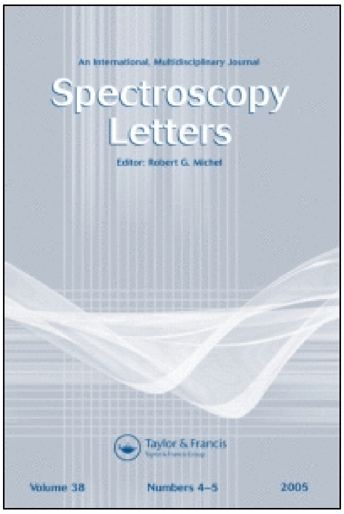

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A THEORETICAL INVESTIGATION OF DEPTQ NMR SPECTROSCOPY FOR I_nS SPIN SYSTEM $(I = 1/2, S = 1/2)$

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ABSTRACT

The product operator technique is used for analytical description of multipulse NMR experiments. DEPTQ NMR spectroscopy is the combination of basic DEPT and SEMUT-90 NMR spectroscopy. This study presents the analytical description of DEPTQ NMR spectroscopy for a weakly coupled spin system I_nS $(I = 1/2, S = 1/2, n = 1, 2, 3)$. The obtained analytical results were found to be in good agreement with the experimental and theoretical ones.

Key Words: DEPTQ NMR; SEMUT pulse sequence; Product operator

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INTRODUCTION

A large variety of homo- and heteronuclear NMR experiments have been developed recently for determination of molecular structure. By the use of simple magnetization vectors and population consideration many of these experiments can be described qualitatively and quantitatively. Whenever multiple-quantum coherences are generated in the experiments, the classical vector descriptions fail. Density matrix formalism has a universal applicability in theoretical description of multipulse NMR experiments and all the other quantum mechanical formalism are founded on it. The elements of density matrix become very cumbersome in systems with a large numbers of spins because the operators are represented by matrices. Alternatively, the product operator formalism, in which requiring no explicit matrix manipulations but the spin operators and using their direct products, is used in theoretical investigation of multipulse NMR experiments.[1–6] The product operator formalism greatly simplifies the description of multipulse NMR experiments and provides a physical picture of what is going on during the experiments on weakly coupled spin systems. Therefore, nowadays, it has become standard practice to describe modern multipulse NMR experiments by using the product operator technique because the product operator technique is a short hand method.[1–13]

It is well known that with the basic DEPT experiment and a single scan the signals of all carbon multiplicities-including nonprotonated (quaternary) carbons may be detected. In a single scan ^{13}C responses of proton-bearing carbons are the superposition of coherences originating from the initial proton and carbon polarization. Since the acquired carbon coherences of different origin are 90° out of phase to each other, line distortions for the signals of proton bearing carbons arise in single scan spectra. Phase cycling is used to get rid of these unwanted line distortions but suppress unfortunately the signals of quaternary carbons as well. Therefore, to distinguish all carbon multiplicities-including quaternary carbons from each other, DEPTQ NMR pulse experiment[14] is used. Pulse experiment used in this article for DEPTQ is the combination of basic DEPT and SEMUT-90 pulse sequences.

The product operator theory for different variant of DEPT experiment, such as 2D DEPT J-Resolved NMR spectroscopy for a weakly coupled I_nS spin system $(I = 1/2, S = 1/2, n = 1, 2, 3)$ has been reported in our previous articles.[15,16]

In this study, by the use of product operator formalism, an analytical description of DEPTQ NMR spectroscopy for a weakly coupled I_nS spin system $(I = 1/2, S = 1/2, n = 1, 2, 3)$ is presented. In Sec. 2, the product operator formalism is briefly introduced. The application of product operator formalism to DEPTQ NMR spectroscopy for I_nS spin system is presented in Sec. 3.

THEORY

The time dependency of the density matrix is governed by the well known Liouville equation,

$$\frac{d\sigma}{dt} = \frac{i}{\hbar}[\sigma, H]. \tag{1}$$

with its formal solution

$$\sigma(t) = \exp(-iHt)\sigma(0)\exp(iHt). \tag{2}$$

Here $[\sigma, H]$ is the commutator of the density matrix, σ, and the total Hamiltonian, H which consists of radio frequency (r.f.) pulse, chemical shift and spin-spin coupling Hamiltonians and $\sigma(0)$ is the density matrix at thermal equilibrium. The general effect of H on σ may be evaluated using the Hausdorff expression[6] which has the form

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

By the use of Hausdorff formula, the r.f. pulse, chemical shift and spin-spin coupling evolution of product operators can easily be obtained[4,6] as in the following:

The Effect of The Radio Frequence (r.f.) Pulse Hamiltonian

$$I_x \xrightarrow{Ht} I_x \tag{4.a}$$

$$I_y \xrightarrow{Ht} I_y \cos\theta + I_z \sin\theta \tag{4.b}$$

$$I_z \xrightarrow{Ht} I_z \cos\theta - I_y \sin\theta \tag{4.c}$$

where $H = \omega_I I_x, \theta = \omega_I t$ and ω_I is the radio frequency.

