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Suppression of Radiation Damping in High-Resolution NMR

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The radiation damping field induced by an intense NMR line can be counterbalanced by a DANTE sequence of small flip angle pulses of opposite phase applied during the free induction decay. The transient NMR signal is acquired, one complex data point at a time, in the intervals between these DANTE pulses. As the intense signal decays, reducing the radiation damping field, the flip angles of the DANTE pulses are reduced at a matching rate. An experimental test on an aqueous solution of D-glucose demonstrates a reduction in linewidth at half height from 13.5 to 0.8 Hz, revealing a weak doublet response previously hidden under the broad water line. © 1999 Academic Press

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The phenomenon of radiation damping, first described by Bloembergen and Pound (*1*), is the source of several potential problems in high-resolution spectra of liquids when the sample has a high spin density, the polarizing field (B_0) is high, and the receiver coil has a high filling factor (ξ) and quality factor (Q). Under such circumstances the NMR signal induced on the receiver coil generates a nonnegligible current, and the resulting magnetic "reaction" field tips the nuclear magnetization toward the $+z$ axis, thus competing with relaxation and accelerating the decay of the free precession signal. The effect is particularly pronounced when water is present (*2*), for this is 110 M in protons, unless heavy water is used. It can have insidious consequences in multipulse experiments, causing *forced nutation* in what would otherwise be periods of *free precession.* Radiation damping is also one of two possible sources of spurious correlation peaks in two-dimensional spectroscopy (*3*). Acceleration of the decay of the transient NMR signal through radiation damping translates into a broader resonance response for the intense line. This often makes it hard to detect weak signals in the skirts of a tall, broad solvent signal such as water, and renders integration particularly difficult because the baseline is affected over an appreciable frequency range. When several adjacent lines are perturbed by radiation damping, the consequences are more complicated, involving phase shifts (*4, 5*) and spurious additional resonances (*5*). Radiation damping also plays havoc with measurements of spin–lattice relaxation times, because a 180° inversion pulse inevitably induces a small transverse NMR signal (through pulse imperfections or circuit noise) which generates a rapidly increasing radiation damping signal in an escalating process (*6–8*).

These problems have prompted several groups to devise methods for suppressing radiation damping. Electronic negative feedback is one solution (*8, 9*), Q-switching is another approach (*10, 11*), and pulsed bipolar field gradients have recently been applied to the problem (*12–14*). (The intriguing idea of detecting the NMR signal in an open series-resonant circuit so that no radiofrequency current flows (*15*) does not yet appear to have been implemented.) Note that these solutions require modifications to the radiofrequency hardware, or the use of pulsed field gradient equipment. They also tend to degrade the sensitivity of the spectrometer by reducing the quality factor of the coil or by seriously limiting the receiver duty cycle. The simple remedy of grossly mistuning the receiver coil suffers the same drawback. We examine here a method based on manipulation of the nuclear magnetization vector, requiring only software modification, with no alterations to the probe, and no significant loss of spectrometer sensitivity.

The basic idea is very simple. Suppose we excite the spins with a hard radiofrequency pulse in the usual manner, and suppose that the solvent line is so intense that radiation damping is appreciable. As the radiation damping field starts to rotate the solvent magnetization vector about the $-x$ axis, we apply a DANTE sequence (*16*) of hard pulses of small flip angle to nudge the solvent magnetization back again by means of a series of tiny rotations about the $+x$ axis. It is well known that a DANTE sequence behaves like a soft radiofrequency pulse, so that with a suitably long duration it only affects the solvent resonance. The DANTE pulse phase must be set to oppose the phase of the radiation damping field. Once these adjustments have been made, the stability of the spectrometer

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[1] On temporary leave at Varian NMR Instruments.

