

Cross Polarization and Cross Relaxation from Laser-Polarized Xenon to Surface Species

Ernesto MacNamara, Gregory Fisher, Jay Smith, Charles V. Rice, Son-Jong Hwang, and Daniel Raftery*

H.C. Brown Laboratory, Department of Chemistry, Purdue University, West Lafayette, Indiana 47907-1393

Received: October 14, 1998

The high polarization of optically pumped ^{129}Xe was transferred to surface carbon and silicon species under magic angle spinning (MAS) conditions to afford enhanced solid-state NMR of surfaces. High-resolution ^{29}Si MAS spectra of fumed silica and ^{13}C spectra of chemisorbed methanol on silica were obtained using a steady flow of hyperpolarized xenon adsorbed onto the surface at 135 K. Cross polarization to ^{29}Si from SPINOE enhanced hydroxyl protons and to ^{13}C from enhanced methyl protons is observed with good efficiency. A direct SPINOE transfer from ^{129}Xe to ^{13}C without cross polarization is observed to give the highest enhancement under these conditions.

Optical pumping represents one of the more promising methods for enhancing the sensitivity of NMR. Pioneering work by Happer and co-workers has led to the generation of hyperpolarized rare gases using optical pumping methods in which the angular momentum of circularly polarized light is transferred to rare gas nuclei via gas-phase spin exchange with Rb atoms.¹ The resulting non-Boltzmann nuclear spin polarizations, and consequently NMR signals, are typically 3–4 orders of magnitude larger than their thermal levels.² This tremendous gain in NMR sensitivity has made possible a number of experiments previously thought intractable. For example, laser-polarized Xe has been used as an inert surface probe to study low surface area materials^{2–11} and as a gas-phase imaging agent.^{12,13} We and others recently introduced a method which combines the enhanced sensitivity afforded by laser-polarized xenon with high-resolution solid-state NMR, a technique we have denoted OPMAS (optical pumping and magic angle spinning).^{14,15} In its current rendition, OPMAS makes use of an incoherent polarization transfer mechanism based on the nuclear Overhauser effect (SPINOE).¹⁶ SPINOE is advantageous in that it has relaxed requirements in terms of temperature necessary to effect xenon polarization transfer compared to other techniques including high-field Hartmann–Hahn cross-polarization (CP)³ and low-field mixing.^{4,17}

We describe below experiments which further improve the potential for using hyperpolarized xenon for surface NMR studies by observing SPINOE enhancements to x-nuclei (i.e., other than hydrogen) under MAS conditions. Recently, Pines and co-workers have obtained SPINOE enhancements of ^{29}Si and ^{13}C under static and MAS conditions.^{10,18,19} Among the advantages in observing x-nuclei are a larger chemical shift range, which is more sensitive to structure, and improved spectral resolution that results from the reduced value of the homonuclear dipolar coupling interaction. We show that the polarization transfer between xenon and the x-nucleus (carbon or silicon in our experiments) can occur in two ways. The high spin polarization of xenon may first enhance surface protons through a SPINOE interaction and subsequently the ^1H enhancement may be transferred to nearby x-nuclei via CP. Alternatively, we show that the x-nucleus may be enhanced

through SPINOE without the CP step and that this path can be very effective for polarization transfer. For our first experiments we have studied the SPINOE enhancement of ^{29}Si in dehydrated fumed silica, and of ^{13}C in methanol chemisorbed on fumed silica. Silica was chosen for these initial studies because of its wide applicability, high surface area, and well understood NMR parameters.²⁰

Our optical pumping apparatus is similar to one designed by Driehuys and co-workers to produce large quantities of laser-polarized Xe under continuous flow conditions.²¹ The pumping cell is situated on a laser table approximately 3 m from our high-field magnet. The field across the pumping cell, required for efficient optical pumping, is provided by the magnet's fringing field and is approximately 5 G. Our optical pumping source is a 100 W diode laser centered at 795 nm (OptoPower Corp., Tucson, AZ) operating at 21.6 A at a temperature of 290 K. The optical pumping gas mixture, consisting of 98% He, 1% N_2 , and 1% natural abundance Xe (26% ^{129}Xe), is introduced into the pumping cell at 6 atm. The optical pumping cell is heated to 383 K to vaporize sufficient quantities of Rb. A monochromator and CCD camera behind the pumping cell allow us to monitor the Rb absorption line. A Teflon needle valve located after the pumping cell drops the pressure to 1 atm and provides flow control. Typical flow rates are $200\text{ cm}^3\text{ min}^{-1}$. Glass tubing connects the pumping cell to the sample chamber in our modified commercial CP-MAS probe. We use a small glass injection tube to deliver the polarized gas mixture to the sample rotor.²² A Kel-F holder situated on top of the rotor housing supports the injection tube which fits into the rotor through a small hole drilled into the cap. All glass surfaces in contact with xenon were coated with Suprasil to minimize xenon polarization losses through wall induced relaxation. Typical xenon polarizations are 1–2%, as measured in high magnetic field.

