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Communication

An alternative tuning approach to enhance NMR signals

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ABSTRACT

By using spin-noise type measurement we show that the resonance frequency of the reception circuit of classical NMR spectrometers does not match the Larmor frequency even if, in emission, the electronic circuit is perfectly tuned at the Larmor frequency and matches the amplifier impedance. We also show that this spin-noise method can be used to ensure a match between the Larmor frequency and the reception circuit resonance frequency. In these conditions, (i) the radiation damping field is in perfect quadrature to the magnetization and (ii) the NMR signal level and potentially the signal-to-noise ratio, are enhanced. This choice induces a change of the probe resonance frequency by several hundreds of kHz for 500 or 700 MHz spectrometer. We show that the resulting mismatch condition for emission can be removed by adding other tuning and matching degrees of freedom located on the excitation line (or by symmetry on the reception line) decoupled to the probe resonance circuit by the crossed diodes.

1. Introduction

We have recently reported the observation of spontaneous multiple chaotic maser emissions [1] using laser-polarized xenon with magnetization anti-aligned with the static magnetic field. This type of phenomenon corresponds to maximal interaction between the transverse nuclear magnetization and the detection coil through the so-called radiation damping effect. This old-story phenomenon corresponds to a non-linear retroaction on the magnetization: the precessing magnetization creates a current in the coil by induction which, in return, creates an oscillating magnetic field at the exact Larmor frequency that interacts with the nuclear magnetization [2,3]. The precessing magnetization and the radiation-damping field in the rotating frame are in exact quadrature only when the coil is perfectly tuned at the Larmor frequency [4]. This was the case for the multiple maser experiments but a preliminary key question was how to ensure such a perfect tuning.

In this article, we show that since the excitation and detection pathways are distinct, the parasite capacities and inductances of diodes and wires modify the resonance frequencies of the two circuits. We illustrate this discrepancy by using principles based on spin-noise detection [5–9], and accordingly an alternative method of frequency tuning, optimized for the reception circuit, is suggested. We also show that when the electronic resonance frequency of the reception circuit matches the Larmor frequency, the NMR signal is improved and the impedance matching of the emission line can however be restored.

2. Results

2.1. Tuning according to the reception channel

Fig. 1 describes a classical NMR probe [10]. The two capacities C_t and C_m ensure that the coil of inductance L and resistance r is tuned at the Larmor frequency of the studied nuclear spins, ω_0. On the other hand, two sets of crossed diodes in positions A and B are used to separate the emission and detection circuits. Classical procedures to ensure that the probe is tuned at the Larmor frequency and matched at the amplifier impedance (usually 50 Ω) consist either in using a Balun circuit with a wobbulator or in using a bidirectional coaxial coupler to monitor reflections towards the amplifier [11]. In any case these methods ensure a proper delivery of the amplifier power to the probe. We define these approaches as frequency tuning according to the emission circuit.

After these steps, the quality of the frequency tuning according to the reception circuit, i.e. through the point B of Fig. 1 was investigated using a spectrum analyzer located at the output of the preamplifier. As observed in Fig. 2A, the Bode diagram revealed that the resonance frequency of the detection circuit was 699.8 MHz while it was tuned in emission at 700.13 MHz. Note that (i) using other reference resistances, when the frequency tuning according to emission circuit is made with a Balun circuit, or (ii) using other tuning schemes based on the concept of minimizing reflections always led to a discrepancy between the Larmor frequency and the resonance frequency of the reception circuit. Moreover the comparison of the noise level in power at these two frequencies (Fig. 2) revealed a difference of 1.1 dB, which meant that the NMR signal could be enhanced by about 25% with proper adjustment.

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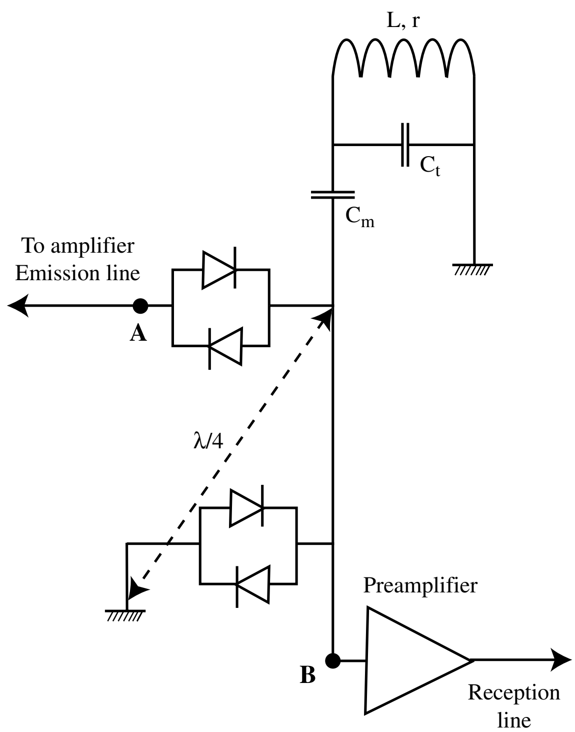

