High-Field Cross Polarization NMR from Laser-Polarized Xenon to Surface Nuclei

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Abstract. A method for NMR investigations of surface nuclei using cross polarization from optically polarized xenon (OPCP) is described. We find this methodology results in enhancement factors of approximately 10^3 upon application to surface protons. The dynamics of ^{129}Xe transfer to protons is examined in some detail, including the time, temperature, and multiple contact dependences of signal intensities. Furthermore, we discuss the sensitivity of the transfer process to spatial diffusion. Finally, we report on application of the OPCP experiment to a low total surface area sample.

1. Introduction

Solid-state NMR is a useful technique for investigating the structure and dynamics of bulk materials; however, because of its low sensitivity, its utility for studying surfaces has been limited to high surface area materials such as zeolites [1–3]. In addition to the problem of sensitivity, *selectivity*, i.e. the problem of distinguishing surface from bulk species, is also an issue. Cross polarization (CP) [4] has been used successfully to selectively probe surface nuclei when the magnetization source, usually protons, resides exclusively at the surface. Maciel and Sindorf have utilized ^{1}H-^{29}Si CP-MAS to investigate the resonances of surface silicon atoms in silica [5]. Oldfield and coworkers used ^{1}H-^{17}O CP to observe surface hydroxyl groups of high surface area metal oxides that are difficult to detect by conventional NMR [6]. This technique is also useful for investigating interfaces. Zumbulyadis and O'Reilly have used ^{1}H-^{29}Si CP to estimate the proximity of the backbone of a polymer to the surface of silica [7].

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For many systems of interest, such as polymers, there are no such distinctive surface nuclei. We have reported recently [8] a method of detecting surface species in such a system by adsorbing optically polarized xenon-129 onto a polymer surface and using the polarized xenon as the source of magnetization in a CP experiment. Gas phase xenon with nuclear spin polarizations up to 10^5 times higher than thermal Boltzmann levels in high magnetic field may be obtained using optically pumped rubidium vapor according to the pioneering work of Happer and coworkers and others [9, 10]. The photon angular momentum of the circularly polarized laser light is transferred via the rubidium electron spins to the xenon nuclear spins. The polarized xenon has been used directly to investigate the surfaces of thin films [11], polymers [12], nanocrystals [13], and clathrate hydrates [14]. Zilm and coworkers have used dipolar demagnetizing fields of polarized xenon to indirectly detect the gas phase spectrum of methane [15].

The primary goal of the optical-pumping cross-polarization experiment is to select and enhance NMR signals from surface nuclei. The difficulties in accomplishing a complete xenon to proton magnetization transfer are twofold. One is that at temperatures below 100 K, a necessary condition for the CP experiment in order to reduce xenon mobility, xenon tends to freeze into the bulk solid phase. The amount of xenon in dipolar contact with the surface, i.e. the *adsorbed* xenon, is limited not just by the total surface area (total number of adsorption sites), but by the adsorption energy of the xenon on the surface. The surface sites are never completely occupied; rather, they are occupied proportionally to the surface area, with the proportionality factor determined from the heat of adsorption. The maximum number of xenon atoms that will adsorb on the surface is thermodynamically limited. This is the major problem for performing these kinds of experiments on the low surface area materials. The general rule to circumvent this problem is to use large amounts of sample to increase the *total* surface area and hence increase the number of adsorbed xenon atoms. The second difficulty is the possible inefficiency of the CP process. It is of course desirable to utilize the full xenon magnetization for the enhancement of the surface proton signal. This inefficiency is the focus of this paper. In this work, we report studies of the dynamics of the cross polarization from laser-polarized xenon to the surface protons of poly(triarylcarbinol), poly(tetrabiphenyl silane) and Aerosil R812.

