Two Dimensional Transfer Modes in CH$_2$ Spin System

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Abstract : Spin-lattice relaxation pathway of CH$_2$ spin system by two dimensional NOESY sequence has been discussed. Two-dimensional spectra governed by dipolar relaxation mechanism were simulated in term of transfer mode, the generalization of conventionally used magnetization mode in one dimension. The transfer matrix directly related to the Redfield relaxation matrix can be constructed by the multiplet of transfer mode. The observable relaxation transfer modes causes to variation of the off-diagonal signal intensity of phase sensitive NOESY spectra from which variable spectral density can be extracted with simple group theoretical calculation. The variation of the J-coupling peak intensity as a function of the mixing time in 2-D spectra for n-Undecane-5-^{13}C and Bromoacetic 2-^{13}C acid has been theoretically traced. Keywords : transfer mode, logitudinal relaxation, NOESY, HOESY, spectral density, magnetization mode

INTRODUCTION

The behavior of a spin system which interacts weakly with a complicated surrounding has been a great concern for many decades ago.[1-5] The spin lattice relaxation process reveal the correlation between the spin and its surrounding at a molecular level. For a complete quantum mechanical description of relaxation one must use the density matrix formalism.[6] The time evolution of full density matrix elements including off-diagonal element for nuclear spin relaxation has been formulated by Redfield. The underlying tenets of his formalism are as follows: Random phase of bath, short molecular correlation time compared to the varying time interval in which spin density matrix element doesn't change considerably, irreversible process of spin relaxation.

Since spin-lattice interaction Hamiltonian is small compared to that of the lattice

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the variation of density operator with time is usually slow, thus Redfiled equation is reduced to the coupled differential equation with constant coefficients. The spin relaxation of $I = 1/2$ nuclei in liquid is due in many cases to the time dependent nuclear magnetic dipolar interactions. The multi-exponential decay of relaxation pathway discovered by Hubbard theoretically is mainly ascribed to the cross-correlation spectral density of dipolar interaction itself even for the identical three spins system.[7] For the scalar coupled spin system dipolar and chemical shift anisotropy cross-correlation also gives rise to the symmetry broken non-exponential relaxation decay which is well reviewed by Grant, Vold, and Canet.[8-12] The normal mode approach proposed by Grant. et al employed the group theoretical argument based on the orthonormal spin operator. The spectral density that contains the dynamic information about the molecular interaction could be extracted from tracing the time dependent density matrix element perturbed by the 1-dimensional pulse trains that create the initial non-equilibrium spin density. The relaxation curve fitting is required to obtain the desired dynamic parameters.[13]

In contrast to the conventional relaxation experiment, new approach has been tried by Bodenhansen in early 1990.[14] They extended the magnetization mode to the 2-dimennsional transfer mode that applied to the homo-nuclear AX system to measure the auto- and cross-correlation spectral density as well as proton chemical shift anisotropy of small molecule, Exifone. They also showed that in small flip angle NOESY the amplitude of the multiplet component obeyed the specific rules and analyzed motional anisotropy and cross-correlation dipolar spectral density for weakly coupled AMX system.[15] However, although hetero-nuclear spin system especially carbon-proton coupled system is widely found in most organic compound and its characterization in a molecular level provides valuable information about molecular tumbling in liquid, such system has not been explained fully yet. So in this paper theoretical strategy of hetero-nuclear CH_2 system has been generally presented in line with the Bodenhausen's concept and briefly applied to n-Uundecane-5-^{13}C and the Bromoacetic 2-^{13}C acid.

MAGNETIZATION MODE

The magnetization mode of coupled system begins with coupling scheme of individual irreducible tensor operators defined for the system.[16-18]

$$T_{q,j}^{(k)}(A,B,C....) = \sum_{q_1} P\sqrt{2k+1}(-1)^{k_1-k_2}\begin{pmatrix} k_1 & k_2 & k \\ q_1 & q_2 & q \end{pmatrix} T_{q_1,j_1}^{(k_1)}(A,B,C....) T_{q_2,j_2}^{(k_2)}(L,M,N....) \quad (1)$$

