Communication

Observation of NMR noise from solid samples

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ABSTRACT

We demonstrate that proton NMR noise signals, i.e. NMR spectra without excitation by radio frequency, can be obtained from solid samples. Experimental results are shown for static and magic-angle spinning conditions. In addition, a tuning procedure based on the probes' NMR noise characteristics and similar to the one described previously for liquids probes can also be used to optimize signal-to-noise ratios in ^{1}H-MAS experiments.

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1. Introduction

Even at equilibrium an ensemble of spins gives rise to a small fluctuating signal. This phenomenon was predicted by Bloch [1] in 1946, and was later detected under a variety of conditions for liquid ^{1}H samples [2–6] . For hyperpolarized solutions, Nuclear Magnetic Resonance (NMR) noise has been reported for both ^{69}Xe [7] and, more recently ^{1}H [8]. NMR noise can also be used as an alternative tuning indicator, leading to the so called spin-noise tuning optimum (SNTO) [6,9,10].

In this report, we demonstrate examples of the detection of NMR noise in solid state NMR under both static and MAS conditions.

In previous communications [5,6] we referred to this noise by the term *spin-noise* only. In view of recent results [8] we prefer to use the term *NMR noise*, which encompasses the proper spin-noise (i.e. residual fluctuations from statistically incomplete cancellation) [1] and the conceptually distinct, but often accompanying effect of absorbed circuit noise (ACN) [8].

2. Experimental

NMR noise spectra of static powders were acquired on a Bruker 500 MHz DRX instrument equipped with a liquids-type high-reso-

lution cryogenically cooled (TXI) triple resonance probe. The solid samples were finely ground powders of hexamethylbenzene (Aldrich) and adamantane (VWR chemicals) filled into standard 5 mm NMR sample tubes.

Magic-angle spinning (MAS) NMR noise data were collected on a Bruker 500 MHz Avance III system using a standard 4 mm triple resonance MAS probe in combination with two different dedicated solids high-power preamplifiers and a low-power, low noise preamplifier. The latter designed for high-resolution liquid state NMR was used, since the higher intrinsic noise levels in the broadband receiving chain of a typical solids spectrometer make detection of NMR noise very demanding. To differentiate between probe and preamplifier effects additional experiments were performed using a 4 mm double resonance MAS probe.

To minimize the pickup from external rf-sources, the ^{1}H-pulse cable coming from the power amplifier was disconnected from the preamplifier and a 50 Ω terminator was attached to the preamplifier instead. The ^{1}H pulse amplifier's mains supply was switched off. The X/Y-channels rf-connectors of the probe were also terminated with 50 Ω.

Data were collected (using a pseudo 2D acquisition sequence (containing no pulse) storing one noise block per row) and processed as detailed in Ref. [6].

For the static wide line experiments 16 K (for adamantane) and 20 K (for hexamethylbenzene) data blocks were collected with 160 ppm spectral width and 256 points in the direct dimension of acquisition, for a total experimental time of approximately 15 min.

