SQUID-EPR and Magnetization of the DNP-MRI Trityl Radical

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Introduction: Dynamic nuclear polarization DNP is an exciting new approach to MRI that transfers the polarization of an electron based paramagnet to the magnetic nuclei of a compound of interest.[1] DNP has the potential to increase carbon based MRI sensitivity by many orders of magnitude, allowing direct visualization of a medicinal agent's flow and bio-interactions through the body.[1] Common paramagnets used for DNP-MRI are carbon centered persistent radicals known as the trityls.[1] The mechanism of polarization transfer is highly dependent on the trityl's EPR linewidth and microwave power absorption at low temperatures and clinical MRI magnetic fields.[2,3]

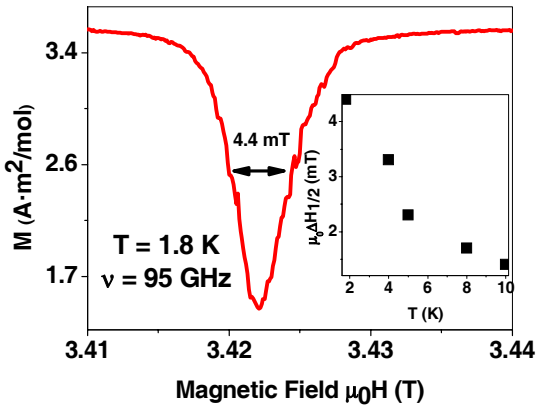

Fig. 1 SQUID-EPR of the trityl radical provides a quantitative account of the EPR interaction. Inset, the EPR $\Delta H_{1/2}$ narrows with temperature

Methods: We use a recently developed EPR technique based on a superconducting-quantum-interference-device SQUID to detect the change in dc magnetic moment due to resonant absorption of rf radiation at clinical MRI fields of 1.5 - 7 Tesla.[4] In contrast to most conventional magnetic resonance this technique is quantitative such that the y-axis is in SI units of A·m^2/mol (Fig.1). Our conventional dc magnetic susceptibility results over 1.8 – 150 K found an S=1/2 Curie-Weiss relationship with little long range interaction. Magnetization vs applied field at 1.8 and 4 K fit a Brillion function with > 90 % electronic polarization at $g\mu_B\mu_0H/kT\sim3$. This result provides information on optimum fields vs temperatures for DNP.

Results and Discussion: In Fig. 1 the dc magnetization M of the Finland trityl as a function of magnetic field under DNP conditions of 1.8 K and microwave irradiation of 95 GHz. This EPR transition has a linewidth of 4.4 mT at 1.8 K and the inset shows significant narrowing to ~ 1.4 mT at 10 K. The narrowing is attributed to faster fluctuations of the dipolar field with increasing temperature. The thermal mixing mechanism of DNP transfer is maximized when the EPR linewidth is comparable to the nuclear Zeeman energy.[2,3] At 3.4 T this corresponds to ~ 5.2 mT for ^{1}H and 1.3 mT for ^{13}C. EPR saturation as a function of incident power is shown in Fig. 2. The beginning of saturation at 40 % suppression of the sample magnetization is attributed to selective excitation of the g-perpendicular powder component.

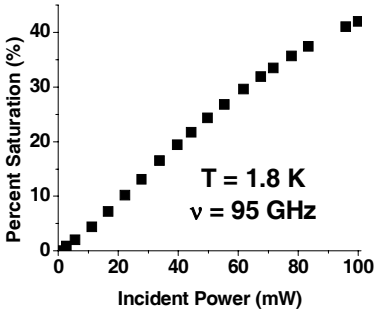

Fig 2 EPR saturation of the trityl as a function of incident microwave power.

Conclusion: This report shows a new quantitative magnetic resonance technique applied to a conventional DNP-MRI compound. These are the first results of the high frequency EPR saturation, linewidth, and dc magnetic susceptibility of the trityl radical in the MRI-DNP temperature range below 10 K. The broadened EPR linewidth of 4.4 mT at 1.8 K is favorable for a thermal mixing mechanism of DNP enhancement using a ^{1}H – ^{13}C cross polarization experiment with a potential increase of the ^{13}C DNP. The saturation data indicate low-power low-cost Gunn diode microwave sources are sufficient for DNP at 1.8 K.

References:

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