With the help of above tensor coupling, CH$_2$ spin system may be formed from the direct products of the zero projection operators for the carbon spin and for the degenerate proton spins as follows

$$T_0^{(0)}(C) = \frac{1}{\sqrt{2}}[E] T_0^{(1)}(C) = \sqrt{2}\left[I_z^C\right] \tag{2-a}$$

$$T_{0E}^{(0)}(H_2) = \frac{1}{2}[E] T_{0X}^{(0)}(H_2) = \frac{2}{\sqrt{3}}\left[\mathbf{I}^H \cdot \mathbf{I}^{H'}\right] = \frac{1}{\sqrt{3}}\left[2I_z^H I_z^{H'} + \left(I_+^H I_-^{H'} + I_-^H I_+^{H'}\right)\right] \tag{2-b}$$

$$T_0^{(1)}(H_2) = \frac{1}{\sqrt{2}}\left[I_z^H + I_z^{H'}\right] \tag{2-c}$$

$$T_0^{(2)}(H_2) = \sqrt{\frac{2}{3}}\left[3I_z^H I_z^{H'} - \mathbf{I}^H \cdot \mathbf{I}^{H'}\right] = \frac{1}{\sqrt{6}}\left[4I_z^H I_z^{H'} - \left(I_+^H I_-^{H'} + I_-^H I_+^{H'}\right)\right] \tag{2-d}$$

where $I_\pm = I_x \pm iI_y$. Then the magnetization modes are defined in terms of irreducible tensor operators and standard single spin angular momentum operators as follows

$$^a v_1 = Tr\left[T_0^{(1)}(C) T_{0E}^{(0)}(H_2)\chi\right] = \frac{1}{\sqrt{2}} Tr\left[I_z^C \chi\right] \tag{3a}$$

$$^a v_2 = Tr\left[T_0^{(0)}(C) T_0^{(1)}(H_2)\chi\right] = \frac{1}{2} Tr\left[\left(I_z^H + I_z^{H'}\right)\chi\right] \tag{3b}$$

$$^a v_3 = \frac{1}{\sqrt{3}} Tr\left[T_0^{(1)}(C)\left(T_{0X}^{(0)}(H_2) + \sqrt{2}T_0^{(2)}(H_2)\right)\chi\right] = \frac{4}{\sqrt{2}} Tr\left[I_z^C I_z^H I_z^{H'} \chi\right] \tag{3c}$$

$$^a v_4 = \sqrt{\frac{3}{8}} Tr\left[T_0^{(1)}(C)\left(T_{0X}^{(0)}(H_2) - \sqrt{2}T_0^{(2)}(H_2)\right)\chi\right] = Tr\left[I_z^C\left(I_+^H I_-^{H'} + I_-^H I_+^{H'}\right)\chi\right] \tag{3d}$$

$$^{s}v_{5} = Tr\left[T_{0}^{(1)}(C)T_{0}^{(1)}(H_{2})\chi\right] = Tr\left[I_{z}^{C}\left(I_{z}^{H} + I_{z}^{H'}\right)\chi\right] \tag{3e}$$

$$^{s}v_{6} = \frac{1}{\sqrt{3}}Tr\left[T_{0}^{(0)}(C)\left(T_{0X}^{(0)}(H_{2}) + \sqrt{2}T_{0}^{(2)}(H_{2})\right)\chi\right] = \sqrt{2}Tr\left[I_{z}^{H}I_{z}^{H'}\chi\right] \tag{3f}$$

$$^{s}v_{7} = \sqrt{\frac{3}{8}}Tr\left[T_{0}^{(0)}(C)\left(T_{0X}^{(0)}(H_{2}) - \sqrt{2}T_{0}^{(2)}(H_{2})\right)\chi\right] = \frac{1}{2}Tr\left[\left(I_{+}^{H}I_{-}^{H'} + I_{-}^{H}I_{+}^{H'}\right)\chi\right] \tag{3g}$$

$$^{s}v_{8} = Tr\left[T_{0}^{(0)}(C)T_{0E}^{(0)}(H_{2})\chi\right] = \frac{1}{2\sqrt{2}}Tr\left[E\chi\right] \tag{3h}$$

These modes defined in spin operators can be rewritten as linear combinations of the populations in spin states and some of them are related to the measurable line intensities From these, it is clear that some of the magnetization modes can be observed through linear combinations of the spectral line intensities. For CH_2 spin system, four out of the eight modes are observable, which are $^{a}v_{1}$, $^{a}v_{2}$, $^{a}v_{3}$, and $^{s}v_{5}$. Among these, $^{a}v_{2}$, which can be denoted as $^{a}v_{X}$, is observable only in the ^{1}H spectra, and this represents the sum of total line intensities in proton doublet. The total carbon nucleus, or carbon magnetization, is given by the mode $^{a}v_{1}$, which is the sum of all the line intensities from carbon triplet. Subtraction of the central line intensity from the sum of the outer two lines intensities in carbon triplet gives the mode $^{a}v_{3}$. Mode $^{s}v_{5}$ can be observed both in proton and carbon spectra where it is the difference of the two lines in the proton doublet and that of the outer lines in the carbon triplet. The four observable magnetization modes are basis for the following transfer mode. And spin-lattice relaxation couples the four longitudinal spin operators.[8] Dipolar and random field spectral densities were obtained from the fitting of experimental data with coupled Redfield equation.[12]

