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INFRARED STUDY ON THE C≡P STRETCHING VIBRATION OF 1-PHOSPHAPROPYNE $CH_3C{\equiv}P$ AND ITS PERDEUTERIUM ANALOG $CD_3C{\equiv}P$

Keiichi OHNO,* Yasumasa YAMAMOTO, Hiroatsu MATSUURA, and Hiromu MURATA
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda-machi, Naka-ku, Hiroshima 730

Unstable molecule 1-phosphapropyne was detected by gas-phase infrared spectroscopy and the vibration-rotation band of the C≡P stretching was analyzed for $CH_3C{\equiv}P$ and $CD_3C{\equiv}P$.

In 1979, an unstable molecule 1-phosphapropyne $CH_3C{\equiv}P$ was first found by microwave and photoelectron spectroscopy.[1)] This initiative work stimulated us to undertake vibration-spectroscopic investigation of this molecule. Mixture samples containing $CH_3C{\equiv}P$ were prepared by the pyrolysis of $C_2H_5PCl_2$[1)] and the infrared bands of $CH_3C{\equiv}P$ were assigned on the basis of the spectral changes with time and of the observed band shapes.[2)] In this work, we have dealt with the vibration-rotation analysis of the C≡P stretching band for $CH_3C{\equiv}P$ and $CD_3C{\equiv}P$ in order to make definite band assignment of 1-phosphapropyne.

The infrared spectra were measured on a JEOL JIR-40X Fourier transform infrared spectrometer with a resolution of 0.08 cm^{-1}. The sample pressure was about 3 kPa in a 12-cm glass cell. In either of the infrared spectra of the pyrolysis products of $C_2H_5PCl_2$ and $C_2D_5PCl_2$, a strong parallel band was observed at 1550-1560 cm^{-1} as shown in Fig. 1. This band exhibited a strong Q branch as well as series of P and R branches with line spacing of about 2B; possible K structures were not resolved under the spectral resolution available. The J-value assignment of the P- and R-branch lines were readily made, as indicated in Fig. 1, up to J=60 for $CH_3C{\equiv}P$ and J=80 for $CD_3C{\equiv}P$. In the spectral analysis, the ground-state constants were first determined by the combination differences method.[3)] The agreement between the derived value for B_0 and the value obtained by microwave spectroscopy[1)] indicated that the parallel band at 1550-1560 cm^{-1} was indeed due to 1-phosphapropyne. This band was thus assigned to the C≡P stretching mode (ν_2). The spectroscopic constants for the ν_2 band were subsequently derived from the observed vibration-rotation wavenumbers by constraining the ground-state constants B_0, $(D_J)_0$, and $(D_{JK})_0$ to the accurately determined microwave values[1)] and assuming $(D_{JK})_2=(D_{JK})_0$, $(D_K)_2=(D_K)_0$, and $[(A_2-B_2)-(A_0-B_0)]=0$. In assigning the quantum number K to each of the unresolved P(J) and R(J) lines, spectral simulation with the Boltzmann factor was employed. Table 1 gives the spectroscopic constants determined for the ν_2 band of $CH_3C{\equiv}P$ and $CD_3C{\equiv}P$. The standard errors of the least-squares fit of 124 lines for $CH_3C{\equiv}P$ and of 178 lines for $CD_3C{\equiv}P$ were ±0.020 and ±0.023 cm^{-1}, respectively.

The fact that the ν_2 wavenumbers for $CH_3C{\equiv}P$ and $CD_3C{\equiv}P$ are almost the same indicates that the C≡P stretching vibration couples negligibly with methyl group

