Electron Relaxation of Hydrophobic Free Radicals at Optimum DNP Concentration

Khamoshi, A.; Lumata, L.L. (U. Texas, Dallas, Physics); Kaur, P.; Song, L. (NHMFL)

Introduction

A central component of dynamic nuclear polarization (DNP), a NMR signal-enhancing technique, is the source of free electrons used as a polarizing agent. The stable, spin-1/2 organic free radicals BDPA, galvinoxyl and DPPH are efficient polarizing agents for dissolution DNP. Despite the hydrophobic nature of these free radicals, these polarizing agents can be dissolved in specialized solvents such as sulfolane or ethyl acetate. In this work, we have investigated the temperature dependence of the spin-lattice relaxation rate $1/T_1$ of these three DNP free radicals at W-band from 250 K down to 4 K. The results obtained here may elucidate the correlation between the relaxation of electrons and the efficiency of these free radicals in DNP.[1]

Experimental Methods

Optimum DNP concentrations of free radicals were prepared for W-band ESR studies. 100 µL 40 mM BDPA or 40 mM DPPH was prepared in 1:1 v/v sulfolane:DMSO solution via sonication. 100 µL 20 mM galvinoxyl solution was prepared in 1:1 v/v EtOAc:$CHCl_3$. Small aliquots of the DNP free radicals were contained in 200-micron capillary tubes. Field-swept ESR spectra were taken at W-band using a Bruker ESR spectrometer E-600-1021 HE. Temperature-dependent relaxation times T_1 were measured from 250 K down to 4 K. Echo-detected inversion recovery technique was used for relaxation measurements.

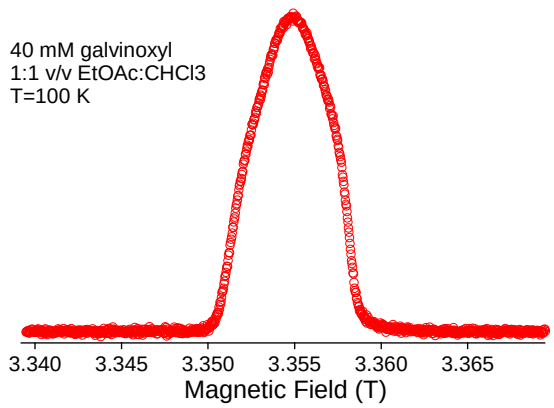

Fig. 1. W-band ESR spectrum of 40 mM galvinoxyl sample taken at 100 K.

Results and Discussion

Fig. 1 shows the W-band ESR spectrum of 40 mM galvinoxyl in 1:1 v/v EtOAc:$CHCl_3$ taken at 100 K. At this concentration, the relaxation times T_1 and T_2 were too fast to be measured above 200 K. The relaxation data were fitted with a double exponential fitting equation where the bigger relaxation component is the relaxation emanating from the free radical electrons and the smaller component has its provenance from the electron-electron interaction effects. Preliminary W-band measurements suggest that for galvinoxyl, the electron spin-lattice relaxation rate follows a behavior close to that of the two-phonon Raman process in the temperature range 125 K down to 40 K. At $T < 40$ K, the electron relaxation rate slows down to a behavior close to the one-phonon direct process. Similar behavior in found in the preliminary results for the free radicals BDPA and DPPH.

Conclusions

Preliminary results for galvinoxyl reveal that at high temperatures above 40 K, the relaxation rate follows a behavior closed to that of the Raman process prediction. Meanwhile, at lower temperatures below 40 K, the relaxation rate slows down and the behavior is close to the direct process prediction. The preliminary data for the other two hydrophobic free radicals BDPA and DPPH also show similar results. Although hydrophobic, these three free radicals can be easily filtered out of the DNP dissolution liquid when water is used as the dissolution solvent.[2]

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References

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[2] Lumata, L., *et al*., Phys. Chem. Chem. Phys., **15**, 9800-9807 (2013).