A Theoretical Application of MAXY NMR for CD$_n$ Groups

İrfan Şaka and Azmi Gençten

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

Reprint requests to İ. Ş.; E-mail: isaka@omu.edu.tr

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Liquid-state NMR experiments including edited-pulse angles are widely used to distinguish protonated and deuterated carbonyl groups in complex molecules. One of them is maximum quantum correlation NMR spectroscopy (MAXY NMR), which is very suitable to separate CH$_n$ groups. The product operator theory is used for the analytical description of these experiments for weakly coupled spin systems. In this study, the MAXY NMR experiment is applied for weakly coupled IS_n ($I = 1/2$; $S = 1$; $n = 1, 2, 3$) spin systems using the product operator theory. A theoretical discussion and experimental suggestions for sub-spectral editing of CD$_n$ groups are also presented.

Key words: MAXY NMR; Product Operator Theory; Spin-1.

1. Introduction

In complex molecules, liquid-state NMR experiments including edited-pulse angles are widely used to distinguish protonated and deuterated carbonyl groups. These experiments can be classified into two subgroups as ^{13}C and ^{1}H NMR experiments. ^{13}C NMR experiments are based on polarization transfer from a high natural abundance nucleus to a low natural abundance nucleus to increase the sensitive enhancement of the NMR spectra such as DEPT [1], INEPT [2] , SEMUT [3,4] and POMMIE [5]. ^{1}H NMR experiments are more useful because of the high natural abundance of the ^{1}H nucleus such as MAXY [6], DEPT-HMQC [7], RINEPT [8] and reverse-POMMIE [9]. ^{2}H NMR spectroscopy became a powerful technique for different applications such as structure elucidation and deuterium labeling [10,11]. ^{13}C and ^{2}H are the most useful stable isotopes for NMR-detected metabolic labeling experiments [11,12].

The product operator theory, as a simple quantum mechanical method, has been developed for the analytical description of multiple-pulse NMR experiments on weakly coupled spin systems in liquids [13 – 21]. In this method, the spin operators themselves and their direct products called product operators, are used. For example, product operator description of 2D DEPT J-resolved and SEMUT NMR spectroscopy for weakly coupled IS_n ($I = 1/2$; $S = 1$; $n = 1, 2, 3$) spin systems are reported elsewhere [22,23]. A complete product operator theory for the IS ($I = 1/2$; $S = 1$) spin system and application to the DEPT-HMQC NMR experiment was recently presented in our previous study [24].

In the POMMIE experiment the first maximum quantum excitation was made for edited detection of CH$_n$ groups [5]. Then, Bulsing et al. have generated the pulse sequence, called reverse-POMMIE, to observe protons [9]. After some modifications, this technique has been edited and named as maximum quantum correlation (MAXY) NMR spectroscopy by Liu et al. [6]. By using the product operator theory, theoretical and experimental studies of some NMR experiments related to MAXY NMR were performed for CH$_n$ groups [6,25 – 31].

In the present study, the MAXY NMR experiment is applied for weakly coupled IS_n ($I = 1/2$; $S = 1$; $n = 1, 2, 3$) spin systems using the product operator theory. Then, a theoretical discussion and experimental suggestions for sub-spectral editing of CD$_n$ groups are presented. To the best of our knowledge, this will be the first application of product operator theory to MAXY NMR spectroscopy for CD$_n$ groups.

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 ($I = 1/2$; $S = 1$) spin system,

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four Cartesian spin angular momentum operators for $I = 1/2$; E_I, 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_z^2, $[S_x,S_z]_+$, $[S_y,S_z]_+$, $[S_x,S_y]_+$, $(S_x^2 - S_y^2)$, can be easily found [32]. So, $4 \times 9 = 36$ product operators are obtained with direct products of these angular momentum operators for the IS ($I = 1/2$; $S = 1$) spin system. Depending on the pulse experiment, the Cartesian spin operator $(S_x^2 - S_y^2)$ is separated into two spin operators of S_x^2 and S_y^2. In this case there exist 40 product operators.

