

A Product Operator Theory of DEPTQ NMR Spectroscopy for IS_n ($I = 1/2$; $S = 1$; $n = 0, 1, 2, 3$) Spin Systems

İ. ŞAKA*, A. GENÇTEN AND S. GÜMÜŞ

Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139, Samsun, Turkey

(Received November 18, 2008; in final form April 20, 2011)

Distortionless enhancement by polarization transfer including the detection of quaternary nuclei is a carbon-editing pulse NMR experiment. In this experiment multiplicity information for all carbons including quaternary carbons are obtained. In the present study, analytical descriptions of DEPTQ NMR experiment have been investigated for weakly coupled IS_n ($I = 1/2$; $S = 1$; $n = 0, 1, 2, 3$) spin systems by using the product operator theory. Then, the theoretical discussion and the experimental suggestions for sub-spectral editing of C, CD, CD₂ and CD₃ groups have been presented. The comparison of the obtained results with those of the basic distortionless enhancement by polarization transfer NMR experiment has been also performed for CD_n groups. It is shown that DEPTQ experiment can be also used for CD_n groups.

PACS: 82.56.Dj, 82.56.Jn

1. Introduction

Polarization transfer experiments such as distortionless enhancement by polarization transfer (DEPT) and insensitive nuclei enhanced by polarization transfer (INEPT) are widely used to simplify the spectra of carbonyl groups in complex molecules [1, 2]. DEPT experiment is used to edit ¹³C NMR spectra into subspectra containing protonated and deuterated carbonyl groups [3, 4]. Distortionless enhancement by polarization transfer including the detection of quaternary nuclei (DEPTQ) experiment was developed by Burger and Bigler [5]. This experiment is based on DEPT and gives multiplicity information for all carbons including quaternary carbons. The advantages of the DEPTQ experiment with respect to similar experiment such as DEPT and subspectral editing with a multiple quantum trap (SEMUT) were also discussed in detail by Burger and Bigler [5]. Improved version of DEPTQ experiment was presented elsewhere [6, 7].

The product operator theory as a quantum mechanical method is widely used for analytical description of multipulse NMR experiments on weakly coupled spin systems in liquids having spin-1/2, spin-1 and spin-3/2 nuclei [8–21]. This method not only allows the confirmation of experimental results but also offers to make some experimental suggestions on NMR experiments. By using product operator theory, SEMUT NMR spectroscopy is applied to CD_n groups [16]. Experimental and theoretical investigation of ¹³C DEPT NMR spectroscopy for CD_n

systems is presented elsewhere [13]. For CD_n groups, product operator theory of 2D DEPT *J*-resolved NMR experiment is also investigated [15]. For weakly coupled IS ($I = 1/2$, $S = 1$) spin system, a complete product operator theory and application to DEPT-heteronuclear multiple quantum coherence (HMQC) NMR experiment has been presented in our study [19]. A product operator description of the DEPTQ experiment for IS_n ($I = 1/2$, $S = 1/2$, $n = 0, 1, 2, 3$) spin systems have been presented [22].

In the present study, by using product operator theory analytical descriptions of DEPTQ experiment have been presented for weakly coupled IS_n ($I = 1/2$; $S = 1$; $n = 0, 1, 2, 3$) spin systems. Then a theoretical discussion and experimental suggestions for subspectral editing of C, CD, CD₂ and CD₃ groups have been presented. The theoretical results are compared with those of DEPT experiment of CD_n groups. To the best of our knowledge, this will be the first application of product operator theory to DEPTQ NMR experiment for IS_n ($I = 1/2$; $S = 1$; $n = 0, 1, 2, 3$) spin systems.

2. Theory

Time dependence of the density matrix is given by [10]:

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

where \mathcal{H} is the total Hamiltonian and $\sigma(0)$ is the density matrix at $t = 0$. In the liquid-state and the solid-state (under magic angle spinning (MAS) conditions) pulse NMR experiments of weakly coupled IS_n spin systems, the total Hamiltonian consists of r.f. pulse, chemical shift

* corresponding author; e-mail: isaka@omu.edu.tr

and spin–spin coupling Hamiltonians can be written as

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

By employing the Hausdorff formula evolutions of the product operators under the r.f. pulse, chemical shift and spin–spin coupling Hamiltonians can be easily obtained [8, 10, 11]. A complete product operator theory for weakly coupled IS ($I = 1/2$, $S = 1$) spin system have been presented in our previous studies [19, 21].

