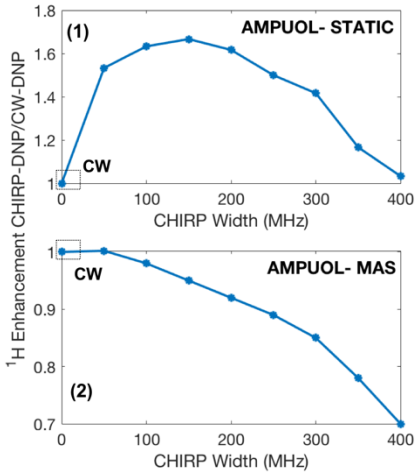
Rotor-synchronous Non-CW DNP Under Magic-Angle Spinning

Asif Equbal, Kan Tagami, Songi Han

University of California, Santa Barbara, CA, USA

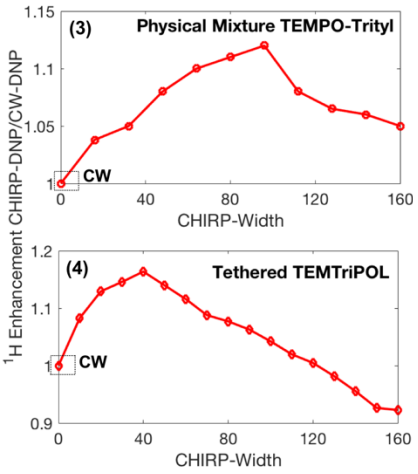
Dynamic nuclear polarization (DNP) has revolutionized the prospects of solid-state NMR spectroscopy by amplifying its sensitivity by several fold. In practice, the polarization transfer process is driven by continuous-wave (CW) microwave (MW) irradiation. In contrast, Hovav *et al.* and Kaminker *et al.*[1] have demonstrated that coherent linear CHIRP or frequency-swept MW irradiation ameliorates the cross-effect (CE) DNP remarkably, compared to the CW for broad bis-nitroxide radicals, and under static high Bo field conditions. This is an effect of the broadband EPR saturation that in turn helps in recruiting more number of electron (*e*) spins into the DNP polarization transfer mechanism. Increasing CHIRP bandwidth augments enhancement before reaching an optimum- that depends on the nuclear (*n*) Larmor frequency and also *e*-spin parameters, as depicted in Fig. 1. The CHIRP-DNP becomes more advantageous for polarizing agents with very broad EPR line, *e.g* paramagnetic metal centers. However, all these interesting developments are so far exclusively achieved under static conditions.



Experimental ^{1}H DNP vs. CHIRP-width at 7T, under static. (Fig.1) and MAS (Fig. 2).

In this presentation, the nuances of broadband MW irradiation for DNP will be explored, for the first time, under Magic-angle spinning (MAS)—an indispensable condition for obtaining high resolution structural information of solid samples, e.g., biosolids and materials. While the CE DNP method that was discovered under static conditions is also valid for rotating samples, the events that meet the CE conditions and/or lead to saturation and polarization exchange under MAS are time-dependent. This is owing to the modulation of *e*-spin energy mainly due to its g-anisotropy, under spinning. A series of periodic energy level crossings and avoided crossings lead to dynamic *e* spin saturation, *e*-*e* polarization exchange, and *e*-*e*-*n* flip-flop-flip transition, as explained using Landau-Zener model.[2] These processes cumulatively lead to the net DNP enhancement. As a consequence of this complexity, the broadband saturation technique developed under the static conditions is not directly transferable to the MAS scenario. This is demonstrated in Fig. 2 which maps DNP enhancement as a function of the CHIRP bandwidth for MAS spin rate at 3 kHz. Unlike under static conditions, CHIRP irradiation becomes deleterious under MAS for AMUPOL. As the CHIRP width increases, deviating from CW conditions, the enhancement decreases sharply. *A priori*, this sharp decrease is not expected. Why does this happen?

The *e*-spin frequency modulation due to g-anisotropy leads to (an orientation dependent) saturation of a large number of *e*-spins as they cross the MW resonance frequency. Therefore, MAS itself helps the recruitment of a large number of *e*-spin pairs to meet the CE-DNP condition. Since the g-tensors of the two *e* spins in bis-nitroxide are similar and their energy trajectories very complicated, the selective saturation of one the two *e*-spins using shaped MW pulse is not straightforward or possible. Apparently, the simple linear-CHIRP irradiation diminishes the extent of saturation of the *e* spins and also the net polarization difference between the two CE *e*-spin pair in steady-state. Therefore, the net CHIRP-DNP enhancement decreases compared to CW, as observed experimentally with AMUPOL (Fig. 2).



CHIRP-DNP at 3kHz (Fig. 3) and 10kHz (Fig.4) spinning, at 7T.

However, if the two *e* spins have distinct EPR line shapes, it becomes feasible to selectively manipulate/saturate one of the two *e*-spins using shaped MW irradiation. Mixed TEMPO-Trityl radical is an ideal system for this scenario. The distinct isotropic g values, separated roughly by the ^{1}H Larmor frequency makes it possible to successfully implement CHIRP irradiation on the narrower Trityl radical, towards more efficient DNP than under CW, as we demonstrate experimentally at 3 kHz MAS in Fig. 3. The numerically simulated CHIRP-DNP enhancement profile for tethered TempTriPol[3] spin-system (Fig. 4) shows ~20% greater enhancement than CW DNP—an exciting proof of principle. Here, two blocks of linear-CHIRP were synchronized with one rotor period at 10 kHz of MAS and 0.2 MHz of MW power. Numerical simulations reveal that the benefit of CHIRP irradiation increases with increase in isotropic exchange (J) coupling between the two *e* spins, since J-coupling splits the spin density of the narrower radical, and mere CW cannot effectively saturate its entire EPR line. In addition, numerical simulations show that optimized Sine-wave and Wurst shaped frequency modulated irradiation can further enhance the DNP performance by up to ~50% using tethered TEMPO-Trityl radicals, as will be presented in the talk. Notably, any shaped pulse can be easily implemented using the digital, quasi-optics based broad-band, and dual DNP-EPR spectrometer system.

References: (**1**) *JPCL, **9**, 3110, 2018.* (**2**) *JCP, **137**, 084508, 2012.* (**3**) Angew.Chem. **54**,11770, 2015.