Time dependency of the density matrix is given by [17]

$$\sigma(t) = \exp(-\mathrm{i}\mathcal{H}t)\sigma(0)\exp(\mathrm{i}\mathcal{H}t), \tag{1}$$

where $\mathcal{H}$ 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 [17]

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

evolutions of product operators under the r. f. pulse, chemical shift and spin-spin coupling Hamiltonians can be easily obtained [13, 17, 19]. For a weakly coupled spin system the spin-spin coupling Hamiltonian, which is the secular part of scalar coupling, is $\mathcal{H}_J = 2\pi J I_z S_z$. For example, the evolution of the $I_x S_x^2$ product operator under the spin-spin coupling Hamiltonian is obtained as

$$\begin{aligned}&I_x S_x^2 \xrightarrow{2\pi J I_z S_z t} \\ &\exp(-2\mathrm{i}\pi J I_z S_z t) I_x S_x^2 \exp(-2\mathrm{i}\pi J I_z S_z t) \\ &= I_x S_x^2 - (\mathrm{i}2\pi Jt)A(1) + \frac{(\mathrm{i}2\pi Jt)^2}{2!}A(2) \\ &- \frac{(\mathrm{i}2\pi Jt)^3}{3!}A(3) + \ldots,\end{aligned} \tag{3}$$

where

$$A(1) = [I_z S_z, I_x S_x^2], \tag{4}$$

$$A(2) = [I_z S_z, A(1)], \tag{5}$$

$$A(3) = [I_z S_z, A(2)]. \tag{6}$$

Table 1. Evolutions of 16 product operators under the spin-spin coupling Hamiltonian $(2\pi J I_z S_z)$ for the IS ($I = 1/2$; $S = 1$) spin system [17 – 19, 23]. $c_{nJ} = \cos(n\pi Jt)$ and $s_{nJ} = \sin(n\pi Jt)$.

Product operator	Evolution under the spin-spin coupling Hamiltonian
I_x	$I_y S_z s_{2J} + I_x(1 + S_z^2(c_{2J} - 1))$
I_y	$-I_x S_z s_{2J} + I_y(1 + S_z^2(c_{2J} - 1))$
S_x	$S_x c_J + 2I_z S_y s_J$
S_y	$S_y c_J - 2I_z S_x s_J$
$I_x S_z$	$I_x S_z c_{2J} + I_y S_z^2 s_{2J}$
$I_y S_z$	$I_y S_z c_{2J} - I_x S_z^2 s_{2J}$
$I_z S_x$	$I_z S_x c_J + \frac{1}{2} S_y s_J$
$I_z S_y$	$I_z S_y c_J - \frac{1}{2} S_x s_J$
$I_x S_x$	$I_x S_x c_J + I_y [S_x, S_z]_+ s_J$
$I_x S_y$	$I_x S_y c_J + I_y [S_y, S_z]_+ s_J$
$I_y S_x$	$I_y S_x c_J - I_x [S_x, S_z]_+ s_J$
$I_y S_y$	$I_y S_y c_J - I_x [S_y, S_z]_+ s_J$
$I_x S_z^2$	$I_x S_z^2 c_{2J} + I_y S_z s_{2J}$
$I_y S_z^2$	$I_y S_z^2 c_{2J} - I_x S_z s_{2J}$
$I_x S_y^2$	$I_x S_y^2 + \frac{1}{2} I_x S_z^2 (c_{2J} - 1) + \frac{1}{2} I_y S_z s_{2J}$
$I_y S_y^2$	$I_y S_y^2 + \frac{1}{2} I_y S_z^2 (c_{2J} - 1) - \frac{1}{2} I_x S_z s_{2J}$

Using the commutation relations,

$$\begin{aligned}I_x S_x^2 &\xrightarrow{2\pi J I_z S_z t} I_x S_x^2 - (\mathrm{i}2\pi Jt)\frac{\mathrm{i}}{2} I_y S_z \\ &+ \frac{(\mathrm{i}2\pi Jt)^2}{2!}\frac{1}{2} I_x S_z^2 - \frac{(\mathrm{i}2\pi Jt)^3}{3!}\frac{\mathrm{i}}{2} I_y S_z + \ldots\end{aligned} \tag{7}$$

is obtained. In order to get the generalized form for the evolution of the $I_x S_x^2$ product operator under the spin-spin coupling Hamiltonian, some addition and subtraction can be made as follows:

