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Theoretical aspects of Magic Angle Spinning - Dynamic Nuclear Polarization

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ABSTRACT

Magic Angle Spinning (MAS) combined with Dynamic Nuclear Polarization (DNP) has been proven in recent years to be a very powerful method for increasing solid-state NMR signals. Since the advent of biradicals such as TOTAPOL to increase the nuclear polarization new classes of radicals, with larger molecular weight and/or different spin properties have been developed. These have led to unprecedented signal gain, with varying results for different experimental parameters, in particular the microwave irradiation strength, the static field, and the spinning frequency. Recently it has been demonstrated that sample spinning imposes DNP enhancement processes that differ from the active DNP mechanism in static samples as upon sample spinning the DNP enhancements are the results of energy level anticrossings occurring periodically during each rotor cycle.

In this work we present experimental results with regards to the MAS frequency dependence of the DNP enhancement profiles of four nitroxide-based radicals at two different sets of temperature, 110 and 160 K. In fact, different magnitudes of reduction in enhancement are observed with increasing spinning frequency. Our simulation code for calculating MAS–DNP powder enhancements of small model spin systems has been improved to extend our studies of the influence of the interaction and relaxation parameters on powder enhancements. To achieve a better understanding we simulated the spin dynamics of a single three-spin system $\{e_a - e_b - n\}$ during its steady state rotor periods and used the Landau–Zener formula to characterize the influence of the different anti-crossings on the polarizations of the system and their necessary action for reaching steady state conditions together with spin relaxation processes. Based on these model calculations we demonstrate that the maximum steady state nuclear polarization cannot become larger than the maximum polarization difference between the two electrons during the steady state rotor cycle. This study also shows the complexity of the MAS–DNP process and therefore the necessity to rely on numerical simulations for understanding parametric dependencies of the enhancements. Finally an extension of the spin system up to five spins allowed us to probe the first steps of the transfer of polarization from the nuclei coupled to the electrons to further away nuclei, demonstrating a decrease in the spin-diffusion barrier under MAS conditions.

1. Introduction

Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) is a common tool for studying structure and dynamics of solid samples. The advent of Dynamic Nuclear Polarization (DNP), using gyrotron microwave (MW) sources, combined with MAS has opened the door to many advanced studies of solids at high magnetic fields [1]. The development and implementation of high field gyrotrons up to the Terahertz range has enabled the construction of high field MAS–DNP instruments, and led to the commercialization of MAS–DNP spectrometers by Bruker Inc. [2] operating up to 18 T. Theses high field DNP instrument developments have triggered a vast interest of the solid-state NMR community in MAS–DNP experiments, both for biological [3–11] and material science [12–22] applications. Most of these experiments performed today are using nitroxide based bi-radicals such as

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TOTAPOL [23,24,2,8,25,26,9], and recently new nitroxide based biradicals have been introduced with varying longitudinal relaxation times, phase memory times (or transverse relaxation time), electron–electron dipolar couplings, and relative $g-$tensor orientations such as AMUPOL, bCTbK, or TEKPOL [27,26,28].

During MAS–DNP nitroxide biradicals dissolved in a glass forming mixture polarize the protons mainly via the Cross Effect (CE) DNP mechanism, while Solid Effect (SE) signal enhancements have been demonstrated in samples with Trityl OX63 and (SA-) BDPA radicals [1,29,23,30–33]. A recent study has revealed the existence of the Overhauser Effect in MAS–DNP on insulating solids [33].

For a long time the DNP mechanisms in samples rotating at the magic angle were considered to be the same as for static samples. Recent theoretical work performed by Thurber and Tycko [34–36] as well as in our group [37,33] has revealed the differences between the static DNP and MAS–DNP mechanism and its underlying complexity. They emphasized that the polarization transfer between the electrons and the nuclei in rotating samples takes place during crossings of the energy levels of the rotating samples. These transfer processes were demonstrated and analyzed by simulating the polarization dynamics of three-spin systems during MW irradiation.

During the CE-DNP process, which is likely to occur when the EPR linewidth is greater than the nuclear Larmor frequency, the enhancement is the result of the electron and nuclear polarization dynamics that takes place at four sequential anticrossings (here called rotor-events) during each rotor cycle. Considering a three-spin system with two electrons e_a and e_b and a nucleus n, with product spin states $|\chi_a\chi_b\chi_n\rangle$, with $\chi = \alpha, \beta$, and time dependent resonance frequencies $\omega_i(t)$, with $i = a, b, n$, the four rotor-events (in arbitrary order of occurrence) during a MW irradiation at frequency ω_{MW} can be characterized as:

