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Neutralization of radiation damping by selective feedback on a 400 MHz NMR spectrometer

Alain Louis-Joseph*, Daniel Abergel and Jean-Yves Lallemand

Groupe de RMN, DCSO, École Polytechnique, F-91128 Palaiseau, France

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Summary

Radiation damping is a phenomenon well known among NMR spectroscopists of proteins as a source of undesirable features, especially in high-field and high-Q probe NMR. In this paper, we present an electronic neutralization network which dramatically reduces radiation damping. It detects the radiation field profile and feeds back into the probe an rf field with identical amplitude and opposite phase. Experimental results of a practical implementation carried out on a 400 MHz Bruker spectrometer are shown.

Radiation damping belongs to a group of magic expressions, often invoked by NMR spectroscopists to explain unexpected signals or artifacts. It is indeed a phenomenon well studied from the early beginnings of NMR spectroscopy (Bloembergen and Pound, 1954). Radiation damping has become an everyday concern in NMR spectroscopy of biomolecules. It causes a broadening of the water resonance line; moreover, it may induce uncontrolled behaviour of the water magnetization during experiments (typically when the water magnetization is tilted from equilibrium by 180°, see also Warren et al. (1989) for radiation damping adapted pulse design). As a result, radiation damping often hampers pulse sequence optimization. With the increase of the magnetic field strength of new spectrometers, larger effects can be detected and radiation damping may become a crucial problem in very high field NMR, further enhanced by the use of high-quality factor (high-Q) probes. During the past few years, the phenomenon has received renewed interest following the observation of unexpected features in high-resolution spectra of water (McCoy and Warren, 1990; Abergel et al., 1992; Warren et al., 1992). Indeed, radiation damping has been shown to be responsible for harmonic peaks in simple high-resolution NMR experiments (Jeener and Vlassenbroeck, 1991; Vlassenbroeck, 1993; Abergel and Lallemand, 1994). These features are likely to be confusing in the interpretation of crowded spectra, since the spurious peaks observed could easily be considered as part of the signal one is looking for. These recent considerations have motivated the need for suppression of the phenomenon of radiation damping.

Radiation damping is due to the interaction between the precessing transverse magnetization $\mathbf{m} = \mathbf{m}_x + i\,\mathbf{m}_y$ of the sample and the detection network. The current induced in the receiver coil produces a reaction field in the xy plane, the intensity of which is proportional to $|\mathbf{m}|$. In the case of a tuned circuit, this field lags the transverse magnetization by 90° (Bloom, 1957):

$$\mathbf{B}_r(t) = i2\pi\eta Q\,\mathbf{m} \qquad (1)$$

This is represented in Fig. 1.

The ringing field acts on the spins and induces a return of the magnetization to the equilibrium state (in the case of a free precession), in a time shorter than the real T_2 relaxation time. The evolution is now cooperative evolution of an assembly of a large number of spins which are coupled together via a common magnetic field. The spins thus behave like a single large momentum (see, for instance, Dicke (1954)). Once the magnetization is tilted by a certain angle from its equilibrium value, and in the ideal case of infinite relaxation times ($T_1 = T_2 = \infty$), it undergoes a movement on a sphere back to its initial state. In this respect it is noteworthy that radiation damping,

*To whom correspondence should be addressed.

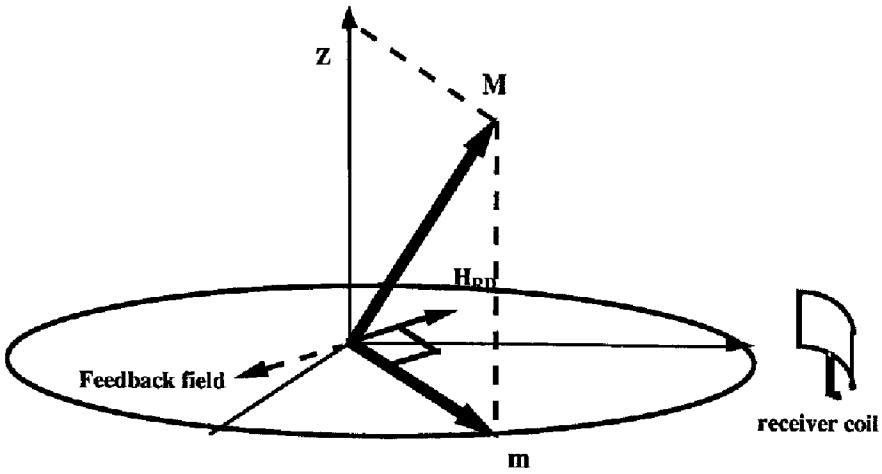

Fig. 1. Schema representing the relative orientations of the magnetization and the radiation damping vector field. The dashed arrow represents the desired feedback field.

