

# Surface NMR Using Laser-Polarized $^{129}\text{Xe}$ under Magic Angle Spinning Conditions

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**NMR signals of surface nuclei of solids may be enhanced by the transfer of spin polarization from laser-polarized noble gases. Until now such experiments have not been feasible under conditions of magic angle spinning. In the present contribution it is shown that laser-polarized  $^{129}\text{Xe}$  can be inserted into a spinning rotor under continuous-flow conditions using helium as a carrier gas. Effective adsorption of xenon on the sample occurs at temperatures of about 163–173 K making possible the observation of a spin polarization induced nuclear Overhauser effect (SPINOE) from the laser-polarized  $^{129}\text{Xe}$  to surface  $^1\text{H}$  nuclei of  $\text{SiO}_2$  (AEROSIL300). This technique opens the way to selectively enhanced high-resolution multinuclear surface NMR experiments.** © 1998 Academic Press

**Key Words:** laser-polarized  $^{129}\text{Xe}$ ; nuclear magnetic resonance; magic angle spinning; solid surfaces; spin polarization induced nuclear Overhauser effect.

## INTRODUCTION

Nuclear magnetic resonance (NMR) is among the most important analytical techniques in numerous fields including clinical imaging, biological research, analytical chemistry, and surface science. However, a serious limitation of NMR is its low sensitivity caused by the relatively low equilibrium nuclear spin polarization in standard experiments. Increasing interest has therefore developed in the enhancement of NMR using laser-polarized noble gas nuclei such as  $^3\text{He}$  or  $^{129}\text{Xe}$  (1–7). Navon *et al.* (5) have demonstrated that spin polarization can be transferred from laser-polarized noble gas nuclei to other nuclei, e.g., protons, via the so-called spin polarization induced nuclear Overhauser effect (SPINOE), provided there is a direct magnetic dipole interaction between the  $^{129}\text{Xe}$  spins and the nuclei to be polarized. Indeed, the  $^1\text{H}$  NMR signals of surface hydroxyl groups of  $\text{SiO}_2$  could be enhanced considerably by SPINOE from laser-polarized  $^{129}\text{Xe}$  (6), which can also be accomplished under the conditions of a continuous flow of laser-polarized  $^{129}\text{Xe}$  through the sample (7). When laser-polarized  $^{129}\text{Xe}$  atoms flow continuously through a sample containing nuclei with

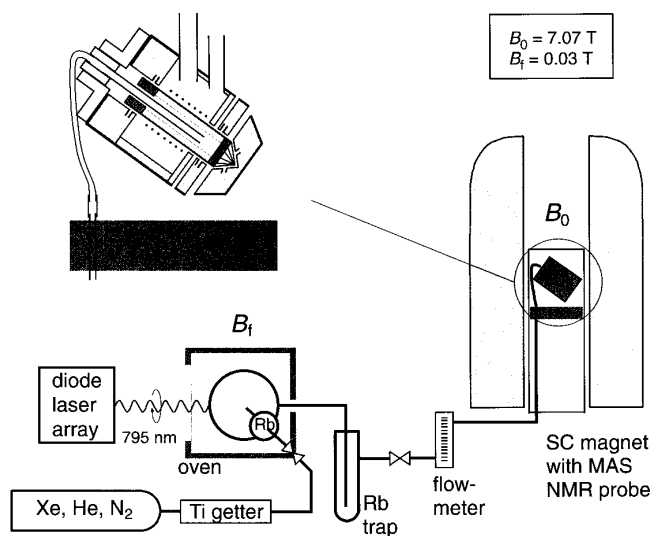
a spin  $I$ , the macroscopic magnetization  $M_I$  of the spins  $I$  may deviate from its equilibrium value  $M_I^0$ . According to the well-known Solomon equations (8),  $M_I$  approaches an equilibrium value  $\langle M_I \rangle$  given by

$$\langle M_I \rangle = M_I^0 - \frac{\sigma_{IS}}{\rho_I} \left( \langle M_S \rangle - M_S^0 \right), \quad [1]$$

where  $S$  denotes the  $^{129}\text{Xe}$  spin,  $\langle M_S \rangle$  denotes the steady-state polarization of the  $^{129}\text{Xe}$  atoms adsorbed on the sample,  $M_S^0$  is the equilibrium spin polarization of  $^{129}\text{Xe}$ ,  $\sigma_{IS}$  denotes the cross relaxation rate, and  $\rho_I$  the longitudinal relaxation rate of the  $I$  spins. The expected behavior was in fact observed for the SPINOE from laser-polarized  $^{129}\text{Xe}$  to surface  $^1\text{H}$  nuclei (7). A useful extension of this approach includes a methodology for extracting high resolution spectral information under conditions that yield surface-enhanced NMR signals. The aim of the present contribution is to show that it is possible (i) to inject laser-polarized  $^{129}\text{Xe}$  into a spinning rotor and (ii) to observe a spin polarization transfer to surface nuclei in magic angle spinning (MAS) (9) experiments under conditions of continuous xenon flow, i.e., to obtain a steady-state nonequilibrium surface spin polarization.

