Analytical Descriptions of DEPT NMR Spectroscopy for $IS_n(I = 1, S = 1; n = 1, 2, 3, 4)$ Spin Systems

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A DEPT pulse sequence is well-known ^{13}C-detected, edited-pulse and cross polarization transfer NMR experiment which offers to selective detection capability of CH, CH$_2$ and CH$_3$ groups from each other. The product operator theory is widely used for analytical descriptions of the cross polarization transfer NMR experiments for weakly coupled spin systems. In this study, analytical descriptions of the DEPT NMR experiment have been presented for $IS_n(I = 1, S = 1; n = 1, 2, 3, 4)$ spin systems by using product operator theory. Then a theoretical discussion and experimental suggestions were made. It has been investigated that this experiment can be used to edit ^{14}N sub–spectra of partly or full deuterated ^{14}ND$_n$ (n=1, 2, 3, 4) groups.

Keywords: NMR; DEPT; Product operator theory; Deuterated nitrogen groups

1. INTRODUCTION

Although nitrogen–14 (^{14}N) isotope has a natural abundance of 99.64%, the magnetic moment is lower than ^{13}C $(\gamma_{^{13}\mathrm{C}}/\gamma_{^{14}\mathrm{N}} \cong 1.8)$, ^{1}H $(\gamma_{^{1}\mathrm{H}}/\gamma_{^{14}\mathrm{N}} \cong 7.0)$ and ^{2}H $(\gamma_{^{2}\mathrm{H}}/\gamma_{^{14}\mathrm{N}} \cong 2.2)$ nuclei, and it is a spin-1 isotope. Because of rapid quadrapolar relaxation spectral line–widths of ^{14}N NMR signals are very broad [1]. In order to overcome those unwanted circumstances, cross polarization transfers are made to increase signal–to–noise ratio in NMR. The cross polarization transfers from high magnetic moment of nuclei to low magnetic moment of nuclei are routine ways to increase sensitive enhancement for heteronuclear weakly coupled spin systems in liquid–state NMR experiments [2–5]. Last decade, the cross polarization transfers in solid compounds have also become a useful technique to increase the sensitivity of nuclei [6–9]. The well–known cross polarization transfer methods are Distortionless Enhancement by Polarization Transfer (DEPT) and Insensitive Nuclei Enhanced by Polarization Transfer (INEPT). The DEPT pulse sequence, which offers to selective detection capability of CH, CH$_2$, CH$_3$ groups from each other, is a ^{13}C-detected, edited-pulse and cross polarization transfer NMR experiment [10-12].

The product operator theory as a quantum mechanical method is widely used for analytical description of the cross polarization transfers on weakly coupled spin systems in liquid–state NMR having spin $-1/2$, spin-1 and spin–3/2 nuclei [10–19]. However, it has been proposed that product operator theory can be used as a new approach for analytical description of solid–state NMR experiments under magic angle spinning (MAS) conditions [20,21]. A complete product operator theory for IS ($I = 1/2$, S=1) spin system and application to DEPT–HMQC (Heteronuclear Multiple Quantum Correlation) NMR experiment has been presented in our previous study [22]. Analytical descriptions of INADEQATE (Incredible Natural Abundance Double Quantum Transfer Experiment) and DQC (Double Quantum Correlation) NMR experiments have been presented for two–spin–1 AX system by Chandrakumar and co–workers [12, 23, 24].

In this study, product operator descriptions of DEPT NMR experiment have been presented for weakly coupled IS_n (I=1, S=1, n=1, 2, 3, 4) spin systems. It has been found that the DEPT NMR experiment can be used to edit ^{14}N sub–spectra for ^{14}ND$_n$ groups if the experiment is performed for the suggested edited-pulse angles.

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 IS (I=1, S=1) spin system, 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 $\left(I_x^2 - I_y^2\right)$ [25]. Similarly, there are also nine Cartesian spin angular momentum operators for S=1. So, $9 \times 9 = 81$ product operators are obtained with direct products of these spin angular momentum operators for IS (I=1, S=1) spin system. Depending on the pulse experiment, $\left(I_x^2 - I_y^2\right)$ 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 $10 \times 10 = 100$ product operators for this spin system. In this study they are used in separated form.

