Effect of Strong Irradiation on Raman Magnetic Resonance in an AX Spin System

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In Raman magnetic resonance an initially prepared multiple quantum coherence (MQC) in a spin system introduces all the possible single quantum (SQ) and multiple quantum (MQ) NMR signals when an irradiation is applied during the detection period. If the irradiation is weak, the induced signals include those MQs up to the very order of this given MQC, while in the strong irradiation case, those MQs beyond the very order of the given MQC will also appear. An analytical approach based on the product formalism is developed to predict the intensities and frequencies of these induced signals. The analysis provides a complete treatment to cover both cases of weak and strong irradiation. It is also demonstrated with an AX spin system. Experimental results are in qualitative agreement with the analysis.

INTRODUCTION

It is well known that multiple quantum (MQ) spectroscopy in pulsed NMR is usually based on an indirect display by a two-dimensional (2D) format.[1] However, in earlier NMR work,[2,3] it was shown that MQ can be displayed by one-dimensional (1D) spectroscopy. In that work, a continuous wave (cw) of strong rf irradiation was employed so that the effect of high order perturbation on the spin system can be manifested. All single and multiple quantum transitions may then be simultaneously and directly probed. Unfortunately, owing to its inherent difficulties CW MQ NMR has not been widely employed as 2D MQ has. It was suggested by Yannoni et al.[4] to merge both 2D and CW MQ together, i.e., first to prepare MQ coherences (MQCs) by pulsed manipulation of the spin system to be studied and then to detect the responses of the spin system by a weak rf irradiation. In this scheme, MQ can be displayed in 1D format as it is done in CW MQ. Moreover the detection sensitivity remains relatively high as is in 2D MQ. This so-called Raman magnetic resonance (RMR) has been studied in quadrupolar system[5] and weakly coupled AX_n (n = 1, 2, 3)[6-8] spin systems, and some practical applications have also been shown.[9,10] It is noted that the RMR experimental scheme is somewhat similar to MQ double resonance.[11] However the applications of RMR emphasize the display of MQ NMR in one dimension. Therefore, in RMR experiments there is no need to introduce a hard pulse to transfer MQCs into directly observable single quantum coherences (SQCs) and response of the MQCs to a CW irradiation is observed during the detection period. Understanding the effects of irradiation to the RMR experiments is of course very important.

In previous studies of RMR[6-10], the irradiation is strictly weak. In the weak regime, an interesting effect is that an initially given MQC will induce all the accessible transitions, which include all the allowed single and forbidden MQs up to the order of this given MQC. In this paper we will extend the RMR study to the strong irradiation case so that we can have a complete understanding on RMR phenomena in a wide range of irradiation strength. For the case of weak irradiation, perturbation theory can be employed to analyze RMR in a spin system.[4-9] On the other hand, for the case of strong irradiation, perturbation analysis is no longer adequate. In this article we will introduce an analytical approach based on the product operator formalism[12] to the study of RMR. The calculation extends the irradiation to an arbitrary strength up to the case when spin decoulping happens, resulting in a more complete treatment. A weakly coupled AX spin system is demonstrated here both theoretically and experimentally. The effects of strong irradiation on the RMR responses of the system is revealed and interpreted in this article.

THEORETICAL FORMALISM

RMR experiment of weak rf irradiation in an AX spin

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system has been studied previously.[6] In this study we conduct a similar experiment but extend the irradiation to a wide range of strength in order to explore new RMR phenomena. For a weakly-coupled spin system AX, we denote nucleus A as spin-I, and X as spin-S. During the preparation period a specific coherent state in the system is prepared. In the detection period, an rf irradiation whose frequency is near the Larmor frequency of spin-S is applied. Therefore, the total Hamiltonian of the system in the double rotating frame during the detection period can be written as

$$H = H_0 + H_1, \quad (1)$$

where

$$H_0 = \delta\, S_z + \delta_I I_z + J S_z I_z, \quad (2)$$

$$H_1 = \frac{1}{2\pi}\cdot\omega_1 S_x, \quad (3)$$

where δ and δ_I are the resonance offsets of S and I spin, respectively, J is the spin coupling constant, and ω_1 is the Larmor frequency along the rf irradiation field.

