obtained under conditions identical to those for (c) and (d). Experiments were performed on a 200 MHz Chemagnetics spectrometer and a Varian 7 mm CPMAS probe. A continuous flow of HP xenon was provided by an optical pumping/delivery described previously¹⁸ that produces a nominal ¹²⁹Xe polarization of 16%.

its applicability for surface NMR studies. By using a combination of a continuous flow HP Xe with magic-angle sample spinning (MAS), we observe HP Xe-mediated CP over a large temperature range (up to 320 K) to materials with low surface areas, measurable amounts of paramagnetic impurities, short (< 1 s) surface T_1 relaxation times, and other conditions where the SPINOE fails. We also demonstrate that high-field HP Xe/surface CP is feasible to low-frequency nuclei, such as ¹³C. The stability in our continuous flow apparatus makes the CP experiment amenable to two-dimensional heteronuclear correlation (HETCOR) experiments, which we use to identify and locate organic adsorbates in a macroscopically heterogeneous zeolite sample.

The unpolarized Bloch decay (BD) and ¹²⁹Xe–¹H CPMAS spectra of a high-surface area (HSA) fumed silica sample (M5 Cab-O-Sil, Cabot) acquired at 135 K are illustrated in Figure 1a and 1b, respectively. The ¹H spectra consist of an isotropic resonance at about 1.7 ppm, corresponding to surface silanols, and a series of spinning sidebands arising primarily from residual homonuclear dipolar couplings. The CP and BD spectra appear to be identical; however, careful inspection indicates that there are noticeable differences in the isotropic resonances and the line widths, possibly due to a site selectivity in the CP process. At such low temperatures, the xenon coverage is high ($\sim 75\%$), and CP from HP Xe produces a surface-selective spectrum with a relative sensitivity of 104%, slightly exceeding that of a standard one-pulse experiment. At this temperature, SPINOE is a more efficient Xe/surface polarization transfer mechanism; however, at warmer temperatures the results are much different. The room temperature (295 K) CP and BD spectra of the HSA silica are shown in Figure 1c and 1d. While the SPINOE gives literally no signal at temperatures above 200 K, CP generates a signal representing roughly 11% of the BD intensity. In fact, the CP continues to generate surface selective spectra at temperatures as high as 320 K.

A primary objective of the HP Xe method for obtaining surface-selective NMR spectra is to study materials where the surface atoms are greatly outnumbered by the bulk. As a representative of this class of materials, we studied 150 mg of a low-surface area (LSA), 5 m²/g, form of SiO₂ (Alfa Aesar) using HP Xe CP. The room-temperature CP and unpolarized BD spectra of the LSA silica are shown in Figure 1e and 1f. The total surface area for this sample was only 0.75 m², resulting in an acquisition time of 60 min for the room-temperature CP spectrum. Again,

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the ^1H resonance around 1.7 ppm in these spectra corresponds to surface silanol groups, but there are slight differences in peak positions and line widths between the two spectra. For this sample, the CP signal represents only 1% of the BD signal, unlike the 11% relative sensitivity observed for the HSA silica. The CP signal of LSA silica is smaller than expected since the surface xenon polarization should increase with the decreasing surface area due to a higher surface-adsorbed xenon replenishment rate. A possible explanation for this discrepancy is a measurable amount of paramagnetic impurities (as evidenced by ESR), although we cannot rule out the possibility of inaccessible proton sites in the particle interior.

High-temperature HP Xe CP is also useful for studying materials with lower-NMR frequency nuclei, such as ^{13}C , ^{29}Si , etc. Room-temperature ^{13}C BD and ^{129}Xe – ^{13}C CP spectra of a $^{13}\text{CD}_3\text{OD}$ treated silica sample were collected and are available in Supporting Information. The CP signal has a relative intensity of about 5% to the BD signal. The methanol spectra consist of a single isotropic resonance centered at 58 ppm, but again show subtle differences in line width and peak position between the BD and CP similar to those observed in the ^1H spectra. On the basis of the NMR frequencies and the results from the room-temperature ^1H CP, a relative CP intensity as large as 44% could be expected. However, due to its lower Larmor frequency and larger atomic radius, ^{129}Xe – ^{13}C dipolar couplings are weaker, requiring longer contact times (~ 100 ms) for maximum polarization transfer. Combined with short xenon $T_{1\rho}$'s (~ 15 ms), the maximum ^{129}Xe – ^{13}C CP signal is limited. Due to limitations on the pulse width from our amplifiers, we were not able to find the optimal contact time for the ^{129}Xe – ^{13}C CP. The ability to CP to lower frequency like ^{23}Na , ^7Li , or ^{27}Al will prove useful for studying surface structure of materials such as zeolites and metal oxide catalysts.

