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(Received 8 January 1996, received in final form 18 March 1996, accepted 18 April 1996)

PACS.76.60.-k — Nuclear magnetic resonance and relaxation
PACS.76.90.+d — Other topics in magnetic resonances and relaxations
PACS.33.25.+k — Nuclear resonance and relaxation

Abstract. — In two-dimensional J-resolved NMR spectrum of radiation damped water with the simple pulse sequence of $\pi/2-t_1/2-\pi-t_1/2$-FID, harmonic peaks spaced by half frequency can either appear or disappear in the indirectly detected dimension, depending on the number of $t_1$ increments and on the sensitivity of probe head. When the experiments are performed with a less sensitive probe having a poor $Q$ factor, the harmonic peaks are hardly observable. The half frequency harmonic peaks observed with a tuned sensitive probe must be due to radiation damping. Theoretically, an inverted, strongly damped magnetization needs an infinitely long time to recover across the $xy$ plane following the radiation damping pathway; while in experiments, it takes less than tens of milliseconds. Therefore, when $t_1$ is long enough compared to the radiation damping time $T_1$, the "echo" is not symmetric about the $\pi$ pulse with respect to the $\pi/2$ pulse, modulating the FID by a pair of angles $\theta$ and $\phi$ that are complicated functions of both $t_1$ and the frequency offset $\Delta\omega$, and producing the harmonic peaks. If $t_1^{\text{max}}$ is short, the radiation damping effects during $t_1$ are wiped out by the spin echo. Consequently, the harmonic peaks disappear. Experimental results have been exactly simulated based on the radiation damping line shape theory.

1. Introduction

In recent years, radiation damping [1-3] has attracted much attention [4-13] in nuclear magnetic resonance (NMR) studies due to its unusual effects in experiments: a single $\pi$ pulse induces an echo-like free induction decay (FID) [2,9,13]; the dependence of the intensity on pulse flip angle becomes a saw tooth function [9,10]; the spin-lattice relaxation time cannot be measured by the mature inversion-recovery method [11,12]. Also in two-dimensional (2D) correlation (COSY) experiments, a radiation-damped sample invariably produces harmonic peaks in the indirectly detected dimension [4-7,13], which has induced heated discussion. Warren et al. [4,5,13] tried to view the harmonic peaks within a quantum mechanical framework, while Jeener et al. [14,15] suggested that a classical picture can also give a satisfactory interpretation.

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In a recent study [16], we have analyzed the radiation damping effects in 2D COSY experiments and found that the harmonic peaks in 2D COSY spectra of water are just artifacts induced by radiation damping. Based on the one-dimensional radiation damping line shape theory [17], a 2D line shape was described and a quantitative explanation of the artifacts was achieved. In this paper, the study is extended to 2D $J$-resolved spectrum that is one of the most important techniques in NMR. We report for the first time the unusual harmonic peaks separated by $\Delta \omega/2$ in the 2D $J$-resolved correlation spectrum of liquid water where $\Delta \omega$ is the frequency offset of the water signal. Trying to interpret them as half-quantum coherences does not seem possible. However, with the radiation damping line shape theory [16, 17], these half-frequency harmonics can be nearly exactly simulated. In the simulations, we emphasize the radiation damping effects during spin inversion, which deviates from what is expected by the mathematical expression of the line shape.

2. Experimental

The sample used was 80% H$_2$O with 20% D$_2$O as the lock substance in a 5 mm sample tube. Two-dimensional proton NMR experiments were conducted on a Bruker ARX-500 spectrometer with a 5 mm inverse probe and a 10 mm normal broad band probe, both being tuned at 500.13 MHz, using the $J$-resolved pulse sequence

$$\pi/2 - t_1/2 - \pi - t_1/2 - t_2.$$  \hspace{1cm} (1)

The transmitter offset was located at 162 Hz up field (lower frequency) from the resonance of water for both dimensions. In 2D data acquisition 512 points were used and the number of $t_1$ increments was changed from 64 to 512. Data matrix for Fourier transformation was $512 \times 512$ with zero filling in the $t_1$ domain only. Before Fourier transformation, no window filtration was performed. For all experiments, only one transient was acquired. The phases of the rf (radio-frequency) pulses and the receiver were fixed in the $x$ direction. Further experimental conditions will be supplemented in the figure notes.

