Radiation damping: Suryan's line broadening revisited in high resolution solution NMR*

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Radiation damping is a combined manifestation of the nuclear spins and the resonant circuit. Radiation damping effects are becoming increasingly important in the high field NMR spectra of biological macromolecules when dissolved in aqueous solutions. This phenomenon was first discovered by Suryan in 1949 and a complete mathematical treatment was provided by Bloembergen and Pound in 1954. In this review, a historical perspective of Suryan's line broadening, commonly known as radiation damping is presented and methods that can suppress or utilize it advantageously are discussed with an emphasis of this phenomenon in the current state of high resolution solution NMR spectroscopy.

THE ability to resolve as many resonances as possible in the nuclear magnetic resonance (NMR) spectra of large biomolecules is an important goal in facilitating their assignment, and ultimately in the determination of the structures of these molecules in the solution state[1,2]. Thus methods that can help narrow the resonance line widths of the very crowded spectra of very large molecules can contribute significantly to the ongoing efforts to push the upper size limits of molecules beyond that of 25 kDa that can be currently studied by NMR spectroscopy[2-4]. Increasing the magnetic field strength (B_0) to up to 18.72 T (ν_H = 800 MHz)[5], combined with heteronuclear and multidimensional NMR experiments[6-8] using ^{15}N, ^{13}C and ^2H isotopic labelling of the molecules[9], have successfully improved the sensitivity of the signals for mid-sizedproteins (10–20 kD). In addition, the resolution of the data has improved with the use of digital signal processing and over-sampling technqiues[10]. However, there is still room for improvement by addressing other factors that can adversely affect the quality of a NMR spectrum.

In most of the experimental methods in use, protons are always detected in the acquisition dimension in order to take advantage of the inherent high sensitivity of these spins. The free induction decay (FID) collected at the end of each transient of an experiment is a mixture of the protons from the molecule of interest and from the solvent molecules. The concentration of protons due to solvent can be thousands of times higher in magnitude than that of the molecule studied, and thus the solvent protons can greatly influence the quality of the NMR data. For example, to observe the exchangeable amide resonances in proteins and imino and amino protons in nucleic acids under biologically relevant conditions, it is necessary to dissolve these molecules in aqueous buffers consisting of 90–95% H_2O. The concentration of water protons is thus approximately 100 M, while that of the sample is typically only 1–2 mM.

Standard NMR methods completely ignore the possibility that the individual spins may be influenced by the bulk nuclear magnetization of the whole sample, predominantly those of the water spins. Detection of the water resonances through a tuned circuit introduces an effect commonly known as radiation damping, which is a combined manifestation of the spin system and the electronic resonance circuit assembly. This effect is directly proportional to the strength of B_0 and the concentration of these spins. Although this phenomenon is commonly referred to today by the name 'radiation damping' given to it by Bloembergen and Pound[11] in 1954, it was first described by Suryan[12] almost 50 years ago in 1949 in a landmark paper. Yet, many researchers fail to acknowledge this original work. Therefore in this manuscript, I would like to revisit and recognize Suryan's 'line broadening' effect with the emphasis on the impact of this phenomenon when using increasingly higher magnetic fields to study biological macromolecules in aqueous solutions. In order to be consistent with the current literature on this subject, the term 'radiation damping' will be used in this review. However, the term does not accurately describe the effect. According to Abragam[13], although this process results in the eventual vanishing of the transverse magnetization, it is not a damping effect since the length of the magnetization vector is unchanged. Jeener and co-workers[14] recently reinforced this concept and agree that it is rather 'unfortunate' to describe this phenomenon as radiation damping. Radiation feedback or Suryan's line broadening effect would have been a more suitable name.

Radiation damping can be best described in the following fashion. The precessing transverse magnetization

*This manuscript is dedicated to Prof. C. L. Khetrapal, Sophisticated Instruments Facility, Indian Institute of Science, Bangalore on the occasion of his 60th birthday.

