Electronic Relaxation of Free Radicals at High Magnetic Fields

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Introduction

The introduction of fast dissolution Dynamic Nuclear Polarization (fd-DNP) has opened the possibility of metabolic imaging in real time with ^{13}C labeled compounds. Traditional nuclear imaging techniques have very high sensitivity, but lack any chemical information. Imaging with ^{13}C labeled metabolic precursors allows chemical reactions to be monitored *in vivo* with high spatial resolution. However, even with fd-DNP, the sensitivity of the magnetic resonance experiment is left wanting. Optimization of the DNP process could potentially lead to a further doubling or tripling of the sensitivity available with current protocols. The DNP process itself is intimately affected by the relaxation times of the free radicals doped into the matrix containing the metabolic precursors. In order to more fully understand the DNP process, we asked the NHMFL EMR Facility to execute a quantitative study of the relaxation properties of three radicals commonly used for DNP experiments at 95 GHz across a range of temperatures. Trityl-OXO63 is a water soluble radical that is the primary agent used in the fd-DNP experiment and was chosen for study at multiple field strengths.

Experimental

Three different radicals, trityl-OXO63, TEMPO, and BDPA, were prepared in a manner consistent with the DNP experiment. All three samples were run on the Bruker E680 spectrometer at 94 GHz at a variety of temperatures (**Figure 1**). The 9, 240, and 336 GHz spectrometers at the EMR Facility were used to study the trityl sample only. The EPR spectra were recorded using an echo detected field sweep method. T_1 measurements were made using a standard saturation recovery experiment.

Results and Discussion

Total line width of the ESR resonance is directly related to the absolute nuclear polarization enhancements that can be realized with DNP. [1] Figure 1a illustrates the ESR spectra of the three radicals and gives immediate insight into the advantages of BDPA and trityl over the nitroxide based radicals for DNP. The W-band (~95 GHz) relaxation for the three radicals as a function of temperature indicates that at around 20 K all the radicals switch from a Raman relaxation mechanism to the direct process. This conclusion had previously been speculated, but no experimental proof had been given. Trityl has a longer T_1 than either BDPA or TEMPO at all field strengths.

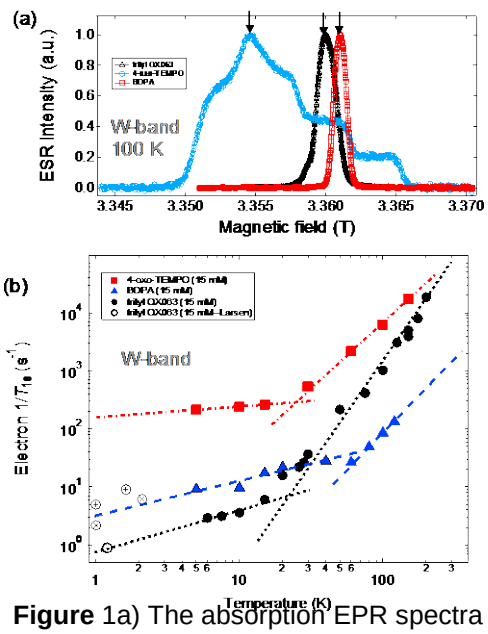

Figure 1a) The absorption EPR spectra of TEMPO (blue), trityl (black), and BDPA (red). b) The W-band temperature dependence of electronic $1/T_1$. The points illustrated by open circles are from reference [2].

Conclusions

DNP systems at higher fields are likely to show superior results to anything produced at lower field strengths.

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References

[1] Heckmann, J., *et al.*, Phys. Rev. B, **74**, 134418 (2006).
[2] Ardenkjaer-Larsen, J.H., *et al.*, Applied Mag. Res., **34**, 509-522 (2008).