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

$$\langle I_y \rangle = \text{Tr}(I_y \sigma(t)), \quad (3)$$

where $\sigma(t)$ 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 free induction decay (FID) signal of a multiple-pulse NMR experiment, density matrix operator should be obtained at the end of the experiment.

3. Results

For the product operator description of the DEPTQ NMR experiment, the pulse sequence illustrated in Fig. 1 is used [5]. In this figure, the density matrix operators at each stage of the experiment are labeled with numbers, and ^{13}C is treated as spin I and ^2H (D) as spin S . The experiment is performed for both the initial 90_y^0 and 90_{-y}^0 pulses in the I channel. In the pulse sequence: τ is the coupling evolution delay and t is the acquisition time. Optimum value of τ is $1/(2J_{IS})$ for the DEPTQ NMR experiment. 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 multispin systems, to follow these processes by hand becomes too difficult. In order to overcome this problem, a computer program written in Mathematica is used [23]. Thus, the density matrix operators at the end of the experiment are obtained for different spin systems such as I , IS , IS_2 and IS_3 ($I = 1/2$, $S = 1$).

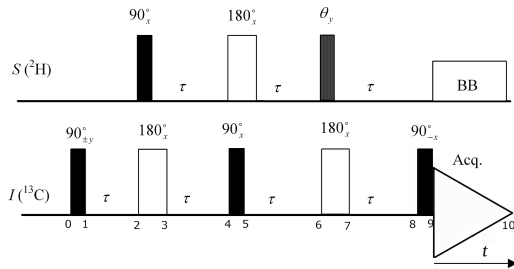


Fig. 1. Pulse sequence for DEPTQ NMR experiment, $\tau = 1/(2J_{IS})$ [5].

3.1. Quaternary carbons (I)

The density matrix at the thermal equilibrium for I spin is $\sigma_0 = I_z$. The evolutions of the density matrix are obtained as follows:

$$\begin{aligned} \sigma_0 &\xrightarrow{90_y^0(I)} \sigma_2 \xrightarrow{180_y^0(I)} \sigma_4 \xrightarrow{90_y^0(I)} \sigma_6 \xrightarrow{180_y^0(I)} \sigma_8 \xrightarrow{90_{-y}^0(I)} \sigma_9 \\ &= I_x. \end{aligned} \quad (4)$$

In the last step, chemical shift takes place and then we obtain

$$\sigma_{10} = I_x \cos(\Omega_I t) + I_y \sin(\Omega_I t). \quad (5)$$

In the last density matrix operator, only the second term contributes to the signals as acquisition is taken along y -axes for spin I . It is necessary to obtain the $\text{Tr}(I_y O)$ values of observable product operators indicated by O . For the IS_n ($I = 1/2$, $S = 1$; $n = 1, 2, 3$) spin systems, $\text{Tr}(I_y O)$ values of all observable product operators can be found elsewhere [19]. For the quaternary carbons $\text{Tr}(I_y I_y) = \frac{1}{2}$ and the magnetization is found as

$$M_y(t) \propto \langle I_y \rangle_{90_y^0} = \text{Tr}(I_y \sigma_{10}) = \frac{1}{2} \sin(\Omega_I t). \quad (6)$$

If the experiment is performed for the initial 90_{-y}^0 I pulse, the magnetization is

$$M_y(t) \propto \langle I_y \rangle_{90_{-y}^0} = \text{Tr}(I_y \sigma_{10}) = -\frac{1}{2} \sin(\Omega_I t). \quad (7)$$

