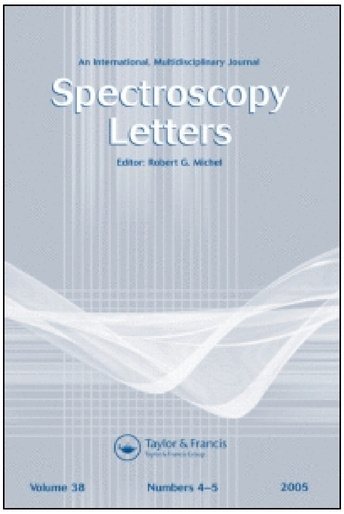

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A PRODUCT OPERATOR THEORY OF 2D DEPT J-RESOLVED NMR SPECTROSCOPY FOR IS_n SPIN SYSTEM (I=1/2, S=1)

Key words: Product operator, NMR, 2D DEPT J-resolved.

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ABSTRACT

By using the product operator technique, analytical description of multipulse NMR experiments can be made. 2D DEPT J-resolved NMR spectroscopy is obtained by combining DEPT and 2D J-resolved NMR spectroscopy. In this study, the analytical description of heteronuclear 2D DEPT J-resolved NMR spectroscopy for a weakly coupled IS_n (I=1/2, S=1, n=1,2,3) spin system is presented and experimental suggestions for ^{13}C 2D DEPT J-resolved NMR spectroscopy of deuterated molecules have been made.

INTRODUCTION

There exists a variety of multipulse NMR experiments for spectral assignments of complex molecules. In order to analyze these pulse experiments applied to large spin systems, a quantum mechanical approach has to be used. In analytical description of multipulse 1D and 2D NMR experiments for a weakly coupled spin systems, product operator formalism can be used [1–10]. Distortionless Enhancement by Polarization Transfer (DEPT) and 2D J–resolved NMR techniques are widely used for spectral assignments of complex molecules. By using DEPT NMR experiment, ^{13}C signals of C, CD, CD_2 and CD_3 groups can be identified. In order to resolve the chemical shift and spin–spin coupling parameters along the two different axes heteronuclear 2D J-resolved NMR spectroscopy is used. Sometimes, spectral assignments of 2D J–resolved NMR spectra become too difficult, due to the complex overlapping spectra. In order to solve this problem, 2D DEPT J–resolved NMR spectroscopy, which is the combination of DEPT and 2D J–resolved NMR spectroscopy techniques, is used [11]. The product operator description of 2D J–resolved NMR spectroscopy for a weakly coupled IS_n spin system (I=1/2, S=1) has been reported elsewhere [12]. In this study, the product operator technique is used for analytical description of heteronuclear 2D DEPT J–resolved NMR spectroscopy for a weakly coupled IS_n spin system (I=1/2, S=1) and experimental suggestions for ^{13}C 2D DEPT J–resolved NMR spectroscopy of deuterated molecules were made. This will probably be the first application of product operator theory to 2D DEPT J–resolved NMR spectroscopy for this system.

THEORY

Time dependency of the density matrix is given as [6]

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

Where H is time independent total Hamiltonian consists of 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 [6]

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

r.f pulse, chemical shift and spin–spin coupling evolution of product operators can easily be obtained [4,6]. The details on the evolution of product operators under the r.f. pulse, chemical shift and spin-spin coupling Hamiltonians can be found elsewhere [4,6,12]. At any time during the experiment, the ensemble averaged expectation value of the spin angular momentum, e.g. for I_y, is given as

$$<I_y>=Tr(I_y\sigma(t)). \tag{3}$$

Where $\sigma(t)$ is the density matrix operator calculated from Eq.(1) at any time. As $<I_y>$ is proportional to the magnitude of the y magnetization, it represents the signal detected on y axis.

ANALYTICAL DESCRIPTION OF 2D DEPT J-RESOLVED NMR

In order to describe the multi–pulse NMR experiment in product operator technique, it is necessary to obtain the $Tr(I_yO)$ values of observable product operators indicated by O. For IS_n spin system (I=1/2, S=1, n=1,2,3), $Tr(I_yO)$ values for some of the observable product operators were calculated by using a computer program and they are given in Table 1.