Fig. 1. Schematic representation of an NMR probe with the decoupling diodes. Probe frequency tuning according to the emission circuit is done through point A, while for the reception circuit, monitoring takes place through B.

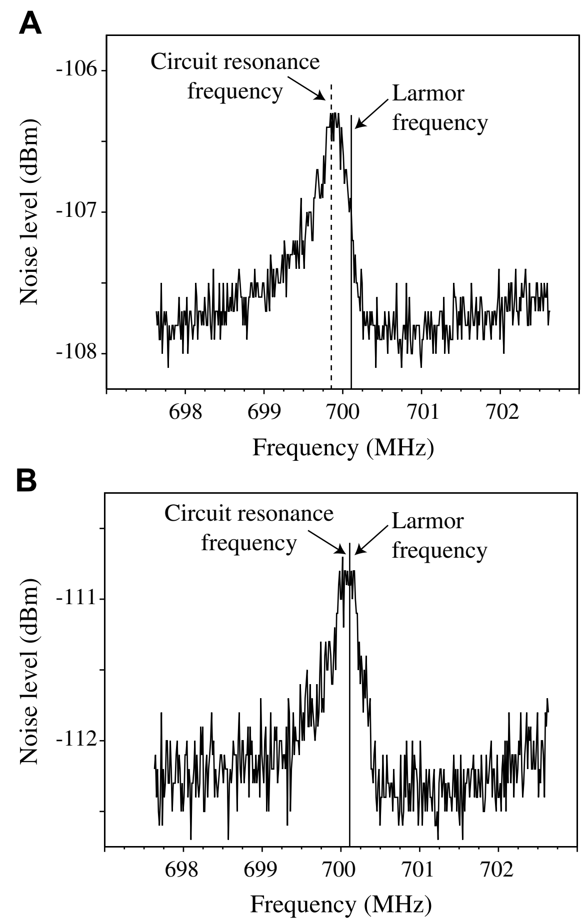

Fig. 2. Noise level measured on a cryoprobe with an ethyl-benzene sample. They were measured after frequency tuning in emission A or in reception B. The Bode diagram illustrates in A, a difference between the probe resonance frequency and the Larmor frequency on the order of 290 kHz. In B, the tuning is correct. The absolute values of the noise level in dB are only indicative since the measurements were not shielded thus they depend on the local-time surrounding noise.

Using this measurement scheme with help of a spectrum analyzer, the tuning of the reception circuit at the proton Larmor frequency was performed by changing the tuning capacity C_t. A Bode diagram as that of Fig. 2B was obtained, revealing a perfect agreement between the amplification of the probe's resonant circuit and the Larmor frequency.

The NMR spectrometer can be used in place of the spectrum analyzer to determine the response of the reception circuit. A high number of FIDs is acquired with a large bandwidth and no rf excitation. They are summed after Fourier transformation and power spectrum calculation. The obtained spectrum corresponds to the frequency response of the reception circuit which is exactly the one used for any NMR acquisition scheme. Maximizing the average noise level ensures that one obtains a perfect match between the reception circuit's resonance frequency and the Larmor frequency. This is the procedure we used in the case of xenon multiple masers [1]. Using this principle, we have also observed a discrepancy in the electronic resonance frequencies of the emission and reception circuit (see Fig. 3). This solution, even if it is slower than resorting to a spectrum analyzer, ensures the correct tuning of the exactly used electronic reception circuit.

We have observed such a discrepancy of resonance frequency between the excitation and detection circuits on all tested apparatus: direct or inverse probeheads, cryoprobe, 500- or 700-MHz spectrometers and even for nuclear spins other than the proton. Depending on the quality factor Q of the probe, the frequency mismatch was found to be about several hundreds of kHz and could be as large as 750 kHz for ^{1}H probe with coil at room temperature.

