Field and Temperature-Dependent ESR Studies of Trityl OX063 at Optimum Concentration for Dynamic Nuclear Polarization

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Introduction

Trityl OX063 is one of the most efficient polarizing agents for dissolution dynamic nuclear polarisation (DNP), a technique which is used to amplify the NMR signals by ~10^4-fold for NMR spectroscopy (NMR) and imaging (MRI) [1]. We have performed temperature-dependent electron spin resonance (ESR) measurements of trityl OX063 at the optimum concentration (15 mM) for dynamic nuclear polarization.

Experimental

The X (9.5 GHz)- and W-band (95 GHz) measurements were done on a Bruker E680 and Bruker E-600-1021 HE spectrometers, respectively. The ESR experiments at 240 GHz and 336 GHz were performed on homebuilt quasi-optical superheterodyne 12.5 T ESR spectrometer where a configuration without a cavity was used. The trityl OX063 (15 mM) ESR spectra and relaxation were measured at 9.5 GHz, 95 GHz, 240 GHz, and 336 GHz.

Results and Discussion

We have found (i) when compared to the W-band ESR properties of other free radicals used in DNP at the same concentration, trityl OX063 has slower electron T_{1e} relaxation than BDPA and 4-oxo-TEMPO. At temperatures above 20 K, the T_{1e}^{-1} vs T of trityl OX063 appears to follow a power law dependence close to the Raman process prediction whereas at temperatures below 10 K, electronic relaxation slows and approaches the direct process behaviour. (ii) Gd^{3+} doping, a factor known to enhance DNP, of trityl OX063 samples measured at W-band resulted in monotonic increases of trityl OX063 T_{1e}^{-1} especially at temperatures below 20-40 K while the ESR lineshapes remained essentially unchanged. (iii) Although the ESR linewidth D monotonically increases with field (Fig. 1), the temperature-dependent electron T_{1e}^{-1} is almost unchanged as the ESR frequency is increased from 9.5 GHz to 95 GHz, but becomes faster at 240 GHz and 336 GHz. These results provide insights into the electron spin dynamics of trityl OX063 at optimum DNP concentration over a wide range of magnetic fields, from 0.35 T to 12 T [2].

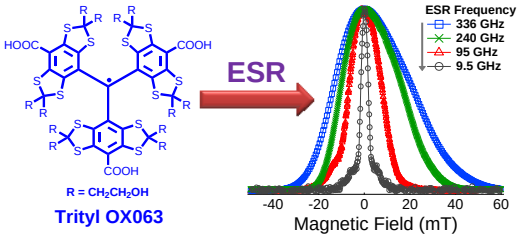

Figure 1. Normalized field-dependent ESR spectra of trityl OX063 taken at 100 K.

Conclusions

W-band data have shown that, at temperatures above ~15 K, the electron relaxation rate T1e-1 vs T can be fitted empirically to a power-law $T^{2.8}$ dependence, close to the T^2 curve predicted by the two-phonon Raman relaxation process. Below 10 K, the relaxation rate slows down close to the linear or temperature-independent behavior indicative of the one-phonon direct process. The ESR lineshape of trityl OX063 monotonically increases as the field is increased from 0.35 T to 12 T. While the X- and W-band electron relaxation of trityl OX063 are very similar, T_{1e}^{-1} increases as the field is increased to 12 T. The relaxation data in this work may be important in elucidating the behavior of DNP performed at different magnetic field strengths [2].

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References

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