$$\begin{aligned}I_x S_x^2 &\xrightarrow{2\pi J I_z S_z t} I_x S_x^2 - (\mathrm{i}2\pi Jt)\frac{\mathrm{i}}{2} I_y S_z \\ &+ \frac{(\mathrm{i}2\pi Jt)^2}{2!}\frac{1}{2} I_x S_z^2 - \frac{(\mathrm{i}2\pi Jt)^3}{3!}\frac{\mathrm{i}}{2} I_y S_z + \ldots \\ &+ \frac{1}{2} I_x S_z^2 - \frac{1}{2} I_x S_z^2.\end{aligned} \tag{8}$$

Then, using sine and cosine series,

$$I_x S_x^2 \xrightarrow{2\pi J I_z S_z t} I_x S_x^2 + \frac{1}{2} I_x S_z^2 (c_{2J} - 1) + \frac{1}{2} I_y S_z s_{2J} \tag{9}$$

is obtained, where $c_{2J} = \cos(2\pi Jt)$ and $s_{2J} = \sin(2\pi Jt)$.

Evolutions of 16 product operators under the spin-spin coupling Hamiltonian for the IS ($I = 1/2$; $S = 1$) spin system are known and can be found in the literature [13, 17 – 19, 23]. They are presented in Table 1.

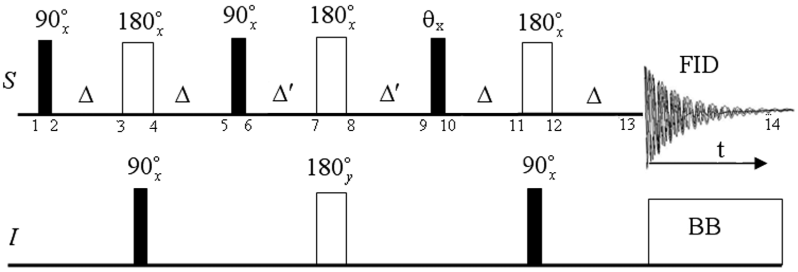

Fig. 1. Pulse sequence of MAXY NMR experiment.

Table 2. Evolutions of 18 product operators under the spin-spin coupling Hamiltonian ($2\pi JI_zS_z$) for the weakly coupled IS ($I = 1/2$; $S = 1$) spin system [24]. $c_{nJ} = \cos(n\pi Jt)$ and $s_{nJ} = \sin(n\pi Jt)$.

Product operator	Evolution under the spin-spin coupling Hamiltonian
S_x^2	$\frac{1}{2}S_x^2(c_{2J}+1) - \frac{1}{2}S_y^2(c_{2J}-1) + I_z[S_y,S_x]_+ s_{2J}$
S_y^2	$\frac{1}{2}S_y^2(c_{2J}+1) - \frac{1}{2}S_x^2(c_{2J}-1) - I_z[S_y,S_x]_+ s_{2J}$
$I_zS_x^2$	$\frac{1}{2}I_zS_x^2(c_{2J}+1) - \frac{1}{2}I_zS_y^2(c_{2J}-1) + \frac{1}{4}[S_y,S_x]_+ s_{2J}$
$I_zS_y^2$	$\frac{1}{2}I_zS_y^2(c_{2J}+1) - \frac{1}{2}I_zS_x^2(c_{2J}-1) - \frac{1}{4}[S_y,S_x]_+ s_{2J}$
$I_x[S_x,S_z]_+$	$I_x[S_x,S_z]_+ c_J + I_yS_xs_J$
$I_x[S_y,S_z]_+$	$I_x[S_y,S_z]_+ c_J + I_yS_ys_J$
$I_y[S_x,S_z]_+$	$I_y[S_x,S_z]_+ c_J - I_xS_xs_J$
$I_y[S_y,S_z]_+$	$I_y[S_y,S_z]_+ c_J - I_xS_ys_J$
$[S_x,S_z]_+$	$[S_x,S_z]_+ c_J + 2I_z[S_y,S_z]_+ s_J$
$[S_y,S_z]_+$	$[S_y,S_z]_+ c_J - 2I_z[S_x,S_z]_+ s_J$
$[S_x,S_y]_+$	$[S_x,S_y]_+ c_{2J} + 2I_z(S_y^2 - S_x^2)s_{2J}$
$I_z[S_x,S_z]_+$	$I_z[S_x,S_z]_+ c_J + \frac{1}{2}[S_y,S_z]_+ s_J$
$I_z[S_y,S_z]_+$	$I_z[S_y,S_z]_+ c_J - \frac{1}{2}[S_x,S_z]_+ s_J$
$I_z[S_x,S_y]_+$	$I_z[S_x,S_y]_+ c_{2J} + \frac{1}{2}(S_y^2 - S_x^2)s_{2J}$
$I_xS_x^2$	$I_xS_x^2 + \frac{1}{2}I_xS_z^2(c_{2J}-1) + \frac{1}{2}I_yS_zs_{2J}$
$I_yS_x^2$	$I_yS_x^2 + \frac{1}{2}I_yS_z^2(c_{2J}-1) - \frac{1}{2}I_xS_zs_{2J}$
$I_x[S_x,S_y]_+$	$I_x[S_x,S_y]_+$
$I_y[S_x,S_y]_+$	$I_y[S_x,S_y]_+$

