Chaotic dynamics in Dynamic Nuclear Polarisation : observations of a solid-state NMR MASER

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Dynamic nuclear polarization (DNP) has been introduced several decades ago as an ensemble of techniques that allows to increase nuclear spin polarisation through their couplings to low-abundance paramagnetic centers under microwave irradiation.[1] In the past decade or so, a series of technological improvements has led to an expanding range of applications in liquid and solid state NMR. For instance, hyperpolarised samples can be dissolved and transferred to a standard high-resolution NMR spectrometer, allowing for the observation of small molecules in solution, in cells or in vivo, with sensitivity enhancements reaching 4 to 5 orders of magnitude, at room temperature (since the seminal paper [2], a rich literature has been published).

In order to achieve such spectacular sensitivity improvements, the nuclear spin bearing molecules to be polarised is dissolved in an aqueous solution containing a relatively small concentration of a stable radical, such as 4-hydroxy-2,2,6,6 tetramethylpiperidine-1-oxyl (TEMPOL), which plays the role of a paramagnetic impurity with respect to the abundant nuclear spins present in the solution. For the instrumentation operating in our lab, the latter is placed in a cryostat at 1.2 K, and at a magnetic field of 6.7 T, where microwave irradiation of the electron spin resonance line is achieved. NMR experiments can then be performed on ^{1}H spins through an excitation/detection coil. Nuclear spin hyperpolarisation results in an extremely large nuclear magnetisation in the sample, which is responsible for the so-called *radiation damping*, very well known to NMR spectroscopists. Radiation damping is due to the back action of the NMR cicuit onto the precessing magnetization through mutual coupling, and is known to give rise to many unexpected effects in liquid state NMR, where it mostly represents a nuisance. One of the most notable features of RD is that it leads to a nonlinear dynamics of the magnetisation. Notably, radiation damping is ordinary observed in the liquid state, where the intensity of the feedback rf field is comparable to the narrow NMR linewidth (a few Hz), but most unlikely in solids, where the homogeneous (dipolar) linewidth is much larger (tens of kHz).

We have recently observed typical manifestations of such nonlinear magnetisation behaviour in the solid state in DNP-hyperpolarised samples :

- Sustained multiple maser pulses extending on $10 - 100$ ms time scales, which represents $\sim$ three orders of magnitude larger than for conventional signals ;
- Chaotic behaviour of the magnetisation, with observations up to several tens of seconds.

The conditions of observation, as well as the transitions between both dynamical regimes will be discussed. A simple set of modified Bloch equations based on previous work[3,4] and adapted to the complex experimental setup will be used to analyse experimental data.

Références

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