2. Experimental

The poly(triarylcarbinol) (DuPont) and poly(tetrabiphenyl silane) (DuPont) have BET surface areas, obtained by nitrogen isotherms, of 835 m^2/g and 1069 m^2/g, respectively [16]. The two materials are of similar chemical structure and morphology. The Aerosil R812 is reported by Degussa to have a surface area of 260 m^2/g. The samples were loosely packed into 10 mm diameter L-shaped sample tubes, evacuated to $5 \cdot 10^{-5}$ torr, and cooled to either 10 or 90 K before the introduction of polarized xenon. The total surface area present in the sample tubes
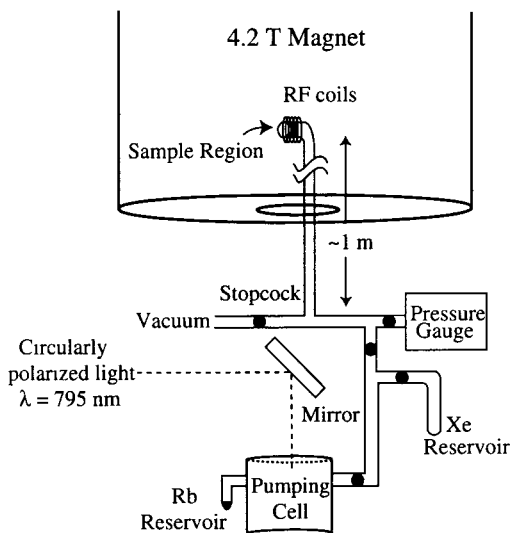
Fig. 1. Optical-pumping apparatus, consisting of a 35 cm³ cylindrical glass cell, Rb reservoir, and a xenon reservoir. These components are linked by glass vacuum lines with a series of stopcocks. One glass line extends into the probe and to the sample. The laser beam passes through a circular polarizer and illuminates the cell where optical pumping takes place. See text for details.

was approximately 300 m² for the poly(triarylcarbinol) and poly(tetrabiphenyl silane) samples and 30 m² for Aerosil R812 sample.

The optical-pumping apparatus, Fig. 1, is located in the fringe magnetic field beneath a superconducting magnet. The sample region in the probe is connected to the pumping cell through a glass transfer line and separated by a series of stopcocks. The pumping cell, a 35 cm³ glass cylinder, is coated with a thin film of rubidium and can be heated by flowing nitrogen gas to maintain the temperature in the range of 80–100°C during laser irradiation. The elevated temperature increases the rubidium vapor pressure to $\sim 6 \cdot 10^{-6}$ torr, which is sufficient to absorb the laser light. The cell is illuminated by circularly polarized light from a 2 W Titanium-Sapphire ring laser (Schwartz Electro-Optics), typically operated at 1–1.5 W, which is pumped with a 10 W Argon laser (Coherent Laser Group Inc.). The laser wavelength is tuned to the rubidium D1 optical transition at 794.7 nm, and the rubidium fluorescence is monitored with an infrared viewer. Enriched ^{129}Xe (80%, EG + G Mound) is stored in a sidearm that also contains rubidium. (The rubidium reacts with impurities in the xenon and serves to purify it before it is loaded into the pumping cell.) Typically, 200–400 torr of xenon ($\sim 3 \cdot 10^{-4}$ moles) are loaded into the pumping cell and irradiated for 20–30 minutes. The cell is then cooled to 40°C to lower the vapor pressure of the rubidium. The xenon gas is introduced to the pre-cooled sample region by opening a stopcock and allowed to equilibrate with the sample surface for a few seconds (5–10) before NMR spectra are acquired.
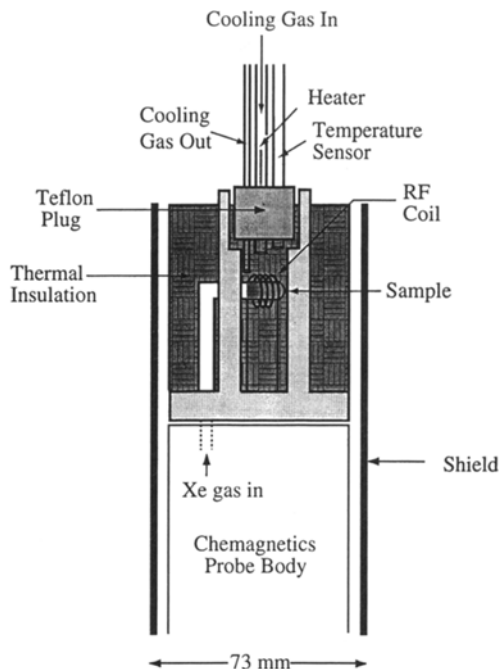
Fig. 2. A schematic drawing of the probe. The probehead consists of an RF coil in a small sample region, surrounded by thermal insulation. A vacuum insulated liquid helium transfer line is used to inject cooled nitrogen gas or liquid helium, which is resistively heated, into the sample region from the top of the magnet. The exit gas is vented through another vacuum insulated line. A shielded thermocouple is installed close to the sample.

