

Relaxation Effects of Glassing Matrix Deuteration on ^{13}C Dynamic Nuclear Polarization

Parish, C. (U. Texas Dallas, Physics); Song, L. (NHMFL); Lumata, L. (U. Texas Dallas, Physics)

Introduction

Glassing solvent deuteration could be beneficial for ^{13}C dynamic nuclear polarization (DNP) using large electron spin resonance (ESR) width free radical such as 4-oxo-TEMPO, whereas the opposite DNP effect was seen for small width radical such as trityl OX063 [1,2]. Herein, we have investigated the influence of ^1H replacement with ^2H spins in the DNP glassing solvent on the ^{13}C nuclear and electron relaxation properties that go along with the effects on ^{13}C DNP intensities.

Experimental

This study examined the effect of solvent deuteration upon ^{13}C and electronic spin-lattice relaxation times of eight solutions containing 2-3 M [$1-^{13}\text{C}$] acetate at 3.35 T and 1.2 K; of these eight, four were doped with the wide linewidth radical 4-oxo-TEMPO while the other four were doped with the narrow linewidth trityl OX063 radical; half of each group of four were dissolved in deuterated or non-deuterated versions of 1:1 v/v glycerol/water while the other half were dissolved in non-deuterated or deuterated variants of 1:1 v/v DMSO/water [1]. The ESR measurements were performed in the W-band at NHMFL on a Bruker E680 ESR spectrometer (Bruker Biospin, Billerica, MA). This spectrometer used a Bruker TE011 cylindrical cavity as well as a CF1200 helium flow cryostat (Oxford Instruments, UK) which was used to control the sample's temperature.

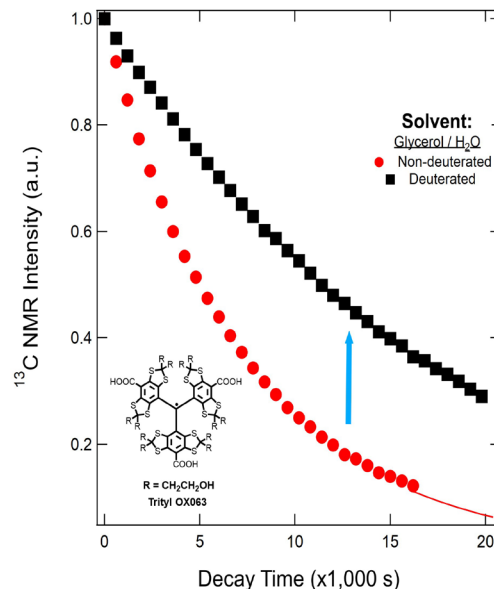


Fig.1 Decay of hyperpolarized ^{13}C NMR signals trityl OX063-doped [$1-^{13}\text{C}$]acetate in deuterated and non-deuterated glassing solvents at 3.35 T and 1.2 K.

Results and Discussion

The main finding of this work was that the ^{13}C T_1 spin-lattice relaxation time generally increases with glassing matrix deuteration regardless of whether trityl OX063 or 4-oxo-TEMPO was used (see Fig.1), which implies a significant contribution of ^2H - ^{13}C dipolar interaction. Meanwhile, deuteration appears to have negligible effect on electron T_1 relaxation times of both free radicals (see Fig.2). However, the electron T_2 spin-spin relaxation times of both free radicals increases upon glassing solvent deuteration.

Conclusions

The overall results indicate that the ^{13}C DNP intensities might be decoupled from the nuclear relaxation behavior, instead the relaxation behavior is ascribed to the dipolar interaction between the nuclear spins and electron spins.

Acknowledgements

The authors would like to acknowledge research support from the Welch Foundation AT-1877-20180324, the US Department of Defense grant number W81XWH-17-1-0303, and the Cancer Prevention and Research Institute of Texas (CPRIT) RP180716. The National High Magnetic Field Laboratory is supported by the National Science Foundation through NSF/DMR-1157490/1644779 and the State of Florida.

References

- [1] Lumata, L., *et al.*, Phys. Chem. Chem. Phys., **15**, 7032-7035 (2013).
- [2] Niedbalski, P., *et al.*, J. Phys. Chem. Lett., **9**, 5481-5489 (2018).

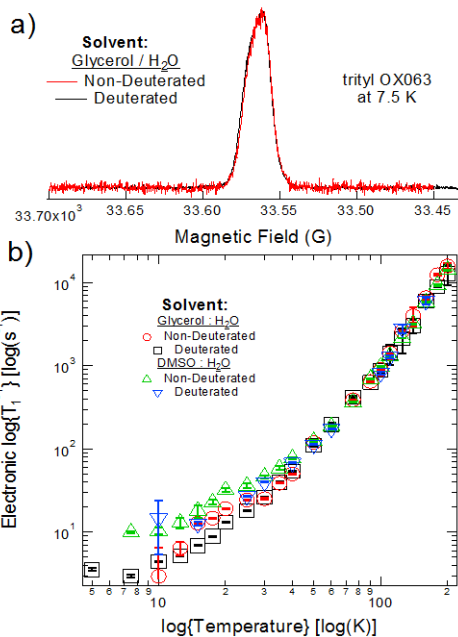


Fig.2 W-band (a) ESR spectra and (b) temperature-dependent electron T_1 relaxation rate of trityl OX063 in deuterated and non-deuterated glassing solvents.