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In order to find the initial noise signal in the MAS experiments and to optimize tuning and matching conditions until a symmetrical dip line shape for the noise signal was observed (this condition is henceforth referred to as spin-noise tuning optimum – SNTO), the rotor was first filled with H_2O and noise measurements were carried out at 3 kHz MAS frequency with 10 ppm spectral width. The experiments on adamantane were performed under similar conditions, albeit using a spectral width of 50 ppm, 8 kHz MAS frequency, and 32–256 K data blocks to obtain sufficient noise signal for total experimental times of approximately 140 min to 18 h.
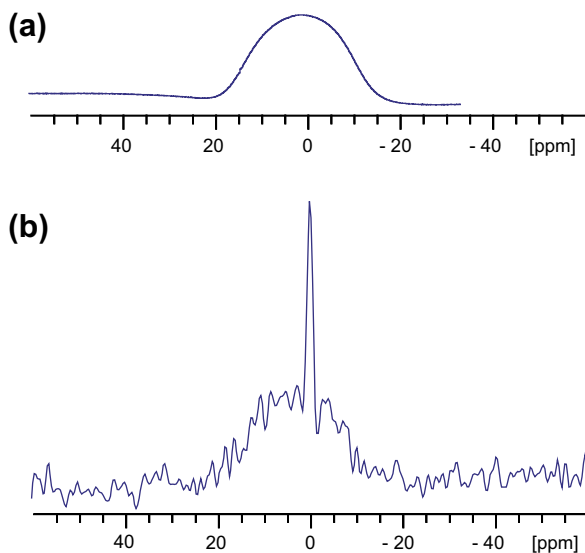
Fig. 1. ^1H single pulse (a) and noise (b) spectra of adamantane powder acquired at 500 MHz with a cryogenically cooled triple resonance probe. Acquisition parameters are given in Section 2.
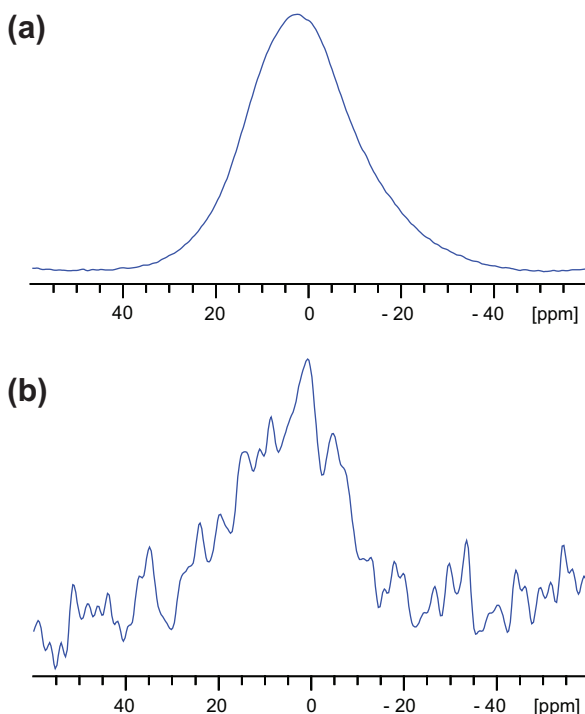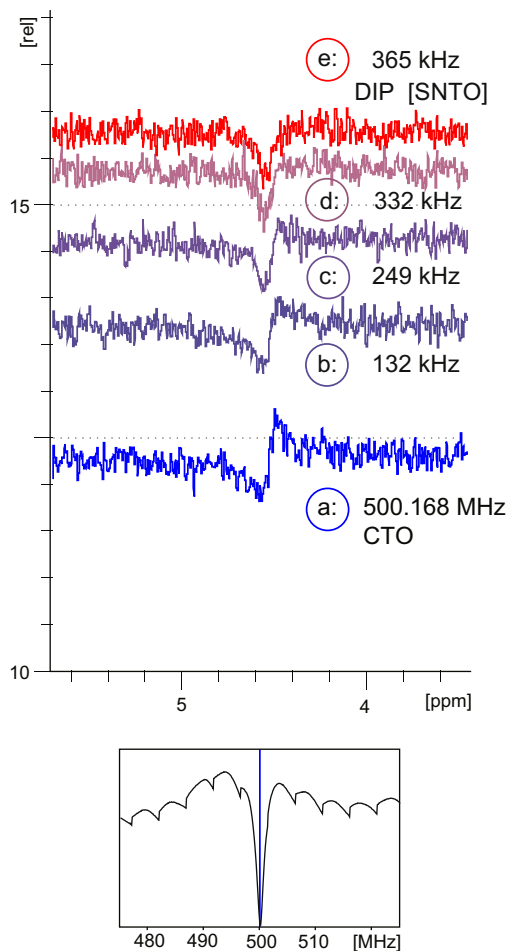

Fig. 2. ^1H single pulse (a) and noise (b) spectra of hexamethylbenzene powder. Acquisition parameters are given in Section 2.

