

PENDANT ^{13}C NMR Spectroscopy Applied to CH_n Groups

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Received 27.03.2006

Abstract

Polarization enhancement nurtured during attached nucleus testing (PENDANT) NMR spectroscopy gives signals of quaternary carbon atoms in addition to signals indicative of CH, CH₂ and CH₃ groups. In this study, using product operator theory, analytical description of PENDANT NMR spectroscopy for CH_n (IS_n , $I = \frac{1}{2}$, $S = \frac{1}{2}$, $n = 0, 1, 2, 3$) spin systems are presented. Simulation and experimental results of PENDANT NMR spectroscopy are also presented. Theoretical results are found to be in exact agreement with the simulation results and in good agreement with the experimental ones.

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

1. Introduction

There exists a large number of one and two-dimensional NMR techniques for ^{13}C spectral editing such as attached proton test (APT), sub spectral editing with a multiple quantum trap (SEMUT), distortionless enhancement by polarization transfer (DEPT), polarization enhancement nurtured during attached nucleus testing (PENDANT). PENDANT NMR spectroscopy has to its advantage that it is also capable of detecting quaternary carbon atoms in addition to the signals of CH, CH₂ and CH₃ groups [1, 2].

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 [see e.g., 3–8]. PENDANT NMR spectroscopy of CH_n groups have been observed for $d_3 = \frac{5}{8}J$ [1, 9]. In this study, by using product operator theory, an analytical description of PENDANT NMR spectroscopy for CH_n (IS_n , $I = \frac{1}{2}$, $S = \frac{1}{2}$, $n = 0, 1, 2, 3$) spin systems are presented. Simulation and experimental results of PENDANT NMR spectroscopy are also presented for these spin systems. Theoretical results were found to be in exact agreement with the simulation results and in good agreement with the experimental results.

2. Theory

Time dependency of the density matrix is given by [6, 7]

$$\sigma(t) = \exp(-iHt)\sigma(0)\exp(iHt), \quad (1)$$

where H is the total Hamiltonian which consists of radio frequency (RF) pulse, chemical shift and spin–spin coupling Hamiltonians and $\sigma(0)$ is the density matrix at $t = 0$. After employing the Hausdorff formula [6, 7], we get

$$\begin{aligned} \exp(-iHt) A \exp(iHt) = & A - (it)[H, A] + \frac{(it)^2}{2!}[H, [H, A]] \\ & - \frac{(it)^3}{3!}[H, [H, [H, A]]] + \dots, \end{aligned} \quad (2)$$

From which the RF pulse, chemical shift and spin–spin coupling evolution of product operators can easily be obtained. Details on the evolution of product operators under these Hamiltonians can be found elsewhere [3, 5–8]. 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 equation (1) at time t . As $\langle I_y \rangle$ is proportional to the magnitude of the y-axis 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, one should obtain density matrix operator at the end of the experiment.

3. Results and Discussion

3.1. Product operator theory

In this section, we present an analytical description of PENDANT NMR spectroscopy for IS_n spin systems (CH_n groups) using product operator theory. The pulse sequence employed for PENDANT is illustrated in Figure 1. Optimum value of d_2 is $(\frac{1}{4}J)$ [9]. Density matrix operator at each stage of the experiment is numerically labeled. We treat ^{13}C as spin I and ^1H as spin S . So CH_n groups can be represented as IS_n ($I = \frac{1}{2}$, $S = \frac{1}{2}$) spin systems.

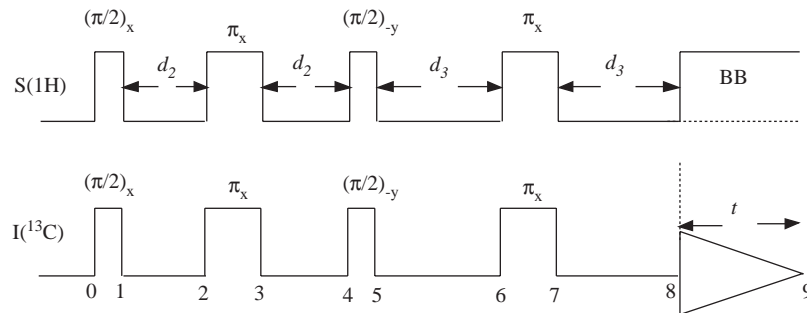


Figure 1. The pulse sequence for ^{13}C PENDANT NMR spectroscopy [1,9]. BB: Broad band.

