

Spectral editing with 2D E-HMQC NMR spectroscopy for CD_n groups: A theoretical study

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In order to get the simplified spectra for separation of carbonyl groups, the spectral editing of NMR signals has become a useful technique for complex molecules. E-HMQC is a ^1H -dedected, edited-pulse angle and two-dimensional NMR experiment which allows the selective detection of CH , CH_2 and CH_3 signals. The product operator theory is widely used for analytical description of the spectral editing NMR experiments for weakly coupled spin systems. In the present study, analytical descriptions of the 2D ^2H -dedected E-HMQC NMR experiment have been presented for weakly coupled IS_n ($I=1/2$; $S=1$; $n=1, 2, 3$) spin systems by using the product operator theory. By using obtained FID values, theoretical discussion and experimental suggestions for sub-spectral editing of CD , CD_2 and CD_3 groups have been made.

Keywords: NMR, E-HMQC, Product operator theory, CD_n

1 Introduction

Editing of NMR signals into sub-signals provides useful structural information, especially distinguishing of protonated and deuterated carbonyl groups in complex molecules. These experiments can be classified into two sub-groups as ^{13}C - and ^1H -dedected NMR experiments. The well-known ^{13}C editing NMR experiments are DEPT (Refs 1,2) and SEMUT (Refs 3,4). The edited-pulse ^1H NMR experiments such as DEPT-HMQC (Refs 5,6), E-HMQC (Ref. 7) and MAXY (Ref. 8) are more useful than ^{13}C -dedected NMR experiments because of high natural abundance of ^1H nucleus. Editing and selective detection methods for ^1H NMR spectroscopy have been reviewed⁹. The basic HMQC is a two-dimensional NMR experiment which provides correlation between scalar coupled heteronuclei^{10,11}. Modified forms of this experiment such as DEPT-HMQC and E-HMQC have been developed in order to edit the signals. The DEPT-HMQC pulse sequence has been designed by Kessler *et. al*⁵. to inverse detection of ^1H nuclei using DEPT for multiplicity editing of CH_n signals into sub-signals. Zhang and Wang⁷ have presented an Editable Heteronuclear Multiple-Correlation (E-HMQC) experiment which allows detecting ^1H nuclei for spectral editing of CH_n signals. The both (DEPT-HMQC and E-HMQC) experiments provide similar information and are called as two-dimensional, edited-pulse and ^1H -dedected NMR experiments. Liquid-state and solid-

state ^2H -dedected NMR experiments are used to investigate the molecular properties of deuterated molecules¹²⁻¹⁵. Therefore, ^2H -dedected version of E-HMQC experiment can be used in deuterated molecules.

It is well known that the product operator theory as a quantum mechanical method is widely used for analytical description of multi-pulse NMR experiments having mostly two spin- $1/2$ system or spin- $1/2$ and spin-1 system in liquids¹⁶⁻²⁸. A complete product operator theory for weakly coupled IS ($I=1/2$, $S=1$) spin system have been presented in our previous study²⁶. By using product operator theory in NMR experiments, new experimental suggestions can be made and also experimental results can be confirmed^{4,23}.

In the present study, by using product operator theory analytical descriptions of 2D ^2H -dedected E-HMQC experiment have been presented for weakly coupled IS_n ($I=1/2$; $S=1$; $n=1, 2, 3$) spin systems. For analytical description of the experiment, we have written a computer program in Mathematica which is very flexible for implementation and evolutions of the product operators under the Hamiltonians²⁹. Then, a theoretical discussion and experimental suggestions for sub-spectral editing of CD , CD_2 and CD_3 groups have been presented. To the best of our knowledge, this will be the first application of product operator theory to 2D ^2H -dedected E-HMQC NMR spectroscopy for weakly coupled IS_n ($I=1/2$; $S=1$; $n=1, 2, 3$) spin systems.