Table 3. Evolutions of nine angular momentum operators under the chemical shift Hamiltonian ($\Omega_S S_z$) for $S = 1$ [24]. $c_{ns} = \cos(n\Omega_s t)$ and $s_{ns} = \sin(n\Omega_s t)$.

Angular momentum operator	Evolution under the chemical shift Hamiltonian
S_x	$S_xc_S + S_ys_S$
S_y	$S_yc_S - S_xs_S$
S_z	S_z
$[S_x,S_y]_+$	$[S_x,S_y]_+ c_{2S} + (S_y^2 - S_x^2)s_{2S}$
$[S_x,S_z]_+$	$[S_x,S_z]_+ c_S + [S_y,S_z]_+ s_S$
$[S_y,S_z]_+$	$[S_y,S_z]_+ c_S - [S_x,S_z]_+ s_S$
S_x^2	$\frac{1}{2}S_x^2(c_{2S}+1) - \frac{1}{2}S_y^2(c_{2S}-1) + \frac{1}{2}[S_x,S_y]_+ s_{2S}$
S_y^2	$\frac{1}{2}S_y^2(c_{2S}+1) - \frac{1}{2}S_x^2(c_{2S}-1) - \frac{1}{2}[S_x,S_y]_+ s_{2S}$
S_z^2	S_z^2

Table 4. Evolutions of nine angular momentum operators under the r. f. pulse Hamiltonian (θS_x) at axes of x for $S = 1$ [24]. $c_{n\theta} = \cos(n\theta)$ and $s_{n\theta} = \sin(n\theta)$.

Angular momentum operator	Evolution under the r. f. pulse Hamiltonian
S_x	S_x
S_y	$S_yc_\theta + S_zs_\theta$
S_z	$S_zc_\theta - S_ys_\theta$
$[S_x,S_y]_+$	$[S_x,S_y]_+ c_\theta + [S_x,S_z]_+ s_\theta$
$[S_x,S_z]_+$	$[S_x,S_z]_+ c_\theta - [S_x,S_y]_+ s_\theta$
$[S_y,S_z]_+$	$[S_y,S_z]_+ c_{2\theta} - (S_y^2 - S_z^2)s_{2\theta}$
S_x^2	S_x^2
S_y^2	$\frac{1}{2}S_y^2(c_{2\theta}+1) - \frac{1}{2}S_z^2(c_{2\theta}-1) + \frac{1}{2}[S_y,S_z]_+ s_{2\theta}$
S_z^2	$\frac{1}{2}S_z^2(c_{2\theta}+1) - \frac{1}{2}S_y^2(c_{2\theta}-1) - \frac{1}{2}[S_y,S_z]_+ s_{2\theta}$

The E, I_z, I_zS_z, S_z, S_z^2 and $I_zS_z^2$ product operators do not change under the spin-spin coupling Hamiltonian for the IS ($I = 1/2$; $S = 1$) spin system. Evolutions for the rest 18 product operators are obtained in our previous work [24]. They are presented in Table 2. For $S = 1$, evolutions of nine angular momentum operators under the chemical shift and the r. f. pulse Hamiltonians are given in Tables 3 and 4, respectively [24].

