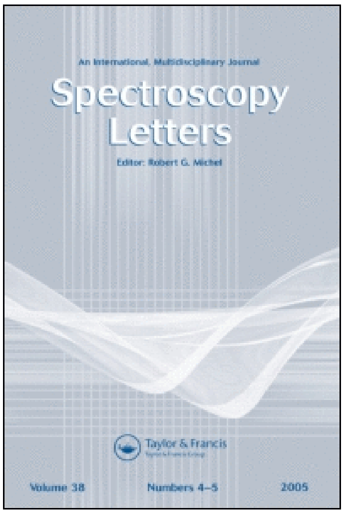

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A Product Operator Description of 2D-J Resolved NMR Spectroscopy for IS_n Spin System (I=1/2, S=1)

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A PRODUCT OPERATOR DESCRIPTION OF 2D-J RESOLVED NMR SPECTROSCOPY FOR IS_n SPIN SYSTEM (I=1/2, S=1)

Key words: Product operator, NMR, J resolved, IS_n system.

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ABSTRACT

Using the product operator technique, an analytical description of heteronuclear 2D-J resolved NMR spectroscopy for a weakly coupled IS_n (I=1/2, S=1, n=1,2,3) spin system is presented. As a pulse sequence, the most commonly used one, the gated decoupler sequence, is used. The obtained analytical results were found to be in good agreement with the experimental ones.

INTRODUCTION

There exists a large number of homo and heteronuclear multi-pulse 2D-NMR experiments which are widely used for molecular structure determination and other purposes [e.g.,1–3]. In order to describe multi–pulse 2D NMR experiments, a quantum mechanical formalism has to be employed. Density matrix formalism has a universal applicability and all other quantum mechanical formalisms were driven from it. In density matrix formalism, operators are represented by the matrices. For example, for N spin-1/2 system, the dimension of the matrices is $2^N \times 2^N$. Therefore to deal with these matrices is cumbersome. On the other hand, in product operator technique, the spin operators themselves and their direct products are used and 2D–NMR experiments can easily be understood. The detailed discussion on product operator formalism and its usage in some 2D NMR experiments can be found elsewhere [4–10].

In one dimensional NMR, as the multiplets from different chemically shifted nuclei overlap, spectral assignments become too difficult. In order to resolve the chemical shift and spin–spin coupling parameters along the two different axes, 2D J resolved spectroscopy is widely used. For example, an experimental result of heteronuclear 2D–J resolved NMR spectroscopy for CD_n (n=1,2,3), in a mixture of toluene, α–[D_1] toluene, α–[D_2] toluene and α–[D_3] toluene sample, is presented by Schmitt et al. [11].

In this study, by using product operator technique, an analytical description of heteronuclear 2D–J resolved NMR spectroscopy for a weakly coupled IS_n spin system (I=1/2, S=1) is given. In section 2, the product operator formalism theory is briefly introduced. The application of product operator technique to heteronuclear 2D–J resolved NMR spectroscopy for IS_n spin system is presented in section 3.

THEORY

Time dependency of the density matrix is governed by Liouville equation;

$$\frac{d\sigma}{dt} = \frac{i}{\hbar}[\sigma, H]. \tag{1}$$

Where $[\sigma, H]$ is the commutator of the density matrix, σ, and the Hamiltonian, H. We neglected the presence of relaxation during the pulse experiment as usually done. Thus, in case of H is time independent, the solution of the Eq.(1) is

$$\sigma(t) = \exp(-iHt)\sigma(0)\exp(iHt). \tag{2}$$

Where H is the total Hamiltonian which consists of radio frequency (r.f.) pulse, chemical shift and spin-spin coupling Hamiltonians and $\sigma(0)$ is the density matrix at t=0. After employing the Hausdorff formula [6]

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

the r.f pulse, chemical shift and spin–spin coupling evolution of product operators can easily be obtained. The effect of the r.f. pulse Hamiltonian on the spin operators is easily obtained:

$$I_x \xrightarrow{Ht} I_x, \tag{4a}$$

$$I_y \xrightarrow{Ht} I_y cos\theta + I_z sin\theta, \tag{4b}$$

$$I_z \xrightarrow{Ht} I_z cos\theta - I_y sin\theta. \tag{4c}$$

Where $H= \omega_l I_x$, $\theta=\omega_l t$ and ω_l is the radio frequency. Chemical shift Hamiltonian evolution of the spin operators can be found:

$$I_x \xrightarrow{Ht} I_x cos\Omega t + I_y sin\Omega t, \tag{5a}$$

$$I_y \xrightarrow{Ht} I_y cos\Omega t - I_x sin\Omega t, \tag{5b}$$

$$I_z \xrightarrow{Ht} I_z. \tag{5c}$$

Where $H=\Omega I_z$. The action of the spin–spin coupling Hamiltonian on the product operators in IS spin system (I=1/2, S=1) yields