In a liquid–state and solid–state (under MAS conditions) pulse NMR experiments of weakly coupled IS_n spin systems, the total Hamiltonian consists of r.f. pulse, chemical shift and spin–spin coupling Hamiltonians can be written as

$$\mathrm{H} = \Omega_I I_z + \sum_{i=1}^{n} \Omega_S S_{iz} + 2\pi \sum_{i=1}^{n} J_i I_z S_{iz}. \qquad (1)$$

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

$$\frac{d\sigma}{dt} = \frac{i}{\hbar}[\sigma, \mathrm{H}] \qquad (2)$$

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

TABLE 1. The evolution of some product operators under the weak spin-spin coupling Hamiltonian for *IS* (*I*=1, *S*=1) spin system where $I_{xz}=[I_x,I_z]_+$, $I_{yz}=[I_y,I_z]_+$, $I_{xy}=[I_x,I_y]_+$, $S_{xz}=[S_x,S_z]_+$, $S_{yz}=[S_y,S_z]_+$, $S_{xy}=[S_x,S_y]_+$and $S_{x-y}^2=\left(S_x^2-S_y^2\right)$ short notations are used.

Product Operator	The evolution under the H_J
$I_xS_x^2$	$\frac{1}{2}I_xS_x^2\left(c_{2J}+1\right)-\frac{1}{2}I_xS_y^2\left(c_{2J}-1\right)+\frac{1}{2}I_xS_z^2\left(c_{2J}-1\right)+\frac{1}{2}\left(I_{xz}S_{xy}+I_yS_z\right)s_{2J}$
$I_xS_y^2$	$\frac{1}{2}I_xS_y^2\left(c_{2J}+1\right)-\frac{1}{2}I_xS_x^2\left(c_{2J}-1\right)+\frac{1}{2}I_xS_z^2\left(c_{2J}-1\right)-\frac{1}{2}\left(I_{xz}S_{xy}-I_yS_z\right)s_{2J}$
$I_yS_x^2$	$\frac{1}{2}I_yS_x^2\left(c_{2J}+1\right)-\frac{1}{2}I_yS_y^2\left(c_{2J}-1\right)+\frac{1}{2}I_yS_z^2\left(c_{2J}-1\right)-\frac{1}{2}\left(I_{yz}S_{xy}-I_xS_z\right)s_{2J}$
$I_yS_y^2$	$\frac{1}{2}I_yS_y^2\left(c_{2J}+1\right)-\frac{1}{2}I_yS_x^2\left(c_{2J}-1\right)+\frac{1}{2}I_yS_z^2\left(c_{2J}-1\right)+\frac{1}{2}\left(I_{yz}S_{xy}+I_xS_z\right)s_{2J}$
I_xS_{xz}	$\frac{1}{2}I_xS_{xz}\left(c_{2J}+1\right)-\frac{1}{2}I_{yz}S_y\left(c_{2J}-1\right)+\frac{1}{2}\left(I_yS_x+I_{xz}S_{yz}\right)s_{2J}$
I_xS_{yz}	$\frac{1}{2}I_xS_{yz}\left(c_{2J}+1\right)+\frac{1}{2}I_{yz}S_x\left(c_{2J}-1\right)+\frac{1}{2}\left(I_yS_y-I_{xz}S_{xz}\right)s_{2J}$
I_yS_{xz}	$\frac{1}{2}I_yS_{xz}\left(c_{2J}+1\right)+\frac{1}{2}I_{xz}S_y\left(c_{2J}-1\right)-\frac{1}{2}\left(I_xS_x-I_{yz}S_{yz}\right)s_{2J}$
I_yS_{yz}	$\frac{1}{2}I_yS_{yz}\left(c_{2J}+1\right)-\frac{1}{2}I_{xz}S_x\left(c_{2J}-1\right)-\frac{1}{2}\left(I_xS_y+I_{yz}S_{xz}\right)s_{2J}$
$I_{xz}S_{xz}$	$\frac{1}{2}I_{xz}S_{xz}\left(c_{2J}+1\right)-\frac{1}{2}I_yS_y\left(c_{2J}-1\right)+\frac{1}{2}\left(I_xS_{yz}+I_{yz}S_x\right)s_{2J}$
$I_{xz}S_{yz}$	$\frac{1}{2}I_{xz}S_{yz}\left(c_{2J}+1\right)-\frac{1}{2}I_xS_y\left(c_{2J}-1\right)+\frac{1}{2}\left(I_{yz}S_y-I_xS_{xz}\right)s_{2J}$
$I_{xz}S_{xy}$	$I_{xz}S_{xy}c_{2J}-I_xS_{x-y}^2s_{2J}$
$I_{yz}S_{yz}$	$\frac{1}{2}I_{yz}S_{yz}\left(c_{2J}+1\right)-\frac{1}{2}I_xS_x\left(c_{2J}-1\right)-\frac{1}{2}\left(I_yS_{xz}+I_{xz}S_y\right)s_{2J}$
$I_{yz}S_{xy}$	$I_{yz}S_{xy}c_{2J}-I_yS_{x-y}^2s_{2J}$

