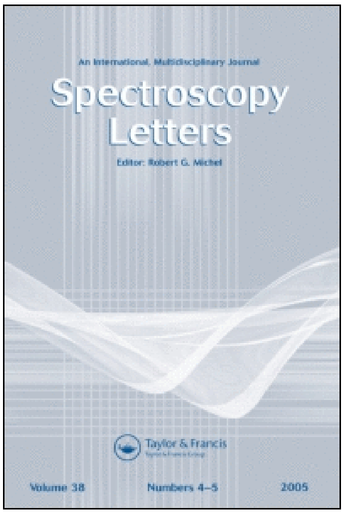

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A THEORETICAL INVESTIGATION OF 3D J-RESOLVED NMR SPECTROSCOPY FOR IS_nK_m ($I = 1/2$, $S = 1/2$ AND 1, $K = 1$) SPIN SYSTEMS

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ABSTRACT

The product operator formalism is widely used for an analytical description of multi-dimensional and multiple-pulse NMR experiments for the weakly coupled spin systems having spin$\frac{1}{2}$ and spin-1. Note that 3D J-resolved NMR spectroscopy is also widely used in order to resolve the chemical shift along the one axis and spin-spin coupling parameters along the two different axes. Therefore, the purpose of this study is to present first the analytical description of heteronuclear 3D J-resolved NMR spectroscopy for both IS_nK_m ($I = 1/2,\ S = 1/2,\ K = 1;\ n = 1, 2,\ m = 1{,}2$) and IS_nK_m($I = 1/2,\ S = 1,\ K = 1;\ n = 1{,}2,\ m = 1{,}2$) spin systems by using the product operator theory.

Key Words: Product operator; 3D J-resolved NMR; Spin-1.

INTRODUCTION

There exists a large number of homo and heteronuclear multiple–pulse 1D, 2D, and 3D NMR experiments. For the analytical description of these multiple–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 axes, 2D and 3D J-resolved NMR spectroscopy are widely used [e.g. 8,9]. In 3D J-resolved NMR spectroscopy, the chemical shift is resolved along one axis and spin-spin coupling parameters along two different axes. The product operator description of heteronuclear 2D J- resolved NMR and 2D DEPT J-resolved NMR spectroscopy for the weakly coupled IS_n ($I = 1/2$, $S = 1$) spin systems has been reported elsewhere [10,11]. In this study, by using the product operator theory, the analytical descriptions of heteronuclear 3D J-resolved NMR spectroscopy for the weakly coupled IS_nK_m ($I = 1/2$, $S = 1/2$, $K = 1$; $n = 1,2$, $m = 1,2$) and IS_nK_m ($I = 1/2$, $S = 1$, $K = 1$; $n = 1,2$, $m = 1,2$) spin systems are presented. To the best of our knowledge, this will be the first application of product operator theory to 3D J-resolved NMR spectroscopy for these spin systems.

THEORY

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

$$\sigma(t) = \exp(-iHt)\sigma(0)\exp(iHt). \tag{1}$$

Where H is the total Hamiltonian which consists of radio frequency (r.f.) pulse, chemical shift and spin-spin coupling Hamiltonians, and where $\sigma(0)$ is the density matrix at t = 0. After employing the Hausdorff formula (6,7)

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

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

$$\langle I_y \rangle = Tr(I_y s(t)). \tag{3}$$

Where $s(t)$ 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 the y-axis. Therefore, in order to estimate the FID signal of a multiple–pulse NMR experiment, the density matrix operator should be obtained at the end of the experiment.

Analytical Description of 3D J-Resolved NMR

In this study, for the analytical descriptions of 3D J-resolved NMR spectroscopy of IS_nK_m ($I = 1/2$, $S = 1/2$, $K = 1$; $n = 1,2$, $m = 1,2$) and IS_nK_m ($I = 1/2$, $S = 1$, $K = 1$; $n = 1,2$, $m = 1,2$) spin systems 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. 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 (between I and S spins) and also during the first half of t_2 (between I and K spins). This section is divided into two subsections for both IS_nK_m ($I = 1/2$, $S = 1/2$, $K = 1$; $n = 1, 2$, $m = 1,2$) and IS_nK_m ($I = 1/2$, $S = 1$, $K = 1$; $n = 1,2$, $m = 1,2$) spin systems.

