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# Enhancement of solid-state proton NMR via the spin-polarization-induced nuclear Overhauser effect with laser-polarized xenon

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We have successfully transferred the spin polarization of laser-polarized $^{129}$Xe to the proton spins of solid-state $^{1}$HCl via spin polarization-induced nuclear Overhauser effect (SPINOE). The key steps include mixing the laser-polarized $^{129}$Xe gas with the $^{1}$HCl gas and cooling them to their condensed state in a flow system. The solid-state nuclear magnetic resonance (NMR) signal enhancement factor of 6 for $^{1}$H was observed, compared with the Boltzmann polarization signal at 1.879 T and 142 K. This method may be valuable for applications in both NMR spectroscopy and chemical physics.

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The sensitivity of the conventional nuclear magnetic resonance (NMR) spectroscopy is usually lower than other detection techniques, such as electron spin resonace (ESR) or optical spectroscopy. The main reason is the low nuclear polarization at thermal equilibrium. A number of methods have been developed to enhance the nuclear polarization,[1] of which the alternative is to use spin-exchange optical pumping (SEOP).[2] Since the nuclear spin polarizations of noble gases $^{3}$He and $^{129}$Xe can be increased via SEOP by four or five orders of magnitude over the equilibrium Boltzmann polarizations, these gases are generally referred to as "hyperpolarized" or "laser-polarized" gases. There have been increasing interests in the applications of these hyperpolarized gases in a wide variety of disciplines.[3–11]

The spin polarization of the hyperpolarized $^{3}$He or $^{129}$Xe can be further transferred to other nuclear spins. With an exception of the solid surface enhancement,[12] proton sensitivity enhancements are generally not significant in most experiments implemented by using gaseous or liquid hyperpolarized xenon.[13–16] The $^{1}$H polarization has been enhanced by a factor of 0.1 to 2, on a 4.2 T NMR spectrometer at room temperature, via cross-relaxation between dissolved hyperpolarized gaseous $^{129}$Xe and the $^{1}$H of liquid benzene. This method has been called the SPINOE by Pines' group.[14] By dissolving compounds in hyperpolarized liquid xenon, the enhanced signal of over 45 for $^{1}$H has been observed at 1.4 T and 200 K by Happer's group.[15] In Xe ice, the large nuclear polarization of hyperpolarized $^{129}$Xe has been transferred to $^{13}$CO$_2$ by low-field thermal mixing.[17] In low magnetic fields (10 G–10 mG) very large SPINOE enhancement factors in the order of $10^3-10^6$ have been reported in organic liquids.[18,19] However, to our knowledge, the solid-state proton polarization enhancement via SPINOE has not been reported before, excluding the surface protons of solids.[4,16]

Considering that hydrogen chloride (HCl) and xenon have almost the same melting points,[20] and the longitudinal relaxation time $(T_1)$ of hyperpolarized $^{129}$Xe in solid-state (4 K) is about 500 h,[21] we can first mix hyperpolarized xenon gas and $^{1}$HCl at room temperature, and then rapidly freeze them into solid. This allows the investigation of the polarization transfer from $^{129}$Xe to $^{1}$H via SPINOE in solid state.

In this letter, we demonstrate how the polarization of hyperpolarized solid-state $^{129}$Xe produced by SEOP can be transferred to the proton of solid-state $^{1}$HCl via SPINOE. This method has yielded the proton signal enhancement of 6 times over the thermal polarization signal at 1.879 T and 142 K. Although the enhancement is modest, it may be valuable for applications in NMR spectroscopy and in chemical physics.

