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The ν_8 Infrared Band of Ethylidynephosphine $CH_3C{\equiv}P$ and Its Perdeuteride $CD_3C{\equiv}P$

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Synopsis. The gas-phase infrared spectra of ethylidynephosphine $CH_3C{\equiv}P$ and its perdeuteride $CD_3C{\equiv}P$ were measured in the 50—400 cm^{-1} region with a resolution of 0.12 cm^{-1}. The molecular constants for the $\nu_8^{\pm1}$ and $2\nu_8^0-\nu_8^{\pm1}$ bands were determined by the ${}^{P,R}Q_K$ branch analysis.

Vibrational spectra of ethylidynephosphine (1-phosphapropyne)$CH_3C{\equiv}P$ and its perdeuteride $CD_3C{\equiv}P$ have been analyzed previously by infrared spectroscopy and the wavenumbers of the fundamental transitions have been determined.[1)] Of the eight fundamentals, the $\nu_8^{\pm1}$ band, which is associated with the lowest vibrational level, has been detected only in the solid state, but no information has been available on this band for the gaseous state. In the present study, we have investigated the gas-phase infrared spectra of $CH_3C{\equiv}P$ and $CD_3C{\equiv}P$ in the 50—400 cm^{-1} region with a resolution of 0.12 cm^{-1} and the molecular constants for the $\nu_8^{\pm1}$ band have been determined. These constants will be eventually important for vibration-rotation analyses of the band systems in which the overtone and/or combination of $\nu_8^{\pm1}$ is involved.

Experimental

Samples of $CH_3C{\equiv}P$ and $CD_3C{\equiv}P$ were prepared by the pyrolyses of $C_2H_5PCl_2$ and $C_2D_5PCl_2$, respectively.[2)] The far-infrared spectra were recorded on a JEOL JIR-40X Fourier transform infrared spectrometer. A globar source, a 6-μm Mylar beam splitter, and a TGS detector with a polyethylene window were used. The sample pressure was about 5 kPa in a 12-cm gas cell fitted with polyethylene windows. Dry nitrogen gas was continuously passed through the instrument during the measurement to get rid of water vapor.