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

$$\langle I_y \rangle = \mathrm{Tr}[I_y \sigma(t)], \tag{10}$$

where $\sigma(t)$ is the density matrix operator calculated from (2) 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. In order to estimate the free induction decay (FID) signal of a multiple-pulse NMR experiment, the density matrix operator should be obtained at the end of the experiment.

3. Results

For the product operator description of the MAXY NMR experiment, the pulse sequence illustrated in Fig. 1 is used [6], where the density matrix operator at each stage of the experiment is labeled with numbers, and ^{13}C is treated as spin I and ^{2}H (D) as spin S. In

Spin system	Product operators (O)	$\sum_{i=1}^{n}\mathrm{Tr}[S_{iy}O]$
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
	$(S_{1y}S_{2j}^2S_{3k}^2+S_{1j}^2S_{2y}S_{3k}^2+S_{1j}^2S_{2k}^2S_{3y})-(S_{1y}S_{2j}^2S_{3k}^2+S_{1j}^2S_{2y}S_{3k}^2+S_{1j}^2S_{2k}^2)$	0

Table 5. Results of $\sum_{i=1}^{n}\mathrm{Tr}[S_{iy}O]$ calculations for some of the observable product operators for the IS_n ($I = 1/2$; $S = 1$; $n = 1$, 2, 3) spin systems ($j = x,y$ and $k = x,y$).

the pulse sequence, Δ is the coupling evolution delay, Δ' is a short compensation delay and t is the acquisition time. The optimum value of Δ is $1/(2J_{IS})$ for this 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-spin systems, to follow these processes by hand becomes too difficult. In order to overcome this problem, a computer program written in Mathematica is used. Thus, the density matrix operators at the end of the experiment are obtained for different spin systems such as IS, IS_2 and IS_3 ($I = 1/2$; $S = 1$).

3.1. IS Spin System

For the IS spin system,

$$\sigma_1 = S_z \tag{11}$$

is the density matrix operator at thermal equilibrium, and then we obtain

$$\sigma_2 = -S_y, \tag{12}$$

$$\sigma_3 = -2I_zS_x, \tag{13}$$

$$\sigma_4 = 2I_yS_x, \tag{14}$$

$$\sigma_5 = -2I_x[S_x,S_z]_+, \tag{15}$$

$$\sigma_6 = 2I_x[S_x,S_y]_+. \tag{16}$$

At this point all spins are excited to their possible highest heteronuclear multiple-quantum level. Then,

$$\sigma_{10} = 2I_x[S_x,S_y]_+c_\theta + 2I_x[S_x,S_z]_+s_\theta, \tag{17}$$

$$\sigma_{13} = -2I_x[S_x,S_y]_+c_\theta + S_ys_\theta, \tag{18}$$

$$\begin{aligned}\sigma_{14} = {}&-2I_x[S_x,S_y]_+c_\theta c_{2S} + S_ys_\theta c_S - S_xs_\theta s_S\\ &+ 2I_xS_x^2c_\theta s_{2S} - 2I_xS_y^2c_\theta s_{2S}\end{aligned} \tag{19}$$

are obtained. In the last density matrix operator, only the second term contributes to the signals, as acquisition is taken along y-axes for spin S. Now, it is necessary to obtain the $\sum_{i=1}^{n}\mathrm{Tr}[S_{iy}O]$ values of observable product operators indicated by O. For the IS_n ($I = 1/2$; $S = 1$; $n = 1$, 2, 3) spin systems, $\sum_{i=1}^{n}\mathrm{Tr}[S_{iy}O]$ values of all observable product operators are calculated by a computer program in Mathematica. The results are given in Table 5. Using Table 5,

$$M_y(t) \propto \langle S_y\rangle = \mathrm{Tr}[S_y\sigma_{14}] = 4s_\theta c_S \tag{20}$$

is obtained. In the above and following equations, $s_{n\theta} = \sin(n\theta)$, $c_{n\theta} = \cos(n\theta)$, $c_{nS} = \cos(n\Omega_St)$ and $s_{nS} = \sin(n\Omega_St)$.