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

where σ(0) is the density matrix at t=0. After employing the Hausdorff formula [15]

$$\exp\left(-i\mathrm{H}t\right)A\exp\left(i\mathrm{H}t\right)=A-\left(it\right)\left[\mathrm{H},A\right]+\frac{(it)^2}{2!}\left[\mathrm{H},\left[\mathrm{H},A\right]\right] -\frac{(it)^3}{3!}\left[\mathrm{H},\left[\mathrm{H},\left[\mathrm{H},A\right]\right]\right]+\cdots, \tag{4}$$

evolutions of the product operators under the r.f. pulse, chemical shift and spin-spin coupling Hamiltonians can be easily obtained. For $IS(I=1,S=1)$ spin system the evolutions of some product operators under the spin-spin coupling Hamiltonian ($\mathrm{H}_J=2\pi JI_zS_z$) are known and they are given in following equations [11, 12, 23, 24]:

$$S_x\xrightarrow{\mathrm{H}_Jt}S_x+I_z^2S_x\left(c_{2J}-1\right)+I_zS_ys_{2J} \tag{5a}$$

$$S_y\xrightarrow{\mathrm{H}_Jt}S_y+I_z^2S_y\left(c_{2J}-1\right)-I_zS_xs_{2J} \tag{5b}$$

$$I_xS_y\xrightarrow{\mathrm{H}_Jt}\frac{1}{2}I_xS_y\left(c_{2J}+1\right)+\frac{1}{2}I_{yz}S_{xz}\left(c_{2J}-1\right)+ \frac{1}{2}\left(I_yS_{yz}-I_{xz}S_x\right)s_{2J} \tag{5c}$$

$$I_xS_z\xrightarrow{\mathrm{H}_Jt}I_xS_zc_{2J}+I_yS_z^2s_{2J} \tag{5d}$$

$$I_xS_z^2\xrightarrow{\mathrm{H}_Jt}I_xS_z^2c_{2J}+I_yS_zs_{2J} \tag{5e}$$

$$I_yS_z\xrightarrow{\mathrm{H}_Jt}I_yS_zc_{2J}-I_xS_z^2s_{2J} \tag{5f}$$

$$I_yS_z^2\xrightarrow{\mathrm{H}_Jt}I_yS_z^2c_{2J}-I_xS_zs_{2J} \tag{5g}$$

$$I_zS_x^2\xrightarrow{\mathrm{H}_Jt}\tfrac{1}{2}I_zS_x^2\left(c_{4J}+1\right)-\tfrac{1}{2}I_zS_y^2\left(c_{4J}-1\right)+\tfrac{1}{2}I_z^2S_{xy}s_{4J} \tag{5h}$$

$$I_zS_y^2\xrightarrow{\mathrm{H}_Jt}\tfrac{1}{2}I_zS_y^2\left(c_{4J}+1\right)-\tfrac{1}{2}I_zS_x^2\left(c_{4J}-1\right)-\tfrac{1}{2}I_z^2S_{xy}s_{4J} \tag{5i}$$

In these equations $I_{yz}=[I_y,I_z]_+$, $I_{xz}=[I_x,I_z]_+$, $S_{xz}=[S_x,S_z]_+$, $S_{yz}=[S_y,S_z]_+$ and $S_{xy}=[S_x,S_y]_+$ short notations are used. Evolutions of the nine Cartesian spin angular momentum operators under the r.f. pulse and the chemical shift Hamiltonians have been presented in our previous works for spin–1 [22, 26]. For *IS* (*I*=1, *S*=1) spin system, evolutions of some product operators under the spin-spin coupling Hamiltonian are given in Table 1.