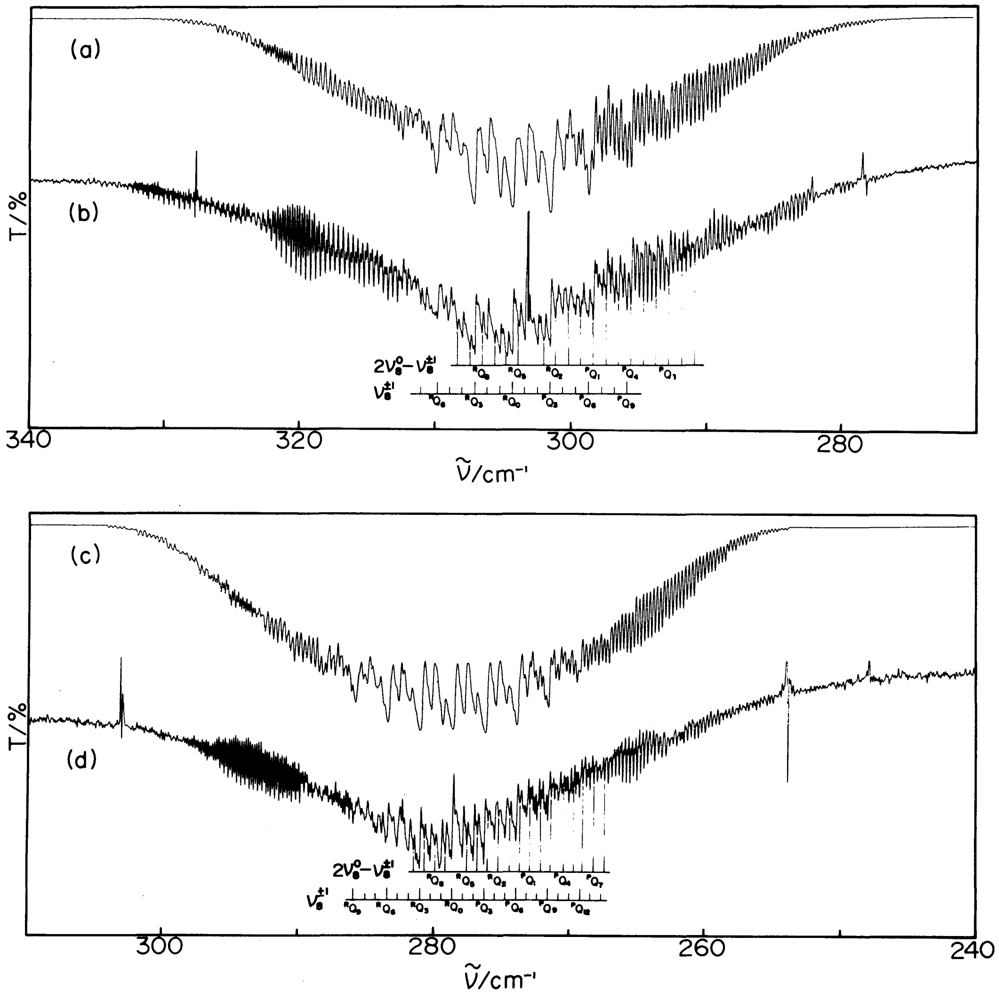

Fig. 1. Infrared spectra of the $\nu_8^{\pm1}$ and $2\nu_8^0-\nu_8^{\pm1}$ bands of $CH_3C{\equiv}P$ and $CD_3C{\equiv}P$. (a) Simulated spectrum of $CH_3C{\equiv}P$, (b) observed spectrum of $CH_3C{\equiv}P$, (c) simulated spectrum of $CD_3C{\equiv}P$, and (d) observed spectrum of $CD_3C{\equiv}P$.

Results and Discussion

Figure 1 shows the infrared spectra of the $\nu_8^{\pm1}$ band region of $CH_3C{\equiv}P$ and $CD_3C{\equiv}P$. The $\nu_8^{\pm1}$ band is due to the perpendicular transition of the prolate symmetric-top molecule. The wavenumbers for the ${}^{P,R}Q_K$ branches of $\nu_8^{\pm1}$ are expressed by

$$\begin{aligned}{}^{R}_{P}\nu^{Q}=&\nu_0+[A'(1-2\zeta^z)-B']\pm2[A'(1-\zeta^z)-B']K\\&+[(A'-B')-(A''-B'')]K^2+(B'-B'')J(J+1),\end{aligned}\qquad(1)$$

where the centrifugal distortion terms are neglected. Thus, the ${}^{P,R}Q_K$ branches were easily assigned on the basis of a successive spacing of approximately $2[A'(1-\zeta^z)-B']=0.8$—$0.9\ cm^{-1}$ and the nuclear spin statistics, i.e., the $K=3|n|$ levels (n: integer) are stronger in intensity than the other K levels in the ground state. The assignments of the ${}^{P,R}Q_K$ branches are shown in Fig. 1. Definitive assignments of the ${}^{P,R}R_K$ and ${}^{P,R}P_K$ branch lines of individual subbands could not be made, because the small spacing of $2[A'(1-\zeta^z)-B']$ made the P and/or R branch lines overlap each other. The molecular constants ν_0, A', and $A'\zeta^z$ in the usual quadratic expression were determined by the least-squares method so as to fit the observed ${}^{P,R}Q_K$ branch wavenumbers, where other rotational and centrifugal distortion constants were constrained to the microwave values.[2] The observed line positions of the ${}^{P,R}Q_K$ branches are given in Table 1. The molecular constants determined are listed in Table 2.

The spectra of the $\nu_8^{\pm1}$ band for $CH_3C{\equiv}P$ and $CD_3C{\equiv}P$ were simulated by using the molecular constants obtained. The simulation spectra have revealed the existence of additional series of lines in the experimental spectra. These lines may be ascribed to hot bands with which $\nu_8^{\pm1}$ is associated. For the hot band $2\nu_8-\nu_8$, which is due to a transition from the most populated excited state, there are three possible cases; i.e., two perpendicular-type bands $2\nu_8^0-\nu_8^{\pm1}$ and

Table 1. Observed ${}^{P,R}Q_K$ Line Positions of the $\nu_8^{\pm1}$ and $2\nu_8^0-\nu_8^{\pm1}$ Bands of $CH_3C{\equiv}P$ and $CD_3C{\equiv}P$[a)]