$IS_nK_m(I = 1/2, S = 1/2$ and $K = 1)$ Spin System

For $IS_nK_m(I = 1/2, S = 1/2, K = 1; n = 1, 2, m = 1,2)$ spin system, in the equations following abbreviations are used: $C_{nJ} = Cos\, n\pi J\frac{t_1}{2}, C'_{nJ} = Cos\, n\pi J' t_2$

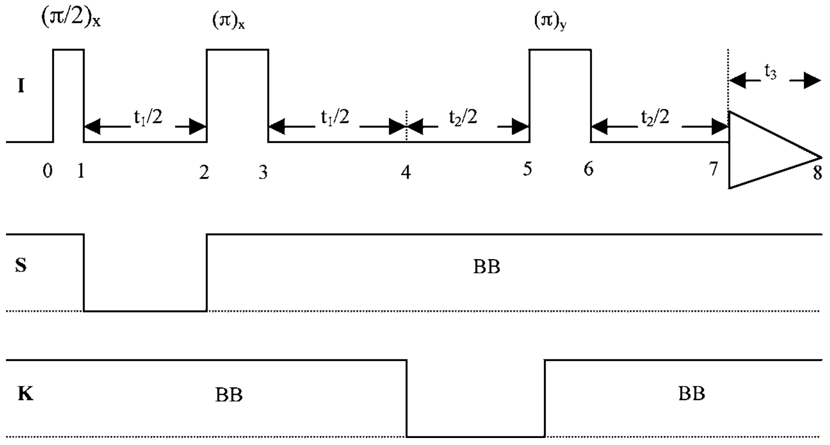

Figure 1. The gated decoupler pulse sequence for heteronuclear 3D J-resolved NMR spectroscopy.

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.

For the ***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 labelled point:

$$\sigma_1 = -I_y, \sigma_2 = -I_y C_J, \tag{4}$$

$$\sigma_3 = \sigma_4 = I_y C_J \tag{5}$$

and

$$\sigma_5 = \sigma_6 = \sigma_7 = I_y C_J + I_y K_z^2 C'_J C_J - I_y K_z^2 C_J. \tag{6}$$

Under the chemical shift evolution during t$_3$, density matrix becomes

$$\sigma_8 = I_y C_J C_I + I_y K_z^2 C'_J C_J C_I - I_y K_z^2 C_J C_I. \tag{7}$$

In density matrix operators, only the terms with observable product operators are kept, as they are the only ones contribute to the signal on y-axis detection. Then, magnetisation along y axis is proportional to $\langle I_y \rangle$ and

$$M_y(t_1, t_2, t_3)\alpha\langle I_y \rangle = Tr(I_y \sigma_8). \tag{8}$$

Now, it is necessary to obtain the $Tr(I_y O)$ values of observable product operators indicated by O. For $IS_n K_m$ spin system ($I = 1/2$, $S = 1/2$, $K = 1$, $n = 1,2$, $m = 1,2$), $Tr(I_y O)$ values were calculated by a computer program and the results are given in Table 1. By using the Table 1, for the $Tr(I_y I_y)$ and $Tr(I_y I_y K_z^2)$ values of ISK spin system,

Table 1. The Results of the $Tr(I_y O)$ Calculations for Some of the Observable Product Operators in $IS_n K_m$ Spin System ($I = 1/2$, $S = 1/2$, $K = 1$; $n = 1, 2$, $m = 1,2$)

