A new solvent suppression method via radiation damping effect*

Cui Xiao-Hong(崔晓红), Peng Ling(彭 凌), Zhang Zhen-Min(张振敏), Cai Shu-Hui(蔡淑惠), and Chen Zhong(陈 忠)†

Department of Electronic Science, Fujian Key Laboratory of Plasma and Magnetic Resonance, State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, *China*

(Received 18 April 2011; revised manuscript received 17 June 2011)

Radiation damping effects induced by the dominated solvent in a solution sample can be applied to suppress the solvent signal. The precession pathway and rate back to equilibrium state between solute and solvent spins are different under radiation damping. In this paper, a series of pulse sequences using radiation damping were designed for the solvent suppression in nuclear magnetic resonance (NMR) spectroscopy. Compared to the WATERGATE method, the solute signals adjacent to the solvent would not be influenced by using the radiation damping method. The one-dimensional (1D) ^{1}H NMR, two-dimensional (2D) gCOSY, and *J*-resolved experimental results show the practicability of solvent suppression via radiation damping effects in 1D and 2D NMR spectroscopy.

Keywords: nuclear magnetic resonance, solvent suppression, radiation damping

PACS: 82.56.–b, 33.25.+k, 76.60.–k **DOI:** 10.1088/1674-1056/20/11/118201

1. Introduction

With the development of solution nuclear magnetic resonance (NMR), higher field magnets, and more sensitive probes have dramatically improved the sensitivity and resolution of NMR signals. In ^{1}H NMR experiments, solvents normally have significantly higher concentrations (e.g., 55 M for water) than solutes (e.g., a few mM for most samples). Therefore, without solvent signal suppression, the intense solvent resonances not only submerge the much weaker resonances of interest, but also saturate the NMR receiver causing many other complications such as baseline distortions and phase roll.[1] Up to now, many solvent suppression approaches have been developed, such as pre-saturation,[2] WET,[3] WATERGATE,[4,5] and so on. Although some of them have been proven to be successful, they still face some problems such as the saturation of exchangeable protons or the loss of solute resonances close to the solvent resonance.[6] The enhanced pre-saturation (pre-saturation utilizing relaxation gradients and echoes, PURGE) sequence[7] and improved WATERGATE sequences,[8] and inversion recovery (IR) excitation sculpting[9] have been proposed to deal with the problems of the original sequences. However, each of these methods is limitative to some extent and not applicable in certain conditions, and some of them may cause new problems.

Radiation damping is a physical phenomenon appearing in highly polarized liquid samples under strong magnetic fields, which originates from the nonlinear coupling between radio-frequency (RF) coil and strong transverse magnetizations.[10−12] Radiation damping may result in some unpredictable phenomena in conventional one-dimensional (1D) and two-dimensional (2D) NMR experiments,[13−16] which should be avoided practically. To eliminate the radiation damping, well-designed pulse sequences and improved experimental conditions are generally required.[17−20] On the other hand, it has been found that radiation damping field can be utilized to improve experimental results in some applications,[21−25] such as radiation damping field enhanced jump-and-return (JR),[22] spin excitation,[23] and magnetic resonance imaging (MRI).[24] Louis-Joseph and co-workers showed that the application of radiation damping enhancement during longitudinal relaxation significantly improved the solvent suppression efficiency of JR.[22] Price *et al.* presented a method of water suppression in which homospoil pulses are used to manipulate the effects of radiation damping on the water resonance

*Project supported by the National Natural Science Foundation of China (Grant Nos. 10974164 and 11074209) and the Fundamental Research Funds for the Central Universities (Grant Nos. 2010121008 and 2010121010).

†Corresponding author. E-mail: chenz@xmu.edu.cn

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and thereby selectively alter the effective longitudinal relaxation time of the water resonance with respect to the protein resonances.[26,27] To our knowledge, so far there is no solvent suppression method just based on radiation damping effects. In this paper, a series of pulse sequences were designed for the solvent suppression in 1D and 2D NMR experiments by using radiation damping effects. The experimental results show that our methods can not only well suppress solvent signal, but also reduce the influence of solvent suppression on the solute signals close to the solvent one.

