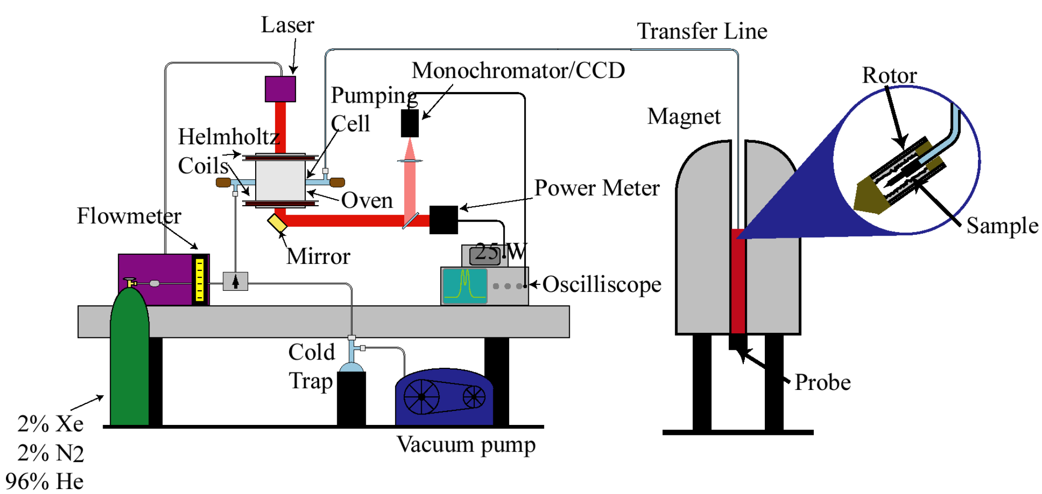
Optical Pumping MAS NMR

Nuclear Magnetic Resonance is a very valuable analytical technique for chemical analysis. However, NMR has two major shortcomings: it is not as sensitive as other analytical techniques and it can only analyze the entire bulk of a sample. This limits the applicability of NMR for surface analysis of samples. Optical pumping magic angle spinning NMR attempts to solve these problems and make NMR more applicable to surface studies.

Optical Pumping Magic Angle Spinning is used to enhance surface species signals of solids in solid state NMR. The samples are spun (2-6 kHz) at a particular angle. This spinning averages out certain NMR interactions, which broaden solid signals and normally back solid state NMR more difficult. Optical pumping enhances the surface species signal of solid samples (it is also used in liquids and for MRIs). An inert gas (xenon in our case) is hyperpolarized by a NIR laser then flowed continuously into the NMR magnet and onto the sample. A diagram of our set-up may be seen below.

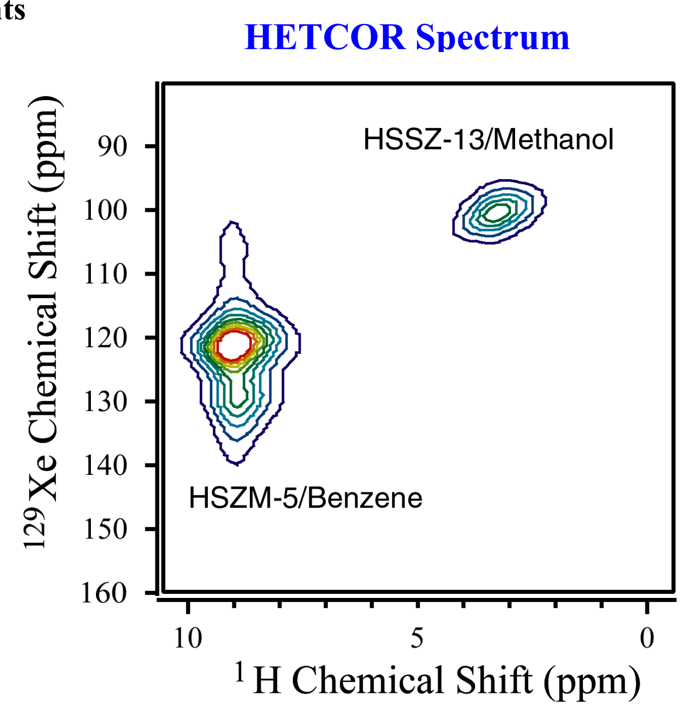


Optical Pumping Set Up

Xenon NMR spectra may then be taken, or polarization may be transferred from the hyperpolarized xenon to the sample. Polarization transfer may occur using one of two mechanisms. Spin Polarization Induced Nuclear Overhauser Effect allows polarization to be naturally transferred over time from one nucleus to another through the Nuclear Overhauser Effect. Cross Polarization (CP) locks both nuclei (xenon and the target of

polarization transfer) with simultaneous electromagnetic fields at two separate frequencies. This creates a quantum transition that allows polarization to be efficiently transferred from xenon to another nucleus (hydrogen).

We have performed a variety of OP/MAS NMR experiments in the Raftery laboratory. SPINOE experiments have performed to enhance the carbon signal of methanol adsorbed on a silica surface. Temperature dependent SPINOE experiments have also been performed on silica to understand the temperature/enhancement relationship. Temperature dependent CP experiments have also been performed in order to compare the effectiveness of CP versus SPINOE at different temperatures. Two-dimensional CP experiments (HETCOR) have also been performed. A mixture of two different zeolites with two different adsorbates was examined using HETCOR in order to determine which adsorbate was on which zeolite. The HETCOR spectrum is shown at the right.



EXSY (EXchange SpectroscopY) experiments were also performed. EXSY is a two-dimensional experiment where xenon is examined over time to characterize how xenon diffuses or moves through a sample. We examined porous silicon using EXSY experiments. The movement of xenon gives an idea of how gas moves through the pores of the silicon and can allow a physical model of porous silicon to be constructed.

There is an array of future experiments for Optical Pumping Magic Angle Spinning NMR. We plan on examining a variety of different substances (low surface area samples, air sensitive catalysts, etc). We also plan on attempting CP from xenon to other nuclei besides hydrogen (currently only Xe-H CP has been performed).

Publications

1. J. Smith, L.J. Smith, K. Knagge, E. MacNamara and D. Raftery, "Hyperpolarized Xenon-Mediated Cross-Polarization to Material Surfaces Observed at Room Temperature and Above," *J. Am. Chem. Soc.* **123**, 2927 (2001).

2. L.J. Smith, J. Smith, E. MacNamara, K. Knagge and D. Raftery, "Variable Temperature Study of the Cross-Relaxation Dynamics in the Hyperpolarized Xenon-Induced Enhancement of Surface Nuclei," *J. Phys. Chem. B* **105**, 1412 (2001).

3. E. MacNamara, C. V. Rice, J. Smith, L. J. Smith and D. Raftery, "Cross- Relaxation Dynamics between Laser-Polarized Xenon and a Surface Species using a Simple Three Spin Model," *Chem. Phys. Lett.* **317**, 165 (2000).

4. E. MacNamara, G. Fisher, J. Smith, C. V. Rice, S.-J. Hwang and D. Raftery, "Cross Polarization and Cross Relaxation from Laser-Polarized Xenon to Surface Species," *J. Phys. Chem. B* **103**, 1158 (1999).

5. D. Raftery, E. MacNamara, G. Fisher, C. V. Rice and J. Smith, "Optical Pumping and Magic Angle Spinning: Sensitivity and Resolution Enhancement for Surface NMR Obtained with Laser-Polarized Xenon", *J. Am. Chem. Soc.* **119**, 8746 (1997).