A Complete Product Operator Theory for *IS* ($I = 1$, $S = 1$) Spin System and Application to 3D HMQC-COSY NMR Experiment

İrfan Şaka, Sedat Gümüş, and Azmi Gençten

Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139, Samsun, Turkey

Reprint requests to A. G.; Fax: +90 362 4576081; E-mail: gencten@omu.edu.tr

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There exist a variety of multi-pulse NMR experiments for spectral assignment of complex molecules in solution. The conventional heteronuclear multiple-quantum coherence (HMQC) NMR experiment provides correlation between weakly coupled hetero-nuclei. The COSY is one of the most popular two-dimensional NMR experiment which is used to correlate J-coupled homo-nuclei of spectral assignment. The combination of the conventional HMQC and COSY NMR experiments yields a new experiment called 3D HMQC-COSY NMR experiment. The product operator theory is widely used for the analytical descriptions of multi-pulse NMR experiments for weakly coupled spin systems in liquids. In this study, complete product operator theory for weakly coupled IS ($I = 1$, $S = 1$) spin system is presented by obtaining the evolutions of the product operators under the spin-spin coupling Hamiltonian. As an application and a verification, analytical descriptions of 3D HMQC-COSY NMR experiment are obtained for weakly coupled $IS_nI'S'_m$ ($I = I' = 1/2$; $S = S' = 1$; $n = 1,2,3$; $m = 1,2$) multi-spin systems. Then the estimated spectra of this experiment for various multi-spin systems are explained in detail.

Key words: Product Operator Theory; Spin-1; 3D HMQC-COSY; NMR.

1. Introduction

It is well-known that the product operator theory as a quantum mechanical method is widely used for the analytical description of multi-pulse NMR experiments on weakly coupled spin systems in liquids having spin-1/2, spin-1 and spin-3/2 nuclei [1 – 16]. For weakly coupled two-spin-1 systems, evolutions of the S_x, S_y, I_xS_y, I_xS_z, $I_xS_z^2$, I_yS_z, $I_yS_z^2$, $I_zS_x^2$ and $I_zS_y^2$ product operators under the weak spin-spin coupling Hamiltonian and analytical descriptions of the INADEQUATE and DQC NMR experiments have been presented by Chandrakumar and co-workers [6, 10, 17, 18]. In our recent study, the complete product operator theory for the IS ($I = 1/2$, $S = 1$) spin system and application to DEPT-HMQC and MAXY NMR experiments have been presented [19, 20]. By using product operator theory in NMR experiments, experimental results can be confirmed and also new experimental suggestions can be made.

The conventional HMQC NMR experiment provides correlation between weakly coupled heteronuclei [21, 22]. The COSY is one of the most popular two-dimensional NMR experiment which is used for the correlation of J-coupled homo-nuclei in order to make spectral assignment [11]. In COSY NMR experiment of complex molecules, the spin-spin coupling multiplets of different chemically shifted nuclei may overlap and then spectral assignment may become too difficult. In order to simplify COSY NMR spectra a new experiment called 3D HMQC-COSY was obtained [23, 24]. This experiment is the combination of HMQC and COSY NMR experiments. The spectrum of this experiment would contain H-H correlations in the F2 and F3 planes. Third dimension (F1) would separate the planes based on ^{13}C chemical shifts of directly bounded ^{13}C atoms.

In the present study, the complete product operator theory has been presented for weakly coupled IS ($I = 1$, $S = 1$) spin system as it is presented before for weakly coupled IS ($I = 1/2$, $S = 1$) spin system [19, 20]. First, the evolutions of all product operators under the scalar spin-spin coupling Hamiltonian have been obtained for the IS ($I = 1$, $S = 1$) spin system. Then, for the first time in this study, the product operator descriptions of the 3D HMQC-COSY NMR experiment are obtained for weakly coupled $IS_nI'S'_m$ ($I = I' = 1/2$; $S = S' = 1$; $n = 1,2,3$; $m = 1,2$) multi-

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spin systems. It is shown that this experiment can be used for spectral assignments of CD_nCD_m groups in complex liquids. Therefore, after obtaining the complete product operator theory for IS ($I = 1$, $S = 1$) spin system an application and a verification of this theory is also presented.

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 the IS ($I = 1$, $S = 1$) spin system, the nine Cartesian spin angular momentum operators for $I = 1$ are E_I, I_x, I_y, I_z, I_z^2, $[I_x,I_z]_+$, $[I_y,I_z]_+$, $[I_x,I_y]_+$ and $(I_x^2 - I_y^2)$ [19,25]. Similarly, there are also nine Cartesian spin angular momentum operators for $S = 1$. So, $9 \cdot 9 = 81$ product operators are obtained with direct products of these spin angular momentum operators for the IS ($I = 1$, $S = 1$) spin system. Depending on the pulse experiment, the $(I_x^2 - I_y^2)$ Cartesian spin angular momentum operator is separated into two spin angular momentum operators as I_x^2 and I_y^2. In this case, there should be $10 \cdot 10 = 100$ product operators for this spin system. In this study they are used in separated form and the complete list of the product operators are given in Table 1.

In a liquid-state pulse NMR experiment of weakly coupled IS_n spin systems, the total Hamiltonian consists of the r. f. pulse, the chemical shift, and the spin-spin coupling Hamiltonians written as

$$\mathcal{H} = \Omega_I I_z + \sum_{i=1}^{n} \Omega_S S_{iz} + 2\pi \sum_{i=1}^{n} J_i I_z S_{iz}. \tag{1}$$

Time dependence of the density matrix is governed by Liouville-von Neumann equation:

$$\frac{\mathrm{d}\sigma}{\mathrm{d}t} = \frac{\mathrm{i}}{\hbar}[\sigma, \mathcal{H}]. \tag{2}$$

When the Hamiltonian is time independent, the solution of (2) is

$$\sigma(t) = \exp(-\mathrm{i}\mathcal{H}t)\sigma(0)\exp(\mathrm{i}\mathcal{H}t). \tag{3}$$

Where $\sigma(0)$ is the density matrix at $t = 0$. After employing the Hausdorff formula [5]

$$\begin{aligned} \exp(-\mathrm{i}\mathcal{H}t)A\exp(\mathrm{i}\mathcal{H}t) &= A - (\mathrm{i}t)[\mathcal{H},A] \\ &+ \frac{(\mathrm{i}t)^2}{2!}[\mathcal{H},[\mathcal{H},A]] - \frac{(\mathrm{i}t)^3}{3!}[\mathcal{H},[\mathcal{H},[\mathcal{H},A]]] + \cdots, \end{aligned} \tag{4}$$

evolutions of product operators under the r. f. pulse, the chemical shift, and the spin-spin coupling Hamiltonians can be easily obtained [5–7, 10, 19].

Table 1. Product operators in terms of direct products of spin angular momentum operators in weakly coupled IS ($I = 1$, $S = 1$) spin system. Only the diagonal and the upper terms are shown and $I_{ab} = [I_a,I_b]_+$, $S_{ab} = [S_a,S_b]_+$ short notations are used.

