Surface-Enhanced NMR Using Continuous-Flow Laser-Polarized Xenon

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Received April 29, 1997

Sensitivity and selectivity pose constant challenges in NMR studies of surfaces.[1] The number of nuclei residing on the surface of a material may be too small for NMR observation, and potentially detectable signals may not be discernible from the spectrum of the bulk material. Some progress has been achieved in recent years by the use of laser-polarized xenon, either by freezing the gas onto the solid surface followed by high-field cross-polarization (CP)[2] or by nuclear Overhauser cross-relaxation from adsorbed polarized xenon,[3] a process dubbed SPINOE[4] (spin polarization induced nuclear Overhauser effect). For both approaches, experiments are typically performed with one batch of isotopically enriched laser-polarized Xe, with subsequent polarization decay either by relaxation in the adsorbed states or by radio frequency driven transfer of the spin polarization. In either case, loss of polarization prevents signal accumulation and the multiple pulse manipulation of spins necessary for spectral resolution. A method for rapid production and continuous delivery of polarized xenon gas to surfaces would clearly be advantageous.

In this communication, we report the use of a fast optical pumping process, combined with a closed gas-circulation NMR probehead designed to deliver a continuous flow of laser-polarized Xe to an Aerosil surface. The technology for the production of ^{129}Xe with nuclear spin polarization several orders of magnitude higher than thermal Boltzmann levels is now well established.[5] In the present study, we exploited the pressure broadening of the rubidium D1 transitions, and recently available high-power diode laser arrays, to pump much denser Rb vapors ($[Rb] = 4 \times 10^{14}$ cm^{-3}), thereby enabling spin-exchange time constants on the order of tens of seconds.[6] The high-pressure optical pumping cell was connected to a gas recirculation system capable of delivering a continuous stream of the polarized xenon gas to the NMR sample, as shown schematically in Figure 1. This new methodology allowed the observation of difference SPINOE's that selectively highlight surface spins, thereby enhancing both sensitivity and selectivity for surface-resolved NMR spectroscopy.

Aerosil300 was obtained from Degussa Inc. and is reported to have a surface area of 300 m^2/g with about 2.5 hydroxyl protons/nm^2. Sample (150 mg) was packed into a 10 mm U-shaped sample tube placed in a double-tuned probe (^{1}H: 178.02 MHz; ^{129}Xe: 49.24 MHz) built on the basic principle of lumped circuit elements published previously.[7] The sample tube and the optical pumping cell were constructed of glass and subsequently glued to $^1/_8$ in. copper tubing. The optical pumping cell was placed in the 150 G fringe field of a 4.2 T superconducting magnet; this assembly was then attached to the recirculation and vacuum pumps, as well as the sample probe. This entire assembly was evacuated to below 10^{-5} Torr for several hours to remove physisorbed water and oxygen; during evacuation, the sample was kept at 50 °C. The evacuated system was then filled with the gas mixture necessary for pumping the pressure-broadened Rb levels; the mixture typically consisted of 300 Torr of natural abundance Xe (Air Products) and 90 Torr of N_2 (Airco Ind.), pressurized with ^{4}He (Aldrich) up to 3 atm. All gases were of research grade (99.995%) and were used without further purification. The NMR sample region was then cooled to the desired temperature, and the optical pumping cell was heated to 180 °C for optical pumping. The Rb atom density was monitored via the IR-absorption profile using an optical fiber positioned behind the pumping cell; the fiber was connected to a monochromator/photodiode setup. The diode laser (Optopower Corp., Model OPC-A150-795-RPCZ) delivered 120 W centered at the Rb D1 transition (794.7 nm), with a fwhm of 2.5 nm using a current of 22 A with the chiller temperature set at 10 °C. Steady-state nuclear spin polarizations of up to 3% for the ^{129}Xe gas could be obtained with a constant flow rate of 30 mL/min with the NMR sample region at ambient temperature. This spin polarization dropped to 0.25% when the gas mixture was circulated over the sample region cooled to −120 °C. ^{129}Xe NMR spectra at these conditions yielded a broad resonance ascribed to adsorbed Xe at 180 ppm (0 ppm: gas signal at 22 °C) with an estimated line width of about 60 ppm. The steady-state laser-polarized Xe layer was then used for SPINOE to surface nuclei. The steady-state polarization signal from the adsorbed xenon on the surface of the Aerosil could be observed shortly (<1 min) after starting the gas circulation pump. The xenon polarization signal may be either emissive or absorptive, depending upon the orientation of the circularly polarized light relative to the magnetic field direction. We observed an emissive signal compared to that obtained at thermal equilibrium. The simultaneous progress of the corresponding "negative" SPINOE to the surface protons was detected (Figure 2), indicating a value of about 200%. The use of 80% enriched ^{129}Xe produced a signal intensity that was 4 times higher. This experiment could be performed for several hours.