- MW rotor-events: MW encounters occurring when $|\omega_a(t) - \omega_{\mathrm{MW}}| \approx 0$ and $(|\alpha_a\chi_b\chi_n\rangle \leftrightarrow |\beta_a\chi_b\chi_n\rangle)$ and when $|\omega_b(t) - \omega_{\mathrm{MW}}| \approx 0$ and $(|\chi_a\beta_b\chi_n\rangle \leftrightarrow |\chi_a\alpha_b\chi_n\rangle)$.
- D rotor-events: electron–electron dipolar anticrossings occurring when $|\omega_a(t) - \omega_b(t)| \approx 0$ and $(|\alpha_a\beta_b\chi_n\rangle \leftrightarrow |\beta_a\alpha_b\chi_n\rangle)$.
- CE rotor-events: CE anticrossings occurring when $|\omega_a(t) - \omega_b(t)| \approx \omega_n$ and $(|\alpha_a\beta_b\alpha_n\rangle \leftrightarrow |\beta_a\alpha_b\beta_n\rangle)$ or $(|\beta_a\alpha_b\alpha_n\rangle \leftrightarrow |\alpha_a\beta_b\beta_n\rangle)$.
- SE rotor-events: ZQ and DQ MW encounters occurring when $|\omega_a(t) - \omega_{\mathrm{MW}}| \approx \omega_n$ and $(|\alpha_a\chi_b\beta_n\rangle \leftrightarrow |\beta_a\chi_b\alpha_n\rangle)$ or $(|\alpha_a\chi_b\alpha_n\rangle \leftrightarrow |\beta_a\chi_b\beta_n\rangle)$ and when $|\omega_b(t) - \omega_{\mathrm{MW}}| \approx \omega_n$ and $(|\chi_a\alpha_b\beta_n\rangle \leftrightarrow |\chi_a\beta_b\alpha_n\rangle)$ or $(|\chi_a\alpha_b\alpha_n\rangle \leftrightarrow |\chi_a\beta_b\beta_n\rangle)$,

where $(|\chi_a, \chi_b, \chi_n\rangle \leftrightarrow |\chi'_a,\ \chi'_b,\ \chi'_n\rangle)$ represents the instantaneous degeneracy of two energy levels in the MW rotating frame. The first two events influence the polarizations of the electrons and the third transfers part of the polarization difference between the two electrons to the nucleus. The fourth event is responsible for the SE-DNP enhancement and polarizes the nucleus on account of one of the electron polarizations with a yield much smaller than during the CE rotor-events.

In this article we extend the earlier discussions concerning the dependence of the nuclear enhancement on the various interaction and relaxation parameters as dictated by the type of radical used [37,34]. During these discussions we use among others the Landau–Zener (LZ) formula used by Thurber et al. [34] for describing MAS–DNP. We begin by showing experimental results that demonstrate changes in the MAS spinning rate dependence of the enhancement at different temperatures for two radicals: TOTAPOL and AMUPOL. In order to understand which parameters influence these experimental observations, and from a more general point of view how each parameter influences the MAS–DNP mechanism, we performed a series of numerical simulations for small spin systems containing up to 5 spins. This has become possible by improving the previously published simulation method. Thus in the third section we present the improvements included in the simulation code in order to speed up the computation times. This code is then used to calculate the time evolution of the energy level populations of a single three-spin $\{e_a - e_b - n\}$ crystal during its “steady state rotor periods” in order to improve our understanding of the combined action of the anticrossing and relaxation mechanisms leading to the steady state MAS–DNP enhancements. Finally, the dependencies of the enhancements on all relevant parameters are simulated and discussed, including the mechanism of polarization transfer from hyperfine coupled nuclei to non-hyperfine coupled nuclei.

2. Experiments

2.1. Experimental conditions

2.1.1. Samples

Glass forming solutions composed of d_8-glycerol-D_2O–H_2O (GDH, 60–30–10 v%) were prepared with 25–30 µl of total volume. 2 mg of uniformly ^{13}C, ^{15}N-labeled proline powder and 1–2 mg of KBr powder were added to the solution. As a second temperature calibration procedure, another sample containing proline, GDH buffer and KBr powder was prepared. In that case, the KBr powder was put at the bottom of the NMR rotor and isolated from the buffer by a silicon rubber seal. The proline was the analyte to be detected via DNP enhanced MAS-NMR experiments, and KBr was used for internal (or in situ) temperature-calibration [38,28,26]. The concentrations of the radicals were set by adding appropriate amounts of 4-amino TEMPO, protonated and deuterated TOTAPOL and AMUPOL [23,26]. Four samples were prepared and studied: 40 mM TEMPO, 20 mM TOTAPOL, 20 mM CD_3-TOTAPOL (called here ^{2}H-TOTAPOL), and 10 mM AMUPOL .

2.1.2. DNP NMR spectroscopy

DNP enhanced MAS NMR experiments were performed at a Bruker DNP-NMR system equipped with a gyrotron operating at 400 MHz/263 GHz ^{1}H/e$^-$ Larmor frequencies, respectively. All spectra were recorded with a Bruker low temperature triple-resonance ^{1}H/^{13}C/^{15}N probe operating at temperatures down to ~100 K. 3.2 mm zirconium oxide MAS NMR rotors were used, and the temperature equilibration of the sample was achieved with a sufficient waiting period after changing the temperature settings. The ^{1}H-DNP enhancements were determined by taking the ratio between the ^{13}C-CPMAS signal intensities of the samples with and without MW irradiation. DNP enhancement is described as:

$$\epsilon_{\mathrm{On/Off}} = \frac{I_{^{13}\mathrm{C,On}}}{I_{^{13}\mathrm{C,Off}}} \tag{1}$$

2.2. Results

The temperature inside the proline sample is kept constant, by using the KBr powder dispersed inside the proline in GDH DNP buffer by using 3.2 mm zirconia rotors. The temperature deviations occur due to changes in MAS frequency and flow for the MAS gas controllers. Following the ^{79}Br chemical shifts [39], we carefully

Table 1
The maximum values of $\epsilon_{\mathrm{On/Off}}$.

Temperature	^{1}H-TOTAPOL	^{2}H-TOTAPOL	TEMPO	AMUPOL
110 K	44.6	49.2	17.4	134.4
160 K	10.7	15.1	2.6	76.3