although a dissipative phenomenon, is a stochastic one. This explains the behaviour of the magnetization, which is very different from that of magnetization returning to equilibrium when subject to, for instance, T_2 relaxation. Radiation damping leads to a broadening of the resonance lines of the abundant spins, usually those of the solvent. Furthermore, radiation damping also causes lineshape distortions, due to the characteristic hyperbolic secant profile of the free induction decay (FID) in this case. This hyperbolic secant FID profile obtained after a 180° pulse is related to the well-known Maser effect in quantum optics, first described by Szöke and Meiboom in the context of NMR (Szöke and Meiboom, 1959). It very clearly illustrates the limits of the exponentially damped model for the FIDs in the case of abundant spins. Note that, as a consequence, a Fourier analysis of the signal will no longer give Lorentzian resonance lines.

Thus, one may think of a means to get rid of radiation damping in the framework of biomolecular NMR. Many techniques involving shaped pulses and gradient field pulses have been proposed in the literature. However, these often involve quite complicated pulse sequences, the implementation of which might be cumbersome. Besides, these methods do not allow suppression of radiation damping during the aquisition period, so that harmonic peaks may still appear. It seems that an instrumental approach, involving a modification of the probe or spectrometer, may be an interesting alternative to really suppress radiation damping (Hobson and Kaiser, 1975; Broekaert and Jeener, 1995; Decorps, M., personal communication).

In this communication, we present the approach developed in our laboratory to this aim. The basic idea is the following. Radiation damping is caused by the abundant spin species in the sample, i.e., in practice, by the spins of the solvent (which is water in the context of biomolecular NMR). According to Eq. 1, one can think of feeding back into the probe through the decoupling network a

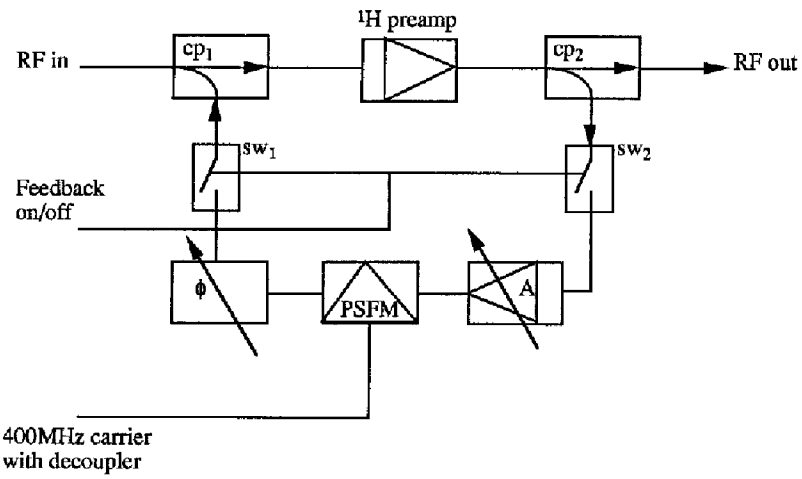

Fig. 2. Block diagram of the electronic neutralization network. One coupler is used to pick up the signal from the detection network, while a second one allows feedback of the signal into the probe. Demodulation and remodulation use a 400.13 MHz carrier frequency centered on the water resonance. Manual phase adjustment is available. Low-noise amplifiers with controlled gain (up to 20 dB) are used for the output signal. The feedback loop is isolated from the rest of the circuit by two switches, SW_1 and SW_2.