$\otimes$	E_S	S_x	S_y	S_z	S_z^2	S_{xz}	S_{yz}	S_{xy}	S_x^2	S_y^2
E_I	E	S_x	S_y	S_z	S_z^2	S_{xz}	S_{yz}	S_{xy}	S_x^2	S_y^2
I_x		I_xS_x	I_xS_y	I_xS_z	$I_xS_z^2$	I_xS_{xz}	I_xS_{yz}	I_xS_{xy}	$I_xS_x^2$	$I_xS_y^2$
I_y			I_yS_y	I_yS_z	$I_yS_z^2$	I_yS_{xz}	I_yS_{yz}	I_yS_{xy}	$I_yS_x^2$	$I_yS_y^2$
I_z				I_zS_z	$I_zS_z^2$	I_zS_{xz}	I_zS_{yz}	I_zS_{xy}	$I_zS_x^2$	$I_zS_y^2$
I_z^2					$I_z^2S_z^2$	$I_z^2S_{xz}$	$I_z^2S_{yz}$	$I_z^2S_{xy}$	$I_z^2S_x^2$	$I_z^2S_y^2$
I_{xz}						$I_{xz}S_{xz}$	$I_{xz}S_{yz}$	$I_{xz}S_{xy}$	$I_{xz}S_x^2$	$I_{xz}S_y^2$
I_{yz}							$I_{yz}S_{yz}$	$I_{yz}S_{xy}$	$I_{yz}S_x^2$	$I_{yz}S_y^2$
I_{xy}								$I_{xy}S_{xy}$	$I_{xy}S_x^2$	$I_{xy}S_y^2$
I_x^2									$I_x^2S_x^2$	$I_x^2S_y^2$
I_y^2										$I_y^2S_y^2$

For the IS ($I = 1, S = 1$) spin system the evolutions of some product operators under the weak spin-spin coupling Hamiltonian ($\mathcal{H}_J = 2\pi J I_z S_z$) are known and they are given in Table 2 [10, 17–20, 26]. In tables and equations, $c_{nJ} = \cos[n\pi Jt]$, $s_{nJ} = \sin[n\pi Jt]$, $I_{yz} = [I_y,I_z]_+$, $I_{xz} = [I_x,I_z]_+$, $S_{xz} = [S_x,S_z]_+$, $S_{yz} = [S_y,S_z]_+$, $S_{xy} = [S_x,S_y]_+$, $I_{x-y}^2 = (I_x^2 - I_y^2)$ and $S_{x-y}^2 = (S_x^2 - S_y^2)$ short notations are used. For example for $I_zS_x^2$ the product operator of IS ($I = 1, S = 1$) spin system can be found as

$$\begin{aligned} &\exp(-\mathrm{i}2\pi J I_z S_z t) I_z S_x^2 \exp(\mathrm{i}2\pi J I_z S_z t) \xrightarrow{\mathcal{H}_J t} \\ &\frac{1}{2} I_z S_x^2 (c_{4J} + 1) - \frac{1}{2} I_z S_y^2 (c_{4J} - 1) + \frac{1}{2} I_z^2 S_{xy} s_{4J}. \end{aligned} \tag{5}$$

The evolutions for the I_x, I_y, I_{xz}, I_{yz}, I_{xy}, I_x^2, and I_y^2 product operators will be similar to those of S_x, S_y, S_{xz}, S_{yz}, S_{xy}, S_x^2, and S_y^2 product operators. For this spin system E, I_z, S_z, I_z^2, S_z^2, I_zS_z, $I_zS_z^2$, $I_z^2S_z$, and $I_z^2S_z^2$ product operators does not change under the spin-spin coupling Hamiltonian. Evolutions of all nine Cartesian spin angular momentum operators under the r. f. pulse and the chemical shift Hamiltonians have been presented in our previous work for spin-1 [19, 20].

At any time during the NMR experiments, the ensemble averaged expectation value of the spin angular momentum, e. g. for I_y, is

$$M_y(t) \propto \langle I_y \rangle \equiv Tr[I_y \sigma(t)], \tag{6}$$

Table 2. Evolutions of the product operators under the spin-spin coupling Hamiltonian $(2\pi J I_z S_z)$ for weakly coupled *IS* $(I = 1, S = 1)$ spin system [10, 17–20, 26].

Product operator	Evolution of the product operator under the spin-spin coupling Hamiltonian $(\mathcal{H} = 2\pi J I_z S_z)$
S_x	$S_x + I_z^2 S_x (c_{2J} - 1) + I_z S_y s_{2J}$
S_y	$S_y + I_z^2 S_y (c_{2J} - 1) - I_z S_x s_{2J}$
S_{xz}	$S_{xz} + I_z^2 S_{xz} (c_{2J} - 1) + I_z S_{yz} s_{2J}$
S_{yz}	$S_{yz} + I_z^2 S_{yz} (c_{2J} - 1) - I_z S_{xz} s_{2J}$
S_{xy}	$S_{xy} + I_z^2 S_{xy} (c_{4J} - 1) - I_z S_{x-y}^2 s_{4J}$
S_x^2	$S_x^2 + \frac{1}{2} I_z^2 S_{x-y}^2 (c_{4J} - 1) + \frac{1}{2} I_z S_{xy} s_{4J}$
S_y^2	$S_y^2 - \frac{1}{2} I_z^2 S_{x-y}^2 (c_{4J} - 1) - \frac{1}{2} I_z S_{xy} s_{4J}$
$I_x S_y$	$\frac{1}{2} I_x S_y (c_{2J} + 1) + \frac{1}{2} I_{yz} S_{xz} (c_{2J} - 1) + \frac{1}{2} (I_y S_{yz} - I_{xz} S_x) s_{2J}$
$I_x S_z$	$I_x S_z c_{2J} + I_y S_z^2 s_{2J}$
$I_x S_z^2$	$I_x S_z^2 c_{2J} + I_y S_z s_{2J}$
$I_y S_z$	$I_y S_z c_{2J} - I_x S_z^2 s_{2J}$
$I_y S_z^2$	$I_y S_z^2 c_{2J} - I_x S_z s_{2J}$
$I_z S_x^2$	$\frac{1}{2} I_z S_x^2 (c_{4J} + 1) - \frac{1}{2} I_z S_y^2 (c_{4J} - 1) + \frac{1}{2} I_z^2 S_{xy} s_{4J}$
$I_z S_y^2$	$\frac{1}{2} I_z S_y^2 (c_{4J} + 1) - \frac{1}{2} I_z S_x^2 (c_{4J} - 1) - \frac{1}{2} I_z^2 S_{xy} s_{4J}$

where $\sigma(t)$ is the density matrix operator calculated from (4) at any time. Since $\langle I_y \rangle$ 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 multi-pulse NMR experiment, the density matrix operator should be obtained at the end of the experiment.

3. The Evolutions of Product Operators under the Spin-Spin Coupling Hamiltonian

As mentioned in section 2, there exist 100 product operators for *IS* $(I = 1, S = 1)$ spin system. Nine of them does not change under the spin-spin coupling Hamiltonian. The evolutions for 21 of them are known in the literature and are given in section 2. In this section the evolutions of 70 product operators under the spin-spin coupling Hamiltonian will be obtained. By using the Hausdorff formula given in (4), the evolutions of product operators under the spin-spin coupling Hamiltonian are derived for weakly coupled *IS* $(I = 1, S = 1)$ spin system. The weak spin-spin coupling Hamiltonian, which is the secular part of the scalar coupling, is $\mathcal{H}_J = 2\pi J I_z S_z$. As an example, evolution of $I_{xz} S_{xz}$ product operator is obtained as following, ($[I_x, I_z]_+ = I_{xz}$ and $[S_x, S_z]_+ = S_{xz}$):

$$\begin{aligned} & I_{xz} S_{xz} \xrightarrow{2\pi J I_z S_z t} \\ & \exp(-2\mathrm{i}\pi J I_z S_z t) I_{xz} S_{xz} \exp(2\mathrm{i}\pi J I_z S_z t) = I_{xz} S_{xz} \\ & -(\mathrm{i}2\pi J t) A(1) + \frac{(\mathrm{i}2\pi J t)^2}{2!} A(2) - \frac{(\mathrm{i}2\pi J t)^3}{3!} A(3) + \cdots \end{aligned} \tag{7}$$