2. Theory description

The phenomenon of radiation damping was discovered early in the history of NMR.[10,28] Radiation damping is a dynamic process that results from the nonlinear coupling between the large transverse magnetization and the RF coil.[29,30] The precessing magnetization induces an oscillating current in the RF coil which in turn generates an oscillating magnetic field that accelerates the return of spin system to its equilibrium state. Under the effects of radiation damping, the solvent spins rotate back to the equilibrium state along the Bloch sphere with a radiation-damping time $T_{\rm rd}$, which is given by (in SI units):[31,32]

$$T_{\rm rd} = 2(\mu_0 \gamma \eta Q M_0)^{-1},$$

where μ_0 is the vacuum magnetic conductance, γ the magnetogyric ratio, η the filling factor of the probe, Q the probe's quality factor, M_0 the thermal equilibrium magnetization. Due to the low concentration of solute, the solute spins are almost immune to the radiation damping effects and rotate back to thermal equilibrium state along the longitudinal relaxation pathway with their T_1. The typical radiation damping time $T_{\rm rd}$ for water protons is around tens of microseconds,[29,33] which is far shorter than the longitudinal relaxation time T_1 of solute.

Based on the different recovery pathway and rate back to the equilibrium state between solute and solvent spins under radiation damping, the 1D solvent suppression sequence via radiation damping effects was proposed and shown schematically in Fig. 1(a). Schematic diagram for solvent and solute magnetization evolution is shown in Fig. 2, where the solvent and solute magnetizations are represented by the blue and red arrows, respectively.

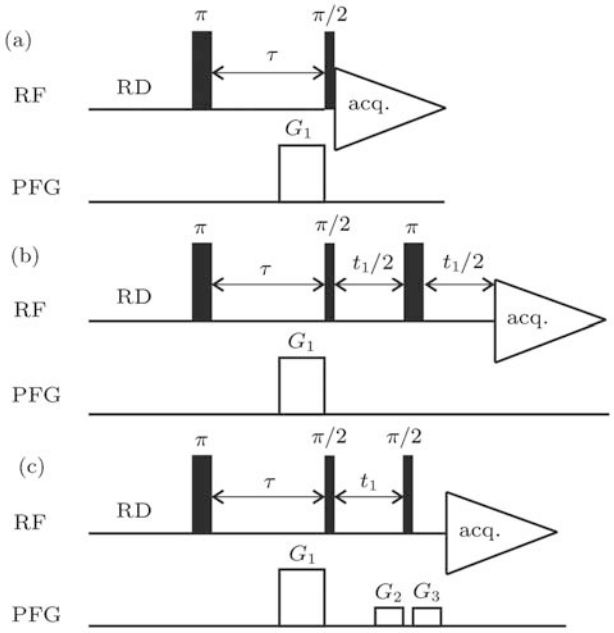


Fig. 1. Pulse sequences for solvent suppression via radiation damping effects: (a) 1D ^{1}H NMR spectroscopy, (b) 2D J-resolved spectroscopy, and (c) 2D gCOSY.

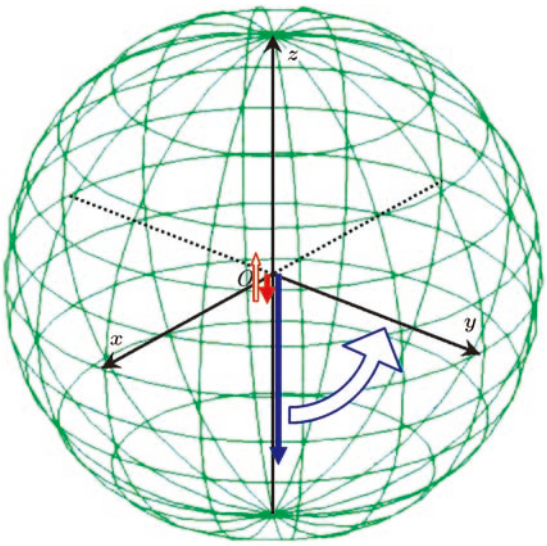


Fig. 2. Schematic diagram showing the evolution pathways of solvent and solute magnetizations. The solvent and solute magnetizations are represented by the blue and red arrows, respectively.