The RMR signal, i.e., the RMR response of a given coherent state of the spin system in the detection period can be written as

$$M_y = Tr[I_y R(t)\rho(0)R(t)^{-1}], \quad (4)$$

where

$$R(t) = \exp(-iHt). \quad (5)$$

When $\rho(0)$ is given and the irradiation is weak in comparison with the coupling constant and the resonant offset, i.e.,

$$\omega_1 << |\delta \pm \frac{1}{2}J|, \quad (6)$$

one can calculate the NMR signal in the time domain in terms of various orders of perturbations. In doing so, the propagator $R(t)$ is divided into two terms, i.e., the major term H_0 and the perturbing term as defined in Eqs. (2) and (3) respectively. However, when the weak irradiation condition in Eq. (6) is not fulfilled, the calculation would become cumbersome, as the perturbation approach is no longer adequate to the analysis.

It has been shown previously by us[13] that the evolution propagators of a coupled spin system, e.g., A_nX_m, ABC, etc., can be decomposed completely into an ordered product of their elementary propagators in terms of product operators[12] when an irradiation is applied to the spin system. Practically, for the AX_n systems, the propagators can be written as

$$R(t) = \exp(-i\delta_I I_z t)\cdot\exp(-i\alpha_1 S_y)\cdot\exp(-i\alpha_2 I_z S_y)\cdot\exp(-i\delta' S_z t)$$
$$\cdot\exp(-iJ' I_z S_z t)\cdot\exp(i\alpha_2 I_z S_y)\cdot\exp(i\alpha_1 S_y), \quad (7)$$

where J' and δ' have the meaning of the effective J and δ when the irradiation ω_1 is applied, respectively. We have

$$J' = J\cos\alpha_1\cos\frac{1}{2}\alpha_2 + 2\omega_1\cos\alpha_1\sin\frac{1}{2}\alpha_2 - 2\delta\sin\alpha_1\frac{1}{2}\alpha_2, \quad (8)$$

$$\delta' = \delta\cos\alpha_1\cos\frac{1}{2}\alpha_2 + \omega_1\sin\alpha_1\cos\frac{1}{2}\alpha_2 - \frac{1}{2}J\sin\alpha_1\sin\frac{1}{2}\alpha_2. \quad (9)$$

The angles α_1 and α_2 are defined by the following equations:

$$\tan\alpha_1 = P - Q\tan\frac{1}{2}\alpha_2, \quad (10)$$

and

$$\tan\frac{1}{2}\alpha_2 = \{(P^2 - Q^2 + 1) - [(P^2 - Q^2 + 1)^2 + 4P^2Q^2]^{1/2}\}/(2PQ), \quad (11)$$

where

$$P = \omega_1/\delta, \quad (12)$$

and

$$Q = \frac{1}{2}J/\delta. \quad (13)$$

Now two examples for the calculation of the response signals in an AX system are demonstrated. It should be noted that the values of ω_1 and δ may be chosen experimentally. However, the choice of $\delta = \pm 1/2\, J$ is certainly prohibited here for an AX system. This may be explained by the fact that in the case of double resonance[14] the irradiation frequency is set at either position of the doublet. Therefore the relevant states are no longer pure states and it is meaningless to distinguish MQ and SQ. A purely given coherent state can be obtained in the AX system with an adequate pulse sequence combined with a designed phase cycle.[6] For example, we can prepare a pure double-quantum coherence (DQC) or zero-quantum coherence (ZQC) in the preparation period in the system. Therefore, expressing the density matrix in spin-operators, we have

$$\rho(0) \infty I_x S_x - I_y S_y \quad (14)$$

for DQC, while for ZQC we have

$$\rho(0) \propto I_xS_x + I_yS_y \tag{15}$$

With the help of Eq. (4), the response signals may be evaluated by

$$\begin{aligned} M_y(DQ) &= Tr\{I_yR(t)[I_xS_x - I_yS_y]R^{-1}(t)\} \\ &= (\cos\alpha_1\sin\tfrac{1}{2}\alpha_2 + \sin\tfrac{1}{2}\alpha_2\cos\tfrac{1}{2}\alpha_2)\exp[-i(\delta_I + \delta')t] \\ &\quad + (\sin\alpha_1\cos\tfrac{1}{2}\alpha_2 - \sin\tfrac{1}{2}\alpha_2\cos\tfrac{1}{2}\alpha_2)\exp[-i(\delta_I + \tfrac{1}{2}J')t] \\ &\quad - (\sin\alpha_1\cos\tfrac{1}{2}\alpha_2 + \sin\tfrac{1}{2}\alpha_2\cos\tfrac{1}{2}\alpha_2)\exp[-i(\delta_I - \tfrac{1}{2}J')t] \\ &\quad - (\cos\alpha_1\sin\tfrac{1}{2}\alpha_2 - \sin\tfrac{1}{2}\alpha_2\cos\tfrac{1}{2}\alpha_2)\exp[-i(\delta_I - \delta')t]. \end{aligned} \tag{16}$$