Spin System	Product Operator (O)	Tr($I_y O$)
ISK	I_y	3
	$I_y K_z^2$	2
IS_2K	I_y	6
	$I_y K_z^2$	4
ISK_2	I_y	9
	$I_y(K_{1z}^2 + K_{2z}^2)$	12
	$I_y K_{1z}^2 K_{2z}^2$	4

$$\begin{aligned}\langle I_y\rangle &= C_J C_I + 2C_J C'_J C_I\\ &= \frac{1}{2}\left[Cos\left(\Omega_I t_3 + \frac{\pi J t_1}{2}\right) + Cos\left(\Omega_I t_3 - \frac{\pi J t_1}{2}\right)\right]\\ &\quad + \frac{1}{2}\left[Cos\left(\Omega_I t_3 + \pi J' t_2 + \frac{\pi J t_1}{2}\right) + Cos\left(\Omega_I t_3 + \pi J' t_2 - \frac{\pi J t_1}{2}\right)\right]\\ &\quad + \frac{1}{2}\left[Cos\left(\Omega_I t_3 - \pi J' t_2 + \frac{\pi J t_1}{2}\right) + Cos\left(\Omega_I t_3 - \pi J' t_2 - \frac{\pi J t_1}{2}\right)\right]\end{aligned} \tag{9}$$

is obtained. This equation represents the FID signals of 3D J-resolved NMR spectroscopy for *ISK* spin system. These are the six signals at $(\frac{J}{4}, 0, \Omega_I)$, $(-\frac{J}{4}, 0, \Omega_I)$, $(\frac{J}{4}, \frac{J'}{2}, \Omega_I)$, $(-\frac{J}{4}, \frac{J'}{2}, \Omega_I)$, $(\frac{J}{4}, -\frac{J'}{2}, \Omega_I)$,$(-\frac{J}{4}, -\frac{J'}{2}, \Omega_I)$with the same relative intensities. In these signal representations, the first, second and the third terms are the values at F_1, F_2 and F_3 axes, 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.

For $\boldsymbol{IS_2K}$ spin system, by using the same pulse sequence we obtain

$$\sigma_7 = I_y C_J^2 + I_y K_z^2 C_J^2 C'_J - I_y K_z^2 C_J^2 \tag{10}$$

and

$$\sigma_8 = \sigma_7 C_I. \tag{11}$$

By using the results in Table 1, the signal representation becomes as

$$\langle I_y\rangle = C_I + 2C'_J C_I + C_{2J} C_I + 2C_{2J} C'_J C_I. \tag{12}$$

This equation represents the signals at $(\frac{J}{2}, 0, \Omega_I)$, $(-\frac{J}{2}, 0, \Omega_I)$, $(\frac{J}{2}, \frac{J'}{2}, \Omega_I)$, $(0, 0, \Omega_I)$, $(0, \frac{J'}{2}, \Omega_I)$, $(0, -\frac{J'}{2}, \Omega_I)$, $(-\frac{J}{2,}, \frac{J'}{2}, \Omega_I)$, $(\frac{J}{2,}, -\frac{J'}{2}, \Omega_I)$, $(-\frac{J}{2,}, -\frac{J'}{2}, \Omega_I)$ with the relative intensities of 1:1:1:2:2:2:1:1:1.

For the $\boldsymbol{ISK_2}$ spin system, by applying the same procedure,

$$\sigma_8 = \left[I_y + I_y\left(K_{1z}^2 + K_{2z}^2\right)[C'_J - 1] + I_y K_{1z}^2 K_{2z}^2\left[\frac{3}{2} + \frac{1}{2}C'_{2J} - 2C'_J\right]\right] C_J C_I \tag{13}$$

is obtained. Then by using the Table 1,

$$\langle I_y\rangle = 3C_J C_I + 4C'_J C_J C_I + 2C_J C_J C_I \tag{14}$$

is found. This equation represents the signals at $(\frac{J}{4}, J', \Omega_I)$, $(-\frac{J}{4}, J', \Omega_I)$, $(\frac{J}{4}, \frac{J'}{2}, \Omega_I)$, $(-\frac{J}{4}, \frac{J'}{2}, \Omega_I)$, $(\frac{J}{4}, 0, \Omega_I)$, $(-\frac{J}{4}, 0, \Omega_I)$, $(\frac{J}{4}, -\frac{J'}{2}, \Omega_I)$, $(-\frac{J}{4}, -\frac{J'}{2}, \Omega_I)$, $(\frac{J}{4}, -J', \Omega_I)$, $(-\frac{J}{4}, -J', \Omega_I)$ with a relative intensity distribution of 1:1:2:2:3:3:2:2:1:1.

