

Cross polarization from laser-polarized solid xenon to $^{13}\text{CO}_2$ by low-field thermal mixing

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The first observation of nuclear spin polarization enhancement in a molecular species by coupling to laser-polarized xenon is reported. The spins of $^{13}\text{CO}_2$ were cooled by inclusion into the xenon solid followed by thermal mixing in magnetic fields comparable to the heteronuclear dipolar interactions. High-field NMR detection yielded enhancement factors of up to 200. Moreover, a change in the sense of the helicity of the optical pumping light results in a sign reversal of the spin temperature and hence an inversion of the ^{13}C NMR signal.

Over thirty years ago, it was demonstrated [1] that the angular momentum of optical photons could be transferred to rare gas nuclear spins by optical pumping and spin exchange with alkali metal atoms. Spin exchange to xenon is particularly efficient due to strong van der Waals complex formation [2]. Xenon nuclear spin polarizations as high as 35% can be obtained in rubidium xenon mixtures using commercially available laser systems [3,4]. It was demonstrated recently that the angular momentum could subsequently be transferred between nuclear spin isotopes of the same element [5], namely between ^{129}Xe and ^{131}Xe . The subject of this Letter is the transfer of ^{129}Xe spin order to molecules, constituting a chemically relevant method of sensitivity enhancement for solid state and surface NMR.

We have previously reported the use of laser-polarized xenon to improve the sensitivity of the NMR of xenon in dynamic equilibrium with the surface of various polycrystalline materials [6,7]. In the present work, cross polarization to a molecular species embedded in laser-polarized xenon solid was achieved by thermal mixing in low magnetic field.

Approximately 2000 Torr cm^3 of xenon gas enriched to 80% ^{129}Xe was polarized by spin exchange with optically pumped rubidium at a temperature of 105°C in a magnetic field of 25 G. A titanium sapphire ring laser pumped by a 10 W argon-ion laser

provided optical pumping fields of 160–200 mW/cm^2 at a wavelength of 794.7 nm (corresponding to the D_1 line of Rb). The remainder of the optical pumping apparatus has been described previously [6] except with the modification that the pumping cell was connected by glassware to an L-shaped NMR sample tube located outside the fringe field of the superconducting magnet. The experimental timing sequence is illustrated in fig. 1. The polarized xenon was combined with 500 Torr cm^3 ($\approx 10^{19}$ molecules) of 99% isotopically enriched $^{13}\text{CO}_2$ (Isotec Inc.) at room temperature and allowed to mix for about 45 s. The mixture was then rapidly frozen into the sample tube, which was immersed in liquid nitrogen. During the freezing process, a static field of 150 G was applied to lengthen the spin–lattice relaxation time of the ^{129}Xe . The cross relaxation was accomplished by rapidly switching the field to a value B_{mix} for a duration τ_{mix} and then returning to 150 G. The sample was then removed from the liquid nitrogen bath and immediately transported to a field of 4.2 T for ^{13}C NMR detection using a chemical shift echo pulse sequence. Similar results were obtained for values of $\{H_{\text{mix}}, \tau_{\text{mix}}\} = \{0.1 \text{ G}, 200 \text{ ms}\}$, $\{10 \text{ G}, \approx 200 \text{ ms}\}$, $\{35 \text{ G}, \approx 10 \text{ s}\}$ and Xe:CO₂ ratios 6:1, 4:1, 1:1 and 1:6.

The sensitivity enhanced spectrum of the 4:1 Xe:CO₂ solid mixture appears in fig. 2a, obtained

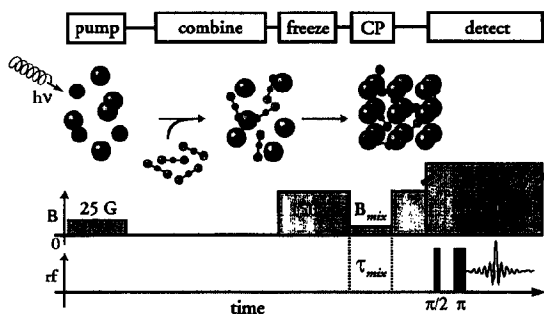


Fig. 1. Timing diagram of the experimental procedure. The experiment begins with optical pumping and spin exchange between the rubidium and xenon for ≈ 20 min. After separation from the rubidium, the xenon is combined with CO₂ gas, mixed for 45 s and expanded into the pre-cooled sample cell placed in a field of 150 G. The field is then reduced to a value B_{mix} for a period τ_{mix} during which thermal mixing occurs. The sample is subsequently removed from the nitrogen bath, immediately transported to high field where the signal is observed during a spin echo pulse sequence.

with right circularly polarized light (i.e. σ^- polarized). As a frequency and sensitivity reference, the conventional NMR spectrum of gaseous ¹³CO₂ for a similar number of molecules is presented in fig. 2c. The measured values of $\sigma_{\perp} = 232.8 \pm 2.3$ and $\sigma_{\parallel} = -82.5 \pm 2.3$ ppm for the axially symmetric chemical shift tensor, extracted from the fit of our spectrum with the best signal-to-noise ratio, differ slightly from $\sigma_{\perp} = 245$ and $\sigma_{\parallel} = -90$ ppm as reported by Beeler et al. [8] for CO₂ in a methane-doped argon matrix at 20 K.