2.2. Spin-noise measurements

The difference of resonance frequency of the excitation and reception circuits has direct effect on the NMR spin dynamics when the magnetization of a studied sample component and the coil properties are sufficient to induce radiation damping [2,3]. Indeed during acquisition, the reception circuit is the relevant one. Hence if its electronic resonance frequency ω_c differs from the Larmor frequency ω_0, the radiation-damping field is no longer in phase quadrature with the magnetization, leading to phase distortions of the NMR signal detected after rf excitations [4].

For such a sample where radiation damping is present, its NMR spectrum can be determined by the spin-noise approach [7]. McCoy and Ernst have shown that, for a system at thermal equilibrium, the spin-noise spectral density $W^U(\omega) - W^U(\infty)$ is proportional to:

$$W^U(\omega) - W^U(\infty) \propto \frac{1 + a(\Delta\omega)\lambda_r}{[1 + a(\Delta\omega)\lambda_r]^2 + [d(\Delta\omega)\lambda_r + 2Q(\omega - \omega_c)/\omega_c]^2} \quad (1)$$

where $\Delta\omega = \omega - \omega_0$, $a(\Delta\omega)$ and $d(\Delta\omega)$ are the normalized absorption and dispersion NMR signals and λ_r is the radiation-damping rate. The inspection of this equation as a function of $\omega - \omega_c$ reveals that the noise level far from spin resonance ($|\omega - \omega_0| \gg \lambda_r$) is maximum for $\omega \simeq \omega_c$. Also only when this tuning condition is matched, Eq. (1) is reduced to a pure absorption Lorentzian function appearing as a dip:

$$W^U(\omega) - W^U(\infty) \propto 1 - \frac{\lambda_r(\lambda_2 + \lambda_r)}{(\lambda_2 + \lambda_r)^2 + \Delta\omega^2} \quad (2)$$

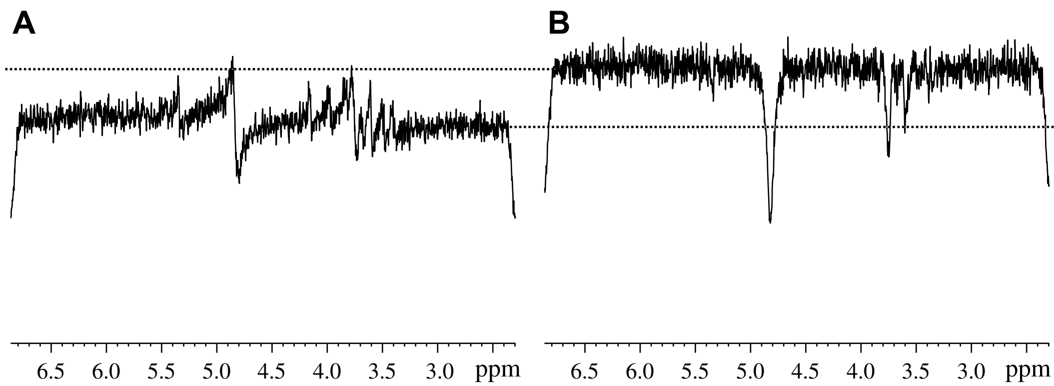

Fig. 3. Spin-noise power spectra of a concentrated saccharose sample at 700 MHz. No baseline correction was applied. A The probe is perfectly tuned and matched according to the emission. The resonance peak shapes are asymmetric. B When the probe is tuned according to the reception, signals of pure absorption Lorentzian shape are obtained (Eq. (2)). One can also notice that the average noise level (materialized by the dotted line) is higher in the case of B, an other illustration of a better adjustment.

with λ_2 the nuclear spin transverse self-relaxation rate. If the condition $\omega \simeq \omega_c$ is not fulfilled, the spin resonance appears as an asymmetric peak superimposing on the average noise level [7,9].

Spectra of Fig. 3 were obtained using this method with a probe tuned according to the emission circuit (A) or according to the reception circuit (B). As measured by the Balun system of the spectrometer ("wobb" command), the electronic resonance frequency of the emission circuit for the spectrum A was 700.13 and 700.49 MHz for the spectrum B. In the first case, the NMR peaks are asymmetric, a feature already observed [7–9]. This is a direct illustration of a difference between the resonance frequencies of the reception circuit ω_c and of the nuclear spins ω_0. When the probe is tuned according to the reception circuit using the method described above, NMR resonance peaks appear as pure absorption Lorentzian shapes (Fig. 3B). Indeed for this experiment, we took benefit from this phase condition to carefully adjust the tuning frequency of the probe according to the reception circuit. These shapes prove that in this tuning condition the radiation-damping field is in perfect quadrature to the transverse magnetization. As discussed in the previous section and in agreement with Eq. (1), one can notice that the average noise level of spectrum B, i.e. out of the nuclear spin resonance peaks, is higher than that of spectrum A. This corresponds to the tuning condition which can be used for all NMR systems, even in the absence of radiation-damping effect. In fact, this result is another illustration that, according to the reception circuit, the frequency tuning is better in B than in A.