	$CH_3C{\equiv}P$				$CD_3C{\equiv}P$			
	$\nu_8^{\pm1}$		$2\nu_8^0-\nu_8^{\pm1}$		$\nu_8^{\pm1}$		$2\nu_8^0-\nu_8^{\pm1}$	
	ν_{obsd}	$\Delta\nu$[b)]	ν_{obsd}	$\Delta\nu$[b)]	ν_{obsd}	$\Delta\nu$[b)]	ν_{obsd}	$\Delta\nu$[b)]
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
${}^RQ_{10}$			308.287*	0.128			281.469	0.042
${}^RQ_9$			307.383	0.046	285.748	−0.018	280.656	−0.017
${}^RQ_8$			306.479	−0.013	285.055	0.062	279.902	−0.010
${}^RQ_7$	310.668	0.056	305.545*	−0.083	284.272	0.057	279.119	−0.026
${}^RQ_6$	309.794	0.040	304.732	−0.014	283.398	−0.034		
${}^RQ_5$	308.860	−0.017	303.828	−0.022	282.674	0.028	277.552	−0.044
${}^RQ_4$	307.926	−0.057			281.831	−0.026	276.768	−0.046
${}^RQ_3$	307.022	−0.051	301.959	−0.061	281.017	−0.049	275.985	−0.043
${}^RQ_2$	306.118	−0.033	301.055	−0.037	280.234	−0.038	275.202	−0.036
${}^RQ_1$	305.184	−0.035	300.121	−0.037	279.451	−0.026	274.388	−0.058
${}^RQ_0$	304.280	0.002	299.247	0.026	278.667	−0.015	273.665	0.013
${}^PQ_1$	303.345	0.012	298.313	0.030	277.853	−0.033	272.912	0.056
${}^PQ_2$	302.381	−0.004	297.349	0.001	277.070	−0.021	272.128	0.068
${}^PQ_3$	301.477	0.042	296.445	0.029	276.286	−0.011	271.345	0.081
${}^PQ_4$	300.543	0.056	295.541	0.051	275.503	−0.001	270.471	0.003
${}^PQ_5$	299.579	0.036	294.607	0.035	274.750	0.037	269.687	0.015
${}^PQ_6$	298.645	0.042	293.673	0.008	273.936	0.012	269.024*	0.147
${}^PQ_7$	297.650	−0.022	292.767	−0.004	273.183	0.045	268.211*	0.126
${}^PQ_8$	296.716	−0.035	291.775*	−0.117	272.399	0.043	267.427*	0.133
${}^PQ_9$	295.812	−0.031	290.991	−0.040	271.616	0.039		
${}^PQ_{10}$					270.832	0.029		
${}^PQ_{11}$					270.049	0.016		
${}^PQ_{12}$					269.265	−0.005		
${}^PQ_{13}$					268.482	−0.030		
${}^PQ_{14}$					267.699	−0.062		

a) The observed wavenumbers with asterisk are not included in the least-squares fit. J values were assumed to be $J=K+1$ for the ${}^RQ_K$ lines and $J=K$ for the ${}^PQ_K$ lines. b) $\nu_{obsd}-\nu_{calcd}$.

Table 2. Molecular Constants for the $\nu_8^{\pm1}$ and $2\nu_8^0-\nu_8^{\pm1}$ Bands of $CH_3C{\equiv}P$ and $CD_3C{\equiv}P$[a)]

Molecular constant	$CH_3C{\equiv}P$		$CD_3C{\equiv}P$	
	$\nu_8^{\pm1}$	$2\nu_8^0-\nu_8^{\pm1}$	$\nu_8^{\pm1}$	$2\nu_8^0-\nu_8^{\pm1}$
$(\nu_0)_v$	308.338 (48)	294.217 (37)	280.330 (37)	271.207 (44)
A_v	5.1703 (14)	5.1692 (35)	2.58820 (53)	2.5878 (10)
$(A\zeta^z)_v$	4.5320 (31)	4.5320[b)]	2.0470 (18)	2.0470[b)]

a) In units of cm^{-1}. The three times standard deviations, given in parentheses, apply to the last significant figures. $A_0=5.17264\ cm^{-1}$ for $CH_3C{\equiv}P$ and $A_0=2.58826\ cm^{-1}$ for $CD_3C{\equiv}P$. b) Assumed.