The Effect of The Chemical Shift Hamiltonian, $H = \Omega I_z$

$$I_x \xrightarrow{Ht} I_x \cos \Omega t + I_y \sin \Omega t, \tag{5.a}$$

$$I_y \xrightarrow{Ht} I_y \cos \Omega t - I_x \sin \Omega t, \tag{5.b}$$

$$I_z \xrightarrow{Ht} I_z. \tag{5.c}$$

The Effect of The Spin-spin Coupling Hamiltonian

$$I_x \xrightarrow{Ht} C_J I_x + 2S_J I_y S_z, \tag{6.a}$$

$$I_y \xrightarrow{Ht} C_J I_y - 2S_J I_x S_z, \tag{6.b}$$

$$I_y S_z \xrightarrow{Ht} C_J I_y S_z - \tfrac{1}{2} S_J I_x, \tag{6.c}$$

$$I_x S_z \xrightarrow{Ht} C_J I_x S_z + \tfrac{1}{2} S_J I_y. \tag{6.d}$$

where, $H = 2\pi J I_z S_z$ is the weak coupling Hamiltonian, $S_J = \sin 2\pi Jt$ and $C_J = \cos 2\pi Jt$.

The product operators used above are the direct products of spin angular momentum operators, e.g. $I_x S_z = I_x \otimes S_z$. At any time during the experiment, the ensemble averaged expectation value of the spin angular momentum, e.g. for I_y, is

$$\langle S_y \rangle = Tr\big(S_y \sigma(t)\big), \tag{7}$$

where $\sigma(t)$ is the density matrix operator calculated from Eq. (2) 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 the following section, the product operator technique is applied to the DEPTQ NMR spectroscopy for $I_n S$ spin system $(I = 1/2, S = 1/2, n = 1, 2, 3)$.

APPLICATION TO DEPTQ NMR

In description of the multipulse NMR experiments by product operator formalism, it is necessary to obtain the $T_r(S_y O)$ values of observable product operators indicated by O. In this study, $T_r(S_yO)$ values of observable product operators for I_nS spin system $(I = 1/2, S = 1/2, n = 1, 2, 3)$ are calculated by a computer program developed and the results are given in Table 1.

In the following, the pulse sequence illustrated in Fig. 1, is used for an analytical description of DEPTQ NMR spectroscopy for I_nS spin system $(I = 1/2, S = 1/2)$. As seen in Fig. 1, the density matrix operator at each stage of the experiment is labeled with numbers. σ_0 is the density matrix operator at thermal equilibrium.

The density matrix evolution for quaternary carbons is as

$$\sigma_0 = S_z, \quad \sigma_1 = S_x, \quad \sigma_3 = -S_x, \quad \sigma_5 = -S_x, \quad \sigma_7 = -S_x = \sigma_8.$$

Here we assumed that during τ, for the evolution density matrix of quaternary carbons, chemical shift and spin-spin coupling do not take place. During detection time, chemical shift take place and than

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

Spin System	Product Operator	$Tr(S_yO)$
IS	S_y	1
I_2S	S_y	2
I_2S	S_y	4

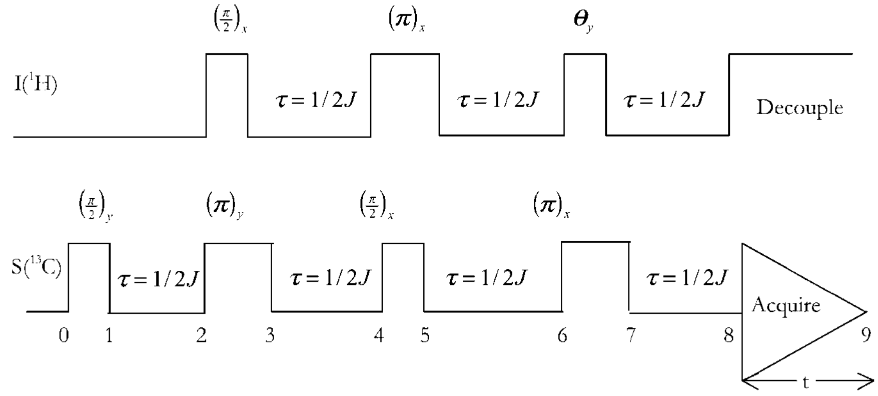

Figure 1. Pulse sequence for DEPTQ NMR spectroscopy.

