Low Field Dynamic Nuclear Polarization for Studying Soft Matter Systems

Alissa Cote

Materials Science and Engineering, University of Illinois at Urbana-Champaign

NNIN REU Site: Nanotech @ UCSB, University of California, Santa Barbara, CA

NNIN REU Principal Investigator(s): Prof. Songi Han, Chemistry and Biochemistry, University of California, Santa Barbara

NNIN REU Mentor(s): Mark Lingwood, Chemistry and Biochemistry, University of California, Santa Barbara

Contact: acote2@illinois.edu, songi@chem.ucsb.edu, mlingwood@chem.ucsb.edu

Abstract:

Nuclear magnetic resonance (NMR) is a versatile technique for soft matter analysis. We can use NMR for imaging, as in the MRI of a brain, or to study the water dynamics in lipid membranes, the structure of proteins and their aggregates, and the aggregation of asphaltene, an element of crude oil. Although NMR is versatile, it also poses some challenges. NMR is an insensitive technique with low contrast. When studying large molecular assemblies, it is difficult to know if we see aggregation because of the insensitivity. In order to solve this problem, we can introduce a probe molecule, which in this case is a nitroxide radical, which gives localized information regarding the area of placement. We can either detect this probe molecule directly, through electron spin resonance (ESR), or transfer the information to the NMR signal of neighboring nuclei by using both ESR and NMR simultaneously; this is known as dynamic nuclear polarization (DNP).

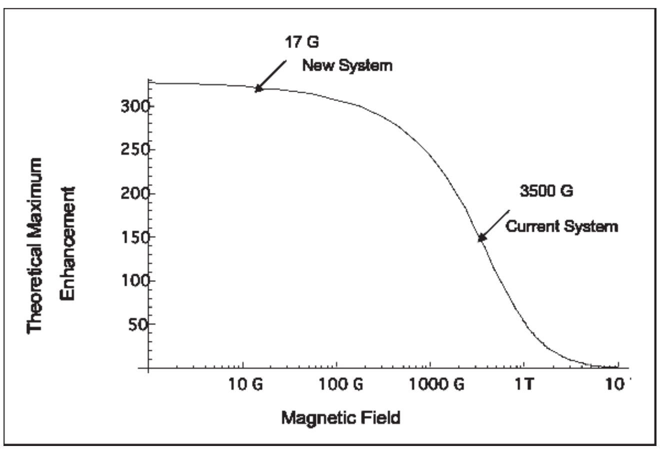


Figure 1; Plot of magnetic field vs. theoretical maximum enhancement

Introduction:

DNP is a method to enhance NMR signal through polarization transfer from electron spins to nuclear spins, and can study water content and viscosity in lipid membranes. At 3500 G, which is the field of our current working DNP system, we have less-than-maximum or even no NMR signal enhancement at all. This project focuses on moving to a magnetic field of about 20 G since the theoretical maximum enhancement increases at a lower field (Figure 1). By moving to a low field, we will be able to both compare the DNP enhancement of samples at different fields and test samples in which no DNP enhancement was observed at 3500 G. We will focus on the design, construction, and testing of this new DNP system, and show some initial results.

In order to understand DNP, one must be able to understand NMR and ESR. When certain nuclei are placed in a magnetic field, the nuclear spin energy splits into different levels. This energy difference can be detected by applying radio frequency radiation to the nuclei. The small differences in the splitting of the energy levels give information on the molecule, seen in the NMR signal. Like NMR, ESR uses electromagnetic radiation to detect differences in energy levels. However, instead of detecting the nuclei, ESR detects the electron spin of free radicals or other paramagnetic species. This is only useful in systems which contain free electrons. Since the free electrons have a higher energy splitting than nuclei, ESR has greater signal sensitivity than NMR. When the free electrons are in close contact with the nuclei, NMR and ESR can be used simultaneously in a process known as DNP. Saturating the electrons with strong electromagnetic radiation perturbs the electron spins, which transfer the higher polarization to the nearby nuclei, and enhances the NMR signal.

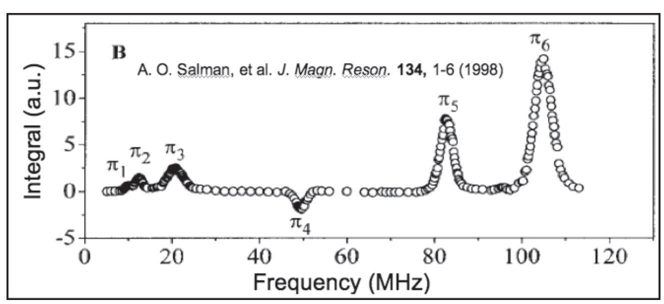


Figure 2: Example of an ESR spectrum at 15.3 G.

Moving to low fields has many advantages, but there are also some disadvantages. The ESR spectrum is much different at low fields than at high fields, and this spectrum can only be detected through DNP. At high fields, the applied magnetic field dominates the spectrum and we see three transitions, one for each spin state of the nitrogen nucleus in the nitroxide. However, at low fields, the applied field no longer dominates, but the nitrogen transitions dominate, and we see many more peaks in the ESR spectrum (Figure 2).

