High-Field Cross Polarization NMR from Laser-Polarized Xenon to a Polymer Surface

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Received May 20, 1993

Surface-selective characterization of materials with NMR has been quite useful in the few cases where sufficient sensitivity and selectivity have been achieved.[1] In this communication we report the use of laser-polarized xenon as the source of magnetization for a high-field cross polarization experiment, obtaining surface-selective magnetization transfer. Gas-phase xenon with nuclear spin polarization several orders of magnitude higher than thermal Boltzmann levels in a high magnetic field can be produced using optically pumped rubidium vapor according to the pioneering work of Happer and co-workers.[2] The angular momentum of circularly polarized laser light is transferred, via the rubidium electron spins, to the (slowly relaxing) xenon nuclear spin system. We have previously used xenon, with a large polarization enhancement (≈10 000), as a probe of low surface area materials.[3] More recently, using thermal mixing in low field,[4] polarization has been transferred between xenon isotopes[5] and from xenon to $^{13}CO_2$ occluded in solid xenon.[6] The approach of low-field mixing has the disadvantages of nonselective magnetization transfer, typically very short spin–lattice relaxation times in low field, and the necessity of rapid field switching or mechanical transport of the sample to high field for detection. High-field cross polarization methods should be advantageous in allowing nuclear spin selectivity in the transfer step as well as circumventing relaxation and transport problems. In the present work, contact between laser-polarized xenon and surface spins was achieved in high field by Hartmann–Hahn matching of the energy levels in the rotating frame with direct NMR detection of the polarized species.[7,8] Proton spins are observed due to their abundance at the surface and the dominant dipolar interactions with adsorbed xenon.

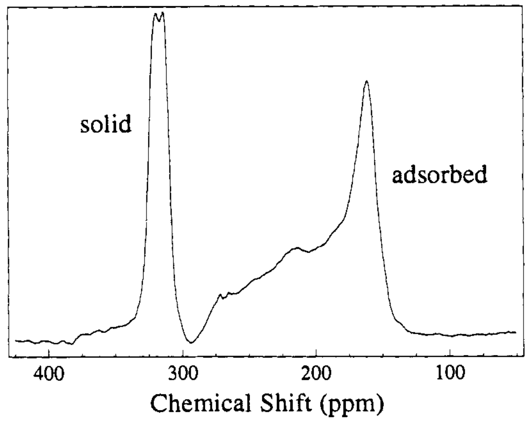


Figure 1. NMR spectrum of ^{129}Xe adsorbed on poly(triarylcarbinol) at $T = -160$ °C, approximately 10 s after the xenon was introduced into the sample region (referenced to low-pressure xenon gas).

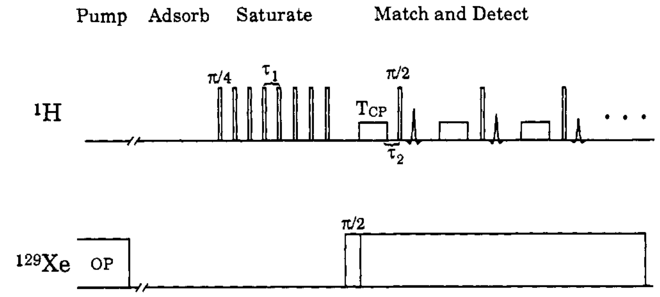
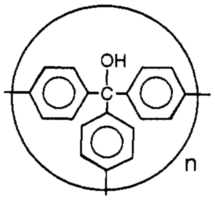


Figure 2. Multiple-contact pulse sequence used for one of the cross polarization experiments. Following optical pumping and adsorption of the xenon, the proton spins of the sample were saturated by a train of 45° pulses and then repeatedly cross polarized by Hartmann–Hahn matching to the xenon with detection using a dipolar echo. The timing parameters were $\tau_1 = 1000$, $\tau_2 = 50$, and $T_{cp} = 200$ μs.

The optical pumping was performed using a slightly modified version of the apparatus described previously.[3] The pumping cell had a volume of ≈35 cm^3, and the laser source was an argon ion (Coherent Laser Group Inc.) pumped Ti:sapphire ring laser (Schwartz Electro-Optics Inc.) with an output of 1–2 W at the rubidium D1 transition (794.7 nm). The double-tuned probe is based on a design of Doty and co-workers[9] and is capable of achieving temperatures as low as −175 °C using cold flowing nitrogen gas. The sample, poly(triarylcarbinol) (**1**), is a microporous, hypercross-linked, rigid-rod polymer, provided by Owen Webster (DuPont). The polymer has a BET surface area, obtained by nitrogen adsorption, of 835 m^2/g and a Langmuir surface area of 1112 m^2/g.[10] Due to the large surface area, at low temperatures this polymer rapidly adsorbs most of the optically polarized xenon present (≈5 × 10^{19} atoms). Before the NMR experiments, the sample was evacuated to <10^{-6} Torr at ≈50 °C for 3 h and then slowly cooled to the set temperature and allowed to equilibrate for several minutes before the xenon was added. We waited typically 5–10 s after adding the xenon before starting the pulse sequence. The T_1 of the ^{129}Xe on the polymer surface is about 20 s. The transmitter power levels for the Hartmann–Hahn matching condition were optimized using a xenon quinol clathrate compound[11] at room temperature.