$$\sigma_9 = -(S_x \cos \omega_s t + S_y \sin \omega_s t)$$

and in the case of detection on the y axis, magnetization along the y axis is proportional to $\langle S_y \rangle$ and

$$M_y(t) \alpha \langle S_y \rangle = Trace(S_y \sigma_9).$$

Then we obtained

$$\langle S_y \rangle = -S_y \sin \omega_s t.$$

For IS spin system $\sigma_0 = I_z + S_z$. The pulse sequence obviously leads to the following density matrix operator evolution

$$\sigma_1 = I_z + S_x.$$

During τ, chemical shift does not exist but spin-spin coupling does. Therefore

$$\begin{aligned}
\sigma_2 &= I_z + 2I_zS_y,\\
\sigma_3 &= -I_y - 2I_yS_y,\\
\sigma_4 &= 2I_xS_z - 2I_yS_y,\\
\sigma_5 &= -2I_xS_y + 2I_yS_z,\\
\sigma_6 &= -2I_xS_y - I_x,\\
\sigma_7 &= 2S_y(C_\theta I_x - S_\theta I_z) - (C_\theta I_x S_\theta I_z),\\
\sigma_8 &= -S_\theta(2I_xS_y - S_x - 2I_yS_z - I_z)
\end{aligned}$$

and during t, chemical shift exist then

$$\sigma_9 = \sin\theta(S_x \cos \omega_s t + S_y \sin \omega_s t).$$

If trace in final stage of the density matrix operator is taken into account, for detection of the magnetization is found as

$$M_y(t) \alpha \langle S_y \rangle = \sin\theta \sin \omega_s t.$$

The density matrix operator evolution for *I_2S spin system* is as

$$\sigma_0 = (I_{1z} + I_{2z}) + S_z,$$

$$\sigma_1 = (I_{1z} + I_{2z}) + S_x,$$

$$\sigma_2 = (I_{1z} + I_{2z}) + 2S_y(I_{1z} + I_{2z})$$

$$\sigma_3 = -(I_{1y} + I_{2y}) - 2S_y(I_{1y} + I_{2y}),$$

$$\sigma_4 = -(I_{1y} + I_{2y}) + 2S_z(I_{1x} + I_{2x}) - 2S_y(I_{1y} + I_{2y}) + 4S_x(I_{1y}I_{2z} + I_{1z}I_{2y}),$$

$$\sigma_5 = -(I_{1z} + I_{2z}) - 2S_y(I_{1x} + I_{2x}) + 2S_z(I_{1y} + I_{2y}) + 4S_x(I_{1y}I_{2z} + I_{1z}I_{2y}),$$

$$\begin{aligned}\sigma_6 = {} & -(I_{1z} + I_{2z}) - 2S_y(I_{1x} + I_{2x}) + 4S_x(I_{1x}I_{2z} + I_{1z}I_{2x}) \\ & -(I_{1x} + I_{2x}) + 2S_z(I_{1y} + I_{2y})\end{aligned}$$

$$\sigma_7 = 4\sin 2\theta(I_{1x}I_{2x} - I_{1z}I_{2z})S_x + 4\cos 2\theta(I_{1x}I_{2z} + I_{1z}I_{2x})S_x$$

$$\sigma_8 = 4\sin 2\theta(I_{1x}I_{2x}S_x + \tfrac{1}{4}S_x).$$

If we take the traces of the product operators, we found that

$$\sigma_8 = S_x \sin 2\theta$$

and during detection time the magnetization is found as

$$\sigma_9 = \sin 2\theta(S_x \cos\omega_s t + S_y \sin\omega_s t)$$

$$M_y(t)\alpha\langle S_y\rangle = 2\sin 2\theta \sin\omega_s t.$$

By using similar procedure, the magnetization for I_3S *spin system*, is briefly found as

$$M_y(t)\alpha\langle S_y\rangle = \tfrac{3}{4}(\sin\theta + \sin 3\theta)\sin\omega_s t$$

In this study, IS, I_2S and I_3S can be considered as CH, CH_2 and CH_3, respectively. As a conclusion, the product operator description of DEPTQ NMR spectroscopy for I_nS $(I = 1/2, S = 1/2, n = 0, 1, 2, 3)$ spin system is presented. By the use of DEPTQ NMR pulse sequence, the density matrix evolution for quaternary carbons are found theoretically. In addition, the subspectra of CH, CH_2 and CH_3 are found as in the DEPT experiment. The obtained analytical results are found to be in good agreement with the experimental and theoretical ones.[16,17]

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