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A THEORETICAL INVESTIGATION OF PENDANT ^{13}C NMR SPECTROSCOPY FOR CD$_n$ GROUPS

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Abstract: Polarization enhancement nurtured during attached nucleus testing (PENDANT) NMR spectroscopy gives signals of quaternary carbon atoms in addition to the signals of CH, CH$_2$ and CH$_3$ groups. In this study, analytical description of PENDANT NMR spectroscopy for CD$_n$ (IS_n, I=½, S=1, n=0, 1, 2, 3) spin systems are presented by using the product operator theory. Simulation results of PENDANT NMR spectroscopy are also presented for CD$_n$ (IS_n, I=½, S=1, n=0, 1, 2, 3) spin systems. Theoretical results are found to be in exact agreement with the simulation results.

Key Words: PENDANT, ^{13}C NMR, Product Operator Theory.

CD$_n$ GRUPLARI İÇİN PENDANT ^{13}C ÇMR SPEKTROSKOPİSİNİN KURAMSAL İNCELENMESİ

Özet: PENDANT (Polarization enhancement nurtured during attached nucleus testing) ÇMR spektroskopisi, CH, CH$_2$ ve CH$_3$ gruplarının sinyallerine ek olarak, kuarterner karbon atomlarının sinyallerini de vermektedir. Bu çalışmada, PENDANT ÇMR spektroskopisinin CD$_n$ (IS_n, I=½, S=1, n=0, 1, 2, 3) spin sistemleri için analitik tanımlanması, çarpım operatör kuramı kullanılarak sunulmaktadır. PENDANT ÇMR spektroskopisinin benzetişim sonuçları da, CD$_n$ (IS_n, I=½, S=1, n=0, 1, 2, 3) spin sistemleri için verilmiştir. Kuramsal sonuçların, benzetişim sonuçlarıyla tam olarak uyuştukları bulunmuştur.

Anahtar Kelimeler: PENDANT, ^{13}C ÇMR, Çarpım Operatör Kuramı.

INTRODUCTION

There exist a large number of one and two dimensional NMR techniques for ^{13}C spectral editing such as APT, SEMUT, DEPT, and PENDANT. The PENDANT NMR spectroscopy gives also the signals of quaternary carbon atoms in addition to the signals of CH, CH$_2$ and CH$_3$ groups (HOMOR & PERRY 1994, 1995). As NMR is a quantum mechanical phenomenon, nuclear spin systems can be treated by quantum mechanical methods. The product operator formalism, as a simple quantum mechanical method, is widely used for the analytical description of multiple pulse NMR experiments on weakly coupled spin systems in liquids (e.g. CHANDRAKUMAR 1984, GENÇTEN & KOKSAL 1997, GENÇTEN et al. 1998, GENÇTEN et al. 2001, GENÇTEN & ŞAKA 2006, PODKORYTOV 1997, SϕRENSEN et al. 1983).

A theoretical and experimental investigation of PENDANT ^{13}C NMR spectroscopy for CH$_n$ groups are presented elsewhere (GENÇTEN et al. 2006). First in this study, by using the product operator theory, analytical description of PENDANT NMR spectroscopy for CD$_n$ (IS_n, I=½, S=1) spin systems are performed. Then simulation results of PENDANT NMR spectroscopy are also presented for CD$_n$ (IS_n, I=½, S=1) spin systems. Theoretical results are found to be in exact agreement with the simulation results.

THEORY

The product operator theory is the expansion of the density matrix operator in terms of matrix representation of angular momentum operators for individual spins. For IS (I=½, S=1) spin system, four Cartesian spin angular momentum operators for I=½; 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 (ALLARD & HÄRD 2001). So, $4\times 9=36$ product operators are obtained with direct products of these angular momentum operators for IS (I=½, S=1) spin systems.