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The ^{129}Xe NMR spectrum of xenon adsorbed on poly(triarylcarbinol) at −160 °C is shown in Figure 1. The two

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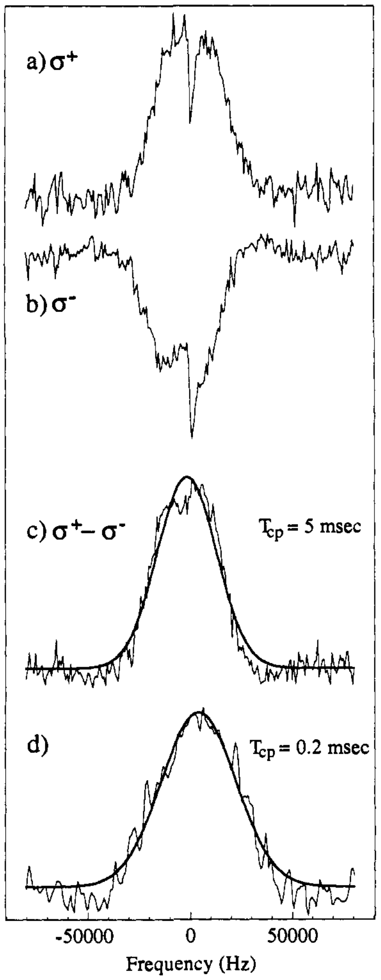

Figure 3. (a) ^{1}H spectrum following cross polarization from ^{129}Xe after using σ^+ pumping light for the Rb/Xe mixture. T_{cp} = 5 ms. (b) Same as spectrum a but with σ^- pumping light. (c) Difference spectrum of a and b, leaving only the signal from those hydrogens in contact with xenon; fwhm = 36 kHz. (d) ^{1}H spectrum following multiple-contact cross polarization from ^{129}Xe after using σ^+ pumping light for the Rb/Xe mixture with background subtracted. T_{cp} = 200 μs; fwhm = 43 kHz.

resonances correspond to frozen xenon and xenon adsorbed on the polymer. Cross polarization *from* protons *to* xenon has been previously demonstrated in this system[12] below about −140 °C, indicating heteronuclear dipolar coupling with an optimal contact time of approximately 5 ms. For the ^{129}Xe *to* ^{1}H cross polarization experiments, Figure 2 shows the multiple contact pulse sequence used. After the xenon is optically pumped and adsorbed on the polymer surface, the proton resonance of the sample is saturated by a train of 45° pulses to destroy any thermal polarization. The xenon is then spin-locked, and a matching field of 13 G is applied to the proton spins. After a contact period, the proton matching field is turned off and the magnetization is refocused using a dipolar echo to reduce the effects of the spectrometer dead time. The resulting spectra are shown in Figure 3. The change in helicity of the pumping light from σ^+ (Figure 3a) to σ^- (Figure 3b) results in a 180° phase shift in the spectrum, which confirms that xenon indeed constitutes the polarization source for the proton spins. No signal from the polymer was obtained when the sequence was run immediately before the xenon was added or when the Hartmann–Hahn matching field amplitudes were deliberately misset. The sharp feature slightly out of phase, near the center of the spectra, arises from proton spins not in contact with xenon, mostly from the probe background. Note that this feature is subtracted out in the difference spectrum of Figure 3c since it is invariant to inversion of the xenon polarization.

The ^{1}H signal was studied at several matching times, using a single contact experiment, and found to be consistent with the expected exponential dependence on the ^{129}Xe–^{1}H contact time. At short contact times ($\leq$0.5 ms), the signal was very weak but could be enhanced by employing the multiple contact sequence of Figure 2. The spectrum at the shortest contact time (0.2 ms, Figure 3d) was perceptibly broader (43 kHz) than the equilibrium spectrum obtained by a simple echo sequence (36 kHz). At longer contact times, the line width approached the bulk equilibrium value, probably due to proton spin diffusion, consistent with a spin diffusion coefficient estimated to be $\approx$0.6 nm^2/ms.[13] The signal from the cross-polarized protons, obtained with the optimal single contact time (20 ms), is estimated to have an enhancement in excess of 70, given that no signal was detected when thermally polarized xenon was used as the magnetization source.

In summary, we have demonstrated that under favorable circumstances (high surface area, long relaxation time), laser-polarized, adsorbed xenon can be used to selectively transfer spin order to surface spins. In more extended studies, variable contact time cross polarization studies should allow "depth profiling" of the nuclei near the surface. The method could also be extended to cross polarization of low gamma and less abundant nuclei such as carbon-13 or silicon-29 on surfaces polarized either directly from the xenon or via the proton spins.

Acknowledgment. The authors are grateful to O. Webster (DuPont) for providing the sample of **1** and to Dr. K. Schmidt-Rohr for helpful discussions. H.C.G. gratefully acknowledges support from the NSF and T.P. from NATO-DAAD. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Material Sciences Division of the U.S. Department of Energy under contract No. DE-AC03-76SF00098 and by a grant from the Shell Development Company.

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