The utility of xenon as a surface probe can be increased when combined with the NMR of other nuclei in a correlation (HETCOR) experiment. A combination of a stable, continuous flow of HP Xe and the coherent polarization transfer afforded by CPMAS makes advanced two-dimensional NMR experiments, like the HECTOR experiment, possible. The incorporation of HP Xe/surface CP into a 2D HETCOR experiment was used to identify the location of benzene and methanol adsorbates in a macroscopically heterogeneous mixture of the zeolites HZSM-5 and HSSZ-13. The HETCOR spectrum depicted in Figure 2 was collected in about 16 min, representing a time savings of roughly 40 over a conventional ^1H – ^{129}Xe correlation experiment, which is obtained by ^1H – ^{129}Xe CP in a high xenon pressure sealed ampule.¹⁶ The difference in pore sizes between zeolites provide differing ^{129}Xe chemical shifts, while the nature of the adsorbates determines the ^1H shifts. A temperature of 225 K was chosen for optimal resolution of the two adsorbed xenon species. Although the xenon resonances in the zeolites and the adsorbate proton resonances can be identified in 1D spectra, the location of the adsorbates in the zeolite mixture is impossible to determine without the 2D correlation experiment. The ^{129}Xe shifts of 100 and 130 ppm in the F_1 dimension correspond to xenon adsorbed in the HSSZ-13 and HZSM-5 zeolites, respectively and were determined by comparison to xenon shifts in the individual zeolites prior to loading. In the F_2 dimension, the ^1H shifts of 3.4 and 9 ppm correspond to the methyl protons of methanol and the benzene protons. The two peaks in the HETCOR spectrum in Figure 2 clearly indicate that methanol is loaded in the HSSZ-13, while the benzene is adsorbed in the HZSM-5.

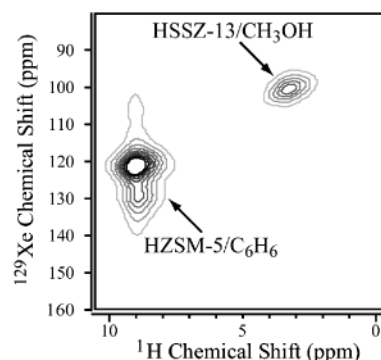


Figure 2. A $^{129}\text{Xe}/^1\text{H}$ 2D-HETCOR (HETeronuclear CORrelation) spectrum showing the correlation between adsorbed xenon and the adsorbate protons of a mixed zeolite sample obtained at a temperature of 225 K. The sample consisted of a mixture of $\text{CH}_3\text{OH}/\text{HSSZ-13}$ and $\text{C}_6\text{H}_6/\text{HZSM-5}$ (~ 50 mg each) with loadings chosen to give proton resonances of roughly equal intensity. The zeolite samples were prepared by dehydration prior to loading the organic adsorbates. The total acquisition time was approximately 16 min.

We report that high field CP from optically pumped ^{129}Xe to surface species shows an unexpectedly large temperature range. Warmer temperature studies allow for resolution improvement in the surface NMR spectra of solid materials using HP Xe by means of either molecular motion or by mechanical sample spinning. At warmer temperatures ($T > 200$ K) the relative CP intensity is small; however, the CP enhancement per adsorbed HP Xe atom is sizable when the low Xe surface coverage (0.5%) is considered. The principle limitation to the experiment is not weak surface/Xe dipolar coupling, but rather low-surface coverages. As the observed CP signal only originates from nuclei in contact with the hyperpolarized ^{129}Xe , the resulting signal is truly surface selective. The recycle delay for the CP experiment is only dependent on the effective Xe T_1 (i.e. the surface replenishment rate, typically < 1 s), so that the resulting experiment times are short. Short recycle delays and temperature-tunable resolution in the xenon dimension makes the CP experiment amenable to rapid 2D correlation experiments. The ability to use high temperatures and to study samples with short T_1 's, even samples with paramagnetic impurities, makes HP Xe CP a reliable surface analysis method. These results as well as preliminary HP Xe CP studies of the acid sites in zeolites and proton-terminated sites in porous silicon¹⁹ are an indication of the diversity of the molecular sites that can be investigated. Observation of CP to low-surface area materials and to lower-frequency nuclei, like ^{13}C , should extend the utility of HP Xe CP for general surface studies using NMR.

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Supporting Information Available: Figure of BD and CP spectra of $^{13}\text{CD}_3\text{OD}$ chemisorbed on silica and CP spectra as a function of magnetic field direction during optical pumping (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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