

## Optical Pumping and Magic Angle Spinning: Sensitivity and Resolution Enhancement for Surface NMR Obtained with Laser-Polarized Xenon

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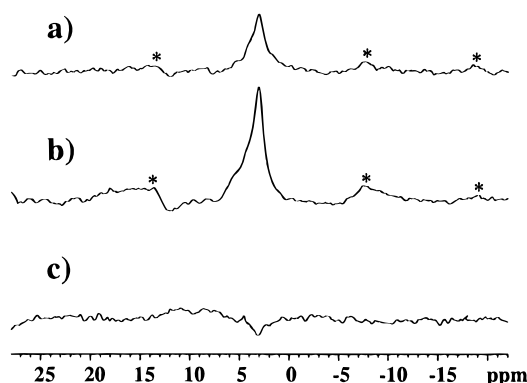
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Enhancement in sensitivity and resolution is a recurring theme in the field of nuclear magnetic resonance (NMR) spectroscopy. The advent of optical pumping methods, as pioneered by Happer and co-workers, has shown a dramatic enhancement in the nuclear spin polarizations, and therefore the NMR signals, of noble gases over equilibrium values.<sup>1</sup> These methods have found applications in a number of areas ranging from atomic physics<sup>2,3</sup> to medical imaging<sup>4,5</sup> and materials science.<sup>6–14</sup> One promising area is the selective enhancement of surface species that can be created by adsorbing the highly polarized gas onto a surface and transferring the polarization. Eventual goals of this research are to detect minority surface species and to differentiate surface nuclei from the bulk. To date, studies in this area have been limited to static samples<sup>7,9,10,14</sup> where the resolution is not optimal.

In this communication, we describe experiments in which we combine optical pumping methods with magic angle spinning (MAS) solid-state NMR. The large, nonequilibrium spin magnetization of laser-polarized <sup>129</sup>Xe is transferred to surface species under MAS conditions. As an example of this methodology, we have enhanced the <sup>1</sup>H MAS NMR signals from the surface of fumed silica, such that highly resolved chemical shift information can be obtained. This method, which we denote OPMAS (Optical Pumping and Magic Angle Spinning), should expand the utility of laser-polarization enhancement for solid-state NMR studies of surfaces where sensitivity and resolution are both at a premium.

Laser-polarized <sup>129</sup>Xe is produced by spin exchange with optically pumped Rb vapor in a continuous flow apparatus similar to one described by Driehuys *et al.*<sup>15</sup> A semiconductor diode array laser (Opto Power Corporation, Tucson, AZ) provides approximately 50 W of circularly polarized light



**Figure 1.** A comparison of the <sup>1</sup>H MAS NMR spectra demonstrating spin polarization transfer from xenon to surface protons. The following xenon polarizations were used: (a) unpolarized xenon (laser light blocked), (b) polarized xenon, and (c) polarized xenon with light helicity reversed ( $\lambda/4$  plate rotated by 90°). In all three spectra, identical flow rates of the gas mixture were used. Each spectrum is the result of 19 signal accumulations, using 90° rf pulses with a recycle delay time of 3 s. Asterisks indicate spinning sidebands. All spectra were acquired with a Varian Unity-Plus spectrometer operating at 300 MHz for protons.

centered at 795 nm with a line width of 4 nm. We use a mixture of 1% xenon (26% <sup>129</sup>Xe), 1% nitrogen, and 98% helium gas at 6 atm and a flow rate of approximately 200 cm<sup>3</sup>/min. A stopcock located after the pumping cell is used to regulate the flow and to drop the pressure to 1 atm at the sample region. The gas mixture is introduced into the spinning sample via a hole in the sample rotor cap with use of a capillary tube as described by Hunger and Horvath in their work on catalytic reactions under flowing conditions.<sup>16</sup> Typical xenon polarizations are 1 to 2%. A more detailed description of the apparatus will be published later.

