Variation of the Overhauser Enhancement with Field-Cycling

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Abstract

Dynamic nuclear polarization (DNP) is an NMR-based technique which enables detection and spectral characterization of endogenous and exogenous paramagnetic substances measured as a transfer of polarization from the saturated unpaired electron spin system to the NMR active nuclei. In case of proton NMR the transfer of polarization leads to an enhancement of the detected proton signal called the Overhauser enhancement [1]. The electron irradiation and the NMR detection may occur at different magnetic field strengths in a DNP spectroscopy experiment. An evaluation of the variation in the Overhauser enhancement with increased separation between the electron irradiation field and the NMR detection field shows that the measured Overhauser enhancement decreases with increasing in field-cycling.

Introduction

Field-cycled DNP spectroscopy is a technique that allows the detection of an electron resonance spectrum of a paramagnetic substance in solution from the water protons which are constantly interacting with the unpaired electrons. The magnetic field is increased progressively in small steps during the electron excitation period while maintaining the electron irradiation frequency constant [2, 3]. The NMR detection occurs at the same magnetic field B_{NMR} post-electron excitation. Therefore FC-DNP spectroscopy provides an electron absorption spectrum as detected from the NMR proton. The ratio of the enhanced NMR signal to the baseline NMR signal is termed the Overhauser enhancement (OE). In order to minimize the non-resonant power deposition in a conductive sample during the electron irradiation field-cycling instrumentation is used to ramp down the magnetic field during electron irradiation. Also in order to increase the signal-to-noise ratio (SNR) of the experiment the magnetic field is ramped up to a higher level for NMR detection. A FC-DNP spectroscopy experiment wherein multiple spectra are acquired at the same electron irradiation field and constant electron frequency but variable NMR detection field (97 G, 200 G, and 587 G) is presented. The OE is determined in each case to evaluate the dependence of OE on the field-cycling.

Materials and methods

A novel variable field DNP spectroscopy system which comprises of two electromagnets to achieve the field-cycling capability has been used. The primary magnet that provides B_{NMR} has a range 0 – 0.38 T. A secondary electromagnet that provides a field in opposition to the primary magnet has a range 0 – 0.1 T. A dual frequency resonator with an EPR component based on the Alderman Grant design that is co-axial with an NMR solenoid was used. The electron excitation resonator was tuned to 282.3 MHz and the NMR solenoid was tuned to 412 kHz, 856 kHz and 2.4 MHz by modification of the tuning capacitor in the solenoid at the respective magnetic fields. The FC-DNP spectra of 1 mM TEMPOL free radical was acquired at different NMR detection field strengths.

Results

Figure 1(a), (b), (c) shows the FC-DNP spectra acquired at increasing magnetic fields with a field resolution of 0.5 G for the electron resonance magnetic field sweep and an electron irradiation pulse of duration 500 ms at a power level of 5W. The OE enhancement measured was -9.4, -5.1and -0.04 at 97 G, 200 G and 587 G respectively.

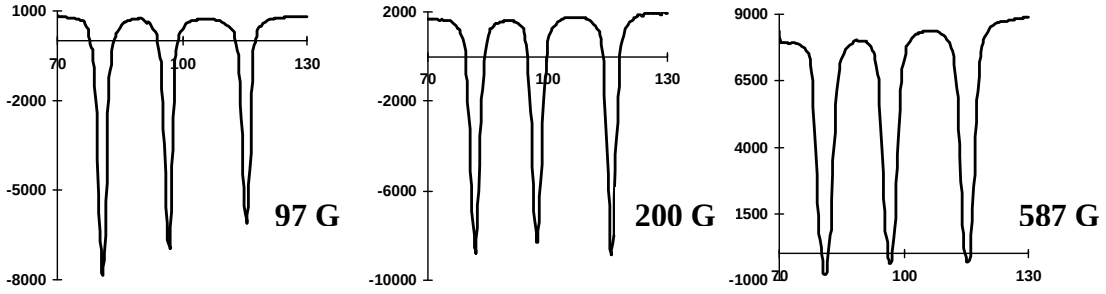

Figure 1. FC-DNP spectra acquired at same B_{EPR} field of 100 G and increasing B_{NMR} (a) 97 G, (b) 200 G, (c) 587 G

Discussion

Increase in field-cycling results in a decrease in the measured Overhauser enhancement; however the SNR increases as B_{NMR} increases as expected. The decrease in OE is attributed to the fact that the depth of the resonance is determined by electron irradiation field and the electron excitation power level and is a constant in this study. As a result at high NMR detection fields the ratio of the non-enhanced NMR baseline signal to the NMR signal at the peak of the EPR resonance decreases as B_{NMR} increases.

References:

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