of the water protons after a radio frequency pulse induces an electromagnetic field (emf) in the receiver coil. This creates an oscillating current that generates a transverse magnetic field at the same frequency. This induced field rotates the magnetization of the solvent spins to its equilibrium position toward the direction of the applied magnetic field before other relaxation mechanisms can take effect. The rate at which the solvent magnetization is rotated to equilibrium is given by a characteristic time constant known as the radiation damping rate, τ_{rd}^{-1}. For example, a sample of water in a NMR spectrometer operating at 400 MHz will have a τ_{rd} value of around 20 ms, while the expected spin lattice (T_1) and spin–spin relaxation (T_2) times of water have durations of the order of more than hundreds of milliseconds. The decay of the time domain signal is thus dominated by the much shorter τ_{rd}, rather than the longer T_2. Yet despite the importance of this effect in causing significant broadening of the NMR signals, a literature search shows that the total number of papers that discuss radiation damping with reference to NMR during the time period from the date of its discovery in 1949 to 1985 is only 15. This number has increased to 100 in the last decade, indicating the increasing awareness of the importance of radiation damping in affecting spectral quality as more experiments were performed on macromolecules in aqueous solutions at higher field spectrometers.

Several interesting papers appeared in the late fifties on the topic of radiation damping based on the equations of Bloembergen and Pound[11]. Bruce *et al.*[15] have experimentally shown the effect of radiation damping on broadening of the resonance line shape, and Bloom[16] has described the analytical solutions of the Bloch equations with radiation damping for slow and fast passage experiments. Szöke and Meiboom[17] have experimentally demonstrated the effect of tuning the receiver coil of the probe on radiation damping, while in a comprehensive work, Hobson and Kaiser[18], simulated the effect with an explicit computer algorithm.

In the absence of collective effects, Bloch's differential equations for the components of average spin magnetization are linear and all standard discussions on spin dynamics are based on this linearity. The presence of an induced magnetic field, such as radiation damping which is explicitly dependent on the average spin magnetization, makes these equations nonlinear. The mathematical analysis of radiation damping in the modified Bloch–Maxwell equations proposed by Bloembergen and Pound[11], in the rotating frame is given by

$$\frac{d}{dt}\begin{bmatrix}\langle I_x\rangle\\ \langle I_y\rangle\\ \langle I_z\rangle\end{bmatrix}=\begin{bmatrix}-R_2 & -\omega & 0\\ \omega & -R_2 & 0\\ 0 & 0 & -R_1\end{bmatrix}\cdot\begin{bmatrix}\langle I_x\rangle\\ \langle I_y\rangle\\ \langle I_z\rangle\end{bmatrix} -\frac{1}{\tau_{rd}}\begin{bmatrix}\langle I_x\rangle\langle I_z\rangle\\ \langle I_y\rangle\langle I_z\rangle\\ \langle I_x\rangle^2+\langle I_y\rangle^2\end{bmatrix}+\begin{bmatrix}0\\ 0\\ R_1\langle I_z^{eq}\rangle\end{bmatrix}. \tag{1}$$

$\langle I_x\rangle$, $\langle I_y\rangle$ and $\langle I_z\rangle$ are the expectation values of the X, Y and Z components magnetization and $\langle I_z^{eq}\rangle$ is the equilibrium value, given by the Boltzman distribution at high field and high temperature approximation. ω is the frequency of spin in the rotating frame rotating at an angular frequency Ω, given by $\omega=\sqrt{\Omega_0^2-\Omega^2}$ and Ω_0 is the applied static magnetic field in frequency units. R_1 (T_1^{-1}) and R_2(T_2^{-1}) are the spin–lattice and spin–spin relaxation rates. τ_{rd} is the classical radiation damping time given in SI units by[11,13]

$$\tau_{rd}^{-1}=2\pi\eta Q_c\gamma M_0. \tag{2}$$

In eq. (2), η is the filling factor defined as the ratio of the probe coil volume to the sample volume enclosed within, Q_c is the quality factor of the resonance circuit ($Q_c=\omega L/C$; ω, L and C are frequency, conductance and capacitance of the resonance circuit) and γ is the gyromagnetic ratio of the observed spin. Substituting for M_0, the thermal equilibrium magnetization for spin half nuclei[19,20], eq. (2) can be rewritten as