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

$$M_y(t)\propto\ \langle I_y\rangle\equiv\mathrm{Tr}\left[I_y\sigma(t)\right]. \tag{6}$$

Where $\sigma(t)$ is the density matrix operator calculated from Equation (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, density matrix operator should be obtained at the end of the experiment.

3. RESULTS

For the analytical descriptions of the DEPT NMR experiment for IS_n(I=1, S=1; n=1, 2, 3, 4) spin systems, the pulse sequence given in Fig. 1 is used. As shown in this figure, the density matrix operator at each stage of the experiment is labeled with numbers and ^{14}N is treated as spin I and ^{2}H as spin S.

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–1 systems, to follow these processes by hand becomes too difficult. In order to overcome this problem a home made computer program has been written in Mathematica which is very flexible for implementation and evolutions of the product operators under the Hamiltonians [27].

For the IS spin system, the density matrix operator at thermal equilibrium is $\sigma_0 = S_z$. Then, the evolutions of density matrices under the Hamiltonians for each labeled point are obtained:

$$\sigma_0 \xrightarrow{90^\circ_x(S)} \sigma_1 = -S_y, \tag{7}$$

$$\sigma_1 \xrightarrow{2\pi J I_z S_z \tau} \sigma_2 = -S_y + I_z^2 S_y + I_z^2 S_y c_{2J} + I_z S_x s_{2J}, \tag{8}$$

$$\sigma_2 \xrightarrow{180^\circ_x(S);90^\circ_x(I)} \sigma_3 = S_y - I_y^2 S_y + I_y^2 S_y c_{2J} - I_y S_x s_{2J}. \tag{9}$$

At above and following equations $c_{2J} = \cos(2\pi J\tau)$ and $s_{2J} = \sin(2\pi J\tau)$. In density matrix operator, only the terms with observable product operators are kept as they are the only ones that contribute to the signal on $y-$axis detection. In the last step

$$\begin{aligned}\sigma_7 = {} & \tfrac{1}{2} I_y S_z^2 \left(1 + c_{2J}\right) s_{2J}^2 s_\theta s_I + \tfrac{1}{4} I_y S_x^2 \left(1 + c_{2J}\right) s_{2J}^2 s_{2\theta} s_I \\ & + \tfrac{1}{4} I_y S_y^2 \left(1 - c_{2J}\right) s_{2J}^2 s_{2\theta} s_I - \tfrac{1}{4} I_y S_z^2 \left(1 + c_{2J}\right) s_{2J}^2 s_{2\theta} s_I\end{aligned} \tag{10}$$

is found. At above and following equations $s_{n\theta} = \sin(n\theta)$, $c_{n\theta} = \cos(n\theta)$ and $s_I = \sin(\Omega_I t)$. If the evolution period is set to $\tau = 1/(2J)$, there is not any observable term in Eq.(10). For the choice of the evolution period as $\tau = 1/(4J)$, we obtain following expression for spin-I:

$$\sigma_7 = \tfrac{1}{2} I_y S_z^2 s_\theta s_I + \tfrac{1}{4} I_y S_x^2 s_{2\theta} s_I + \tfrac{1}{4} I_y S_y^2 s_{2\theta} s_I - \tfrac{1}{4} I_y S_z^2 s_{2\theta} s_I \tag{11}$$

At any time during the experiment, the ensemble averaged expectation value of the spin angular momentum, $\langle I_y \rangle$, is proportional to the magnitude of the y–magnetization and

$$M_y(t) \propto \langle I_y \rangle = \mathrm{Tr}\left[I_y \sigma(t)\right] \tag{12}$$

is written. It represents the free induction decay (FID) signal of a multiple-pulse NMR on y-axis. $\mathrm{Tr}\left[I_y O\right]$ values of observable product operators, indicated by O, have been calculated by a home made computer program in Mathematica and results are given in Table 2 for IS_n (I=1, S=1; n=1, 2, 3, 4) spin systems. Using Table 2,

$$M_y(t) \propto \langle I_y \rangle (IS) = \mathrm{Tr}\left[I_y \sigma_7\right] = \left(2 s_\theta + s_{2\theta}\right) s_I \tag{13}$$

is obtained for IS spin system.