3. Results and Discussion

Sequence (1) is among the simplest 2D experiments with only two pulses. One can quickly go through the analysis of the simple spin echo sequence with the normal model of exponentially decaying free precession. The $\pi$ pulse in the middle of $t_1$ focuses the chemical shift effect in the $F_1$ dimension. Since in a water molecule, the two protons are magnetically equivalent with a single Larmor frequency, neither direct nor indirect coupling between the two equivalent nuclei need to be considered. If the sample is free of radiation damping, only a single signal should appear on the 2D map at $\omega_1 = 0$, irrespective of the transmitter offset. However, for 80% H$_2$O in a 11.74 Tesla magnet with a tuned sensitive probe like the inverse one, the radiation damping time $T_\gamma$ is as short as 13 milliseconds, far shorter than the relaxation times ($T_1 = T_2 = 2.3$ s, $T_2^* = 0.2$ s.). This is a typical radiation-damped sample. The $J$-resolved spectrum (Fig. 1) shows a number of resonances in the indirectly detected dimension $F_1$, separated by a frequency of $\Delta \omega/2$, where $\Delta \omega$ is the chemical shift offset. This feature is quite different from 2D COSY spectrum [14, 16], where the harmonic peaks are spaced by $\Delta \omega$. It was not possible to interpret the observed multiple frequencies using intermolecular multiple quantum coherences, since half-integer quantum coherences cannot be described in NMR multiple quantum spectroscopy.
Fig. 1. — Absolute representation of two-dimensional J-resolved spectrum of 80% H₂O recorded with an inverse probe head. Data matrix for acquiring FID was 512 × 256 and zero filling to 512 × 512 for Fourier transformation was applied. The spectral width was 1000 Hz in both dimensions, so that the maximum t₁ was 256 ms (the t₁ increment was 1 ms). The transmitter offset with respective to the water signal was Δω = 162 Hz. As a result, the harmonic peaks in the indirectly detected dimension F₁ (the vertical dimension) are separated by 81 Hz. Shown as the projection is the F₁-slice with ω₂ = Δω.

Unfortunately, according to formal radiation damping theory, these multiple frequencies in the F₁ dimension are not expected, either. The evolution of the radiation-damped magnetization under the spin-echo pulse sequence can be explicitly analyzed. The first (π/2)₀ pulse flips the magnetization onto the y direction. During the first half of the evolution period, the magnetization precesses and decays as usual, but it returns to the equilibrium state not under the influence of relaxation, but following the radiation damping pathway [18]. In other words, the radiation damping effects become the dominant mechanism for the recovery of the magnetization. At the end of the first t₁/2 the magnetization points in a direction characterized by a pair of angles θ₁ and φ₁. The angle θ₁ must be smaller than π/2 and is described by [3]

\[ \tan(\theta₁/2) = \tan(θ₀/2) \exp(-t₁/2T₁) = \exp(-t₁/2T₁) \]

where the initial angle θ₀ is π/2 and tan(θ₀/2) = 1. The angle φ₁ is caused by the chemical shift precession and is apparently expressed by φ₁ = Δωt₁/2 in the rotating frame. The subsequent π pulse with x phase turns the magnetization to another direction denoted by θ₂ and φ₂, which
are found to be

\[ \theta_2 = \pi - \theta_1 = \pi - 2 \tan^{-1}[\exp(-t_1/2T_r)], \quad \phi_2 = \pi - \Delta \omega t_1/2. \]  

(3)

At the end of the second \( t_1/2 \), the angle between the magnetization and the \( B_1 \) field (denoted by \( \theta_3 \)) happens to be \( \pi/2 \), since

\[ \tan(\theta_3/2) = \tan(\theta_2/2) \exp(-t_1/2T_r), \]

(4)

and the corresponding phase \( \phi_3 \) that is related to the chemical-shift precession is just \( \pi \), since

\[ \phi_3 = \Delta \omega t_1/2 + \phi_2. \]

(5)

In this case, an echo forms with the magnetization lying along the \(-y\) axis. It turns out that the \( \pi \) pulse in the sequence could eliminate radiation damping. Since \( \theta_3 = \pi/2, \phi_3 = \pi, \) both being constants instead of functions of \( t_1 \), in the final 2D spectrum, there would be only one signal appearing at \( \omega_1 = 0 \). The harmonic peaks observed in \( F_1 \) dimension fail to be predicted.