Figure 2 shows a schematic drawing of the probe, a modified commercial double resonance probe (Chemagnetics). The main modification is the small size of the cold region; this facilitates fast change of sample temperature. A vacuum insulated liquid helium transfer line is used to inject cooled nitrogen gas or liquid helium into the sample region from the top of the magnet. The exit gas is vented through another vacuum insulated line. A shielded thermocouple is installed very close to the sample. The probe can be cooled to liquid nitrogen temperature in about 10 minutes and can be warmed up quickly when flushed with warm nitrogen gas. When liquid helium is used, the sample can be cooled down to ~10 K. The temperature in the probe can be controlled to an accuracy of a few Kelvins. In our apparatus the xenon and proton NMR frequencies are 49.45 and 178.75 MHz, respectively. The typical 90° pulse lengths used are 6 μs for xenon and 4 μs for proton.

Figure 3 shows the timing diagrams for the experimental procedures, including the pulse sequences. Fig. 3a shows the multiple contact sequence used for the optical-pumping cross-polarization (OPCP) experiment. In this experiment, after the polarized xenon is adsorbed onto the sample surface and allowed to equilibrate, a 90° pulse is applied to the xenon spins, which are then spin-locked for the dura-
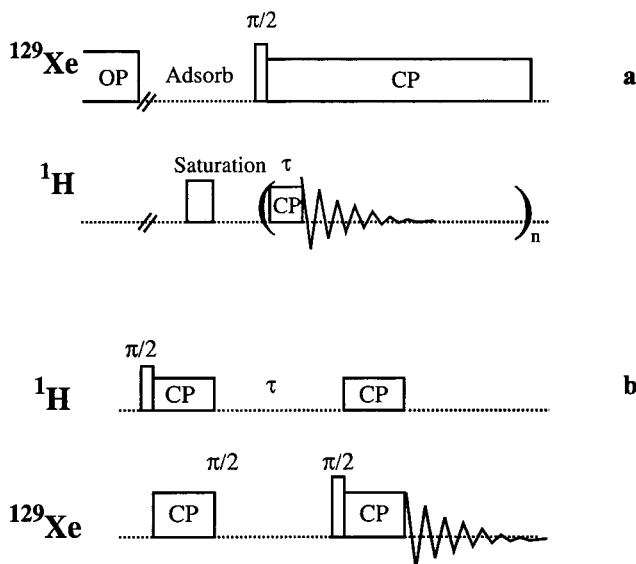
Fig. 3. Pulse sequences used in the experiments. In **a**, the optical-pumping multiple contact cross-polarization sequence is shown. The xenon is spinlocked for the duration of the experiment. The proton spins are repeatedly cross polarized (up to 8 times) to the xenon by Hartmann-Hahn matching. **b** The DRAIN sequence is shown. An initial CP sequence is followed by storage of xenon magnetization along the z-axis for a fixed time τ, and a second cross-polarization step. The second contact time is varied and τ is set to 1 s.

tion of the acquisition. A Hartmann-Hahn matching pulse is applied to the proton spins for a time τ to establish a dipolar contact between ^{1}H and ^{129}Xe, and the proton signal is acquired immediately afterward. This ^{1}H-^{129}Xe contact and signal acquisition are repeated up to 8 times while the xenon spins remain spin-locked. Fig. 3b shows a sequence used to examine the efficiency of polarization transfer from the xenon to the proton reservoir. The first step of the sequence is a proton to xenon cross polarization to establish the xenon signal. The enhanced xenon magnetization is then stored along the z axis for at time τ. The xenon and proton reservoirs are again brought into dipolar contact and the xenon magnetization is consequently drained away. The xenon signal is measured as a function of the second contact time. We will refer to this sequence as the DRAIN experiment.