Time dependency of the density matrix is given by (CHANDRAKUMAR & SUBRAMANIAN 1987)

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

Where $\mathcal{H}$ is the total Hamiltonian which consists of 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 (CHANDRAKUMAR & SUBRAMANIAN 1987)

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

evolutions of product operators under the r.f pulse, chemical shift and spin–spin coupling Hamiltonians can be easily obtained (CHANDRAKUMAR & SUBRAMANIAN 1987, ERNST et al. 1987, SϕRENSEN et al. 1983). A complete product operator theory for IS (I=½, S=1) spin system and its application to DEPT–HMQC NMR experiment is presented recently (GENÇTEN & ŞAKA 2006), where the evolutions of all product operators under these Hamiltonians are obtained. At any time during the experiment, the ensemble averaged expectation value of the spin angular momentum, e.g. for I_y, is

$$\langle I_y \rangle = \mathrm{Tr}[I_y \sigma(t)] \ , \tag{3}$$

where $\sigma(t)$ is the density matrix operator calculated from Equation (1) at any time. As $\langle I_y \rangle$ is proportional to the magnitude of the *y*–magnetization, it represents the signal detected on *y*-axis. In order to estimate the free induction decay (FID) signal of a multiple–pulse NMR experiment, density matrix operator should be obtained at the end of the experiment.

RESULTS AND DISCUSSION

a) Product Operator Theory

In this section of the study, by using the product operator theory, analytical description of PENDANT NMR spectroscopy for IS_n spin systems (CD_n groups) will be presented. The pulse sequence employed for PENDANT is illustrated in Figure 1. Optimum value of d_2 is ($1/_{4J}$) (BRAUN et al. 1998). Density matrix operator at each stage of the experiment is labeled with numbers. In this study, ^{13}C is treated as spin *I* and ^{2}D as spin *S*. Then CD_n groups can be represented as IS_n (I=½; S=1; n=0,1,2,3) spin systems. The evolutions of density matrix operators during the experiment were calculated using a program written in Mathematica (WOLFRAM 1996).

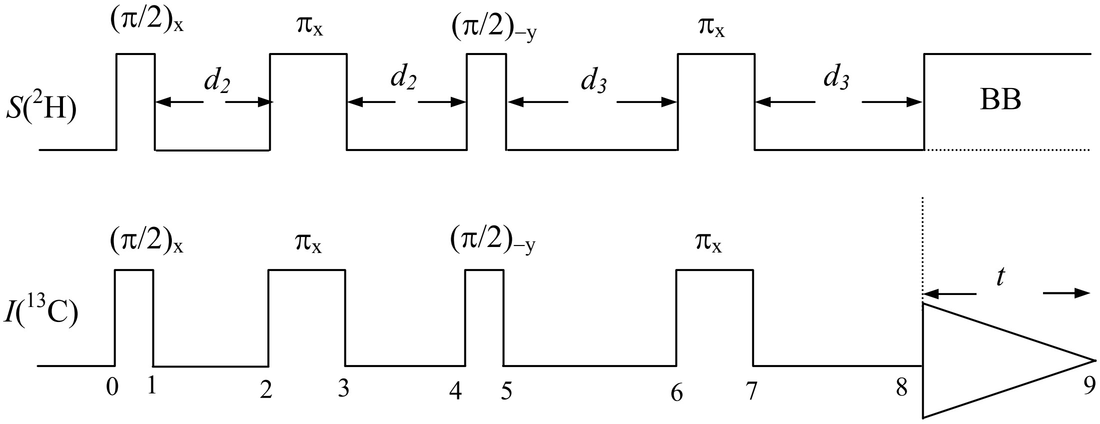

Figure 1. The pulse sequence for ^{13}C PENDANT NMR spectroscopy (HOMOR & PERRY 1994, BRAUN et al. 1998). BB: Broad band.

For *IS* spin system, σ_o is the density matrix operator at thermal equilibrium and $\sigma_o = S_z$. The pulse sequence in Figure 1 (where $d_2 = \frac{1}{4J}$) obviously leads to the following density matrices for each labeled point:

$$\sigma_1 = -S_y , \tag{4}$$

$$\sigma_5 = 2I_x S_z \tag{5}$$

$$\sigma_6 = 2I_x S_z \cos(2\pi J d_3) + 2I_y S_z^2 \sin(2\pi J d_3) \tag{6}$$

$$\sigma_8 = -2I_x S_z c_{4J} - 2I_y S_z^2 s_{4J} \tag{7}$$

In this and in the following equations $c_{nJ} = \cos(n\pi J d_3)$ and $s_{nJ} = \sin(n\pi J d_3)$. It is assumed that during d_2 and d_3 relaxation and evolution under chemical shift do not exist. The chemical shift evolution takes place only during t. As the density operator at point 8 in Figure 1 tells everything, the calculation is stopped at this point. For *IS* spin system only the observable $I_y S_z^2$ terms are kept in σ_8. In the case of detection on the *y*–axis, magnetization along the *y*–axis is proportional to $\langle I_y \rangle$ and we have

$$M_y(t) \alpha \langle I_y \rangle = \mathrm{Tr}(I_y \sigma_8) = -2S_{4J}\,\mathrm{Tr}(I_y\, I_y S_z^2). \tag{8}$$