The experimental setup is similar to that in Ref. 22. It mainly consists of an optical pumping system and a cross-relaxation and detection system. The two parts are connected by a cylindrical Pyrex tube and separated by stopcocks. Before beginning the experiment the whole system was evacuated to $1.5\times10^{-5}$ Torr and kept for several hours. The cylindrical pump cell with a volume of 600 cm$^3$, containing a few drops of Cs metal, was loaded with 760 Torr natural-abundance xenon gas at room temperature. The pump cell, placed in a 25 G magnetic field generated by Helmholtz coils, was afterwards maintained at approximately $333\pm4$ K by a resistance heater during the optical pumping. The inner surfaces of the cylindrical Pyrex tube and the pump cell were coated with silane in order to slow down the relaxation of the $^{129}$Xe upon collision with the tube wall. The laser light from a 15 W cw tunable semiconductor-diode laser array (Opto Power Co. Model OPC-D015-850-FCPS) at wavelength $\lambda=852.1$ nm was used as pumping light. After passing through the beam expander, Glan prism, $\lambda/4$ plate and convex lens, the laser light became circularly polarized, and illuminated almost 4/5 of the pump cell volume. The direction of the laser beam was parallel to the direction of the magnetic field. The circularly polarized laser resonated with the Cs $D_2$ absorption line and induced an electron spin polarization in the Cs atoms via a standard optical pumping process.[2] By spin-exchange collision with the polarized Cs atoms, the hyperpolarized $^{129}$Xe gas was produced in about 25 min.

In the cross-relaxation and detection system part, there was a liter of $^{1}$HCl gas at room temperature and an atmosphere in the HCl tank. The hyperpolarized $^{129}$Xe and $^{1}$HCl were mixed and then transferred to a 10 mm NMR probe, pre-cooled at $172\pm2$ K, of a Bruker WP-80SY NMR spectrometer (1.879 Tesla). In an evacuated glass dewar, the tem-

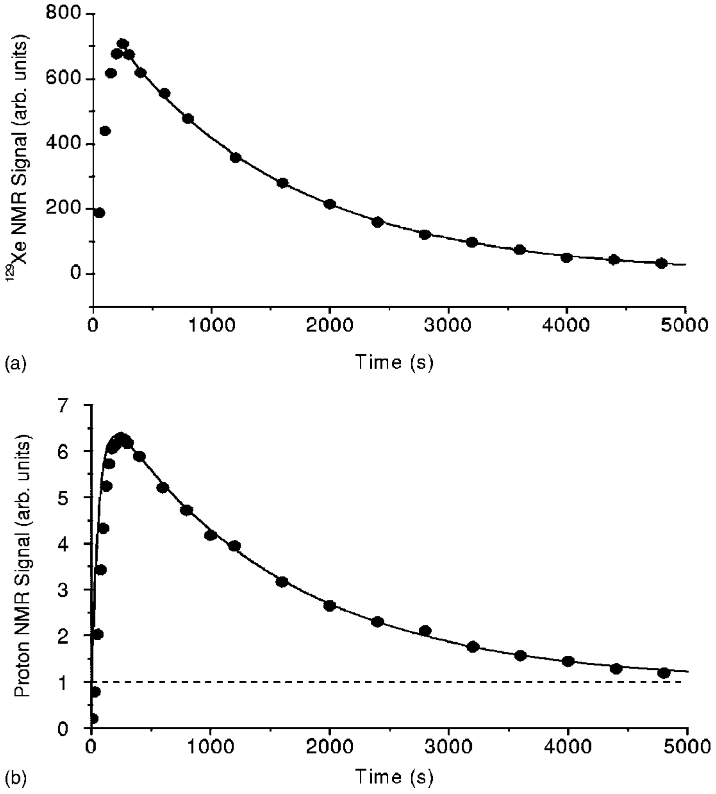

FIG. 1. (a) Time dependence of the solid-state $^{129}$Xe NMR signal (solid circle) observed after the mixing of hyperpolarized $^{129}$Xe and $^{1}$HCl at 1.879 T and 142 K. The solid line, a single exponential fit to data after the peak, represents how much $^{129}$Xe magnetization is left after a SPINOE experiment. (b) Time dependence of the solid-state proton NMR signal (solid circle) from the same sample. It relaxes towards its thermal equilibrium value (dashed line) at the same rate as the hyperpolarized $^{129}$Xe signal.

perature of the probe was subsequently reduced to 142 K by flowing cold nitrogen gas around the NMR probe, which was controlled by a Bruker variable temperature unit. We kept this temperature with a variation less than 2 K at all the time, so that the mixture is in the solid-state. Since a polarization imbalance exists between the hyperpolarized $^{129}$Xe and the thermally polarized proton, a modulated magnetic dipole interaction between them will induce a spin polarization transfer (SPINOE). NMR experiments were performed with a probe tuned at 80.13 MHz for $^{1}$H or at 22.16 MHz for $^{129}$Xe. The pulse flip angles of 4° and 9° were applied to $^{129}$Xe and $^{1}$H, respectively, for acquisitions unless otherwise indicated.

