The Microwave Spectrum of Phosphaethene, $CH_2{=}PH$

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Summary A detailed assignment and accurate analysis of the *R*-band microwave spectrum of phosphaethene $CH_2{=}PH$, has been carried out and the rotational constants A_0 = 138 503·20(21), B_0 = 16 418·105(26), and C_0 = 14 649·084(28) were derived together with all *five* quartic centrifugal distortion coefficients; this simplest phospha-alkene has been obtained by pyrolysis of $SiMe_3CH_2PH_2$ (at 710 °C) as well as of $(CH_3)_2PH$ and CH_3PH_2 (at 1000 °C), though less efficiently.

OUR original detection of phosphaethene, $CH_2{=}PH$, in the pyrolysis products of dimethylphosphine $(CH_3)_2PH$ was reported together with the detections of *P*-chlorophosphaethene, $CH_2{=}PCl$, and *C*-difluorophosphaethene $CF_2{=}PH$.[1] We here report the detailed assignment and accurate analysis of the microwave spectrum of $CH_2{=}PH$ together with results of studies of an alternative method of production.

TABLE 1. Observed frequencies of $CH_2{=}PH$.

Assignment						Frequency /MHz	Obs. − calc. /MHz
1	0	1	0	0	0	31 067·120	−0·001
3	0	3	2	1	2	27 208·936	−0·002
5	1	4	5	1	5	26 518·826	0·001
6	1	5	6	1	6	37 118·709	0·000
11	1	10	10	2	9	29 067·941	0·004
14	2	12	14	2	13	32 692·832	0·007
17	2	15	16	3	14	38 429·902	0·014
16	1	16	15	2	13	39 680·356	−0·026
17	1	17	16	2	14	35 752·041	−0·049
18	1	18	17	2	15	34 530·133	−0·049

$CH_2{=}PH$ was originally produced by pyrolysing CH_3PH_2 as well as $(CH_3)_2PH$ at *ca.* 1000 °C. However, the strongest spectra have now been obtained by passing $Me_3SiCH_2PH_2$ *via* a heated quartz tube (8 mm i.d. and 400 mm long; 710 °C) followed by a cold trap (−78 °C) through a 1 m cell of a Hewlett Packard 8460A microwave spectrometer operating between 26·5 and 40 GHz. Ten lines, including the 1_{01}–0_{00} line originally detected,[1] have been measured (Table 1) and fitted, using a least squares criterion to the Watson Hamiltonian[2] with quartic centrifugal distortion coefficients. It was found that to fit these lines all 5 quartic coefficients were necessary, otherwise relatively large inaccuracies creep into the derived A_0, B_0, and C_0 rotational constants. The results are listed in Table 2. The dipole moment (Table 2) has been obtained by analysis of the Stark effects of the 1_{01}–0_{00}, 3_{03}–2_{12}, and 5_{14}–5_{15} transitions.

TABLE 2. Derived rotational constants (MHz) and dipole moment components (Debye)[a]

A_0	138 503·20(21)
B_0	16 418·105(26)
C_0	14 649·084(28)
Δ_J	0·01696(17)
Δ_{JK}	0·2133(31)
Δ_K	2·418(31)
δ_J	0·001891(10)
δ_K	0·1581(12)

μ_A = 0·731(2) μ_B = 0·470(3) (Debye)

[a] Standard deviations for last figures in parentheses.

This work confirms the original preliminary detection and the rotational constants indicate that the ∠(CPH) angle is *ca.* 97·5°, much more acute than the equivalent ∠(CNH) angle in $CH_2{=}NH$ where it is 110·4°.[3]

The new method of production, from $Me_3SiCH_2PH_2$, promises to be efficient enough to allow study of the isotopically substituted variants necessary for an accurate structure analysis and the use of Me_3SiX elimination reactions from $Me_3SiCH_2PX_2$ precursors appears to have a wide application in $CH_2{=}PX$ synthesis.[4]

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