Results of the $\mathrm{Tr}(I_y\, O)$ calculations for some of the observable product operators in *IS*$_n$ spin systems (*I*=½; *S*=1; n=1, 2, 3) are given in Table 1. Using these trace values in

Table 1;

$$\langle I_y \rangle (IS) = -2S_{4J} \tag{9}$$

is obtained.

Table 1. Results of the $\mathrm{Tr}(I_y\, O)$ calculations for some of the observable product operators in *IS*$_n$ spin systems (*I*=½; *S*=1; n=1, 2, 3).

Spin System	Product Operator (*O*)	$\mathrm{Tr}(I_y\, O)$
IS	$I_y S_z^2$	1
IS$_2$	$I_y(S_{1z}^2 + S_{2z}^2)$	6
	$I_y S_{1z}^2 S_{2z}^2$	2
IS$_3$	$I_y(S_{1z}^2 + S_{2z}^2 + S_{3z}^2)$	27
	$I_y(S_{1z}^2 S_{2z}^2 + S_{1z}^2 S_{3z}^2 + S_{2z}^2 S_{3z}^2)$	18
	$I_y S_{1z}^2 S_{2z}^2 S_{3z}^2$	4

For *IS*$_2$ spin system the density matrix operator at thermal equilibrium is

$$\sigma_o = S_{1z} + S_{2z}.$$

With the same pulse sequence we obtain

$$\begin{aligned}\sigma_8 = {} & -4I_y S_{1z}^2 c_{2J} s_{2J} - 4I_y S_{2z}^2 c_{2J} s_{2J} + 8I_y S_{1z}^2 S_{2z}^2 c_{2J} s_{2J} \\ & -4I_y S_{1z}^2 S_{2z}^2 c_{2J}^3 s_{2J} - 4I_y S_{1z}^2 S_{2z}^2 c_{2J} c_{4J} s_{2J} + 4I_y S_{1z}^2 S_{2z}^2 c_{2J} s_{2J}^3\end{aligned}. \tag{10}$$

Using trace values in Table 1

$$\langle I_y \rangle (IS_2) = -4(s_{8J} + s_{4J}) \tag{11}$$

is obtained.

Applying the same procedure for IS_3 spin system we obtain

$$\langle I_y \rangle (IS_3) = -6(s_{12J} + 2s_{8J} + 2s_{4J}). \tag{12}$$

For IS, IS_2 and IS_3 spin systems, $\langle I_y \rangle = \mathrm{Tr}(I_y \sigma_8)$ values represent the FID signals of PENDANT ^{13}C NMR spectroscopy for CD, CD_2 and CD_3 groups, respectively. $\langle I_y \rangle = \mathrm{Tr}(I_y \sigma_8)$ values can be normalized by multiplication with $6/\mathrm{Tr}(E)$. Here E is the unity product operator for corresponding spin system. $\langle I_y \rangle = \mathrm{Tr}(I_y \sigma_8)$ values and their normalized forms are given in Table 2.

Table 2. $\langle I_y \rangle = \mathrm{Tr}(I_y \sigma_8)$ values and their normalized forms for CD_n (IS_n Spin System I=½, S=1) groups.