A series of SPINOE experiments with $^{129}$Xe detection was performed to check the time evolution of the $^{129}$Xe NMR signals. Figure 1(a) shows the time dependence of the $^{129}$Xe NMR signal intensity (solid circle) observed after mixing hyperpolarized $^{129}$Xe and $^{1}$HCl. The point $t=0$ is the time at which the hyperpolarized $^{129}$Xe gas and $^{1}$HCl gas became mixed. Each solid circle represents the integral of the NMR spectrum, proportional to the instantaneous total $^{129}$Xe nuclear magnetization inside the probe. The $^{129}$Xe NMR signal reaches the peak value at $t_0=280$ s, and then it relaxes back to its thermal equilibrium value at a rate of $(29.6\pm0.6\ \text{min})^{-1}$. The solid line is a single exponential fit to the data after the maximum. The initial rise of the $^{129}$Xe NMR signals manifests the accumulation of the hyperpolarized $^{129}$Xe in the probe, similar to that in Ref. 14. The maximum of $^{129}$Xe signal can be explained by the fact that the accumulated Xe magnetization increases up to a point where the absolute value of the $^{129}$Xe magnetization decay rate ($T_1$ decay) is equal the accumulation rate. Note that after the maximum, the hyperpolarized Xe magnetization decays due mainly to Xe autorelaxation and through the Xe-$^{1}$H SPINOE mechanism. Note also that the fitted spin relaxation time is close to the spin-lattice relaxation time of pure solid Xe (at 142 K and 1.435 T: $T_1 \sim 30$ min).[21]

We also carried out proton NMR investigations to manifest that the spin polarization could be transferred via SPINOE from the hyperpolarized $^{129}$Xe to the proton. Figure 1(b) shows the time dependence of the solid-state proton NMR signal (solid circle). It should be noted that the rapid growth of the proton signal after $t=0$ is due to the combination of two effects: (1) The cross-relaxation from $^{129}$Xe to $^{1}$H and the autorelaxation of $^{1}$H, and (2) the progressive filling of the sample cell. However, by comparing Fig. 1(b) with Fig. 1(a) at $t<280$ s, we find that the observed fast growth rates are very similar for $^{1}$H and for $^{129}$Xe. Hence the fast growth of the proton signal is due mainly to the finite rate of filling of the cell and not to cross-relaxation. The proton NMR signal reaches the peak value at a time $t_0=280$ s after the mixing, and then decays towards its thermal equilibrium value (dashed line) at a rate of $(33.0\pm1.1\ \text{min})^{-1}$. Based on the Solomon equations,[23] in the case of small cross-relaxation rates compared with the autorelaxation, the time evolution of the proton NOE signals satisfies the following equation:[4]

$$I(t) = A + B(e^{-t/T_{\text{dec}}} - e^{-t/T_{\text{pol}}}). \tag{1}$$

Using Eq. (1) to fit the data [solid line in Fig. 1(b)], we can obtain the two time constants $T_{\text{pol}}=1.4\pm0.1$ min and $T_{\text{dec}}=33.0\pm1.1$ min. Under ideal conditions, i.e., neglecting the dynamics of the progressive accumulation of the $^{129}$Xe-$^{1}$HCl mixture in the sample cell, the shortest time $T_{\text{pol}}$ should agree with the proton spin-lattice relaxation