3. Results and discussion

3.1. Static samples

The static solid samples used, adamantane and hexamethylbenzene, are not considered "typical" solids, since high internal mobil-

Fig. 3. Tuning dependence of the line shape of the H_2O ^1H noise signal for a triple resonance MAS probe in combination with a high-power $^1H/^{19}F$ preamplifier. Data were acquired using the general parameters, given in Section 2. The line shape at the CTO (a) has a dispersive character (shown in blue colour, marked with "CTO"). The "dip" line shape (e) was found by de-tuning the probe by 365 kHz. Spectra (b), (c) and (d) illustrate the line shape changes while de-tuning. In addition the conventional tuning curve (sweep width 50 MHz) is shown as a screen shot in the inset frame, which exhibits a notably different shape compared to those in Fig. 4).

Table 1
Tuning frequency at the NMR noise dip (found with H_2O) for different probe – preamplifier – combinations (using the preamplifiers' manufacturer's shorthand designations).

Probe	Preamplifier	Tuning offset (kHz)
Triple	LP LNA ^1H	1365[a]
	HP LNA ^1H	0
	HPHP $^1H/^{19}F$	365
Double	LP LNA ^1H	7165[b]
	HP LNA ^1H	0
	HPHP $^1H/^{19}F$	Dip not found within tuning range

[a] The probe had to be slightly dematched to arrive at the "dip".
[b] Significant de-matching of the probe lead to a "dip". In that case the tuning frequency is the frequency of a secondary very broad global minimum, which occured after de-matching.

ity in these plastic solids narrows the spectra [11]. However, due to the spectral width limitations imposed by the hardware of a liquid state spectrometer, these samples were chosen to demonstrate the feasibility of noise NMR on static solids. In Figs. 1 and 2 we compare conventional NMR spectra (called *pulse spectra* in the following) to noise NMR spectra for the two plastic solids. The short transverse relaxation times in solids allow for very short noise

