High-Field NMR of Adsorbed Xenon Polarized by Laser Pumping

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Optical pumping has been used to enhance the pulsed NMR signal of ^{129}Xe, allowing the detection of low-pressure xenon gas and of xenon adsorbed on powdered solids. We observe an increase in sensitivity of more than 2 orders of magnitude over conventional NMR, the current limitation being the laser power. Adsorbed xenon is observed at 298 K on graphitized carbon (10 m^2/g) and on powdered benzanthracene ($\sim$0.5 m^2/g) below 170 K. The increased sensitivity of this technique allows the study of a large class of amorphous materials with surface areas below 10 m^2/g including semiconductors, polymers, metal oxides, and catalysts.

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Recent experiments in two areas have created the possibility of extending the already powerful methods of pulsed NMR (Ref. 1) to the study of surfaces of materials with moderate to low surface areas. In the pioneering work of Happer and co-workers,[2] xenon and other noble-gas atoms, polarized during the lifetime of van der Waals collisions with optically pumped rubidium,[3,4] have been used to study surface interactions with glass cell walls[5] and to measure fundamental physics quantities.[6] Most recently, Cates *et al.* have observed the NMR of solid ^{129}Xe by transfer of optically pumped xenon to a magnet.[7] Meanwhile, there has been much activity in the use of conventional ^{129}Xe NMR to help elucidate the structure of zeolites[8] and clathrates,[9] as well as to characterize dispersed metals[10] and adsorbed guest molecules inside Na-Y zeolite.[11] Because of its large diameter and the sensitivity of its NMR parameters to perturbations, xenon is a useful probe of microscopic chemical environments. The main drawback of these NMR experiments is that, unless the temperature is extremely low,[12] the sensitivity is unfavorable, and one is often limited to systems with high surface area.[13]

In this Letter we report the initial results of our experiments on pulsed high-field NMR of laser-pumped ^{129}Xe in which we have observed spectra corresponding to low-pressure xenon gas and to the adsorption of xenon on powdered solids of moderate surface area (less than 10 m^2/g), a result of potential significance in surface science and catalysis. Ordinary amorphous solid materials with particle sizes on the order of 10 μm have surface areas around 1 m^2/g, so that adsorption studies on a wide range of materials should be possible using this technique.

A direct comparison of the ^{129}Xe NMR signal in xenon gas was made with and without optical pumping in our 4.4 T magnet in order to estimate the enhanced xenon nuclear polarization afforded by optical pumping. In Fig. 1(a) we show the conventional Fourier-transformed NMR spectrum of a 3.3-cm^3 sample volume containing 206 torr of natural-abundance (26%) ^{129}Xe at room temperature. Approximately 1000 torr of oxygen was added to reduce the ^{129}Xe relaxation time to 1.3 s,[14] which also had the effect of shifting the xenon resonance frequency by 80 Hz relative to the pure gas, in agreement with Ref. 14. After 100 acquisitions, the signal-to-noise ratio is 14 indicating that the detection limit for a signal-to-noise ratio of 1 is about 4×10^{18} ^{129}Xe nuclear spins for our spectrometer (corresponding to about 3×10^{14} 100%-polarized ^{129}Xe nuclear spins at 4.4 T) with a spectral bandwidth of 40 kHz. The linewidth is

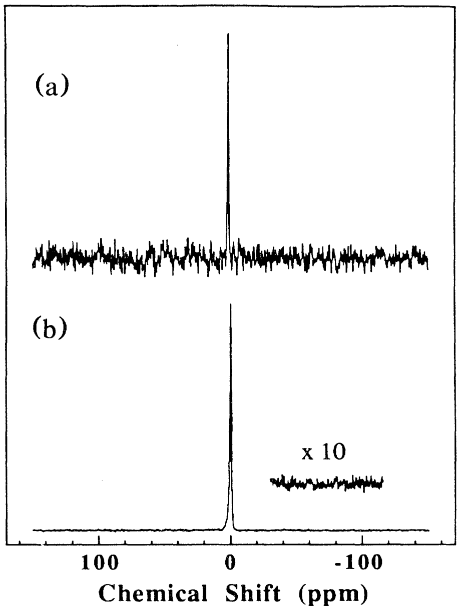

FIG. 1. Room-temperature (298 K) NMR spectra of natural-abundance ^{129}Xe: (a) conventional NMR, 3.3 cm^3 containing 206 torr xenon and 1000 torr oxygen, 100 acquisitions; (b) with optical pumping, 8 cm^3 containing 32 torr xenon, single acquisition.

