Nuclear Magnetic Spin Noise Spectra

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Observation of nuclear magnetic spin noise is straightforward with modern high-resolution NMR spectrometers, in particular when using cryogenically cooled probes. Previously, we have introduced **spin noise imaging** [N. Müller and A. Jerschow, Proc. Nat. Acad. Sci. USA, 103, 6790 (2006)]. We report recent experiments on solutions and solids investigating the fundamentals and application potential of **spin noise spectroscopy**.

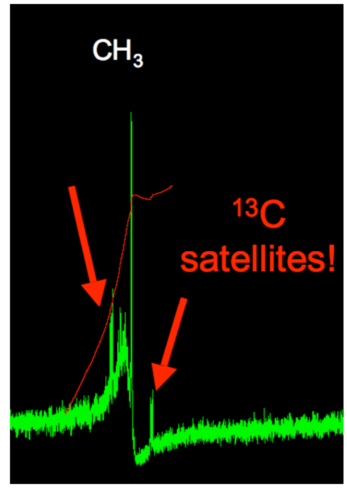

Figure 1: In this 500 MHz ^{1}H spin noise power spectrum of a sample of 80% iso-propanol in DMSO-d_6 the methyl region exhibits "oversized" ^{13}C-satellites. This effect is ascribed to radiation damping of the central resonances. The "dispersion-like" line shape is an effect of the tuning-offset, as explained in the text. The acquisition time on a cryogenic probe for this spin noise spectrum at 500 MHz was 10 min.

High-resolution spin noise NMR spectra can be obtained easily, but **quantification** of the spin noise response depends heavily on the relative rates of transverse relaxation and radiation damping. This is exemplified most impressively in Figure 1 by the observation of ^{13}C-satellites on methyl ^{1}H signals at natural isotope abundance. Only if radiation damping is quenched, e.g. by a weak magnetic field gradient, a linear dependence between the power spectral amplitude and the number of spins is maintained.

The independence of spin noise from longitudinal relaxation may be of advantage for detecting very slowly relaxing spins. In an optimized sampling strategy a **continuous stream of noise data** would be recorded. The stream can be dissected into chunks adapted to the intrinsic line widths (which may be determined by radiation damping, homogeneous or inhomogeneous broadening) to give optimal sensitivity after processing (alternatively, the correlation function can be calculated on the same time-domain stream data).

The **dependence of spin noise on the tuning** of the receiving resonance circuit observed in our experiments deviates significantly from what is predicted by the formulae given by Ernst and McCoy [Chem. Phys. Lett. 139, 587 (1989)]. According to their theory, based on the notion of Nyquist noise in a resonance circuit with frequency dependent resistance and inductance, the presence of spins would cause a "dip" in the noise power spectrum, when their Larmor frequency is at the tuning optimum. On multiply tuned probes (which are standard on today's high performance NMR spectrometers), however, we find surprisingly large offsets from this condition as is shown in Figure 2. Far from the tuning optimum positive noise peaks are observed, in an intermediate range "dispersion-like" line shapes occur in the power spectra, as can be seen in both figures. This tuning dependence, which – at this time – is only qualitatively understood, may serve to **characterize receiver circuits** in magnetic resonance probes. This application appears to be of particular interest under circumstances, where direct physical access to the resonance circuit is impossible, as is the case in cryogenically cooled probes.

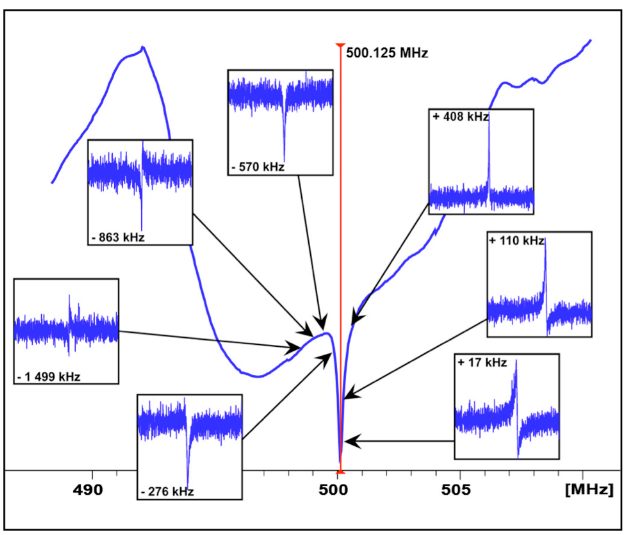

Figure 2: The ^{1}H tuning ("wobble") curve (blue trace) of a cryogenically cooled 500 MHz NMR probe containing a sample of 90%H_2O/10%D_2O (for field stabilization). The ^{1}H spin noise power spectra are shown at selected offset frequencies. Theory predicts a sharp "dip" in the thermal noise at the tuning optimum (red line). We observed the dip at an offset of –570 kHz on this probe. Different probes showed different behavior. Note the changing line shapes of the power spectra as a function of the tuning offset.

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