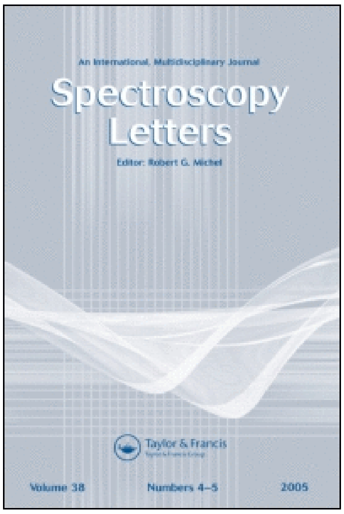

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A PRODUCT OPERATOR THEORY OF ^{13}C SPIN-ECHO J-MODULATION NMR SPECTROSCOPY FOR CD_n (n = 1,2,3) GROUPS

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ABSTRACT

Product operator formalism is widely used for analytical description of multiple–pulse NMR experiments for a weakly coupled spin systems. ^{13}C spin-echo J-modulation NMR spectroscopy for CH_n ve CD_n groups is used for identification of different carbon groups. In this study, by using the product operator technique, the analytical description of ^{13}C spin-echo J-modulation NMR spectroscopy for CD_n (n = 1,2,3) groups is presented and the experimental identifications of ^{13}C NMR signals of CD_3, CD_2 and CD groups and also quaternary carbons are discussed.

INTRODUCTION

In order to analyze multiple–pulse NMR experiments applied to large spin systems, a quantum mechanical approach has to be used. In analytical description of multiple–pulse 1D and 2D NMR experiments, the product operator formalism is widely used for weakly coupled spin systems[1–7]. Spin-echo J-modulation is a well known and widely applied technique, *e.g.* for signal assignments in ^{13}C NMR spectroscopy and for 2D ^{13}C NMR spectroscopy[8,9]. So, by using spin-echo J-modulation, ^{13}C NMR signals coming from CH_n ($n = 0,1,2,3$) groups can be assigned[10]. It also can be used for the elimination of ^{13}C NMR signals from deuterated solvents and for the ^{13}C NMR analysis of partially deuterated compounds[11]. The product operator description of heteronuclear 2D J-resolved NMR and 2D DEPT J-resolved NMR spectroscopies for the weakly coupled IS_n spin systems ($I = 1/2$, $S = 1$) has been reported elsewhere[12,13]. In this study, the product operator technique is used for analytical description of ^{13}C spin-echo J-modulation NMR spectroscopy for CD_n ($n = 1,2,3$) groups by representing CD_n as $\mathrm{I}S_n$ ($n = 1,2,3$, $\mathrm{I} = 1/2$, $S = 1$). Then the experimental identifications of ^{13}C NMR signals coming from CD_3, CD_2, CD and quaternary carbons are discussed. To the best of our knowledge, this will be the first application of product operator theory to ^{13}C spin-echo J-modulation NMR spectroscopy for CD_n ($n = 1,2,3$) groups.

THEORY

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

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

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

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

the r.f pulse, chemical shift and spin-spin coupling evolution of product operators can easily be obtained[1,6,7]. The details on the evolution of product operators under these Hamiltonians can be found elsewhere[1,6,7,12]. At any time during the experiment, the ensemble averaged expectation value of the spin angular momentum, *e.g.* for I_y, is

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

Where $s(t)$ is the density matrix operator calculated from Eq. (1) at any time. As $\langle I_y \rangle$ is proportional to the magnitude of the y magnetization, it represents the signal detected on y axis. So, in order to estimate the FID signal of a multiple–pulse NMR experiment, density matrix operator should be obtained at the end of the experiment.

^{13}C Spin-Echo J-Modulation NMR For CD$_n$ (n = 1,2,3)

When the simple pulse sequence of spin-echo J-modulation is used, there exists some sources of errors[14]. In order to eliminate these sources of errors, a new pulse sequence called ESCORT editing has been developed[14]. In this study, for the analytical description of ^{13}C spin-echo J-modulation NMR spectroscopy of CD$_n$ (IS_n) groups, the pulse sequence of ESCORT editing, illustrated in Figure 1, is used. In the pulse sequence τ_0 takes an average value found from average coupling constant J_0 as $\tau_0 = 1/J_0$ and it is kept constant. As seen in Figure 1, the density matrix operator at each stage of the experiment is labeled with numbers.