In the following, the pulse sequence, illustrated in Fig.1, is used for an analytical description of 2D DEPT J–resolved NMR spectroscopy for IS_n spin system (I=1/2, S=1). 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 and for ***IS* spin system** $\sigma_0=S_z$. The pulse sequence in Fig.1 obviously leads to the following density matrices for each labeled point:

$$\sigma_1=-S_y,\ \sigma_2=2S_xI_z. \tag{4}$$

Here it is assumed that during τ and t_1 between pulses, relaxation and evolution under chemical shift do not exists. Therefore,

$$\sigma_5=2S_{2\theta}(I_xS_z^2-I_xS_x^2). \tag{5}$$

TABLE 1

The results of the $Tr(I_yO)$ calculations for some of the observable product operators ($i=x,z$; $j=x,z$ and $k=x,z$) in IS_n spin system ($I=1/2$, $S=1$, n=1,2,3).

Spin System	Product Operator (O)	$Tr(I_yO)$
IS	I_y	3/2
	$I_yS_i^2$	1
IS_2	I_y	9/2
	$I_y(S_{1i}^2+S_{2j}^2)$	6
	$I_yS_{1i}^2S_{2j}^2$	2
IS_3	I_y	27/2
	$I_y(S_{1i}^2+S_{2j}^2+S_{3k}^2)$	27
	$I_y(S_{1i}^2S_{2j}^2+S_{1i}^2S_{3k}^2+S_{2j}^2S_{3k}^2)$	18
	$I_y\,S_{1i}^2S_{2j}^2S_{3k}^2$	4

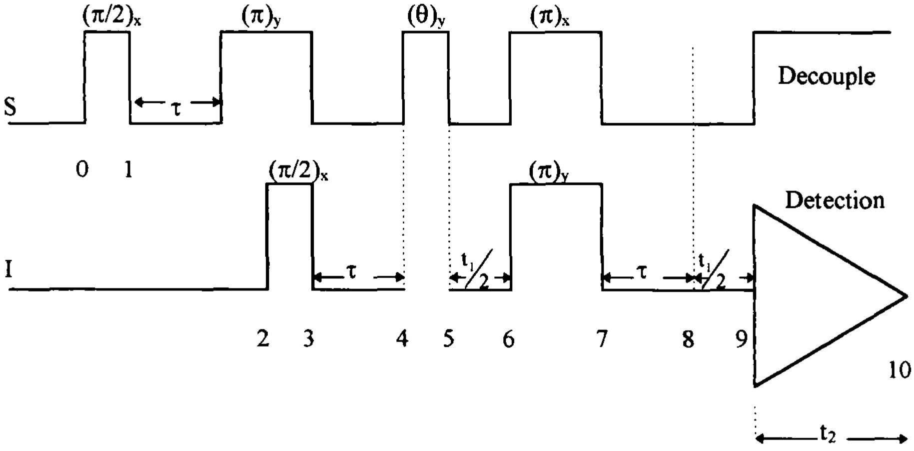

Figure 1. The pulse sequence for 2D DEPT J-resolved NMR spectroscopy.

Furthermore, under the chemical shift evolution during t_2, the density matrix becomes

$$\sigma_{10} = 2S_{2\theta}(I_x C_I + I_y S_I)[1/2(C_J - 1)S_z^2 + S_x^2]. \qquad (6)$$

In this and in the following equations, $C_I = \cos\Omega_I t_2$, $S_I = \sin\Omega_I t_2$, $S_{nJ} = \sin(n2\pi J t_1)$, $C_{nJ} = \cos(n2\pi J t_1)$ and $S_{n\theta} = \sin n\theta$. In the case of on y axis detection, magnetization along y axis is proportional to $<I_y>$ and

$$M_y(t_1,t_2)\,\alpha <I_y> = Tr(I_y \sigma_{10}). \qquad (7)$$

Then, we obtained

$$<I_y> = S_{2\theta}(1 + C_J)S_I. \qquad (8)$$

This equation shows that 2D DEPT J–resolved NMR signal for IS spin system depends on $\sin 2\theta$ and for $\theta = 45^0$ it gives signals at (J,Ω_I), (Ω_I) $(-J,\Omega_I)$ with an intensity distribution of (1,2,1) which is consistent with the study reported elsewhere [13].

