Optimal Illumination for Optical Overhauser DNP

D.J. Cheney, C.J. Wedge
School of Applied Sciences, University of Huddersfield, Queensgate, Huddersfield. UK
c.wedge@hud.ac.uk

NMR spectroscopy while offering a wealth of information on molecular structure and dynamics has always suffered from inherently low sensitivity which limits applications, not least in the case of volume-limited biological samples. Several spin chemical mechanisms result in spin polarization which can potentially be used to tackle this challenge, with photo-CIDNP methods based on the radical pair mechanism and parahydrogen based PHIP methods well known. A less explored route is the use of laser pumping to hyperpolarize electrons via the radical triplet pair mechanism (RTPM) which we have previously shown can lead to ^{1}H NMR enhancements in solution after Overhauser driven polarization transfer to nuclear spins. Not only does this offer a route to DNP-NMR enhancements in aqueous solution without the technical demands of microwave pumping, but using hyperpolarized electrons means the maximum theoretical enhancements exceed the Boltzmann limited values of microwave pumped Overhauser DNP [1]. Here we show that the attainable NMR signal enhancements are also significantly greater for reduced sample volumes (Fig. 1). While at first glance this may seem problematic due to the reduced filling factor and hence lower sensitivity of NMR detection for small volume samples it does in fact mean that Optical Overhauser DNP is fortuitously well suited to tackle the sensitivity challenge for volume-limited samples.

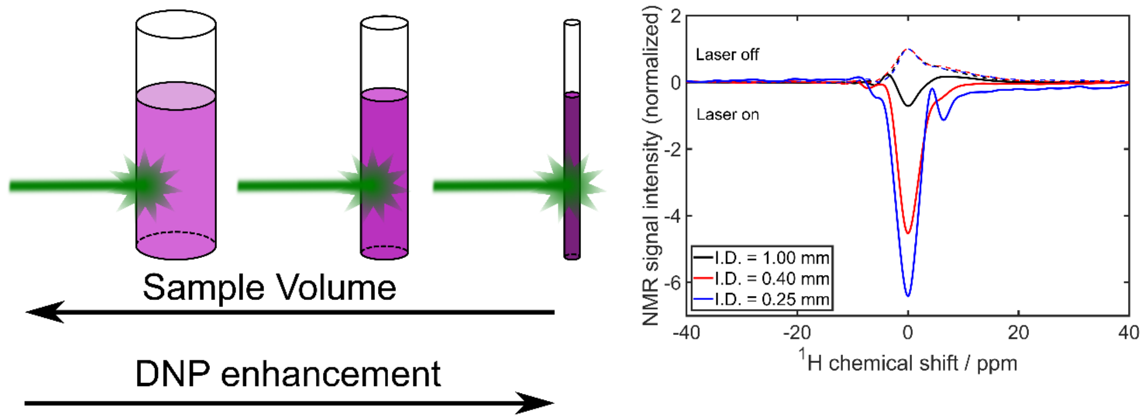

Fig. 1 Reducing the sample tube internal diameter while optimising concentrations of radical and dye leads to increased laser-on vs laser-off DNP enhancement of the ^{1}H NMR signal of water. Figure reproduced from [2].

We use numerical simulations to explore the optimal illumination conditions for RTPM based DNP, considering pulsed illumination regimes [3] and showing the now experimentally verified prediction of significant sample volume effects [2]. We show that for low-volume samples simultaneous optimization of coupling and leakage factors in the well-known Overhauser equation is possible and predict even greater enhancement factors in the case of volume optimized NMR detection, adding Optical Overhauser DNP to the growing number of hyperpolarization methods that show potential for integration with microfluidic NMR [4].

References

[1] M. W. Dale and C. J. Wedge, *Chem. Commun.*, 52, 13221–13224 (2016).
[2] D.J. Cheney and C.J. Wedge, *J. Magn. Reson.*, 337, 107170 (2022).
[3] D.J. Cheney and C.J. Wedge, *J. Chem. Phys.*, 152, 034202 (2020).
[4] J. Eills, W. Hale and M. Utz, *Prog. Nucl. Magn. Reson. Spectrosc.*, 128, 44-69 (2022).