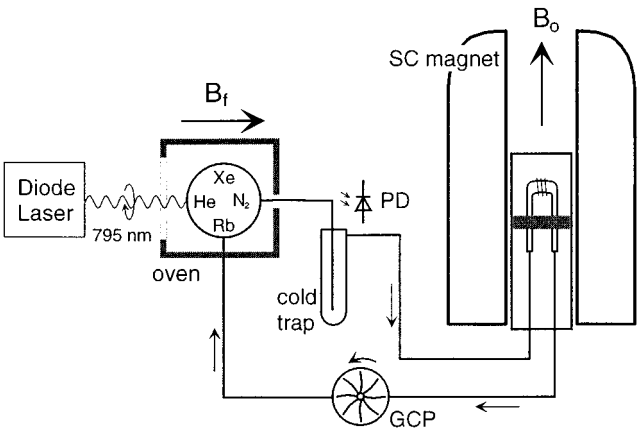

Figure 1. Gas recirculation setup including the superconducting magnet, field strength $B_o \approx 4.2$ T, housing the sample in a dewared region of a NMR probe. The optical pumping cell is placed in the fringe field at $B_f \approx 150$ G heated by an air stream heater. The transmitted light is detected by a photodiode (PD). GCP denotes the gas circulation pump, located in the back line of the optical pumping cell.

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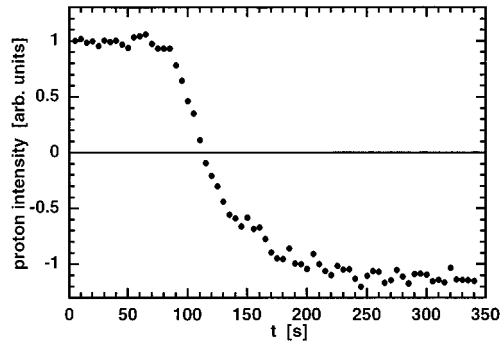


Figure 2. ^{1}H NMR signal intensities from surface protons on 150 mg of Aerosil300 at −120 °C; signals were obtained every 5 s using an 18° proton excitation pulse ($T_1(^1H) \approx 9$ s). The diode-laser was started after 1 min. The surface SPINOE from adsorbed laser-polarized Xe begins 40 s later. Steady-state optical pumping conditions were achieved at 250 s and could be followed for several hours.

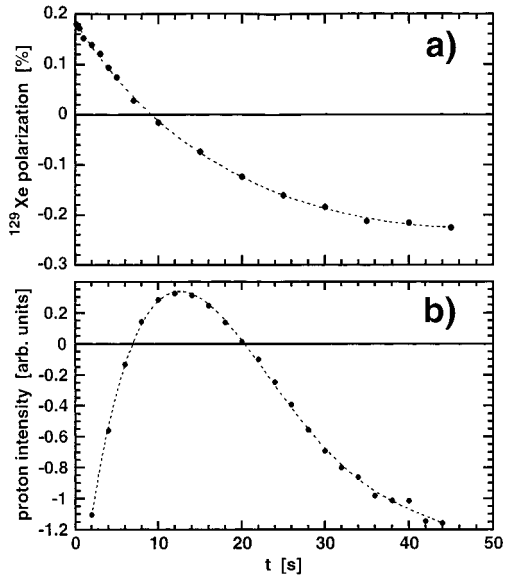


Figure 3. (a) ^{129}Xe NMR signal intensities from an inversion recovery experiment of the steady-state laser-polarized Xe layer on the Aerosil surface at −120 °C under continuous-flow conditions. The intensities are given in percent of polarization, calibrated with the adsorbed signal at thermal equilibrium. (b) Corresponding ^{1}H NMR signal intensities from the surface protons that follow the spin inversion of the steady-state Xe layer through the effective SPINOE. Units are on scale with those of Figure 1.

