Surface Relaxation Mechanisms of Laser-Polarized ^{129}Xe

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We have determined the dominant mechanism for nuclear spin relaxation of laser-polarized ^{129}Xe in silicone coated cells. The ^{129}Xe relaxation rate is found to be strongly dependent on magnetic field, which indicates that ^{129}Xe becomes trapped in the coating for extraordinarily long times ($\tau > 10\ \mu$s). Relaxation is caused by dipolar coupling between the trapped ^{129}Xe and the protons in the coating, which we confirm with a novel double resonance scheme. This result should aid the development of improved coatings, and offers new possibilities for using laser-polarized ^{129}Xe as a probe of other polymer and biological systems.

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The number and variety of applications of noble gases, particularly ^{3}He and ^{129}Xe, polarized through spin-exchange optical pumping [1,2] have grown rapidly over the past few years. Most recently, the enhanced NMR signals of laser-polarized ^{129}Xe, which are about 5 orders of magnitude larger than those from thermally polarized ^{129}Xe, have made possible the first high-speed biological magnetic resonance imaging (MRI) of a gas [3], opening many new avenues of research. Historically, polarized ^{129}Xe has been used for fundamental symmetry studies [4], nuclear spin relaxation studies of solids [5], high resolution NMR spectroscopy [6], and cross polarization to other nuclei [5,7,8]. Polarized ^{3}He is an important nuclear target [9] and has also been shown to be an excellent nucleus for gas-phase MRI [10]. All these applications require that the highly nonequilibrium polarizations of the noble gas nuclei be long lived; i.e., the decay to thermal equilibrium must be slow. However, interactions of the polarized noble gas nuclei with surfaces can cause rapid relaxation, often resulting in relaxation times T_1 that are undesirably short. Understanding these mechanisms is vital for continued progress in a large variety of experiments using polarized noble gases.

Zeng and co-workers made substantial progress in reducing ^{129}Xe surface relaxation by introducing the use of the silicone coating SurfaSil [11,12]. Relaxation times of order $T_1 \sim 20$ min are routinely attained but are still some 2 orders of magnitude shorter than what is expected for gaseous ^{129}Xe at a density of 1 amagat [13]. The spin-rotation interaction $\gamma \mathbf{N} \cdot \mathbf{I}$ between the ^{129}Xe nuclear spin $\mathbf{I}$ and the molecular angular momentum $\mathbf{N}$ during ^{129}Xe-Xe collisions limits the gas-phase relaxation time to $T_1 = 56/\rho$ h amagat [14]. To achieve relaxation times approaching this gas-phase limit, a better understanding of the ^{129}Xe surface interactions is needed.

The experiments use several 1 cm^3 spherical Pyrex cells treated with the SurfaSil coating as described in [12]. The cells are attached to a glass manifold and connected to a vacuum system (base system pressure of $P = 1 \times 10^{-8}$ Torr). The manifold is baked out under vacuum at 150°C for 1–2 d. Each cell contains a few mg of Rb and is filled under liquid nitrogen with roughly 0.5 amagat of isotopically enriched Xe (72.9% ^{129}Xe) and 0.1 amagat of N$_2$, both purified by flowing through zirconium getters [15].

In order to measure the ^{129}Xe relaxation rates, the nuclei are first polarized to ~25% through optical pumping and spin exchange. A cell is placed in a 30 G magnetic field and is heated to 85°C, resulting in a Rb density $[\mathrm{Rb}] \approx 2 \times 10^{12}$ cm^{-3}. The Rb atoms are optically pumped with 2–4 W of circularly polarized 795 nm Rb D_1 light from a Ti:sapphire laser while polarization of the ^{129}Xe nuclei proceeds through Rb-Xe spin-exchange collisions [2,16]. After ~20 min the cell is removed from the pumping oven and cooled to room temperature. It is then placed in a cryostat (77–300 K) in a Helmholtz pair, variable in field from 0 to 2000 G. For the double resonance experiments the magnetic field is locked and stabilized near 97 G using an optically pumped ^{85}Rb magnetometer [17].

