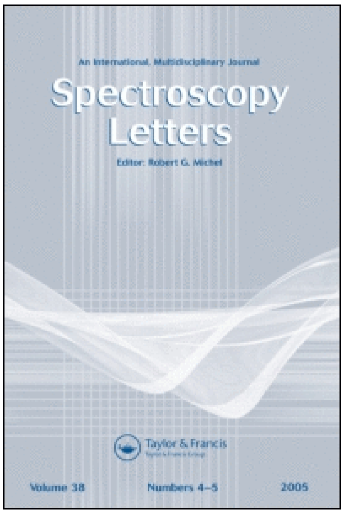

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THEORETICAL AND EXPERIMENTAL APT AND DEPT BEHAVIOR OF METHANE

Key Words: NMR; APT; DEPT; methane.

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ABSTRACT

The theoretically developed Attached Proton Test (APT) and Distortionless Enhancement by Polarization Transfer (DEPT) curves for methane were compared with the corresponding experimentally measured data for ^{13}C enriched methane. As expected, in both cases the CH_4 curves have a similar shape than the corresponding CH_2 curves and show a minimum intensity when $\tau = 1/2J$. In the APT case the CH_2 curve takes larger values than the CH_4 curve except at $\tau = 0, 1/2J$ and $1/J$ values where they have the same intensity. In the DEPT experiment, the maximum

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polarization transfer for CH_4 takes place at $\tau = 1/6J$ and $5/6J$, while for CH_2 this happen at $\tau = 1/4J$ and $3/4J$. This fact could be useful to distinguish the CH_2 and CH_4 signals using APT and DEPT experiments.

INTRODUCTION

For a long time the methane molecule has been a useful model to understand the origin of physicochemical and spectroscopic properties of structurally more complex molecules. In NMR spectrometry it has been the subject of several studies related to deuterium induced isotope shifts,[1-3] to the mechanism of spin relaxations,[4] for effects of Van der Waals interactions,[5] temperature and electronegativity of substituents on chemical shifts,[6-8] etc. In contrast, the theoretical basis to edit pulse sequences for methane have been neglected probably due to their structural simplicity. For example, since the early eighties the APT[9] (*Attached Proton Test*) and DEPT[10,11] (*Distortionless Enhancement by Polarization Transfer*) knowledge for CH, CH_2 and CH_3 fragments were implemented as analytical tools to distinguish them, but the CH_4 case was not considered. This fact encouraged us to develop the equations for the APT and DEPT curves of methane that predict the dependence of the signals intensity with variable time delay periods. These behaviors were tested experimentally, and are described herein.

RESULTS AND DISCUSSION

The APT sequence is one of the first NMR methods taking into account the time dependence of $^1J(^{13}C-^1H)$modulated ^{13}C magnetization for the differentiation of methyl (CH_3), methylene (CH_2), methylene (CH) and quaternary carbon atom (C) subspectra. The APT mathematical expressions for these molecular fragments have been established as:[9]

$$C \;:\; S/So = 1 \tag{1}$$

$$CH \;:\; S/So = \cos \pi J\tau \tag{2}$$

$$CH_2 : S/So = \frac{1}{2}(1+\cos 2\pi J\tau) \tag{3}$$

$$CH_3 : S/So = \frac{1}{4}(3 \cos \pi J\tau + \cos 3\pi J\tau) \tag{4}$$

where S and So are the intensities of the magnetization in the x-y plane at $\tau \neq 0$ and $\tau = 0$, respectively.