Prior to preparation on a gas rack, samples were loaded in the rotor and "spun-out" to ensure cylindrical sample packing and to allow room for the injection tube. The rotor was then inserted into a glass tube and connected to a gas rack for sample preparation. Sample preparation for the fumed silica sample (Aldrich, specific surface area $389\text{ m}^2/\text{g}$) involved heating to 413 K for 4 h under vacuum (10^{-5} Torr). The chemisorbed

* To whom correspondence should be addressed.

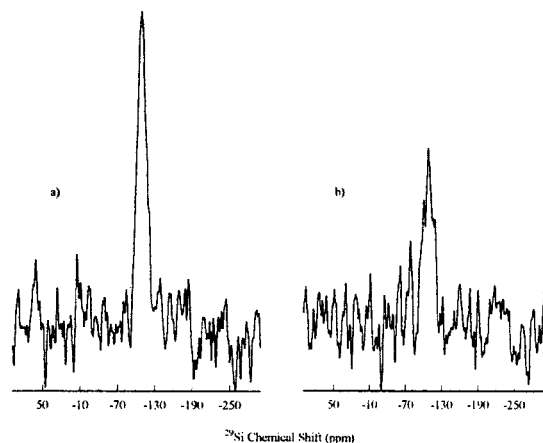


Figure 1. ^{29}Si SPINOE-CP spectra acquired at 59.6 MHz on a Varian UnityPlus 300 spectrometer. The MAS spectra were acquired at 135 K and a spinning speed of 3 kHz using a ^1H – ^{29}Si CP pulse sequence. Each spectrum is the result of 100 scans with a 32 s recycle delay time. The contact time was 2.5 ms. (a) SPINOE-CP using σ^+ pumping light; (b) SPINOE-CP using σ^- light.

methanol samples were prepared by similarly dehydrating the silica surface and loading 0.23 mmol of $^{13}\text{CH}_3\text{OH}$ (Cambridge Isotopes), heating at 673 K for 3 h, and then evacuating to 1×10^{-4} Torr.²³ After the rotor had been transferred to the MAS probe and connected to the optical pumping apparatus, a flow of dry N_2 was initiated while the sample was warmed to 320 K to remove any water which had adsorbed during the setup procedure. ^1H MAS NMR spectra were used to monitor the desorption of water. Probe temperatures were calibrated with $\text{Pb}(\text{NO}_3)_2$.²⁴

Under continuous flowing conditions at 135 K, Xe forms a steady-state surface adsorbed layer comprised of 6×10^{17} atoms on the 10 mg silica sample (calculated from BET isotherm data). The surface adsorbed Xe peak on silica is located at 167 ppm (referenced to the room-temperature Xe gas-phase peak) and has a line width of 31 ppm, whereas on the methanol sample the surface peak occurs at 142 ppm with a line width of 15 ppm. The line shapes for both samples are asymmetric indicating a heterogeneous distribution of surface adsorption sites. At this temperature and low xenon partial pressures we do not observe solid Xe.

Figure 1 shows ^{129}Xe – ^1H – ^{29}Si SPINOE-CP spectra for the silica sample using left (denoted σ^+) and right (σ^-) circularly polarized light. The surface Si peak is at -105 ppm relative to TMS and its line width is 17 ppm. The σ^+ spectrum is approximately 38% larger than the σ^- , and we therefore estimate a SPINOE enhancement factor ($S_+ - S_- / S_+ + S_-$) to be approximately 16%. Here, S_+ and S_- represent the integrated signals for the σ^+ and σ^- experiments, respectively. In separate experiments, we measured the ^1H enhancement to be 27%, although a higher value (100%) was observed previously under more hydrated conditions.¹⁴ Therefore, the majority of the initial ^{129}Xe – ^1H SPINOE enhancement was transferred to ^{29}Si during the CP step. These Si SPINOE-CP experiments were acquired with prolonged signal averaging which is only possible when Xe is continuously flowing across the sample, and are in contrast to many previous laser-polarized Xe experiments which were conducted under one-shot batch conditions.