For the IS_2 spin system, the density matrix at the thermal equilibrium is $\sigma_0 = S_{1z} + S_{2z}$. At the end of the experiment forty–one observable terms are obtained as shown in following equation:

$$\begin{aligned}
\sigma_7 = {} & \tfrac{1}{2} \begin{pmatrix} I_y S_{1z}^2 + I_y S_{2z}^2 - \tfrac{1}{4} I_y S_{1z}^2 S_{2x}^2 - \tfrac{1}{4} I_y S_{1z}^2 S_{2y}^2 \\ -\tfrac{1}{4} I_y S_{1x}^2 S_{2z}^2 - \tfrac{1}{4} I_y S_{1y}^2 S_{2z}^2 - \tfrac{3}{2} I_y S_{1z}^2 S_{2z}^2 \end{pmatrix} s_\theta s_I \\
& + \tfrac{1}{4} \begin{pmatrix} I_y S_{1x}^2 + I_y S_{2x}^2 + I_y S_{1y}^2 + I_y S_{2y}^2 - I_y S_{1z}^2 - I_y S_{2z}^2 \\ -\tfrac{1}{2} I_y S_{1x}^2 S_{2x}^2 - \tfrac{1}{2} I_y S_{1y}^2 S_{2x}^2 - \tfrac{1}{2} I_y S_{1x}^2 S_{2y}^2 - \tfrac{1}{2} I_y S_{1y}^2 S_{2y}^2 \\ -\tfrac{1}{2} I_y S_{1z}^2 S_{2x}^2 - \tfrac{1}{2} I_y S_{1z}^2 S_{2y}^2 - \tfrac{1}{2} I_y S_{1x}^2 S_{2z}^2 - \tfrac{1}{2} I_y S_{1y}^2 S_{2z}^2 \\ +\tfrac{7}{2} I_y S_{1z}^2 S_{2z}^2 \end{pmatrix} s_{2\theta} s_I \\
& + \tfrac{1}{8} \left(I_y S_{1z}^2 S_{2x}^2 + I_y S_{1z}^2 S_{2y}^2 + I_y S_{1x}^2 S_{2z}^2 + I_y S_{1y}^2 S_{2z}^2 - 2 I_y S_{1z}^2 S_{2z}^2 \right) c_{2\theta} s_\theta s_I \\
& + \tfrac{1}{4} \left(I_y S_{1z}^2 S_{2x}^2 + I_y S_{1z}^2 S_{2y}^2 + I_y S_{1x}^2 S_{2z}^2 + I_y S_{1y}^2 S_{2z}^2 - 2 I_y S_{1z}^2 S_{2z}^2 \right) c_\theta s_{2\theta} s_I \\
& + \tfrac{1}{8} \begin{pmatrix} I_y S_{1x}^2 S_{2x}^2 + I_y S_{1y}^2 S_{2x}^2 + I_y S_{1x}^2 S_{2y}^2 + I_y S_{1y}^2 S_{2y}^2 + I_y S_{1z}^2 S_{2z}^2 \\ -I_y S_{1z}^2 S_{2x}^2 - I_y S_{1z}^2 S_{2y}^2 - I_y S_{1x}^2 S_{2z}^2 - I_y S_{1y}^2 S_{2z}^2 \end{pmatrix} c_{2\theta} s_{2\theta} s_I
\end{aligned} \tag{14}$$

Using the Trace values in Table 2;