The ^{129}Xe polarization decay was monitored by adiabatic fast passage NMR (AFP) [18], which allows the magnetization to be detected with negligible loss of polarization. A field H_1, rotating at a frequency ω_0, is first applied perpendicular to the static field H_0. The static field is then swept slowly through the NMR resonance condition $\omega_0 = (7402\ \mathrm{s}^{-1}\,\mathrm{G}^{-1})H_0$, inverting the entire magnetization as the transverse component is detected with a tuned pickup coil and lock-in amplifier. The decay of the AFP signal height versus time is fit to an exponential to determine the longitudinal relaxation time T_1 or spin-locked relaxation time $T_{1\rho}$ [19]. Spin locking of the ^{129}Xe is achieved by stopping the field sweep exactly on resonance when the magnetization is aligned with H_1 in the frame rotating at ω_0.

Figure 1 shows the static magnetic field dependence of the ^{129}Xe relaxation rate from 0 to 100 G at temperatures ranging between 250 and 297 K. This magnetic field dependence provides a means to determine a limit on the surface dwell time of the ^{129}Xe atoms. During a surface dwell time τ_d the ^{129}Xe nuclear spin I can couple to a

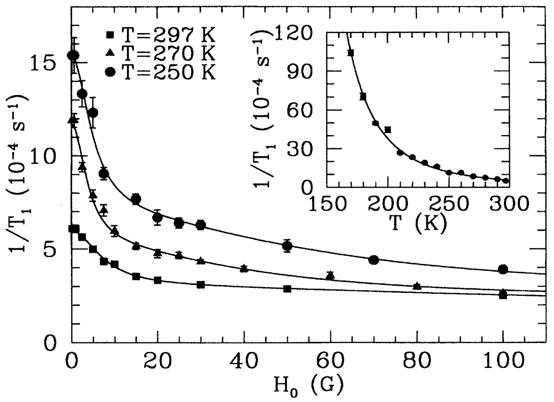

FIG. 1. Magnetic field dependence of the nuclear spin relaxation of polarized ^{129}Xe on the SurfaSil coating at $T = 297$, 270, and 250 K. The relaxation curves are fit to a sum of two expressions of the form of (1), with different correlation times, the longest of which is $\tau_c = 8.1 \pm 1.0$ μs. The inset shows the exponential temperature dependence of the ^{129}Xe relaxation rate at zero magnetic field, consistent with a Xe surface binding energy $E_s = -0.10 \pm 0.005$ eV.

neighboring nuclear or electronic spin S through dipolar interactions. The fields from the surface spins at the ^{129}Xe nucleus fluctuate randomly as a result of ^{129}Xe hopping from site to site, motion of the coating molecules, or spin-spin interactions between neighboring surface spins. We assume that such fluctuations can be characterized by correlation functions $\langle H_s(t) H_s(t + \tau)\rangle = H_s^2 e^{(-|\tau|/\tau_c)}$, where τ_c is the characteristic time of the fluctuations [18]. The ^{129}Xe dipolar relaxation rate resulting from this time-dependent coupling depends on magnetic field [18]. Neglecting scalar contributions which may be important for relaxation due to paramagnetic sites, the rate is given by

$$\frac{1}{T_1} = \frac{1}{10T_0}\left(\frac{1}{1 + (\omega_{0I} - \omega_{0S})^2\tau_c^2} + \frac{3}{1 + \omega_{0I}^2\tau_c^2} + \frac{6}{1 + (\omega_{0I} + \omega_{0S})^2\tau_c^2}\right), \quad (1)$$

where $\omega_{0I} = \gamma_I H_0$ and $\omega_{0S} = \gamma_S H_0$ are the ^{129}Xe and surface spin Larmor frequencies, respectively, and $1/T_0$ is the ^{129}Xe relaxation rate at zero magnetic field

$$\frac{1}{T_0} = \frac{4}{3} f(T) S(S + 1)\gamma_I^2 \gamma_S^2 \hbar^2 \tau_c \sum_i r_i^{-6}. \quad (2)$$

Here, $f(T)$ is the fraction of ^{129}Xe atoms occupying sites on the coating, γ_I and γ_S are the gyromagnetic ratios of the ^{129}Xe and surface spin, and r_i are the distances from the ^{129}Xe to the neighboring spins. A fit of the field-dependent ^{129}Xe relaxation data in Fig. 1 by (1) will determine the correlation time τ_c of the fluctuations and provide a lower bound on the ^{129}Xe dwell time at a given site.