As mentioned earlier, after excited by a π pulse, the solvent and solute spins return to their equilibrium states via radiation-damping and longitudinal relaxation effects, respectively. Since the typical $T_{\rm rd}$ for solvent is far shorter than the T_1 for solute, when the solvent magnetization rotates onto the xy plane, the solute magnetization can be considered to be still along $-z$ direction. At this moment, the solvent magnetization is dephased by a pulse field gradient (PFG) G_1 with strong intensity and short duration, which

hardly affects the solute magnetization. Subsequently, a read pulse rotates the solute magnetization to the xy plane for acquisition. Note that the time τ in the sequence must be optimized to make sure the residual solvent magnetization is minimal.

The solvent suppression module via radiation damping effects can be incorporated into the 2D J-resolved and gCOSY experiments. The pulse sequences are shown in Figs. 1(b) and 1(c).

3. Experiments

All experiments were carried out at 25 °C on a Varian NMR System spectrometer with a proton frequency of 500.13 MHz and an indirect detection (ID) probe. The samples were 20-mM glucose in 90%H_2O/10%D_2O and 100%D_2O, respectively. In order to maximize the effects of radiation damping, the probe was well tuned. To overcome the inhomogeneity of π pulse, a $(\pi/2)_x$–$(\pi)_y$–$(\pi/2)_x$ composite pulse instead of a single π pulse was used. In all the three pulse sequences, the time τ was optimized to be 19.3 ms and the duration and strength of gradient G_1 was 50 μs and 0.32 T/m, respectively.

The 2D J-resolved experiments were performed with the standard pulse sequence and the sequence shown in Fig. 1(b). The spectral width was set to 2500 Hz and 100 Hz in the F2 and F1 dimensions, respectively. The initial echo time t_1 is 20 ms and 6500(F2)×64(F1) complex data points with 16 scans were acquired. The time domain data were zero filled to 16384(F2)×256(F1) before FFT. No window function was applied in the data processing.

The 2D gCOSY experiments were performed using the standard pulse sequence and the sequence shown in Fig. 1(c), with 2048(F2)×128(F1) complex data points and 16 scans. A pair of PFGs (G_2 and G_3) with duration 2 ms and strength 0.1 T/m were applied for coherence selection. The time domain data were weighted using a sinebell ($\pi/2$–$\pi/2$) window function and zero filled to 2048(F2)×512(F1) before FFT.

4. Results and discussion

The 1D ^{1}H NMR spectra of 20-mM glucose in 90%H_2O/10%D_2O are shown in Fig. 3. In the spectrum acquired with a single $\pi/2$ hard pulse (Fig. 3(a)), the intensity of solvent peak is extremely strong and the solute signals are hardly seen. In addition, the 50% line width of the solvent peak is about 41 Hz in the well-shimmed magnetic field. The broad line width may result from the radiation damping to a certain extent. When the signal intensity is amplified by 2000 times, the peaks of the solute which are far away from the solvent peak are present themselves, but the peaks near the solvent peak is seriously enshrouded by the broad solvent peak (Fig. 3(b)). The peak 227 Hz away from the solvent peak (α–H from glucose, see Fig. 3(e) for a reference) is lifted on the shoulder of the broad solvent peak, and another peak 70 Hz away from the solvent peak (β-H from glucose, see Fig. 3(e)) is almost submerged under the strong solvent peak.

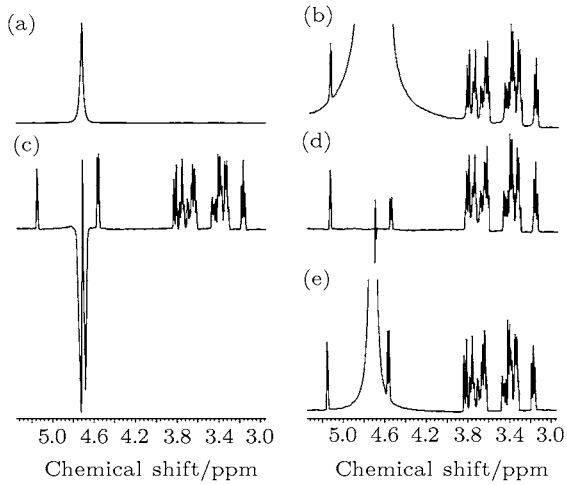


Fig. 3. 1D ^{1}H NMR spectra of 20-mM glucose in 90%H_2O/10%D_2O (panels (a)–(d) and in 100%D_2O panel (e)). (a) Acquired with a single $\pi/2$ hard pulse, (b) the spectrum of (a) amplified by 2000 times, (c) acquired with the pulse sequence shown in Fig. 1(a), (d) acquired using the WATERGATE (W5) scheme, and (e) acquired with a single $\pi/2$ hard pulse.