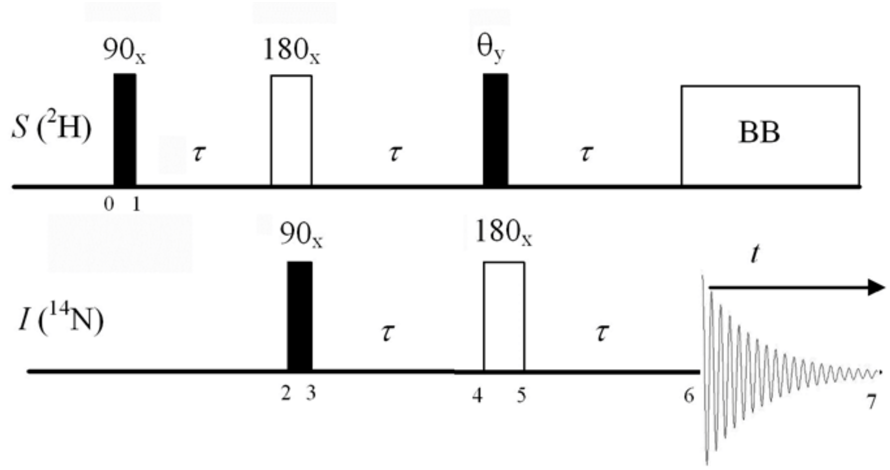

FIG. 1: DEPT NMR pulse sequence for the cross polarization transfer from ^{2}H (S=1) nuclei to ^{14}N (I=1) nuclei. τ : Evolution period for optimum polarization transfer, t: acquisition period, BB: Broad Band for decouple.

TABLE 2. Results of the Tr $[I_yO]$ calculations for some of the observable product operators in IS_n (I=1, S=1; n=1, 2, 3, 4) spin systems $(i = x,y,z;\ j = x,y,z;\ k = x,y,z \text{ and } l = x,y,z)$.

Spin system	Operator (O)	Tr $[I_yO]$
IS	$I_yS_i^2$	4
IS_2	$I_yS_{1i}^2\,;\,I_yS_{2j}^2$	12
	$I_yS_{1i}^2S_{2j}^2$	8
IS_3	$I_yS_{1i}^2\,;\,I_yS_{2j}^2\,;\,I_yS_{3k}^2$	36
	$I_yS_{1i}^2S_{2j}^2\,;\,I_yS_{1i}^2S_{3k}^2\,;\,I_yS_{2j}^2S_{3k}^2$	24
	$I_yS_{1i}^2S_{2j}^2S_{3k}^2$	16
IS_4	$I_yS_{1i}^2\,;\,I_yS_{2j}^2\,;\,I_yS_{3k}^2\,;\,I_yS_{4l}^2$	108
	$I_yS_{1i}^2S_{2j}^2\,;\,I_yS_{1i}^2S_{3k}^2\,;\,I_yS_{1i}^2S_{4l}^2\,;\,I_yS_{2j}^2S_{3k}^2\,;\,I_yS_{2j}^2S_{4l}^2\,;\,I_yS_{3k}^2S_{4l}^2$	72
	$I_yS_{1i}^2S_{2j}^2S_{3k}^2\,;\,I_yS_{1i}^2S_{2j}^2S_{4l}^2\,;\,I_yS_{1i}^2S_{3k}^2S_{4l}^2\,;\,I_yS_{2j}^2S_{3k}^2S_{4l}^2$	48
	$I_yS_{1i}^2S_{2j}^2S_{3k}^2S_{4l}^2$	32

$$M_y(t) \propto \langle I_y\rangle\,(IS_2) = \mathrm{Tr}\,[I_y\sigma_7] = (1+4c_\theta+c_{2\theta})\,(2s_\theta+s_{2\theta})\,s_I \tag{15}$$

is found for the IS_2 spin system.