TRANSFER MODE

Bodenhausen introduced the transfer mode, which may be regarded as two dimensional analogues of magnetization mode.[15] They introduced the transfer mode for the weakly coupled proton scalar coupled two spin system. There are three longitudinal spin order and nine transfer modes. For the heteronuclear CH_2 spin system 16 independent

transfer mode with four longitudinal spin order can be generalized by the same token as below

$$\{I_z^C \to I_z^C\} \tag{4a}$$

$$\{I_z^C \to (I_z^H + I_z^{H'})\} \tag{4b}$$

$$\{I_z^C \to I_z^C (I_z^H + I_z^{H'})\} \tag{4c}$$

$$\{I_z^C \to I_z^C I_z^H I_z^{H'})\} \tag{4d}$$

$$\{(I_z^H + I_z^{H'}) \to (I_z^H + I_z^{H'})\} \tag{5a}$$

$$\{(I_z^H + I_z^{H'}) \to I_z^C\} \tag{5b}$$

$$\{(I_z^H + I_z^{H'}) \to I_z^C (I_z^H + I_z^{H'})\} \tag{5c}$$

$$\{(I_z^H + I_z^{H'}) \to I_z^C I_z^H I_z^{H'})\} \tag{5d}$$

$$\{I_z^C (I_z^H + I_z^{H'}) \to I_z^C\} \tag{6a}$$

$$\{I_z^C (I_z^H + I_z^{H'}) \to (I_z^H + I_z^{H'})\} \tag{6b}$$

$$\{I_z^C (I_z^H + I_z^{H'}) \to I_z^C (I_z^H + I_z^{H'})\} \tag{6c}$$

$$\{I_z^C (I_z^H + I_z^{H'}) \to I_z^C I_z^H I_z^{H'})\} \tag{6d}$$

$$\{I_z^C I_z^H I_z^{H'} \to I_z^C\} \tag{7a}$$

$$\{I_z^C I_z^H I_z^{H'} \to (I_z^H + I_z^{H'})\} \tag{7b}$$

$$\{I_z^C I_z^H I_z^{H'} \to I_z^C (I_z^H + I_z^{H'})\} \tag{7c}$$

$$\{I_z^C I_z^H I_z^{H'} \to I_z^C I_z^H I_z^{H'})\} \tag{7d}$$

Here we may construct the 16 different ordered pairs $\{\sigma_i\} \to \{\sigma_j\}$ from 1-dimensional

Table.1 The multiplets originated from the transfer modes

Multiplet	Transfer Mode	
M_{CC}	(4a),(4d), (6c), (7a),(7d)	(4b),(6a),(6d),(7c)
M_{HH}	(5b),(5d), (6c), (7b),(7d)	(5c),(6a),(6b),(7c)
M_{CH}	(4b),(4d),(6c), (7b),(7d)	(4c),(6b),(6d),(7c)
M_{HC}	(5b),(5d), (6c), (7a),(7d)	(5c),(6b),(6d),(7c)

four longitudinal spin order. The operators $\{\sigma_i\}, \{\sigma_j\}$ in each pair refer to the state at the

beginning and at the end of the mixing period. Each longitudinal spin order can be inter-converted during the mix time through its own longitudinal relaxation pathway. If the dipolar-CSA cross-correlation does not be considered the transfer mode of CH_2 spin system reduced from 16 to 10 due to the symmetry property of the dipolar interaction. That means only seven independent transfer modes are enough to extract the spectral density of the relaxation pathway via 2-dimensional signal intensity. The corresponding multiplets can be treated in a same manner as in Bodenhausen's paper[14] although the extra multiplets can arise from the three spin longitudinal order, like $\{I_z^C I_z^H I_z^{H'} \rightarrow I_z^C I_z^H I_z^{H'})\}$. The muliplets arising from the transfer mode $\{I_z^C I_z^H I_z^{H'} \rightarrow I_z^C I_z^H I_z^{H'})\}$ are centered at $(\varpi_C, \varpi_C), (\varpi_C, \varpi_H), (\varpi_H, \varpi_C), (\varpi_H, \varpi_H)$. The 2-dimensional multiplet corresponding to the transfer mode are summarized in Table.1 The multiplets from the third column in Table.1 originate from the inter-conversion of symmetric and antisymmetric longitudinal spin order under the operation of spin inversion. The symmetry property of the relaxation process causes the M_{CH} and M_{HC} to be equal intensity and phase. Thus the ^1H-^{13}C HOESY are enough to consider the independent experimental data set. So we could only consider three multiplets (ϖ_C, ϖ_C), (ϖ_C, ϖ_H), (ϖ_H, ϖ_H) to extract the dynamic parameter.