As is evident from (1), the correlation time obtained from the fit is dependent on the magnetic moment of the surface spin to which the ^{129}Xe nucleus is assumed to couple. For a paramagnetic site $\gamma_S \approx 2 \times 10^7$ s^{-1} G^{-1}, whereas for protons $\gamma_S \approx 2.7 \times 10^4$ s^{-1} G^{-1}. The 10^3 difference in precession frequency between electronic and nuclear spins results in a 10^3 difference in the correlation time obtained from the fit. Relaxation by electronic spins yields $\tau_c = 8$ ns, whereas for protons the necessary correlation time is $\tau_c = 8$ μs.

The temperature dependence of the ^{129}Xe relaxation rate yields further insight into the nature of the ^{129}Xe binding sites. As the temperature is lowered, the ^{129}Xe dwell time at a site should increase exponentially depending on its binding energy.

$$\tau_d = \tau_0 e^{-E_s/k_B T}, \quad (3)$$

where $\tau_0 \approx 10^{-12}$ s. The widths of the magnetic field dependence curves in Fig. 1 are independent of temperature, indicating that the correlation time is different from the ^{129}Xe site dwell time. This also demonstrates that $\tau_d > \tau_c$, since narrowing of the magnetic field dependence would be expected as the temperature is lowered if $\tau_d \leq \tau_c$. For ^{129}Xe relaxation due to electronic spins this means $\tau_d > 8$ ns, and for relaxation by the coating protons the required dwell time is $\tau_d > 8$ μ s.

The inset of Fig. 1 shows that the zero-field relaxation rate of the ^{129}Xe is exponentially dependent on temperature. This temperature dependence must result from the increasing fraction $f(T)$ of ^{129}Xe bound to the coating at lower temperatures. If the binding energy of a ^{129}Xe atom at a surface site is E_s and there are N_s such sites of volume V_s, the fraction of bound ^{129}Xe is roughly given by

$$f(T) = \frac{N_s V_s}{V} e^{-E_s/k_B T}, \quad (4)$$

where V is the total volume of the cell and we assume $N_s V_s \exp(-E_s/k_B T) \ll V$. A fit of the temperature dependence of the zero-field relaxation rate by (2) and (4) gives a ^{129}Xe binding energy $E_s = -0.10 \pm 0.01$ eV. However, using this binding energy in (3) to estimate the ^{129}Xe dwell time at a given site gives only $\tau_d \approx 50$ ps, 2 orders of magnitude shorter than the shortest possible dwell time $\tau_d = 8$ ns set by the field dependence of the ^{129}Xe relaxation rate. Thus, simple adsorption of the xenon on the coating surface cannot account for the long correlation times observed.

It appears that there must be some additional energy barrier E_b, which hinders the escape of a ^{129}Xe atom from a given site. For instance, it is possible that ^{129}Xe atoms become trapped at these sites by a mechanism akin to Xe clathrate formation [20]. Then, even the extremely long (>8 μs) trapping times necessary for ^{129}Xe relaxation by protons are conceivable. For 8 μs trapping times, an energy barrier of at least $E_b > kT \ln[(8\ \mu\text{s})/(1\ \text{ps})] \approx 0.4$ eV is needed.

We have proven that dipolar coupling of the magnetic moments of the coating protons and the ^{129}Xe nuclei is indeed the dominant cause of relaxation by observing a ^{129}Xe-proton double resonance signature at 297 K. As is typical of double resonance, this experiment requires spin locking the ^{129}Xe magnetization to a resonant rotating field H_{1I} while a separate field H_{1S} is applied to the protons [19]. Since the ^{129}Xe and proton Zeeman energies are quantized independently, the ^{129}Xe relaxation rate can be changed by manipulating only the proton spin system. A calculation of the rotating frame relaxation rate $1/T_{1\rho}$ of a spin I due to coupling to a spin S has been presented by O'Reilly, Peterson, and Tsang [21]. A minor modification of their analysis to include the effects of a second field H_{1S} gives the relaxation rate of the spin-locked ^{129}Xe magnetization under double resonance conditions:

$$\frac{1}{T_{1\rho}} = \frac{1}{10T_0}\left(\frac{1}{1+(\omega_{1I}+\omega_{1S})^2\tau_c^2} + \frac{1}{1+(\omega_{1I}-\omega_{1S})^2\tau_c^2} + \cdots\right), \quad (5)$$

where the $[\cdots]$ represent the 22 remaining terms which are dependent on the static field but are only weakly dependent on the resonant fields H_{1I} and H_{1S}.