3. Results and Discussion

To study the details of the CP process, we have performed multiple contact experiments in order to monitor the complete magnetization transfer process. The basic idea is that the observed ^{1}H signal is proportional to the ^{129}Xe magnetization prior to the cross-polarization contact, and thus it is a measure of the de-

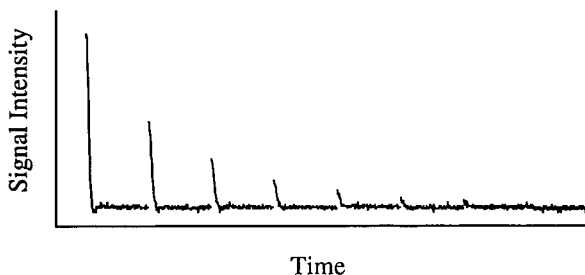cay of ^{129}Xe polarization during the complete CP experiment. Moreover, this experiment may yield multiple signals from a single OPCP run, and it is possible to combine these signals to further increase the signal-to-noise ratio.

Figure 4 shows a typical multiple contact signal for the ^{129}Xe-^{1}H OPCP of xenon adsorbed on poly(tetrabiphenyl silane) at 90 K. Each of the signals is a free induction decay (FID) immediately after one contact. The acquisition time for each FID is 128 μs. In this example, there are 8 contacts of 4 ms each, with resulting signals in the first seven contacts. The FID signal intensity decays with each contact. It is clear that the ^{129}Xe spin magnetization is not transferred completely to the ^{1}H spins during the first contact period.

The CP process can be understood as the transfer of nuclear Zeeman energy in the rotating frame. The energy of each nuclear spin reservoir is given by $N(\gamma H_1)P$, where N represents the number of spins, H_1 is the radiofrequency (RF) magnetic field for each nucleus, and γ is the gyromagnetic ratio of the nucleus, and P is the polarization of each nuclear species. Conservation of energy dictates that the energy gain in the proton spin reservoir equals the energy loss in the xenon spin reservoir,

$$N_{\mathrm{H}}(\gamma H_1)_{\mathrm{H}} P_{\mathrm{H}} = N_{\mathrm{Xe}}(\gamma H_1)_{\mathrm{Xe}}(P_0 - P_{\mathrm{Xe}}) \ , \tag{1}$$

where P_0 represents the initial xenon polarization prior to the contact period. Under the Hartmann-Hahn matching condition, the ratio of the RF field at the NMR frequency of ^{129}Xe and ^{1}H equals the inverse of the γ ratio, $(\gamma H_1)_{\mathrm{Xe}} = (\gamma H_1)_{\mathrm{H}}$. We assume that during the contact period, a thermal equilibrium is reached between the proton and xenon spin systems in the rotating frame, so that the final polarizations of the two spin systems are the same, $P_{\mathrm{Xe}} = P_{\mathrm{H}} \equiv P$. The final polarization after each contact becomes:

$$P = P_0\left(1 + \frac{N_{\mathrm{H}}}{N_{\mathrm{Xe}}}\right)^{-1} . \tag{2}$$