THE SIMULATION OF THE TWO DIMENSIONAL NOESY SPECTRA

Typical ^1H-, ^{13}C-NOESY and ^1H-^{13}C HOESY pulse sequence is shown in Fig.1. It consists of three pulses, each of 90 degree. The first pulse converts the one spin longitudinal z magnetization into transverse magnetization. During the subsequent period t_1, the spin magnetization processes through the angle with respect to the given chemical shift and coupling constant. The second mixing pulse brings the magnetization to the z-axis. The spurious transverse magnetization following the second pulse can be canceled out by suitable phase cycling. Thus the only longitudinal z-magnetization can be obtained right before the mixing period. The frequency labeled magnetization modulated both chemical shift and coupling constant gives the phase sensitive indirect multiplets.

The density operator at time d in Fig. 1 for ^{13}C-NOESY pulse sequence gives

$$\sigma_d \rightarrow I_Z^C \cos^2(\pi J t_1)\cos(\omega_C t_1) + 2I_Z^C (I_Z^H + I_Z^{H'})\sin(2\pi J t_1)\sin(\omega_C t_1).$$

$$+ I_Z^C I_Z^H I_Z^{H'} \sin^2(\pi J t_1)\cos(\omega_C t_1).. \qquad (8)$$

The first terms gives the in-phase multplet, while the second out-of phase multiplet in F1 axis. At $\tau_m = 0$, each longitudinal spin order has its own 2-D peak intensity modulated both ω_C and J_{CH} likewise in F1 axis which can be simulated in Fig. 2. In Fig. 2, in-phase $I_z - I_z$ transfer mode in pure phase sensitive as well as in mixed phased are displayed. The mixed phase spectrum has the same information of relaxation driven by each transfer mode as the pure absorption peak. But due to the inherent weakness susceptible to pulse imperfection it has not been used to interpret the experimental data but only for second check-up. Other multiplet pattern from ^{13}C NOESY pulse sequence can be simulated and their spectra are shown in Fig. 3. The multiplet in Fig.3 corresponding the second term of Eq.(8) shows the two diagonal and two anti-phase off diagonal peak with equal intensity. The longitudinal three spin order, $I_Z^C I_Z^H I_Z^{H'}$, yields the same absolute peak intensity with I_Z^C NOESY pattern except the negative peak at the (ν_c, $\nu_c \pm J$), ($\nu_c \pm J$, ν_c).
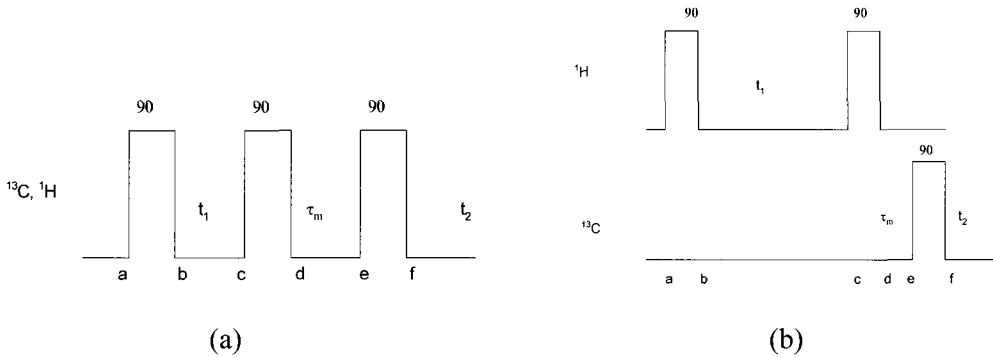