For an 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 $d_2 = \frac{1}{4}J$) obviously leads to the following density matrices for each labeled point:

$$\sigma_1 = -S_y, \quad (4)$$

$$\sigma_2 = -S_y \cos(\pi J d_2) + 2I_z S_x \sin(\pi J d_2) \quad (5)$$

$$\sigma_3 = S_y \cos(\pi J d_2) - 2I_z S_x \sin(\pi J d_2) \quad (6)$$

$$\sigma_4 = -2I_z S_x \quad (7)$$

$$\sigma_5 = 2I_x S_z \quad (8)$$

$$\sigma_6 = 2I_x S_z C_J + I_y S_J. \quad (9)$$

Here and in the following equations $C_{nJ} = \cos(n\pi J d_3)$, $S_{nJ} = \sin(n\pi J d_3)$ and $C_I = \cos(\Omega_I t)$. So we obtain

$$\sigma_8 = -2I_x S_z C_{2J} - I_y S_{2J}. \quad (10)$$

Under the chemical shift evolution during time t , the density matrix becomes

$$\sigma_9 = -I_y S_{2J} C_I. \quad (11)$$

For an IS spin system, only the observable I_y terms are kept in σ_9 . For detection along the y-axis, magnetization along the y-axis is proportional to $\langle I_y \rangle$ and we have

$$\begin{aligned} M_y(t) \alpha \langle I_y \rangle &= Tr(I_y \sigma_9) \\ &= -S_{2J} C_I Tr(I_y I_y). \end{aligned} \quad (12)$$

For an IS($I = 1/2$, $S = 1/2$) spin system, since $Tr(I_y I_y) = 1$, we obtain

$$\langle I_y \rangle (IS) = -\sin(\pi J d_3) \cos(\Omega_I t). \quad (13)$$

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

$$\sigma_o = S_{1z} + S_{2z} \quad (14)$$

$$\sigma_5 = 2I_x S_{1z} + 2I_x S_{2z} \quad (15)$$

and

$$\sigma_9 = -I_y \sin(4\pi J d_3) \cos \Omega_I t. \quad (16)$$

Since $Tr(I_y I_y) = 2$, we have

$$\langle I_y \rangle (IS_2) = -2 \sin(4\pi J d_3) \cos(\Omega_I t). \quad (17)$$

Applying the same procedure for IS_3 spin system we obtained

$$\sigma_o = S_{1z} + S_{2z} + S_{3z}, \quad (18)$$

$$\sigma_5 = 2I_x S_{1z} + 2I_x S_{2z} + 2I_x S_{3z} \quad (19)$$

and

$$\langle I_y \rangle (IS_3) = -\{3 \sin(6\pi J d_3) + 3 \sin(2\pi J d_3)\} \cos(\Omega_I t), \quad (20)$$

where $Tr(I_y I_y) = 4$ is used.

For IS_n spin systems values of $\langle I_y \rangle = Tr(I_y \sigma_9)$ and their normalized forms by multiplication with $4/Tr(E)$ are given in Table 1, apart from $\cos(\Omega_I t)$. Here E is the unity product operator for corresponding spin system. Values of $\langle I_y \rangle = Tr(I_y \sigma_9)$ represent the FID signals of PENDANT NMR spectroscopy for IS_n spin system.

Table 1. $\langle I_y \rangle = Tr(I_y \sigma_9)$ values and their normalized forms for IS_n spin systems apart from $\cos(\Omega_I t)$ product.

Spin System	$\langle I_y \rangle = Tr(I_y \sigma_8)$	$\frac{4}{Tr(E)}$	$\frac{4}{Tr(E)} Tr(I_y \sigma_8)$
CH(IS_1)	$-\sin(2\pi J d_3)$	1	$-\sin(2\pi J d_3)$
CH ₂ (IS_2)	$-2 \sin(4\pi J d_3)$	1/2	$-\sin(4\pi J d_3)$
CH ₃ (IS_3)	$-3[\sin(6\pi J d_3) + \sin(2\pi J d_3)]$	1/4	$-\frac{3}{4}[\sin(6\pi J d_3) + \sin(2\pi J d_3)]$

The relative signal intensity plots of ¹³C PENDANT NMR spectroscopy for CH, CH₂ and CH₃ groups are given in Figure 2 as a function of time, d_3 . As one can see, PENDANT experiment for CH_n groups can be performed for different d_3 values and the signals of C, CH, CH₂ and CH₃ groups can be identified. Quaternary carbons will always give a negative signal, as they do not depend on the time, d_3 . The expected signs of PENDANT NMR signals of CH_n groups for different d_3 values obtained from Figure 2 are given in Table 2.

