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A new phosphorus bearing derivative of the methyl radical, CH$_2$CP, studied by microwave spectroscopy and *ab initio* calculation

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The microwave spectrum of the CH$_2$CP radical in its $^2B_1$ ground electronic state was detected for the first time using a source-modulated microwave spectrometer. The radical was generated in the cell by a dc-glow discharge in a mixture of PH$_3$ and C$_2$H$_2$. Fine structure was observed but no hyperfine structure pertaining to the phosphorus and hydrogen nuclei could be resolved. In total 110 spectral lines were measured for the K-structure and fine structure of eight rotational transitions in the 300–380 GHz region. The rotational, centrifugal distortion, and spin-rotation coupling constants were obtained by a least-squares analysis of the measured frequencies. On the basis of accompanying coupled cluster calculations an accurate equilibrium structure could be established; $r_e(\text{CH}) = 1.0816(5)$ Å, $\alpha_e(\text{HCH}) = 118.22(5)°$, $R_{1e}(\text{CC}) = 1.3418(10)$ Å, and $R_{2e}(\text{CP}) = 1.5889(10)$ Å. The equilibrium dipole moment is predicted to be $\mu_e = -1.15$ D, with the negative end at the phosphorus site. © *1998 American Institute of Physics.* [S0021-9606(98)00335-3]

I. INTRODUCTION

While phospha-alkenes and phospha-alkynes have been extensively studied over the past 20 years (see Refs. 1–4 for reviews), very little is known about radicals with multiple CP bonds. In particular, high-resolution spectroscopic studies of such species are almost completely missing. Only diatomic CP (Refs. 5, 6) and HCCP (Ref. 7) could be investigated so far. The former radical is one of the two phosphorus bearing molecules which could be observed in the interstellar medium so far.[8] It may be due to a lack of suitable laboratory data that the chemistry of interstellar phosphorus is largely unexplored. Speculations about the role of phosphorus in interstellar cloud chemistry have been reported repeatedly.[9–11] In space, the formation of CP bonds is postulated to occur by the reaction of PH$_n^+$ with hydrocarbons and terminal CP bonds of carbon-chain molecules are thought to be formed in the dissociative recombination of organo-phosphorus ions.[10]

In the search for reactive species with CP multiple bonds, a phosphine-acetylene discharge system was investigated by means of microwave spectroscopy. For the first time, a polyatomic phosphorus bearing radical, HCCP, could be recently detected by this spectroscopic technique.[7] Several paramagnetic spectral lines found in the same chemical system remained unassigned. As will be shown in the present paper, they should be attributed to a new phosphorus bearing radical, CH$_2$CP. To our knowledge, no *ab initio* calculations have yet been published for CH$_2$CP although a cyclic form of C$_2$H$_2$P was investigated by Gonbeau and Pfister-Guillouzo.[12]

Formally, the CH$_2$CP radical is a derivative of the methyl radical resulting from substitution of one of the hydrogen atoms by a CP group. The CH$_3$ radical and some of its halogenated derivatives have been thoroughly studied by mi-

crowave and infrared spectroscopy,[13–17] and many discussions have centered on the planarity of their structures. CH$_3$ and CH$_2$F were shown to have planar and quasiplanar structures, respectively, whereas CHF$_2$ and CF$_3$ were found to be of pyramidal structure. The differences in structure were explained by the fact that the electrons are delocalized from the central carbon atom towards the more electronegative halogen atoms.[16] The CH$_2$CN radical, the nitrogen analog of CH$_2$CP, was confirmed to have a planar structure.[18]

The present paper reports on a joint experimental/theoretical study of CH$_2$CP. The experimental work was carried out at the Institute for Molecular Science (IMS) while the theoretical investigations were performed at the Abteilung für Theoretische Chemie of the Georg-August-Universität Göttingen.

II. MICROWAVE MEASUREMENTS AND ANALYSIS

A source-modulated microwave spectrometer covering the range up to 620 GHz in conjunction with a 2 m free space cell was employed at the IMS.[19] Outputs of frequency multipliers driven by millimeter-wave klystrons were used as higher millimeter and submillimeter-wave sources. CH$_2$CP radicals were generated by a premixture of phosphine and acetylene gases to which a dc glow discharge was applied in the aforementioned cell. Such experimental conditions are known to readily produce another phosphorus bearing radical, HCCP.[7] In that particular investigation, CH$_2$CP spectral lines were considerably weaker than those of HCCP and remained unassigned, instigating the present study as described above. In addition to HCCP, very intense PH$_2$ lines were observed as well as many diamagnetic lines. After eliminat-

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ing all known lines by comparison with their corresponding cited literature frequencies,[7,20,21] the remaining paramagnetic lines were examined.

On surveying a wider region (357–380 GHz), a distinct spectral pattern emerged which was repeated about every 10.8 GHz. Such patterns suggested a-type R-branch transitions of an asymmetric top radical in a doublet state and the spacing of the lines gave an estimation of the sum of the rotational constants, $B+C$. Thus the species was suspected to be CH_2CP in the $^2B_1$ ground electronic state. Various assignments of the K_a components were made in an attempt to find a reasonable set of molecular constants, and, in this way, $K_a=0$, 2 and 4 lines were initially assigned. Upon further inspection, much weaker lines were measured and could be assigned to $K_a=1$, 3, 5, and 6, though these proved difficult to detect. Spectral lines with $K_a=$ even were found to be much more intense than lines with $K_a=$ odd. Since the electronic ground state of the related radical CH_2CN is of $^2B_1$ symmetry,[18] it was presumed that CH_2CP will also adopt a $^2B_1$ ground electronic state. This was confirmed by comparing the relative intensities of the K_a components. The two hydrogen nuclei of $I(H)=\frac{1}{2}$ are identical under C_2 operation around the a molecular axis so that the symmetric rotational level of $K_a=$ even combines with the symmetric nuclear spin function of $I(H)=1$ whereas the antisymmetric rotational level of $K_a=$ odd combines with the antisymmetric level of $I(H)=0$ to give a line intensity ratio of 3:1 for $K_a=$ even components: $K_a=$ odd components.