For comparison, the NMR spectra of 20-mM glucose in 90%H_2O/10%D_2O with solvent suppression via radiation damping effects and the W5 method[8] are given in Figs. 3(c) and 3(d), respectively. In Fig. 3(c), the two peaks from α–H and β–H of glucose are clearly shown, and the base line is smooth enough for qualitative analysis. In Fig. 3(d), the peak of β–H from glucose is suppressed to some extent. These results suggest that the solvent suppression method via radiation damping effects is much fitter than the W5 method for the samples with solute peaks close to the solvent one. However, carefully examining the spectra in Figs. 3(c) and 3(e), it has been found that the intensity ratio of peaks in the spectrum of Fig. 3(c) is slightly changed, which may result from the different relaxation attenuations of various solute spins during the τ period. Hence, this method would not be suitable for quantitative analysis.

As is known, 2D J-resolved spectrum is one of the most fundamental and important 2D spectra for NMR

study. In a 2D J-resolved spectrum, chemical shift and J coupling information are separated and displayed on different axes of the spectrum, thus avoiding the peak crowding in 1D NMR spectrum. To suppress the solvent peak, the solvent suppression module via radiation damping effects was applied in 2D J-resolved experiment. The 2D J-resolved spectra of glucose in $90\%H_2O/10\%D_2O$ acquired using the standard pulse sequence without solvent suppression and the pulse sequence shown in Fig. 1(b) are presented in Figs. 4(a) and 4(b), respectively. From Fig. 4(a), it can be noticed that the intensities of solute peaks are so weak that the J-coupling information for the peaks close to the solvent (α–H and β–H of glucose) cannot be obtained at all. When the solvent peak is suppressed via radiation damping effects, the intensities of solute peaks are increased relatively and useful J-coupling information for the peaks close to the solvent (α–H and β–H of glucose) is presented distinctly.

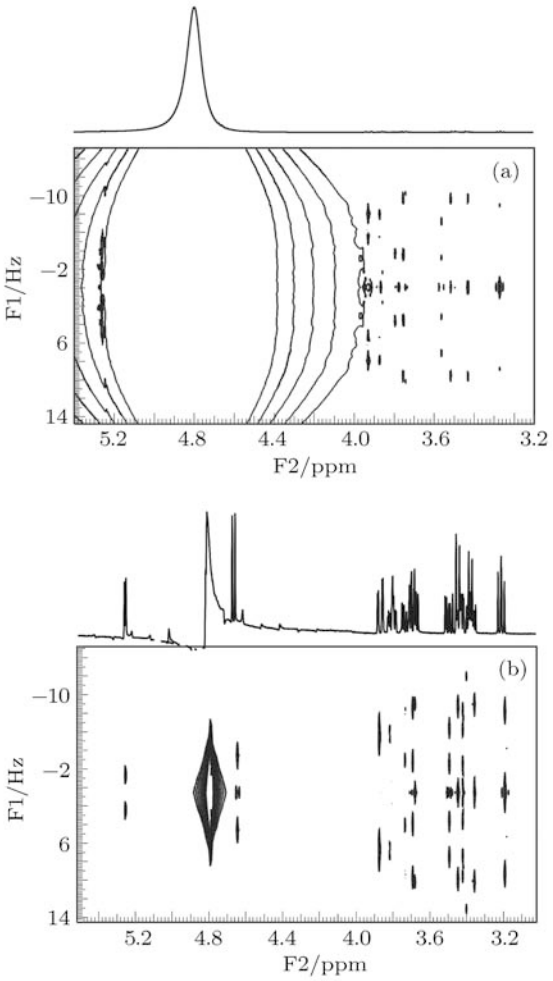


Fig. 4. The 2D J-resolved spectra of glucose in $90\%H_2O/10\%D_2O$. (a) Acquired with the standard pulse sequence without solvent suppression, and (b) acquired using the pulse sequence shown in Fig. 1(b) with solvent suppression via radiation damping effects.

