

A Product Operator Formalism of 3D J-Resolved NMR Spectroscopy for $IS_nK_m(I = 1/2, S = 1/2, K = 1/2)$ Spin System

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Abstract

Product operator formalism is widely used for analytical description of multiple-pulse NMR experiments for weakly coupled spin systems. 3D J-resolved NMR spectroscopy is widely used in order to resolve the chemical shift along one axis and spin-spin coupling parameters along the two other axis. In this study, product operator theory is used for analytical description of heteronuclear 3D J-resolved NMR spectroscopy for the $IS_nK_m(I = 1/2, S = 1/2, K = 1/2; n = 1, 2, m = 1, 2, 3)$ spin system.

Key Words: Product operator, 3D J-Resolved NMR spectroscopy.

1. Introduction

There exists a large number of homo and heteronuclear multi-pulse 1D, 2D and 3D NMR experiments. For the analytical description of these multi-pulse NMR experiments product operator formalism is widely used [1-7]. In this formalism, the spin operators themselves and their direct products, called product operators, are used. 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 different axis, 2D and 3D J-resolved NMR spectroscopies are widely used [8,9]. In 3D J-resolved NMR spectroscopy, the chemical shift is resolved along the one axis and spin-spin coupling parameters along the two different axis. The product operator description of heteronuclear 2D J-resolved NMR and 2D DEPT J-resolved NMR spectroscopies for the weakly coupled $IS_n(I = 1/2, S = 1/2 \text{ and } 1)$ spin systems has been reported elsewhere [10-13]. In this study, by using the product operator theory, an ana-

lytical description of heteronuclear 3D J-resolved NMR spectroscopy for a weakly coupled IS_nK_m ($I = 1/2, S = 1/2, K = 1/2; n = 1, 2, m = 1, 2, 3$) spin system is presented. This will probably be the first application of product operator theory to 3D J-resolved NMR spectroscopy for this system.

2. Theory

The density operator is expressed as a linear combination of base operators (B_s):

$$\sigma(t) = \sum_s b_s(t) B_s. \quad (1)$$

For a spin system a set of base operators can be obtained by [1]

$$B_s = 2^{(q-1)} \prod_{k=1}^N (I_{kv})^{a_{sk}}. \quad (2)$$

Here, N is the total number of spins in the spin system under consideration, k is an index for the spin, ν represents x, y or z axis and q ($0 \leq q \leq N$) is the number of single spin operators in the product. For q nuclei $a_{sk} = 1$ and for the $N - q$ remaining nuclei $a_{sk} = 0$. The complete base set, for a system with N spins $1/2$, consists of 4^N product operators. For ISK ($I = 1/2, S = 1/2, K = 1/2$) spin system there exists 64 product operators such as $\frac{1}{2}E, I_x, S_y, K_z, 2I_xS_y, 4I_xS_yK_z$.

Time dependency of the density matrix is given by [6,7]

$$\sigma(t) = \exp(-iHt)\sigma(0)\exp(iHt), \quad (3)$$

where H is the total Hamiltonian which consists of a 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 [6,7]

$$\begin{aligned} \exp(-iHt)A\exp(iHt) &= A - (it)[H, A] + \frac{(it)^2}{2!}[H, [H, A]] \\ &\quad - \frac{(it)^3}{3!}[H, [H, [H, A]]] + \dots, \end{aligned} \quad (4)$$

the r.f pulse, chemical shift and spin-spin coupling evolution of product operators can easily be obtained [1,6,7]. The details on the evolution of product operators under these Hamiltonians can be found elsewhere [1,6,7,10]. At any time during the experiment, the ensemble averaged expectation value of the spin angular momentum, e.g. for I_y is

$$\langle I_y \rangle = \text{Tr}(I_y(t)), \quad (5)$$

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 FID signal of a multiple-pulse NMR experiment, a density matrix operator should be obtained at the end of the experiment.

3. Results and Discussion

In this study, for the analytical description of 3D J-resolved NMR spectroscopy of IS_nK_m ($I = 1/2, S = 1/2, K = 1/2; n = 1, 2, m = 1, 2, 3$) spin system by using product operator theory the pulse sequence illustrated in Figure 1 is used. As seen in Figure 1, the density matrix operator at each stage of the experiment is labeled with numbers.

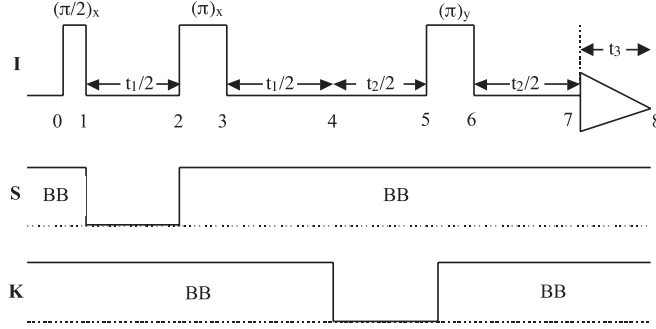


Figure 1. The gated decoupler pulse sequence for heteronuclear 3D J-Resolved NMR spectroscopy. There exist spin-spin couplings between I and S spins during the first half of t_1 and between I and K spins during the first half of t_2 . BB: Broadband decoupling.