where

$$A(1) = [I_z S_z, I_{xz} S_{xz}], \tag{8}$$

$$A(2) = [I_z S_z, A(1)], \tag{9}$$

$$A(3) = [I_z S_z, A(2)]. \tag{10}$$

Commutation relations for $S = 1$ can be found elsewhere [10]. Using the commutation relations

$$A(1) = \frac{\mathrm{i}}{2} I_z^2 I_x S_{yz} + \frac{\mathrm{i}}{2} I_{yz} S_x S_z^2, \tag{11}$$

is obtained, where

$$I_z^2 I_x = \frac{1}{2}(I_x + \mathrm{i} I_{yz}), \tag{12}$$

$$S_x S_z^2 = \frac{1}{2}(S_x - \mathrm{i} S_{yz}). \tag{13}$$

In this study, for the evolution of all product operators for the *IS* $(I = 1, S = 1)$ spin system, we have used some new relations between the angular momentum operators of spin-1. These new relations are given in the Appendix. After replacing all results in (7),

$$\begin{aligned} I_{xz} S_{xz} \xrightarrow{2\pi J I_z S_z t} & I_{xz} S_{xz} - (\mathrm{i}2\pi J t) \frac{\mathrm{i}}{2} (I_x S_{yz} + I_{yz} S_x) \\ & + \frac{(\mathrm{i}2\pi J t)^2}{2!} \frac{-1}{2} (I_y S_y - I_{xz} S_{xz}) \\ & - \frac{(\mathrm{i}2\pi J t)^3}{3!} \frac{\mathrm{i}}{2} (I_x S_{yz} + I_{yz} S_x) + \cdots \end{aligned} \tag{14}$$

is obtained. In order to get the generalized form for the evolution of $I_{xz} S_{xz}$ product operator under the spin-spin coupling Hamiltonian some additions and subtractions can be made as follows:

$$\begin{aligned} I_{xz} S_{xz} \xrightarrow{2\pi J I_z S_z t} & I_{xz} S_{xz} - (\mathrm{i}2\pi J t) \frac{\mathrm{i}}{2} (I_x S_{yz} + I_{yz} S_x) \\ & + \frac{(\mathrm{i}2\pi J t)^2}{2!} \frac{-1}{2} (I_y S_y - I_{xz} S_{xz}) \\ & - \frac{(\mathrm{i}2\pi J t)^3}{3!} \frac{\mathrm{i}}{2} (I_x S_{yz} + I_{yz} S_x) + \cdots \\ & + \frac{1}{2} (I_y S_y - I_{xz} S_{xz}) - \frac{1}{2} (I_y S_y - I_{xz} S_{xz}). \end{aligned} \tag{15}$$

Then, using sine and cosine series,

$$\begin{aligned} I_{xz} S_{xz} \xrightarrow{2\pi J I_z S_z t} & \frac{1}{2} I_{xz} S_{xz} (c_{2J} + 1) \\ & - \frac{1}{2} I_y S_y (c_{2J} - 1) + \frac{1}{2} (I_x S_{yz} + I_{yz} S_x) s_{2J} \end{aligned} \tag{16}$$

Table 3. Evolution of the product operators under the spin-spin coupling Hamiltonian $(2\pi J I_z S_z)$ for weakly coupled *IS* $(I = 1, S = 1)$ spin system.

Product operator	Evolution of the product operator under the spin-spin coupling Hamiltonian $(\mathcal{H} = 2\pi J I_z S_z)$
I_xS_x	$\frac{1}{2}I_xS_x(c_{2J}+1)-\frac{1}{2}I_{yz}S_{yz}(c_{2J}-1)+\frac{1}{2}(I_yS_{xz}+I_{xz}S_y)s_{2J}$
I_xS_{xz}	$\frac{1}{2}I_xS_{xz}(c_{2J}+1)-\frac{1}{2}I_{yz}S_y(c_{2J}-1)+\frac{1}{2}(I_yS_x+I_{xz}S_{yz})s_{2J}$
I_xS_{yz}	$\frac{1}{2}I_xS_{yz}(c_{2J}+1)+\frac{1}{2}I_{yz}S_x(c_{2J}-1)+\frac{1}{2}(I_yS_y-I_{xz}S_{xz})s_{2J}$
I_xS_{xy}	$I_xS_{xy}c_{2J}-I_{xz}S^2_{x-y}s_{2J}$
$I_xS_x^2$	$\frac{1}{2}I_xS_x^2(c_{2J}+1)-\frac{1}{2}I_xS_y^2(c_{2J}-1)+\frac{1}{2}I_xS_z^2(c_{2J}-1)+\frac{1}{2}(I_{xz}S_{xy}+I_yS_z)s_{2J}$
$I_xS_y^2$	$\frac{1}{2}I_xS_y^2(c_{2J}+1)-\frac{1}{2}I_xS_x^2(c_{2J}-1)+\frac{1}{2}I_xS_z^2(c_{2J}-1)-\frac{1}{2}(I_{xz}S_{xy}-I_yS_z)s_{2J}$
I_yS_y	$\frac{1}{2}I_yS_y(c_{2J}+1)-\frac{1}{2}I_{xz}S_{xz}(c_{2J}-1)-\frac{1}{2}(I_xS_{yz}+I_{yz}S_x)s_{2J}$
I_yS_{xz}	$\frac{1}{2}I_yS_{xz}(c_{2J}+1)+\frac{1}{2}I_{xz}S_y(c_{2J}-1)-\frac{1}{2}(I_xS_x-I_{yz}S_{yz})s_{2J}$
I_yS_{yz}	$\frac{1}{2}I_yS_{yz}(c_{2J}+1)-\frac{1}{2}I_{xz}S_x(c_{2J}-1)-\frac{1}{2}(I_xS_y+I_{yz}S_{xz})s_{2J}$
I_yS_{xy}	$I_yS_{xy}c_{2J}-I_{yz}S^2_{x-y}s_{2J}$
$I_yS_x^2$	$\frac{1}{2}I_yS_x^2(c_{2J}+1)-\frac{1}{2}I_yS_y^2(c_{2J}-1)+\frac{1}{2}I_yS_z^2(c_{2J}-1)-\frac{1}{2}(I_{yz}S_{xy}-I_xS_z)s_{2J}$
$I_yS_y^2$	$\frac{1}{2}I_yS_y^2(c_{2J}+1)-\frac{1}{2}I_yS_x^2(c_{2J}-1)+\frac{1}{2}I_yS_z^2(c_{2J}-1)+\frac{1}{2}(I_{yz}S_{xy}+I_xS_z)s_{2J}$
I_zS_{xz}	$I_zS_{xz}c_{2J}+I_z^2S_{yz}s_{2J}$
I_zS_{yz}	$I_zS_{yz}c_{2J}-I_z^2S_{xz}s_{2J}$
I_zS_{xy}	$I_zS_{xy}c_{4J}-I_z^2S^2_{x-y}s_{4J}$
$I_z^2S_{xz}$	$I_z^2S_{xz}c_{2J}+I_zS_{yz}s_{2J}$
$I_z^2S_{yz}$	$I_z^2S_{yz}c_{2J}-I_zS_{xz}s_{2J}$
$I_z^2S_{xy}$	$I_z^2S_{xy}c_{4J}-I_zS^2_{x-y}s_{4J}$
$I_z^2S_x^2$	$\frac{1}{2}I_z^2S_x^2(c_{4J}+1)-\frac{1}{2}I_z^2S_y^2(c_{4J}-1)+\frac{1}{2}I_zS_{xy}s_{4J}$
$I_z^2S_y^2$	$\frac{1}{2}I_z^2S_y^2(c_{4J}+1)-\frac{1}{2}I_z^2S_x^2(c_{4J}-1)-\frac{1}{2}I_zS_{xy}s_{4J}$
$I_{xz}S_{xz}$	$\frac{1}{2}I_{xz}S_{xz}(c_{2J}+1)-\frac{1}{2}I_yS_y(c_{2J}-1)+\frac{1}{2}(I_xS_{yz}+I_{yz}S_x)s_{2J}$
$I_{xz}S_{yz}$	$\frac{1}{2}I_{xz}S_{yz}(c_{2J}+1)-\frac{1}{2}I_xS_y(c_{2J}-1)+\frac{1}{2}(I_{yz}S_y-I_xS_{xz})s_{2J}$
$I_{xz}S_{xy}$	$I_{xz}S_{xy}c_{2J}-I_xS^2_{x-y}s_{2J}$
$I_{xz}S_x^2$	$\frac{1}{2}I_{xz}S_x^2(c_{2J}+1)-\frac{1}{2}I_{xz}S_y^2(c_{2J}-1)+\frac{1}{2}I_{xz}S_z^2(c_{2J}-1)+\frac{1}{2}(I_xS_{xy}+I_{yz}S_z)s_{2J}$
$I_{xz}S_y^2$	$\frac{1}{2}I_{xz}S_y^2(c_{2J}+1)-\frac{1}{2}I_{xz}S_x^2(c_{2J}-1)+\frac{1}{2}I_{xz}S_z^2(c_{2J}-1)-\frac{1}{2}(I_xS_{xy}-I_{yz}S_z)s_{2J}$
$I_{yz}S_{yz}$	$\frac{1}{2}I_{yz}S_{yz}(c_{2J}+1)-\frac{1}{2}I_xS_x(c_{2J}-1)-\frac{1}{2}(I_yS_{xz}+I_{xz}S_y)s_{2J}$
$I_{yz}S_{xy}$	$I_{yz}S_{xy}c_{2J}-I_yS^2_{x-y}s_{2J}$
$I_{yz}S_x^2$	$\frac{1}{2}I_{yz}S_x^2(c_{2J}+1)-\frac{1}{2}I_{yz}S_y^2(c_{2J}-1)+\frac{1}{2}I_{yz}S_z^2(c_{2J}-1)+\frac{1}{2}(I_yS_{xy}-I_{xz}S_z)s_{2J}$
$I_{yz}S_y^2$	$\frac{1}{2}I_{yz}S_y^2(c_{2J}+1)-\frac{1}{2}I_{yz}S_x^2(c_{2J}-1)+\frac{1}{2}I_{yz}S_z^2(c_{2J}-1)-\frac{1}{2}(I_yS_{xy}+I_{xz}S_z)s_{2J}$
$I_{xy}S_{xy}$	$I_{xy}S_{xy}$
$I_{xy}S_x^2$	$I_{xy}S_x^2+\frac{1}{2}I_{xy}S_z^2(c_{4J}-1)-\frac{1}{2}I^2_{x-y}S_zs_{4J}$
$I_{xy}S_y^2$	$I_{xy}S_y^2+\frac{1}{2}I_{xy}S_z^2(c_{4J}-1)-\frac{1}{2}I^2_{x-y}S_zs_{4J}$
$I_x^2S_x^2$	$I_x^2S_x^2+\frac{1}{4}(I^2_{x-y}S_z^2+I_z^2S^2_{x-y})(c_{4J}-1)+\frac{1}{4}(I_zS_{xy}+I_{xy}S_z)s_{4J}$
$I_x^2S_y^2$	$I_x^2S_y^2+\frac{1}{4}(I^2_{x-y}S_z^2+I_z^2S^2_{x-y})(c_{4J}-1)+\frac{1}{4}(I_zS_{xy}+I_{xy}S_z)s_{4J}$
$I_y^2S_y^2$	$I_y^2S_y^2+\frac{1}{4}(I^2_{x-y}S_z^2+I_z^2S^2_{x-y})(c_{4J}-1)+\frac{1}{4}(I_zS_{xy}+I_{xy}S_z)s_{4J}$