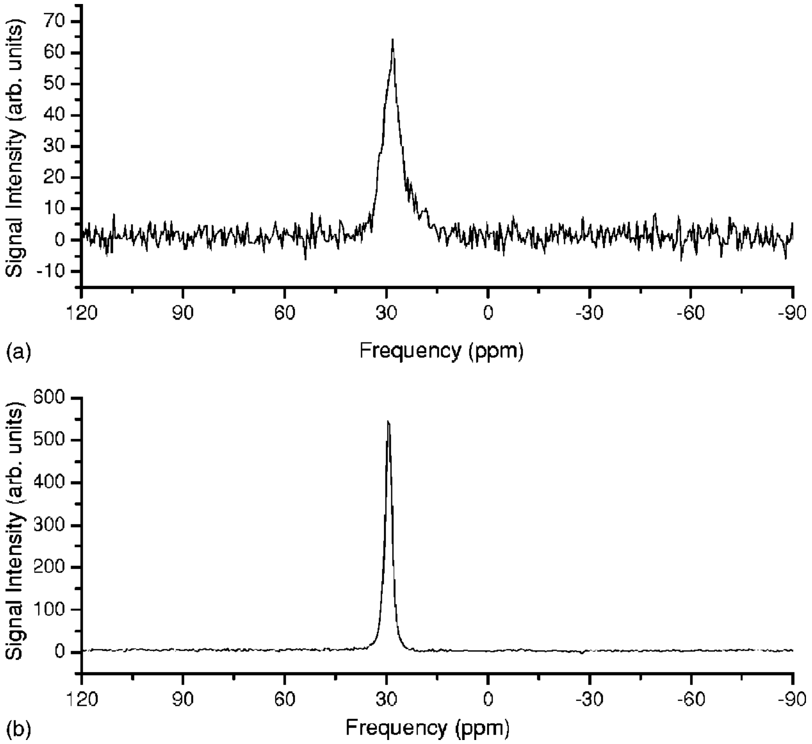

FIG. 2. Single scan solid-state proton NMR spectra of $^1$HCl under the conditions of (a) thermal equilibrium and (b) enhancement via SPINOE with hyperpolarized $^{129}$Xe at 1.879 T and 142 K, obtained with 90° pulses.

time.[4] However, because of the accumulation effect, the $1/T_{\mathrm{pol}}$ does not provide quantitative information on the autorelaxation rate of $^1$H, but results in a lower limit. We did not measure the proton spin-lattice relaxation time in the presence of the hyperpolarized $^{129}$Xe in our current experiments. This should be an interesting and useful measurement, which remains to be investigated. It is also obvious that the longest time constant $T_{\mathrm{dec}}$ should be, within error, in agreement with the decay time constant of the $^{129}$Xe spin polarization.[15]

In order to obtain the maximal $^1$H NMR signal in our SPINOE experiments, we used a 90° pulse and a single acquisition at time $t_0=280$ s. Figure 2(b) shows a typical enhanced $^1$H NMR spectrum, while Fig. 2(a) is the one at thermal equilibrium under otherwise identical conditions. By comparing their integrated intensity, the acquired signal enhancement factor of the solid-state proton was about 6. In terms of the relation of the magnetization versus the nuclear spin polarization given by Abragam,[24] this enhancement corresponds to a proton spin polarization of about $8.55\times10^{-5}$. It is equivalent to a proton thermal spin polarization on a 10 T NMR spectrometer at 300 K.

According to the Solomon equations,[14,23,24] the maximum fractional enhancement of polarizations of the solid-state protons ($I$ spins) due to cross relaxation with the hyperpolarized $^{129}$Xe ($S$ spins) can be read as:

$$\frac{I_z(t_0)-I_0}{I_0}=-\frac{\sigma_{IS}}{\rho_I}\frac{\gamma_S S(S+1)}{\gamma_I I(I+1)}\frac{S_z(t_0)-S_0}{S_0}, \tag{2}$$

where $\gamma_I$ and $\gamma_S$ are the corresponding gyromagnetic ratios of $I$ and $S$ spins, and $t_0$ is the time at which $I_z$ goes through the maximum value. $I_z(t_0)$ and $S_z(t_0)$ are $z$ components of $I$ and $S$ spins at time $t_0$, and $I_0$ and $S_0$ are their thermal equilibrium values. $\sigma_{IS}$ is the cross-relaxation rate between them, $\rho_I$ is the autorelaxation rate of the $I$ spin. In our experiments, the enhancement of hyperpolarized solid-state $^{129}$Xe magnetization, $[S_z(t_0)-S_0]/S_0\approx S_z(t_0)/S_0$, was about 6000,[22] and the enhancement of proton magnetization was about 6, so we can calculate $\sigma_{IS}/\rho_I$ to be about $1/280$ by using Eq. (2). Therefore, we indeed achieved the limit $\rho_I\gg\sigma_{IS}$, and the dynamics of the proton NOE signal could be described by Eq. (1) neglecting the accumulation effect,[4] as shown in Fig. 1(b).