Equations (1)-(4) can be written in the generalized form

$$\mathrm{CH_n{:}\,S/So} = \cos^{n} \pi J\tau \tag{5}$$

Considering the series:

$$\cos^{2n} \alpha = \frac{1}{2^{2n}}\genfrac{[}{]}{0pt}{}{2n}{n} + \frac{1}{2^{2n-1}}\left[\cos\, 2n\alpha + \genfrac{[}{]}{0pt}{}{2n}{1}\cos(2n-2)\alpha + \cdots + \genfrac{[}{]}{0pt}{}{2n}{n\text{-}1}\cos 2\alpha\right] \tag{6}$$

it can be found that:

$$\mathrm{CH_4{:}\ S/So} = \frac{1}{8}(3 + 4\cos\, 2\pi J\tau + \cos\, 4\pi J\tau) \tag{7}$$

The five equations (1-4 and 7) can be solved numerically over the range from 0° to 180°, or 0 to π, as shown in Table 1, or they can be plotted as shown in figure 1a.

Equation (7) was tested experimentally through the classical APT pulse sequence using a τ array from 0.5 to 8 ms, in 0.5 ms increments, and the graphical results are shown in figure 1b. As can be seen, these results are in good agreement with the theorical curve and further show a similar trend than the CH_2 curve, giving, as expected only positive values. The only difference between the CH_4 and CH_2 curves is that the CH_2 curve takes larger or the same intensity values than the CH_4 curve, a fact that makes it possible to distinguish these carbons by their signal intensities, for instance at $\pi = 3/4$ (6 ms for $^1J_{CH} = 125$ Hz) in a natural gas sample.

The motion of the ^{13}C magnetization vectors for $^{13}CH_4$ is shown in figure 2. According to the APT sequence, the first 90° pulse aligns the five components of the quintet (a) along the y-axis in the rotating reference frame. After a $1/8J$ delay,

TABLE 1

Relative ^{13}C Signal Intensities for C_n Arrangements in the APT Experiment.

(o)	**0**	**45**	**60**	**90**	**120**	**135**	**180**
π	**0**	**1/4**	**1/3**	**1/2**	**2/3**	**3/4**	**1**
C	1	1	1	1	1	1	1
CH	1	$1/\sqrt{2}$	1/2	0	-1/2	$-1/\sqrt{2}$	-1
CH_2	1	1/2	1/4	0	1/4	1/2	1
CH_3	1	$1/2\sqrt{2}$	1/8	0	-1/8	$-1/2\sqrt{2}$	-1
CH_4	1	1/4	1/16	0	1/16	1/4	1