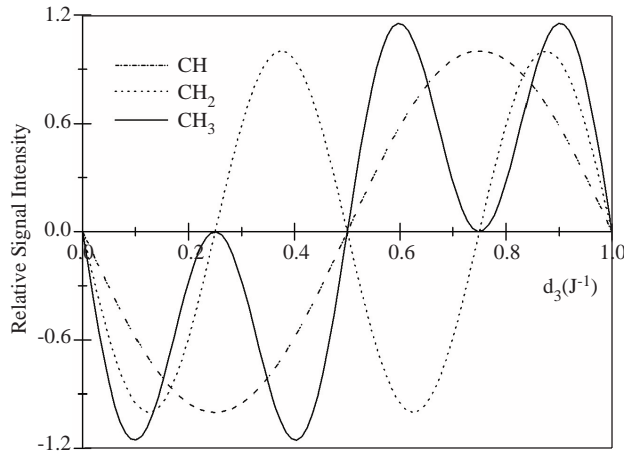


Figure 2. The relative signal intensity plots for ¹³C PENDANT NMR spectroscopy for CH, CH₂ and CH₃ groups.

Table 2. The expected signs of PENDANT NMR signals of CH_n groups at different d_3 values.

Group	$d_3=3/(8J)$	$d_3=5/(8J)$	$d_3=6/(8J)$	$d_3=4/(8J)$
C	–	–	–	–
CH	–	+	+	No signal
CH_2	+	–	No signal	No signal
CH_3	–	+	No signal	No signal

3.2. Simulation

Simulations of PENDANT NMR spectroscopy were performed using the NMR-Sim program. In simulation, an artificial spin system was established with the following chemical shift values: C (60 ppm), CH (50 ppm), CH_2 (40 ppm) and CH_3 (30 ppm). The simulated PENDANT spectra are shown in Figure 3 for different values of d_3 . They are in exact agreement with theoretical results presented in Figure 2 and Table 2.

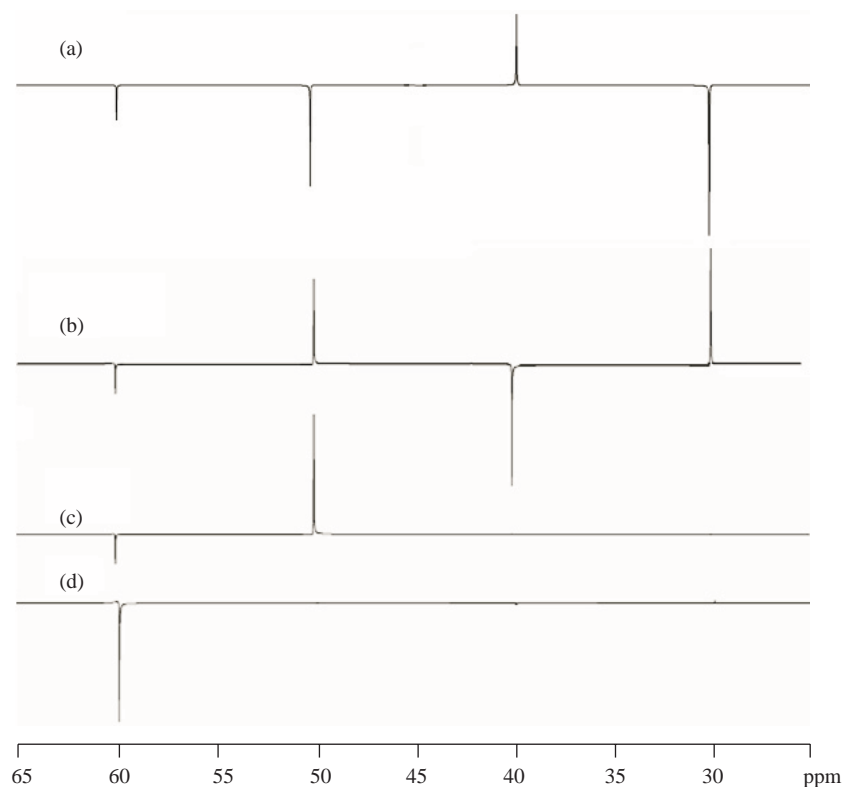


Figure 3. Simulated PENDANT ^{13}C NMR spectra for different d_3 values: (a) $3/(8J)$, (b) $5/(8J)$, (c) $6/(8J)$ and (d) $4/(8J)$.