However, in real situations, a \( \pi \) pulse cannot always refocus the effects of radiation damping. If the evolution time \( t_1 \) is shorter than the radiation damping time \( T_r \), it is certain that radiation damping effects are refocused at the end of \( t_1 \); but this is not true when \( t_1 \) is much longer than \( T_r \). There is an apparent discrepancy between the real situation and the ideal situation. Ideally, the radiation damped FID is expressed by a hyperbolic secant function [14,17]

\[ s(t) = M_0 \sec h\{t/T_r - \ln[\tan(\theta_0/2)]\} \exp(i\Delta \omega t) \]

(6)

where \( \theta_0 \) is the initial angle of the magnetization during a free evolution. If the magnetization is inverted, i.e., \( \theta_0 = \pi \), it would take an infinitely long time for the magnetization to recover, across the \( xy \) plane. However, in a real situation, the magnetization cannot stay at the inverted state for long. One need not wait longer than a second, as has been analyzed in a recent paper [18] dealing with the spin-spin relaxation time measurements. Therefore, as far as inversion is concerned, great care should be taken in a quantitative analysis. In recording the spectrum in Figure 1, the maximum of \( t_1/2 \) was as long as 128 ms, much longer than \( T_r \). For many experiments with long \( t_1 \), before the \( \pi \) pulse the magnetization has recovered nearly completely to the \( z \) direction already, owing to the fast drive of the radiation damping field. Thus, \( \theta_2 = \pi \), if the inversion is exact (see Eq. (3)). Theoretically according to equation (6), with an exact inversion (i.e., \( \theta_0 = \pi \)) the “echo” will not form until time is infinitely long. However, in experiments the “echo” can be observed within tens of milliseconds, i.e., the “echo” does not form at the end of the second \( t_1/2 \), but at a certain time in advance! This is the effect of radiation damping during spin inversion. Thus, when \( t_1 \) is much longer than \( T_r \), radiation damping cannot be focused out by a \( \pi \) pulse.

The reason is understandable based on the facts described below. The quantum mechanical response system is not an ideal system. Incoherent and nonlinear effects may occur, which could force the magnetization to leave the inverted position before relaxation takes place. The incoherent effect may be brought about by the inhomogeneity of the rf field, and the nonlinear effect may be due to some imperfection of the rf pulse. More reasonably, the inverted state is semi-stable, and its life time could not be long because of the intrinsically existing spin noise [19–21]. Therefore, even if the inversion is exact, the initial angle \( \theta_0 \) in equation (6) seems as if it were smaller (or greater) than \( \pi \). Meanwhile, an accurate inversion is hardly achieved in experiments. A small deviation from 180°, for example, 1% or 2%, is very likely to occur. This can lead to the same results as the finite life time of the inverted state can do. It would be rather difficult to isolate these two effects, and distinguishing them from each
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Fig. 2. — a) Six spin echoes of water recorded with the spin-echo pulse sequence \((\pi/2)_x - \tau - (\pi/2)_x(\pi/2)_y\)-FID where \(\pi\) pulse was replaced by the composite pulse in order to achieve an accurate inversion. The water signal was set on resonance, i.e. \(\Delta\omega = 0\). The varied \(\tau\) values are indicated along each trace. The arrows point where the echo should appear. It is clear that when \(\tau\) was short, the echoes were observed where they should be, but when \(\tau\) was long, the echoes appeared much earlier.
b) Computer simulated radiation damped spin echoes with the pulse sequence of \((\pi/2)_x - \tau - (0.983\pi)_y\)-FID. In this example, the 1.7 percent error in the \(\pi\) pulse can account for the radiation damping effect during inversion.