Two methods can be considered for observing the ^{129}Xe-proton coupling. One is to spin lock the ^{129}Xe magnetization to a strong field H_{1I} such that $\omega_{1I}\tau_c \gg 1$ and then to observe increased relaxation when a second field H_{1S} is applied to the protons at the Hartmann-Hahn matching condition $\omega_{1I} = \omega_{1S}$. However, with $\tau_c = 8\ \mu$s this requires $H_{1I} \geq 17$ G, which is difficult to maintain for the necessary time scales. Instead, we have chosen to lock the ^{129}Xe to a small field $H_{1I} = 1.1$ G ($\omega_{1I}\tau_c \ll 1$) and to slow down the ^{129}Xe relaxation rate by increasing the strength of the resonant proton field H_{1S}. When H_{1S} is large enough to cause proton Rabi precession which is faster than the intrinsic frequency of the proton dipolar fluctuations ($\gamma_S H_{1S} > 1/\tau_c$), the ^{129}Xe relaxation rate is slowed down.

Because of the long ^{129}Xe relaxation times and relatively infrequent coupling between a given ^{129}Xe and coating protons, extremely long spin-locking times, of order 100 s or more, are required in order to observe the double resonance effect. Relaxation from inhomogeneities in both the static and spin-locking fields can contribute significantly to the ^{129}Xe relaxation rate, effects that were thoroughly investigated by Cates and co-workers [22]. The results of [22] can be simplified for our experimental conditions, giving an inhomogeneity contribution to the spin-locked ^{129}Xe relaxation rate of

$$\frac{1}{T'_{1\rho}} = D\left[\frac{|\nabla H_{0z}|^2}{H_{1I}^2} + \frac{|\nabla H_{1I}|^2}{H_{1I}^2}\right], \quad (6)$$

where D is the xenon diffusion coefficient, $|\nabla H_{0z}|$ is the $\hat{z}$ component of the static field inhomogeneity, and $|\nabla H_{1I}|$ is the inhomogeneity of the ^{129}Xe spin-locking field. Since $\nabla H_{1I} \propto H_{1I}$, the second term in (6) is independent of H_{1I} and dominates the relaxation rate for sufficiently large H_{1I}. At 97 G the static field inhomogeneity of our apparatus was $|\nabla H_{0z}| = 19.0$ mG/cm, so that this condition was met for $H_{1I} > 500$ mG, giving $T'_{1\rho} = 600$ s.

Figure 2 shows the slowing of the spin-locked ^{129}Xe relaxation rate measured at 297 K as a function of the resonant proton field strength H_{1S}. The inset figure shows that the slowing is dependent on the detuning of H_{1S} from the proton resonance. This signature unmistakably demonstrates that dipolar relaxation due to protons is the dominant source of ^{129}Xe surface relaxation and confirms the surprisingly long trapping times of the Xe in the coating. Fitting the H_{1S} dependence to (5) yields a correlation time $\tau'_c = 17\ \mu$s twice as long as $\tau_c = 8\ \mu$s expected from the static field dependence. Furthermore, the spin-locked ^{129}Xe relaxation rate with no H_{1S} is 2.5 times larger than expected when the static field fit parameters are inserted into (5). While these discrepancies have little effect on the basic conclusions, it is evident that our models are not yet sufficiently accurate to rigorously assess the polymer dynamics which give rise to the relaxation.