2 Theory

The product operator formalism is the expansion of the density matrix operator in terms of matrix representation of angular momentum operators for individual spins. For IS ($I=1/2, S=1$) spin system, four Cartesian spin angular momentum operators for $I=1/2$; E, I_x, I_y, I_z and nine Cartesian spin angular momentum operators for $S=1$; $E_S, S_x, S_y, S_z, S_x^2, (S_x, S_z)_+, (S_y, S_z)_+, (S_x, S_y)_+, (S_x^2 - S_y^2)$ can be easily found³⁰. So, $4 \times 9 = 36$ product operators are obtained with direct products of these angular momentum operators for IS ($I=1/2, S=1$) spin system. Depending on the pulse experiment, Cartesian spin operator $(S_x^2 - S_y^2)$ is separated into two spin operators as S_x^2 and S_y^2 . In this case, there exist 40 product operators.

Time dependency of the density matrix is given by²¹:

$$\sigma(t) = \exp(-iHt)\sigma(0)\exp(iHt) \quad \dots(1)$$

where H is the total Hamiltonian which consists of radio frequency (rf) pulse, chemical shift and spin-spin coupling Hamiltonians and $\sigma(0)$ is the density matrix at $t=0$. After employing the Hausdorff formula²¹:

$$\begin{aligned} \exp(-iHt)A\exp(iHt) &= A - (it)[H, A] \\ &+ \frac{(it)^2}{2!}[H, (H, A)] - \frac{(it)^3}{3!}[H, \{H, (H, A)\}] + \Lambda \quad \dots(2) \end{aligned}$$

evolutions of the product operators under the rf pulse, chemical shift and spin-spin coupling Hamiltonians can easily be obtained^{16,21,22}. The effect of x -axis rf pulse on some of Cartesian spin angular momentum operators for IS ($I=1/2, S=1$) spin system are given in following equations²⁶:

$$S_y \xrightarrow{H_{rf}t} S_y c_{2\theta} + S_z s_{2\theta} \quad \dots(3a)$$

$$S_z \xrightarrow{H_{rf}t} S_z c_{2\theta} - S_y s_{2\theta} \quad \dots(3b)$$

$$(S_x, S_y)_+ \xrightarrow{H_{rf}t} (S_x, S_y)_+ c_{2\theta} + (S_x, S_z)_+ s_{2\theta} \quad \dots(3c)$$

$$(S_x, S_z)_+ \xrightarrow{H_{rf}t} (S_x, S_z)_+ c_{2\theta} - (S_x, S_y)_+ s_{2\theta} \quad \dots(3d)$$

$$\begin{aligned} S_y^2 \xrightarrow{H_{rf}t} &\frac{1}{2}S_y^2(c_{2\theta} + 1) - \frac{1}{2}S_z^2(c_{2\theta} - 1) \\ &+ \frac{1}{2}(S_y, S_z)_+ s_{2\theta} \quad \dots(3e) \end{aligned}$$

where the rf pulse Hamiltonian for x -axes is $H_{rf} = \omega_{rf} S_x$, $\theta = \omega_{rf}t$, $c_{n\theta} = \cos(n\theta)$ and $s_{n\theta} = \sin(n\theta)$. The effect of the spin-spin coupling Hamiltonian on some of product operators in a weakly coupled IS ($I=1/2, S=1$) spin system is given as following equations²⁶:

$$I_x \xrightarrow{H_{rf}t} I_y S_z s_{2J} + I_x [1 + S_z^2(c_{2J} - 1)] \quad \dots(4a)$$

$$I_y \xrightarrow{H_{rf}t} -I_x S_z s_{2J} + I_y [1 + S_z^2(c_{2J} - 1)] \quad \dots(4b)$$

$$I_x S_z \xrightarrow{H_{rf}t} I_x S_z c_{2J} + I_y S_z^2 s_{2J} \quad \dots(4c)$$

$$I_y S_z \xrightarrow{H_{rf}t} I_y S_z c_{2J} - I_x S_z^2 s_{2J} \quad \dots(4d)$$

$$\begin{aligned} S_x^2 \xrightarrow{H_{rf}t} &\frac{1}{2}S_x^2(c_{2J} + 1) - \frac{1}{2}S_y^2(c_{2J} - 1) + I_z (S_y, S_x)_+ s_{2J} \\ &\dots(4e) \end{aligned}$$

$$\begin{aligned} I_z S_y^2 \xrightarrow{H_{rf}t} &\frac{1}{2}I_z S_y^2(c_{2J} + 1) - \frac{1}{2}I_z S_x^2(c_{2J} - 1) \\ &- \frac{1}{4}(S_y, S_x)_+ s_{2J} \quad \dots(4f) \end{aligned}$$

In the Eqs 4(a-f), $H_J = 2\pi J I_z S_z$ is the weak coupling Hamiltonian, $c_{nJ} = \cos(n\pi Jt)$ and $s_{nJ} = \sin(n\pi Jt)$. All evolutions under the rf pulse, spin-spin coupling and chemical shift Hamiltonians can be found elsewhere²⁶.