3.2. IS spin system

$\sigma_0 = I_z + S_z$ is the density matrix operator at the thermal equilibrium for IS spin system and the following evolutions are obtained:

$$\sigma_0 \xrightarrow{90_{+y}^0(I)} I_x + S_z = \sigma_1, \quad (8a)$$

$$\sigma_1 \xrightarrow{\mathcal{H}_J \tau (\tau=1/2J)} I_x + S_z - 2I_x S_z^2, \quad (8b)$$

$$\sigma_2 \xrightarrow{90_x^0(S)+180_x^0(I)} I_x - S_y - 2I_x S_y^2, \quad (8c)$$

$$\sigma_3 \xrightarrow{\mathcal{H}_J \tau (\tau=1/2J)} I_x + 2I_x S_x - 2I_x S_y^2 = \sigma_4, \quad (8d)$$

$$\begin{aligned} \sigma_7 &= I_x - 2I_x S_y^2 + 2I_x [S_x, S_z]_+ c_{2\theta} + 2I_x S_x^2 s_{2\theta} \\ &\quad - 2I_x S_z^2 s_{2\theta}, \end{aligned} \quad (8e)$$

and

$$\begin{aligned} \sigma_{10} &= I_x c_I + I_y s_I - 2I_x S_y^2 c_I - 2I_y S_y^2 s_I - 2I_x S_x c_{2\theta} \\ &\quad + 2I_x S_x^2 s_{2\theta} c_I + 2I_y S_x^2 s_{2\theta} s_I. \end{aligned} \quad (8f)$$

In above and following equations $c_I = \cos(\Omega_I t)$, $s_I = \sin(\Omega_I t)$, $c_{n\theta} = \cos(n\theta)$ and $s_{n\theta} = \sin(n\theta)$. Using the trace values, magnetization for IS spin system is

$$\text{Tr}(I_y \sigma_{10}) = -\frac{1}{2} s_I + 2s_{2\theta} s_I. \quad (9)$$

For the initial 90_{-y}^0 I pulse, the magnetization is found as

$$\text{Tr}(I_y \sigma_{10}) = \frac{1}{2} s_I + 2s_{2\theta} s_I. \quad (10)$$

3.3. IS_2 spin system

For the IS_2 spin system, $\sigma_0 = I_z + S_{1z} + S_{2z}$ is the density matrix at the thermal equilibrium. For the initial $90_y^0 I$ pulse, density matrix at the end of the experiment is

$$\begin{aligned} \sigma_{10} = & I_y s_I - 2I_y (S_{1y}^2 + S_{2y}^2) s_I + 4I_y S_{1y}^2 S_{2y}^2 s_I \\ & + 2I_y (S_{1x}^2 + S_{2x}^2) s_{2\theta} s_I - 4I_y S_{1x}^2 S_{2x}^2 s_{2\theta} s_I \\ & + 4I_y S_{1x}^2 S_{2x}^2 c_{2\theta} s_{2\theta} s_I. \end{aligned} \quad (11)$$

Using the trace values for IS_2 spin system,

$$\text{Tr}(I_y \sigma_{10}) = \frac{1}{2} s_I + 4s_{2\theta} s_I + 8c_{2\theta} s_{2\theta} s_I \quad (12)$$

is found and for the initial $90_{-y}^0 I$ pulse,

$$\text{Tr}(I_y \sigma_{10}) = -\frac{1}{2} s_I + 4s_{2\theta} s_I + 8c_{2\theta} s_{2\theta} s_I \quad (13)$$

is obtained.

3.4. IS_3 spin system

Applying the same procedure for IS_3 spin system, following results are obtained for 90_y^0 and $90_{-y}^0 I$ pulses, respectively:

$$\begin{aligned} \text{Tr}(I_y \sigma_{10}) = & -\frac{1}{2} s_I + 6s_{2\theta} s_I + 24c_{2\theta} s_{2\theta} s_I \\ & + 24c_{2\theta}^2 s_{2\theta} s_I, \end{aligned} \quad (14)$$

$$\begin{aligned} \text{Tr}(I_y \sigma_{10}) = & \frac{1}{2} s_I + 6s_{2\theta} s_I + 24c_{2\theta} s_{2\theta} s_I \\ & + 24c_{2\theta}^2 s_{2\theta} s_I. \end{aligned} \quad (15)$$