Having confirmed the long trapping times and the dominant relaxation mechanism, it is possible to estimate the minimum number of trapping sites which could give rise to the measured ^{129}Xe relaxation rate. Using $\tau_c = 8\ \mu$s and assuming a separation of $r \approx 2$ Å between a trapped ^{129}Xe and a neighboring proton, the zero-field ^{129}Xe relaxation rate calculated using (2) is $1/T_0 \approx 6 \times 10^3 f(T)\,\mathrm{s}^{-1}$. The measured zero-field relaxation rate of the cell used in Fig. 2 is $1/T_0 = 1 \times 10^{-2}\ \mathrm{s}^{-1}$ at 297 K, which implies a fraction of trapped ^{129}Xe of $f(T) \approx 2 \times 10^{-6}$. Using (4) and assuming a trapping volume

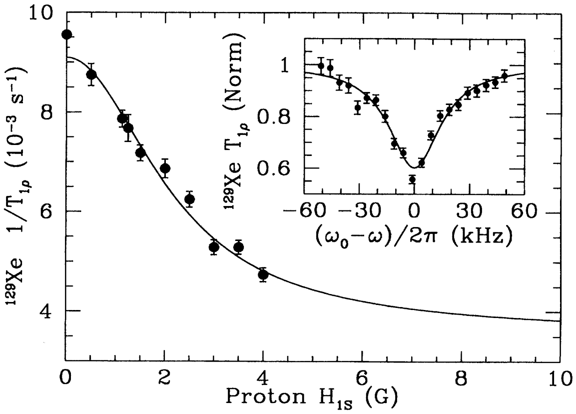

FIG. 2. Resonant decoupling of the spin-locked ^{129}Xe relaxation rate $1/T_{1\rho}$ with $H_{1I} = 1.1$ G. Application of a second field H_{1S} to the proton resonance decreases the ^{129}Xe relaxation rate, consistent with a correlation time of $\tau_c = 17\ \mu$s. The inset shows that the slowing of the ^{129}Xe relaxation is dependent on detuning from the proton resonance with maximum slowing occurring when H_{1S} is applied exactly on resonance. The resonance curve was obtained with a constant proton field strength $H_{1S} = 4$ G while the frequency was varied.

$V_s \sim (5\ \text{Å})^3$, at least $N_s \approx 3 \times 10^{14}$ trapping sites must be involved in the relaxation. While this is roughly the same number of surface sites predicted by the geometric surface area, it is possible that ^{129}Xe could enter into the bulk of the coating as well. Xenon is known to be soluble in many polymer systems [23], and work by Wu *et al.* on ^{131}Xe relaxation in SurfaSil coated cells is also suggestive of Xe entering the bulk of the polymer [24].

One final consideration is the possibility of multiple Xe atoms trapping within a single site [25]. If Xe atoms are moving freely within the cavity ($\tau_c \approx 10^{-12}$ s) then the spin-rotation interaction between Xe atoms [14] should be considered. The pressure within a cavity is $\sim\exp(-E_s/k_BT)$ higher than the cell pressure and the resulting relaxation rate is $1/T_1 \approx 1 f(T)\ \text{h}^{-1}\,\text{amagat}^{-1}$, which is negligible for our cells. If, on the other hand, the correlation time is $\tau_c = 8\ \mu\text{s}$ as for ^{129}Xe-proton relaxation then dipolar relaxation between ^{129}Xe atoms could play a role [26]. However, the smaller moment of ^{129}Xe compared to protons ensures that this mechanism will be at least a factor of $\gamma_I^2/\gamma_S^2 \approx 10$ smaller than the relaxation due to protons.

Several possibilities for improving the coating can be considered based on the results that have been presented. One is to replace the coating protons with deuterons as first demonstrated by Bouchiat in her pioneering work on alkali metal relaxation on paraffins [27]. The deuterium magnetic moment is 6.5 times smaller than that of the proton so that the ~1 h relaxation times currently attainable could increase to ~15 h for the deuterated coating. A second approach is to decrease the permeability of the coating to Xe, for example, by fluorinating the coating [28]. In addition to the practical implications for improvements in polarized noble gas technology, this work has also demonstrated that ^{129}Xe relaxation studies can provide a unique probe of polymer surfaces or membranes in biological systems. Studies of ^{129}Xe relaxation in a variety of environments should be of particular interest to the further development of MRI with laser-polarized noble gases.