3.2. IS$_2$ Spin System

For the IS_2 spin system, σ_1 is the density matrix operator at thermal equilibrium:

$$\sigma_1 = S_{1z} + S_{2z}. \tag{21}$$

22 observable terms are obtained at the end of the experiment:

$$\begin{aligned}\sigma_{14} = {}&\frac{1}{2}(2S_{1y} + 2S_{2y} - S_{1y}S_{2x}^2 - S_{1x}^2S_{2y}\\ &- S_{1y}S_{2y}^2 - S_{1y}^2S_{2y})s_\theta c_S\\ &- \frac{1}{2}(S_{1y}S_{2x}^2 + S_{1x}^2S_{2y} + S_{1y}S_{2y}^2 + S_{1y}^2S_{2y})c_{2\theta}s_\theta c_S\\ &- \frac{1}{2}(S_{1y}S_{2x}^2 - S_{1x}^2S_{2y} + S_{1y}S_{2y}^2 - S_{1y}^2S_{2y})s_\theta c_{2S}c_S\\ &- \frac{1}{2}(S_{1y}S_{2x}^2 - S_{1x}^2S_{2y} + S_{1y}S_{2y}^2 - S_{1y}^2S_{2y})\\ &\cdot c_{2\theta}s_\theta c_Sc_{2S}\end{aligned}$$

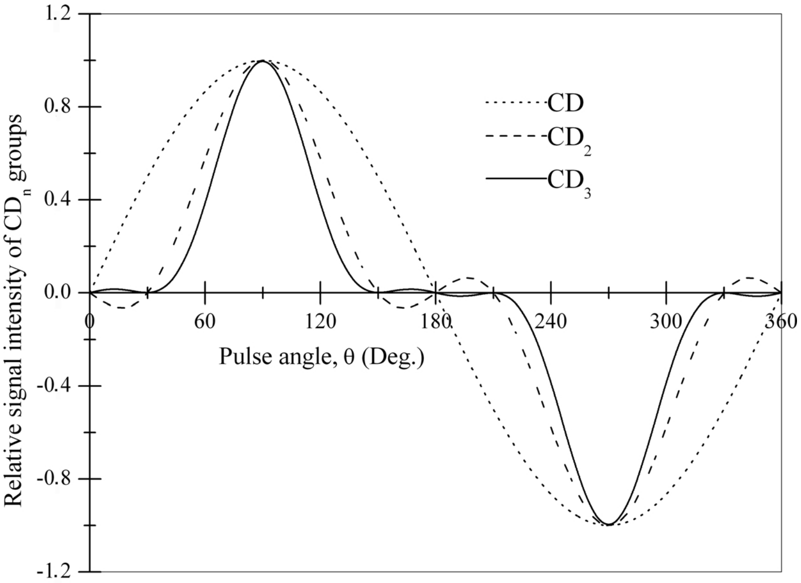

Fig. 2. Relative signal intensity of MAXY NMR for CD, CD_2 and CD_3 groups as function of the pulse angle θ.

$$-\frac{1}{2}(S_{1y}S_{2x}^2 - S_{1x}^2S_{2y} + S_{1y}S_{2y}^2 - S_{1y}^2S_{2y}) \cdot c_\theta s_{2\theta} s_S s_{2S}. \quad (22)$$

Using the trace values for the observable terms given in Table 5,

$$M_y(t) \propto \langle S_{1y}\rangle + \langle S_{2y}\rangle = \mathrm{Tr}[S_{1y}\sigma_{14}] + \mathrm{Tr}[S_{2y}\sigma_{14}], \quad (23)$$

$$\langle S_{1y}\rangle + \langle S_{2y}\rangle = 8(s_\theta c_S - 2c_{2\theta}s_\theta c_S) \quad (24)$$

is obtained.

3.3. IS_3 Spin System

For the IS_3 spin system, applying the same procedure, 188 observable terms are obtained at the end of the experiment by using the computer program. Using the trace values in Table 5,

$$\begin{aligned}&\langle S_{1y}\rangle + \langle S_{2y}\rangle + \langle S_{3y}\rangle \\ &= 12(s_\theta c_S - 4c_{2\theta}s_\theta c_S + 4c_{2\theta}^2 s_\theta c_S)\end{aligned} \quad (25)$$

is found.