The product operators are the direct products of the spin angular momentum operators, *e.g.*, $I_x S_y$ is $I_x \theta S_z$. At any time during the experiment, the ensemble averaged expectation value of the spin angular momentum, *e.g.* for I_y , is:

$$M_y(t) \propto \langle I_y \rangle \equiv \text{Tr}[I_y \sigma(t)] \quad \dots(5)$$

where $\sigma(t)$ is the density matrix operator calculated from Eq. (1) at any time. As $\langle I_y \rangle$ is proportional to the magnitude of the y -magnetization, it represents the signal detected on y -axis. So, in order to estimate the free induction decay (FID) signal of a multiple-pulse NMR experiment, density matrix operator should be obtained at the end of the experiment.

3 Results and Discussion

For the product operator description of the 2D E-HMQC NMR experiment for CD_n groups, the pulse sequence is shown in Fig. 1, is used. The density matrix operator at each stage of the experiment is labeled with numbers and ^{13}C is treated as spin I and ^2H (D) as spin S . In the pulse sequence; Δ is the

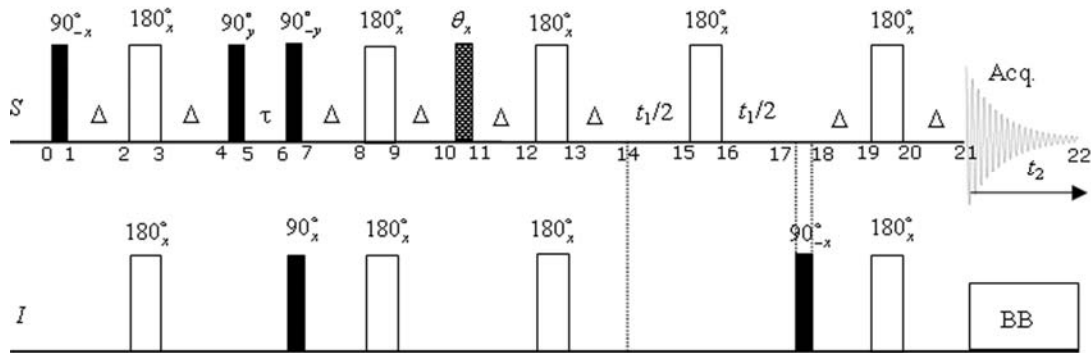


Fig 1 — Pulse sequence for the 2D ²H-detected E-HMQC experiment where Δ=1/(4J), BB: Broad Band for the decoupling⁷.

coupling evolution delay, τ delay is applied for recovery of magnetic field homogeneity, t₁ and t₂ delays are the chemical shift evolution period for I and S, respectively. Optimum value of Δ is 1/(4J_{IS}) for the 2D E-HMQC experiment. Starting from the density matrix operator at thermal equilibrium, one should apply the required Hamiltonians during the pulse sequence and obtain the density matrix operator at the end of the experiment. For multi-pulse NMR experiments and multi-spin systems, to follow these processes by hand becomes too difficult. In order to overcome this problem, a home made computer program written in Mathematica is used. Thus, the density matrix operators for every stage and at the end of the experiment are obtained for different spin systems such as IS, IS₂ and IS₃ (I=1/2, S=1).

For IS spin system, the density matrix at thermal equilibrium is σ₀∝S_z. The density matrices evolutions under Hamiltonians for some labeled point are obtained as follows:

$$\sigma_0 \xrightarrow{90_x(S)} S_y \xrightarrow{H_I \Delta (\Delta=1/4J)} -\sqrt{2} I_z S_x + \frac{1}{\sqrt{2}} S_y \equiv \sigma_2 \quad \dots(6)$$

$$\sigma_2 \xrightarrow{180_x(S)+180_x(I)} -\sqrt{2} I_z S_x - \frac{1}{\sqrt{2}} S_y \xrightarrow{H_I \Delta} 2 I_z S_x \xrightarrow{90_y(S)} -2 I_z S_z \quad \dots(7)$$