29 Hz (FWHM), due primarily to residual field inhomogeneities over the sample volume, and is shown in Fig. 1(a) with a 20-Hz Lorentzian line broadening. The spectrum for a *single acquisition* of optically pumped, natural-abundance ^{129}Xe at only 32 torr, with no added oxygen gas, is shown in Fig. 1(b), and has a signal-to-noise ratio of 300 with a linewidth of 39 Hz. We have estimated the spin-lattice relaxation time (T_1) for pure, gas-phase ^{129}Xe at high field to be more than 20 min in our coated-glass (see text below), 8-cm^3 sample region. The enhancement over conventional xenon NMR in our apparatus is about 750.

The apparatus, shown schematically in Fig. 2(a), consists of an optical-pumping cell located in the fringe magnetic field (250 G) underneath a superconducting NMR magnet and a sample and detection cell located in high magnetic field. The two regions are connected by a glass tube and separated by a series of stopcocks. Separate connections allow the evacuation and pressure measurement of the sample region. Natual-abundance rubidium is contained in a reservoir region connected with the pumping cell, and is heated in an oven with warm flowing nitrogen gas. The rubidium is optically pumped to a polarization level approaching 100% using circularly polarized light from a temperature-stabilized, 30-mW, single-mode semiconductor-diode laser operating at 794.7 nm. The laser illuminates approximately $\frac{2}{3}$ of the cell volume. The entire glass manifold has been coated with Surfrasil,[15] a siliconizing agent that reduces the wall-induced relaxation rate of ^{129}Xe to less than 2 per hour. The cylindrical optical-pumping cell of approximately 11 cm^3 volume is filled with between 200 and 600 torr of natural-abundance or enriched (70%) spin-$\frac{1}{2}$ xenon-129. The samples were evacuated for several hours to about 10^{-5} torr at room temperature (benzanthracene and graphitized carbon) or at 350 °C (Na-Y zeolite) before beginning the experiment.

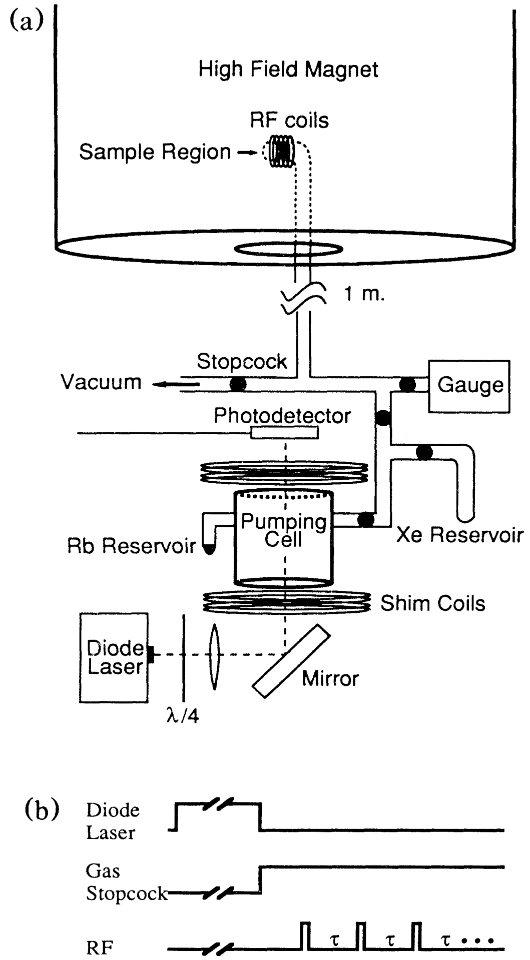

FIG. 2. Schematic diagram of the (a) experimental apparatus and (b) timing diagram. Circularly polarized 794.7-nm laser light is focused onto the optical-pumping cell. A silicon photodetector is used to detect the rubidium absorption. The oven used to heat the pumping cell, and the nitrogen cooling system for the sample region are not shown. Shim coils can be used to cancel gradients or reduce the overall magnetic field in the pumping cell.