$2\nu_8{}^{\pm 2}-\nu_8{}^{\pm 1}$ and one parallel-type band $2\nu_8{}^{\mp 2}-\nu_8{}^{\pm 1}$. Of these, only the $2\nu_8{}^0-\nu_8{}^{\pm 1}$ band is likely to be observed in this region, since the microwave analysis of $CH_3C\equiv P$[2)] has given the anharmonicity constant g_{88} to be 6.11 ± 0.86 cm^{-1} which includes a Coriolis term $A_8(\zeta_8{}^z)^2$. The wavenumbers for the $^{P,R}Q_K$ branches of $2\nu_8{}^0-\nu_8{}^{\pm 1}$ are given by

$$\begin{aligned}{}^{R}_{P}\nu^{Q} &= \nu_0 + A'-B' \pm 2[A'-A''\zeta^z-B']K \\ &\quad +[(A'-B')-(A''-B'')]K^2+(B'-B'')J(J+1). \end{aligned} \tag{2}$$

The successive spacing of $2[A'-A''\zeta^z-B']$ is nearly equal to that for the $\nu_8{}^{\pm 1}$ band. The transitions with the $|K-l|=3|n|$ levels in the lower vibrational state, i.e., …, $^RQ_5$, $^RQ_2$, $^PQ_1$, $^PQ_4$, … are stronger than the others. The assignments of the $^{P,R}Q_K$ branches of $2\nu_8{}^0-\nu_8{}^{\pm 1}$ were made, as shown in Fig. 1, on the basis of the above criterion and the anharmonicity constant x_{88} for $CH_3C\equiv N$[3)] and $x'_{88}\simeq(\omega'_8/\omega_8)x_{88}$. The observed line positions of the $^{P,R}Q_K$ branches are given in Table 1 and the molecular constants determined are given in Table 2.

The composite simulation spectrum of the $\nu_8{}^{\pm 1}$ and $2\nu_8{}^0-\nu_8{}^{\pm 1}$ bands is shown in Fig. 1(a) for $CH_3C\equiv P$ and in Fig. 1(c) for $CD_3C\equiv P$. It is seen that the $\nu_8{}^{\pm 1}$ band is well simulated but the intensities of $2\nu_8{}^0-\nu_8{}^{\pm 1}$ are not reproduced satisfactorily with the Boltzmann factor alone.

Table 3. Vibrational Parameters of the $\nu_8{}^{\pm 1}$ Band of $CH_3C\equiv P$ and $CD_3C\equiv P$

Compound	$\omega_8{}^0$/cm^{-1}	x_{88}/cm^{-1}	g_{88}/cm^{-1}
$CH_3C\equiv P$	303.18	−0.95	6.11[a)]
$CD_3C\equiv P$	277.38	−0.81	3.75[b)]

a) Microwave value (Ref. 2). b) The anharmonic terms in g_{88} are assumed to be the same as those for $CH_3C\equiv P$.

The determined band origins for $\nu_8{}^{\pm 1}$ of $CH_3C\equiv P$ and $CD_3C\equiv P$ in the gaseous state are smaller by 8—7 cm^{-1} than those observed in the solid state: 316 cm^{-1} for the former and 287 cm^{-1} for the latter.[1)] The band origins for $\nu_8{}^{\pm 1}$ and $2\nu_8{}^0-\nu_8{}^{\pm 1}$ and the microwave value[2)] for g_{88} of $CH_3C\equiv P$ yield the vibrational parameters for $CH_3C\equiv P$ and $CD_3C\equiv P$ as given in Table 3. By using these parameters, the band origin for $3\nu_8{}^{\pm 1}$ of $CD_3C\equiv P$ is estimated to be 828.6 cm^{-1}. An experimental value of 829.7 ± 0.4 cm^{-1} has been obtained for this band origin from the $^{P,R}Q_K$ branch analysis of a Fermi-interacting band system $\nu_7{}^{\pm 1}$ and $3\nu_8{}^{\pm 1}$ with the assumption that $(\zeta_{\text{eff}}{}^z)_{888}=0.791$.[1)] The Coriolis constant $\zeta_8{}^z$ was obtained to be 0.876 for $CH_3C\equiv P$ and 0.791 for $CD_3C\equiv P$, in good agreement with 0.865 and 0.772, respectively, calculated from the molecular force field.[1)] The molecular parameters for $CH_3C\equiv P$ may also be compared with those for $CH_3C\equiv N$: $\omega_8{}^0=360.27$ cm^{-1}, $x_{88}=-0.963$ cm^{-1}, $g_{88}=5.75$ cm^{-1}, and $\zeta_8{}^z=0.874$.[3)]

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