Applying the procedure, the following density matrices are obtained in steps 11, 17 and 22:

$$\sigma_{11} = -2 I_x (S_x, S_z)_+ c_\theta + 2 I_x (S_x, S_y)_+ s_\theta \quad \dots (8)$$

$$\sigma_{17} = 2 I_y S_x c_\theta c_I - 2 I_x (S_x, S_y)_+ s_\theta c_I - 2 I_x S_x c_\theta s_I - 2 I_y (S_x, S_y)_+ s_\theta s_I \quad \dots(9)$$

$$\sigma_{22} = S_y c_\theta c_I c_S - 2 I_x (S_x, S_y)_+ s_\theta c_I - 2 I_y (S_x, S_z)_+ c_\theta s_I + 2 I_z (S_x, S_y)_+ s_\theta s_I - S_x c_\theta c_I s_S \quad \dots(10)$$

In Eqs (8-10) and following equations, H_I=2πJ_{Iz}S_z, c_{nθ}=cos(nθ), s_{nθ}=sin(nθ), c_{nI}=cos(nΩ_It₁), s_{nI}=sin(nΩ_It₁), c_{nS}=cos(nΩ_St₂) and S_{nS}=sin(nΩ_St₂). In the last density matrix operator in Eq. (10), only the first term contributes to the signals since acquisition is taken along y–axes for spin S. Then, the magnetization along the y–axis is proportional to ∑_{i=1}ⁿ⟨S_{iy}⟩ and

$$M_y(t_1, t_2) \propto \sum_{i=1}^n \langle S_{iy} \rangle = \sum_{i=1}^n \text{Tr}(S_{iy} \sigma_{22}) \quad \dots(11)$$

Now, it is necessary to obtain the ∑_{i=1}ⁿ Tr(S_{iy}O) values of observable product operators indicated by O. For the IS_n (I=1/2, S=1; n=1, 2, 3) spin systems, ∑_{i=1}ⁿ Tr(S_{iy}O) values of observable product operators are calculated by using Mathematica and results are given in Table 1. Using Table 1 for the IS spin system:

$$M_y(t_1, t_2) \propto \langle S_y \rangle = \text{Tr}(S_y \sigma_{22}) = 4 c_\theta c_I c_S, \quad \dots (12)$$

is obtained.

For IS₂ spin system, the density matrix at thermal equilibrium is σ₀∝S_{1z}+S_{2z}. At the end of the experiment, following observable terms are obtained using the computer program:

$$\begin{aligned} \sigma_{22} = & \frac{1}{2} (2S_{1y} + 2S_{2y} - S_{1y}S_{2x}^2 - S_{1y}S_{2y}^2 - S_{1x}^2S_{2y}) \\ & - S_{1y}^2S_{2y})c_\theta c_I c_S + \frac{1}{2} (S_{1y}S_{2x}^2 + S_{1x}^2S_{2y} + S_{1y}S_{2y}^2 \\ & + S_{1y}^2S_{2y})c_{2\theta} c_I c_S + \frac{1}{2} (-S_{1y}S_{2x}^2 - S_{1x}^2S_{2y} + S_{1y}S_{2y}^2 \\ & + S_{1y}^2S_{2y})c_\theta c_I c_{2S} c_S + \frac{1}{2} (S_{1y}S_{2x}^2 + S_{1x}^2S_{2y} - S_{1y}S_{2y}^2 \\ & - S_{1y}^2S_{2y})c_{2\theta} c_\theta c_S c_{2S} \end{aligned} \quad \dots(13)$$

Table 1—Results of the $\sum_{i=1}^n \text{Tr}(S_{iy}O)$ calculations for some of the observable product operators for IS_n ($I=1/2, S=1; n=1, 2, 3$) spin systems ($j = x, y$ and $k = x, y$)