$$I_x \xrightarrow{Ht} I_y S_z s_J + I_x(1+S_z^2(c_J-1)), \tag{6a}$$

$$I_y \xrightarrow{Ht} -I_x S_z s_J + I_y(1+S_z^2(c_J-1)), \tag{6b}$$

$$I_x S_z \xrightarrow{Ht} I_x S_z c_J + I_y S_z^2 s_J, \tag{6c}$$

$$I_y S_z \xrightarrow{Ht} I_y S_z c_J - I_x S_z^2 s_J, \tag{6d}$$

$$I_x S_z^2 \xrightarrow{Ht} I_x S_z^2 c_J + I_y S_z s_J, \tag{6e}$$

$$I_y S_z^2 \xrightarrow{Ht} I_y S_z^2 c_J - I_x S_z s_J. \tag{6f}$$

Where, $H = 2\pi J I_z S_z$ is the weak coupling Hamiltonian, $s_J = sin2\pi Jt$, $c_J = cos2\pi Jt$ and the product operators are the direct products of spin angular momentum operators, e.g. $I_y S_z$ is $I_y \otimes S_z$. At any time during the experiment, the ensemble averaged expectation value of the spin angular momentum, e.g. for I_y, is

$$\langle I_y \rangle = Tr(I_y \sigma(t)). \tag{7}$$

Where $\sigma(t)$ is the density matrix operator calculated from Eq.(2) 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. In the following section, the product operator technique is applied to heteronuclear 2D–J resolved NMR spectroscopy for IS_n spin system (I=1/2, S=1, n=1,2,3).

APPLICATION TO 2D-J RESOLVED NMR SPECTROSCOPY

In description of the multi–pulse NMR experiment by product operator technique, it is necessary to obtain the $Tr(I_y O)$ values of observable product operators indicated by O. For IS_n spin system (I=1/2, S=1, n=1,2,3), $Tr(I_y O)$ values for some of the observable product operators were calculated by a computer program developed in this study and the results are given in Table 1.

In the following, the gated decoupler pulse sequence (illustrated in Fig.1) is used for an analytical description of heteronuclear 2D–J resolved NMR spectroscopy for IS_n spin system (I=1/2, S=1). As seen in Fig.1, the density matrix operator at each stage of the experiment is labeled with numbers. σ_1 is the density matrix operator at thermal equilibrium and

$$\sigma_1 = I_z . \tag{8}$$

IS Spin System:

For IS spin system, the pulse sequence in Fig.1 obviously leads to the following density matrices for each labeled point:

$$\sigma_2 = -I_y, \ \sigma_3 = -I_y \text{ and } \sigma_4 = I_y. \tag{9}$$

Here we assumed that during t_1, relaxation and evolution under chemical shift do

TABLE 1

The results of the *$Tr(I_yO)$* calculations for some of the observable product operators in IS_n spin system (I=1/2, S=1, n=1,2,3).

Spin System	Product Operator (O)	$Tr(I_yO)$
IS	I_y	3/2
	$I_yS_z^2$	1
IS_2	I_y	9/2
	$I_y(S_{1z}^2+S_{2z}^2)$	6
	$I_yS_{1z}^2S_{2z}^2$	2
IS_3	I_y	27/2
	$I_y(S_{1z}^2+S_{2z}^2+S_{3z}^2)$	27
	$I_y(S_{1z}^2S_{2z}^2+S_{1z}^2S_{3z}^2+S_{2z}^2S_{3z}^2)$	18
	$I_y\,S_{1z}^2S_{2z}^2S_{3z}^2$	4

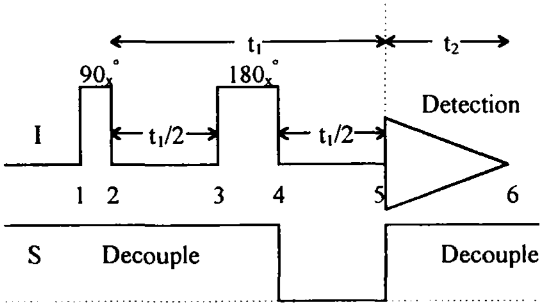

FIG. 1. The gated decoupler pulse sequence for heteronuclear 2D–J resolved NMR spectroscopy.

not take place. Spin–spin coupling obviously exist only during the second half of t_1 and therefore,

$$\sigma_5 = -I_x S_z s_J + I_y(1 + S_z^2(c_J - 1)). \qquad (10)$$

Where $s_J = \sin \pi J t_1$, $c_J = \cos \pi J t_1$. Furthermore, under the chemical shift evolution during t_2, the density matrix becomes

$$\sigma_6 = -(I_x c_I + I_y s_I) S_z s_J + (I_y c_I - I_x s_I) + (I_y c_I - I_x s_I) S_z^2 (c_J - 1). \qquad (11)$$