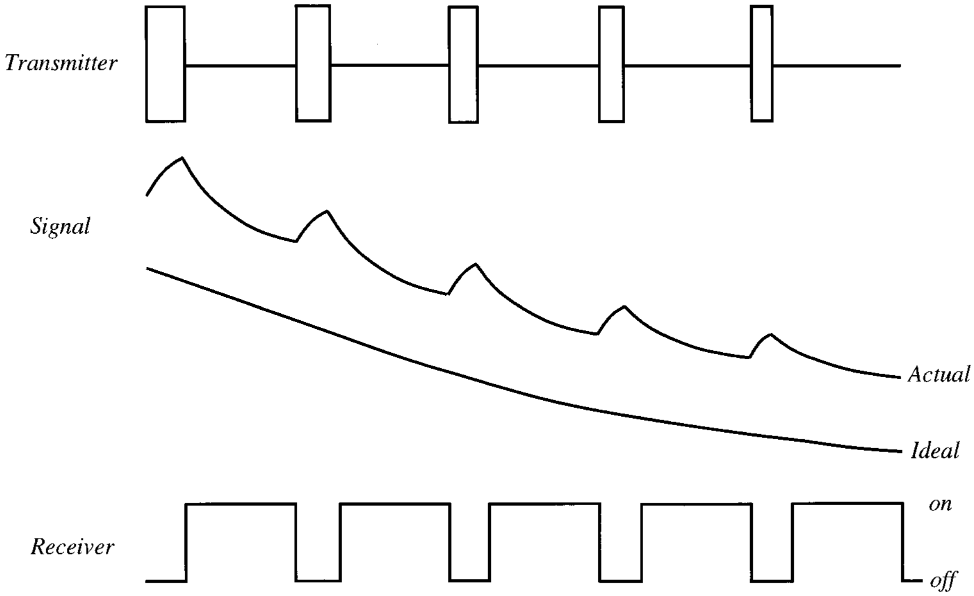

FIG. 1. Schematic diagram of the time evolution of the transverse NMR signal of water, showing compensation for the effects of radiation damping by DANTE pulses of steadily decreasing flip angle. The receiver duty cycle remains high and constant throughout.

field/frequency ratio is sufficient to sustain them. As the NMR signal decays through spin–spin relaxation and field inhomogeneity, causing a corresponding decay of the induced radiation damping field, the flip angle of the DANTE pulses is reduced at a matching rate. This maintains a delicate balance between the continuous torque caused by the radiation damping field and the (opposed) intermittent torques generated by the pulses. If the flip angle of the initial hard excitation pulse is rather less than 90°, then the compensation is stable.

The key to the implementation of this strategy is to acquire the NMR signal, one complex data point at a time, in the windows between the DANTE pulses (*17, 18*). The time evolution of the signal is shown schematically in Fig. 1; the actual zigzag trajectory closely approximates the ideal slow decay of a signal in the absence of radiation damping. Note that this is *not* a solvent suppression scheme; the initial amplitude of the time-domain signal is unchanged. The solvent resonance becomes narrower and much taller. Signals only a few hertz from the solvent frequency remain essentially unaffected by the DANTE pulses.

The sequence of operations is similar to one employed in an earlier investigation of signals detected during a shaped soft pulse (*18*). The software program is straightforward except for one minor complication. Relatively high pulse repetition rates are required if the Nyquist sampling condition is to be satisfied for large spectral widths. A problem then arises from the necessity for matching the decay of the radiation damping signal by decreasing the DANTE flip angles according to a decaying exponential. At high pulse repetition rates, the software loop written to control interleaved pulses and signal acquisition would need to run faster than the corresponding commands can be generated, and the FIFO (first in, first out) buffer would be emptied too quickly. This was remedied by nesting within the software loop a small number of cycles ($N \leq 4$) of a "hardware loop" (a repeated sequence of operations in which the parameters were all held constant). In this manner the DANTE pulse flip angle is only decremented every N cycles, but this slight coarsening of the digitization steps of the exponential curve proved to have no significant adverse effect.