If $N_H = N_{Xe}$, then $P = 0.5 P_0$. Therefore, if the number of protons is equal to the number of xenon atoms, each signal in the multiple contact sequence should be half the intensity of the previous signal. If $N_{Xe} \gg N_H$, there should be little decay of the signal in subsequent contacts. Conversely, if $N_H \gg N_{Xe}$, then the proton signal should decay rapidly. For multiple contact experiments, one would expect the intensity of each subsequent FID to decay exponentially:

$$P_n = P_{n-1} \left(1 + \frac{N_H}{N_{Xe}} \right)^{-1} = P_0 \exp(-\alpha \cdot n) \ , \tag{3}$$

where $\alpha = \ln(1 + N_H/N_{Xe})$. If the thermal equilibrium is not reached, the decay factor α may also be dependent on the length of the contact time, and, in general, should be smaller than $\ln(1 + N_H/N_{Xe})$. Experimentally, the observed decay factor α is close to $\ln 2$. Fig. 5 shows the signal intensity as a function of the number of dipolar contacts for the contact times of 0.5, 1, 4, and 10 ms for OPCP on the poly(tetrabiphenyl silane) sample. The decay factors α for the four contact times are 0.43, 0.54, 0.55, and 0.76, respectively. The dependence of α on contact time is qualitatively consistent with the above considerations. Nuclear relaxation certainly contributes to the signal decay, however, since the $T_{1\rho}$ of xenon under these conditions is measured to be 33 ms, this contribution may be neglected in all but the longest contact time experiments.
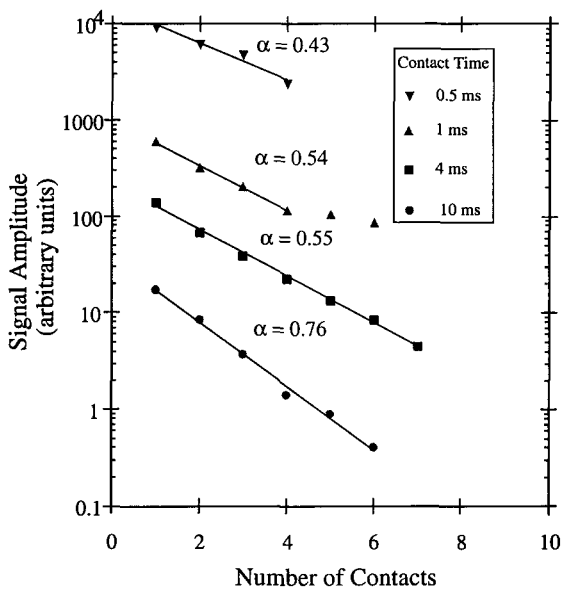
Fig. 5. Signal intensity versus number of contacts for contact times of 0.5, 1, 4, and 10 ms, obtained by OPCP experiments on poly(tetrabiphenyl silane). The signal intensities have been scaled for clarity.
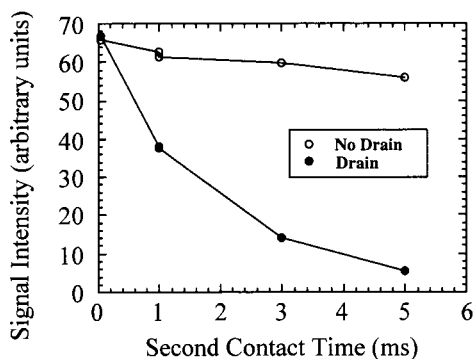
Fig. 6. The ^{129}Xe signal intensity is compared with and without the second proton matching pulse in the DRAIN experiment. Without the matching pulse, the xenon signal intensity decays quite slowly. With the matching pulse, the xenon signal is essentially drained with a 5 ms contact time.

To further address the question of CP efficiency, we have directly observed the ^{129}Xe signal as a function of the contact time in the DRAIN experiment. This experiment was performed on a sample of poly(triarylcarbinol) sealed with 2 atm pressure of xenon gas and a poly(tetrabiphenyl silane) sample connected to the glassware of the optical pumping cell with ^{129}Xe pre-adsorbed and equilibrated for at least 20 minutes. The results from both samples are similar. The data for the poly(triarylcarbinol) sample are displayed in Fig. 6. The xenon signal observed after a proton matching pulse decays very rapidly, while the xenon signal observed when the experiment is performed without the proton matching pulses shows only a very slight decay, likely due to (rotating frame) spin-lattice relaxation of ^{129}Xe magnetization. We conclude that the proton matching pulse establishes dipolar contact between ^{129}Xe and ^{1}H and effectively drains away the xenon nuclear Zeeman energy in the rotating frame. The polarization is transferred completely from the xenon to the proton spin reservoir within a 4–5 ms contact period, indicating efficient magnetization transfer. We have also investigated the effects of xenon spin diffusion by varying the delay times between the contacts in the DRAIN experiment, and preliminary results indicate that xenon spin diffusion does not limit the cross polarization efficiency.