The timing diagram for the experiment is shown in Fig. 2(b). We normally optically pump for approximately 30 min at temperatures between 80 and 120 °C, so that the absorption of incident pumping light is between 50% and 100%. After pumping, the cell is rapidly cooled to approximately 40 °C to reduce the vapor pressure of rubidium in the pumping cell. The ^{129}Xe does not relax appreciably during this cooling period. The stopcock is then opened and polarized xenon flows (in about 1 s) up to the sample region where it can adsorb onto the sample. Spectra are recorded by Fourier transformation of the signal following a radio-frequency pulse at 51.4 MHz. The sample region is located inside a glass Dewar and cooled using cold nitrogen gas. The NMR signal is typically obtained in a single scan with sufficient signal-to-noise ratio.

Figure 3 shows spectra for polarized, enriched ^{129}Xe in the presence of 0.96 g of 1,2-benzanthracene (surface area ~0.5 m^2/g as estimated by average particle size from electron micrographs) at several temperatures. At room temperature only a narrow peak due to gas-phase ^{129}Xe is observed at the same resonance frequency as the optically pumped pure xenon gas, and which we use as the reference frequency, defined as 0 ppm (parts per million) chemical shift.[16] When polarized xenon gas is admitted to the sample at lower temperatures, additional peaks appear. At 158 K, xenon adsorbed onto the surface has a resonant frequency which is shifted by 10 ppm compared to the gas peak. At 153 K, the peak associated with adsorbed xenon is observed at 32 ppm relative to the gas and has a somewhat asymmetric line shape. The chemical shift and linewidth increases with decreasing temperature, indicating a continual increase in the residence time and decrease of the mobility of the ad-

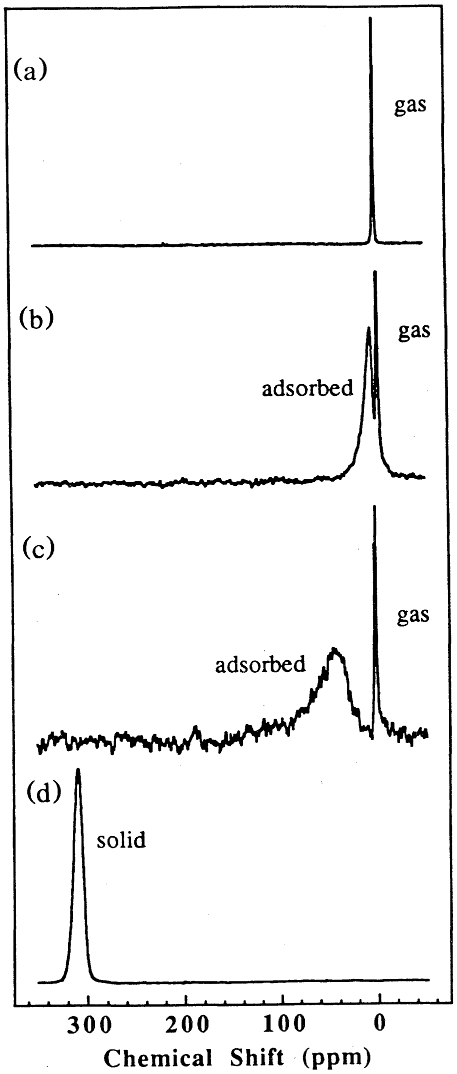

FIG. 3. NMR spectra of enriched ^{129}Xe in the presence of powdered benzanthracene following optical pumping: (a) xenon gas peak only, $T=298$ K, $P=20$ torr; (b) xenon gas and adsorbed, $T=158$ K, $P=21$ torr; (c) xenon gas and adsorbed, $T=153$ K, $P=22$ torr; (d) solid xenon, $T=123$ K.

sorbed xenon. The line shape of the adsorbed xenon signal at 153 K may arise from a distortion of the xenon electron cloud on the surface of the benzanthracene. Indeed, Ripmeester has recorded chemical-shift anisotropies as large as 160 ppm for xenon trapped in β-quinol clathrate.[17] Below 130 K, we detect the NMR signal of polarized solid xenon with a temperature-dependent linewidth in agreement with previous work,[18] corrected for isotopic enrichment. However, the measured chemical shift of the solid is 10 ppm larger than in Ref. 18.