As the DANTE pulse flip angle decreases with time, a compensating delay ensures that the sampling operation remains uniform in time. Accuracy of timing proved to be very important for obtaining artifact-free spectra. With this modification, sampling rates in excess of 8 kHz were readily achieved. The receiver duty cycle was held constant at 0.65, although other experiments indicated that a duty cycle as high as 0.9 is quite feasible. This ensures that the sensitivity (proportional to the square root of the receiver duty cycle) was not appreciably degraded.

The setting-up procedure proved to be quite straightforward. An exponential time constant of 0.5 s was found empirically to match the decay of the water signal (in the absence of radiation damping). The only other adjustable parameter is the transmitter frequency, set roughly by centering on the broad water resonance, and then finely tuned by trial and error to give a water resonance with the narrowest linewidth and the best lineshape. In this application the widths near the base of the resonance line (measured at 0.55% and 0.11% of the peak height) are rather more important that the width at half-height.

The idea was tested on a Varian INOVA 500 MHz spectrometer (in Palo Alto) operated remotely (from Cambridge)

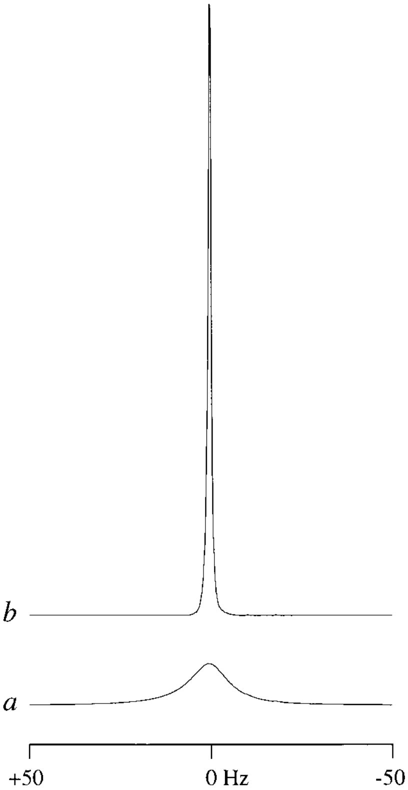

FIG. 2. Narrowing of the residual HDO line from a width of 13.5 Hz at half-height (a) to 0.8 Hz (b) by compensation of the radiation damping field with a DANTE sequence.

TABLE 1
Narrowing of the Residual Water Resonance by Compensating the Radiation Damping Field

Linewidth	Before	After
At 50%	13.5 Hz	0.8 Hz
At 0.55%	182 Hz	10.6 Hz
At 0.11%	>500 Hz[a]	20.1 Hz

[a] Ill-defined for such a broad response.

using the "X-windows" facility. We examined the proton resonance spectrum of an approximately 75 mM solution of an equilibrium mixture of α and β D-glucose in 50% H_2O/D_2O. The proton resonance of water was broadened to 13.5 Hz through radiation damping. At the chosen probe temperature of 35.5°C, the 8.0 Hz doublet from the anomeric proton of β-D-glucose lies under the skirts of the radiation-damped water resonance and thus provides a stringent test to see whether the proposed technique can narrow the water line sufficiently to expose this doublet response.

A nonspinning sample was used and the initial hard pulse flip angle was 45°. The flip angle of the DANTE pulses was programmed to decrease exponentially in steps of 12.5 ns from a maximum at the beginning of the sequence to a minimum of 100 ns at the end of the compensation sequence. This limit was only reached near the tail of the free induction decay, where radiation damping was already weak and compensation was no longer necessary. Then the DANTE pulses were extinguished, but the receiver duty cycle remained unchanged so as not to introduce a step in the signal intensity. Even quite small distortions of the time-domain signal are unwelcome when the solvent resonance is so intense. The usual precautions were taken to avoid the introduction of digitization noise.