$$\begin{aligned} M_y(ZQ) &= Tr\{I_yR(t)[I_xS_x + I_yS_y]R^{-1}(t)\} \\ &= (\cos\alpha_1\sin\tfrac{1}{2}\alpha_2 - \sin\tfrac{1}{2}\alpha_2\cos\tfrac{1}{2}\alpha_2)\exp[-i(\delta_I + \delta')t] \\ &\quad + (\sin\alpha_1\cos\tfrac{1}{2}\alpha_2 + \sin\tfrac{1}{2}\alpha_2\cos\tfrac{1}{2}\alpha_2)\exp[-i(\delta_I + \tfrac{1}{2}J')t] \\ &\quad - (\sin\alpha_1\cos\tfrac{1}{2}\alpha_2 - \sin\tfrac{1}{2}\alpha_2\cos\tfrac{1}{2}\alpha_2)\exp[-i(\delta_I - \tfrac{1}{2}J')t] \\ &\quad - (\cos\alpha_1\sin\tfrac{1}{2}\alpha_2 + \sin\tfrac{1}{2}\alpha_2\cos\tfrac{1}{2}\alpha_2)\exp[-i(\delta_I - \delta')t]. \end{aligned} \tag{17}$$

It is interesting to notice from Eqs. (16) and (17) that a pure MQC, e.g., DQC in Eq. (16), and ZQC in Eq. (17), will introduce DQ (the first term in the equations), SQ (the second and the third terms), and ZQ (the last term) signals. For simplicity, we call these RMR response signals DQT, SQTs, and ZQT respectively in the following discussions, an expressing simplicity in the text. From these two equations, when the practical spin system and the experimental conditions are given, i.e., when the parameters J, δ_I, δ, and ω_1 are known, the RMR responses of a given MQC can be predicted, including the signal intensity and the observed frequency of each induced signal or transition. The calculations are straightforward without any approximation.

EXPERIMENTAL AND DISCUSSIONS

In the present work the RMR responses of DQC and ZQC in formic acid (E. Merck) are measured with a Bruker MSL 400 at ambient temperature. The ^{13}C-^{1}H in this sample is a typical AX system, where $J = 220$ Hz. δ is set at 200 Hz in the experiment. Fig. 1 shows the RMR response spectra of DQC. (during the preparation period a pure DQC was created.) Fig. 1(a) shows the traditional ^{13}C spectrum for reference and Fig. 1(b) shows that the DQ RMR spectrum includes a DQT (the far left signal) and two SQTs when ω_1 is weak. In this situation, there is no obvious frequency shift for the two SQTs, though the intensity of one SQT (the right side one) was changed and its phase reversed. As shown in Fig. 1(c), when ω_1, is comparable to J, an additional ZQT (in the far right side) appears and its intensity is much less than that of the DQT. Besides, the frequency separation of the two SQT lines become smaller since their frequency shifts have opposite signs. Fig. 1(d) shows the case when the strength of irradiation is further increased. The intensities of both the DQT and the ZQT are decreased and their absolute frequency shifts become large, and the frequency spacing of the SQTs become even smaller and

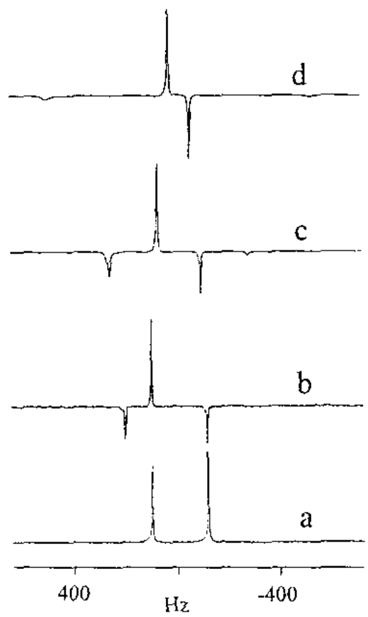

Fig. 1. (a) Traditional 1D spectrum of carbon in formic acid. The ^{13}C-^{1}H group is a typical AX spin system. $J = 220$ Hz, (b)-(d). Response RMR spectra of a pure DQC in the same system. $\delta = 200$ Hz. (b) $\omega_1/2\pi = 35$ Hz. The irradiation is weak, therefore the DQC only induces DQT (the reverse peak on the left side) and two SQTs, and the frequency shift of the two SQTs can be neglected in this situation. (c) $\omega_1/2\pi = 185$ Hz, the stronger irradiation induces additional ZQT (the reversed weak signal on the right side). The effective coupling constant J' has become smaller than that of weak irradiation, therefore the two SQTs are notably closer than that in (b). (d) $\omega_1/2\pi = 450$ Hz J' becomes even smaller, and both DQC and ZQT intensities have decreased and they move further away from the center of the spectrum.

their absolute intensities becoming equal as the decoupling case is reached.