For $\boldsymbol{IS_2}$ **spin system,**

$$\sigma_0 = S_{1z} + S_{2z}. \qquad (9)$$

By using the same pulse sequence, we obtain

$$<I_y> = 4(S_{2\theta} + S_{4\theta})\left(\frac{3}{2} + 2C_J + C_{2J}\right)S_I. \qquad (10)$$

Where $C_{2J} = \cos(4\pi J t_1)$. As seen from this equation 2D DEPT J–resolved NMR signal for IS_2 spin system depends on $(\sin 2\theta + \sin 4\theta)$.

By using the same procedure for $\boldsymbol{IS_3}$ **spin system**, we obtain

$$<I_y> = 2(2S_{2\theta} + 2S_{4\theta} + S_{6\theta})\left(\frac{7}{2} + 6C_J + 3C_{2J} + C_{3J}\right)S_I. \qquad (11)$$

This equation represents the FID signal of IS_3 spin system at any angle.

EXPERIMENTAL SUGGESTIONS

$Tr(I_y\sigma_{10})$ values for IS, IS_2 and IS_3 spin systems represent the FID signals of ^{13}C 2D DEPT J–resolved NMR spectroscopy for CD, CD_2 and CD_3 groups, respectively. By adding the $Tr(I_y\sigma_{10})$ values of all these three groups, total $Tr(I_y\sigma_{10})$ value can be found as:

$$[Tr(I_y\sigma_{10})]_{tot}= S_{2\theta}(1+C_J)S_I+4(S_{2\theta}+S_{4\theta})(\frac{3}{2}+2C_J+C_{2J})S_I$$

$$+2(2S_{2\theta}+2S_{4\theta}+S_{6\theta})(\frac{7}{2}+6C_J+3C_{2J}+C_{3J})S_I. \qquad (12)$$

This corresponds to total FID signal for all three groups. At θ=60° the relative intensity for CD is nonzero, but for both CD_2 and CD_3 it is zero. Therefore, FID taken at θ=60° will give the spectrum for only CD groups. In order to have complete separation of ^{13}C 2D DEPT J–resolved NMR spectrum into CD, CD_2 and CD_3 subspectra FID signals should be taken at θ=27°, θ=60° and θ=74° and their combinations should be made as following:

$$I_{CD}=[Tr(I_y\sigma_{10})]_{tot}(60^o) \qquad (13)$$

$$I_{CD_2}=[Tr(I_y\sigma_{10})]_{tot}(27^o)+a[Tr(I_y\sigma_{10})]_{tot}(60^o)-b[Tr(I_y\sigma_{10})]_{tot}(74^o) \qquad (14)$$

$$I_{CD_3}=[Tr(I_y\sigma_{10})]_{tot}(27^o)-c[Tr(I_y\sigma_{10})]_{tot}(60^o)+d[Tr(I_y\sigma_{10})]_{tot}(74^o). \qquad (15)$$

Where a=8.19, b=14.91, c=3.85 and d=4.77. These values were found here and some of them are different from those reported for DEPT NMR elsewhere [13]. After these combinations, the theoretical representations of FID signals for CD, CD_2 and CD_3 groups are obtained as:

$$I_{CD}\,\alpha\,(1+C_J)S_I \qquad (16)$$

$$I_{CD_2}\,\alpha\,(\frac{3}{2}+2C_J+C_{2J})S_I \qquad (17)$$

$$I_{CD_3}\,\alpha\,(\frac{7}{2}+6C_J+3C_{2J}+C_{3J})S_I. \qquad (18)$$

These theoretical combinations can be applied to ^{13}C 2D DEPT J–resolved NMR experiments of deuterated molecules. And therefore CD, CD_2 and CD_3 groups can be easily identified.

In conclusion, product operator description of 2D DEPT J–resolved NMR spectroscopy for IS_n (I=1/2, S=1, n=1,2,3) spin system is presented. Theoretical representations of ^{13}C 2D DEPT J–resolved NMR spectra of CD, CD_2 and CD_3

groups were separately obtained and experimental suggestions for ^{13}C 2D DEPT J–resolved NMR spectroscopy of deuterated molecules were made.

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