A comparison of the normal and enhanced proton spectra is shown in Figure 1 for an untreated 10-mg sample of fumed silica (BET surface area 420 m<sup>2</sup>/g, Aldrich) at approximately 150 K in the presence of the flowing gas mixture, using normal and laser-polarized xenon. The <sup>1</sup>H MAS spectrum (Figure 1a) shows an isotropic peak at 3.1 ppm (referenced to TMS) with a line width of approximately 450 Hz, along with two spinning sidebands that result either from residual dipolar coupling or from chemical shift anisotropy.<sup>17</sup> The signal is attributed to adsorbed water on the silica surface.<sup>18</sup> In Figure 1b, the observed proton spectrum is enhanced due to dipole–dipole interactions between the protons and adsorbed, laser-polarized xenon. A 2-fold increase over that of the nonenhanced spectrum (Figure 1a) is obtained, with the spinning sidebands similarly enhanced. This transfer of spin polarization has been termed SPINOE (Spin Polarization-Induced Nuclear Overhauser Effect).<sup>19</sup> The enhancement is negative when the xenon spin polarization is inverted by reversing the helicity of the circularly polarized laser light (Figure 1c).

Figure 2 shows the solid-state MAS NMR signal of adsorbed <sup>129</sup>Xe on the silica surface. At 150 K, xenon condenses readily, forming a steady-state quantity under continuous flow conditions. The spectrum shows a gas peak, which we reference as 0 ppm, and an adsorbed peak at 144 ppm, along with two spinning sidebands. <sup>1</sup>H decoupling did not change the observed spectrum. No solid xenon was observed at this temperature.

We can describe the dynamics of spin magnetization between two coupled spin systems using a modified version of the

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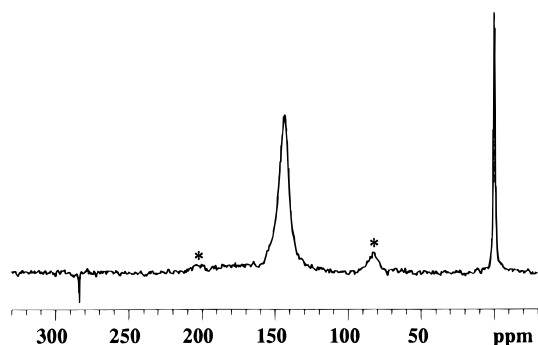
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**Figure 2.**  $^{129}\text{Xe}$  MAS NMR spectrum of laser-polarized xenon on the surface of fumed silica at 150 K. The spinning speed was 5 kHz. Gas phase (0 ppm) and surface adsorbed xenon (144 ppm) are observed, along with two spinning sidebands denoted by asterisks.

Solomon equations:<sup>20,21</sup>

$$\frac{dI_z}{dt} = -\rho_I(I_z - I_o) - \sigma_{IS}(S_z - S_o) \quad (1)$$

$$\frac{dS_z}{dt} = -\rho_S(S_z - S_o) - \sigma_{SI}(I_z - I_o) + \rho_S^{\text{in}}(S_z^g - S_o) - \rho_S^{\text{out}}(S_z - S_o) \quad (2)$$

Here,  $\rho_I$  and  $\rho_S$  are the relaxation rates of the proton spins  $I$ , and xenon spins  $S$ , respectively at the surface.  $\sigma$  denotes the cross relaxation between the two spin systems, which gives rise to the Nuclear Overhauser Effect. Equation 2 has been modified for our open system to include a feeding term  $\rho_S^{\text{in}}(S_z^g - S_o)$ , which describes the additional xenon magnetization that is delivered to the sample via the continuous flow of xenon with a nonequilibrium magnetization given by  $S_z^g$ , and an additional loss term,  $\rho_S^{\text{out}}(S_z - S_o)$ , which denotes the loss rate of magnetization due to xenon efflux. At steady state,  $\rho_S^{\text{in}} = \rho_S^{\text{out}} = \rho_S^{\text{flow}}$ , where  $\rho_S^{\text{flow}}$  is the replenishment rate of  $^{129}\text{Xe}$  atoms, relative to the number of xenon on the silica sample surface. We assume that adsorption and desorption processes are fast compared to the flow rate.

At steady state, the left-hand sides of eqs 1 and 2 are each equal to zero. Equation 1 can be rewritten in terms of the Boltzmann spin magnetization in the high-temperature approximation;  $S_o \approx S(S+1)\gamma_S\hbar B_o/(3kT)$  and  $I_o \approx I(I+1)\gamma_I\hbar B_o/(3kT)$ , such that

$$\frac{I_z - I_o}{I_o} = \frac{-\sigma_{IS} \gamma_S S(S+1) S_z - S_o}{\rho_I \gamma_I I(I+1) S_o} \quad (3)$$