4. Discussion

The $\text{Tr}(I_y \sigma_{10})$ values obtained in the previous section for I , IS , IS_2 and IS_3 spin systems represent the FID signals of the DEPTQ NMR experiment for C, CD, CD_2 and CD_3 groups, respectively. Generalized forms of these results obtained for 90_y^0 and $90_{-y}^0 I$ pulses are

$$\begin{aligned} \text{Tr}(I_y \sigma_{10})_{90_{+y}^0} (CD_n) = & (-1)^n \frac{1}{2} s_I \\ & + 2n(1 + 2c_{2\theta})^{n-1} s_{2\theta} s_I \end{aligned} \quad (16)$$

and

$$\begin{aligned} \text{Tr}(I_y \sigma_{10})_{90_{-y}^0} (CD_n) = & (-1)^{n+1} \frac{1}{2} s_I \\ & + 2n(1 + 2c_{2\theta})^{n-1} s_{2\theta} s_I. \end{aligned} \quad (17)$$

In order to distinguish the signals of C, CD, CD_2 and CD_3 groups from each other, addition and subtraction of FID signals obtained for 90_y^0 and $90_{-y}^0 I$ pulses can be made as following:

$$\begin{aligned} \text{Tr}(I_y \sigma_{10})_{90_{+y}^0} (CD_n) + \text{Tr}(I_y \sigma_{10})_{90_{-y}^0} (CD_n) \\ = 4n(1 + 2c_{2\theta})^{n-1} s_{2\theta} s_I, \end{aligned} \quad (18)$$

$$\begin{aligned} \text{Tr}(I_y \sigma_{10})_{90_{+y}^0} (CD_n) - \text{Tr}(I_y \sigma_{10})_{90_{-y}^0} (CD_n) \\ = (-1)^n s_I. \end{aligned} \quad (19)$$

Equation (18) can be normalized by multiplying with $3/(2\text{Tr}(E))$. Here E is the unity product operator for corresponding spin system. Then the normalized FID form is

$$\begin{aligned} \text{Tr}(I_y \sigma_{10})_{90_{+y}^0} (CD_n) + \text{Tr}(I_y \sigma_{10})_{90_{-y}^0} (CD_n) \\ = \frac{3n}{3^n} (1 + 2c_{2\theta})^{n-1} s_{2\theta} s_I. \end{aligned} \quad (20)$$

These normalized $\text{Tr}(I_y \sigma_{10})_{90_{+y}^0} + \text{Tr}(I_y \sigma_{10})_{90_{-y}^0}$ and $\text{Tr}(I_y \sigma_{10})_{90_{+y}^0} - \text{Tr}(I_y \sigma_{10})_{90_{-y}^0}$ values are given in Table. In Table, the added FID values depend on θ and these results are the same with those of DEPT NMR experiment [4, 12]. On the other hand, the subtracted results give the FID values for quaternary carbons in addition to CD, CD_2 and CD_3 groups. The relative signal intensity plots of DEPTQ NMR experiment for CD_n groups as functions of the editing pulse angle, θ , are presented in Fig. 2. As seen from Table and Fig. 2, added and subtracted signals can be used to distinguish the signals of C, CD, CD_2 and CD_3 groups from each other by using several pulse angles such as 30° , 60° and 75° .

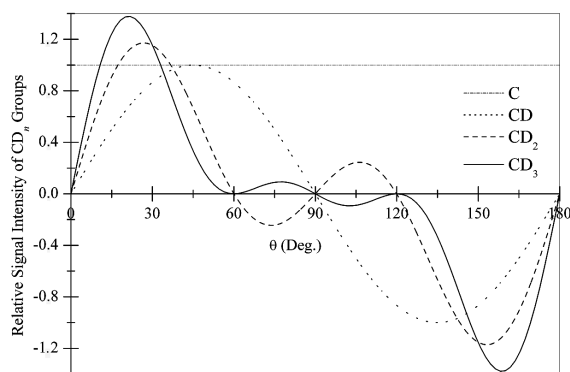


Fig. 2. The relative signal intensity plots of DEPTQ NMR experiment for CD_n groups as functions of the editing pulse angle, θ .

TABLE

Normalized $\text{Tr}(I_y \sigma_{10})_{90_{+y}^0} + \text{Tr}(I_y \sigma_{10})_{90_{-y}^0}$ and $\text{Tr}(I_y \sigma_{10})_{90_{+y}^0} - \text{Tr}(I_y \sigma_{10})_{90_{-y}^0}$ values for IS_n ($I = 1/2$; $S = 1$; $n = 0, 1, 2, 3$) spin systems.