block acquisition times and therefore permit highly efficient collection of NMR data as compared to pulse spectra, as longitudinal relaxation is irrelevant in the absence of excitation. In spite of the large number of acquired data blocks the total duration of acquisition (excluding buffer transfer times and internal spectrometer delays) for the spectra shown in Figs. 1b and 2b was only several seconds for each. These remarkably short pure acquisition
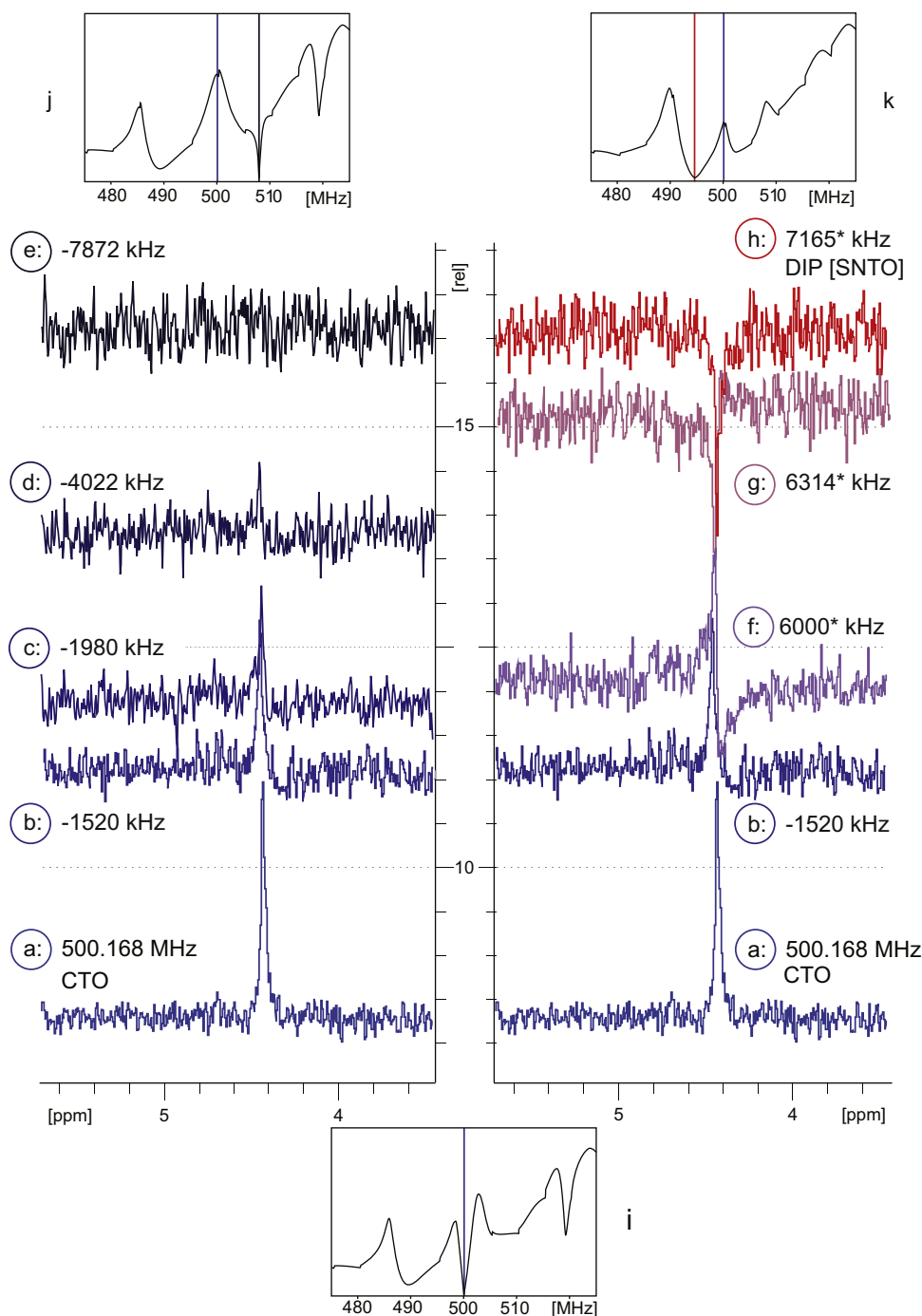
Fig. 4. Tuning and matching dependence of the ^1H_2O noise signal for the double resonance MAS probe connected via a low-power, low noise liquids preamplifier. The left part of the figure shows that de-tuning does not change the line shape of the signal much, while the (thermal) noise level increases, starting from the CTO (a), gradually de-tuning more and more (b), (c) and (d) up to almost −8 MHz offset (e). Significant de-matching starting from point (b) resulted in the line shape (f). De-matching of the probe lead to a new global minimum in the conventional tuning curve (tuning offsets under "de-matched conditions" are marked by asterisks). The dip-type noise signal (h) was found by trial and error adjustments of the tuning and matching capacitors from situation (f). Data were acquired using the parameters, given in Section 2. The line shape at the CTO has a pure positive character ("bump", shown in blue, marked with "CTO"). Conventional tuning curves (sweep width 50 MHz) (i, j, k) correspond to the spectra (a, e, h), respectively. Light blue lines mark the centre frequencies (500.16 MHz), the dark blue line in (j) shows the position of the maximum tuning offset (e) accessible by the tuning capacitor and the red line in (h) designates the SNTO.

times for noise spectra of static solids highlight an application potential of NMR noise detection for specialized applications to very slowly relaxing nuclei, such as, for example, found in nano-diamond powder [12].

To compensate for the non-uniform rf-background noise of the narrow-band spectrometer system used, baseline corrections were required for wide line spectra. For this purpose a noise power spectrum obtained with an empty NMR tube under identical conditions was subtracted from the initial noise power spectra of each sample.

In the ^{1}H noise spectrum of adamantane (Fig. 1b) obtained in this way one can see a spike near zero frequency arising from incomplete cancellation of coherent artifacts near the carrier frequency. While such artifacts are usually negligible in noise spectra of liquid samples [6,9], they can be prominent in wide line noise NMR spectra, because the energy spectral density of the wide line solid signal is much weaker than a corresponding high resolution NMR noise signal. Since the decoherence times of these electronic artifacts is much longer than the solid samples' ^{1}H transverse relaxation time, which determines the line shapes of NMR noise signals under conditions, where radiation damping can be neglected [6,8,13], there is a simple remedy: the coherent electronic signals are efficiently suppressed by pair-wise subtraction of subsequent noise data blocks before Fourier transform. This is demonstrated in the noise spectrum of solid hexamethylbenzene shown in Fig. 2b, which was otherwise processed like the spectrum in Fig. 1b. Due to the random nature of the NMR noise signal this subtraction procedure results in a signal loss by a factor $(\sqrt{2})^{-1}$.