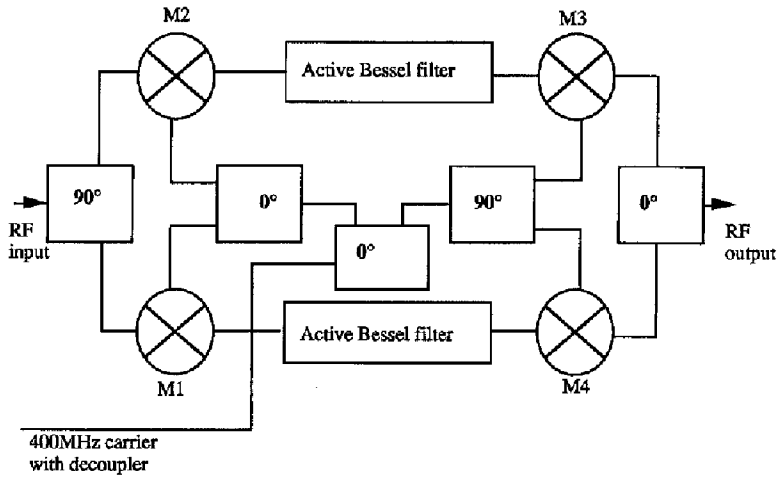

Fig. 3. The combination of demodulator-filter-remodulator results in a phase-sensitive filtering modulator. M1 to M4 are mixers, 90° and 0° devices are splitters/combiners. The active Bessel filter is used to obtain a good amplitude attenuation outside the bandwidth Δf and a constant group delay. The gain is set to compensate the insertion loss.

correction derived from the water signal to minimize the effects of the radiation damping field. It is possible to limit the correction to only a small bandwidth containing the water frequency, with the appropriate amplitude and phase correction. This strategy was expected to avoid any degradation of the signal-to-noise ratio in the rest of the spectrum.

A schema of the network used for that purpose is given in Fig. 2. The signal of the water is detected, filtered and analyzed with respect to its phase and envelope, and fed back into the probe with appropriate gain and phase corrections, as well as transposition at the water frequency. The rf signal is picked up by means of a directional coupler, located at the output of the ^{1}H pream-