3.3. Experimental results

Experimental measurements are performed using a Bruker DRX-400 NMR Spectrometer using 50% Crotonic acid ethyl ester (**I**). The ^1H broad band decoupled ^{13}C NMR spectrum of this sample is shown in Figure 4(a). ^{13}C PENDANT NMR spectra obtained for $d_3 = 3/(8J)$ and $5/(8J)$ are shown in Figures 4(b) and 4(c). Experimental spectra obtained for $d_3 = 6/(8J)$ and $4/(8J)$ values are not in agreement with theory and simulation. So they are not presented here. This is because spin–spin coupling constants are different for CH, CH_2 and CH_3 groups. The experimental results obtained for $d_3 = 3/(8J)$ and $5/(8J)$ are in agreement with theory (Figure 2 and Table 2) and simulation (Figure 3). These values can be called

optimum values for this experiment as all groups give signals of maximum intensity. For these values, spectra are not affected by the difference of spin–spin coupling constants.

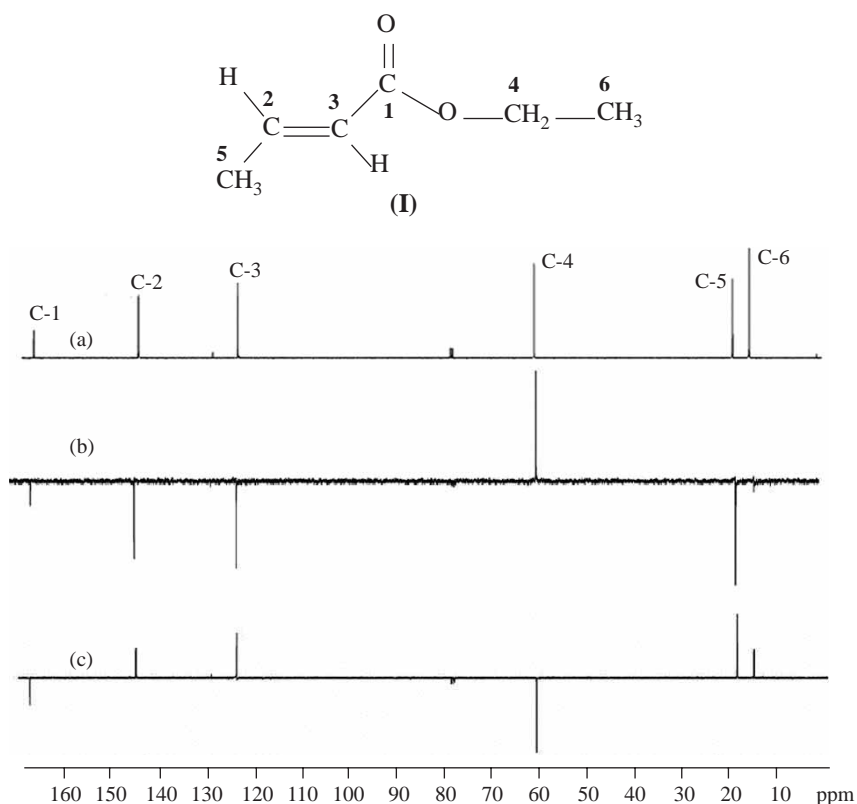


Figure 4. (a) The ^1H broad band decoupled ^{13}C NMR spectrum. ^{13}C PENDANT NMR spectra obtained for (b) $d_3 = 3/(8J)$ and (c) $d_3 = 5/(8J)$.

4. Conclusion

One can perform PENDANT NMR experiment for $d_3 = 3/(8J)$ and $5/(8J)$. For both values quaternary carbons give negative signals. For $d_3 = 3/(8J)$, while CH_2 groups are giving positive signals, CH and CH_3 groups give negative signals. For $d_3 = 5/(8J)$, CH_2 groups give negative signals, CH and CH_3 groups give positive signals. For each d_3 value the signs of CH and CH_3 groups signals are the same but CH and CH_3 groups can be identified from each other by looking at their chemical shifts. As a result ^{13}C PENDANT NMR spectroscopy can be used for identification of C, CH, CH_2 and CH_3 groups.

Acknowledgment

We would like to thank Dr Matthias Findeisen and Prof. Dr. Stefan Berger (Univ Leipzig, Inst Analyt Chem, D-04103 Leipzig, Germany) for providing us simulation and experimental results.

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