Relaxometry and Overhauser Dynamic Nuclear Polarisation

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One of its most severe limitations of NMR is the inherent low sensitivity. Among extensive efforts to overcome this limitation, dynamic nuclear polarization (DNP) is emerging as a promising tool to hyperpolarize nuclear spins for NMR. Overhauser DNP is ascribed to the magnetization transfer occurring in a magnetic field from unpaired electrons to nuclei through stochastic modulation of the magnetic hyperfine interaction between electron and nuclear spins. The transfer requires a non-Boltzmann distribution of the populations of electronic and nuclear spin energy levels, which is achieved by microwave irradiation at the electron Larmor frequency. The Overhauser DNP enhancements strongly depend on the correlation times modulating the dipole-dipole interaction between nuclei and unpaired electrons. The analysis of the relaxation profiles of polarizing agents thus represents a valuable tool for their characterization, because they can provide information on these parameters.

DNP is usually performed using nitroxide radicals as polarizing agents, characterized by sharp EPR lines, fast rotation, fast diffusion, and favourable distribution of the unpaired electron. The relaxation profiles of solvent water protons in the presence of nitroxide radicals or paramagnetic metal complexes have been collected and analyzed to obtain the correlation times and the coupling factors [1-5], which report on the largest Overhauser DNP enhancements achievable at full electron saturation, as a function of the applied magnetic field.

For ^1H, molecular motion leads predominantly to a modulation of the magnetic electron-nuclear dipole-dipole interaction at a time scale of tens of ps. This makes the Overhauser DNP enhancements achievable at room temperature and magnetic fields > 1 T relatively small (< 10^2). On the other hand, the enhancement of ^{13}C nuclei in $CHCl_3$ or CCl_4 solutions can be up to 1000 at magnetic fields of 3 Tesla [6]. ^{13}C relaxometry indicated that ^{13}C relaxation is dominated by the contact interaction with the nitroxide radicals, with a correlation time of about 1 ps. A higher relaxivity was measured at low fields for $CHCl_3$ than for CCl_4, as the result of the additional contribution arising from the H atom in $CHCl_3$. Notably, the ^{13}C relaxation profile of $CHCl_3$ could be reproduced with the same parameters as CCl_4 plus an additional contribution mediated by the H-atom. In both solvents, a dipolar contribution to the total relaxivity should also be included. The best-fit values of the parameters obtained from the ^{13}C relaxation profiles can account for coupling factors of -0.47 (CCl_4) and -0.37 ($CHCl_3$), as measured at 3.35 T.

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