is obtained. For the remainder, the same procedure is applied and the obtained results are presented in Table 3. The calculations are made only for the diagonal and upper terms of Table 1. Because of the symmetry, the evolutions for the lower terms can be written easily from the evolutions of the upper terms. As an example, evolution for $I_yS_x^2$ as given in Table 2 is

$$I_yS_x^2 \xrightarrow{\mathcal{H}_J t} \frac{1}{2}I_yS_x^2(c_{2J}+1)-\frac{1}{2}I_yS_y^2(c_{2J}-1) + \frac{1}{2}I_yS_z^2(c_{2J}-1)-\frac{1}{2}(I_{yz}S_{xy}-I_xS_z)s_{2J}. \quad (17)$$

Then, the evolution for $I_x^2S_y$ will be

$$I_x^2S_y \xrightarrow{\mathcal{H}_J t} \frac{1}{2}I_x^2S_y(c_{2J}+1)-\frac{1}{2}I_y^2S_y(c_{2J}-1) + \frac{1}{2}I_z^2S_y(c_{2J}-1)-\frac{1}{2}(I_{xy}S_{yz}-I_zS_x)s_{2J}. \quad (18)$$

4. 3D HMQC-COSY NMR Experiment for $IS_nIS'_m$ Multi-Spin Systems

For the analytical description of the 3D HMQC-COSY NMR experiment of $IS_nI'S'_m$ multi-spin systems, the pulse sequence given in Figure 1 is used. As shown in this figure, the density matrix operator at each stage of the experiment is labelled with numbers where ^{13}C is treated as spins $I;I'$ and ^{2}H as spins $S;S'$.

In this pulse sequence, τ is the evolution delay for hetero-nuclei and its optimum value is $1/(2J_{IS})$. t$_1$ is the chemical shift delay for both spins I and I'. t$_2$ is the homonuclear weak spin-spin coupling and chemical shift delay for both spins-S and S'. t$_3$ is the acquisition time for both spins S and S' along the x-axis. During the t$_2$ and t$_3$ homonuclear weak spin-spin coupling between S and S' spins takes place. 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 this experiment following r. f. pulse, chemical shift, and spin-spin coupling Hamiltonians are applied:

$$\mathcal{H}_{rf}(I,I') = \omega_{rf}I_\varphi + \omega_{rf}I'_\varphi, \quad (\varphi = x,y) \quad (19)$$

$$\mathcal{H}_{rf}(S,S') = \omega_{rf}S_\varphi + \omega_{rf}S'_\varphi, \quad (\varphi = x,y) \quad (20)$$

$$\mathcal{H}_I(I,I') = \Omega_I I_z + \Omega'_I I'_z, \quad (21)$$

$$\mathcal{H}_C(S,S') = \Omega_S S_z + \Omega'_S S'_z, \quad (22)$$

$$\mathcal{H}_J(I-S,I'-S') = 2\pi J_{IS}I_zS_z + 2\pi J_{I'S'}I'_zS'_z, \quad (J_{IS} = J_{I'S'}) \quad (23)$$

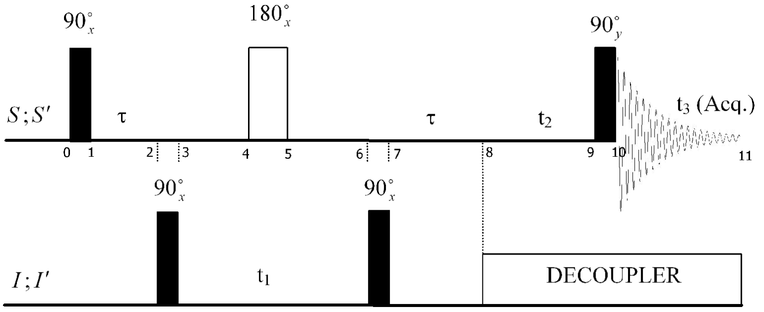

Fig. 1. 3D HMQC-COSY NMR pulse sequence [23, 24].

$$\mathcal{H}_J(S-S') = 2\pi J_{SS'}S_zS'_z. \tag{24}$$

For multi-spin systems, to follow these processes (applications of required Hamiltonians during the pulse sequence) by hand becomes too difficult. In order to overcome this problem a computer program was written in Mathematica for this study [27]. This program is used to obtain the density matrix operator at the end of the experiment for different multi-spin systems.