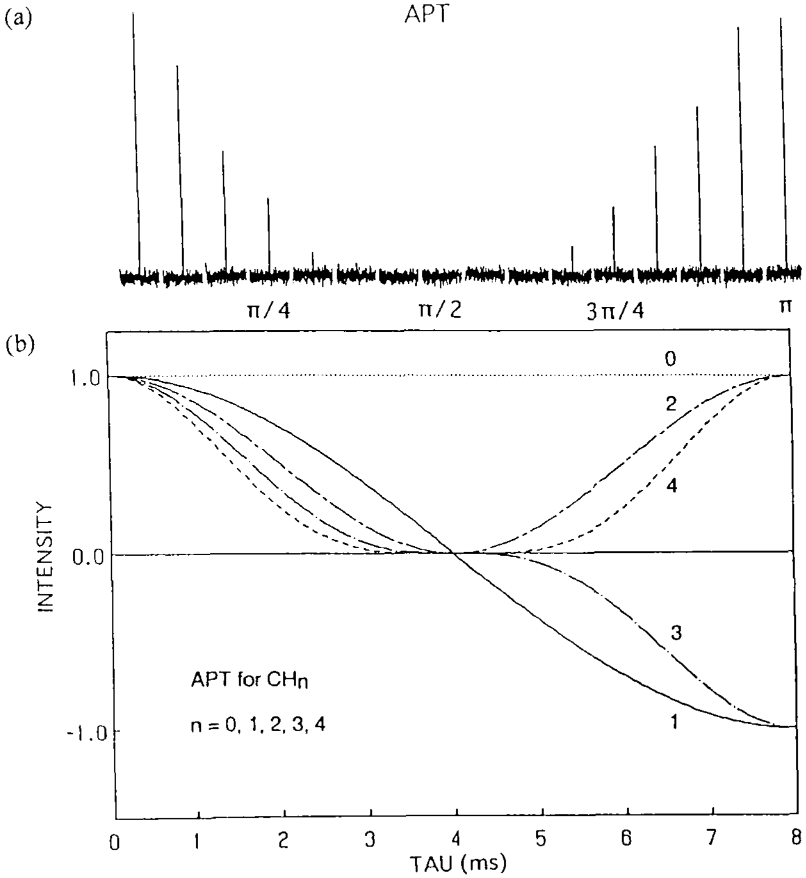

FIG. 1. (a) Theorical curves for APT with variable τ delays for C, CH, CH_2, CH_3 and CH_4 groups; (b) experimental arrayed APT spectra for $^{13}CH_4$ showing the variation of the net magnetisation (signal intensity) with variable τ delays.

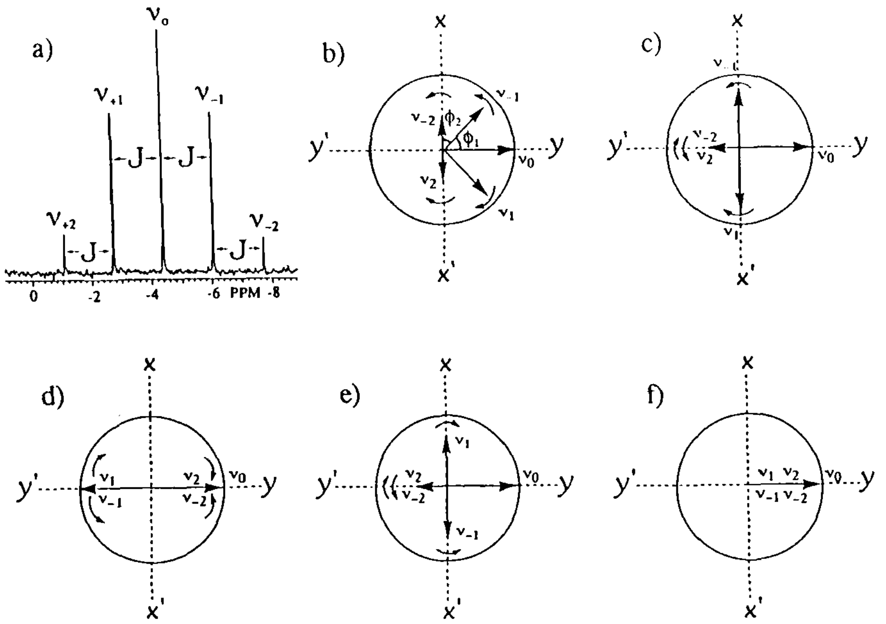

FIG. 2. a) ^1H coupled ^{13}C NMR spectrum of $^{13}CH_4$; b)-f) motion of the five vectors of the $^{13}CH_4$ carbon at the τ delay:

	b)	*c)*	*d)*	*e)*	*f)*
τ	1/8J	1/4J	1/2J	3/4J	1/J
ϕ_1	45°	90°	180°	270°	360°
ϕ_2	90°	180°	360°	540°	720°

the macroscopic magnetization has evolved into the five vectors (b), where υ_0 represents the vector moving at the rotating frame frequency, υ_1 and υ_{-1} are the vectors moving $+J$ and $-J$ Hz away from the vector υ_0; while the υ_2 and υ_{-2} vectors correspond to those moving two times away ($+2J$ and $-2J$ Hz) from υ_0. The angles ϕ_1 and ϕ_2 describe the radial magnitude of the evolution for the vectors giving the 4:4 and 1:1 relative intensity lines, respectively. It can be seen that the $4\cos 2\pi J\tau$ term in equation (7) corresponds to the ϕ_1 and ϕ_2 angles, and for each τ value, ϕ_2

will always be twice the ϕ_1 angle. The remaining pictorial representations (c-f) in Figure 2, modulate the net magnetization producing a signal with variable intensity. This signal becomes zero (d) when the delay reach *1/2J* seconds. At the time *1/J* seconds (f) the five components join again together along the *y*-axis, thus giving a signal with positive amplitud for the $^{13}CH_4$ molecule.

