Dramatic Enhancement of Cross-Peak Signals in Hyperpolarized NMR Exchange Spectroscopy by Interruption of the Gas Flow

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Introduction

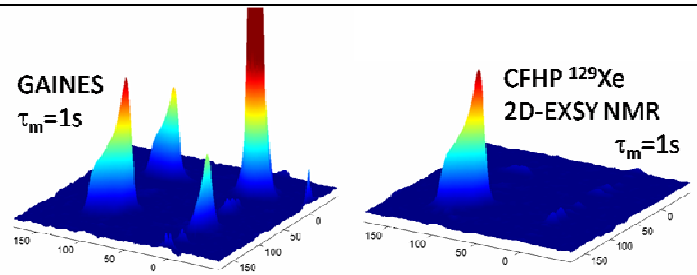
In our recent JACS article[1] we presented a study of the exchange kinetics of Xe atoms localized near the openings of self-assembled L-Alanyl-L-Valine (AV) dipeptide nanotubes[2,3] utilizing continuous-flow hyperpolarized 2D-EXSY NMR. In CFHP 2D-EXSY, hyperpolarized gas is transported from the optical pumping cell to the sample space at a constant flow rate, enabling the 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 suppress diagonal- and cross-peak signals, and we suggested that the undesired signal suppression could be mitigated simply by interrupting the gas flow during the mixing time of the 2D-EXSY pulse sequence.[1] Here we present the dramatic experimental confirmation of this effect in AV.

Experimental

A 15mg AV sample was evacuated in-situ to ~10^{-5}torr at 100 °C for 2-3 hours prior to experiments. The gas mixture consisted of 2% ^{129}Xe, 2% N_2 and 96% ^{4}He at a total pressure of 4600mbar. A fractional nanotube occupancy of $\theta = 0.047$ was inferred from the Xe shift tensor. The continuous-flow hyperpolarized ^{129}Xe NMR setup is the same as that described in Ref. 1, except for one modification: the outlet of the sample space was connected to a two-way solenoid valve. An auxiliary TTL gate on the Bruker spectrometer was used to switch the solenoid valve from the pulse program to stop the flow of gas.

Results and Discussion

The CF and IF mode hyperpolarized ^{129}Xe 2D-EXSY spectra acquired in AV nanotubes at $\tau_m = 1$s are presented below. The continuous-flow sequence barely yielded any cross-peaks. In contrast, the IF mode spectrum exhibits intense gas phase diagonal and exchange cross-peak signals. Thus, by interrupting the gas flow during the EXSY pulse sequence, the cross-peak signals were enhanced by a factor of ~60.[4]



Hyperpolarized xenon-129 EXSY spectra in AV nanotubes acquired under continuous (right) and interrupted gas flow conditions using a mixing time of 1s. Spectra were acquired at −10 °C at 9.4T.

Conclusions

Our new method will provide greater accuracy in rate constant determination, and facilitate measurement of smaller exchange rate constants. It may also be applicable to other hyperpolarized species such as ^{1}H or ^{13}C generated from parahydrogen or DNP. 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 nanotubes or nanoporous materials in general.

Acknowledgements

Construction of the Xenon-129 polarizer was supported by the NHMFL In-House Research Program and UF.

References

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[4] C.-Y. Cheng, J.P. Pfeilsticker and C.R. Bowers, *submitted for publication* (2007).