$\boldsymbol{IS_nK_m(I = 1/2, S = 1}$ and $\boldsymbol{K = 1)}$ Spin System

The abbreviations used in the $IS_nK_m(I = 1/2, S = 1, K = 1;\ n = 1,2,\ m = 1,2)$ spin system are: $C_{nJ} = Cosn\pi Jt_1$, $C'_{nJ} = Cosn\pi J't_2$ and $C_I = Cos\Omega_I t_3$. Spin-spin coupling parameters are the same as explained in the previous subsection.

For the ***ISK*** spin system $\sigma_0 = I_z$ is the density matrix operator at thermal equilibrium and the density matrices for each labelled point are as following

$$\sigma_1 = -I_y, \sigma_2 = -I_y - I_yS_x^2(C_J - 1), \tag{15}$$

$$\sigma_3 = \sigma_4 = I_y + I_yS_z^2(C_J - 1) \tag{16}$$

and

$$\begin{aligned}\sigma_5 = \sigma_6 = \sigma_7 = I_y + I_yS_z^2(C_J - 1) + I_yK_z^2(C'_J - 1)\\ + I_yS_z^2K_z^2(C_J - 1)(C'_J - 1).\end{aligned} \tag{17}$$

Under the chemical shift evolution during t$_3$, density matrix becomes

$$\sigma_3 = \left[I_y + I_yS_x^2(C_J - 1) + I_yK_z^2(C'_J - 1) + I_yS_z^2K_z^2(C_J - 1)(C'_J - 1)\right]C_I. \tag{18}$$

For the IS_nK_m spin system ($I = 1/2$, $S = 1$, $K = 1$, $n = 1,2$, $m = 1,2$), calculated $Tr(I_yO)$ values are given in Table 2. By using the Table 2,

$$\langle I_y\rangle = \frac{1}{2}C_I + C_JC_I + C'_J C_I + 2C_JC'_JC_I \tag{19}$$

is obtained. This equation represents the FID signals of 3D J-resolved NMR spectroscopy for the *ISK* spin system. These are the nine signals at $(\frac{J}{2}, \frac{J'}{2}, \Omega_I)$, $(0, \frac{J'}{2}, \Omega_I)$, $(-\frac{J}{2}, \frac{J'}{2}, \Omega_I)$, $(\frac{J}{2}, 0, \Omega_I)$, $(0, 0, \Omega_I)$, $(-\frac{J}{2}, 0, \Omega_I)$, $(\frac{J}{2}, -\frac{J'}{2}, \Omega_I)$, $(0, -\frac{J'}{2}, \Omega_I)$, $(-\frac{J}{2}, -\frac{J'}{2}, \Omega_I)$ with the same relative intensities.

For the ***ISK₂*** spin system,

$$\langle I_y\rangle = \frac{3}{2}C_I + 3C_JC_I + 2C'_JC_I + 4C'_JC_JC_I + C'_{2J}C_I + 2C'_{2J}C_JC_I \tag{20}$$

is found. This equation represents fifteen signals at $(\frac{J}{2}, J', \Omega_I)$, $(0, J', \Omega_I)$, $(-\frac{J}{2}, J', \Omega_I)$, $(\frac{J}{2}, \frac{J'}{2}, \Omega_I)$, $(0, \frac{J'}{2}, \Omega_I)$, $(-\frac{J}{2}, \frac{J'}{2}, \Omega_I)$, $(\frac{J}{2}, 0, \Omega_I)$, $(0, 0, \Omega_I)$, $(-\frac{J}{2}, 0, \Omega_I)$, $(\frac{J}{2}, -\frac{J'}{2}, \Omega_I)$, $(0, -\frac{J}{2}, \Omega_I)$, $(-\frac{J}{2}, -\frac{J'}{2}, \Omega_I)$, $(\frac{J}{2}, -J', \Omega_I)$, $(0, -J', \Omega_I)$, $(-\frac{J}{2}, -J', \Omega_I)$ with relative intensities 1:1:1:2:2:2:3:3:3:2:2:2:1:1:1.