Spin system	Product operators (O)	$\sum_{i=1}^n \text{Tr}(S_{iy}O)$
IS	S_y	4
IS_2	$S_{1y} + S_{2y}$	24
	$S_{1y}S_{2j}^2 + S_{1j}^2S_{2y}$	16
	$S_{1y}S_{2j}^2 - S_{1j}^2S_{2y}$	0
IS_3	$S_{1y} + S_{2y} + S_{3y}$	108
	$S_{1y}S_{2j}^2 + S_{1y}S_{3j}^2 + S_{1j}^2S_{2y} + S_{2y}S_{3j}^2 + S_{2j}^2S_{3y} + S_{1j}^2S_{3y}$	144
	$(S_{1y}S_{2j}^2 + S_{1y}S_{3j}^2 + S_{2y}S_{3j}^2) - (S_{1j}^2S_{2y} + S_{1j}^2S_{3y} + S_{2j}^2S_{3y})$	0
	$S_{1y}S_{2j}^2S_{3k}^2 + S_{1j}^2S_{2y}S_{3k}^2 + S_{1j}^2S_{2k}^2S_{3y}$	48
	$(S_{1y}S_{2j}^2S_{3k}^2 + S_{1j}^2S_{2y}S_{3k}^2 + S_{1j}^2S_{2k}^2S_{3y}) - (S_{1y}S_{2j}^2S_{3k}^2 + S_{1j}^2S_{2y}S_{3k}^2 + S_{1j}^2S_{2k}^2S_{3y})$	0

Using trace values for the observable terms given in Table 1:

$$M_y(t_1, t_2) \propto \sum_{i=1}^2 \langle S_{iy} \rangle = \sum_{i=1}^2 \text{Tr}(S_{iy}\sigma_{22}) = 8c_\theta c_I c_S \dots (14)$$

$$+ 16c_{2\theta} c_\theta c_I c_S$$

is found.

For IS_3 spin system, applying the same procedure:

$$M_y(t_1, t_2) \propto \sum_{i=1}^3 \langle S_{iy} \rangle = \sum_{i=1}^3 \text{Tr}(S_{iy}\sigma_{22}) \dots (15)$$

$$2c_\theta c_I c_S + 48c_{2\theta} c_\theta c_I c_S + 48c_{2\theta}^2 c_\theta c_I c_S$$

is obtained.

The $\sum_{i=1}^n \text{Tr}(S_{iy}\sigma_{22})$ values obtained for IS, IS_2 and IS_3 spin systems represent the FID signals of the 2D 2H -dedected E-HMQC experiment for CD, CD₂ and CD₃ groups, respectively. These $\sum_{i=1}^n \text{Tr}(S_{iy}\sigma_{22})$ values for IS_n ($I=1/2; S=1; n=1, 2, 3$) spin systems can be generalized as following:

$$\sum_{i=1}^n \text{Tr}(S_{iy}\sigma_{22})(CD_n) = 4n(1 + 2c_{2\theta})^{n-1} c_\theta c_I c_S \dots (16)$$

However, the $\sum_{i=1}^n \text{Tr}(S_{iy}\sigma_{22})$ values can be normalized by multiplication with $6/[4n\text{Tr}(E)]$. Here E is the unity product operator for the corresponding spin system. Then, the normalized FID values became as following:

$$\text{Tr}(S_y\sigma_{22})(CD) = c_\theta c_I c_S \dots (17)$$

$$\sum_{i=1}^2 \text{Tr}(S_{iy}\sigma_{22})(CD_2) = \frac{1}{3}(1 + 2c_{2\theta})c_\theta c_I c_S \dots (18)$$

$$\sum_{i=1}^3 \text{Tr}(S_{iy}\sigma_{22})(CD_3) = \frac{1}{9}(1 + 2c_{2\theta})^2 c_\theta c_I c_S \dots (19)$$

These normalized $\sum_{i=1}^n \text{Tr}(S_{iy}\sigma_{22})$ values can be also written in a generalized form as:

$$\sum_{i=1}^n \text{Tr}(S_{iy}\sigma_{22})(CD_n) = \frac{1}{3^{n-1}}(1 + 2c_{2\theta})^{n-1} c_\theta c_I c_S \dots (20)$$

The plots of these FID functions are shown in Fig. 2. As seen in Fig. 2, the relative signal intensities of CD, CD₂ and CD₃ groups vary as functions of θ .