For $ISI'S'$ multi-spin system, the density matrix at thermal equilibrium is $\sigma_0 = S_z + S'_z$. By using the computer program following density matrices are obtained for each labelled point:

$$\sigma_0 \xrightarrow{90^\circ_x(S,S')} -S_y - S'_y \equiv \sigma_1, \tag{25}$$

$$\sigma_1 \xrightarrow{\mathcal{H}_J(I-S)\tau+\mathcal{H}_J(I'-S')\tau} 2I_zS_x + 2I'_zS'_x, \quad \text{where} \quad \tau = 1/(2J_{IS}), \tag{26}$$

$$\sigma_2 \xrightarrow{90^\circ_x(I,I')} -2I_yS_x - 2I'_yS'_x, \tag{27}$$

$$\begin{aligned}&\sigma_3 \xrightarrow{\mathcal{H}_C(I,I')t_1+180^\circ_x(S,S')}\\ &-2I_yS_x\cos[\Omega_It_1] + 2I_xS_x\sin[\Omega_It_1]\\ &-2I'_yS'_x\cos[\Omega'_It_1] + 2I'_xS'_x\sin[\Omega'_It_1],\end{aligned} \tag{28}$$

$$\begin{aligned}\sigma_6 \xrightarrow{90^\circ_x(I,I')} &-2I_zS_x\cos[\Omega_It_1] + 2I_xS_x\sin[\Omega_It_1]\\ &-2I'_zS'_x\cos[\Omega'_It_1] + 2I'_xS'_x\sin[\Omega'_It_1],\end{aligned} \tag{29}$$

$$\begin{aligned}&\sigma_7 \xrightarrow{\mathcal{H}_J(I-S)\tau+\mathcal{H}_J(I'-S')\tau}\\ &-S_y\cos[\Omega_It_1] + 2I_xS_{xz}\sin[\Omega_It_1]\\ &-S'_y\cos[\Omega'_It_1] + 2I'_xS'_{xz}\sin[\Omega'_It_1],\end{aligned} \tag{30}$$

$$\begin{aligned}&\sigma_8 \xrightarrow{\mathcal{H}_J(S-S')t_2+\mathcal{H}_C(S,S')t_2}\\ &\sigma_9 \xrightarrow{90^\circ_y(S,S')} \sigma_{10} \xrightarrow{\mathcal{H}_J(S-S')t_3+\mathcal{H}_C(S,S')t_3} \sigma_{11}.\end{aligned} \tag{31}$$

In the last step, the density matrix consists of many product operator terms. So, for the simplification of the density matrix only the observable terms should be taken into account. As the acquisition is taken along the x-axes for spins-S and S', at the end of the experiment the following density matrix is obtained:

$$\begin{aligned}\sigma_{11} &= \frac{1}{2}(2S_x - S_xS'^2_x - S_xS'^2_y - S_xS'^2_z)c_I(t_1)c_S(t_2)s_S(t_3)\\ &+ \frac{1}{2}(2S'_x - S^2_xS'_x - S^2_yS'_x - S^2_zS'_x)c'_I(t_1)c'_S(t_2)s'_S(t_3)\\ &+ \frac{1}{2}(S_xS'^2_x + S_xS'^2_y - S_xS'^2_z)c_{2J}(t_2)c_I(t_1)c_S(t_2)s_S(t_3)\\ &+ \frac{1}{2}(S^2_xS'_x + S^2_yS'_x - S^2_zS'_x)c_{2J}(t_2)c'_I(t_1)c'_S(t_2)s'_S(t_3)\\ &- \frac{1}{2}(S_xS'^2_x - S_xS'^2_y)(1 - c_{2J}(t_2))c_J(t_3)c_I(t_1)c_S(t_2)\\ &\qquad \cdot s_S(t_3)c'_{2S}(t_3)\\ &- \frac{1}{2}(S^2_xS'_x - S^2_yS'_x)(1 - c_{2J}(t_2))c_J(t_3)c'_I(t_1)c'_S\\ &\qquad \cdot (t_2)s'_S(t_3)c_{2S}(t_3)\\ &+ \frac{1}{2}S_xS^2_z(1 + c_{2J}(t_2))c_{2J}(t_3)c_I(t_1)c_S(t_2)s_S(t_3)\\ &+ \frac{1}{2}S^2_zS'_x(1 + c_{2J}(t_2))c_{2J}(t_3)c'_I(t_1)c'_S(t_2)s'_S(t_3)\\ &+ S_xS^2_zs_{2J}(t_2)s_{2J}(t_3)c'_I(t_1)c'_S(t_2)s_S(t_3)\\ &+ S^2_zS'_xs_{2J}(t_2)s_{2J}(t_3)c_I(t_1)c_S(t_2)s'_S(t_3).\end{aligned} \tag{32}$$

At above and in following equations $c_I(t_1) = \cos[\Omega_It_1]$, $c'_I(t_1) = \cos[\Omega'_It_1]$, $c_S(t_2) = \cos[\Omega_St_2]$, $c'_S(t_2) = \cos[\Omega'_St_2]$, $c_{nS}(t_3) = \cos[n\Omega_St_3]$, $c'_{nS}(t_3) = \cos[n\Omega'_St_3]$, $s_{nS}(t_3) = \sin[n\Omega_St_3]$, $s'_{nS}(t_3) = \sin[n\Omega'_St_3]$, $c_{nJ}(t_2) = \cos[n\pi Jt_2]$, $s_{nJ}(t_2) = \sin[n\pi Jt_2]$, $c_{nJ}(t_3) = \cos[n\pi Jt_3]$ and $s_{nJ}(t_3) = \sin[n\pi Jt_3]$.

For $IS_nI'S'_m$ multi-spin systems the ensemble averaged expectation value of the spin angular momentum, $\sum_{i=1}^{n}\langle S_{ix}\rangle + \sum_{j=1}^{m}\langle S'_{jx}\rangle$, is proportional to the magni-

Table 4. Results of the $\sum_{i=1}^{n}\mathrm{Tr}[S_{ix}O]$ calculations for the observable product operators of $IS_nI'S'_m$ multi-spin systems ($k=x,y,z$; $l=x,y,z$; $o=x,y,z$).

Spin System	Product Operator (O)	$\sum_{i=1}^{n}\mathrm{Tr}[S_{ix}O]$
$ISI'S'$	S_x	24
	$S_xS'^2_k$	16
$IS_2I'S'$	$S_{1x}+S_{2x}$	144
	$S_{1x}(S^2_{2k}+S'^2_k)+S_{2x}(S^2_{1k}+S'^2_k)$	192
	$S_{1x}S^2_{2k}S'^2_l+S^2_{1k}S_{2x}S'^2_l$	64
$IS_3I'S'$	$S_{1x}+S_{2x}+S_{3x}$	648
	$S_{1x}(S^2_{2k}+S^2_{3k}+S'^2_k)+S_{2x}(S^2_{1k}+S^2_{3k}+S'^2_k)$ $+S_{3x}(S^2_{1k}+S^2_{2k}+S'^2_k)$	1296
	$S_{1x}(S^2_{2k}S^2_{3l}+S^2_{2k}S'^2_l+S^2_{3k}S^2_l)$ $+S_{2x}(S^2_{1k}S^2_{3l}+S^2_{1k}S'^2_l+S^2_{3k}S'^2_l)$ $+S_{3x}(S^2_{1k}S^2_{2l}+S^2_{1k}S'^2_l+S^2_{2k}S'^2_l)$	864
	$S_{1x}S^2_{2k}S^2_{3l}S'^2_o+S^2_{1k}S_{2x}S^2_{3l}S'^2_o+S^2_{1k}S^2_{2l}S_{3x}S'^2_o$	192

Table 5. Results of the $\sum_{j=1}^{m}\mathrm{Tr}[S'_{jx}O']$ calculations for the observable product operators of $IS_nI'S'_m$ multi-spin systems ($k=x,y,z$; $l=x,y,z$; $o=x,y,z$).

