Spin Dynamics at Fast MAS in ^{1}H – ^{14}N Double Cross Polarization and TRAPDOR – HMQC Experiments Involving Spin 3/2 Nuclei

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Abstract

Experiments probing correlations between spin-1/2 nuclei (I) and nuclear spins (S) with large anisotropic interactions (quadrupolar or chemical shift anisotropy) often offer valuable access routes to molecular structure and dynamics. In such experiments, development of efficient correlation schemes is not trivial and constitutes an ever-evolving theme of research. As these experiments are performed routinely under MAS, interference between the RF field and the large time-dependent quadrupolar or chemical shift anisotropic interaction leads to complex spin dynamics, often leading to poor and orientation-dependent transfer efficiency.

The work presented in this thesis is a theoretical and numerical investigation of the spin-dynamics in two recently demonstrated experiments involving long periods of RF irradiation on the quadrupolar nuclei channel, the ^{1}H - ^{14}N double cross polarization (double CP) under fast MAS experiment by Carnevale et al. and the ^{1}H - ^{35}Cl TRAPDOR-HMQC experiment of Hung et al. Creation and evolution of various coherences generated in these proton-detected experiments are explored. To analyse the rich and complex spin dynamics due to the interference between the large time-dependent quadrupolar interaction and the radio-frequency (RF) field, an exact effective Hamiltonian is constructed numerically using the *matrix logarithm* approach. Structure of the effective Hamiltonian is connected with transfer amplitudes to various coherences, the output signal, etc. and, when possible, features of the spin dynamics are derived theoretically. The analysis also provides insight on the efficiency of these experiments under different experimental conditions.