## EXPERIMENTAL

A schematic diagram of the experimental setup is shown in Fig. 1. It consists mainly of (i) a homebuilt apparatus similar to that designed by Driehuys *et al.* (10) providing a continuously flowing gas stream carrying the Xe gas, and (ii) a homebuilt double resonance probe (Doty design (11)) equipped with a commercial variable-temperature magic angle spinning unit (Chemagnetics, Pencil rotor with 7.5 mm outer diameter). The gas mixture containing 10% Xe (natural isotopic distribution so that only 2.6% of the gas mixture is  $^{129}\text{Xe}$ ), 1.5%  $\text{N}_2$ , and 88.5% He is compressed to an initial pressure of about 800 kPa in a gas tank. The



**FIG. 1.** Schematic depiction of the experimental setup.  $B_0$  denotes the magnetic field of 7.07 T at the site of the sample and  $B_f$  is the fringe field of about 0.03 T at the site of the pump cell. Rb denotes the rubidium metal contained in a glass bulb directly connected to the pump cell. The Rb trap is filled with a mixture of ice and water maintaining the trap at a temperature of 273 K.

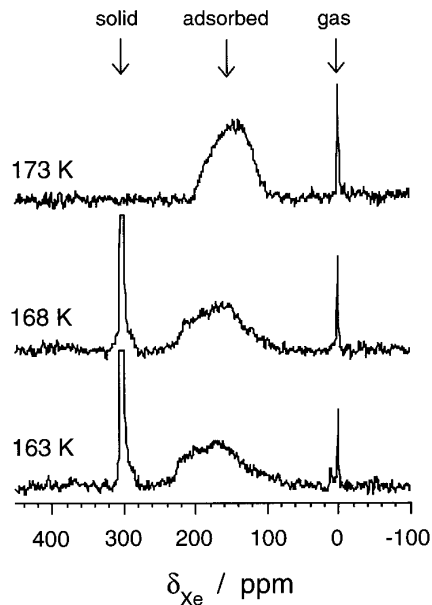
gas stream leaving the tank flows through a tube containing titanium powder heated up to about 423 K (Ti getter) in order to oxidize any spurious oxygen before entering the heated pump cell (about 465 K) containing a small amount of rubidium metal. The Rb atoms are optically pumped at the wavelength of the Rb  $D_1$  transition (794.8 nm) with circularly polarized light from a diode laser (Optopower Corp., Model OPC-A150-795-RPCZ) delivering about 90 W light power at wavelengths of  $795 \pm 1$  nm. After passing the pump cell the gas is expanded to normal pressure and inserted into the probe via copper and Teflon tubing connected to a glass capillary directed into the spinning rotor. This arrangement is similar to that used for continuous-flow NMR investigations of chemical reactions (12, 13). The spin polarization of  $^{129}\text{Xe}$  was measured to be about 0.7% with the gas in the rotor, about three orders of magnitude higher than the equilibrium spin polarization at 293 K.

The sample (fumed silica AEROSIL300, Degussa (14)) was chosen as a suitable model compound for which the SPINOE was already studied under static (i.e., nonspinning) conditions (6, 7). After activation at 473 K in high vacuum the sample was filled into the rotor in a glove box under nitrogen atmosphere. The filled rotor was inserted into the probe and purged with the gas mixture during the entire duration of the experiment. Furthermore, the sample was heated initially up to about 373 K in order to remove water or oxygen which may have been adsorbed during the insertion of the rotor into the probe. After this procedure the sample was cooled down to the desired measurement temperature between 213 and 163 K. The temperature inside the