other does not seem necessary. Because we lack knowledge about the life time of the inverted state, we propose a small deviation \(\delta\) from the ideal \(\pi\) pulse to describe both these effects in the following discussion, i.e., \(\theta_2\) is not equal to \(\pi\) any more, but will be \(\pi - \delta\). The small deviation from \(\pi\) does not induce appreciable change in the echo when \(t_1\) is short. However, in the case of long \(t_1\), at the beginning of \(t_2\) the magnetization is not perpendicular to the \(z\) direction but has an angle smaller than \(\pi/2\), and the initial value of FID (or the amplitude of FID) is modulated by radiation damping during \(t_1\) (or more accurately speaking, during the second \(t_1/2\)). The radiation damping effects are thus still effective. What we have detected after the second \(t_1/2\) is the truncated echo-like NMR maser [2] signal. This can be illustrated in Figure 2, where the left column lists the experimental spin echoes, and the right column the simulated ones by \(90^\circ - \tau - 177^\circ - \tau\)-echo. We see that for a damped magnetization, when \(\tau\) is
short, the echo appears at $2\tau$, but when $\tau$ is long, the echo forms before the acquisition starts. Therefore, with a long $t_1$ just before the detection, the angle $\theta_3$ should be smaller than $\pi/2$, and becomes $t_1$-dependent. Due to the same reason, the chemical shift offset will be important when $t_1$ is long, and cannot be refocused by the spin-echo sequence.

The analysis above offers us a qualitative picture for the radiation damping effects in a 2D $J$-resolved experiment. Quantitative description will provide a deeper insight into the origin of radiation damping. The one-dimensional line shape equation (6) can be easily extended to describe the two-dimensional FID:

$$s(t_1, t_2) = M_0 \sec h \left\{ t_2/T_\tau - \ln \left[ \tan \frac{\theta(t_1)}{2} \right] \right\} \exp[i\Delta \omega t_2 + \phi(t_1)]. \quad (7)$$

Now the initial angle $\theta_0$ is replaced by $\theta(t_1)$, and the initial phase is changed from zero in equation (6) into $\phi(t_1)$ in equation (7) which is a function of $t_1$. Equation (7) is the general expression for radiation damped 2D FID. For any 2D experiment, if $\theta(t_1)$ and $\phi(t_1)$ are known, the damped 2D spectrum can be calculated through double Fourier transformation. Specifically in the current problem, in order to keep accordance with the previous discussion, $\theta(t_1) = \theta_3$ and $\phi(t_1) = \phi_3$.

It is known that Fourier transformation of equation (7) with respect to $t_2$ gives an expression complicated by the superposition of a series of Lorentzian line shapes [17]. Since we are interested in the $F_1$ slice at $\omega_2 = \Delta \omega$ only, where the harmonic peaks appear, we need not discuss the whole 2D spectrum. For this single slice, the calculation can be dramatically simplified and the expression becomes

$$S(t_1, \omega_2 = \Delta \omega) = M_0 T_\tau \theta(t_1) \exp[i\phi(t_1)]$$

$$= M_0 T_\tau \theta_3 \exp[i\phi_3]. \quad (8)$$

What we should do is to determine $\theta_3$ and $\phi_3$ at first, then take the Fourier transform of $S(t_1, \omega_2 = \Delta \omega)$ with respect to $t_1$. It should be pointed out that at this time $\theta_3$ and $\phi_3$ are not respectively equal to $\pi/2$ and $\pi$ any more, although equations (4, 5) are still valid. In order to derive $\theta_3$ and $\phi_3$, we replace $\pi$ by $\pi - \delta$ for the second pulse in sequence (1), where $\delta$ is a very small quantity to account for the radiation damping effects in real systems. The deviation in $\pi$ affects not only $\theta_2$ but also $\phi_2$. As a result, $\theta_2$ and $\phi_2$ are determined by equations (9, 10), respectively

$$\cos \theta_2 = -\cos \theta_1 \cos \delta - \cos(\Delta \omega t_1/2) \sin \theta_1 \sin \delta, \quad (9)$$