Spin System	$\langle I_y \rangle = \mathrm{Tr}(I_y \sigma_8)$	$\frac{6}{\mathrm{Tr}(E)}$	$\frac{6}{\mathrm{Tr}(E)}\mathrm{Tr}(I_y \sigma_8)$
CD(IS)	$-2\sin(4\pi J d_3)$	1	$-2\sin(4\pi J d_3)$
CD_2(IS_2)	$-4[\sin(8\pi J d_3)+\sin(4\pi J d_3)]$	1/3	$-\frac{4}{3}[\sin(8\pi J d_3)+\sin(4\pi J d_3)]$
CD_3(IS_3)	$-6\begin{bmatrix}\sin(12\pi J d_3)+ \\ 2\sin(8\pi J d_3)+2\sin(4\pi J d_3)\end{bmatrix}$	2/9	$-2\begin{bmatrix}\sin(12\pi J d_3)+ \\ 2\sin(8\pi J d_3)+2\sin(4\pi J d_3)\end{bmatrix}$

The relative signal intensity plots of PENDANT ^{13}C NMR spectroscopy for CD, CD_2 and CD_3 groups are given in Figure 2 as a function of time, d_3. In these plots maximum relative signal intensities normalized to 1. As one can see from these plots, PENDANT experiment for CD_n groups can be performed for different d_3 values and then the signals of C, CD, CD_2 and CD_3 groups can be identified. Quaternary carbons will always give negative signal, as they do not depend on the time, d_3. The relative signal intensities of PENDANT NMR spectroscopy of CD_n groups for different d_3 values obtained from Figure 2 are given in Table 3. As seen in Figure 2 and Table 3, when the experiment is performed for d_3=3/(10J) value, CD and CD_3 groups will give positive signals with the relative signal intensities of 0.59 and 0.14, respectively. On the other hand, for d_3=3/(10J) value, CD_2 groups will give negative signal with the relative intensity of 0.21. It is obvious from Table 3 that the difference spectrum for d_3=7/(16J) and d_3=5/(16J) values will give only positive signals of CD_2 and CD_3 groups with a relative intensity of 1.15 and 0.49, respectively.

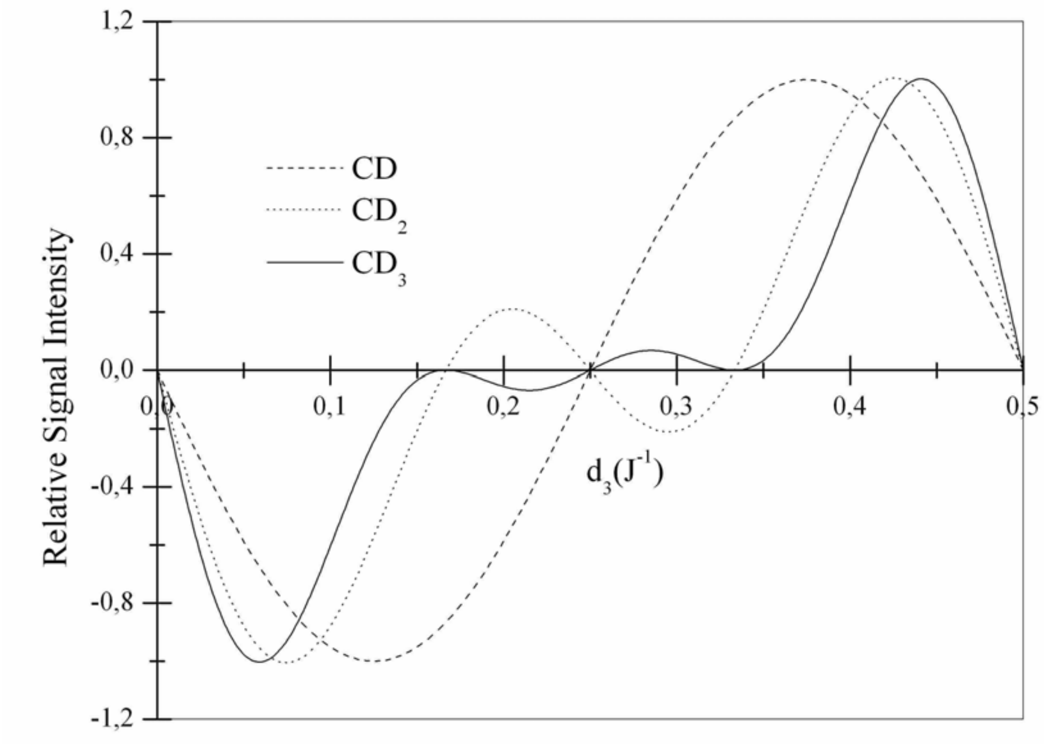

Figure 2. The relative signal intensity plots for ^{13}C PENDANT NMR spectroscopy for CD, CD_2 and CD_3 groups.