Fig.1. The (a) ^{1}H,^{13}C-NOESY and (b) ^{1}H-^{13}C HOESY pulse sequence

As shown in Table.1 the experimental intensities of all possible 2D multiplet can be regarded as the component of vectors in nine-dimensional space. The spin inversion symm-
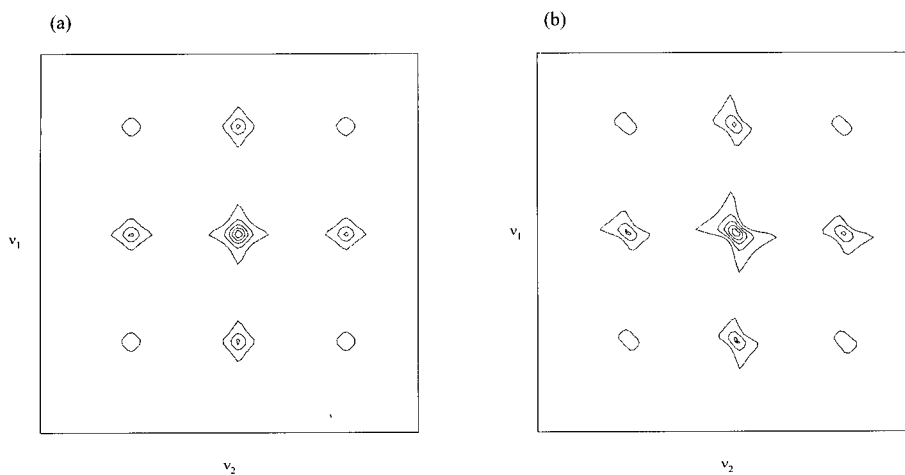
(a)

(b)

Fig. 2.   The 2D-multiplet of (a) pure absorption and (b) mixed phase contour from
I_z --- I_z transfer mode

etry reduces the possible multiplet from nine transfer modes to five. The resulting 2D multiplet component of (ω_c, ω_c) can be constructed by the corresponding transfer mode.

The multiplet vector, M^{CC}, ^{13}C-NOSY peak intensity centered at (ω_c, ω_c) is

associated with the transfer mode, $\{\sigma_i\} \rightarrow \{\sigma_j\}$ with its characteristic peak intensity.

Therefore the

$$M^{CC} = \sum_{ij} \alpha_{ij}^{CC} M_{ij}^{CC} \tag{9}$$

where the coefficient α_{ij}^{CC} is the weight of the transfer mode, $\{\sigma_i\} \rightarrow \{\sigma_j\}$, which is

directly related to the mixing time and the relaxation process. It is possible to simulate the ^{13}C-NOSY peak intensity centered at (ω_c, ω_c) with Eq. (9). The J-coupled multiplet of the total 2D contour spectrum at mixing time zero comes fom the linear combination of the thr-

ee multuplets and their results is shown in Fig. 4(a). The experimental results for the *n*-Uundecane-5-^{13}C is given in Fig. 4(b).   The two spectra show that there is only diagonal peak without any J-coupled peak. The α_{ij}^{CC} oppositely added to vector M^{CC} at zero mixing time yields the zero intensity of off-diagonal peak. It is evident that the off-diagonal J-coupling peak would arise as the time evolves during mixing time due to the relaxation process. Likewise ^{1}H-NOESY as well as ^{13}C-^{1}H HOESY can be applied analogously with the same definition of multiplet vectors, M^{HH} M^{CH} with coefficient α_{ij}^{HH} , α_{ij}^{CH} respectively.

^{1}H-NOESY the density operator at time d is

$$\sigma_d^{'} \rightarrow (I_Z^H + I_Z^{H'})\cos(\pi Jt_1)\cos(\omega_H t_1) + I_Z^C(I_Z^H + I_Z^{H'})\sin(\pi Jt_1)\sin(\omega_H t_1)... \qquad (10)$$

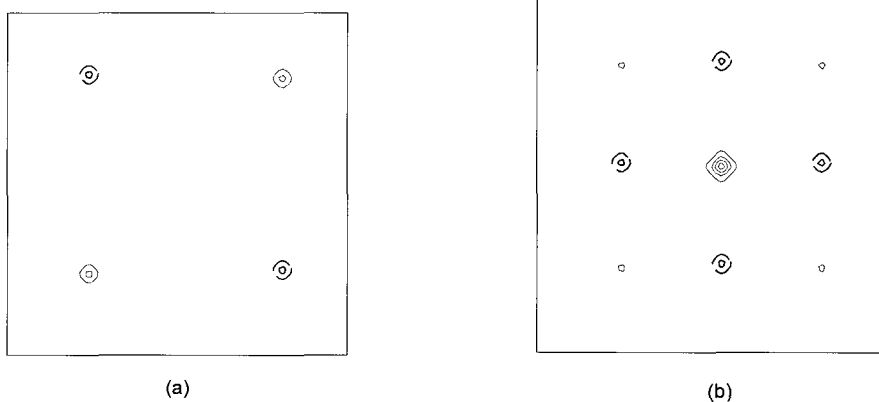(a)   (b)

Fig. 3. The ^{13}C-NOESY 2D-multiplet from transfer mode (a) Eq.(6c) and (b) Eq.(7d)
        Dashed contour denotes the negative peak.

