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Phase Modulation in APT Spectra for ABX Patterns

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Anomalous APT spectra are reported for an organophosphorus compound containing methylene ^{13}C nuclei coupled to two ^{31}P nuclei. Strong coupling effects in these ABX spin systems are shown to account for the anomalous phases and intensities of the APT spectra by density matrix simulations. © 1997 by John Wiley & Sons, Ltd.

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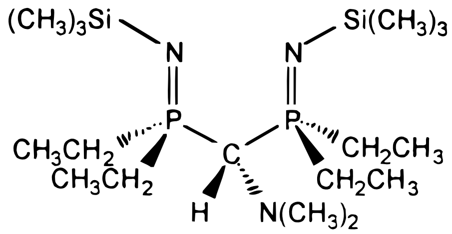
INTRODUCTION

APT,[1] a ^{13}C spin-echo pulse sequence[2] with the ^{1}H decoupler gated off during the delay period between the excitation and refocusing pulses, is used routinely in ^{13}C NMR spectroscopy to determine ^{13}C resonance multiplicities. Generally the APT spectrum is obtained with the delay equal to $1/J_{CH}$, where J_{CH} is the one-bond proton–carbon coupling constant. This gives ^{13}C spectra in which resonances from quaternary and methylene carbons are 180° out of phase from those originating from methine and methyl carbons. False multiplicity assignments are possible in ^{13}C dilabelled compounds because of J modulation of the ^{13}C resonances caused by homonuclear coupling during the spin-echo pulse sequence[3] or when the compound contains CH_n groups with very large J_{CH} values.[4] In this paper we report observations of phase modulation in APT spectra caused by strong coupling effects.

RESULTS AND DISCUSSION

The $^{13}C\{^{1}H\}$ spectra of organophosphorus molecules containing chemically equivalent phosphorus nuclei such as structure **1** (the synthesis of **1** and related molecules is described elsewhere[5]) often show second-order coupling patterns and such spectra can be analyzed fully.[6] The two pairs of chemically non-equivalent methylene carbons form the X parts of two nearly coincident ABX patterns shifted by 0.08 ppm as shown in Fig. 1(A). The quantities D_+ and D_- used in Fig. 1 and the angles ϕ_+ and ϕ_- used in Table 1 follow the definitions of Pople *et al.*[7] The ABX patterns arise because the methylene carbons couple differently to the two phosphorus nuclei which are magnetically non-equivalent because the phosphorus which is directly bonded to the ^{13}C nucleus experiences a small isotope shift. The ABX spectra are similar to those given in Ref. 6.

The APT spectrum of **1**, obtained with a $45–\tau_1–180–\tau_1–\tau_2–180–\tau_2$–Acquire sequence with the ^{1}H decoupler gated off during the τ_1–180 time interval, is shown in Fig. 1(B). The anomalous lineshapes in this APT spectrum are rather striking—the outermost lines in each of the six line patterns [at frequencies $\nu_X \pm (D_+ + D_-)$] have dispersion lineshapes, the innermost pairs of lines [at frequencies $\nu_X \pm (D_+ - D_-)$] have absorption lineshapes with much lower intensities than in the $^{13}C\{^{1}H\}$ spectrum in Fig. 1(A), while the intense lines at frequencies $\nu_X \pm (J_{AX} + J_{BX})/2$ have absorption lineshapes with amplitudes similar to those in the normal spectrum. The effect of strong coupling on spectral amplitudes has been reported for several spin-echo experiments,[8] but not for APT. The results of a density matrix analysis of the behavior of the X part of an ABX spin system when subjected to the APT pulse sequence, and to the simpler $90–\tau_1–180–\tau_1$–Acquire Hahn spin-echo sequence, are given in Table 1. The origin of the phase and amplitude anomalies observed in the APT spectrum is due to the mixing of magnetizations from lines at $\nu_X \pm (D_+ + D_-)$ and $\nu_X \pm (D_+ - D_-)$ produced by the 180° pulses. On the other hand, the magnetizations of the $\nu_X \pm (J_{AX} + J_{BX})/2$ lines are not mixed