2.3. Signal improvement and signal-to-noise ratio

As expected from the Bode diagram (Fig. 2) or average noise level (Fig. 3), by matching the resonance frequency of the reception electronic circuit to the Larmor frequency, an enhancement of NMR signal amplitude is observed (Fig. 4). The net signal improvement computed as $(I_B - I_A)/I_A$, corresponds to 28% as measured in signal amplitude and 31.5% as measured in integrals.

This improvement in signal amplitudes can also be observed when looking at the signal-to-noise ratio. Fig. 5 reveals an improvement on the order of 30% for a large range of receiver gain. For the largest receiver gains, the two values saturate at the same level. A similar behavior was observed for the noise level computed on a 200-Hz range. Indeed, the improvement of the probe sensitivity by tuning according to the reception circuit increases the NMR signal but also the noise; keeping *a priori* the ratio constant. Now, the receiver gain level defines the number of digits available to quantify the noise and the signals. This adds a new noise source, referenced as the digitalization noise, which is predominant in our experiments

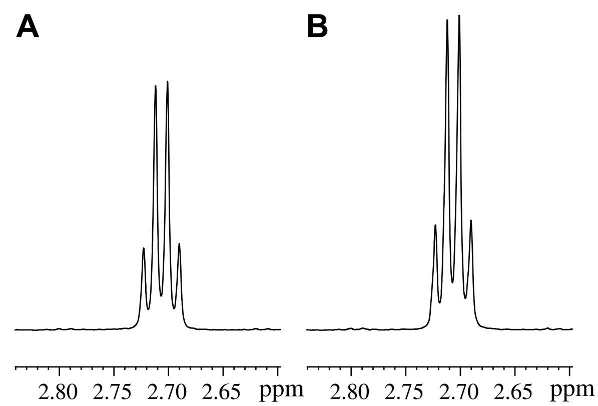

Fig. 4. Comparison on a reference sample (0.1% ethyl-benzene in chloroform) of the improvement in signal amplitude allowed by the tuning according to the reception circuit (B) relative to the classical procedure (A).

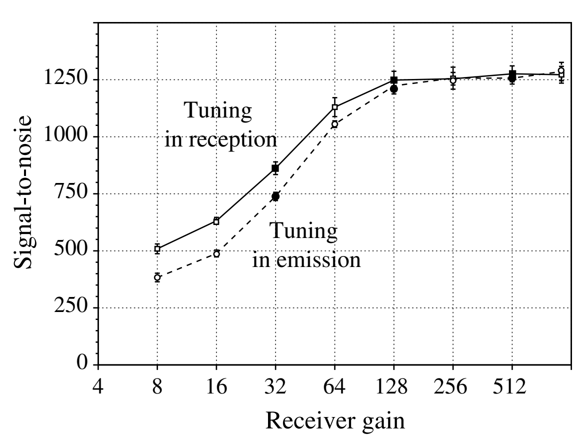

Fig. 5. Evolution of the signal-to-noise ratios as a function of the receiver gain for the tuning according to emission (dotted line) and to reception (solid line). The values are averaged performed on five (open symbols) or 10 (solid symbol) independent measurements. The signal was measured on the methylene signal of a 0.02% sample of ethyl-benzene in chloroform and the noise computed on 2 ppm.

at low receiver gain levels: for the largest gain levels, the sensitivity of the receiver allows a proper measurement of the electronic noise and the whole noise of the experiment is then mainly defined by the probe noise, whereas for small receiver gain levels, only the signal is correctly digitalized. Hence, the NMR signal improvement allowed by the correct tuning of the probe is reproduced after digitalization while the increase of the probe electronic noise level is truncated by the resolution of the digitizer. This derivation does not take into account the preamplifier noise. When its contribution is non negligible compared to the probe noise, a rapid calculation indicates that the tuning according to reception always leads to a better signal-to-noise ratio, whatever the receiver gain level.

3. Discussion

Adjusting the C_t and C_m values of the probe for matching the electronic resonance frequency of the reception circuit to the Larmor frequency exhibits two advantages:

- It allows the obtaining of larger signals and potentially larger signal-to-noise ratio than those obtained with the classical tuning procedure;
- It ensures that radiation-damping field is in quadrature to the transverse magnetization. Hence the resonance line of nuclear magnetization exhibiting radiation damping remains symmetric [4]. It is consequently easier to suppress them by classical techniques (see for instance Refs. [12,13]). Also maser responses become more predictable.