Table 3. The relative signal intensities of PENDANT ^{13}C NMR experiment of CD_n groups for different d_3 values.

Group	d_3=3/(10*J*)	d_3=5/(16*J*)	d_3=7/(16*J*)
C	−1	−1	−1
CD	0.59	0.70	0.70
CD_2	−0.21	−0.17	0.98
CD_3	0.14	0.10	0.59

b) Simulation

The simulations of PENDANT NMR spectroscopy were performed by using NMR-SIM program. In simulation an artificial spin system was established with the following chemical shift values: C(60ppm), CD(50ppm), CD_2(40ppm) and CD_3(30ppm). The simulated PENDANT ^{13}C NMR spectrum is shown in Figure 3(a) for d_3=3/(10*J*). As mentioned in section (a), in the simulated spectrum for d_3=3/(10*J*), CD and CD_2 groups have positive signals while quaternary carbon and CD_2 group are giving negative signals. In Figure 3(b), simulated difference spectrum for d_3=7/(16*J*) and d_3=5/(16*J*) values are presented. In the difference spectrum CD_2 and CD_3 groups with positive signals are observed. Simulated spectra are in exact agreement with theoretical results presented in section (a).

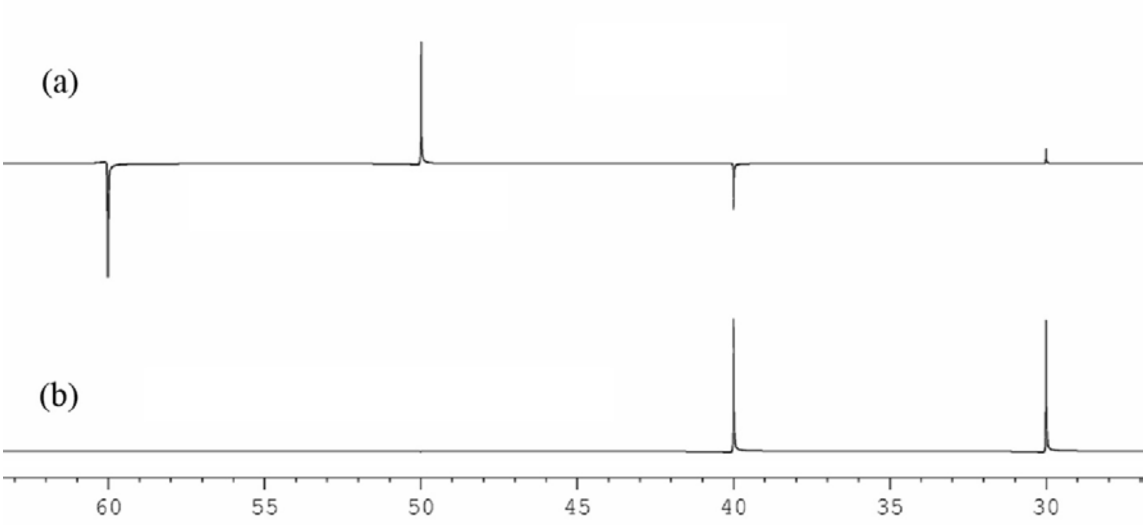

Figure 3. Simulated PENDANT ^{13}C NMR spectra: (a) d_3=3/(10J) and (b) difference spectrum for d_3=7/(16J) and d_3=5/(16J).

CONCLUSION

Product operator theory and simulation of PENDANT ^{13}C NMR spectroscopy for CD_n (IS_n, I=½, S=1) spin systems are investigated. In order to identify C, CD, CD_2, and CD_3 groups from each other, PENDANT ^{13}C NMR experiment can be performed for 3/(10J), 5/(16J) and 7/(16J) values of d_3. For any d_3 value quaternary carbons will always give negative signals. For d_3=3/(10J), while CD_2 groups are giving negative signals, CD and CD_3 groups give positive signals. The difference spectrum for d_3=7/(16J) and d_3=5/(16J) values will give only positive signals of CD_2 and CD_3 groups. These experimental suggestions made from the theoretical results are found to be in exact agreement with the simulated spectra.

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