Comparing the pulse spectra to the noise spectra in Figs. 1 and 2 one can see that the line shapes are well reproduced. It is noteworthy here that, if the temperature ratio $T_{\text{sample}}/T_{\text{coil}} > 2$, these wide line noise spectra are always positive (i.e. the ^{1}H noise is always adding to the thermal noise) irrespective of the tuning offset, since $T_2 \ll T_{\text{rd}}$, as can be rationalized from Eqs. (2) to (4) in Ref. [6].

3.2. Magic-angle spinning experiments

Using MAS NMR we observed ^{1}H NMR noise spectra for liquid H_2O and adamantane powder using both a triple and a double resonance probe in combination with three different preamplifiers.

According to the description of the line shape of the spin-noise signal by McCoy and Ernst [13], a pure Lorentzian absorption signal ("dip") should occur, if the resonance frequency of the rf-circuit coincides with the Larmor frequency. As described for liquid state NMR noise experiments [6,9] the tuning required to obtain this dip line shape may deviate from the conventional tuning optimum (CTO). This offset also does not generally coincide with the optimum determined by minimizing reflected power through an external reflection bridge. This was also the case for the triple and double resonance probes in combination with two preamplifiers, where the noise power signal exhibits a dispersive line shape at the CTO.

Fig. 3 shows noise spectra of H_2O at different tuning offsets obtained using the triple resonance probe connected to a high-power ^{1}H/^{19}F preamplifier. Note that both the observed line shape and the average (thermal) noise level are tuning-dependent. De-tuning of the other channels had no influence on the ^{1}H noise signal. The SNTO [6], where a pure "dip" power line shape (i.e. a noise level lower than average thermal noise) was seen, was at a tuning offset of 365 kHz from the resonance frequency. This offset varies between different probes and preamplifiers as shown in Table 1.

Using a (^{1}H/^{13}C) double resonance MAS probe instead, surprisingly, only positive noise signals could be found within the entire tuning and matching range. We concluded that the SNTO for this probe/amplifier connection lay outside the range accessible by the tuning capacitors.

Using a high-power (solids) low noise preamplifier, the dip tuning offset was zero. This was the case for this preamplifier with all probes used.

In combination with a low-power preamplifier the shape of the tuning curve was significantly different. The pure dip signal was not found with the normal routine within the tuning ranges of both probes. De-matching had a significant influence on both the noise line shape and the average thermal noise level. In the case of the triple resonance probe, slight de-matching, in case of the double resonance probe (Fig. 4), significant de-matching (a new minimum occurred in the tuning curve) together with de-tuning allowed us to find settings that gave rise to a dip line shape of the noise signal, in a trial-and-error approach. A more systematic approach is under investigation in our laboratories.

Apparently there can be more than one combination of tuning and matching adjustments that yield an NMR noise dip signal, at least on some probes.

The MAS tuning and matching conditions found for the H_2O sample were also used for adamantane. In this case, where a dip was found by de-tuning only, the probe was tuned to the same SNTO frequency as found for H_2O. If de-tuning and de-matching were necessary to find the dip, the controls were adjusted until the conventional tuning curve resembled as closely as possible the one found with H_2O.
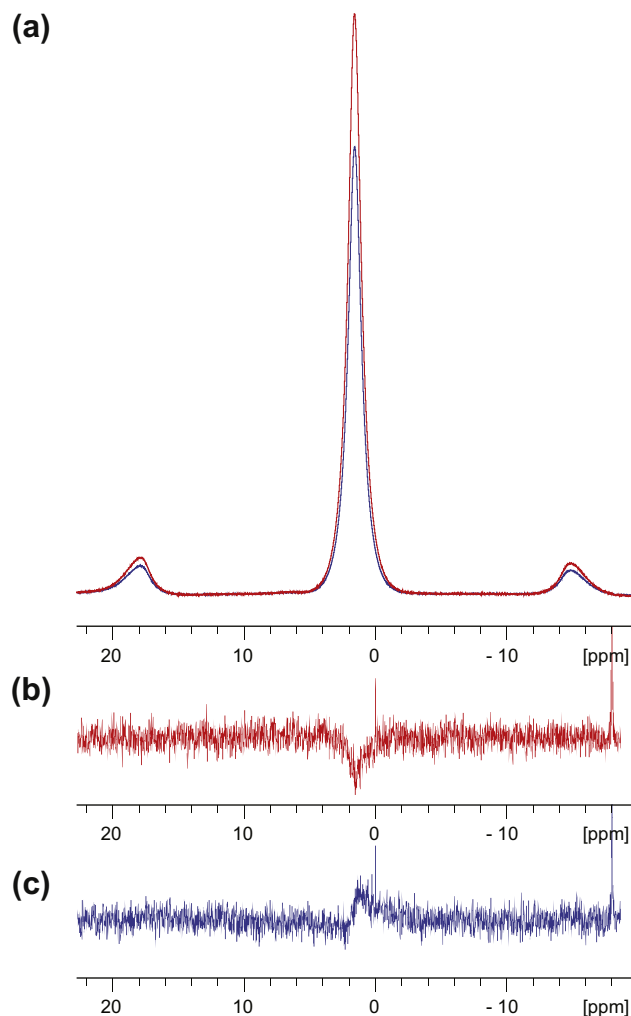