$$\tau_{rd}^{-1}=\frac{\eta Q_c\gamma^3 h^2 N_0 B_0}{8\pi kT}, \tag{3}$$

where h is Planck's constant (6.6262×10^{-34} m^2 kgs^{-1}), N_0 is the number of spins per unit volume (typically 1.3×10^{22} protons per 200 µl of water)[20], B_0 is the strength of the magnetic field in Tesla, k is the Boltzman constant (1.3806×10^{-23} m^2 kg s^{-2} K^{-1}) and T is the temperature of the sample in K. Eq. (3) clearly shows that the rate at which the magnetization vector is rotated is directly proportional to the experimental parameters, quality factor and choice of the spectrometer frequency. De-tuning the probe will thus decrease the effect of radiation damping by reducing the sensitivity of the solute signals. Following the formulation provided by Mao and Ye[21], the value of τ_{rd} can be evaluated from the water line width, $\Delta\nu_{1/2}$ measured in the spectrum obtained using a non-selective 90° pulse as:

$$\tau_{rd}^{-1}=\frac{\Delta\nu_{1/2}}{0.8384}. \tag{4}$$

The magnitude of the radiation damping field can be calculated using the equation provided by Abragam[22] as

$$B_{rd}=\frac{-\sin\theta}{\gamma\tau_{rd}}. \tag{5}$$

For example, a magnetic field of 11.7 T (500 MHz), ηQ of 10, and $\theta = 90°$, yields a radiation damping field of 16 Hz (ref. 23). This field is significantly smaller than the radio frequency field of 25 kHz, generated by typical 90° pulse (pulse width of 10 µs) in a high field NMR spectrometer.

Radiation damping effects even simple NMR experiments in unexpected and novel ways. Solutions to eq. (1) for a single spin with radiation damping is by itself one of the interesting problems. Many attempts have been made to obtain an analytical solution for the most general case. One such solution was presented recently by Barbara[24] using an elegant projection technique. Here a numerical integration procedure is adopted to solve eq. (1). Self-consistent numerical integration procedures[25] that can automatically adjust the step size of the integration are used in the calculations. Standard Fortran-77 is used for the code (available on request from the author). It should be mentioned here that the radiation damping phenomenon can also be explained by using a quantum mechanical treatment of the spin system. Shrivastava[26] was first to treat Suryan's line broadening using quantum mechanical treatment and the readers are referred to the work by Abergel and Lalleman[27] and Jeener and coworkers[28] for a detailed description of this method.

In order to demonstrate the effect of radiation damping as a function of the excitation pulse angle, Figure 1 shows the calculated plots of the time domain signal as the water spins are flipped increasingly away from their equilibrium positions along B_0. The plots were obtained by numerical integration of eq (1). The FID in Figure 1 *c*, which was obtained after a 135° pulse, already shows the signs of radiation damping. The echo-like shape of the FID in Figure 1 *d* after near inversion (pulse angle of 179.99°) is typical of a strongly radiation damped signal. The effect to applied magnetic field on radiation damping can be more easily seen in the simulated spectra shown in Figure 2. For a flip angle of 150°, the line width of the water signal increases with a corresponding linear decrease in τ_{rd} as the magnetic field is increased. For example, τ_{rd} decreases from 40 ms to 15 ms by increasing the field from 300 MHz (Figure 2 *a*) to 800 MHz (Figure 2 *e*), respectively. It is inevitable that radiation damping will be a part of every spectrum of molecules in solvents containing a high concentration of protons. The increased sensitivity of high field NMR spectrometers is a double-edged sword. On the one hand, the increased sensitivity allows the acquisition of NMR data for samples at lower concentrations, but at the same time, it makes it possible to observe radiation damping effects which were once considered negligible only a short time ago.

Re-examining the effect of radiation damping on the quality of NMR spectra opens up several new avenues of research in high field NMR spectroscopy, since optimization of the sample signals alone does not guarantee an improvement in the quality of the data. Techniques to suppress, utilize and control radiation damping during the entire course of an experiment need to be developed. Examples of techniques to suppress radiation damping include simple pre-saturation[29] of the water signal to multiple excitation pulses[30], in combination with pulsed field gradients[31-37]. Radiation damping is difficult to control during the course of a multiple pulse experiment since the water spins undergo the same set of pulses as that of the sample protons. Recently, there has been some effort reported in the literature to actually use radiation damping to improve the performance of some pulse sequences. Pulsed field gradients are applied after inverting the water magnetization to effectively control the rate at which the magnetization