On the other hand, it is well known that the DEPT[10,11] pulse sequence is a useful method to differentiate CH, CH_2 and CH_3 groups. The edited version of the individual spectra allows to obtain their separate traces. In this case the amplitudes of the signals depend on the polarization transfer from the hydrogen atoms to the carbon nuclei, and the equations that describe the magnitudes of these transfers are the following:

$$\mathrm{CH}:\ \sin\theta = \sin\theta\ \cos^0\theta \qquad (8)$$

$$\mathrm{CH_2}:\ \sin 2\theta = 2\sin\theta\ \cos^1\theta \qquad (9)$$

$$\mathrm{CH_3}:\ \frac{3}{4}(\sin\theta + \sin 3\theta) = 3\sin\theta\ \cos^2\theta \qquad (10)$$

which can be generalized as:

$$\mathrm{CH_n}:\ \mathrm{n}\sin\theta\ \cos^{\mathrm{n-1}}\theta \qquad (11)$$

As was done above for the APT case, the theorical and experimental DEPT curves for $^{13}CH_4$ were determined at first glance. From equation (11) it can be deduced that

$$\mathrm{CH_4}:\ 4\ \sin\theta\ \cos^3\theta \qquad (12)$$

and considering the corresponding trigonometrical identities, it was finally found that

$$\mathrm{CH_4}:\ 4\,sin\theta\ \cos^3\theta = sin\,2\theta + \frac{1}{2}(sin\,4\theta) \qquad (13)$$

which describes the sinoidal dependence of the polarization transfer with the θ pulse, as shown in figure 3a. As can be seen, the behavior of the CH_4 curve is very