Figure 4(a) shows optically enhanced NMR spectra of xenon adsorbed on graphitized carbon[19] (surface area 10 m^2/g) at a pressure of 20 torr. Graphitized carbon has been used to study two-dimensional phase transitions of monolayers of xenon adsorbed on graphite surfaces.[20] Our spectrum indicates that the material is very homogeneous, with a narrow line (200 Hz linewidth) at 10 ppm. The chemical-shift value is somewhat lower than that for xenon adsorbed on other types of amorphous carbon,[21] when extrapolated to zero xenon pressure. We were unable to detect a conventional NMR signal for xenon adsorbed on our graphitized carbon sample after 5000 accumulations using a delay time of 1 s.

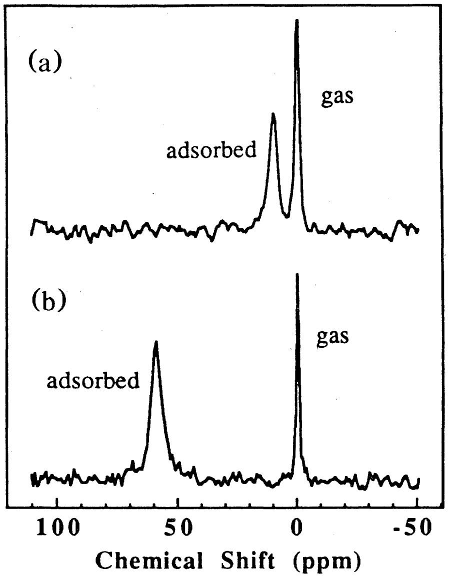

FIG. 4. Room-temperature (298 K) ^{129}Xe NMR spectra using optically pumped, natural-abundance ^{129}Xe adsorbed onto (a) graphitized carbon, $P=20$ torr, chemical shift=10 ppm, linewidth=200 Hz; (b) Na-Y zeolite, $P=16$ torr, chemical shift=59 ppm, linewidth=250 Hz.

It is also possible to study surfaces on which xenon has relatively short spin-lattice relaxation times. Figure 4(b) shows the spectrum of ^{129}Xe adsorbed on Na-Y zeolite at 16 torr. The measured T_1 relaxation time for Na-Y zeolite is about 100 ms, so several data acquisitions with a short delay (100 ms) between them were made to observe the signal. Multiple data acquisitions may be used to follow the time development of the xenon adsorption. In fact, the linewidth of the adsorbed xenon signal in Na-Y zeolite decreases from 450 Hz in the first scan after the xenon arrives in the probe to 300 Hz taken 100 ms later. The chemical shift of 59 ppm is measured at a pressure of 16 torr. This is the lowest pressure for xenon NMR reported to date, and the chemical shift is in agreement with the reported values (extrapolated to zero xenon pressure) for xenon adsorbed in Na-Y zeolite.[22]

Our observed enhancement for xenon adsorbed in Na-Y zeolite is approximately 350. The reduced enhancement compared to the pure-xenon-gas experiments is probably due to contaminants which can reduce the pumping efficiency, or relaxation of xenon at the surface, for the case of Na-Y. However, optical pumping allows us to observe xenon on surfaces where the xenon relaxation time is long (the xenon T_1 on benzanthracene is many tens of seconds), and signal averaging is impractical. Our observed NMR signals of the xenon gas correspond to a nuclear polarization of about 0.5%, which, accounting for our laser power and operating conditions is consistent with results of Bhaskar and Happer.[4] It should be straightforward to increase our polarizations by up to 2 orders of magnitude using higher-power lasers currently available.

We have demonstrated an enhancement of nuclear-spin polarization which extends to the possibilities of high-field NMR to the study of adsorption on low- to moderate-surface-area materials. An exciting possibility currently being investigated is the selective enhancement of other surface spins by cross polarization[23] from optically polarized xenon following adsorption.

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[1] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, Germany, 1990), 3rd ed.; A. Pines, in *Proceedings of the Bloch Symposium,* edited by W. A. Little (World Scientific, Singapore, 1990).

[2] R. J. Knize, Z. Wu, and W. Happer, Adv. Atom. Mol. Phys. **24**, 223 (1989).

[3] B. C. Grover, Phys. Rev. Lett. **40**, 391 (1978).

[4] N. D. Bhaskar and W. Happer, Phys. Rev. Lett. **49**, 25 (1982).