$$\sin \phi_2 = \sin(\Delta \omega t_1/2) \sin \theta_1 / \sin \theta_2. \quad (10a)$$

$$\cos \phi_2 = [\cos \theta_1 \sin \delta - \cos(\Delta \omega t_1/2) \sin \theta_1 \cos \delta] / \sin \theta_2. \quad (10b)$$

where the value of $\phi_2$ varies in the range from 0 to $2\pi$. Obviously, when $\delta = 0$, equations (9, 10) are reduced to the expressions in equation (3). This is just the situation we analyzed above. The angles $\theta_3$ and $\phi_3$ are still given by equations (4, 5) respectively, but since $\theta_2$ and $\phi_2$ are affected by $\delta$ that describes the radiation damping effects during inversion, $\theta_3$ and $\phi_3$ become complicated functions of $t_1$ and $\Delta \omega$. Inserting $\theta_3$ and $\phi_3$ into equation (8), we see that $S(t_1, \omega_2 = \Delta \omega)$ is frequency modulated by chemical shift offset, and multiple frequencies will be expected in the final 2D spectrum in the $F_1$ dimension.

One may have the difficulty in performing an analytical Fourier transformation of $S(t_1, \omega_2 = \Delta \omega)$ with respect to $t_1$. However, with the help of a computer, we obtained the calculated spectrum depicted in Figure 3. For the simulations we set $\delta = 2$ degree, deviating about 1% from $\pi$. It can be seen that only 1% inaccuracy for the $\pi$ pulse produces the half-frequency-spaced harmonic peaks in 2D $J$-resolved spectrum. Calculations show that a negative value
Fig. 3. — Simulation of the $F_1$-slice of $\omega_2 = \Delta \omega$ in Figure 1 with $\delta = 2^\circ$ (see the text). (A) and (B) are respectively the real and the imaginary part of the signal $s(t_1, \omega_2 = \Delta \omega)$ (see Eq. (8) and the related equations), while (C) is the final spectrum of $S(\omega_1, \omega_2 = \Delta \omega)$. Not only the frequencies, but also the relative intensities of the harmonic peaks have been nearly exactly simulated.

for $\delta$ yields the same result. However, when $\pi$ is used for calculation, no harmonic peaks can be simulated. On the other hand, if $\Delta \omega = 0$, from equations (9), (10) and (4), we see that $\phi_2 = \phi_3 = 0$, $\theta_2 = \pi - \delta - \theta_1$ and $\theta_3$ is independent of $\Delta \omega$. In this case, equation (8) is no longer a function of $\Delta \omega$ and the harmonic peaks are not expected to appear in the $F_1$ dimension.

It should be once-more emphasized that when we used $\pi - \delta$ instead of $\pi$ for calculation, we did not only mean the inaccuracy of the $\pi$ pulse, which may happen frequently in experiments; more importantly we meant that the real damped spin system cannot stay at the inverted state for long. Since the fast recovery of the damped, inverted system is much like the situation due to the inaccuracy in $\pi$ pulse, we therefore introduced the small deviation quantity $\delta$.

The simulation shown in Figure 3 explains well that the harmonic peaks in the indirectly detected dimension of the $J$-resolved spectrum of liquid water are due to the fact that the inverted magnetization forms an echo with a time shorter than what is expected by the mathematical expression, particularly when $t_1$ is much longer than $T_\gamma$. This implies that if the maximum of $t_1$ is not much longer than the damping time, harmonic peaks will disappear. Experiments confirm the implication. In the left column of Figure 4 we show four projections of 2D $J$-resolved spectra with different experimental numbers: (A) 64, (B) 128, (C) 256, (D) 512. The dwell time in the $t_1$ dimension or the $t_1$ increment was fixed at 500 microseconds. For (A) and (B), the maximum of $t_1/2$ were not long enough and the harmonic peaks did
not appear. When $t_1^{\text{max}}/2$ became long in experiment C, harmonic peaks began to appear. Finally when $t_1^{\text{max}}/2$ in experiment D was as long as $10T_r$, harmonic peaks were strong. These experimental spectra have been exactly simulated by computer and the results are shown in the right column of Figure 4.

