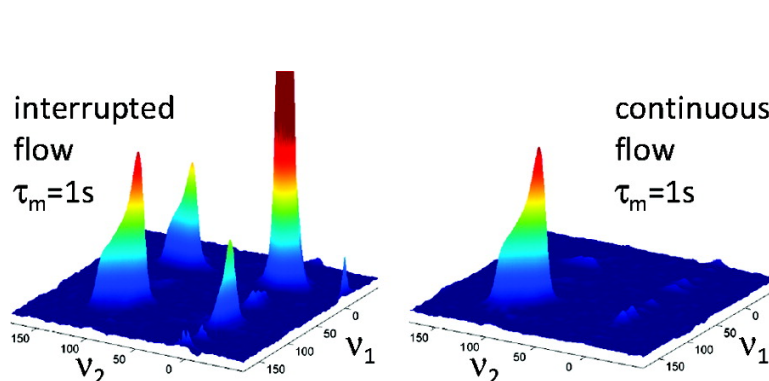## Communication

Dramatic Enhancement of Hyperpolarized Xenon-129 2D-NMR Exchange Cross-Peak Signals in Nanotubes by Interruption of the Gas Flow

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Dramatic Enhancement of Hyperpolarized Xenon-129 2D-NMR Exchange Cross-Peak Signals in Nanotubes by Interruption of the Gas Flow

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In our recent JACS article,[1] we presented a study of the exchange dynamics of Xe gas atoms localized near the openings of self-assembled L-alanyl-L-valine (AV) dipeptide nanotubes[2,3] utilizing continuous-flow hyperpolarized two-dimensional NMR exchange spectroscopy (CFHP 2D-EXSY).[4−14] In this method, hyperpolarized gas is transported from the spin-exchange optical pumping cell to the NMR sample space at a constant flow rate, enabling rapid acquisition of 2D spectra with enhanced sensitivity. In deriving the expressions for the cross-peak signals under flow conditions, we noted that the finite residence time of the hyperpolarized gas inside the sample space may under certain conditions suppress the gas-phase diagonal-peak and cross-peak signals associated with exchange between the surface and gas phases. Moreover, we suggested that the undesired signal suppression could be mitigated simply by incorporating a brief pause in the gas flow during the mixing time of the 2D-EXSY pulse sequence. Here we present the dramatic experimental verification of this effect in AV nanotubes.

As in ref 1, a 15 mg AV sample was evacuated in-situ to $\sim 10^{-5}$ Torr at 100 °C for 2−3 h prior to experiments. The gas mixture (Spectra Gases) consisted of 2% natural abundance ^{129}Xe, 2% N_2, and 96% He at a total pressure of 4600 mbar. The ^{129}Xe spin polarization is estimated to be $\sim 20\%$. Only hyperpolarized ^{129}Xe yields observable NMR signal, since the thermally polarized gas cannot be detected at this density without signal averaging. A fractional occupancy of $\theta = 0.047$ in AV nanotubes was inferred from the Xe chemical shift tensor, as described in ref 5. Spectra were acquired at -10 °C in a magnetic field of 9.4 T (110.6 MHz ^{129}Xe Larmor frequency). The isotropic chemical shift difference between the gaseous and adsorbed phases of ^{129}Xe is about 110 ppm. The continuous-flow hyperpolarized ^{129}Xe NMR setup is the same as that described in ref 1, except for one modification: to control the flow of hyperpolarized gas, the outlet of the sample space was connected to a two-way solenoid valve (Jefferson Solenoid Valves). An auxiliary transistor-to-transistor logic (TTL) gate on the Bruker Avance NMR spectrometer was used to switch the solenoid valve from the pulse program.

Two different 2D-EXSY NMR pulse sequences, adapted for experiments with hyperpolarized gas, are presented in Figure 1. In the continuous flow sequence (Figure 1a), the stream of hyperpolarized gas is circulated through the sample space at a steady rate of 100 mL/min during the experiment, with no interruption.

In principle, spectra acquired in CF mode will not be affected by gas flow if the spin relaxation time of the gas is much shorter than the residence time of Xe atoms in the sample space (i.e., $T_{1g} \ll \tau_R$). In diamagnetic materials devoid of paramagnetic defects or impurities, ^{129}Xe spin relaxation times in the gaseous or adsorbed phases are typically much longer than any of the other time-scales relevant to the experiment. In such cases, spin relaxation may be neglected, and the diagonal gas peak and all cross-peak signals representing exchange will generally depend on τ_R and the exchange rate. For example, the expressions for the cross-peak signal for
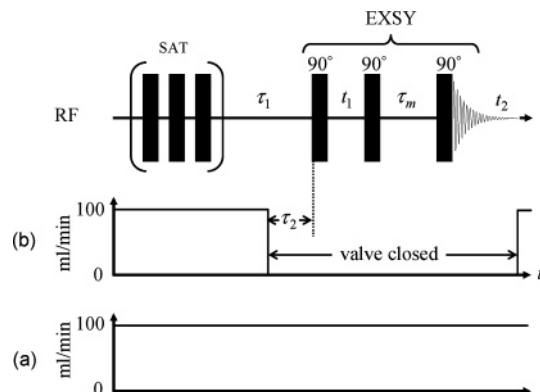

Figure 1. Pulse sequences for (a) continuous flow (CF) and (b) interrupted flow (IF) hyperpolarized 2D-EXSY. The solenoid valve is closed in advance of the first pulse of the EXSY sequence for a fixed period $\tau_2 = 1$ s to allow settling. The SAT pulse train destroys all ^{129}Xe nuclear magnetization in the sample holder.