In 2D the 2H -dedected E-HMQC experiment, as the observed nuclei is 2H , Eq. (20) is multiplied by n for the real relative signal intensities of CD_{*n*} groups. Then, the obtained real relative signal intensities for several angles are given in Table 2. As seen in Table 2 and in Figure 2, when the experiment is performed for the angle of 60°, only CD groups will be observed as positive signals. For the angle of 75°, CD and CD₃ groups will give positive signals and CD₂ groups will give negative signals. By comparing the signs and the relative intensities of signals for the angles of 60° and 75°, one can easily identify all CD, CD₂ and CD₃ groups from each other. Therefore, 2D

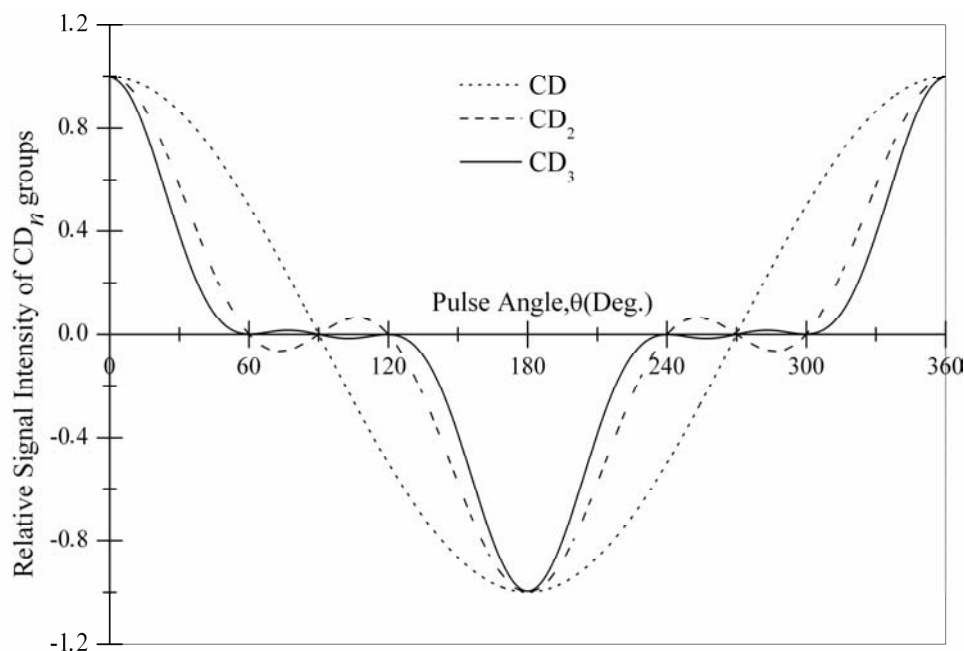


Fig. 2 — Plots of relative signal intensity of the 2D ^2H -dedected E-HMQC experiment for CD_n groups as functions of the editing pulse angle, θ

Table 2—Real relative signal intensities of the ^2H -dedected E-HMQC experiment of CD_n groups for several pulse angles of θ

Spin System	$\theta=60^\circ$	$\theta=75^\circ$	$\theta=180^\circ$
$IS(\text{CD})$	0.5	0.26	-1
$IS_2(\text{CD}_2)$	0	-0.19	-2
$IS_3(\text{CD}_3)$	0	0.14	-3

^2H -dedected E-HMQC experiment can be used for the sub-spectral editing of CD, CD_2 and CD_3 groups. In deuterium labeling, it is of interest to determine whether the methyl-group is transferred as a whole leading to $^{13}\text{CD}_3$ - containing compounds or leading to $^{13}\text{CD}_2\text{H}$ - or $^{13}\text{CDH}_2$ - containing compounds^{13,14}. So, 2D ^2H -dedected E-HMQC experiment of CD_n groups can be also used for this purpose.

4 Conclusions

Multi-pulse NMR experiments including editing pulse angles have become a powerful technique for selective detection of protonated and deuterated carbonyl groups in complex molecules. The product operator theory is a useful technique for the analytical description of multi-pulse and editing pulse NMR experiments for weakly coupled spin systems¹⁶⁻²⁸. In this study, by using product operator theory, an analytical description of 2D ^2H -dedected E-HMQC NMR experiment is presented for IS_n ($I=1/2$; $S=1$;

$n=1, 2, 3$) spin systems. Then, it is shown this experiment can be easily used for the identification of CD, CD_2 and CD_3 groups from each other.

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