Spin System	Product Operator (O')	$\sum_{j=1}^{n}\mathrm{Tr}[S'_{jx}O']$
$ISI'S'$	S'_x	24
	$S^2_kS'_x$	16
$IS_2I'S'$	S'_x	72
	$(S^2_{1k}+S^2_{2k})S'_x$	96
	$S^2_{1k}S^2_{2l}S'_x$	32
$IS_3I'S'$	S'_x	216
	$(S^2_{1k}+S^2_{2k}+S^2_{3k})S'_x$	432
	$(S^2_{1k}S^2_{2l}+S^2_{1k}S^2_{3l}+S^2_{2k}S^2_{3l})S'_x$	288
	$S^2_{1k}S^2_{2l}S^2_{3o}S'_x$	64

tude of the x-magnetization at any time during the experiment. So, the magnetization of 3D HMQC-COSY NMR experiment can be written as following:

$$\begin{aligned} M_y(t_1,t_2,t_3) &\propto \sum_{i=1}^{n}\langle S_{ix}\rangle+\sum_{j=1}^{m}\langle S'_{jx}\rangle \\ &= \sum_{i=1}^{n}\mathrm{Tr}[S_{ix}\sigma_{11}]+\sum_{j=1}^{m}\mathrm{Tr}[S'_{jx}\sigma_{11}]. \end{aligned} \tag{33}$$

Now it is necessary to obtain the $\sum_{i=1}^{n}\mathrm{Tr}[S_{ix}O]$ and $\sum_{j=1}^{m}\mathrm{Tr}[S'_{jx}O']$ values of the observable product operators indicated by O and O'. The $\sum_{i=1}^{n}\mathrm{Tr}[S_{ix}O]$ and $\sum_{j=1}^{m}\mathrm{Tr}[S'_{jx}O']$ values are calculated by a computer program in Mathematica and the results for several multi-spin systems are given in Table 4 and Table 5, respectively. For example, the trace value for the observable product operator S_x of $IS'S'$ multi-spin systems is calculated as following:

$$\begin{aligned} &\mathrm{Tr}[S_{ix}O]=\mathrm{Tr}[S_xS_x]= \\ &\mathrm{Tr}[(E_I\otimes S_x\otimes E'_I\otimes E'_S)(E_I\otimes S_x\otimes E'_I\otimes E'_S)]=24. \end{aligned} \tag{34}$$

By using Table 4 and Table 5,

$$\begin{aligned} \langle S_x\rangle+\langle S'_x\rangle &= \left\{\begin{matrix} 8c_{2J}(t_2)+8c_{2J}(t_3) \\ +8c_{2J}(t_2)c_{2J}(t_3) \end{matrix}\right\} c_I(t_1)c_S(t_2)s_S(t_3) \\ &\quad +16s_{2J}(t_2)s_{2J}(t_3)c_I(t_1)c_S(t_2)s'_S(t_3) \\ &\quad +16s_{2J}(t_2)s_{2J}(t_3)c'_I(t_1)c'_S(t_2)s_S(t_3) \\ &\quad +\left\{\begin{matrix} 8c_{2J}(t_2)+8c_{2J}(t_3) \\ +8c_{2J}(t_2)c_{2J}(t_3) \end{matrix}\right\} c'_I(t_1)c'_S(t_2)s'_S(t_3) \end{aligned} \tag{35}$$

is obtained for the $IS'S'$ multi-spin system. This equation is divided into four parts which represents the FID values of 8, 4, 4 and 8 signals for 3D HMQC-COSY NMR experiment. The first part of (35) represents nine diagonal signals at the coordinates of $(\Omega_I,\Omega_S-2\pi J,-\Omega_S-2\pi J)$, $(\Omega_I,\Omega_S-2\pi J,-\Omega_S)$, $(\Omega_I,\Omega_S-2\pi J,-\Omega_S+2\pi J)$, $(\Omega_I,\Omega_S,-\Omega_S-2\pi J)$, $(\Omega_I,\Omega_S,-\Omega_S)$, $(\Omega_I,\Omega_S,-\Omega_S+2\pi J)$, $(\Omega_I,\Omega_S+2\pi J,-\Omega_S-2\pi J)$, $(\Omega_I,\Omega_S+2\pi J,-\Omega_S)$, and $(\Omega_I,\Omega_S+2\pi J,-\Omega_S+2\pi J)$ with the intensity distribution of $1:2:1:2:0:2:1:2:1$, respectively. The second part of (35) represents nine cross signals at the coordinates of $(\Omega_I,\Omega_S-2\pi J,-\Omega'_S-2\pi J)$, $(\Omega_I,\Omega_S-2\pi J,-\Omega_S)$, $(\Omega_I,\Omega_S-2\pi J,\Omega'_S+2\pi J)$, $(\Omega_I,\Omega_S,-\Omega'_S-2\pi J)$, $(\Omega_I,\Omega_S,-\Omega'_S)$, $(\Omega_I,\Omega_S,-\Omega'_S+2\pi J)$, $(\Omega_I,\Omega_S+2\pi J,-\Omega'_S-2\pi J)$, $(\Omega_I,\Omega_S+2\pi J,-\Omega'_S)$, and $(\Omega_I,\Omega_S+2\pi J,-\Omega'_S+2\pi J)$ with the relative intensities of $1:0:-1:0:0:0:-1:0:1$, respectively. The third part of (35) represents nine cross signals at the coordinate of $(\Omega'_I,\Omega'_S-2\pi J,-\Omega_S-2\pi J)$, $(\Omega'_I,\Omega'_S-2\pi J,-\Omega_S)$, $(\Omega'_I,\Omega'_S-2\pi J,-\Omega_S+2\pi J)$, $(\Omega'_I,\Omega'_S,-\Omega_S-2\pi J)$, $(\Omega'_I,\Omega'_S,-\Omega_S)$, $(\Omega'_I,\Omega'_S,-\Omega_S+2\pi J)$, $(\Omega'_I,\Omega'_S+2\pi J,-\Omega_S-2\pi J)$, $(\Omega'_I,\Omega'_S+2\pi J,-\Omega_S)$, and $(\Omega'_I,\Omega'_S+2\pi J,-\Omega_S+2\pi J)$ with the intensity distribution of $1:0:-1:0:0:0:-1:0:1$, respectively. The last part of (35) represents nine diagonal signals at the coordinates of $(\Omega'_I,\Omega'_S-2\pi J,-\Omega'_S-2\pi J)$, $(\Omega'_I,\Omega'_S-2\pi J,-\Omega'_S)$, $(\Omega'_I,\Omega'_S-2\pi J,-\Omega'_S+2\pi J)$, $(\Omega_I,\Omega'_S,-\Omega'_S-2\pi J)$, $(\Omega_I,\Omega'_S,-\Omega'_S)$, $(\Omega'_I,\Omega'_S,-\Omega'_S+2\pi J)$, $(\Omega'_I,\Omega'_S+2\pi J,-\Omega'_S-2\pi J)$, $(\Omega'_I,\Omega'_S+2\pi J,-\Omega'_S)$, and $(\Omega'_I,\Omega'_S+2\pi J,-\Omega'_S+2\pi J)$ with the relative intensities of $1:2:1:2:0:2:1:2:1$, respectively. The appearance of 3D spectrum of the signals indicated above is shown in Figure 2. In a COSY spectrum of SS' spin system all these 36 (12 with zero intensity)