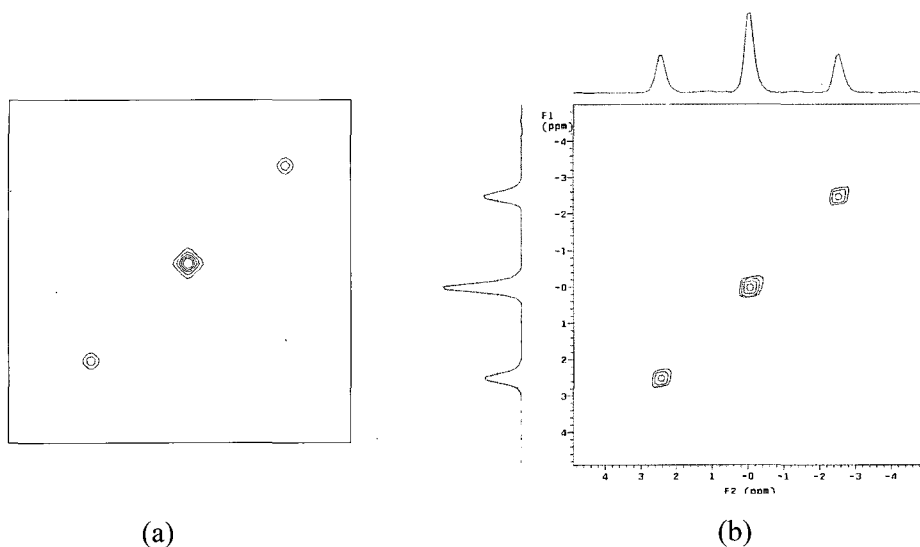(a)   (b)

Fig. 4. The ^{13}C-NOESY 2D-multiplet of CH_2 system at zero mixing (a) simulated and (b) experimental spectrum of enriched n-undecane central carbon(Varian 200MHz)

The first and second term of Eq.(10) give the J-coupled ^{1}H-NOESY multiplet, which is shown in Fig.5 The coefficient $\alpha_{ij}^{HH}(i,j=(I_Z^H+I_Z^{H'}))$ matrix from Eq.(4c) has the element (1,1,1,1) and α_{ij}^{HH} from Eq.(5c) transfer mode is the (-1,1,-1,1). With Eq.(9) the total multiplet of ^{1}H-NOESY from possible transfer mode at zero mixing time yields the following 2D intensity multiplet, which is shown in Fig6. The experimental ^{1}H-NOESY spectrum of Bromo-2-^{13}C acetic acid is also shown in Fig.6. Only Diagonal peak is observable while off-diagonal peaks appears as the relaxation between the magnetization modes become active during the mixing time. The intensity of the J-cross peak can be traced theoretically provided that the spectral density of the system is known.

The another independent experimental data set comes from the ^{1}H-^{13}C HOESY pulse sequence. The only observable spin magnetization is the carbon-proton two spin order
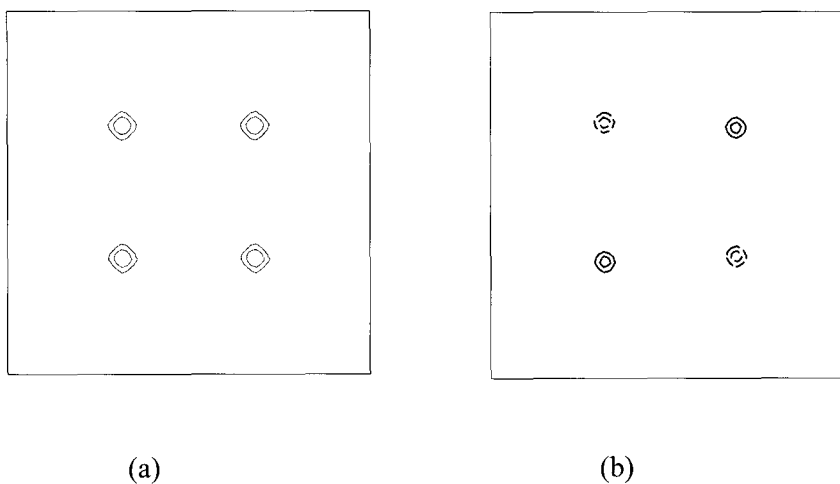
(a)   (b)