Fig. 5. Comparison of noise spectra (b and c) and pulse spectra (a) of adamantane, obtained using the triple resonance probe connected to a low-power, low noise liquids preamplifier, at SNTO (red) and CTO (blue) conditions.

Table 2

Tuning dependence of the pulsed ^{1}H-NMR signal of solid adamantane, rms-noise, derived S/N, and 90° pulse length (p90) obtained on a triple resonance probe in combination with a low-power low noise preamplifier under CTO and SNTO conditions. Because of the long 90° pulse lengths and to allow us to use a higher receiver gain (RG set to 80.6, sufficient to avoid digitization noise problems on this spectrometer system) the spectra were acquired at 1/40 of the 90° pulse lengths. Note the small difference in the SNTO-frequencies obtained for adamantane (shown here) and for water (Table 1).

Triple	Tuning-offset (kHz)	Signal amplitude	Noise	S/N	p90 (µs) 0 dB
CTO	0	0.851×10^6	330.841	1285.7	6.0
SNTO	1329	1.104×10^6	456.842	1208.1	10.0
Difference	1329	+29.7%	+38.1%	−6.0%	4.0

Table 3

Tuning dependence of the pulsed ^{1}H-NMR signal of solid adamantane, rms-noise, derived S/N, and 90° pulse length (p90) obtained on a double resonance probe under CTO and SNTO conditions. Because of the long 90° pulse lengths and to allow us to use a higher receiver gain (RG set to 71.8, sufficient to avoid digitization noise problems on this spectrometer system), the spectra were acquired at 1/20 of the 90° pulse lengths.

Double	Tuning offset (kHz)	Signal	Noise	S/N	p90 (µs), 0 dB
CTO	0	1.180×10^6	649.042	908.955	5.5
SNTO	5941[a]	1.425×10^6	730.267	975.512	9.0
Difference	5941	+20.8%	+12.5%	+29.7%	3.5

[a] Tuning offset of a "new" very broad global minimum, which resulted from significantly de-matching the probe.

In Fig. 5 pulse and noise spectra of adamantane obtained under conventional tuning (CTO) and SNTO conditions are compared. In the pulse spectra one can see that a substantial signal gain is achieved for both probes at the SNTO compared to the CTO: about 30% and 20% (for the triple and double resonance probes, respectively). As reported for liquid state spectra [6] and as a consequence of the tuning offsets and sub-optimal matching for pulse conditions the pulse durations increase concomitantly. The thermal noise also depends on the tuning and matching. The noise level is somewhat bigger at SNTO-conditions for the probes tested (Tables 2 and 3).

Comparing the wide line noise spectra and the MAS noise spectra, a most noteworthy difference is that a dip noise signal is found for the MAS case only. This behavior can be understood well within the modified Nyquist treatment by considering the difference of scale between T_2 and T_{rd} in line with Eqs. (2)–(4) in Ref. [6].