For ISK spin system $\sigma_0 = I_z$ is the density matrix operator at thermal equilibrium and the pulse sequence in Figure 1 obviously leads to the following density matrices for each labeled point:

$$\sigma_1 = -I_y, \sigma_2 = -I_y C_J \quad (6)$$

$$\sigma_3 = \sigma_4 = I_y C_J \quad (7)$$

and

$$\sigma_5 = \sigma_6 = \sigma_7 = I_y C_J C'_J. \quad (8)$$

In the pulse sequence, it is assumed that during t_1 and t_2 , relaxation and evolution under chemical shift do not take place. Spin-spin couplings obviously exist during the first half of t_1 and also during the first half of t_2 . Under the chemical shift evolution during t_3 , the density matrix becomes

$$\sigma_8 = I_y C_J C'_J C_I. \quad (9)$$

Here and in the following equations $C_{n,J} = \cos n\pi J \frac{t_1}{2}$, $C'_{n,J} = \cos n\pi J' \frac{t_2}{2}$ and $C_I = \cos \Omega_I t_3$, where J and J' are the spin-spin coupling parameters between I and S spins;

and I and K spins, respectively. In density matrix operators only observable I_y product operator terms are kept, as they are the only ones that contribute to the signal on y axis detection. Then, magnetization along y axis is proportional to $\langle I_y \rangle$ and

$$M_y(t_1, t_2, t_3)\alpha\langle I_y \rangle = Tr(I_y\sigma_8). \quad (10)$$

Now, it is necessary to obtain the $Tr(I_yO)$ values of observable product operators indicated by O . For IS_nK_m spin system ($I = 1/2, S = 1/2, K = 1/2; n = 1, 2, m = 1, 2, 3$), $Tr(I_yO)$ values were calculated by a computer program and the results are given in Table 1.

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

Spin System	Product operator (O)	$Tr(I_yO)$
ISK	I_y	1
ISK_2	I_y	2
ISK_3	I_y	4
IS_2K_2	I_y	4

By using the Table 1 for the $Tr(I_yI_y)$ value of ISK spin system,

$$\begin{aligned} \langle I_y \rangle &= Tr(I_yI_y)C_JC'_JC_I \\ &= \frac{1}{4} \left[\cos(\Omega_I t_3 + \frac{\pi J' t_2}{2} + \frac{\pi J t_1}{2}) + \cos(\Omega_I t_3 + \frac{\pi J' t_2}{2} - \frac{\pi J t_1}{2}) \right. \\ &\quad \left. + \cos(\Omega_I t_3 - \frac{\pi J' t_2}{2} + \frac{\pi J t_1}{2}) + \cos(\Omega_I t_3 - \frac{\pi J' t_2}{2} - \frac{\pi J t_1}{2}) \right] \end{aligned} \quad (11)$$

is obtained. This equation represents the FID signals of 3D J-resolved NMR spectroscopy for ISK spin system. These are the four signals at $(\frac{J}{4}, \frac{J'}{4}, \Omega_I), (-\frac{J}{4}, \frac{J'}{4}, \Omega_I), (\frac{J}{4}, -\frac{J'}{4}, \Omega_I), (-\frac{J}{4}, -\frac{J'}{4}, \Omega_I)$ with an intensity distribution of (1,1,1,1). In these signal representations, the first, second and the third terms are the values along the F_1, F_2 and F_3 axis, respectively. Since the gated decoupler pulse sequence is used, spin-spin couplings in F_1 and F_2 dimensions are scaled by a factor of 0.5.

By using the same pulse sequence for ISK_2 spin system, we obtain

$$\sigma_1 = -I_y \quad (12)$$

$$\sigma_4 = I_y C_J \quad (13)$$

$$\sigma_7 = I_y C_J C_J'^2 \quad (14)$$

and

$$\sigma_8 = \frac{1}{2}I_y C_J C_I + \frac{1}{2}I_y C_J C'_{2J} C_I. \quad (15)$$

Then by using Table 1,

$$\begin{aligned} \langle I_y \rangle &= C_J C_I + C_J C'_{2J} C_I \\ &= \frac{1}{2} \left[\cos(\Omega_I t_3 + \frac{\pi J t_1}{2}) + \cos(\Omega_I t_3 - \frac{\pi J t_1}{2}) \right] + \frac{1}{4} \left[\cos(\Omega_I t_3 + \pi J' t_2 + \frac{\pi J t_1}{2}) \right. \\ &\quad \left. + \cos(\Omega_I t_3 + \pi J' t_2 - \frac{\pi J t_1}{2}) + \cos(\Omega_I t_3 - \pi J' t_2 + \frac{\pi J t_1}{2}) + \cos(\Omega_I t_3 - \pi J' t_2 - \frac{\pi J t_1}{2}) \right]. \end{aligned} \quad (16)$$