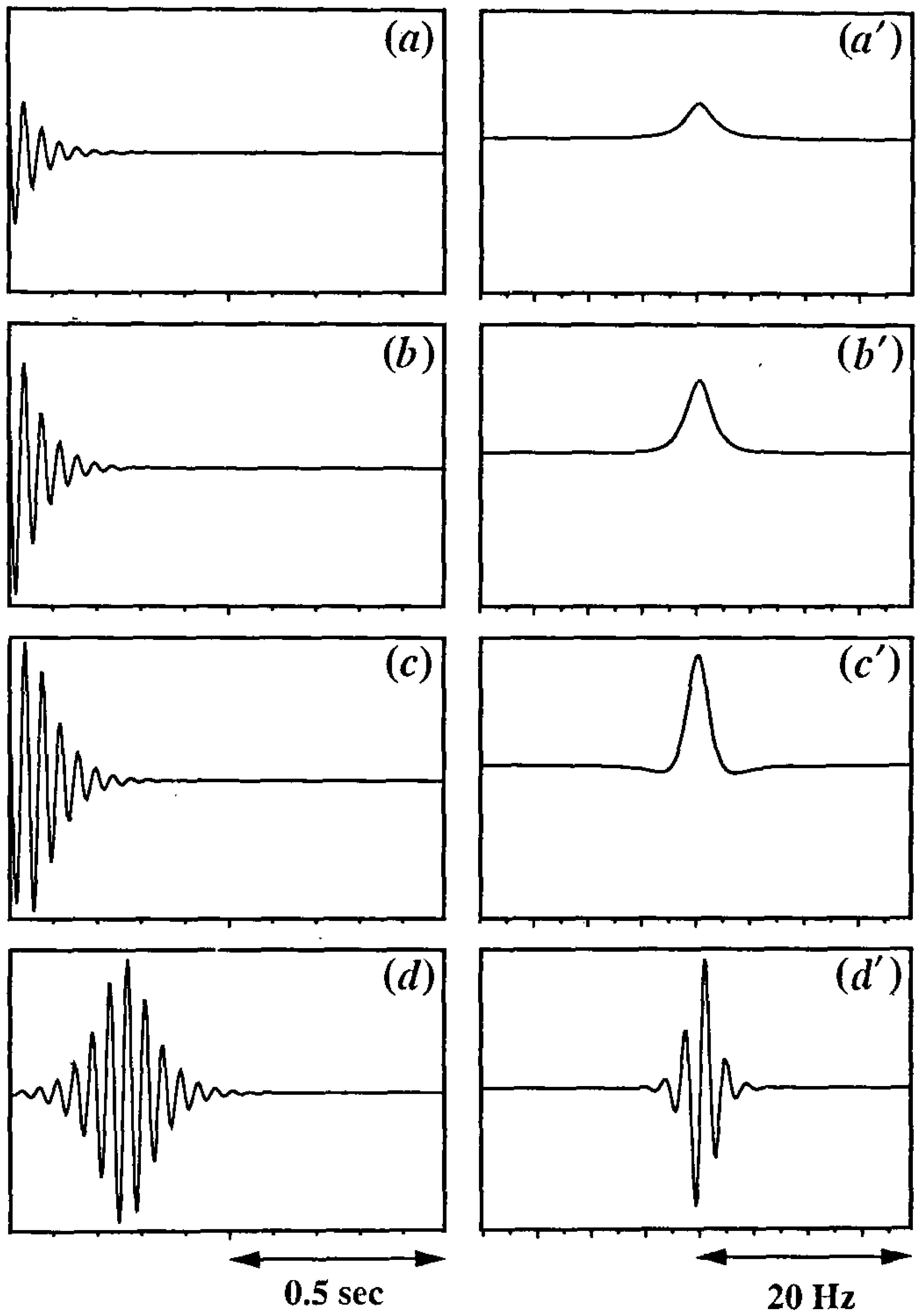

Figure 1. Flip angle dependence of water resonance: Panels *a*, *b*, *c* and *d* are the simulated water free induction decay (FID) acquired after a 45°, 90°, 135° and 179.99° pulses respectively, while the panels *a'*, *b'*, *c'* and *d'* are the corresponding Fourier transformed spectra. The time domain data are simulated by numerical integration of eq. (1) with the parameters; τ_{rd} = 25 ms, $R_1 = R_2$ = 10 Hz and ω = 50 Hz. The calculations are performed over 1024 complex points with a spectral width of 250 Hz and the time domain data are fast Fourier transformed using FELIX-97 (MSI Inc.) without any apodization. The time and frequency domain data are normalized with respect to panels *d* and *d'* respectively.