For **IS spin system** s_I is the density matrix operator at thermal equilibrium and

$$\sigma_1 = I_z. \tag{4}$$

The pulse sequence obviously leads to the following density matrices for each labeled point:

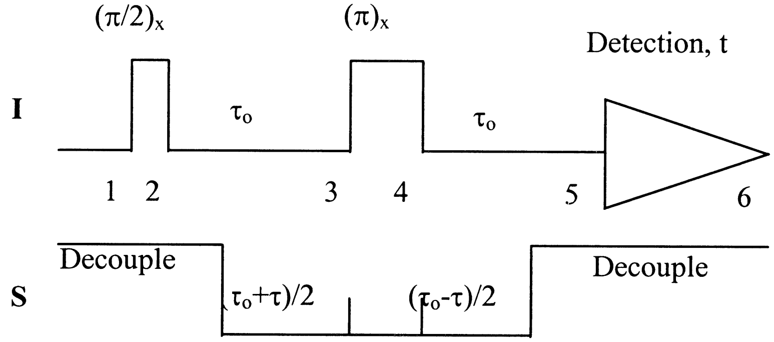

Figure 1. The pulse sequence of ESCORT editing for spin-echo J-modulation NMR spectroscopy[14].

$$\sigma_2 = -I_y \tag{5}$$

$$\sigma_3 = I_x S_z S_{J0} - I_y(1 + S_z^2(C_{J0} - 1)) \tag{6}$$

$$\sigma_4 = I_x S_z S_{J0} + I_y(1 + S_z^2(C_{J0} - 1)). \tag{7}$$

In the preceding and following equations $S_{J0} = \sin \pi J(\tau_0 + \tau)$, $C_{J0} = \cos \pi J(\tau_0 + \tau)$, $C_{nJ} = \cos 2\pi n J \tau$ and $C_I = \cos \Omega_I t$. It is assumed that during τ_o, relaxation and evolution under chemical shift do not exist. The chemical shift evolution take place only during t_1. Then,

$$\sigma_5 = I_y(1 + S_z^2(C_J - 1)) \tag{8}$$

and

$$\sigma_6 = I_y(1 + S_z^2(C_J - 1))C_I \tag{9}$$

As seen in Figure 1, s_6 is the density matrix operator at the end of the experiment. For IS spin system in s_6 only the observable I_y and $I_y S_z{}^2$ terms are kept. Now, it is necessary to obtain the $Tr(I_y O)$ values of observable product operators indicated by O. For IS_n spin system ($I = 1/2$, $S = 1$, n = 1,2,3), $Tr(I_y O)$ values for some of the observable product operators were calculated by a computer program and the results are given in Table 1. So using Table 1

$$\langle I_y \rangle = Tr(I_y \sigma_6) = \left(\frac{1}{2} + C_J\right) C_I \tag{10}$$

is obtained.

By using the same pulse sequence for **IS_2 spin system**, we obtain

$$\sigma_6 = I_y(1 + (S_{1z}^2 + S_{2z}^2)(C_J - 1) + S_{1z}^2 S_{2z}^2 (C_J - 1)^2) C_I. \tag{11}$$

Table 1. The Results of the $Tr(I_y O)$ Calculations for Some of the Observable Product Operators in IS_n Spin System ($I = 1/2$, $S = 1$, $n = 1, 2, 3$)

Spin System	Product Operator (O)	Tr ($I_y O$)
IS	I_y	3/2
	$I_y S_Z^2$	1
IS_2	I_y	9/2
	$I_y(S_{1z}^2 + S_{2z}^2)$	6
	$I_y S_{1z}^2 S_{2z}^2$	2
IS_3	I_y	27/2
	$I_y(S_{1z}^2 + S_{2z}^2 + S_{3z}^2)$	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

Then,

$$Tr(I_y\sigma_6) = \left(\frac{3}{2} + 2C_J + C_2J\right)C_I \tag{12}$$

is obtained.

For **IS$_3$ spin system**, applying the same procedure we obtain

$$\sigma_6 = I_y\begin{pmatrix} 1+(S_{1z}^2+S_{2z}^2+S_{3z}^2)(C_J-1)+(S_{1z}^2S_{2z}^2+S_{1z}^2S_{3z}^2+S_{2z}^2S_{3z}^2)(C_J-1)^2 \\ +S_{1z}^2S_{2z}^2S_{3z}^2(C_J-1)^3 \end{pmatrix}C_I \tag{13}$$

and

$$Tr(I_y\sigma_6) = \left(\frac{7}{2} + 6C_J + 3C_{2J} + C_{3J}\right)C_I \tag{14}$$

DISCUSSION

$Tr(I_y\sigma_6)$ values obtained in the preceding section for IS, IS$_2$ and IS$_3$ spin systems represents the FID signals of ^{13}C spin-echo J-modulation NMR spectroscopy for CD, CD$_2$ and CD$_3$ groups, respectively. $Tr(I_y\sigma_6)$ values can be normalized multiplying by $4/Tr(E)$. Here E is the unity product operator for the corresponding spin system. Then the normalized values become as following:

$$Tr(I_y\sigma_6)(IS) = \frac{2}{3}\left(\frac{1}{2} + C_J\right)C_I \tag{15}$$

$$Tr(I_y\sigma_6)(IS_2) = \frac{2}{9}\left(\frac{3}{2} + 2C_J + C_{2J}\right)C_I \tag{16}$$

$$Tr(I_y\sigma_6) = \frac{2}{27}\left(\frac{7}{2} + 6C_J + 3C_{2J} + C_{3J}\right)C_I \tag{17}$$