In the DRAIN experiment the xenon magnetization is completely transferred in 4–5 ms; however, in the multiple contact experiments, signal is still obtained after seven 4 ms contacts! This implies that in the multiple contact experiment ^{129}Xe magnetization is added into the xenon spin reservoir during or after each contact period. One possible explanation is that after xenon is released into the sample region, some of the xenon atoms may not contact the surface immediately. Due to the long T_1 of xenon in the gas phase, these xenon atoms remain polarized. As these xenon atoms condense onto the surface during the course of the experiment, they can replenish the polarization of the xenon reservoir and contribute to the second and subsequent CP ^{1}H signals.

The DRAIN sequence was also used to calculate the enhancement of the surface ^{1}H signal obtained using OPCP. For this purpose, however, the ^{1}H signal, rather than the xenon signal, was detected. By utilizing the two CP steps in this manner, only the surface protons (i.e., the protons near xenon) contribute to the detected signal. This proton signal obtained by signal averaging can be directly compared to the signal obtained via the OPCP experiment, which also detects only surface protons. Thirty-two signal averages using the DRAIN sequence were accumulated on the sample of poly(triarylcarbinol) after xenon gas was adsorbed at 90 K in the same fashion as in an OPCP experiment. A single shot acquisition of xenon adsorbed on poly(triarylcarbinol) using OPCP resulted in an enhancement of roughly 800. Although encouraging, this factor is still an order of magnitude less than the direct enhancement in the [129]Xe signal obtained for laser-polarized xenon over thermal [129]Xe. These figures suggest that not all of the polarized xenon is in close contact with the surface for magnetization transfer to occur. The main difference in the procedure of the DRAIN and OPCP experiments, besides the polarization of [129]Xe, is that in the OPCP experiment the xenon is rapidly introduced to the sample and may not be sufficiently cooled to the sample temperature prior to the execution of the experiments. This difference introduces the possibility that the cross-polarization enhancement obtained using OPCP is partly limited by diffusion of the xenon from the gas phase to the sample surface.

Xenon mobility may be reduced at lower temperatures. We have performed cross-polarization experiments from ^{1}H to [129]Xe adsorbed on poly(triarylcarbinol) at 10 K, and they clearly demonstrate increased efficiency of dipolar contact and polarization transfer. Fig. 7 shows a comparison of the signal intensity as a function of the contact time for the CP experiments at 10 and 90 K. At 10 K the signal reaches the maximum after a 2 ms contact time, while at 90 K, the signal
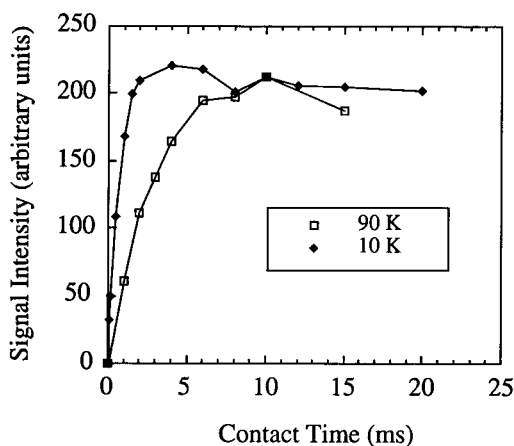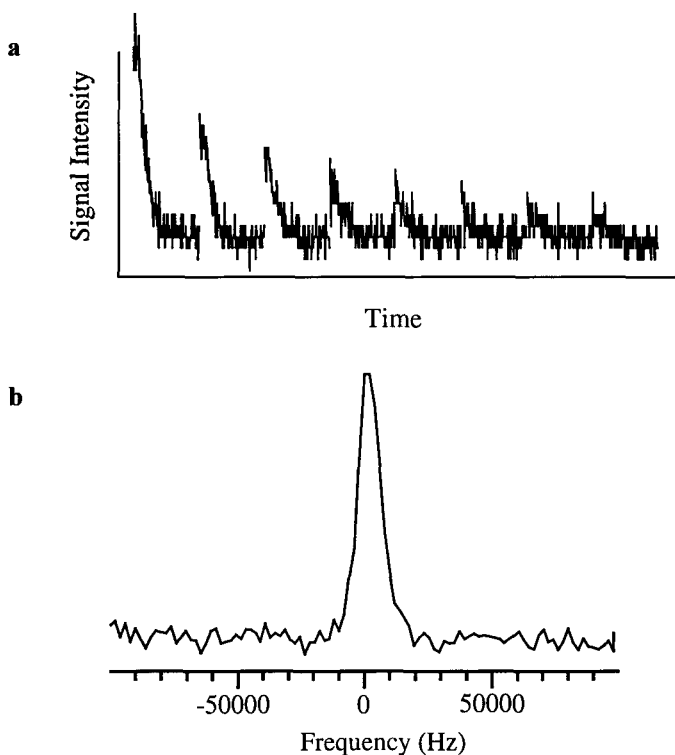