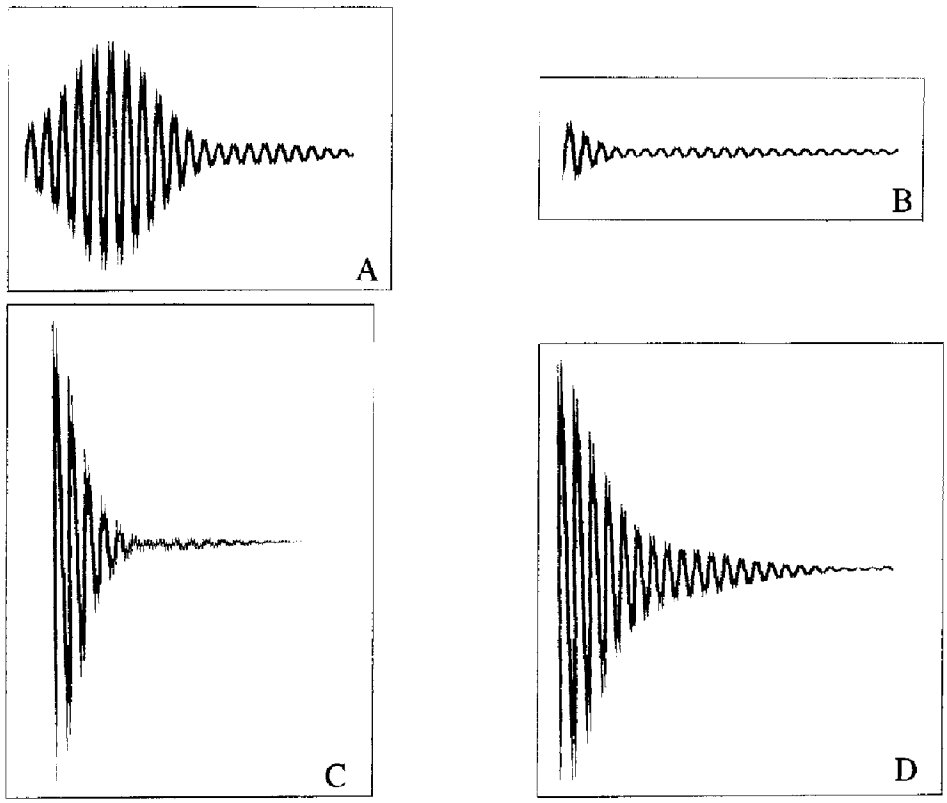

Fig. 4. Results of a simple pulse acquisition on a sample containing a mixture of H_2O with dioxane (1%) and D_2O (10%), showing the effects of the neutralization network. The observation frequency was offset by 50 Hz in order to more conveniently observe the shapes of the FIDs. The acquisition time was 205 ms in all cases. Experiments were performed on a 400 MHz Bruker AM spectrometer. (A) A 'Maser' pulse due to radiation damping occurs after a pulse close to 180°. (B) Suppression of radiation damping with feedback on after a (close to) 180° pulse. Note the exponentially damped decay of the FID. (C) and (D) A 90° pulse excitation is followed by a faster decay of the FID in the presence of radiation damping. The neutralization of radiation damping dramatically increases the duration of the FID.

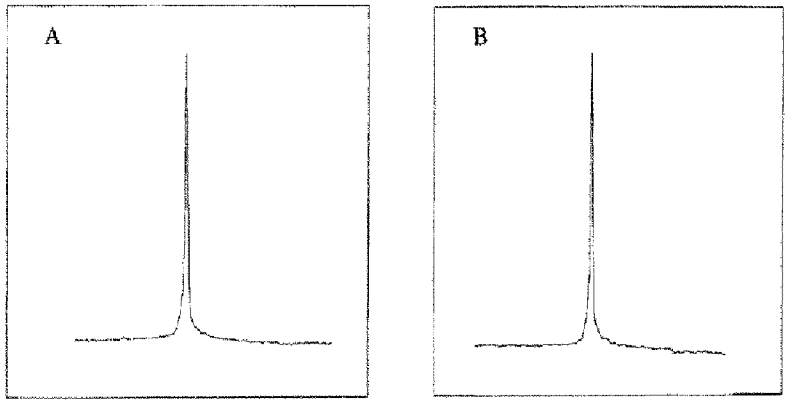

Fig. 5. The dioxane resonance line, obtained after a 90° pulse, shows no deterioration and the signal-to-noise ratio is not affected by the action of the neutralization network. Extracts of the spectra obtained with and without the use of the network are shown in (A) and (B), respectively. The resonance frequency offset of the dioxane is 560 Hz from the water line, and the linewidth is 10 Hz.

plifier receiver, and fed into a phase-sensitive detector where demodulation at 400 MHz takes place. The real and imaginary components are then fed into low-pass active filters in order to reduce the frequency domain to a bandwidth ($\Delta f = 300$ Hz) centered on the water resonance frequency. In order to achieve good selectivity, we used second-order Bessel filters, which also minimize phase and group delay distortions. The gain of the filter compensates the losses and allows for adjustment of the levels in the next modulator, where back-conversion to 400 MHz takes place. In this step, we use the decoupler frequency synthesizer, which allows precise frequency adjustment. This part of the network is depicted in Fig. 3. Additional phase- and amplitude-tuning facilities of this signal have been implemented. Finally, the signal is fed back into the probe via a directional coupler, standardly used in homonuclear decoupling on NMR spectrometers. Note that a coherent modulation is needed, and that the decoupler carrier must be locked to the ^{1}H carrier of the spectrometer.

The feedback system was implemented on a 400 MHz Bruker AM spectrometer with very little modification of the standard circuits. The decoupler frequency synthesizer must be locked to the ^{1}H frequency synthesizer and is used as the carrier. Two test experiments were carried out, using a single 90° or 180° pulse with various offsets from the water resonance. The observed FIDs clearly show the modification of the envelope of the transient.