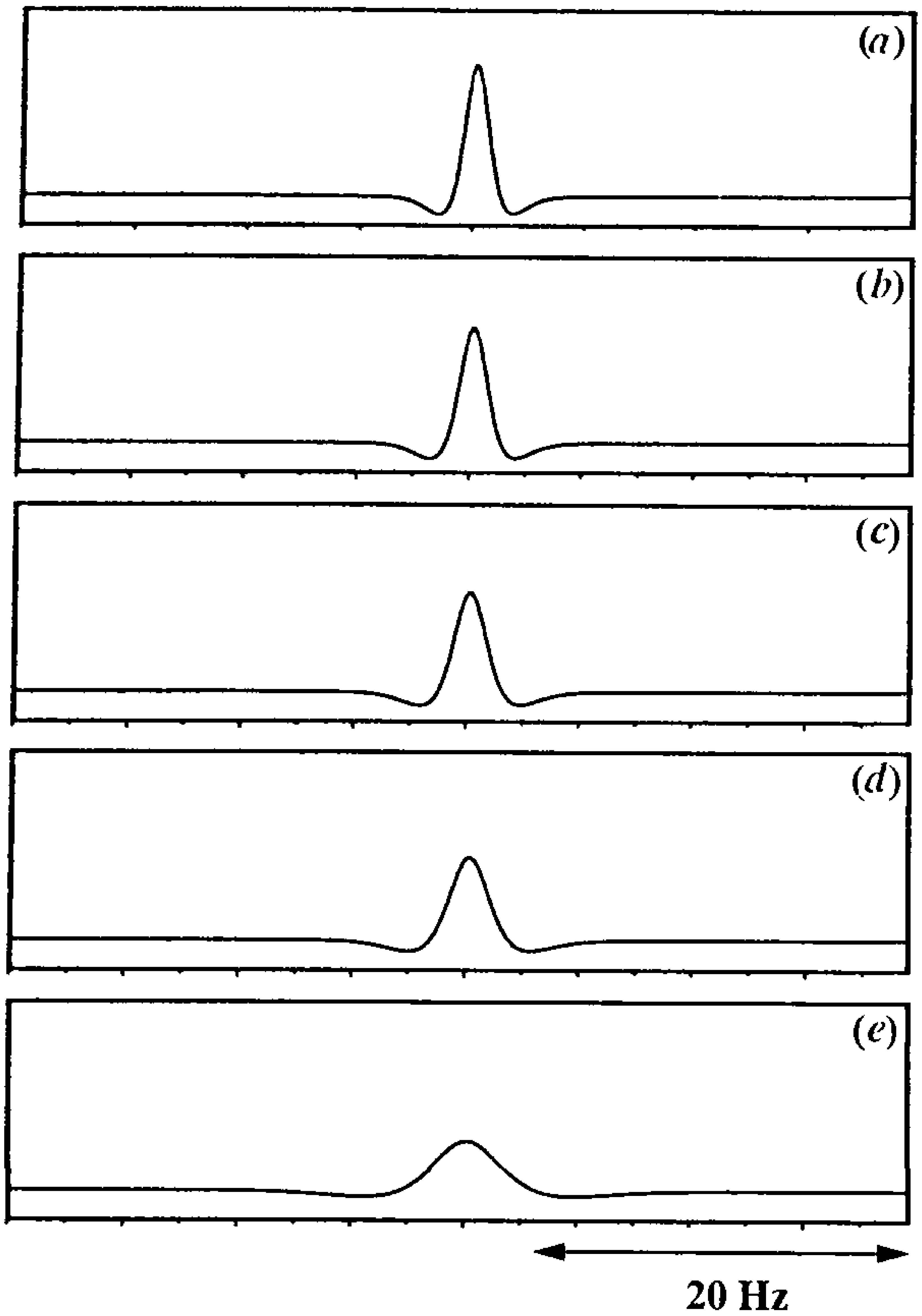

Figure 2. Simulation of Suryan's line-broadening effect as a function of the spectrometer frequency. Panels *a, b, c, d* and *e* correspond to spectrometer field strengths in terms of proton frequencies 300 (7.02 T), 400 (9.36 T), 500 (11.7 T), 600 (14.04 T) and 800 MHz (18.72 T), respectively, τ_{rd} at 300 MHz is assumed to be 40 ms, the rest are scaled according to eq. (3). The tip angle of the read pulse is 150°, while the rest of the simulation parameters remain the same as in Figure 1, ignoring the field dependency of relaxation rates.