Experimental Procedures:

Because DNP instruments are not commercially available, we built our own. First we built the electromagnet, a Helmholtz coil design, which consists of two coils placed on the same axis with the same current flowing through each one producing a homogeneous magnetic field. Our sample can be easily inserted or removed from the magnet.

The NMR system contains four parts: a laptop, an NMR spectrometer, the magnet, and a coil. The laptop first sends a signal to the spectrometer to send a radiofrequency pulse to the sample, which in our case is a 1 mM radical solution (4-amino-TEMPO). The spectrometer then sends the pulse to the sample, which in turn perturbs the nuclei from the water. This perturbation is then picked up by the NMR coil and sent back to the spectrometer, and the laptop collects information about the molecule.

For the ESR system, we have a frequency source, an amplifier, a tuning circuit, and a second coil. The frequency source sends a fixed frequency through the amplifier. From the amplifier, the frequency is sent to a tuned and matched circuit into the coil. This allows for the most power to get to the sample. A normal NMR experiment is conducted with the ESR saturation on in order to perform DNP. This setup is shown in Figure 3.

Results and Conclusions:

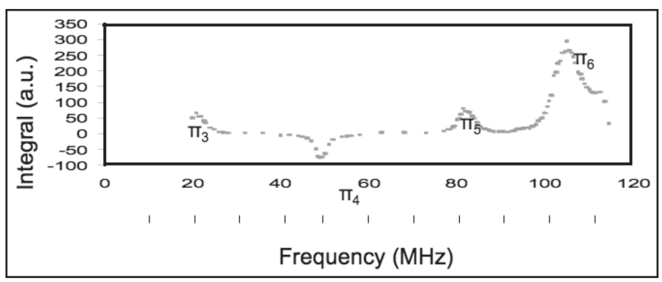
In order to prove that our new low field DNP system worked, we reproduced previous results found in the literature. We successfully obtained a similar ESR spectrum through DNP (Figure 4). When using DNP, 117-fold enhancement with respect to the normal NMR signal was observed. Compare this to our current system of 3500 G with the same radical concentration in which the maximum enhancement is about 32-fold. This proves that the enhancement is greater at low fields.

Future Work:

We can now use this low-field to test other systems, for example, studying the water dynamics in lipid membranes using this low field system compared with results with those taken at high fields. Also, we can now study crude oil in which no DNP enhancement was observed at high fields.

Acknowledgements:

Thanks to Professor Songi Han, Mark Lingwood, and the Han group for all of their help with this project. Also thank you to the National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program, the NSF and Angela Berenstein for opportunity to participate in this program at UCSB.



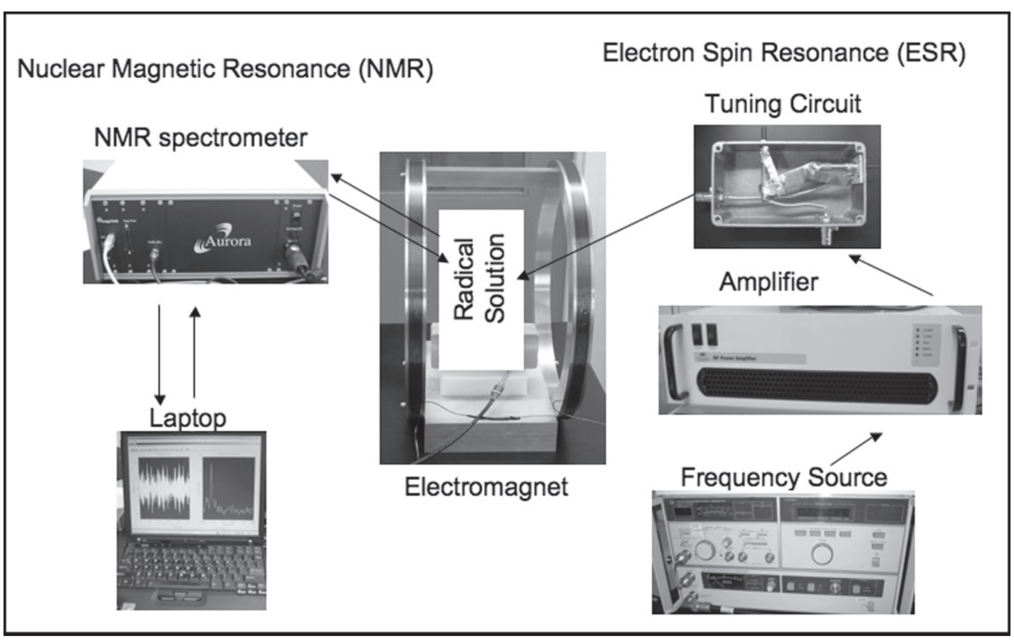


Figure 3, left: Experimental setup.

Figure 4, above: ESR spectrum at 15.3 G with our homebuilt system