

# High Frequency Dynamic Nuclear Polarization in Solids and Liquids: Why Two Electrons Are Better Than One

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Over the last few years we have developed two gyrotron microwave sources that operate at frequencies of 140 GHz ( $\lambda = 2.14$  mm) and 250 GHz ( $\lambda = 1.2$  mm), and a third that is under development at ~460 GHz ( $\lambda = 0.65$  mm) that permit DNP enhanced NMR (DNP/NMR) experiments in magnetic fields of 5-16.4 T ( $^1\text{H}$  NMR frequencies of 211, 380, and 700 MHz, respectively). We review the instrumentation (low temperature MAS probes, microwave transmission lines, and gyrotron sources) used for these experiments. In addition, we discuss two mechanisms that are currently used for DNP experiments in insulating solids at high fields – the solid effect and thermal mixing/cross effect -- and the paramagnetic polarizing agents appropriate for each. These include a new class of biradicals that enable increased enhancements at reduced concentrations of the paramagnetic center. In addition, we discuss applications of DNP/NMR that illustrate its utility in enhancing signal-to-noise in MAS NMR spectra of a variety of biological systems including bacteriorhodopsin and its photocycle intermediates and amyloid fibrils whose structures are of considerable scientific interest. In particular we review results that illustrate enhancements that are routinely available and range from 40-340 depending on experimental variables such as temperature, magnetic field, microwave  $B_1$ , polarizing agent, etc. Finally, we describe extensions of these experiments that permit observation of  $^{13}\text{C}$  liquid state spectra where we have observed enhancements of 140-400 in small molecules and a protein.