For the ***IS₂K*** spin system

$$\langle I_y\rangle = \frac{3}{2}C_I + 3C'_JC_I + 2C_JC_I + 4C_JC_JC_I + C_{2J}C_I + 2C_{2J}C'_JC_I \tag{21}$$

Table 2. The Results of the $Tr(I_y O)$ Calculations for Some of the Observable Product Operators in the $IS_n K_m$ Spin System $I = 1/2$, $S = 1$, $K = 1; n = 1{,}2$, $m = 1{,}2$)

Spin System	Product Operator (O)	$Tr(I_y O)$
ISK	I_y	18/4
	$I_y S_z^2$	3
	$I_y S_z^2 (K_{1z}^2 + K_{2z}^2)$	3
	$I_y S_z^2 K_z^2$	8/4
IS_2K	I_y	54/4
	$I_y S_z^2$	9
	$I_y (K_{1z}^2 + K_{2z}^2)$	18
	$I_y S_z^2 (K_{1z}^2 + K_{2z}^2$	12
	$I_y K_{1z}^2 K_{2z}^2$	6
	$I_y S_z^2 K_{1z}^2 K_{2z}^2$	4
ISK_2	I_y	54/4
	$I_y K_z^2$	9
	$I_y (S_{1z}^2 + S_{2z}^2)$	18
	$I_y (S_{1z}^2 + S_{2z}^2) K_z^2$	12
	$I_y S_{1z}^2 S_{2z}^2$	6
	$I_y S_{1z}^2 S_{2z}^2 K_z^2$	4

is found. As seen in this equation, there exist fifteen signals at $(J, \frac{J'}{2}, \Omega_I)$, $(J, 0, \Omega_I)$, $(-J, \frac{J'}{2,}, \Omega_I)$, $(\frac{J}{2}, \frac{J'}{2}, \Omega_I)$, $(\frac{J}{2}, 0, \Omega_I)$, $(-\frac{J}{2}, \frac{J'}{2}, \Omega_I)$, $(0, \frac{J'}{2}, \Omega_I)$, $(0, 0, \Omega_I)$, $(0, -\frac{J'}{2}, \Omega_I)$, $(\frac{J}{2}, -\frac{J'}{2}, \Omega_I)$, $(-\frac{J}{2}, 0, \Omega_I)$, $(-\frac{J}{2}, -\frac{J'}{2}, \Omega_I)$, $(J, -\frac{J'}{2}, \Omega_I)$, $(-J, 0, \Omega_I)$, $(-J, -\frac{J}{2}, \Omega_I)$, with relative intensities of 1:1:1:2:2:2:3:3:3:2:2:2:1:1:1.

CONCLUSION

It is known that 3D J-resolved NMR spectroscopy is widely used for resolving the chemical shift along the one axis and spin-spin coupling parameters along the two different axes. And the product operator formalism became a technique to use in analytical description of multi-dimensional and multiple-pulse NMR experiments for the weakly coupled spin systems having spin$\frac{1}{2}$ and spin-1. Therefore, by using the product operator theory analytical description of heteronuclear 3D J-resolved NMR spectroscopy for both $IS_n K_m (I = 1/2, S = 1/2, K = 1; n = 1{,}2, m = 1{,}2)$ and $IS_n K_m (I = 1/2, S = 1, K = 1; n = 1, 2, m = 1, 2)$ spin systems are first presented in this study. One can easily show that these results found here are consistent with those of classical formalism.

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