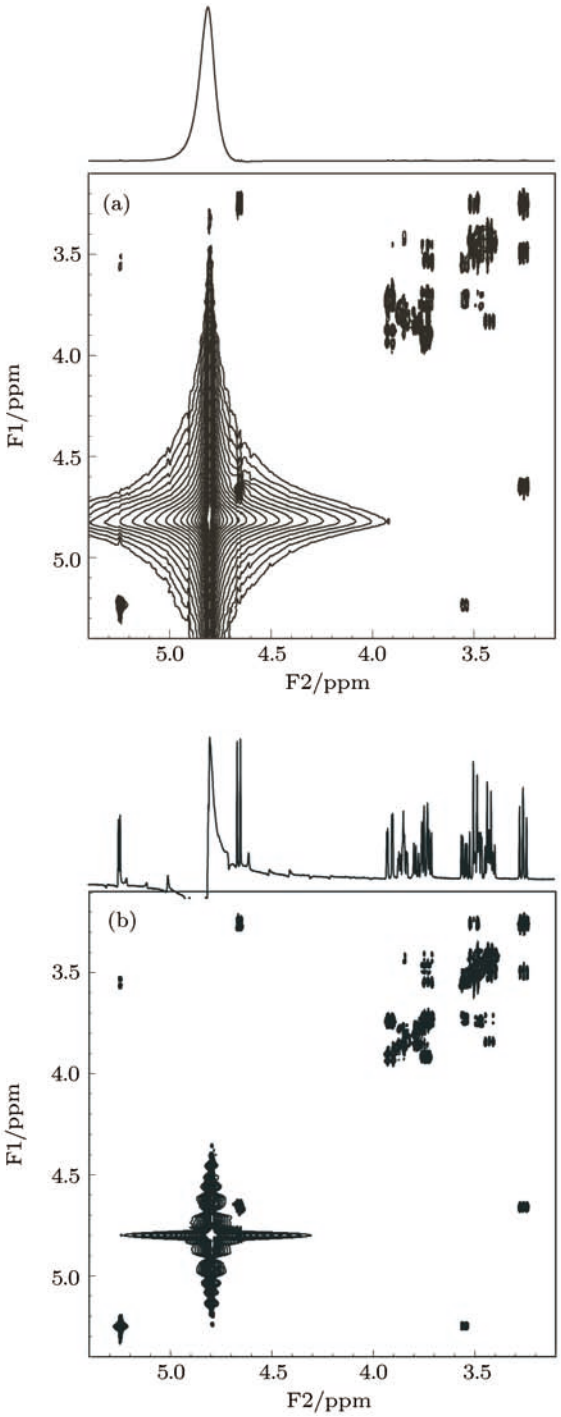


Fig. 5. The 2D gCOSY spectra of glucose in $90\%H_2O/10\%D_2O$. (a) Acquired with the standard pulse sequence without solvent suppression, and (b) acquired using the pulse sequence shown in Fig. 1(c) with solvent suppression via radiation damping effects.

The 2D COSY is another important NMR spectroscopic technique. From a COSY spectrum, it is possible to trace out the whole J-coupling network in the molecule. Similar to the 2D J-resolved experiment, solvent suppression module via radiation

damping effects was also applied in 2D gCOSY. The 2D gCOSY spectra of glucose in 90%H_2O/10%D_2O acquired with the standard pulse sequence without solvent suppression and the pulse sequence shown in Fig. 1(c) are illustrated in Figs. 5(a) and 5(b), respectively. In contrast with the spectrum without solvent suppression, it can be found that the solvent peak is well suppressed in Fig. 5(b). This indicates that the radiation damping can be applied for solvent suppression in 2D gCOSY experiments.

5. Conclusion

In this paper, a solvent suppression method via radiation damping effects was proposed. The solvent signal was well suppressed by introducing this solvent suppression method into the 1D ^{1}H NMR, 2D J-resolved, and gCOSY experiments. Compared to the W5, our method can suppress solvent signal without the suppression of the solute signals adjacent to the solvent. Although there are some disadvantages, such as possibly not suitable for quantitative analysis, this method still can be a good complement to conventional solvent suppression methods, especially for the samples with solute peaks adjacent to the solvent signal.

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