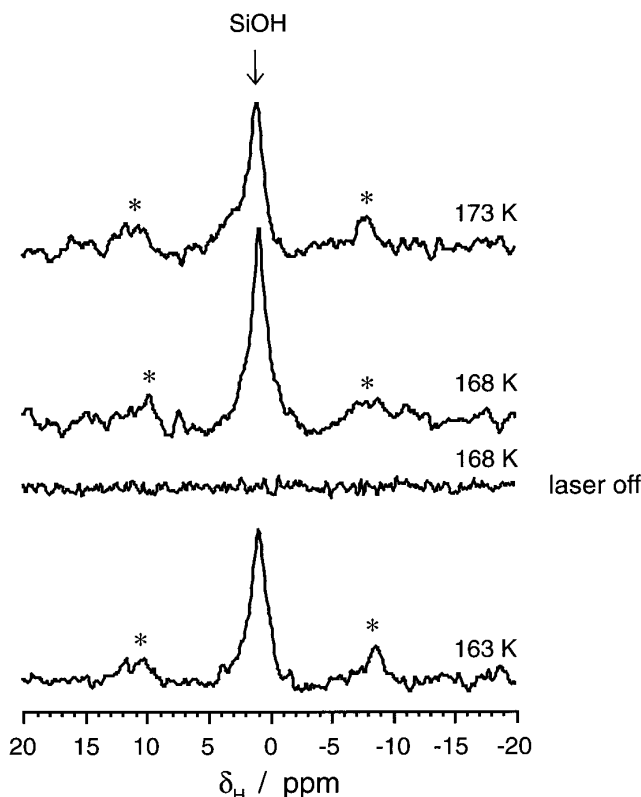
rotor was calibrated by  $^{207}\text{Pb}$  NMR spectroscopy making use of the temperature dependence of the chemical shift of  $\text{Pb}(\text{NO}_3)_2$  (15, 16). The spatial temperature variation within the rotor was less than 10 K.

## RESULTS AND DISCUSSION

Effective adsorption of laser-polarized  $^{129}\text{Xe}$  atoms on the sample under study is a necessary condition for the observation of spin polarization transfer via SPINOE. Figure 2 shows the  $^{129}\text{Xe}$  MAS NMR spectra of laser-polarized  $^{129}\text{Xe}$  adsorbed on AEROSIL300 under continuous-flow conditions measured at sample temperatures of 163–173 K where the maximum amount of adsorbed xenon is observed. At 173 K the spectrum exhibits a narrow signal at 0 ppm due to a small amount of gaseous xenon and a broad signal at a mean chemical shift of about 150 ppm with a linewidth (full-width at half-maximum height) of about 70 ppm. The latter signal is known to be due to  $^{129}\text{Xe}$  adsorbed at the surface of the sample (7). The mean chemical shift of this signal increases up to about 170 ppm if the temperature is decreased to 168 K, and the linewidth then amounts to about 90 ppm. Quantitative analysis indicates a slight increase of about 10% of the intensity of the signal due to adsorbed  $^{129}\text{Xe}$  compared to the spectrum observed at 173 K. Furthermore, one observes a narrow signal at  $302 \pm 1$  ppm characteristic of solid  $^{129}\text{Xe}$ . It should be noted that the chemical shift of the latter



**FIG. 2.** Variable temperature  $^{129}\text{Xe}$  MAS NMR spectra of laser-polarized  $^{129}\text{Xe}$  adsorbed on  $\text{SiO}_2$  (AEROSIL300). The spectra were acquired at a resonance frequency of 83.3 MHz with a sample spinning rate of about 3 kHz (four scans with a repetition time of 10 s). The flip angle of the excitation pulse was  $45^\circ$ . (Note that the sharp signals at 302 ppm due to solid  $^{129}\text{Xe}$  are cutted.)



**FIG. 3.** Variable temperature  $^1\text{H}$  MAS NMR difference spectra of  $\text{SiO}_2$  (AEROSIL300) acquired at a resonance frequency of 301.2 MHz and a sample spinning rate of about 3 kHz (four scans with a repetition time of 10 s). The flip angle of the excitation pulse was  $30^\circ$ . The spectra shown in this figure are the difference between the spectrum obtained if the  $^{129}\text{Xe}$  flowing into the rotor is laser-polarized (laser on) and the spectrum obtained if  $^{129}\text{Xe}$  is not laser-polarized (laser off). These spectra therefore quantitatively represent the observed SPINOE intensities (for  $T = 168$  K the figure also shows the difference between two spectra subsequently measured when the laser was turned off). \* denotes spinning sidebands.

signal increases with decreasing temperature (17). A chemical shift of  $316.4 \pm 1$  ppm could be observed for solid xenon at a temperature of 77 K (18). At a temperature of 163 K the intensity of the broad signal due to adsorbed xenon drops down to about 80% of the value observed at 168 K and the intensity of the signal at 302 ppm due to solid  $^{129}\text{Xe}$  increases. Advantageous conditions for spin polarization transfer are therefore expected at about 168 K. Other subtleties regarding these  $^{129}\text{Xe}$  MAS NMR spectra, such as the asymmetry in the lineshape centered at about 170 ppm, and the appearance of an additional peak near 0 ppm, will be addressed in a later publication.