This equation represents the signals at $(\frac{J}{4}, \frac{J'}{2}, \Omega_I)$, $(-\frac{J}{4}, \frac{J'}{2}, \Omega_I)$, $(\frac{J}{4}, 0, \Omega_I)$, $(-\frac{J}{4}, 0, \Omega_I)$, $(\frac{J}{4}, -\frac{J'}{2}, \Omega_I)$, $(-\frac{J}{4}, -\frac{J'}{2}, \Omega_I)$ with an intensity distribution of (1,1,2,2,1,1)

For **ISK**₃ spin system, by applying the same procedure,

$$\sigma_8 = I_y C_J C_J^3 C_I \quad (17)$$

is obtained and

$$\begin{aligned} \langle I_y \rangle &= 3C_J C'_J C_I + C_J C'_{3J} C_I \\ &= \frac{3}{4} \left[\cos(\Omega_I t_3 + \frac{\pi J' t_2}{2} + \frac{\pi J t_1}{2}) + \cos(\Omega_I t_3 + \frac{\pi J' t_2}{2} - \frac{\pi J t_1}{2}) \right. \\ &\quad \left. + \cos(\Omega_I t_3 - \frac{\pi J' t_2}{2} + \frac{\pi J t_1}{2}) + \cos(\Omega_I t_3 - \frac{\pi J' t_2}{2} - \frac{\pi J t_1}{2}) \right] \\ &\quad + \frac{1}{4} \left[\cos(\Omega_I t_3 + \frac{3\pi J' t_2}{2} + \frac{\pi J t_1}{2}) + \cos(\Omega_I t_3 + \frac{3\pi J' t_2}{2} - \frac{\pi J t_1}{2}) \right. \\ &\quad \left. + \cos(\Omega_I t_3 - \frac{3\pi J' t_2}{2} + \frac{\pi J t_1}{2}) + \cos(\Omega_I t_3 - \frac{3\pi J' t_2}{2} - \frac{\pi J t_1}{2}) \right] \end{aligned} \quad (18)$$

is found. This equation represents the signals at $(\frac{J}{4}, \frac{3J'}{4}, \Omega_I)$, $(-\frac{J}{4}, \frac{3J'}{4}, \Omega_I)$, $(\frac{J}{4}, \frac{J'}{4}, \Omega_I)$, $(-\frac{J}{4}, \frac{J'}{4}, \Omega_I)$, $(\frac{J}{4}, -\frac{J'}{4}, \Omega_I)$, $(-\frac{J}{4}, -\frac{J'}{4}, \Omega_I)$, $(\frac{J}{4}, -\frac{3J'}{4}, \Omega_I)$, $(-\frac{J}{4}, -\frac{3J'}{4}, \Omega_I)$ with intensities of (1,1, 3,3,3,3, 1,1).

For **IS₂K₂** spin system, we obtain

$$\sigma_8 = \frac{I_y}{4}(1 + C_{2J} + C'_{2J} + C_{2J}C'_{2J})C_I. \quad (19)$$

Then,

$$\langle I_y \rangle = (1 + C_{2J} + C'_{2J} + C_{2J}C'_{2J})C_I$$

$$\begin{aligned}
&= \cos \Omega_I t_3 + \frac{1}{2} [\cos(\Omega_I t_3 + \pi J t_1) + \cos(\Omega_I t_3 - \pi J t_1)] \\
&+ \frac{1}{2} [\cos(\Omega_I t_3 + \pi J' t_2) + \cos(\Omega_I t_3 - \pi J' t_2)] + \frac{1}{4} [\cos(\Omega_I t_3 + \pi J' t_2 + \pi J t_1) \\
&+ \cos(\Omega_I t_3 + \pi J' t_2 - \pi J t_1) + \cos(\Omega_I t_3 - \pi J' t_2 + \pi J t_1) + \cos(\Omega_I t_3 - \pi J' t_2 - \pi J t_1)]
\end{aligned} \quad (20)$$

is found. As seen in this equation, there exist the signals at $(\frac{J}{2}, \frac{J'}{2}, \Omega_I)$, $(-\frac{J}{2}, \frac{J'}{2}, \Omega_I)$, $(\frac{J}{2}, 0, \Omega_I)$, $(-\frac{J}{2}, 0, \Omega_I)$, $(0, 0, \Omega_I)$, $(0, \frac{J'}{2}, \Omega_I)$, $(0, -\frac{J'}{2}, \Omega_I)$, $(\frac{J}{2}, -\frac{J'}{2}, \Omega_I)$, $(-\frac{J}{2}, -\frac{J'}{2}, \Omega_I)$ with intensities of (1,1, 2,2,4,2,2, 1,1).

As a conclusion, in this study an application of product operator description of 3D J-resolved NMR spectroscopy for IS_nK_m ($I = 1/2, S = 1/2, K = 1/2$) spin system is presented. Obtained analytical results are consistent with those of classical formalisms.

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