4. Conclusion

The properties of NMR noise signals with respect to line shape, thermal noise level and tuning dependence resemble those observed for liquid state NMR [6]. The static solids investigated on a high-resolution cryogenically cooled liquids probe showed a positive (bump) NMR noise response, which indicates prevailing of pure spin-noise as opposed to absorbed circuit noise [8]. The short transverse relaxation times in static solids efficiently quench radiation damping, allowing straightforward observation of pure spin-noise.

The line shape of the NMR noise signal from MAS probes does not only depend on tuning but is also significantly influenced by the matching adjustment and the preamplifier used. In some cases, only significant de-matching allowed to arrive at the spin-noise tuning optimum (SNTO).

The SNTO offsets are not influenced significantly by the sample properties. For example, it is nearly the same for liquid H_2O and solid adamantane. For this reason, it suffices to determine the spin-noise tuning offset only once for a particular probe/preamplifier pair.

At SNTO conditions with large offsets from the Larmor frequency the signal of MAS pulse spectra can be enhanced by up to 20–30% as compared to the conventional tuning conditions. Similarly, large tuning offsets have been reported recently by Rossini et al. [14] for optimized NQR spectra of [75]As and [35]Cl.

With respect to NMR probe circuits, we propose that a probe design, which makes the conventional tuning and noise optima coincide, can help to obtain probes performing better under both pulse and receiving conditions, thus ultimately making special tuning protocols such as finding the SNTO [6,9] obsolete.

References

[1] F. Bloch, Nuclear induction, Phys. Rev. 70 (1946) 460–475.
[2] T. Sleator, E.L. Hahn, C. Hilbert, J. Clarke, Nuclear-spin noise, Phys. Rev. Lett. 55 (1985) 1742–1746.
[3] T. Sleator, E.L. Hahn, C. Hilbert, J. Clarke, Nuclear-spin noise and spontaneous emission, Phys. Rev. B 36 (1987) 1969–1981.
[4] M. Guéron, J.L. Leroy, NMR of water protons. The detection of their nuclear-spin noise, and a simple determination of absolute probe sensitivity based on radiation damping, J. Magn. Reson. 85 (1989) 209–215.
[5] N. Müller, A. Jerschow, Nuclear spin noise imaging, Proc. Natl. Acad. Sci. USA 103 (2006) 6790–6792.
[6] M. Nausner, J. Schlagnitweit, V. Smrecki, X. Yang, A. Jerschow, N. Müller, Non-linearity and frequency shifts of nuclear magnetic spin-noise, J. Magn. Reson. 198 (2009) 73–79.
[7] H. Desvaux, D.J.Y. Marion, G. Huber, P. Berthault, Nuclear spin-noise spectra of hyperpolarized systems, Angew. Chem. Int. Ed. 48 (2009) 4341–4343.
[8] P. Giraudeau, N. Müller, A. Jerschow, L. Frydman, ^{1}H NMR noise measurements in hyperpolarized liquid samples, Chem. Phys. Lett. 489 (2010) 107–112.
[9] D.J.-Y. Marion, H. Desvaux, An alternative tuning approach to enhance NMR signals, J. Magn. Reson. 193 (2008) 153–157.
[10] M. Nausner, M. Goger, E. Bendet-Taicher, J. Schlagnitweit, A. Jerschow, N. Müller, Signal enhancement in protein NMR using the spin noise tuning optimum, J. Biomol. NMR, doi:10.1007/s10858-010-9446-4.
[11] W.P. Slichter, Nuclear magnetic relaxation in organic crystals, Mol. Cryst. Liq. Cryst. 9 (1969) 81–99.
[12] E.M. Levin, X.W. Fang, S.L. Bud'ko, W.E. Straszheim, R.W. McCallum, K. Schmidt-Rohr, Magnetization and ^{13}C NMR spin-lattice relaxation of nanodiamond powder, Phys. Rev. B 77 (2008) 054418.
[13] M.A. McCoy, R.R. Ernst, Nuclear spin noise at room temperature, Chem. Phys. Lett. 159 (1989) 587–593.
[14] A.J. Rossini, H. Hamaed, R.W. Schurko, The application of frequency swept pulses for the acquisition of nuclear quadrupole resonance spectra, J. Magn. Reson. 207 (2010) 32–40.