Applying the same procedure for the IS_3 and IS_4spin systems, as one can guess huge amount of observable terms are obtained at the end of the DEPT experiment by using the computer program. Then, replacing the Trace values of observable terms in Table 2 we obtain

$$M_y(t) \propto \langle I_y\rangle\,(IS_3) = \frac{3}{4}\,(1+4c_\theta+c_{2\theta})^2\,(2s_\theta+s_{2\theta})\,s_I, \tag{16}$$

$$M_y(t) \propto \langle I_y\rangle\,(IS_4) = \frac{1}{2}\,(1+4c_\theta+c_{2\theta})^3\,(2s_\theta+s_{2\theta})\,s_I. \tag{17}$$

4. DISCUSSION

$\mathrm{Tr}\,[I_y\sigma_7]$ values obtained in Section 3 for IS, IS_2, $IS_3$and IS_4 spin systems represent FID signals of DEPT NMR experiment for ^{14}ND, ^{14}ND$_2$, ^{14}ND$_3$ and ^{14}ND$_4$ groups, respectively. These $\mathrm{Tr}\,[I_y\sigma_7]$ values for ^{14}ND$_n$ (n=1, 2, 3, 4) spin systems can be generalized as following

$$\langle I_y\rangle\,\left(^{14}\mathrm{ND}_n\right) = \frac{n}{2^{n-1}}\,(1+4c_\theta+c_{2\theta})^{n-1}\,(2s_\theta+s_{2\theta})\,s_I. \tag{18}$$

The $\mathrm{Tr}\,[I_y\sigma_7]$ values can be normalized by multiplication with $3/(\mathrm{Tr}(E))$. Here E is the unity product operator for the corresponding spin system. Then, the normalized FID values become as follows:

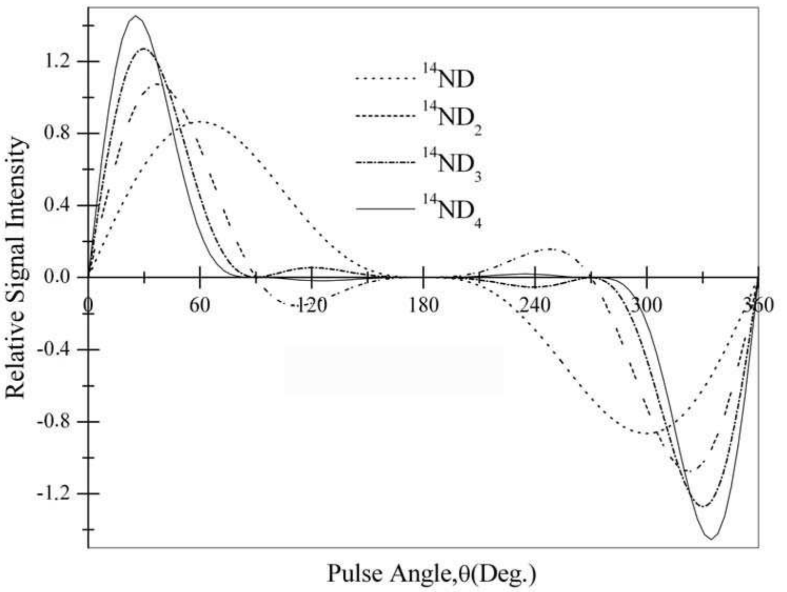

FIG. 2: The relative signal intensity plots of DEPT NMR spectroscopy for ^{14}ND$_n$ groups as functions of θ.

$$\langle I_y\rangle\left(^{14}\mathrm{ND}\right)=\frac{1}{3}\left(2s_\theta+s_{2\theta}\right)s_I, \tag{19}$$

$$\langle I_y\rangle\left(^{14}\mathrm{ND}_2\right)=\frac{1}{9}\left(1+4c_\theta+c_{2\theta}\right)\left(2s_\theta+s_{2\theta}\right)s_I, \tag{20}$$

$$\langle I_y\rangle\left(^{14}\mathrm{ND}_3\right)=\frac{1}{36}\left(1+4c_\theta+c_{2\theta}\right)^2\left(2s_\theta+s_{2\theta}\right)s_I, \tag{21}$$

$$\langle I_y\rangle\left(^{14}\mathrm{ND}_4\right)=\frac{1}{162}\left(1+4c_\theta+c_{2\theta}\right)^3\left(2s_\theta+s_{2\theta}\right)s_I. \tag{22}$$

These normalized $\mathrm{Tr}\left[I_y\sigma_7\right]$ values can be also written in a generalized form as

$$\langle I_y\rangle\left(^{14}\mathrm{ND}_n\right)=\frac{n}{2^{n-1}3^n}\left(1+4c_\theta+c_{2\theta}\right)^{n-1}\left(2s_\theta+s_{2\theta}\right)s_I. \tag{23}$$

TABLE 3. The real relative signal intensities of DEPT NMR experiment of ^{14}ND$_n$ groups for several pulse angles of θ.

