

Effect of Solvent Deuteration upon Nuclear and Electronic Spin-Lattice Relaxation Times

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Nuclear magnetic resonance (NMR) is a tad insensitive when examining low gyromagnetic ratio (γ) nuclei. Yet, electron paramagnetic resonance (EPR) has considerable sensitivity because electrons have a γ three orders of magnitude larger than the γ of protons. This difference is used by dynamic nuclear polarization (DNP) to enhance the sensitivity of NMR through transferring the high electron polarization to the nuclei under consideration. DNP does this via microwave irradiation of a sample at cryogenic temperatures (~ 1 K) and within high magnetic fields (>1 T).

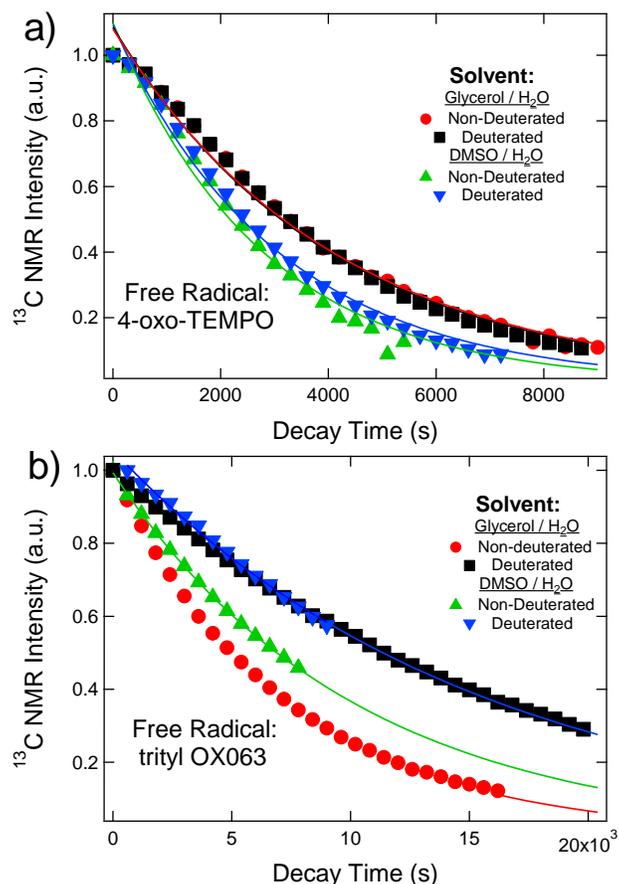


Fig. 1: a) ¹³C polarization decay of the samples doped with 4-oxo-TEMPO; b) ¹³C polarization decay of the samples doped with trityl OX063.

Deuteration of one's glassing solvent is often used in ¹³C DNP to improve the resulting NMR signal. Yet, the mechanism behind this boost is poorly understood. In particular, Lumata et al. found that use of a wide (narrow) EPR line-width radical combined with glassing solvent deuteration led to a significant increase (decrease) in the hyperpolarization.¹ Later, Kiswandhi et al. determined that solvent deuteration doubled the ¹³C DNP build-up rate.² However, there have not been any investigations into the effect of glassing solvent deuteration upon electronic and nuclear spin-lattice relaxation times (T_{1s}) – a situation this study seeks to rectify.

With this goal in mind, our study examined the ¹³C and electronic T_{1s} of eight solutions containing 2-3 M [¹⁻¹³C] acetate at 3.35 T and 1.2 K. This group of eight samples was separated into groups of two in order to examine the effect of solvent deuteration when the radical or glassing matrix were varied. Half of the samples were polarized until they plateaued. This was immediately followed by irradiating the samples with a 2° pulse every 10 minutes in order to monitor the ¹³C NMR signals' decays. The other half of the samples underwent EPR measurements at the National High Magnetic Field Laboratory (NHMFL) in Florida.

As seen in figure 1 a), the solid-state relaxation of the 4-oxo-TEMPO-doped [¹⁻¹³C] acetate was virtually unchanged by deuteration. Yet, when these samples were instead doped with trityl OX063, shown in figure 1 b), deuteration led to an increase in the ¹³C T_{1s} . These two observations were explained via recourse to each free radical's EPR line-width combined with considerations from the thermal mixing regime of DNP. On the other hand, the EPR spectra and the electronic longitudinal relaxation rates showed no significant difference between deuterated and non-deuterated samples. This observation was

explained through noting the difference in magnitude between an electron's γ and ¹³C's γ . The same observations and reasoning also applied to the samples doped with the trityl OX063 radical.

References

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- ² A. Kiswandhi, B. Lama, P. Niedbalski, M. Goderya, J. Long, and L. Lumata, *RSC Adv.* **6**, 38855 (2016).

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