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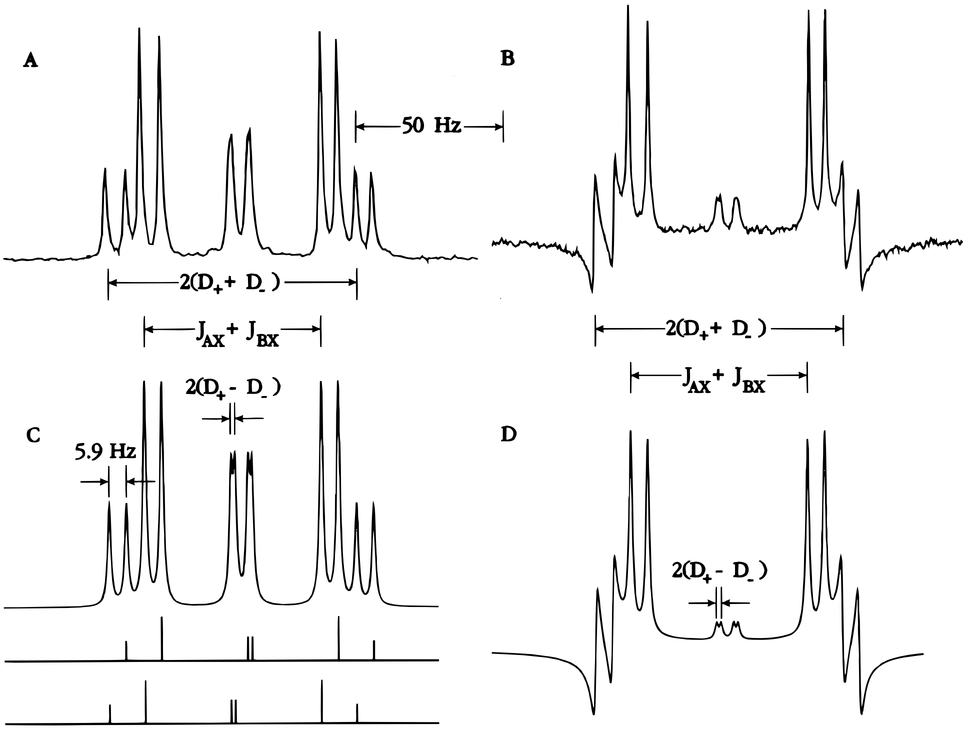

Figure 1. CH_2 region of the 75 MHz $^{13}C\{^1H\}$ and APT spectra of **1**: (A) observed $^{13}C\{^1H\}$; (B) observed APT; (C) calculated $^{13}C\{^1H\}$ with 'stick' spectra below; (D) calculated APT. Calculated spectra are based on a pair of ABX patterns with identical spectral parameters ($\nu_A - \nu_B = 1.0$ Hz, $J_{AB} = 31.7$ Hz, $J_{AX} = 59.0$ Hz, $J_{BX} = 2.0$ Hz) offset by 5.9 Hz. For APT, $\tau_1 = 0.007$ s and $\tau_2 = 0.001$ s.

by the 180° pulses and are completely refocused during the next delay period. The simulated $^{13}C\{^1H\}$ and APT spectra of **1** are shown in Fig. 1(C) and (D), respectively.

The relative magnitudes of the absorptive and dispersive components of the lines in the APT spectra at frequencies $\nu_X \pm (D_+ + D_-)$ and $\nu_X \pm (D_+ - D_-)$ are determined by the magnitudes of the delays τ_1 and τ_2, and by the magnitudes of the magnetic parameters D_+ and D_-. In general, the dispersive components of the inner lines at frequencies $\nu_X \pm (D_+ - D_-)$ are very small when $\nu_A - \nu_B$ is small as in compound **1**. The magnitudes of the absorptive components of the inner lines vary strongly with D_+, D_- and τ_1 provided $D_+\tau_1$, $D_-\tau_1 > 0.1$. The dispersive components of the outer lines at frequencies $\nu_X \pm (D_+ + D_-)$ are also significant when $D_+\tau_1$, $D_-\tau_1 > 0.1$, and when the coupling constants satisfy the relationship $0.3\,|J_{AX} - J_{BX}| \lesssim J_{AB} \lesssim 0.6\,|J_{AX} - J_{BX}|$. When $\nu_A - \nu_B \approx 0$ as in compound **1**, $D_+ \approx D_- = D$, and the magnitudes of the absorptive components of the inner lines are approximately proportional to $1 - 2\sin^2(\phi_+ - \phi_-)\,[1 - \cos(4\pi D\tau_1)]$. Furthermore, the magnitudes of the dispersive components of the outer lines are approximately proportional to $\sin(4\pi D\tau_1)\,[1 - \cos(4\pi D\tau_1)]$ in this limit,

