

¹³C Dynamic Nuclear Polarization using BDPA and trityl OX063

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Nuclear magnetic resonance (NMR) is relatively insensitive when it comes to monitoring nuclei with gyromagnetic ratios lower than the proton's gyromagnetic ratio ($\gamma = 42.577$ MHz/T). Electron paramagnetic resonance, on the other hand, has incredible sensitivity due to the electron's high gyromagnetic ratio ($\gamma = 28,020$ MHz/T). One method by which NMR's insensitivity may be reduced is dynamic nuclear polarization (DNP). DNP manages this feat by transferring the high electron polarization to the nuclei under consideration. There has been much recent effort to optimize ¹³C DNP at low temperatures and within high magnetic fields. This has been largely motivated by the 2003 invention of dissolution DNP which nets liquid-state samples with NMR signals enhanced by several thousand-fold.¹

Many of these optimization efforts were examined previously under magic angle spinning (MAS) DNP. However, the results acquired under MAS-DNP frequently differ from those gotten with DNP due to the different experimental conditions. For example, the trityl biradical, while commonly used in MAS-DNP, is far less effective under temperatures around 1 K – temperatures normal for DNP.² This suggests that studies on biradicals and on radical mixtures could improve the current understanding of the physics behind DNP.

With this goal in mind, our study examined ¹³C DNP performed using a 1:1 v/v ¹³C acetic acid/sulfolane solution doped with a 1:1 mixture of two narrow linewidth free radicals: trityl OX063 (trityl) and BDPA. The samples' polarization levels were monitored every 3 minutes while the samples were irradiated at the spin-up peak's microwave frequency of 94.10 GHz. In this manner, we acquired the build-up times and maximum magnetizations for various concentrations of the 1:1 trityl-to-BDPA radical mixture.

As seen in Fig. 1(a), it was found that the ¹³C DNP spectra of the control and combined radical samples have substantial differences in the peak locations of optimum microwave irradiation frequencies. This is attributed to the differences in the EPR spectra of each free radical. Fig. 1(b) shows the representative polarization buildup curves of ¹³C samples doped with different concentrations of BDPA:trityl radicals. The optimum BDPA:trityl mixture appears to be 10 mM:10 mM wherein there appears to be sufficient polarizing centers for the ¹³C spins and at the same time the expected nuclear T1 reduction is not yet detrimental to DNP. The increase in polarization prior to the peak was attributed to the rising number of polarizing centers. The fall in polarization following the peak was attributed to the increased concentration of spin diffusion barriers and the rise in the rate of nuclear spin-lattice relaxation.

References

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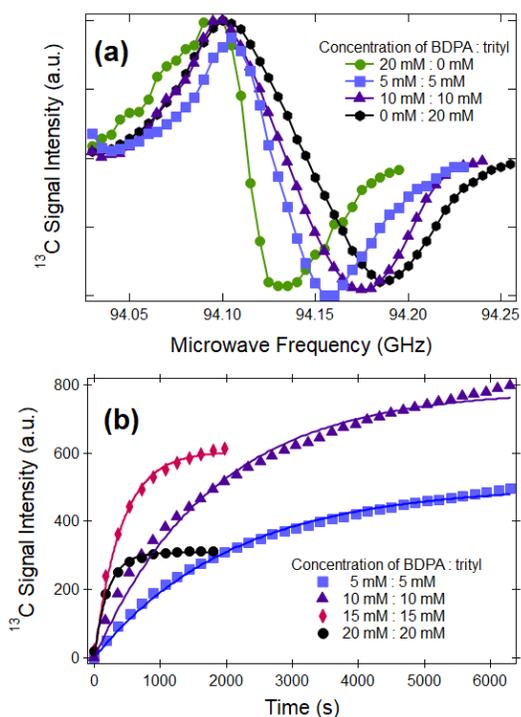


Fig. 1: a) ¹³C microwave DNP spectra showing the optimum polarization peaks for each sample. b) ¹³C polarization build-up times versus radical mixture concentration. These data were taken at 3.35 T and 1.2 K.