Fig. 7. The contact time dependence of [129]Xe signal from CP from ^{1}H on poly(triarylcarbinol) at 10 and at 90 K. At 10 K, the signal maximum is reached with a 2 ms contact time, as compared to 90 K, when the signal maximum is not reached until 8–10 ms. The lines are provided to guide the eye.

Fig. 8. a ^{1}H signals from the Aerosil R812 sample in a multiple contact optical pumping cross-polarization experiment performed at 90 K. **b** The spectrum obtained by Fourier transform of the first signal in **a**. The full-width-half-maximum is 20 kHz.

reaches the maximum around 8–10 ms. These results suggest that significant motion of the adsorbed xenon atoms does indeed exist on the time scale of a few milliseconds at 90 K. From a two-exponential fit to the 10 K experiment, we have obtained a value of 0.7 ms for T_{IS}, which is comparable to the values expected for [13]C-[1]H (~0.1–1 ms) [4].

The previous experiments were all performed on poly(triarylcarbinol) or poly-(tetrabiphenyl silane), both of which are ultra-high surface area and microporous. The first OPCP ^{1}H spectra obtained from a lower total surface area sample, Aerosil R812, are shown in Fig. 8. The surface area of the Aerosil R812 is quite high, 260 m^2/g, yet the sample mass used in our study was only 0.1 g. Thus the total surface area of this sample is around 30 m^2, a factor of 10 less than for the other two samples. Obtaining OPCP surface ^{1}H signals from the Aerosil sample represents an encouraging step toward investigating lower surface areas. Adsorbing xenon onto samples with a stronger xenon-surface interaction may produce more effective wetting and, therefore better proton-xenon dipolar contact; this should enable lower surface area materials to be studied by this method.

4. Conclusions

Optical Pumping Cross Polarization can be an effective way of obtaining surface selective NMR signals, particularly when combined with techniques such as multiple contact CP. We found that the magnetization transfer process depends not only on the contact times used during the CP experiments, but also on the diffusion of polarized xenon to the surface. The continual diffusion of polarized xenon allows for a number of acquisitions to be obtained and possibly averaged. The signal enhancement of the surface protons was found to be approximately 10^3, although this might be improved by dispersing the sample onto the cold surface of the sample cell and allowing the xenon to equilibrate longer before beginning acquisition. The first OPCP experiment on a sample with $30 \, m^2$ total surface area is reported, representing an encouraging step towards observing low surface area materials. Transferring magnetization to other nuclei such as ^{13}C [17] or ^{29}Si, which are more sensitive to local structural and chemical properties, would be another valuable extension of this method. Experimental efforts in this direction are currently in progress in our lab.

Acknowledgements

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