Table 1. Amplitudes for lines in the spin-echo and APT spectra for the X part of an ABX spin system[a]

Spectra	Frequency	Absorption intensity	Dispersion intensity
Spin-echo	$\nu_X \pm (D_+ + D_-)$	SA_i	$\pm SA_r$
	$\nu_X \pm (J_{AX} + J_{BX})/2$	1	0
	$\nu_X \pm (D_+ - D_-)$	$-CB_i$	$\pm CB_r$
APT	$\nu_X \pm (D_+ - D_-)$	$S\,\{C^2[-A_r \sin(\Omega_+\tau_2) + A_i \cos(\Omega_+\tau_2)] + CS\,(B_r[-\sin(\omega_+\tau_2) + \sin(\omega_-\tau_2)] + B_i[\cos(\omega_+\tau_2) + \cos(\omega_-\tau_2)]) - S^2 A_i\}$	$\mp S\,\{C^2[A_r \cos(\Omega_+\tau_2) + A_i \sin(\Omega_+\tau_2)] + CS\,(B_r[\cos(\omega_+\tau_2) - \cos(\omega_-\tau_2)] + B_i[\sin(\omega_+\tau_2) + \sin(\omega_-\tau_2)]) + S^2 A_r\}$
	$\nu_X \pm (J_{AX} + J_{BX})/2$	1	0
	$\nu_X \pm (D_+ - D_-)$	$C\,\{S^2[B_r \sin(\Omega_-\tau_2) - B_i \cos(\Omega_-\tau_2)] + CS\,(A_r[\sin(\omega_+\tau_2) + \sin(\omega_-\tau_2)] - A_i[\cos(\omega_+\tau_2) + \cos(\omega_-\tau_2)]) + C^2B_i\}$	$\pm C\,\{S^2[B_r \cos(\Omega_-\tau_2) + B_i \sin(\Omega_+\tau_2)] + CS\,(A_r[\cos(\omega_+\tau_2) - \cos(\omega_-\tau_2)] + A_i[\sin(\omega_+\tau_2) - \sin(\omega_-\tau_2)]) + C^2B_r\}$

[a] $D_\pm = \frac{1}{2}\sqrt{[\nu_A - \nu_B \pm (J_{AX} - J_{BX})/2]^2 + J_{AB}^2}$;
$C = \cos(\phi_+ - \phi_-)$;
$S = \sin(\phi_+ - \phi_-)$;
$\omega_\pm = 4\pi D_\pm$;
$\Omega_\pm = \omega_+ \pm \omega_-$;
$A_r = SC^2[\sin(\omega_+\tau_1) + \sin(\omega_-\tau_1) - \sin(\Omega_+\tau_1)]$;
$A_i = S\{1 + C^2[-1 + \cos(\omega_+\tau_1) + \cos(\omega_-\tau_1) - \cos(\Omega_+\tau_1)]\}$;
$B_r = CS^2[-\sin(\omega_+\tau_1) + \sin(\omega_-\tau_1) + \sin(\Omega_-\tau_1)]$;
$B_i = -C\{1 + S^2[-1 + \cos(\omega_+\tau_1) + \cos(\omega_-\tau_1) - \cos(\Omega_-\tau_1)]\}$.

so the APT lineshapes are very sensitive to the value of τ_1 and to the values of J_{AB} and $|J_{AX} - J_{BX}|$ which define the parameter D. The APT lineshapes are much more sensitive to the values of the magnetic parameters than the standard $^{13}C\{^1H\}$ spectra are, so APT and/or spin-echo spectra may be used to refine estimates of magnetic parameters obtained from analysis of $^{13}C\{^1H\}$ spectra. INEPT[9] and DEPT[10] spectra of **1** show very little phase distortion because the delay periods in these sequences are much shorter than the long delay period τ_1 used in APT.

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