By adding the $Tr(I_y\sigma_6)$ values of all these three groups, total $Tr(I_y\sigma_6)$ value can be found as:

$$(Tr(I_y\sigma_6))_{\text{tot}} = \begin{pmatrix} \frac{2}{3}\left(\frac{1}{2} + C_J\right) + \frac{2}{9}\left(\frac{3}{2} + 2C_J + C_{2J}\right) \\ + \frac{2}{27}\left(\frac{7}{2} + 6C_J + 3C_{2J} + C_{3J}\right) \end{pmatrix}C_I. \tag{18}$$

This corresponds to total FID signal for all three groups. This does not include the FID signal of quaternary carbons. By taking $\theta = 2\pi J_0\tau$, FID signals can be estimated for different angles (for different τ values). When the experiment performed at 120° or 240° angles, only the signals coming from quaternary carbons are observed as $(Tr(I_y\sigma_6))_{\text{tot}}$ value becomes zero at these angles. For identification of ^{13}C NMR signals of CD, CD_2 and CD_3 groups, the FID signals of ^{13}C spin-echo J-modulation NMR spectroscopy should be obtained at 90° and 180° angles (at corresponding τ values). Then, from their combinations, following results are obtained:

$$I(CD_2) = 4.5\{(Tr(I_y\sigma_6))_{\text{tot}}(90^\circ) + (Tr(I_y\sigma_6))_{\text{tot}}(180^\circ)\} \quad (19)$$

$$I(CD) + \frac{1}{9}I(CD_3) = 1.5\{(Tr(I_y\sigma_6))_{\text{tot}}(90^\circ) - Tr(I_y\sigma_6))_{\text{tot}}(180^\circ)\} \quad (20)$$

where $I(CD_n)$ represents the relative signal intensity of indicated group. The combination in Equation (19) gives the FID signal of CD_2 group only. And the combination in Equation (20) results in the FID signals of CD and CD_3 groups. It is obvious from Equation (20) that CD signals can be easily separated from CD_3 signals as CD_3 signals will have small relative intensities.

In conclusion, product operator theory is applied to ^{13}C spin-echo J-modulation NMR spectroscopy for CD_n (n = 1,2,3) groups. In order to identify the CD_3, CD_2 and CD groups and also quaternary carbons, experimental suggestions for ^{13}C spin-echo J-modulation NMR spectroscopy of deuterated molecules were made.

REFERENCES

1. Sfrensen, O.W.; Eich, G.W.; Levitt, M.H.; Bodenhausen, G.; Ernst, R.R. Product Operator Formalism for the Description of NMR Pulse Experiments. Prog. NMR Spectrosc. **1983**, *16*, 163.
2. Van de Ven, F.J.M.; Hilbers, C.W. A Simple Formalism for the Description of Multiple–Pulse Experiments. Application to a Weakly Coupled Two-Spin (I = 1/2) System. J. Magn. Res. **1983**, *54*, 512.
3. Packer, K.J.; Wright, K.M. The Use of Single–Spin Operator Basis Sets in the NMR Spectroscopy of Scalar-Coupled Spin Systems. Mol. Phys. **1983**, *50*, 797.
4. Shriver, J. Product Operators and Coherence Transfer in Multiple–Pulse NMR Experiments. Concepts Magn. Res. **1992**, *4*, 1.
5. Howarth, M.A.; Lian, L.Y.; Hawkes, G.E.; Sales, K.D. Formalisms for the Description of Multiple–Pulse NMR Experiments. J. Magn. Res. **1986**, *68*, 433.

6. Ernst, R.R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Oxford: Clarendon Press, 1987.
7. Chandrakumar, N.; Subramanian, S. *Modern Techniques in High Resolution FT NMR*; New York: Springer, 1987.
8. Patt, S.L.; Shoolery, J.N. Attached Proton Test for Carbon-13 NMR. J. Magn. Res. **1982**, *46*, 535.
9. Benn, R.; Günther, H. Modern Pulse Methods in High–Resolution NMR Spectroscopy. Angew. Chem. Int. Ed. Engl. **1983**, *22*, 350.
10. Jakobsen, H.J.; Sfrensen, O.W.; Brey, W.S.; Kanyha, P. The Magic Angle for the Differentiation Between CH_3 and CH Multiplicities in ^{13}C Spin-Echo J-Modulation Experiments. J. Magn. Res. **1982**, *48*, 328.
11. Schmitt, P.; Wesener, J.R.; Günther, H. ^{13}C Spin-Echo Modulation through ^{13}C, ^{2}H Spin–Spin Coupling: Elimination of Solvent Signals and Analysis of Partially Deuterated Systems. J. Magn. Res. **1983**, *52*, 511.
12. Gençten, A.; Köksal, F. A Product Operator Description of 2D–J Resolved NMR Spectroscopy for IS_n Spin System ($I = 1/2$, $S = 1$). Spect. Lett. **1997**, *30* (1), 71.
13. Gençten, A.; Özdoğan, T.; Köksal, F. A Product Operator Theory of 2D DEPT J-Resolved NMR Spectroscopy for IS_n Spin System ($I = 1/2$, $S = 1$). Spect. Lett. **1998**, *31* (5), 981.
14. Madsen, J.C.; Bildsøe, H.; Jakobsen, H.J. ESCORT Editing. An Update of the APT Experiment. J. Magn. Res. **1986**, *67*, 243.

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