De Novo Prediction of Cross-Effect Efficiency for Magic Angle Spinning Dynamic Nuclear Polarization

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Introduction

Magic Angle Spinning Dynamic Nuclear Polarization (MAS-DNP) pushes the boundaries of NMR experiments through high sensitivity gains. These gains are mostly determined by the hardware and the properties of the biradicals used to boost the sensitivity. To date, AMUPol and TEKPol [1,2] are the most efficient biradicals used in MAS-DNP under 18.8T. In this work we used recently developed simulations [3–5] combined with high-field EPR and DFT to predict their DNP capabilities.

Experimental

This solvent mixture was chosen as it forms a relatively good and reproducible glass. The AMUPol sample was prepared by dissolution in a 2 M ^{13}C–urea D_8-glycerol/D_2O/H_2O (60/30/10 v%) mixture to form a 10 mM solution. For each sample, the experiments have been carried out in 3.2 mm outer-diameter sapphire MAS rotors. We carried out part of our experiments on the 600 MAS-DNP system and the 240 GHz Pulsed high field EPR at NHMFL in Tallahassee.

Results and Discussion

Using DFT we have been able to predict many of geometrical parameters of the biradicals. These parameters have been used as input parameters to fit the High Field EPR spectra. The corresponding fit are reported in **Fig.1** for AMUPol at 240 GHz. Using the pulsed capability of the EPR system the electron relaxation time was measured across the EPR line. This revealed an orientation dependent relaxation time $T_{1,e}$. The fitted parameters from the EPR and the orientation dependent relaxation time were then used as input for the MAS-DNP simulation tool previously developed [5]. The simulations were used to compare the experimental enhancement as a function of the main magnetic field value (DNP field profile). After adjusting the microwave irradiation strength, a very good agreement between experiment and theory was obtained. This is illustrated in the case of AMUPol at 14.1T in **Fig.2**.

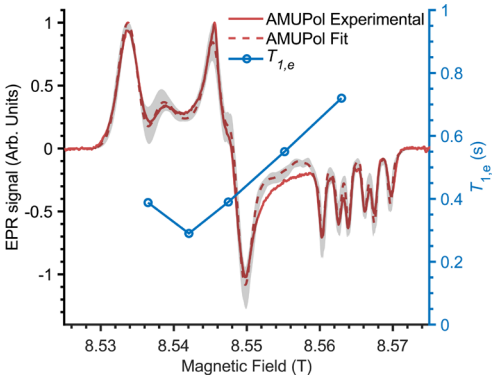

Fig.1 Experimental CW spectrum (red line), Fitted EPR spectrum (red dotted line). The blue line reports the T_{1e}.

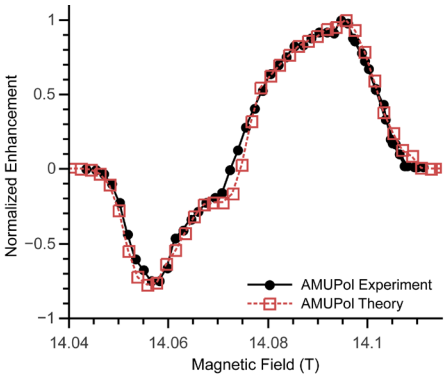

Fig.2 Experimental (black squares) and theoretical (open red squares) DNP field profile.

Conclusions

The combined approach of DFT, High-Field EPR and MAS-DNP simulations permits prediction of the behavior and the DNP properties of a given biradical. This allows in turn to predict additional properties such as the build-up times, the depolarization and the gain. This work was submitted to Physical Chemistry Chemical Physics in November 2018 and has been accepted.

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