However, since we have shown that the emission and detection circuits are not tuned at the same frequency, in conditions optimized for reception, the emission circuit is no longer tuned at the Larmor frequency and matched to the amplifier impedance. An obvious consequence effectively observed is the increase of the 90° pulse durations. Using the same amplifier power, it was equal to 6.35 μs when the probe was tuned according to emission and 7.10 μs when the reception was optimized (case of Fig. 4). Indeed since the system is no longer matched at the amplifier impedance, part of the power it delivers is lost in the transmission line and reflected to the amplifier. If this appears of little importance for standard 1D experiments, it is clear that acquiring spectra with pulse sequences requiring strong rf irradiations, for instance for decoupling or recoupling, would become problematic. Supplementary tuning and matching capabilities are consequently needed. This supplementary adjusting electronic circuits, typically composed of inductance or capacitance elements, can be put at point A of Fig. 1 (before the diodes on the amplifier line) and/or B (after the diodes on the reception line) in order to have, as much as possible, no influence on the resonance frequency of the other part of the circuit.

As an illustration, after having optimized the probe tuning according to the reception circuit and thus keeping the C_m and C_t values constant, we have modulated the length of the wire between point A and the amplifier, i.e. changing the impedance of the emission line. The monitoring of the quality of the frequency matching according to the emission circuit was performed by using a bi-directional coaxial coupler. Thanks to this matching capability, at constant power, the duration of the ^{1}H 90° hard pulse was reduced back from 7.10 to 6.65 μs, revealing a concomitant decrease of reflected power. We have checked by spin-noise measurements that the correctness of the frequency tuning according to the reception was conserved. Also signal-to-noise measurements clearly indicated that this impedance matching, performed on the emission line, did not affect at all the improvement in sensitivity allowed by ensuring a proper matching between the electronic resonance frequency of the reception circuit and the Larmor frequency.

4. Conclusions

We have observed that tuning a probehead according to the emission circuit systematically leads to a mismatch between the reception circuit's resonance frequency and the Larmor frequency. We have shown that the tuning in reception is possible using a protocol based on the spin-noise measurement method. Using this approach an improvement in signal with respect to the classical approach on the order of 25–30% was achieved, and when the probe is tuned in these conditions, the radiation-damping field is exactly in quadrature relative to the magnetization. This ensures symmetric resonance lines and thus easier conditions to suppress solvent signals. Obviously, by tuning the circuit according to the reception, impedance matching between the amplifier and the probe requires extra degrees of freedom. By adding these degrees, we have shown that power reflection in the emission line can be minimized while the advantages associated to reception tuning are conserved. The potential of the present method in terms of sensitivity enhancement when the gain amplifier is limited by large signals, for instance resulting from solvents or buffers, and in terms of the quality of solvent signal suppressions makes us believing that these simple improvements should rapidly be implemented on commercial spectrometers.

5. Experimental

All experiments reported here were performed at 293 K on a Bruker Avance 700 spectrometer equipped with a TCI cryoprobe. The sample was either the standard ^{1}H signal-to-noise reference sample (ethyl-benzene at 0.1% in deuterated chloroform) from Bruker, a degassed diluted version (0.02% of ethyl-benzene) or a D_2O solution containing 0.7 g of saccharose.

The signal-to-noise measurements were performed using the standard protocol (Bruker "sinocal" automatic program). It consisted after signal acquisition, exponential line-broadening and Fourier transformation, in the calculation of the ratio of the methylene peak signal (2.8 ppm) to a base-line corrected root-mean square deviation of the noise in a 200-Hz or 2 ppm domain located between 2.8 and 7 ppm. Its location was automatically chosen to optimize the signal-to-noise ratio. For each gain value, the values of signal-to-noise ratio of Fig. 5 correspond to mean values computed on 5 or 10 different spectra (same number for the two frequency tuning schemes).

Spin-noise spectra (Fig. 3) were obtained by acquiring, without excitation, 700 FIDs composed of 2048 points on a spectral bandwidth of 6410 Hz. Each one was Fourier-transformed, and the power spectrum calculated. They were then summed.

Bode diagram of the Fig. 2 were obtained using a E4411B spectrum analyzer from Agilent Technologies. The pulse sequence used on the spectrometer was just a very fast succession of long acquisitions with no rf excitation.

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