

Overhauser Dynamic Nuclear Polarization for Online NMR Spectroscopy

Kerstin Münnemann

*Laboratory for Advanced Spin Engineering – Magnetic Resonance (LASE-MR), RPTU Kaiserslautern
Laboratory of Engineering Thermodynamics (LTD), RPTU Kaiserslautern, Germany*

NMR spectroscopy is an attractive analytical technique for reaction and process monitoring. The robust benchtop NMR spectrometers that have become available recently have extended the applicability of the method to industrial processes. Process monitoring is often carried out on-line: the mixture that is to be analysed is pumped through the analytic instrument, which is operated in flow mode. In these setups, the volume of the line between process and analysis should be small and flow rates should be high to enable a fast transport to the analytic instrument. In NMR spectroscopy, this is in conflict with the time needed for sufficient polarization build-up, which is particularly problematic for benchtop NMR spectrometers because of their compact design. However, hyperpolarization methods like Overhauser Dynamic Nuclear Polarization (ODNP) are well suited to overcome this problem because hyperpolarization build-up happens on very short timescales and can be performed under continuous flow [1]. We demonstrate continuous-flow ODNP enhanced ^1H and ^{13}C NMR measurements with a 1T benchtop spectrometer with immobilized TEMPO radicals [2] in pure solvents and in binary solvent mixtures and show that the range of accessible flow rates can be greatly expanded by the application of ODNP.

However, a challenge in combining online NMR with ODNP is quantitative analysis, because the ODNP efficiency varies greatly depending on the solvent, receptor molecule, type of radical, sample temperature, measured nucleus, and polarization field. To take these effects into account and to understand the underlying physical effects in detail, Molecular Dynamics (MD) simulations combined with quantum mechanical calculations can be performed [3]. However, these simulations are tedious and were demonstrated so far only for a radical dissolved in a pure solvent. For more complex and temporarily changing systems, as being present in chemical reactions, simulations would be extremely time-consuming if possible at all. A better strategy is to enable quantitative analysis by means of calibration. We demonstrate continuous-flow ODNP enhanced ^1H and ^{13}C NMR measurements in binary solvent mixtures (acetonitrile + water, acetonitrile + 1,4-dioxane, acetonitrile + chloroform) with varying compositions. Quantitative analysis of the hyperpolarized mixtures is enabled by means of calibration and the benefits and drawbacks of the method are discussed.

References

- [1] R. Kircher, H. Hasse, K. Münnemann, *Analytical Chemistry* 93, 25, 8897–8905 (2021).
- [2] R. Kircher, S. Mross, H. Hasse, K. Münnemann, *Molecules* 27, 6402 (2022).
- [3] D. Sezer, M.J. Prandolini, T.F. Prisner, *Physical chemistry chemical physics* 11 (31), 6626-6637 (2009).