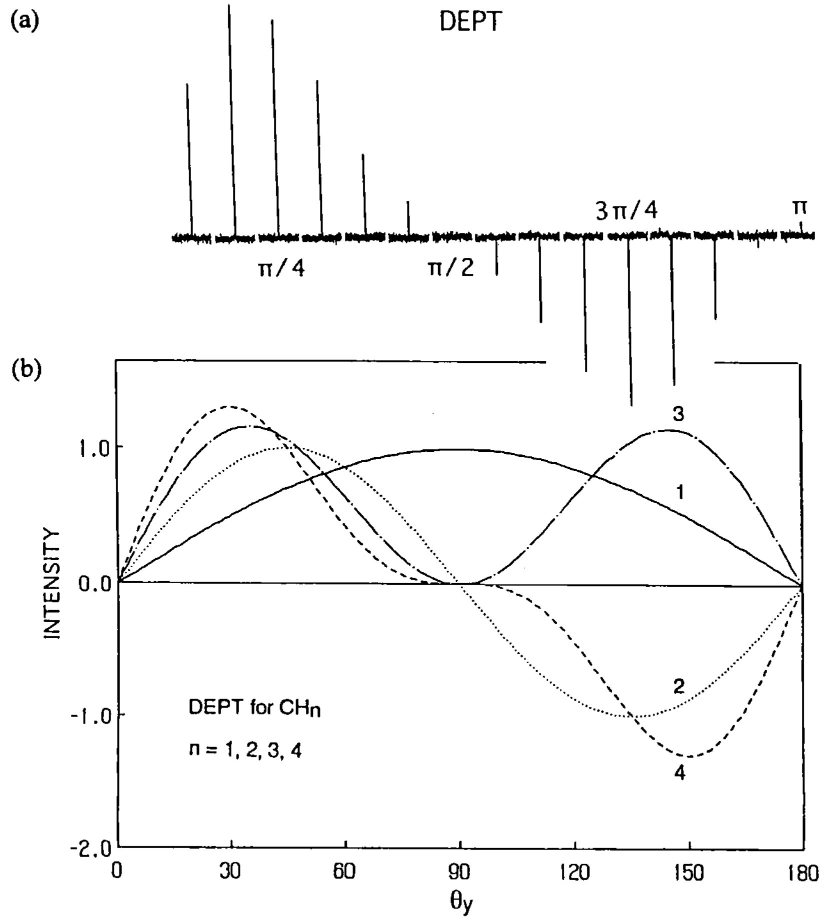

FIG. 3. (a) Sine modulations in the amplitude of the ^{13}C signals for CH, CH_2, CH_3 and CH_4 arrangements as a function of the θ pulse angle given during the polarization transfer pulse; (b) DEPT experiment (^1H-decoupled) for $^{13}CH_4$ showing the dependence of the polarization transfer (signal intensity) with the θ pulse angle.

similar to that of the CH_2 case, both being curves with negative and positive values, At $\tau = 1/6J$ and $\tau = 5/6J$ the maximum polarization transfer takes place for H_4. This fact makes it possible to differentiate the signals of CH_2 and CH_4, since the maximum intensity for CH_2 will be at $\tau = 1/4J$ and $\tau = 3/4J$. Table 2 shows the relative signal intensities for the CH, CH_2, CH_3 and CH_4 arrangements, where it can be seen that the maximum polarization transfer for CH_4 is reached when θ is equal to 30° and 150°, since the carbon holds four hydrogen atoms. Figure 3b shows a series of spectra acquired at variable θ pulse and the experimental curve shows close agreement with the theorical expression (eq. 13). In this case the vector analysis is difficult to show since heteronuclear multiple quantum coherence takes place in the DEPT sequence, although a representation has been attempted.[12]

The small differences between the theorical and experimental curves in both APT and DEPT experiments could in part be attributed to the "alfa" delay requiered by the spectrometer software, which is inserted in the pulse train before the acquisition time and, particularly for the DEPT sequence, to natural relaxations during the short delay given after each transient.

EXPERIMENTAL

The APT and DEPT spectra were recorded on a Varian XL 300GS spectrometer at an observe frequency of 75.4 MHz, using C_6H_6 as the solvent and TMS as the internal reference. The D_2 delay (τ) in the APT experiment was increased from 0.5 to 8 ms each 0.5 ms. For the DEPT experiment a variable θ pulse from 0 to 180°, obtained through an arrayed *mult*, was used. In both experiments 400 transients were acquired with an acquisition time of 1.8 s and a relaxation time of 2 s. The recycling time was set around 4 s and at least 8320 data points were acquired.

Preparation of ^{13}C labeled methane.

To a cooled (0°C) solution of 0.5 g (3.5 mmol) of CH_3I 99%-^{13}C in 10 ml of anhydrous ethyl ether were added 90 mg (3.7 mmol) of Mg powder under a N_2 atmosphere. The mixture was allowed to warm to the room temperature and stirred for 30 min. The temperature was lowered to 0°C, then was added dropwise 1 ml of

TABLE 2

Relative ^{13}C signal intensities for C_n arrangements in the DEPT experiment.

θ	**0**	**30**	**45**	**60**	**90**	**120**	**135**	**150**	**180**
π	**0**	**1/6**	**1/4**	**1/3**	**1/2**	**2/3**	**3/4**	**5/6**	**1**
CH	0	1/2	$1/\sqrt{2}$	$\sqrt{3}/2$	1	$\sqrt{3}/2$	$1/\sqrt{2}$	1/2	0
CH_2	0	$\sqrt{3}/2$	1	$\sqrt{3}/2$	0	$-\sqrt{3}/2$	-1	$-\sqrt{3}/2$	0
CH_3	0	9/8	$3/2\sqrt{2}$	$3\sqrt{3}/8$	0	$3\sqrt{3}/8$	$3/2\sqrt{2}$	9/8	0
CH_4	0	$3\sqrt{3}/4$	1	$\sqrt{3}/4$	0	$\sqrt{3}/4$	-1	$-3\sqrt{3}/4$	0

H_2O and the gas that evolved was bubbled into a cooled (10°C) 5 mm nmr tube containing 0.5 ml of C_6H_6, which was sealed.

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