A corresponding "positive" SPINOE could be established with reversed xenon polarization obtained by changing the pumping conditions appropriately. However, this approach is not suitable for triggering double-resonance experiments. Alternatively, we applied a 180° (Xe) pulse to invert the nuclear spin polarization in the sample region. The result of such an inversion−recovery experiment under continuous-flow conditions, where the "recovery" arises from replacement of freshly polarized Xe on the surface, is shown in Figure 3a. The time constant for this experiment, 17 s, corresponds to the lifetime of the inverted Xe spin pool on the sample surface, whereas the relaxation time of ^{129}Xe at stopped gas flow is 32 s. The polarization reversal of the surface xenon atoms affects also the surface proton spins, as is shown in Figure 3b by monitoring the proton signal. The proton spins initially experience a "positive" SPINOE, reaching a signal maximum after approximately 12 s, followed by a "negative" SPINOE returning again the signal to its initial steady-state value, shown in Figure 2.

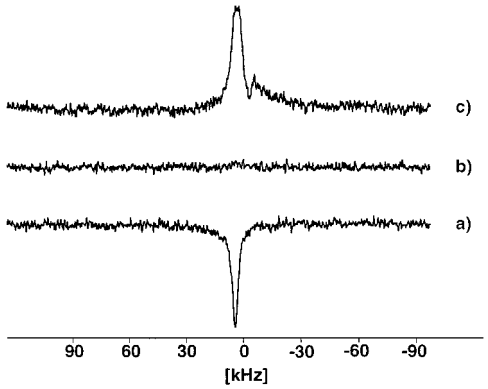
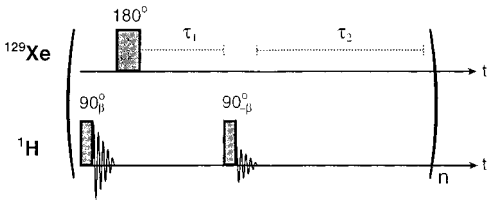


Figure 4. (a) ^{1}H NMR spectrum of the Aerosil sample using the difference SPINOE pulse sequence (Scheme 1) with the laser-light "on". (b) Application of the same sequence as in part a but with laser-light cut "off", i.e., without SPINOE. (c) Spectrum at thermal equilibrium after eight scans.

Scheme 1



The polarization inversion experiment is the key element in developing a difference surface SPINOE since only those protons cross-relaxed by the surface xenon atoms experience a polarization change with the xenon 180° pulse. The following pulse sequence was therefore applied during continuous-flow conditions.

After a 90°$_\beta$(H) pulse and subsequent signal acquisition, we applied a 180°(Xe) pulse to invert the spin polarization of the Xe surface layer and waited 10 s (τ_1) to allow the "positive" SPINOE to build up. The second 90°$_{-\beta}$ (H) pulse subtracted the reduced SPINOE spectrum from the first FID, thereby canceling the bulk proton signal. The result after eight scans is displayed in Figure 4a using a recovery time τ_2 of 60 s. Applying the same sequence without laser irradiation yielded a spectrum (Figure 4b) in which the difference SPINOE is absent. In contrast to the difference SPINOE spectrum, the proton signal at thermal equilibrium (Figure 4c) additionally showed a broad background.

The results of our experiments demonstrate that under continuous-flow conditions a steady-state laser-polarized Xe layer can be exploited for surface-sensitive NMR detection. The surface SPINOE experiments do not require isotopically enriched Xe and, given a recirculating gas system, can be conducted over long periods of time, thereby affording steady state enhanced sensitivity. A further characteristic of the present approach is the possibility of directly polarizing dilute heteronuclei on surfaces using long contact times, in the range of thousands of seconds, with laser-polarized xenon. Besides polarization transfer experiments, this technique should also facilitate the direct observation of Xe to probe porosity[8] of materials and catalyst activity.[9]

Acknowledgment. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Science, Materials Science Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. M.H. thanks the Studienstiftung des Deutschen Volkes and the BASF Co. for a postdoc fellowship. R.S. acknowledges support from the Swiss National Science Foundation. We thank T. Lawhead for his expert glassblowing.

JA9713587

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