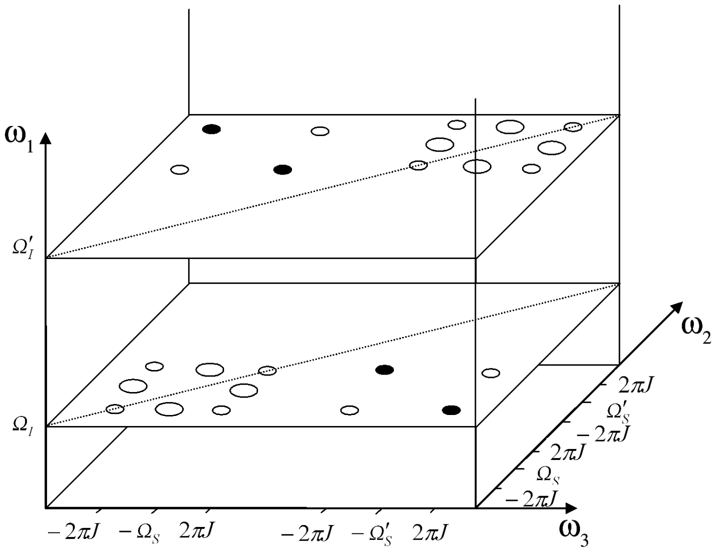

Fig. 2. Appearance of 3D HMQC-COSY NMR spectrum for $ISI'S'$ multi-spin system. The solid and open cycles represent negative and positive signals, respectively.

signals will be in one plane. In this 3D HMQC-COSY NMR experiment these signals will be observed in two planes of Ω_I and Ω_I' frequencies in F1 dimension as shown in Figure 2. In this Figure ^{2}D-^{2}D correlations are shown in F$_2$-F$_3$ planes. Chemical shifts of ^{13}C are in different planes. Intensity distributions for the diagonal peaks $(1:2:1:2:0:2:1:2:1)$ and for the cross peaks $(1:0:-1:0:0:0:-1:0:1)$ in two planes are in exact agreement with results predicted by Chandrakumar for COSY experiment [10].

For $IS_2I'S'$ multi-spin system, the density matrix at thermal equilibrium is $\sigma_0 = S_{1z} + S_{2z} + S_z'$. By using the computer program following density matrices are obtained for each labelled point:

$$\sigma_0 \xrightarrow{90^\circ_x(S_1,S_2,S')} -S_{1y} - S_{2y} - S_y' \equiv \sigma_1, \tag{36}$$

$$\sigma_1 \xrightarrow{\mathcal{H}_{1J}(I-S_1)\tau+\mathcal{H}_{2J}(I-S_2)\tau+H_J'(I'-S')\tau} 2I_zS_{1x} + 2I_zS_{2x} + 2I_z'S_x', \tag{37}$$

$$\sigma_2 \xrightarrow{90^\circ_x(I,I')} -2I_yS_{1x} - 2I_yS_{2x} - 2I_y'S_x', \tag{38}$$

$$\begin{aligned} \sigma_3 &\xrightarrow{\mathcal{H}_C(I,I')t_1+180^\circ_x(S_1,S_2,S')} \\ &-2I_yS_{1x}\cos[\Omega_It_1] + 2I_xS_{1x}\sin[\Omega_It_1] \\ &-2I_yS_{2x}\cos[\Omega_It_1] + 2I_xS_{2x}\sin[\Omega_It_1] \\ &-2I_y'S_x'\cos[\Omega_It_1] + 2I_x'S_x'\sin[\Omega_It_1]. \end{aligned} \tag{39}$$

As one can guess, after this step product operator calculations of $IS_2I'S'$ multi-spin system will be more complicated than those of $ISI'S'$ multi-spin system. By using the trace values of the observable product operators in Table 4 and 5 we obtain following expression for the magnetization at the end of the experiment:

$$\begin{aligned} &\sum_{i=1}^{2}\langle S_{ix}\rangle + \langle S_x'\rangle = \\ &\left\{\begin{array}{l} 48c_{2J}(t_2) + 48c_{2J}(t_3) \\ +48c_{2J}(t_2)c_{2J}(t_3) \end{array}\right\} c_I(t_1)c_S(t_2)s_S(t_3) \\ &+\left\{\begin{array}{l} 32s_{2J}(t_2)s_{2J}(t_3) \\ +64s_{2J}(t_2)s_{2J}(t_3)c_{2J}(t_3) \end{array}\right\} c_I(t_1)c_S(t_2)s_S'(t_3) \\ &+\left\{\begin{array}{l} 32s_{2J}(t_2)s_{2J}(t_3) \\ +64s_{2J}(t_2)c_{2J}(t_2)s_{2J}(t_3) \end{array}\right\} c_I'(t_1)c_S'(t_2)s_S(t_3) \\ &+\left\{\begin{array}{l} 8c_{2J}^2(t_2) + 16c_{2J}(t_2)c_{2J}(t_3) \\ +16c_{2J}^2(t_2)c_{2J}(t_3) + 8c_{2J}^2(t_3) \\ +16c_{2J}(t_2)c_{2J}^2(t_3) + 8c_{2J}^2(t_2)c_{2J}^2(t_3) \end{array}\right\} \\ &\cdot c_I'(t_1)c_S'(t_2)s_S'(t_3). \end{aligned} \tag{40}$$

This equation is also divided into four parts which represent the FID values of 8, 8, 8 and 25 signals for 3D HMQC-COSY NMR experiment. The signal coordinates and intensity distribution of the expected 3D HMQC-COSY NMR spectrum are presented in Fig. 3 for $IS_2I'S'$ multi-spin system. 3D spectrum will be observed in two planes for Ω_I and Ω_I' frequencies in F1 dimension as indicated in this figure.

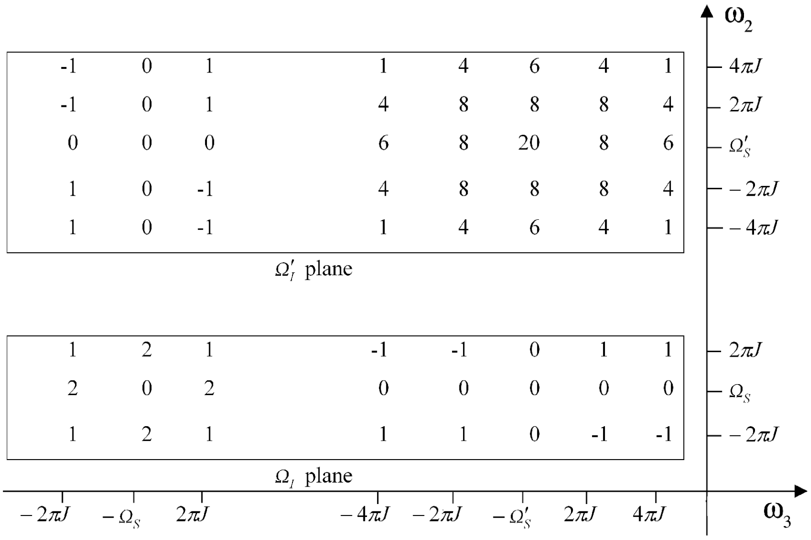

Fig. 3. Schematic signal coordinates and intensity distributions of the 3D HMQC-COSY NMR spectrum for the $IS_2I'S'$ multi-spin system.