Fig. 5.   The ¹H-NOESY 2D-multiplet from transfer mode (a) Eq.(5a) and (b) Eq.(6c)
          Dashed contour denotes the negative peak
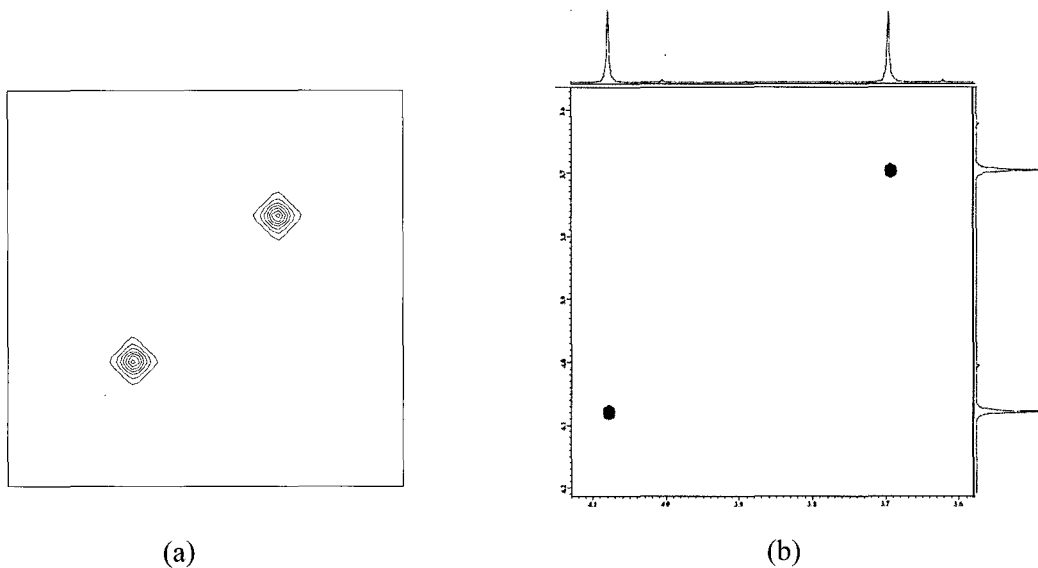

(a)   (b)

Fig. 6. The ¹H-NOESY 2D-multiplet of CH_2 system at zero mixing (a) simulated and (b)
        experimental spectrum of Bromoacetic 2-^{13}C acid (JEOL 400MHz)

$\{I_z^C(I_z^H + I_z^{H'})\}$ which gives the phase twisted 2-dimensional multiplet with equal intensity

at $(\omega_H, \omega_C \pm J)$, while zero intensity at (ω_H, ω_C). The HOESY multiplet obtained with $\tau_m = 0$

in absolute mode is given in Fig. 7. The carbon magnetization that has not been frequency

labeled in t_1 dimension gives only axial-like peak, which can be suppressed by phase cycling and does not consider any more.

THE TRANSFER MATRIX AND THE RELAXATION MATRIX

The general relaxation equation can be written as

$$\frac{d\sigma_i(t)}{dt} = \sum_j R_{ij}[\sigma_j(t) - \sigma_j(\infty)] \quad \text{or} \quad \frac{d\sigma}{dt} = R[\sigma - \sigma(\infty)] \tag{10}$$

where R represents the relaxation matrix in a given magnetization mode basis. For AX_2 spin system, the relaxation matrix, R, with equations of motion have been treated in various ways reflecting diverse concept in the definitions of the magnetization modes.[8-10] The formal solution of Eq(10) is
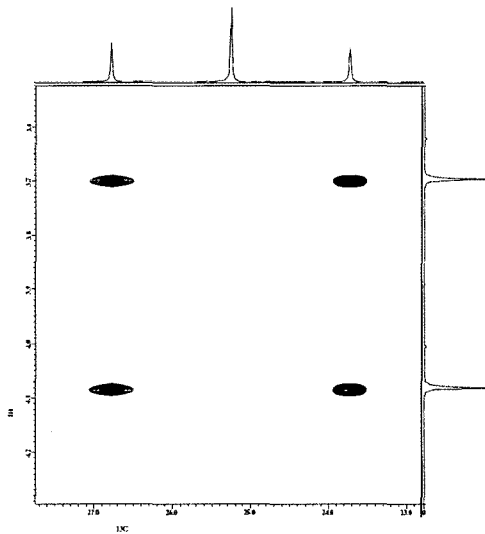