4. Discussion

The $\sum_{i=1}^n \mathrm{Tr}[S_{iy}\sigma_{14}]$ values obtained in the preceding section for IS, IS_2 and IS_3 spin systems represent the FID signals of MAXY NMR for CD, CD_2 and CD_3 groups, respectively. The $\sum_{i=1}^n \mathrm{Tr}[S_{iy}\sigma_{14}]$ values for the IS_n ($I = 1/2$; $S = 1$; $n = 1$, 2, 3) spin systems can be generalized as

$$\sum_{i=1}^{n} \mathrm{Tr}[S_{iy}\sigma_{14}](\mathrm{CD}_n) = 4n(1-2c_{2\theta})^{n-1}s_\theta c_S. \quad (26)$$

The $\sum_{i=1}^n \mathrm{Tr}[S_{iy}\sigma_{14}]$ values can be normalized by multiplication with $6/(4n\mathrm{Tr}(E))$. Here E is the unity product operator for the corresponding spin system. Then, normalized values become as follows:

$$\mathrm{Tr}[S_y\sigma_{14}](\mathrm{CD}) = s_\theta c_S, \quad (27)$$

$$\sum_{i=1}^{2} \mathrm{Tr}[S_{iy}\sigma_{14}](\mathrm{CD}_2) = \frac{1}{3}(1-2c_{2\theta})s_\theta c_S, \quad (28)$$

$$\sum_{i=1}^{3} \mathrm{Tr}[S_{iy}\sigma_{14}](\mathrm{CD}_3) = \frac{1}{9}(1-2c_{2\theta})^2 s_\theta c_S. \quad (29)$$

Normalized $\sum_{i=1}^n \mathrm{Tr}[S_{iy}\sigma_{14}]$ values can be written in a generalized form of

$$\sum_{i=1}^{n} \mathrm{Tr}[S_{iy}\sigma_{14}](\mathrm{CD}_n) = \frac{1}{3^{n-1}}(1-2c_{2\theta})^{n-1}s_\theta c_S. \quad (30)$$

The plots of these generalized functions are presented in Figure 2. As seen in this figure, the relative signal intensities of CD, CD_2 and CD_3 groups vary as functions of θ. In the MAXY NMR experiment of CD_n groups, the real relative signal intensities found from (26) are given in Table 6. As seen in Table 6 and Fig. 2, when

Table 6. Real relative signal intensities of MAXY NMR experiment of CD$_n$ groups for several pulse angles θ.

Spin system	$\theta = 30°$ and $150°$	$\theta = 45°$ and $135°$	$\theta = 90°$
IS(CD)	$\frac{1}{2}$	0.707	1
IS_2(CD$_2$)	0	1.414	6
IS_3(CD$_3$)	0	2.121	27

the experiment is performed for the angle of 30°, only CD groups will be observed, giving a positive signal. For the angle 90°, all CD, CD$_2$ and CD$_3$ groups will give positive signals with the real relative signal intensities of $1:6:27$. When the pulse angle is 45°, real relative signal intensities of the CD, CD$_2$ and CD$_3$ groups will be $0.707:1.414:2.121$. By comparing their relative signal intensities obtained for the angles of 90° and 45°, one can easily identify CD$_2$ and CD$_3$ groups from each other. As a result, the MAXY NMR experiment can be used for sub-spectral editing of CD$_n$ groups. In deuterium labeling it is of interest to determine whether the methyl group is transferred as a whole, leading to ^{13}CD$_3$-containing compounds, or leading to ^{13}CD$_2$H- or ^{13}CDH$_2$-containing compounds [11, 33]. MAXY NMR of CD$_n$ groups can be also used for this purpose.

5. Conclusions

The product operator formalism became a useful technique for the analytical description of multiple-pulse and edited-pulse NMR experiments for weakly coupled spin systems including spin-1/2 and spin-1 [6, 13–24]. In this study, by using the product operator theory, an analytical description of the MAXY NMR experiment is presented for IS_n ($I = 1/2$; $S = 1$; $n = 1, 2, 3$) spin systems. Then, theoretical discussion and experimental suggestions are presented in order to distinguish CD, CD$_2$ and CD$_3$ groups from each other.

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