The response signal intensities of DQC in this AX system have been calculated and are shown in Fig. 2. The calculations were carried out using Eq. (16) where ω_l was taken as a variable, with $J = 220$ Hz and $\delta = 200$ Hz was set by the experiment. As we can see from Fig. 2, the theoretical predictions are in fairly good qualitative agreement with the experiment.

The RMR response spectra of ZQC in the AX system are shown in Fig. 3. Again, Fig. 3(b) shows the spectrum when the irradiation is weak. The response signals include ZQT, i.e., the inverse peak on the right side and the two inevitable SQTs. Figs. 3(c-e) show the spectra when the irradiation strength ω_l is further increased. The relevant theoretical calculations of the ZQC response are displayed in Fig. 4.

These experiments show that when the irradiation is relatively weak, a given MQC in the system induces the MQT of the very order and two SQTs, as had been indicated in our previous studies.[6-8] However, when the irradiation field increases, another possible MQT, i.e., ZQT in the DQC responses and DQT in the ZQC responses also appears in an AX system. The effective coupling constant J' in Equation (8) is monotonously decreasing with increasing irradiation power. Therefore the frequencies of the two SQTs in the response spectra come closer and their absolute intensities equalize while the MQTs first go through a maximum and then drop towards zero intensity. Calculations show that the behavior of these responses are fully predictable by our theoretical model. It is not our intention in this short communication to make a quantitative comparison between the calculations and the experiments. Hence, we can see from the experimental spectra in Figs. 1 and 3 that the linewidths of the RMR signals increase with increasing irradiation power. However, in our theoretical study this effect of irradiation broadening has not been considered.

Fig. 5 shows the effective constant J' as a function of irradiation strength ω_l. The calculations were based on Eq. (8). The curve shows that J' is monotonously decreasing with increasing ω_l towards complete decoupling. Since the effective offset δ' can be obtained by Eq. (9), therefore the frequencies of all the signals can be predicted provided the offset δ_l is known. A full paper related to a complete study

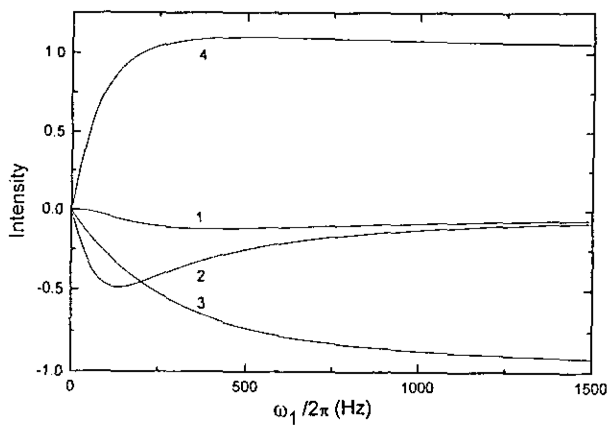

Fig. 2. Response signal intensities of a pure DQC in an AX system as a function of irradiation strength ω_l. $J = 220$ Hz, $\delta = 200$ Hz. The calculations were based on Eq. (16). 1 — ZQT, 2 — DQT, 4 — the SQT which is related to the positive peak in Fig. 1(b)-(d). 3 — the SQT which is related to the reversed peak in Fig. (b)-(d). The intensities of both DQT and ZQT increase first to their respective maximum and then goes down towards zero as ω_l increases, while the absolute intensities of the two SQTs equalize. The spin system will eventually reach a completely decoupled status.