Using eq 2 and the high-temperature approximation, one can write an expression for the surface xenon polarization enhancement:

$$\frac{S_z - S_o}{S_o} = \frac{\sigma_{SI} \gamma_I I(I+1) (I_z - I_o)}{\rho_S + \rho_S^{\text{flow}} \gamma_S S(S+1) I_o} + \frac{\rho_S^{\text{flow}} (S_z^g - S_o)}{\rho_S + \rho_S^{\text{flow}} S_o} \quad (4)$$

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and combining eqs 3 and 4 to eliminate  $(S_z - S_o)/S_o$  results in an expression that describes the proton polarization enhancement in terms of the relaxation and  $(S_z^g - S_o)/S_o$ :

$$\frac{I_z - I_o}{I_o} = \frac{\frac{-\sigma_{IS} \rho_S^{\text{flow}} \gamma_S S(S+1) (S_z^g - S_o)}{\rho_I \rho_S + \rho_S^{\text{flow}} \gamma_I I(I+1)} S_o}{1 - \frac{\sigma_{IS} \sigma_{SI}}{\rho_I (\rho_S + \rho_S^{\text{flow}})}} \quad (5)$$

In our experiments, we measure all quantities except for the cross relaxation rates  $\sigma_{IS}$  and  $\sigma_{SI}$ , which are related to each other by  $\sigma_{IS} = \{I(I+1)N_S\}/\{S(S+1)N_I\}\sigma_{SI}$ , where  $N_S$  and  $N_I$  are the number of surface  $^{129}\text{Xe}$  and  $^1\text{H}$  spins, respectively. A measurement of the apparent  $T_1$  of xenon on the surface yielded a value of 16 s. Using the following measured values,  $N_S = 6 \times 10^{17}$  (determined from xenon BET isotherms),  $N_I = 4 \times 10^{18}$  (determined by external calibration with a  $^1\text{H}$  standard),  $\rho_I = 0.23 \text{ s}^{-1}$ ,  $\rho_S = 0.062 \text{ s}^{-1}$ ,  $\rho_S^{\text{flow}} = 2.0 \times 10^{17} \text{ }^{129}\text{Xe s}^{-1}/N_S = 0.33 \text{ s}^{-1}$ ,  $S_z^g/S_o = 1250$ , and  $(I_z - I_o)/I_o = 2$ ,<sup>22</sup> we calculate  $\sigma_{IS} = 2 \times 10^{-3} \text{ s}^{-1}$ .

The observed  $^1\text{H}$  enhancement corresponds to approximately  $2 \times 10^{14}$  proton spins polarized by the xenon in the 3 s period between signal acquisitions. Since we polarize  $9 \times 10^{15}$  xenon atoms every 3 s, this corresponds to a transfer efficiency of approximately 2% per atom. We expect the transfer efficiency to be quite dependent on the surface species as well as experimental parameters such as temperature.

The theoretical maximum value for  $\sigma_{IS}$  in the motionally narrowed regime is given by  $\rho_S^I N_S/2N_I$ , where  $\rho_S^I$  is the relaxation of xenon due solely to coupling with the surface protons. This expression yields a value of  $5 \times 10^{-3} \text{ s}^{-1}$  for  $\sigma_{IS}$  assuming  $\rho_S^I \approx \rho_S$ . It is likely that  $\rho_S$  contains contributions from other relaxation mechanisms, such as spin-rotation relaxation, CSA induced relaxation, and paramagnetic relaxation.

In summary, we have shown that optically pumped  $^{129}\text{Xe}$  can be used to enhance surface proton spins under high-resolution solid-state MAS NMR conditions. Although the enhancement factor is modest for a high surface area material such as fumed silica, the observed signals represent an increase of signal that corresponds to  $4 \times 10^{18}$  spins (at equilibrium polarization), which could constitute a significant fraction of the surface species on a material with a smaller surface area. Optimizing the optical pumping setup as well as the polarization transfer step should increase the enhancements significantly. Continuing work in this area will ensure applications of OPMAS to surface studies, some of which are currently underway in our laboratory.

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(22) Using our experimental parameters (90° pulses every 3 s), we actually observed  $(I_z - I_o)/I_o = 1.0$  (see Figure 1). Numerical integration of the modified Solomon eqs 1 and 2 yields a value of  $2 \times 10^{-3}$  for  $\sigma_{IS}$ . Using small tipping pulses, where a steady-state approximation is strictly valid, would give an enhancement factor of 2, although the signal-to-noise ratios would suffer.