In this and in the following equations, $c_I = \cos \Omega_I t_2$ and $s_I = \sin \Omega_I t_2$. Here only observable I_y and $I_y S_z^2$ product operator terms contribute to the signal on y axis detection. As a result, σ_6 in Eq.(11) simplifies to:

$$\sigma_6 = I_y c_I + I_y S_z^2 c_I (c_J - 1). \qquad (12)$$

In the case of on y axis detection, magnetization along y axis is proportional to $\langle I_y \rangle$ and

$$M_y(t_1, t_2) \alpha \langle I_y \rangle = Tr(I_y \sigma_6). \qquad (13)$$

Then, using Table 1, we obtained

$$\langle I_y \rangle = Tr(I_y I_y) c_I + Tr(I_y I_y S_z^2) c_I (c_J - 1)$$

$$= \frac{1}{2} c_I + c_I c_J . \qquad (14)$$

In this equation, the first term represents the chemical shift on F_2 axis. The second term shows that the spin–spin coupling information appears on F_1 axis and represents two separate coherence with phases $\Omega_I t_2 \pm \pi J t_1$ and half of the amplitude in each component. Therefore, this gives a triplet of signals at $(J/2, \Omega_I)$, (Ω_I) and $(-J/2, \Omega_I)$ with an intensity distribution of (1,1,1) and since the gated decoupler pulse sequence is used, spin–spin coupling in F_1 dimension is scaled by a factor of 0.5.

IS_2 Spin System:

By using the same pulse sequence for IS_2 spin system, we obtain

$$\sigma_4 = I_y, \qquad (15)$$

$$\sigma_5 = -I_y S_{1z} S_{2z} s_J^2 - I_x (S_{1z} + S_{2z}) s_J - I_x (S_{1z} S_{2z}^2 + S_{1z}^2 S_{2z})(c_J - 1) s_J + I_y + I_y (S_{1z}^2 + S_{2z}^2)(c_J - 1)$$
$$+ I_y S_{1z}^2 S_{2z}^2 (c_J - 1)^2 \qquad (16)$$

and

$$\sigma_6 = I_y c_I + I_y (S_{1z}^2 + S_{2z}^2) c_I (c_J - 1) + I_y S_{1z}^2 S_{2z}^2 c_I (c_J - 1)^2. \qquad (17)$$

Then,

$$Tr(I_y\sigma_6)=\frac{3}{2}\,c_I+2c_Jc_I+c_{2J}c_I \tag{18}$$

is obtained. Here $c_{2J}=cos2\pi Jt_1$. In a similar manner to IS system, Eq.(18) represents the signals at (J,Ω_I), $(J/2,\Omega_I)$, (Ω_I), $(-J/2,\Omega_I)$, and $(-J,\Omega_I)$ with an intensity distribution of (1,2,3,2,1).

<u>IS$_3$ Spin System:</u>

Applying the same procedure, we obtain

$$\sigma_6=I_yc_I+I_y(S_{1z}^2+S_{2z}^2+S_{3z}^2)c_I(c_J-1)+I_y(S_{1z}^2S_{2z}^2+S_{1z}^2S_{3z}^2+S_{2z}^2S_{3z}^2)c_I(c_J-1)^2$$
$$+I_yS_{1z}^2S_{2z}^2S_{3z}^2c_I(c_J-1)^3 \tag{19}$$

and

$$Tr(I_y\sigma_6)=\frac{7}{2}\,c_I+6c_Ic_J+3c_Ic_{2J}+c_Ic_{3J}\,. \tag{20}$$

In Eq.(20) $c_{3J}=cos3\pi Jt_1$ and as a result this equation represents the signals at $(3J/2,\Omega_I)$, (J,Ω_I), $(J/2,\Omega_I)$, (Ω_I), $(-J/2,\Omega_I)$, $(-J,\Omega_I)$ and $(-3J/2,\Omega_I)$ with intensities of (1,3,6,7,6,3,1).

One dimensional ^{13}C NMR spectrum and 2D–J resolved ^{13}C NMR spectroscopy of a mixture of toluene, α–[D$_1$] toluene, α–[D$_2$] toluene and α–[D$_3$] toluene sample were presented elsewhere [11]. In one dimensional spectrum, it is too difficult to assign the multiplets but in 2D–J resolved spectrum, chemical shift and spin–spin coupling information are well separated into two axes. For $IS_n(CD_n)$ spin system, analytical results obtained here are consistent with the experimental results of Schmitt et al. [11].

As a conclusion, in this study an application of product operator description to 2D–J resolved NMR spectroscopy for IS_n (I=1/2, S=1, n=1,2,3) spin system is presented. Obtained analytical results are compared with the experimental ones and found to be in good agreement.

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