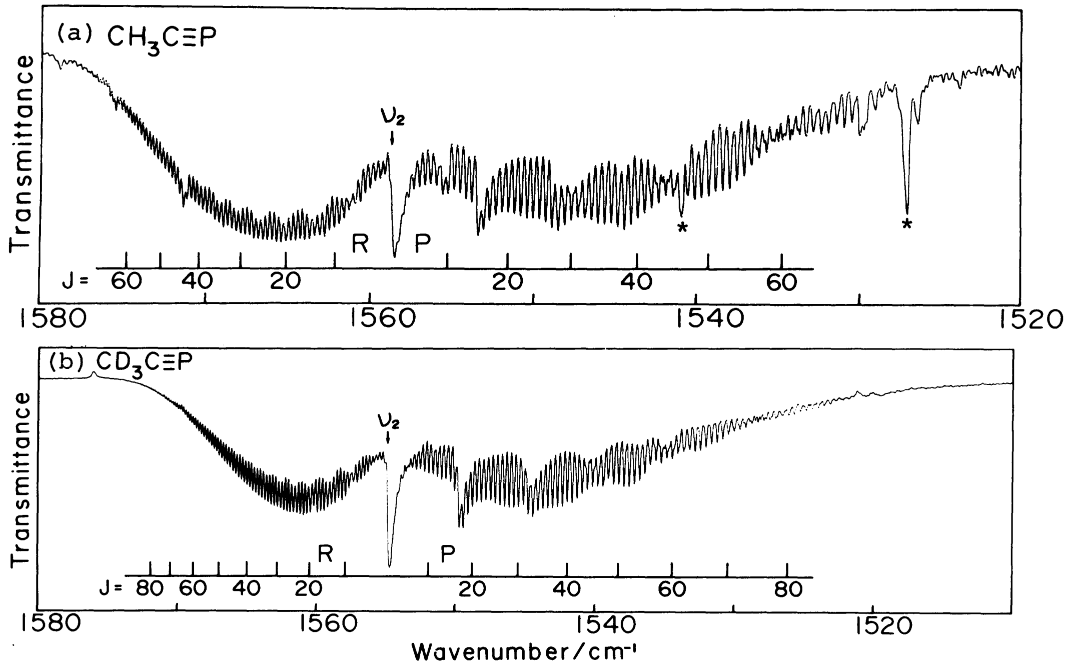

Fig. 1. Vibration-rotation spectra of the ν_2 band region of $CH_3C{\equiv}P$ (a) and $CD_3C{\equiv}P$ (b). The peaks marked with asterisks are ${}^{R}Q_K$ branches of the ν_6 band.

vibrations. This contrasts with the large coupling of the C≡P stretching vibration with the skeletal stretching vibration; the observed C≡P stretching wavenumbers are in fact spread over in the 1270-1680 cm^{-1} region for HC≡P, FC≡P, and $CH_3C{\equiv}P$.[2)]

The Q branches of the hot bands, $\nu_2+\nu_8-\nu_8$ and $\nu_2+2\nu_8-2\nu_8$, were also observed at 1553.63 and 1548.67 cm^{-1}, respectively, for $CH_3C{\equiv}P$ and at 1549.91 and 1544.91 cm^{-1} for $CD_3C{\equiv}P$. The anharmonicity constant x_{28} was therefore derived to be -5.03(7) cm^{-1} for either of the isotopic species.

In conclusion, the parallel band at 1550-1560 cm^{-1} was assigned to the C≡P stretching vibration of 1-phosphapropyne, on the basis of the derived value for the rotational constant B and the small wavenumber shift of this band on deuteration.

Table 1. Spectroscopic constants (cm^{-1}) of the ν_2 band for $CH_3C{\equiv}P$ and $CD_3C{\equiv}P$[a)]

Constant	$CH_3C{\equiv}P$		$CD_3C{\equiv}P$	
	ν_2	Ground state	ν_2	Ground state
$(\nu_0)_v$	1558.724(25)	-	1554.962(25)	-
B_v	0.165368(15)	0.16649312[b)]	0.1423070(74)	0.14322105[b)]
$(D_J)_v \times 10^8$	2.45(43)	2.74[b)]	2.53(10)	2.67[b)]
$(D_{JK})_v \times 10^6$	$=(D_{JK})_0$	2.2212[b)]	$=(D_{JK})_0$	1.4343[b)]

a) Errors (3σ) for the last significant figures in parentheses. b) Microwave value.

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