The spectrum in fig. 2b demonstrates the inversion of the NMR signal occurring when the helicity of the optical pumping light is changed from positive to negative because the density matrix of the xenon following optical pumping corresponds to positive spin temperature for σ^- light and to a negative spin temperature for σ^+ light. The population inversion may be interpreted as a reversal in sign of the spin temperature. With our laser optical pumping apparatus, the fractional polarization can reach values as high as 0.3 [4]. Demagnetization of the spin system to low field, wherein the difference in the Larmor frequencies is comparable to the heteronuclear dipolar interaction, conserves the sign of the spin temperature [9,10]. After thermal mixing during a time on the order of T_2 , the density matrix becomes pro-

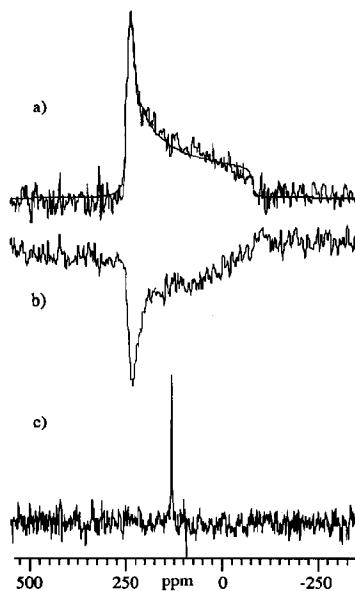


Fig. 2. (a) ¹³C NMR spectrum of $\approx 1.6 \times 10^{19}$ molecules of 99% isotopically pure ¹³CO₂ obtained after thermal mixing in zero field at 77 K with $\approx 6.4 \times 10^{19}$ atoms of laser-polarized ¹²⁹Xe (80% isotopic purity). The signal was acquired in a single scan at 4.2 T using a spin echo pulse sequence. The optical pumping light was σ^- circularly polarized. The solid line represents a fit of the theoretical anisotropic chemical shift line shape to the experimental spectrum. (b) Spectrum obtained with the same procedure as in (a), but with σ^+ light. (c) ¹³C NMR spectrum of $\approx 5 \times 10^{18}$ molecules of 99% isotopically pure ¹³CO₂ gas at 300 K after 64 averaged scans. The chemical shift of 124.6 ppm is referenced to an external standard of liquid TMS.

portional to $\exp(-\beta H)$, where H is the low-field Hamiltonian and β is the common inverse spin temperature. The sign of β is thereby determined by the sense of the circular polarization of the light. Negative spin temperatures correspond to emissive NMR transitions as illustrated in fig. 2b.

An enhancement factor of 200 is estimated by comparison of the integrated intensity of the laser-enhanced signal with that of the reference, corrected for differences in the number of ¹³C spins. This is substantially smaller than the xenon enhancement factor of approximately 18000, corresponding to a polarization of about 10%. However, this calculation does not account for the possibility that only a fraction of the total number of CO₂ molecules are in dipolar contact with the polarized xenon. This raises the question of the degree of dispersion of the CO₂

in the frozen Xe. The solid mixtures were prepared by opening a stopcock separating the two gases, waiting 45 s, and allowing them to expand into the precooled NMR sample tube. No special measures were taken to confirm that a homogeneous matrix was formed. Xenon enriched to 80.0% isotopic purity of ^{129}Xe and depleted to 1.2% ^{131}Xe was used to avoid potential losses due to low-field cross relaxation from the former to the latter. This is the dominant spin-lattice relaxation mechanism [5] at 4.2 K for magnetic fields lower than 1000 G. The spin-lattice relaxation time for the xenon in the sample was extremely long, as is characteristic of the pure solid.

In summary, the spin order of laser-polarized xenon was transferred to the nuclear spins of a molecular species for the first time. Thermal mixing in low magnetic fields was used to achieve this transfer, yielding an anisotropic chemical shift spectrum, substantially enhanced in sensitivity over that which can be obtained by conventional NMR. Phase inversion of the signal, reflecting a reversal in sign of the spin temperature, accompanied the change in helicity of the polarized pumping light. Additional experiments are under way to implement high-field cross polarization [11] for the transfer of the enhanced xenon spin order to other nuclei. Finally, the Xe-CO₂ system studied here serves as a model for polarization transfer to surface nuclei. The number of surface spins on $\approx 1 \text{ m}^2$ of a typical powdered solid is on the order of 10^{19} , approximately the same number of ^{13}C nuclei detected in the current experiment. Thus, it is expected that sufficient sensitivity for single shot detection of a broad ($\approx 15 \text{ kHz}$) surface resonance can

be obtained by cross polarization from laser-polarized xenon.

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