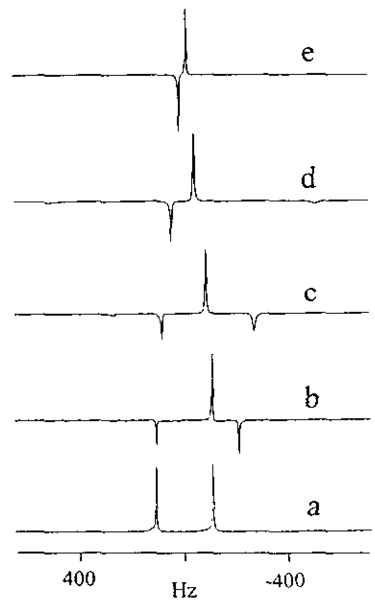

Fig. 3. (a) The traditional ^{13}C spectrum of formic acid. (b)-(e), The RMR response spectra of a pure ZQC in the AX spin system. $\delta = 200$ Hz. (b) $\omega_l/2\pi = 35$ Hz. The irradiation is weak, hence the RMR signals include only ZQTs (the reversed peak on the right side) and the two SQTs. J' has no apparent change than that in (a). (c) $\omega_l/2\pi = 185$ Hz. (d) $\omega_l/2\pi = 450$ Hz. (e) $\omega_l/2\pi = 970$ Hz. When the irradiation becomes rather strong, DQT (the reversed and very small peak on the left side) appears and drops out when ω_l further increases, while J' becomes smaller and the reversed SQT intensity equalizes and moves closer to another SQT, indicating that the spin system is reaching its completely decoupled status.

on AX_n (n = 1, 2, 3) spin systems will be presented elsewhere.

In a more complex system, we anticipate that the RMR response signals of a given MQC will introduce all the possible transitions including the SQTs and possible forbidden MQTs not only up to the very order of the given MQ in the weak irradiation, but also those MQTs with even higher order and eventually reaching the highest order as long as they are available in the system with increasing irradiation strength. For the AX system, DQC and SQC have different symmetries as indicated in Eqs. (14) and (15), therefore they have different behavior in the RMR responses. Consequently, the much weaker ZQ signal appears in the DQC response only when the irradiation is strong although ZQT is actually a double quantum process which involves simultaneously a flip-flop of S and I-spins, and vice versa for the DQ signal in the ZQC response spectra.

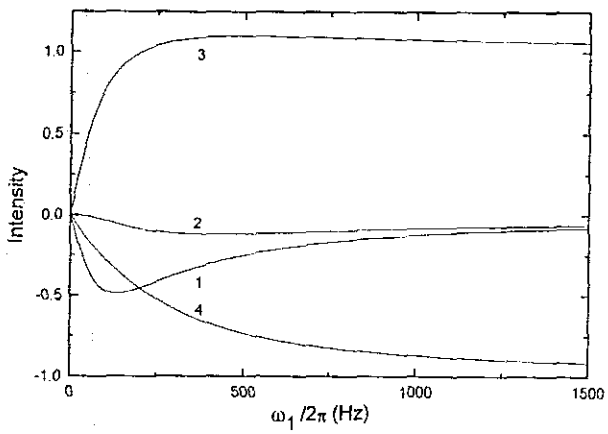

Fig. 4. The response signal intensities of a pure ZQC in an AX spin System as a function of irradiation strength ω_1. J = 220 Hz, δ = 200 Hz. The calculations were based on Eq. (17). 1 — ZQT, 2 — DQT, 3 — the SQT which is related to the positive peak in Fig. 3(b). 4 — the SQT, which is related to the downward peak in Fig. 3(b). The trends with increasing ω_1 are similar to those in Fig. (2). The difference here from that of Fig. (2) is that the ZQT intensity is much larger than that of DQT since the initial state is a ZQC in this experiment.

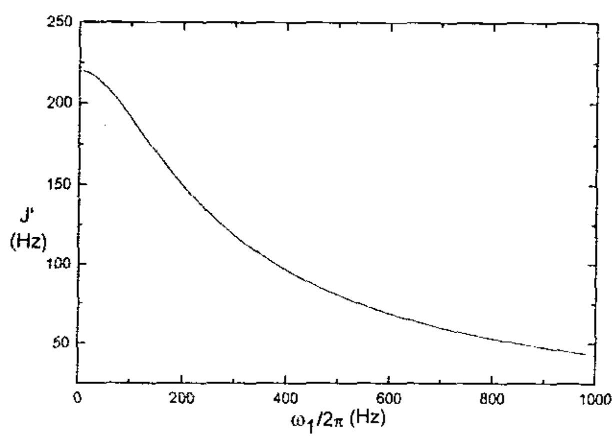

Fig. 5. Effective coupling constant J' as a function of irradiation strength ω_1. J = 220 Hz, δ = 200 Hz. J' is monotonously decreasing with an increasing ω_1, therefore moving towards complete decoupling. The calculation was based on Eq. (8).

In conclusion, we have shown with an AX system that a theoretical analysis based on the product operator formalism can readily be employed to handle both weak and strong irradiation. Therefore RMR experiments can be properly interpreted and consequently the MQ process in RMR experiments can be clearly understood, e.g., the effects of a stronger irradiation on the RMR responses in the spin system can then be revealed. Further studies following this line is under way.

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Key Words

Raman magnetic resonance; Multiple quantum NMR; Double resonances.

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