Spin System	$\theta=60^\circ$	$\theta=90^\circ$	$\theta=120^\circ$
$IS(^{14}\mathrm{ND})$	$\frac{3\sqrt{3}}{2}$	2	$\frac{\sqrt{3}}{2}$
$IS_2(^{14}\mathrm{ND}_2)$	$\frac{15\sqrt{3}}{4}$	0	$-\frac{3\sqrt{3}}{4}$
$IS_3(^{14}\mathrm{ND}_3)$	$\frac{225\sqrt{3}}{32}$	0	$\frac{27\sqrt{3}}{32}$
$IS_4(^{14}\mathrm{ND}_4)$	$\frac{375\sqrt{3}}{32}$	0	$-\frac{27\sqrt{3}}{32}$

The plots of the normalized FID functions are presented in Fig. 2. As seen in this Figure, the relative signal intensities of ^{14}ND, ^{14}ND$_2$, ^{14}ND$_3$ and ^{14}ND$_4$ groups vary as functions of θ. The real relative signal intensities can be found from Eq. (18) for ^{14}ND, ^{14}ND$_2$, ^{14}ND$_3$ and ^{14}ND$_4$ groups for several pulse angles which are given in Table 3. As seen in Fig. 2 and Table 3, when the experiment is performed for the angle of 60 °, all groups will give positive signal. For the pulse angle of 90 °, only ^{14}ND groups will be observed giving positive signal. For the pulse angle of 120 °, ^{14}ND and ^{14}ND$_3$ groups will give positive signals and ^{14}ND$_2$ and ^{14}ND$_4$ groups will give negative signals. ^{14}ND$_3$ group can be easily separated by comparison of spectra for θ=90 ° and θ=120 °. To selectively enhance of ^{14}ND$_2$ and ^{14}ND$_4$ groups, one might collect FIDs at θ=60 ° and θ=120 ° and take the linear combinations:

$$I_{\mathrm{ND}_2}=\mathrm{FID}(60^\circ)+5\,\mathrm{FID}(120^\circ)=0,$$

$$I_{\mathrm{ND}_4}=\mathrm{FID}(60^\circ)+5\,\mathrm{FID}(120^\circ)=\frac{15\sqrt{3}}{2}.$$

According to these results, deuterated nitrogen groups can be separated from each other if the experiment is performed for the angles of 60 °, 90 ° and 120 °.

Studies on full or partially deuterated nitrogen molecules by using liquid- and solid-state NMR spectroscopies offer new features in biological and material science [28–32]. In determination of deuteration degree, it is of interest to determine whether the ammonium ions (^{14}NH$_4^+$) are transferred as a whole leading to ^{14}ND$_4^+$ or partially deuterated ^{14}ND$_3$H$^+$, ^{14}ND$_2$H$_2^+$ and ^{14}NDH$_3^+$ groups. In addition, a sample can contain some deuterated nitrogen groups such as

$^{14}ND_4-$, $^{14}ND_3^+-$, $^{14}ND_2H^+-$, $^{14}ND_2-$ or $^{14}NDH-$ containing molecules. As a result, a DEPT NMR experiment can be employed for determination of deuteration degree of nitrogen groups in molecules if one uses the suggested angels found in this study.

5. CONCLUSION

The cross polarization transfers between nuclei became a useful technique to increase NMR signal intensity in both liquid– and solid–state NMR experiments. In this study, analytical descriptions of DEPT NMR experiment have been presented for weakly coupled IS_n (I=1; S=1; n=1, 2, 3, 4) spin systems by using product operator theory. Thus a theoretical discussion and experimental suggestions for DEPT NMR spectroscopy have been performed in order to edit ^{14}N signals of ^{14}ND, $^{14}ND_2$, $^{14}ND_3$ and $^{14}ND_4$ groups.

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