Fig. 7. The ^1H-^{13}C HOESY 2D-multiplet of CH_2 system at zero mixing of Bromoacetic 2-^{13}C-acid (JEOL 400MHz)

$$\sigma(t) = \exp(R\tau_m)\,\Delta\sigma(0) \;=\; A(\tau_m)\,\Delta\sigma(0) \tag{11}$$

The matrix $A(\tau_m)$, the transfer matrix, contains the information about the various relaxation process that occur the mixing time and unique transfer amplitude of the given molecular system. The transfer matrix can be rewritten by eigenvector and eigenvalue of the Redfield relaxation matrix. That is

$$A = U\exp(U^{-1}RU\tau_m)U^{-1} \quad \text{or} \quad R = \frac{1}{\tau_m}U\ln[U^{-1}AU]\,U^{-1} \tag{12}$$

Since the relaxation matrix is real and symmetric the transfer matrix is also symmetric and their elements are obtained from the experimental 2-D peak intensity ratio at mixing time zero and time t.

$$A(\tau_m = t)_{ij} = \alpha_{ij}(\tau_m = t)/\alpha_{ij}(0) \tag{13}$$

where the α_{ij} is considered the coefficient of the multiplet of the peak intensity constituent the transfer modes. The intensity ratio of the element of the two dimensional NOESY spectra with $\tau_m = 0$ to $\tau_m = t$ gives the transfer matrix, A, and relaxation matrix can be constructed from the Eq.(13) with applying the projection operator technique to disentangle the multiplets into respective components. Here we constructed the transfer
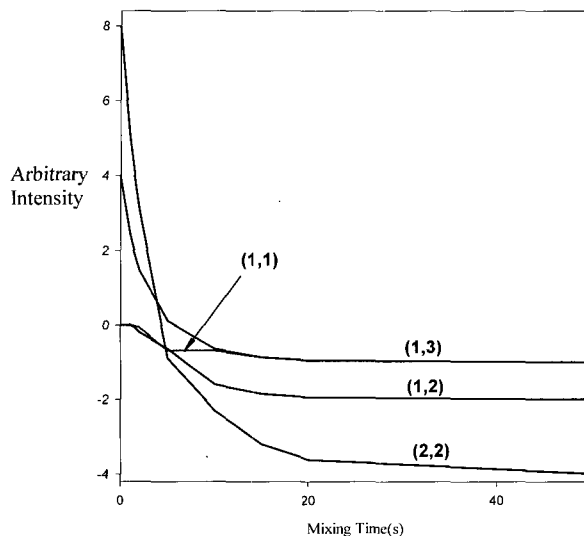
Fig. 8. Theoretical intensity of ^{13}C NOESY multiplet of n-undecane as a function of mixing time. (1,1),(1,2),(1,3) denote the 2D multiplet component taken in the order upper left, middle, to right, respectively. (2,2) denotes the center component.

matrix from the known spectral densities[13] of n-Undecane-5-^{13}C and the 2D multiplet of ^{13}C NOESY spectrum theoretically, which is shown in Fig. 8. It can be seen from that curve that the diagonal peaks gradually decrease as the off-diagonal peak arise. As the mixing time goes far enough to reach the equilibrium state the 1:2:1 J-coupled intensity pattern has apparently obtained.

CONCLUSION

In this paper, general transfer mode of heteronuclear CH_2 spin system have been discussed. J-coupled multiplets of 2D-NOESY pulse sequence are simulated based on the dipolar relaxation with symmetry conserved pathway, which is experimentally confirmed with small molecules, n-Undecane as well as Bromoacetic acid.   With previously reported

auto- and cross-correlation spectral densities the 2D multiplet components as a function of mixing time have been theoretically reproduced. Although the molecular parameter extracted by the projection operator technique needs the precise determination of the peak intensity of phase sensitive NOESY spectrum, it deserved the useful method complementary to the 1-dimensional coupled relaxation experiment in that this new approach only utilizes the simple pulse sequence with time saving. The practical extension to the more complex heteronuclear coupled spin system is being underway.

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