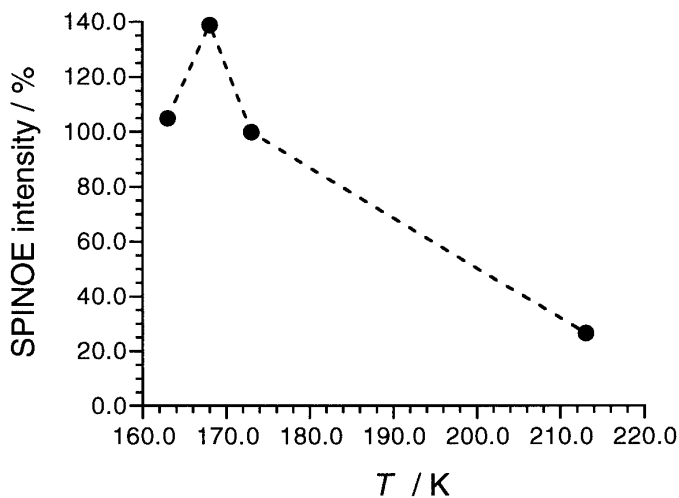
$^1\text{H}$  MAS NMR investigations were carried out in order to show that spin polarization is transferred via SPINOE from the highly spin polarized adsorbed  $^{129}\text{Xe}$  to the surface of the sample. The room-temperature  $^1\text{H}$  MAS NMR spectrum of the sample investigated here (AEROSIL300) exhibits a single signal at about  $1.5 \pm 0.2$  ppm which can be assigned

to isolated (i.e., nonhydrogen bonded) SiOH groups at the surface of  $\text{SiO}_2$  (19–21). At low temperatures (163–173 K) the signal is shifted to a position of about  $1.1 \pm 0.2$  ppm. A possible explanation of this temperature-dependent shift is the presence of paramagnetic sites. Figure 3 shows  $^1\text{H}$  MAS NMR spectra measured as the difference between the spectrum obtained when the  $^{129}\text{Xe}$  flowing into the rotor is laser-polarized (i.e., when the laser is switched on) and the spectrum obtained when the  $^{129}\text{Xe}$  only exhibits its equilibrium polarization (i.e., when the laser is switched off). Signals observed in these difference spectra therefore represent a spin polarization transfer via SPINOE. The result of the quantitative analysis of these difference spectra is shown in Fig. 4. As a measure for the strength of the SPINOE we have defined a SPINOE intensity according to the equation

$$\text{SPINOE intensity} = \left( \frac{I_{\text{on}}}{I_{\text{off}}} - 1 \right) 100\%, \quad [2]$$

where  $I_{\text{on}}$  and  $I_{\text{off}}$  denote the intensities of the above-described  $^1\text{H}$  MAS NMR signal of SiOH groups observed when the laser was switched on and off, respectively. The highest SPINOE intensity of about 140% could be observed at 168 K, as anticipated. The efficiency of the spin polarization transfer strongly decreases with increasing temperature in agreement with earlier observations (6, 7).

The experiments described above demonstrated that spin polarization transfer experiments using laser-polarized  $^{129}\text{Xe}$  can be carried out under conditions of magic angle spinning. It is encouraging that the observed SPINOE intensities of up to 140% were obtained with a relatively low polarization of the  $^{129}\text{Xe}$  spins of about 0.7%. Since the SPINOE intensity is directly proportional to the  $^{129}\text{Xe}$  polarization, one goal



**FIG. 4.** SPINOE intensities observed for the  $^1\text{H}$  MAS NMR signal of SiOH groups in  $\text{SiO}_2$  (AEROSIL300) as a function of the temperature. The dashed lines are drawn to guide the eye.

of our future work will be the improvement of the optical pumping apparatus; the use of isotopically enriched xenon gas will also lead to higher SPINOE intensities. The application of this technique to other surface nuclei with long longitudinal relaxation times, e.g.,  $^{13}\text{C}$  and  $^{29}\text{Si}$  is in progress. In these studies we anticipate much higher SPINOE intensities than for  $^1\text{H}$  nuclei (cf. Eq. [1]). Provided that the spectral resolution is sufficient, this new method also provides a tool for the distinction between nuclei accessible and nonaccessible to the xenon atoms since the direct magnetic dipole interaction between  $^{129}\text{Xe}$  and the nuclei is a necessary condition for the observation of the SPINOE.

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*Note Added in Proof.* After submission of the present article a paper that also deals with laser-polarized xenon in MAS experiments was published (D. Raftery, E. MacNamara, G. Fisher, C. V. Rice, and J. Smith, *J. Am. Chem. Soc.* **119**, 8746 (1997)).

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