recovers to equilibrium between the lower and upper limiting rates governed by radiation damping and other relaxation processes, respectively[38]. Price *et al.*[36,37] have utilized this method in combination with the WEFT method of Patt and Sykes[39] as a water-suppression technique. Radiation damping has been successfully used to control water magnetization in experiments designed to measure amide proton exchange rates in ^{15}N labelled proteins (V. V. Krishnan and M. Rance, unpublished results) and in triple resonance experiments to optimize the sensitivity of rapidly exchanging protons[40]. Methods that leave the water magnetization close to its equilibrium orientation significantly reduce radiation damping during the course of a pulse sequence, and these methods when incorporated in a standard pulse sequence are called water-flip back experiments[41–44].

More recently, schemes to eliminate radiation damping based on novel probe and electronic circuit designs have been proposed[45–49]. These methods include high gain electronic feedback[45], FID compensation by decoupling the input signal[46], and a probe with a multiple coil design with Q switching[47–49]. Broekaert *et al.*[50] have recently speculated that a combination of pulse sequences and specially designed probes may soon make the deleterious effects of radiation damping history.

The induced magnetization process of radiation damping is one of two collective effects, which result from placing a high density of protons in an external magnetic field. The other effect, known as a dipolar field[51,52], is sometimes confused with radiation damping[53–57]. Therefore, a brief description of the dipolar field is included here to complete the discussion on radiation damping, and the reader is referred to articles by Jeener and co-workers[28,50,58,59], and Levitt[60] for further details about dipolar fields and the differences between these two effects. A dipolar field refers to creation of additional magnetic field in each spin. As in the case of radiation damping, a dipolar field is proportional to the nuclear spin density and the strength of the external magnetic field. However, unlike radiation damping, it has a strong dependency on the shape of the sample and the spatial distribution of the nuclear spin magnetization[51,52,59–61]. In addition, dipolar effects are independent of the quality factor (Q_c) of the resonance coil[51,52,59–61]. More importantly, radiation damping diminishes the quality of the spectra to a greater extent than does the dipolar field. For example, a typical 600 μl sample of water in a 5 mm diameter cylindrical tube placed on a 600 MHz spectrometer produces a dipolar field resulting in a shift of the NMR signal of the protons of the order of 1 Hz, while τ_{rd}^{-1} is of the order of 100 Hz (refs 58, 59).

In summary, I have tried to present an overview of Suryan's line broadening effect or so-called radiation damping with a historic perspective and by revisiting the phenomenon's impact on the quality of the spectra of samples in aqueous solutions obtained using high field NMR spectrometers. The classical description of radiation damping based on the Bloch–Maxwell equation was presented and solved by numerical integration methods. Various methods that suppress or use radiation damping have been discussed. The effect of radiation damping on the relaxation rate of a water signal was demonstrated by calculating the FID as a function of different excitation pulse widths. In addition, the effect of increasing the magnetic field strength on broadening the line width was demonstrated by computer simulation. Reinvestigating the effects of radiation damping in high field NMR spectra of samples in aqueous solutions challenges commonly held theoretical assumptions as well as opened up several new avenues for research in pulse sequence development, electronic circuit, and probe design. The impact of collective spin effects such as radiation damping on the quality of NMR spectra of molecules dissolved in aqueous solution using high field magnets cannot be ignored. The ultimate goal of obtaining high resolution, accurate structure of biomolecules in solution depends on obtaining high quality NMR data. Consideration of methods that can either eliminate or beneficially use radiation damping will enable researchers to reach this goal.

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ACKNOWLEDGEMENTS. My sincere thanks to Dr Monique Cosman for her critical reading of the manuscript and for many suggestions to improve the contents. I would also like to thank Professor Mark Rance, who first pointed out the importance of radiation damping and helped me to understand this phenomenon in detail. This work was performed under the auspices of the US Department of Energy by the Lawrence Livermore National Laboratory under contract W-7405-ENG-48 and supported by the Lawrence Livermore National Laboratory LDRD Director's Initiative grant 96-DI-010.

Received 23 January 1998; accepted 25 March 1998