One may be curious about the half frequency that is so seldom in 2D spectra and may occur only when $t_1^{\text{max}}/2$ is long. A simple physical picture may help people to get a good understanding. When $t_1$ is much longer than $T_r$, the recorded FID cannot remember what happened during the first $t_1/2$, because before the $\pi$ pulse, the magnetization has arrived at equilibrium due to radiation damping. The $t_1$ information contained in the 2D FID, which takes the form of $\Delta \omega t_1/2$, is actually contributed by the evolution during the second $t_1/2$. However, the Fourier transformation is performed with respect to the whole $t_1$. Therefore, the factor $1/2$ is given to the precession frequency $\Delta \omega$, resulting in a half frequency in the 2D spectrum.

We have seen that many factors affect the forming of the harmonic artifacts: the frequency offset, the number of $t_1$ increments or the maximum value of $t_1$, and the error in the $\pi$ pulse. An interesting question would be that if the system is free of radiation damping, can the half-frequency spaced harmonic peaks be expected? It has been pointed out [22] that in the usual
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Fig. 5. — Experimental spectrum for the same sample obtained by using the modified J-resolved pulse sequence \((\pi/2)_x - (\tau - \pi_y - 2\tau - \pi_y - \tau)_m\)-FID where \(m\) is increased in accordance with the \(t_1\) increment. The CPMG sequence was inserted in the evolution in order to eliminate radiation damping. As a result, the harmonic peaks disappeared in the \(F_1\) dimension.

cases where radiation damping is neglected, an imperfect \(\pi\) pulse in 2D J-resolved experiment also leads to a number of artifacts in \(F_1\) dimension. However, the intensities of such artifacts are weak, roughly proportional to \(\cos^2[(\pi - \delta)/2]\), while the main peak is \(\sin^2[(\pi - \delta)/2]\). If \(\delta = 2^\circ\), as assumed in the above simulation, the intensities of the artifacts are about 0.0003 times of the main peak. It is too weak to account for the artifacts in Figure 1. Thus, it can be concluded that the harmonic peaks in Figure 1 are caused by radiation damping.

This conclusion can be verified by experiments. When the radiation damping effects are removed, the 2D J-resolved spectrum of water should be free or nearly free of half-frequency harmonics. Although in recent years, various techniques for the suppression of radiation damping have been available \([8, 23-25]\), in order not to introduce side effects that may occur in the \(Q\)-switch, pulsed field gradient, or current feed-back experiments, we replaced the \(\pi\) pulse in sequence (1) by the CPMG pulse sequence that has proven useful for the suppression of radiation damping \([18]\). The experimental result is presented in Figure 5. The spectrum is free of artifacts. Another useful and simple method to avoid radiation damping is to use a 10 mm broad band probe head. With this probe, the proton signal was observed by the decoupling coil whose \(Q\) factor is very low and the filling factor for the 5 mm sample in 10 mm probe is rather poor. The radiation damping times are estimated to be increased by a factor of 40. The 2D J-resolved spectrum recorded by this probe is shown in Figure 6, where the half-frequency
signals become negligibly small. The non vanishing of the artifacts may be partly due to the contribution from $\cos^2[(\pi - \delta)/2]$ and partly due to weak radiation damping effects.

4. Conclusion

The half-frequency-spaced harmonic peaks in the $F_1$ dimension of two-dimensional $J$-resolved spectra of water are caused by radiation damping. Because the spin system cannot stay at the inverted state for long, the radiation damping effects during inversion resemble very much the effect of the imperfection of the $\pi$ pulse. Bearing this important feature in mind, we have simulated the experimental results by radiation damping line shape theory. When the evolution time is not long compared to radiation damping time, or when the radiation damping effects are removed by CPMG pulse sequence or weakened by using an insensitive probe, the harmonic artifacts disappear or become negligible.

Acknowledgments

This work has been supported by the National Natural Science Foundation of China. Helpful discussion with Prof. J. Jeener, Prof. G. Bodenhausen and Prof. B. C. Sanctuary are acknowledged. The authors are grateful to Prof. J. Jeener for his preprints before publication.
References