In solid HCl-Xe, the Xe-H correlation time $\tau_c$ might be very long, probably longer than 1 $\mu$s. So the situation in solid $(\omega\tau_c\gg1)$ might be completely different from that in solution.[25] Since the Xe correlation times in solution are ps order, one can always use the fast-motion limit $(\omega\tau_c\ll1)$ to treat the SPINOE in solution. But in the slow-motion limit $(\omega\tau_c\gg1)$, the proton polarization enhancement via SPINOE in solid states might be decreased by a factor about $\tau_c/[1+(\omega\tau_c)^2]$, relative to the short correlation case.

In terms of Eq. (2), the proton polarization enhancement provided by SPINOE depends on the xenon polarization enhancement $([S_z(t_0)-S_0]/S_0)$, the cross-relaxation rate $(\sigma_{IS})$ and the autorelaxation rate $(\rho_I)$ of the proton. Similar to the discussions in Ref. 15, the $^1$H autorelaxation $\rho_I$ can be expressed as the sum of $\rho_I^{IS}$ and $\rho_I^0$. $\rho_I^{IS}$ is the contribution from the dipole-dipole coupling between the $^1$H and the hyperpolarized $^{129}$Xe spins, and $\rho_I^0$ is the relaxation rate from H-H dipole-dipole interaction, spin rotation, paramagnetism and all other interactions, such as the H-$^{35}$Cl (or $^{37}$Cl), H-$^{131}$Xe interactions, etc. In fact, in the solid mixture of $^1$HCl and Xe, there exist complicated couplings, including H-H, H-Xe, H-Cl, Xe-Cl, Xe-Xe, Cl-Cl. Due to the very fast quadrupolar relaxation of both $^{35}$Cl and $^{37}$Cl, the nuclear polarization of Cl can be treated as permanently in equilibrium with the lattice; hence the Cl can be neglected in our discussion. The dipolar H-H spin flip-flop (zero quantum transition) interaction does not affect the SPINOE enhancement, because this conserves the total proton spin. But the single quantum H-H transitions, which do not conserve the total spin, do matter in the SPINOE enhancement. The H-Cl and H-$^{131}$Xe coupling plays a role to leak the proton enhancement as well as the proton depolarization with the lattice. Because it is the natural xenon (26.4% $^{129}$Xe, 21.2% $^{131}$Xe) that has been used in our experiments, the cross-relaxation between $^{129}$Xe and Xe can decrease the efficiency of polarization transfer from $^{129}$Xe to $^{1}$H at 142 K.[21,26] The polarization loss owing to relaxation with the wall as well as the freezing will diminish the value of $[S_z(t_0)-S_0]/S_0$.[26] In addition, the inhomogeneous mixture of hyperpolarized Xe in the solid HCl matrix would cut down the SPINOE enhancement.[25] All of these factors reduce the proton enhancement via SPINOE with the hyperpolarized $^{129}$Xe, so it could be expected that the enhancement might be larger with the optimization.

In conclusion, we have obtained the solid-state enhanced proton NMR signal of $^{1}$HCl via SPINOE with the solid-state hyperpolarized $^{129}$Xe at 1.879 T and 142 K in a flow system. The measured enhancement factor of the proton NMR signal was about 6. Solid-state signal enhancement via SPINOE with hyperpolarized $^{129}$Xe is not limited to the proton, i.e., it can be extendible to other nuclei, such as $^{13}$C, $^{15}$N, $^{31}$P, etc. Meanwhile, this method should be readily extended to chemical physics and the determination of the three-dimensional (3D) structure of large biomolecules, since NOE can provide unique information on molecular structure. Traditional NOE needs to irradiate one nucleus so as to observe another. However, by using this method, it is very convenient and available to probe interactions between nuclei, without any additional conditions. In addition, much remains to be studied, both theoretically and experimentally, about SPINOE in solids at high-magnetic fields.

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