[5] T. M. Kwon, J. G. Mark, and C. H. Volk, Phys. Rev. A **24**, 1894 (1981); Z. Wu, W. Happer, and J. M. Daniels, Phys. Rev. Lett. **59**, 1480 (1987); Z. Wu, W. Happer, M. Kitano, and J. Daniels, Phys. Rev. A **42**, 2774 (1990); V. Lefevre-Seguin and J. Brossel, J. Low Temp. Phys. **72**, 165 (1988).

[6] T. E. Chupp, R. J. Hoare, R. A. Loveman, E. R. Oteiza, J. M. Richardson, M. E. Wagshul, and A. K. Thompson, Phys. Rev. Lett. **63**, 1541 (1989); T. E. Chupp and R. J. Hoare, Phys. Rev. Lett. **64**, 2261 (1990); M. Kitano, M. Bourzutschky, F. P. Calaprice, J. Clayhold, W. Happer, and M. Musolf, Phys. Rev. C **34**, 1974 (1986).

[7] G. D. Cates, D. R. Benton, M. Gatzke, W. Happer, K. C. Hasson, and N. R. Newbury, Phys. Rev. Lett. **65**, 2591 (1990).

[8] M. A. Springuel-Huet and J. Fraissard, Chem. Phys. Lett. **154**, 299 (1989); T. Ito and J. Fraissard, Zeolites **8**, 350 (1988); E. W. Scharpf, R. W. Creceley, B. C. Gates, and C. Dybowski, J. Chem. Phys. **90**, 9 (1986); M. E. Davis, C. Saldarriaga, C. Montes, and B. Hanson, J. Chem. Phys. **92**, 2557 (1988).

[9] J. A. Ripmeester, C. I. Ratcliffe, and J. S. Tse, J. Chem. Soc. Faraday Trans. 1 **84**, 3731 (1988).

[10] B. F. Chmelka, L. C. de Menorval, R. Csencsits, R. Ryoo, S.-B. Liu, C. J. Radke, E. E. Petersen, and A. Pines, in *Structure and Reactivity of Surfaces,* edited by C. Morterra *et al.* (Elsevier, Amsterdam, 1989), p. 269.

[11] L. C. de Menorval, D. Raftery, S.-B. Liu, K. Takegoshi, R. Ryoo, and A. Pines, J. Phys. Chem. **94**, 27 (1990); B. F. Chmelka, J. G. Pearson, S.-B. Liu, R. Ryoo, L. C. de Menorval, and A. Pines, J. Phys. Chem. **95**, 303 (1991).

[12] O. Gonen, P. L. Kuhns, J. S. Waugh, and J. P. Fraissard, J. Phys. Chem. **93**, 504 (1989).

[13] C. P. Slichter, Ann. Rev. Phys. Chem. **37**, 25 (1986); B. F. Chmelka, D. Raftery, A. V. McCormick, L. C. de Menorval, R. D. Levine, and A. Pines, preceding Letter, Phys. Rev. Lett. **66**, 580 (1991).

[14] C. J. Jameson, A. K. Jameson, and J. K. Hwang, J. Chem. Phys. **89**, 4074 (1988).

[15] Pierce Chemical Company, Rockford, IL 61105.

[16] C. J. Jameson, A. K. Jameson, and S. M. Cohen, J. Chem. Phys. **59**, 4540 (1973).

[17] J. A. Ripmeester, J. Am. Chem. Soc. **104**, 290 (1982).

[18] D. Brinkmann and H. Y. Carr, Phys. Rev. **150**, 174 (1966); W. M. Yen and R. E. Norberg, Phys. Rev. **131**, 269 (1963).

[19] Thermax (graphitized carbon) courtesy of the Vanderbilt Co., Norwalk, CT 06852.

[20] G. Neue, Z. Phys. Chem. Neue Folge, Bd. **152**, 271 (1987); H. Hong, C. J. Peters, A. Mak, R. J. Birgeneau, P. M. Horn, and H. Suematsu, Phys. Rev. B **40**, 4797 (1989).

[21] R. Ryoo (private communication).

[22] T. Ito and J. Fraissard, J. Chem. Phys. **76**, 5225 (1982).

[23] S. R. Hartmann and E. L. Hahn, Phys. Rev. **128**, 2042 (1962); A. Pines, M. G. Gibby, and J. S. Waugh, J. Chem. Phys. **59**, 569 (1973).