OPMAS experiments were also conducted to transfer the enhanced Xe polarization to ^{13}C in chemisorbed methanol. The number of methanol molecules was approximately 10^{19} , calculated using an external ^{13}C sample, which constitutes nearly a monolayer surface coverage on the 10 mg of silica used. In

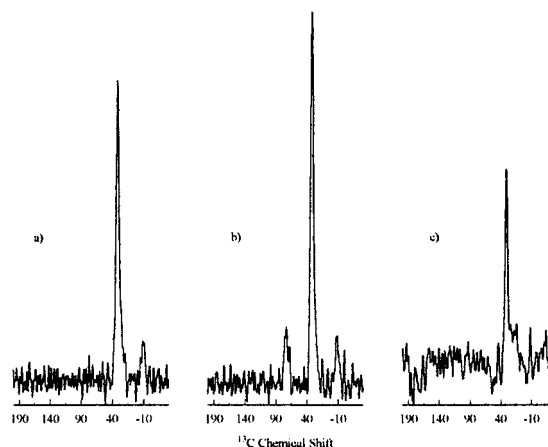


Figure 2. ^{13}C SPINOE Bloch decay spectra: (a) control SPINOE using linearly polarized pumping light; (b) SPINOE using σ^+ light; (c) SPINOE using σ^- light.

contrast to the ^{29}Si experiments, the enhancement factor for ^{13}C SPINOE-CP (not shown) was only 7.6% relative to the control CP signal, whereas it was 21% for the SPINOE transfer to the methyl protons. The lower transfer efficiency may be due to polarization losses during CP via $T_{1\rho}$ relaxation, and more detailed investigations will be reported in a future publication.

Alternatively, the Xe polarization can be transferred to ^{13}C without the ^1H – ^{13}C CP step. Figure 2 shows the control ^{13}C Bloch decay (BD) spectrum (a), and ^{13}C direct SPINOE BD spectra using σ^+ (b) and σ^- (c) light for the chemisorbed methanol sample at 135 K. The methanol carbon peak appears at 25 ppm relative to TMS with a line width of 4 ppm. Two spinning sidebands can also be observed. The ^{13}C direct SPINOE enhancement is 30% compared to the control BD signal, and is larger than the ^1H SPINOE in the same sample. The observed ^{13}C enhancement corresponds to 3×10^{18} ^{13}C spins at Boltzmann polarization levels, or 7×10^{13} polarized spins. The number of polarized ^{129}Xe atoms delivered to the sample during a single acquisition period is 1.5×10^{16} , making the transfer efficiency to ^{13}C equal to 0.5% per Xe atom. As described above, the ^1H SPINOE enhancement to methyl ^1H 's was 21%. The corresponding SPINOE transfer efficiency to ^1H was 4% per Xe. A calculation of the expected ^{129}Xe – $^{13}\text{C}/^{129}\text{Xe}$ – ^1H transfer efficiency ratio based on differences in the ^{129}Xe – ^1H and ^{129}Xe – ^{13}C dipolar couplings due to different distances and gyromagnetic ratios yields an extrapolated value of 0.02, whereas we measured 0.08. Although this simple calculation ignores dynamical aspects of the SPINOE transfer process, it nevertheless underlines our unanticipated results. One possible explanation is that the protons may act as intermediaries in a two-step polarization transfer. Recent experiments have shown it possible to measure and control the spin diffusion pathways in multistep NOE transfers in oligonucleotides,²⁵ and such experiments should be useful to investigate the relaxation pathways in the present system.

In summary, we have shown the possibility of transferring a sizable fraction of the large, nonequilibrium xenon polarization generated by optical pumping to surface ^{13}C and ^{29}Si nuclei. The transfer process can occur in two ways, via CP from SPINOE-enhanced ^1H or more simply without using the CP step. We expect that with advances in optical pumping methods and improvements in the transfer efficiency, significant surface enhancements may be realized and would therefore be able to provide useful surface information on a variety of surface systems.

Acknowledgment. This research was supported by the National Science Foundation (CHE 95-31693) and the Research Corporation. E.M. thanks the NSF for a graduate fellowship. The authors thank Brian Saam and Mark Conradi for generously loaning the laser diode array used to carry out this research.