desorption from a surface consisting of equivalent adsorption sites to the gas phase is as follows:[1]

$$I_{c \to g}(\tau_1, \tau_m) \propto M_c^o(\tau_1) \frac{k_d}{\tau_R^{-1} - k_d}(e^{-k_d \tau_m} - e^{-\tau_m / \tau_R}) \quad (1)$$

A similar expression describes the reverse process. Here, M_c^o is the magnetization of the adsorbed gas at the end of the repolarization delay, τ_1, and k_d is the desorption rate constant. Equation 1 reveals the onset of cross-peak suppression when $\tau_R^{-1} \geq k_d$. Furthermore, the mixing time τ_m for which maximum cross-peak signals are obtained is shifted to shorter values, and in the $\tau_R \to 0$ limit, the cross-peaks vanish entirely. In this regime, the decay of the gas-phase diagonal-peak signal is also dominated by the flow of tagged gas atoms out of the sample region. Because gas atoms are constantly purged from the sample space on the time-scale of the residence time, τ_R, the cross-peaks for both the forward and reverse exchange processes are suppressed. Although τ_R can be increased simply by reducing the flow rate, this is not usually favorable for retaining high polarization due to relaxation losses in the gas handling system during transport from the pumping cell to the sample space.[14]

In the interrupted flow (IF) pulse sequence shown in Figure 1b, the hyperpolarized gas flow is halted prior to the 2D-EXSY pulse sequence. The solenoid valve is closed at the end of τ_1 and a settling time of $\tau_2 = 1$ s is allowed prior to application of the $\pi/2$ EXSY preparation pulse. Immediately following the acquisition time, the polarized gas flow is resumed. Stopping the flow during the mixing time allows molecules desorbing from the surface, or nanotube channels, as in the present case, to accumulate in the sample space for detection. For the reverse process, a longer residence time increases the probability that gas atoms tagged by the preparation
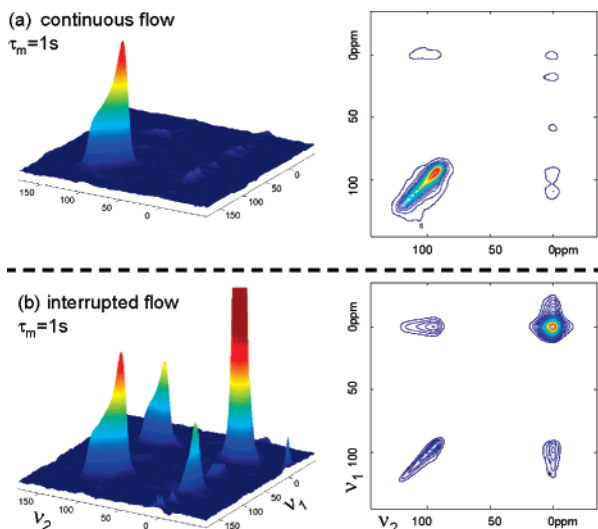
Figure 2. Hyperpolarized ^{129}Xe 2D-EXSY spectra of Xe in AV at −10 °C using a mixing time $\tau_m = 1$ s, with $\tau_1 = 4$ s, and $\tau_2 = 1$ s. Spectrum a was acquired in continuous flow (CF) mode. Spectrum b was acquired in interrupted flow (IF) mode (see text). At each t_1 point, 8 transients were signal averaged. Spectra were collected with 100 and 1024 points in the t_1 and t_2 dimensions with a 26 kHz spectral width. A 300 Hz line-broadening was applied with respect to both time dimensions prior to Fourier transformation. Chemical shifts are referenced to dilute Xe gas. The total experiment time for each 2D spectrum was ∼65 min. In spectrum b, the gas-phase diagonal peak is cropped to facilitate comparison of the cross-peaks.

pulse will be adsorbed by the nanotubes during the mixing time. In principle, the mixing time dependences of the cross- and diagonal-peak signal integrals in IF mode spectra should be essentially the same as in a thermally polarized experiment.

The CF and IF mode hyperpolarized ^{129}Xe 2D-EXSY spectra acquired in AV nanotubes at $\tau_m = 1$ s are presented in Figure 2. Clearly, the signal-to-noise ratios of both the gas-phase diagonal and exchange cross-peaks are much higher in the spectra acquired in IF mode. The CFHP 2D-EXSY pulse sequence barely yielded any cross-peaks. In contrast, the IF mode spectrum exhibits intense gas-phase diagonal and exchange cross-peak signals. The differences in the spectra obtained under interrupted and continuous flow conditions are particularly dramatic in the 3D representations. Thus, by interrupting the gas flow during the EXSY pulse sequence, the cross-peak signals were enhanced by a factor of ∼60. We refer to this experimental method as IFHP-EXSY.

To summarize, a simple but highly effective modification of the continuous flow hyperpolarized EXSY experiment has been demonstrated in AV, a polycrystalline nanotube material. IFHP-EXSY appears particularly well-suited for studies of diffusion-limited gas exchange kinetics, as in nanotube systems. Since the experimental uncertainty in kinetic parameters extracted from 2D-EXSY spectra is highly sensitive to the signal-to-noise ratio, IFHP-EXSY will provide greater accuracy in rate constant determination and facilitate measurement of smaller exchange rate constants. IFHP-EXSY may also be applicable to other hyperpolarized species such as ^{1}H or ^{13}C generated from parahydrogen[15,16] or DNP.[17] In principle, mixing times in the interrupted flow experiment are limited only by the intrinsic spin relaxation times. The ability to probe longer mixing times will facilitate extension of hyperpolarized 2D-EXSY to slower exchange processes or longer diffusion time/length scales for characterization of pore−space architecture, exchange and transport processes in nanotubes and other nanoporous materials.

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