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[1] N. D. Bhaskar, W. Happer, and T. McClelland, Phys. Rev. Lett. **49**, 25 (1982).
[2] W. Happer, E. Miron, S. Schaefer, W. A. van Wijngaarden, and X. Zeng, Phys. Rev. A **29**, 3092 (1984).
[3] M. S. Albert, G. D. Cates, B. Driehuys, W. Happer, B. Saam, C. S. Springer, and A. Wishnia, Nature (London) **370**, 188 (1994).
[4] T. E. Chupp, R. J. Hoare, R. L. Walsworth, and Bo Wu, Phys. Rev. Lett. **72**, 2363 (1994.
[5] M. Gatzke, G. D. Cates, B. Driehuys, D. Fox, W. Happer, and B. Saam, Phys. Rev. Lett. **70**, 690 (1993).
[6] D. Raftery, H. Long, T. Meersmann, P. J. Grandinetti, L. Reven, and A. Pines, Phys. Rev. Lett. **66**, 584 (1991).
[7] B. Driehuys, G. D. Cates, W. Happer, H. Mabuchi, B. Saam, M. S. Albert, and A. Wishnia, Phys. Lett. A **184**, 88 (1993).
[8] H. W. Long, H. C. Gaede, J. Shore, L. Reven, C. R. Bowers, J. Kritzenberger, T. Pietrass, A. Pines, P. Tang, and J. A. Reimer, J. Am. Chem. Soc. **115**, 8491 (1993).
[9] P. L. Anthony *et al.,* Phys. Rev. Lett. **71**, 959 (1993); H. Middleton, Ph.D. thesis, Princeton University, 1994 (unpublished).
[10] H. Middleton *et al.,* Mag. Res. Med. **33**, 271 (1995).
[11] Pierce Scientific Inc, Rockland, IL 61105.
[12] X. Zeng, E. Miron, W. A. van Wijngaarden, D. Schreiber, and W. Happer, Phys. Lett. **96A**, 191 (1983).
[13] 1 amagat = 2.689×10^{19} atoms/cm^3, the density of an ideal gas at 273 K and 1 atm.
[14] E. R. Hunt and H. Y. Carr, Phys. Rev. **130**, 2302 (1963); H. C. Torrey, Phys. Rev. **130**, 2306 (1963).
[15] Ultrapure Inc., Noble gas purifier part #00600-VCR-HE-XL, nitrogen purifier part #0050-VCR-N2-XL.
[16] G. D. Cates, R. J. Fitzgerald, A. S. Barton, P. Bogorad, M. Gatzke, N. R. Newbury, and B. Saam, Phys. Rev. A **45**, 4631 (1992).
[17] N. R. Newbury, A. S. Barton, P. Bogorad, G. D. Cates, M. Gatzke, H. Mabuchi, and B. Saam, Phys. Rev. A **48**, 558 (1993).
[18] A. Abragam, *Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961).
[19] S. R. Hartmann and E. L. Hahn, Phys. Rev. **128**, 2042 (1962).
[20] C. Dybowski, N. Bansal, and T. M. Duncan, Annu. Rev. Phys. Chem. **42**, 433 (1991).
[21] D. E. O'Reilly, E. M. Peterson, and T. Tsang, Phys. Rev. **160**, 333 (1967).
[22] G. D. Cates *et al.,* Phys. Rev. A **38**, 5092 (1988); G. D. Cates, S. R. Schaefer, and W. Happer, Phys. Rev. A **37**, 2877 (1988).
[23] J. B. Miller, Rubber Chem. Tech. **66**, 455 (1993).
[24] Z. Wu, W. Happer, M. Kitano, and J. Daniels, Phys. Rev. A **42**, 2774 (1990).
[25] B. F. Chmelka, D. Raftery, A. V. McCormick, L. C. de Menorval, R. D. Levine, and A. Pines, Phys. Rev. Lett. **66**, 580 (1991).
[26] R. Chapman and M. Bloom, Can. J. Phys. **54**, 861 (1976).
[27] M. A. Bouchiat and J. Brossel, Phys. Rev. **147**, 41 (1966).
[28] J. D. LeRoux, V. V. Teplyakov, and D. R. Paul, J. Membr. Sci. **90**, 55 (1994).