References and Notes

- (1) Walker, T. G.; Happer, W. *Rev. Mod. Phys.* **1997**, *69*, 629 and references therein.
- (2) Raftery, D.; Long, H.; Meersmann, T.; Grandinetti, P. J.; Reven, L.; Pines, A. *Phys. Rev. Lett.* **1991**, *66*, 584.
- (3) Long, H. W.; Gaede, H. C.; Shore, J.; Reven, L.; Bowers, C. R.; Kritzenberger, J.; Pietrass, T.; Pines, A. *J. Am. Chem. Soc.* **1993**, *115*, 8491.
- (4) Driehuys, B.; Cates, G. D.; Happer, W.; Mabuchi, H.; Saam, B.; Albert, M. S.; Wishnia, A. *Phys. Lett. A* **1993**, *184*, 88.
- (5) Raftery, D.; Reven, L.; Long, H.; Pines, A.; Tang, P.; Reimer, J. A. *J. Phys. Chem.* **1993**, *97*, 1649.
- (6) Bowers, C. R.; Pietrass, T.; Barash, E.; Pines, A.; Grubbs, R. K.; Alivisatos, A. P. *J. Chem. Phys.* **1994**, *98*, 9400.
- (7) Gaede, H. C.; Song, Y.-Q.; Taylor, R. E.; Munson, E. J.; Reimer, J. A.; Pines, A. *Appl. Magn. Reson.* **1995**, *8*, 373.
- (8) Song, Y.-Q.; Gaede, H. C.; Pietrass, T.; Barrall, G. A.; Chingas, G. C.; Ayers, M. R.; Pines, A. *J. Magn. Reson. A* **1995**, *115*, 127.
- (9) Pietrass, T.; Bifone, A.; Pines, A. *Surf. Sci.* **1995**, *334*, L730.
- (10) Room, T.; Appelt, S.; Seydoux, R.; Hahn, E. L.; Pines, A. *Phys. Rev. B* **1997**, *55*, 11604.
- (11) Haake, M.; Pines, A.; Reimer, J. A.; Seydoux, R. *J. Am. Chem. Soc.* **1997**, *119*, 11711.
- (12) Albert, M. S.; Cates, G. D.; Driehuys, B.; Happer, W.; Saam, B.; Springer Jr., C. S.; Wishnia, A. *Nature* **1994**, *370*, 199.
- (13) Middleton, H.; Black, R. D.; Saam, B.; Cates, G. D.; Cofer, G. P.; Guenther, R.; Happer, W.; Hedlund, L. W.; Johnson, G. A.; Juvan, K.; Swartz, J. *Magn. Reson. Med.* **1995**, *33*, 271.
- (14) Raftery, D.; MacNamara, E.; Fisher, G.; Rice, C. V.; Smith, J. J. *Am. Chem. Soc.* **1997**, *119*, 8746.
- (15) Brunner, E.; Seydoux, R.; Haake, M.; Pines, A.; Reimer, J. A. *J. Magn. Reson.* **1998**, *130*, 145.
- (16) Navon, G.; Song, Y.-Q.; Riim, T.; Appelt, S.; Taylor, R. E.; Pines, A. *Science* **1996**, *271*, 1848.
- (17) Bowers, C. R.; Long, H. W.; Pietrass, T.; Gaede, H. C.; Pines, A. *Chem. Phys. Lett.* **1993**, *205*, 168.
- (18) Pietrass, T.; Seydoux, R.; Pines, A. *J. Magn. Reson.* **1998**, *133*, 299.
- (19) Brunner, E.; Haake, M.; Pines, A.; Reimer, J. A.; Seydoux, R. *Chem. Phys. Lett.* **1998**, *290*, 112.
- (20) Liu, C. C.; Maciel, G. E. *J. Am. Chem. Soc.* **1996**, *118*, 5103.
- (21) Driehuys, B.; Cates, G. D.; Miron, E.; Sauer, K.; Walter, D. K.; Happer, W. *Appl. Phys. Lett.* **1996**, *69*, 1668.
- (22) Hunger, M.; Horvath, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1423.
- (23) Pelmentschikov, A. G.; Morosi, G.; Gamba, A.; Zecchina, A.; Bordiga, S.; Paukshtis, E. A. *J. Phys. Chem.* **1993**, *97*, 11979.
- (24) Bielecki, A.; Burum, D. P. *J. Magn. Reson. A* **1995**, *116*, 215.
- (25) Zwahlen, C.; Vincent, S. J. F.; Bari, L. D.; Levitt, M. H.; Bodenhausen, G. *J. Am. Chem. Soc.* **1994**, *116*, 362.