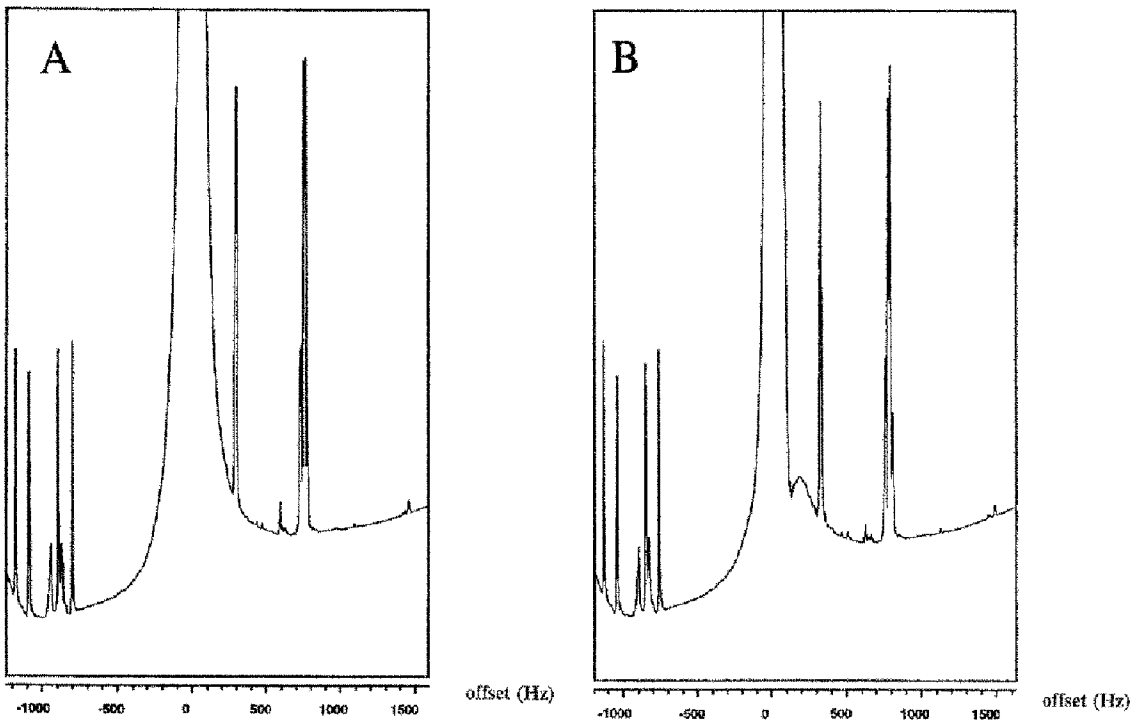

Fig. 6. Pulse-acquisition experiments performed on a 10 mM ^{15}N-labeled asparagine sample. (A) The reference spectrum. (B) The spectrum obtained with the neutralization network contains only minor differences in the vicinity of the filter cutoff frequency (see text).

For a 90° pulse, the damping of the signal is strongly reduced. For a 180° pulse, the characteristic Maser effect is eliminated, and the hyperbolic secant signal is transformed into a small residual exponential decay. Results are depicted in Figs. 4A–D.

The signal-to-noise ratio strongly depends on the amount of noise originating from the detection circuit, and possibly from the neutralization network. Both have a characteristic noise factor, which is proportional to the hardware working bandwidth (typically 300 Hz). Thus, the use of a reduced bandwidth in the feedback system maintains a low level of the noise power in the loop. Furthermore, the overall gain of the feedback loop was kept to a rather low value, which again allowed the noise level to remain low in the loop. In order to check the effects on the signal-to-noise ratio and other artifacts, the test sample contained 1% dioxane in water with 10% D_2O for the lock system. In practice, the signal-to-noise ratio of the signal of interest was found to be only weakly altered (Fig. 5), and the whole system displayed quite satisfactory phase and gain stability. This prevented the system from oscillating, while adjustment of the overall gain and phase of the loop was allowed. Moreover, spectra obtained from a 10 mM ^{15}N-labeled asparagine sample show minor spectral distortions, corresponding to the limits of the filter bandwidth (Fig. 6).

Finally, note also that opposite use could be made of the same network. If a faster return of the water magnetization back to its equilibrium position is desired, the phase of the output signal of the loop can simply be inversed.

During this work, we have noted related work developed by P. Broekaert and J. Jeener, relying on a lock-in-system approach with the purpose of cancelling the signal at the receiver coil. We would like to emphasize that in our setup, the correction takes place outside the probe network and is reduced to the water signal. The effective gain of the feedback loop must be around unity. The perturbation due to this circuit is thus expected to be smallest in this case.

In this communication, we have presented an electronic neutralization network capable of eliminating the ringing field responsible for radiation damping. The design of the circuit relies to some extent on a modification of the proton decoupler. Although we used continuous irradiation during FID acquisition, it should also be possible to use a time-shared mode homodecoupling strategy for better insulation of the receiver. Lastly, this network could easily be implemented on standard spectrometers and is able to compensate radiation damping during any evolution period, complex mixing time processes or detection period in multidimensional NMR experiments.

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