For the $IS_3I'S'$ multi-spin system, the FID values of 3D HMQC-COSY NMR experiment are obtained applying the same procedure as above. At the end of the experiment following FID values are obtained:

$$\begin{aligned}
&\sum_{i=1}^{3}\langle S_{ix}\rangle+\langle S'_x\rangle=\\
&\left\{\begin{matrix}216c_{2J}(t_2)\\+216c_{2J}(t_3)\\+216c_{2J}(t_2)c_{2J}(t_3)\end{matrix}\right\}c_I(t_1)c_S(t_2)s_S(t_3)\\
&+\left\{\begin{matrix}48s_{2J}(t_2)s_{2J}(t_3)\\+192s_{2J}(t_2)s_{2J}(t_3)c_{2J}(t_3)\\+192s_{2J}(t_2)s_{2J}(t_3)c^2_{2J}(t_3)\end{matrix}\right\}c_I(t_1)c_S(t_2)s'_S(t_3)\\
&+\left\{\begin{matrix}48s_{2J}(t_2)s_{2J}(t_3)\\+192s_{2J}(t_2)c_{2J}(t_2)s_{2J}(t_3)\\+192s_{2J}(t_2)c^2_{2J}(t_2)s_{2J}(t_3)\end{matrix}\right\}c'_I(t_1)c'_S(t_2)s_S(t_3)\\
&+\left\{\begin{matrix}8c^3_{2J}(t_2)+8c^3_{2J}(t_3)+24c^2_{2J}(t_2)c_{2J}(t_3)\\+24c_{2J}(t_2)c^2_{2J}(t_3)+24c^3_{2J}(t_2)c_{2J}(t_3)\\+24c_{2J}(t_2)c^3_{2J}(t_3)+48c^2_{2J}(t_2)c^2_{2J}(t_3)\\+24c^3_{2J}(t_2)c^2_{2J}(t_3)+24c^2_{2J}(t_2)c^3_{2J}(t_3)\\+24c^3_{2J}(t_2)c^3_{2J}(t_3)\end{matrix}\right\}\\
&\cdot c'_I(t_1)c'_S(t_2)s'_S(t_3).
\end{aligned}\tag{41}$$

This equation is also divided into four parts which represents the FID values of 8, 12, 12 and 49 signals for 3D HMQC-COSY NMR experiment. The signal coordinates and intensity distribution of the expected 3D HMQC-COSY NMR spectrum are shown in Fig. 4 for the $IS_3I'S'$ multi-spin system. Again 3D spectrum will be observed in two planes for Ω_I and Ω'_I frequencies in F1 dimension. The calculations for the other multi-spin systems such as $IS_2I'S'_2$ and $IS_3I'S'_2$, can be also made.

5. Conclusion

As a result, a complete product operator theory for *IS* ($I=1$, $S=1$) spin system has been presented and applied. For this spin system, first the evolutions of all the product operators under the spin-spin coupling Hamiltonian were obtained. This is the first complete presentation of product operator theory for this spin system in the literature. Therefore, it will be useful for the future studies on product operator theory and pulse NMR experiments. For example theoretical results found here can be used for the confirmation of experimental results in some pulse NMR experiments. Then, as an application and a verification, the product operator description of 3D HMQC-COSY NMR experiment was obtained for $IS_nI'S'_m(I=I'=1/2;\ S=S'=1;\ n=1,2,3;\ m=1,2)$ multi-spin systems. The spectra of 3D HMQC-COSY NMR experiment contain ^{2}D-^{2}D correlations in F$_2$-F$_3$ planes. Also the chemical shifts of different CD$_n$ groups will be in different planes. By presenting the estimated spectra of $IS_nI'S'_m$ groups, it is shown that NMR experiment can be used for the spectral assignments of CD$_n$CD$_m$ groups in complex liquids.

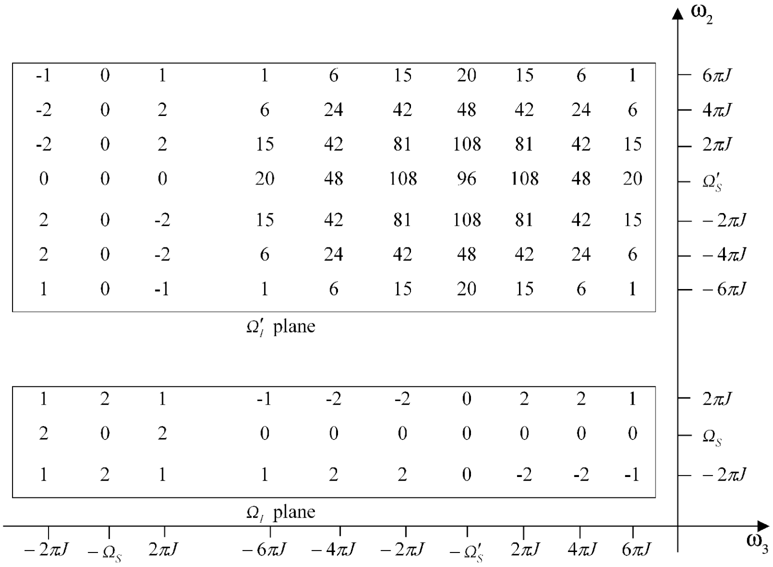

Fig. 4. Schematic signal coordinates and intensity distributions of the 3D HMQC-COSY NMR spectrum for the $IS_3I'S'$ multi-spin system.

Appendix: Some New Relations between the Angular Momentum Operators for Spin-1

$$S_zS_x^2 = \tfrac{1}{2}(S_z + \mathrm{i}[S_x,S_y]_+)$$
$$S_x^2S_z = \tfrac{1}{2}(S_z - \mathrm{i}[S_x,S_y]_+)$$
$$S_zS_y^2 = \tfrac{1}{2}(S_z - \mathrm{i}[S_x,S_y]_+)$$
$$S_y^2S_z = \tfrac{1}{2}(S_z + \mathrm{i}[S_x,S_y]_+)$$
$$(S_x^2 - S_y^2)S_z = -\mathrm{i}[S_x,S_y]_+$$
$$S_z(S_x^2 - S_y^2) = \mathrm{i}[S_x,S_y]_+$$
$$S_z[S_x,S_y]_+ = -\mathrm{i}(S_x^2 - S_y^2)$$
$$[S_x,S_y]_+S_z = \mathrm{i}(S_x^2 - S_y^2)$$
$$S_zS_x = \tfrac{1}{2}([S_x,S_z]_+ + \mathrm{i}S_y)$$
$$S_xS_z = \tfrac{1}{2}([S_x,S_z]_+ - \mathrm{i}S_y)$$
$$S_zS_y = \tfrac{1}{2}([S_y,S_z]_+ - \mathrm{i}S_x)$$
$$S_yS_z = \tfrac{1}{2}([S_y,S_z]_+ + \mathrm{i}S_x)$$
$$S_yS_z^2 = \tfrac{1}{2}(S_y + \mathrm{i}[S_x,S_z]_+)$$
$$S_z^2S_y = \tfrac{1}{2}(S_y - \mathrm{i}[S_x,S_z]_+)$$
$$S_xS_z^2 = \tfrac{1}{2}(S_x - \mathrm{i}[S_y,S_z]_+)$$
$$S_z^2S_x = \tfrac{1}{2}(S_x + \mathrm{i}[S_y,S_z]_+)$$
$$S_z[S_y,S_z]_+ = \tfrac{1}{2}(S_y - \mathrm{i}[S_x,S_z]_+)$$
$$[S_y,S_z]_+S_z = \tfrac{1}{2}(S_y + \mathrm{i}[S_x,S_z]_+)$$
$$S_z[S_x,S_z]_+ = \tfrac{1}{2}(S_x + \mathrm{i}[S_y,S_z]_+)$$
$$[S_x,S_z]_+S_z = \tfrac{1}{2}(S_x - \mathrm{i}[S_y,S_z]_+)$$

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