Novel Concepts in Direct and Site-Specific Dynamic Nuclear Polarization of Insensitive Nuclei

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Dynamic nuclear polarization (DNP) is capable to enhance the sensitivity of MAS NMR by several orders of magnitude. To achieve this aim, paramagnetic polarizing agents are usually added to the sample of interest in the form of persistent radicals (e.g., bis-nitroxides). Alternatively, paramagnetic metal ions (e.g., Gd^{3+}, Mn^{2+}) may be used, either exogenously introduced as chelate complexes, or as endogenously bound ions. Their large electron spin polarization is then transferred to nuclei by microwave irradiation. If ^{1}H is hyperpolarized by DNP, the enhanced polarization will effectively and uniformly spread throughout the sample by spin diffusion and may then be utilized by cross-polarization of insensitive (low-γ) nuclei (e.g., ^{13}C, ^{15}N), leading to significant NMR signal enhancement of typically all compounds present in the sample. If low-γ nuclei are directly hyperpolarized, spin diffusion is greatly attenuated and specificity may potentially be introduced by spatial relationship between the polarizing agent and the target to be polarized.

In this presentation, several routes towards site-specific DNP are introduced and discussed. Results will be shown on several sample systems, including RNA and protein systems featuring localized metal ion polarized agents. The prospect of extracting distance constraints by analyzing the build-up of enhanced nuclear polarization of specific target sites is demonstrated on a model protein, ubiquitin, which has been paramagnetically labeled on three different positions with a Gd(III)-tag. Furthermore, an alternative method which relies on specific cross relaxation enhancement by active motions under DNP (SCREAM-DNP) will be introduced. By this technique it is possible to specifically probe intermolecular contacts with excellent selectivity.