Compensation reduced the water linewidth at half-height by more than an order of magnitude (Figs. 2 and 3). (An even larger effect was observed for a sample that contained 90% H_2O, reducing the width at half-height from 41 Hz to 0.8 Hz.) For the purpose of retrieving signals in the skirts of the water line the important parameters are the linewidths near the base

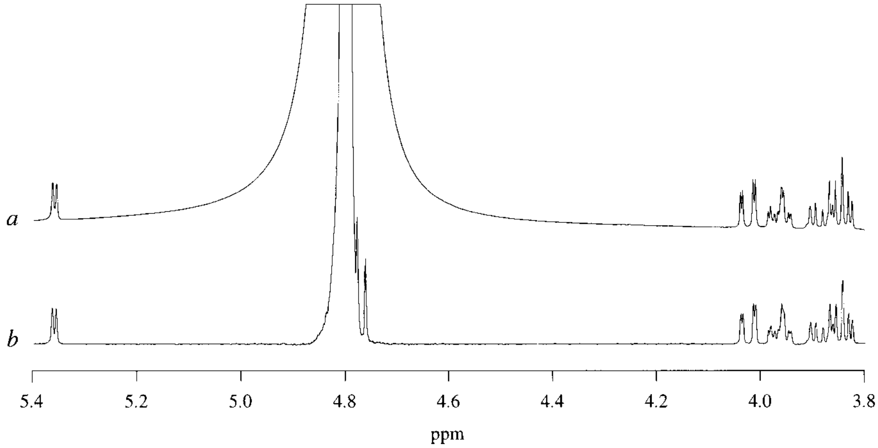

FIG. 3. Part of the 500 MHz proton spectrum of D-glucose in D_2O with added H_2O (a) with radiation damping (16 scans) and (b) after compensation with a DANTE sequence (32 scans). Baseline correction was employed in (b) but was not feasible in (a). Note the appearance in (b) of the previously hidden 8 Hz doublet from the anomeric proton of the β isomer.

of the resonance (Table 1). In principle, only resonances lying within the effective bandwidth of the DANTE pulses (about 1 Hz) would fail to be detected by this compensation scheme. The center of the 8 Hz doublet of the anomeric proton of β-D-glucose lies 14 Hz from the center of the water response, and after compensation, this doublet becomes clearly visible. The remainder of the spectrum is essentially unaffected. However, artifacts in the skirts of the water resonance generated by residual spectrometer instabilities, together with any sidebands arising from spurious modulation, become more apparent when not broadened by radiation damping. This experiment serves as a sensitive test for any shortcomings of the spectrometer.

A much simpler pulse program can be used in situations when signal acquisition is not required. For example, in certain circumstances it may be advantageous to *enhance* radiation damping (*9*) by applying a sequence of DANTE pulses *in phase* with the radiation damping field. This could be useful for avoiding the dynamic range problem by delaying acquisition until the intense water signal has decayed to a low level, through radiation damping assisted by DANTE pulses. Preliminary experiments indicate that a delay of as little as 5 ms is sufficient to reduce the water signal to a level below that of the anomeric proton doublet from β-D-glucose. However, the resulting frequency-dependent phase shift needs to be compensated by linear prediction of the missing initial section of the time-domain signal. Furthermore, the suppression ratios achieved are not competitive with standard solvent suppression schemes such as WATERGATE (*19*), partly because of a weak, long-lived component of the water response that is enhanced by the linear prediction program.

Radiation damping is now emerging as a serious problem in several areas of NMR—in very-high-field spectrometers, in probes with superconducting receiver coils (*20*) with quality factors as high as 20,000, and in experiments with hyperpolarized noble gases, such as ^{3}He and ^{129}Xe (*21*). Compensation of radiation damping by a regular sequence of pulses of small flip angle is demonstrated here experimentally. It appears to be instrumentally less demanding than schemes based on Q-switching or on negative feedback circuitry, and it does not degrade the spectrometer sensitivity to any significant extent. Another application is the suppression of radiation damping during the evolution period of a two-dimensional experiment, offering a simple alternative to the bipolar field gradient method (*12*).

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