Spin system	$\text{Tr}(I_y \sigma_{10})_{90_{+y}^0} + \text{Tr}(I_y \sigma_{10})_{90_{-y}^0}$	$\text{Tr}(I_y \sigma_{10})_{90_{+y}^0} - \text{Tr}(I_y \sigma_{10})_{90_{-y}^0}$
$I(C)$	0	s_I
$IS(CD)$	$s_{2\theta} s_I$	$-s_I$
$IS_2(CD_2)$	$\frac{2}{3}(1 + 2c_{2\theta}) s_{2\theta} s_I$	s_I
$IS_3(CD_3)$	$\frac{1}{3}(1 + 2c_{2\theta})^2 s_{2\theta} s_I$	$-s_I$

5. Conclusions

In this study, by using product operator theory, analytical descriptions of the DEPTQ NMR experiment have been presented for IS_n ($I = 1/2$; $S = 1$; $n = 0, 1, 2, 3$) spin systems. Obtained results are compared with those of DEPT experiment for CD_n groups. Then a theoretical discussion and experimental suggestions for subspectral editing of C, CD, CD_2 and CD_3 groups have been presented. As a result, DEPTQ NMR experiment can be used for subspectral editing of CD_n groups including quaternary carbons in liquids.

References

- [1] O.W. Sorensen, *Prog. NMR Spectrosc.* **21**, 503 (1989).
- [2] P. Nolis, T. Parella, *Curr. Analyt. Chem.* **3**, 47 (2007).
- [3] D.M. Doddrell, D.T. Pegg, M.R. Bendall, *J. Magn. Reson.* **48**, 323 (1982).
- [4] N. Chandrakumar, *J. Magn. Reson.* **60**, 28 (1984).
- [5] R. Burger, P. Bigler, *J. Magn. Reson.* **135**, 529 (1998).
- [6] P. Bigler, R. Kümmerle, W. Bermel, *Magn. Reson. Chem.* **45**, 469 (2007).
- [7] P. Bigler, *Spectrosc. Lett.* **41**, 162 (2008).
- [8] O.W. Sørensen, G.W. Eich, M.H. Levitt, G. Bodenhausen, R.R. Ernst, *Prog. NMR Spectrosc.* **16**, 163 (1983).
- [9] O.W. Sørensen, R.R. Ernst, *J. Magn. Reson.* **51**, 477 (1983).
- [10] N. Chandrakumar, S. Subramanian, *Modern Techniques in High Resolution FT NMR*, Springer-Verlag, New York 1987.
- [11] R.R. Ernst, G. Bodenhausen, A. Wokaun, *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*, Clarendon Press, Oxford 1987.
- [12] N. Chandrakumar, *Spin-1 NMR*, Springer, Berlin 1996.
- [13] T.T. Nakashima, R.E.D. McClung, B.K. John, *J. Magn. Reson.* **58**, 27 (1984).
- [14] A. Gençten, F. Köksal, *Spectrosc. Lett.* **30**, 71 (1997).
- [15] A. Gençten, T. Özdoğan, F. Koksall, *Spectrosc. Lett.* **31**, 981 (1998).
- [16] A. Gençten, Ö. Tezel, A. Köroğlu, *Appl. Magn. Reson.* **20**, 265 (2001).
- [17] İ. Şaka, Ö. Tezel, A. Gençten, *Z. Naturforsch.* **58a**, 139 (2003).
- [18] A. Tokath, A. Gençten, M. Şahin, Ö. Tezel, S. Bahçeli, *J. Magn. Reson.* **169**, 68 (2004).
- [19] A. Gençten, İ. Şaka, *Mol. Phys.* **104**, 2983 (2006).
- [20] İ. Şaka, A. Gençten, *J. Mol. Struct.* **834-836**, 521 (2007).
- [21] İ. Şaka, A. Gençten, *Z. Naturforsch.* **62a**, 259 (2007).
- [22] T. Özdoğan, M. Orbay, *Spectrosc. Lett.* **35**, 447 (2002).
- [23] S. Wolfram, *The Mathematica Book*, 3rd ed., Wolfram Media/Cambridge University Press, Cambridge 1996.