Both the observed spectral patterns and the production chemistry verified the identification of CH_2CP in the gas phase. Optimum conditions for the production of the observed species were partial pressures of 22 mTorr of PH_3 and 26 mTorr of C_2H_2. Throughout the experiments the discharge current was set to 80 mA and the temperature of the cell was maintained at around $-100\,^\circ$C by flowing liquid nitrogen around a copper jacket attached to the cell.

A total of 110 spectral lines for eight rotational transitions ranging from $N=28-27$ to $N=35-34$ were recorded over the 300–380 GHz region. All are relatively high N rotational transitions, and hyperfine structures due to the phosphorus and hydrogen nuclei could not be resolved. Assuming that the spin densities on the P and H atoms are not too different from those of CH_2CN,[18] the preceding statement is consistent with the predicted lack of observation of hyperfine structures. Lines of isotopomers of CH_2CP have been hithero unobserved. Each line frequency was determined by averaging five pairs of upward and downward frequency sweep measurements. In the final fit, a total of 87 lines was included from among 110 measured lines. Lines that were disturbed or overlapped were eliminated from the final set of spectral lines. The observed line frequencies are listed in Table I. An example of the observed spectral lines is shown in Fig. 1.

The observed spectral lines of CH_2CP were analyzed using the appropriate Hamiltonian, the matrix elements of which are given in the literature[22,23] with the angular momentum coupling scheme of $J=N+S$. A least-squares fitting program was utilized to analyse the observed spectral lines and the required energy levels were calculated by numerical diagonalization of the Hamiltonian matrices. Rota-

TABLE I. Observed transition frequencies of the CH_2CP ($^2B_1$) radical (MHz).[a]

$N'_{Ka'Kc'}-N''_{Ka''Kc''}$	$F_1\nu_{obs}(\Delta\nu)$[b]	$F_2\nu_{obs}(\Delta\nu)$[b]
$35_{0\,35}-34_{0\,34}$	378 917.376 (0.055)	378 940.317 (0.046)
$35_{1\,35}-34_{1\,34}$	377 217.451 (−0.331)[d]	377 228.474 (−0.234)[d]
$35_{1\,34}-34_{1\,33}$	380 914.215 (0.027)	380 949.115 (−0.049)
$35_{2\,34}-34_{2\,33}$	379 057.340 (0.053)	379 071.504 (0.026)
$35_{2\,33}-34_{2\,32}$	379 265.713 (0.050)	379 283.845 (−0.054)
$35_{3\,33}-34_{3\,32}$	379 069.872 (−0.167)[d,e]	379 069.872 (−0.167)[d,e]
$35_{3\,32}-34_{3\,31}$	379 071.504 (−0.739)[d,e]	379 071.504 (−0.739)[d,e]
35_4-34_4	378 989.538 (−0.015)	378 968.274 (−0.200)[d]
35_5-34_5	378 886.989 (0.333)[d]	
35_6-34_6	378 746.717 (0.273)[d]	
$34_{0\,34}-33_{0\,33}$	368 112.303 (−0.031)	368 135.458 (−0.050)
$34_{1\,34}-33_{1\,33}$	366 452.566 (−0.140)[d]	
$34_{1\,33}-33_{1\,32}$	370 043.778 (−0.085)[c]	370 078.763 (0.045)
$34_{2\,33}-33_{2\,32}$	368 239.129 (−0.051)	368 252.630 (−0.053)
$34_{2\,32}-33_{2\,31}$	368 447.576 (0.027)	
$34_{3\,32}-33_{3\,31}$	368 247.206 (−0.213)[d]	
$34_{3\,32}-33_{3\,31}$		368 249.068 (0.039)
$34_{3\,31}-33_{3\,30}$	368 250.755 (0.017)	
34_4-33_4	368 172.119 (−0.051)	368 147.975 (−0.230)[d]
34_5-33_5		368 021.086 (0.090)
34_6-33_6	367 938.753 (−0.034)	367 851.611 (−0.019)
$33_{0\,33}-32_{0\,32}$	357 305.640 (0.162)[d]	357 328.459 (−0.413)[d]
$33_{1\,33}-32_{1\,32}$	355 686.495 (−0.048)	355 697.197 (0.004)
$33_{2\,32}-32_{2\,31}$	357 420.051 (−0.013)	357 432.674 (−0.138)[d]
$33_{2\,31}-32_{2\,30}$	357 594.739 (−0.019)	357 611.095 (−0.012)
$33_{3\,31}-32_{3\,30}$	357 427.173 (0.080)[c]	357 423.651 (−0.200)[d]
$33_{3\,30}-32_{3\,29}$	357 425.602 (0.080)[c]	
33_4-32_4	357 354.118 (−0.011)	357 326.685 (−0.310)[d]
33_6-32_6	357 130.617 (−0.045)	
$32_{0\,32}-31_{0\,31}$	346 496.823 (0.016)	346 520.451 (0.037)
$32_{1\,32}-31_{1\,31}$	344 919.338 (0.012)	344 929.732 (−0.077)[c]
$32_{1\,31}-31_{1\,30}$	348 299.715 (−0.053)	348 334.291 (−0.032)
$32_{2\,31}-31_{2\,30}$	346 599.956 (−0.017)	346 611.919 (0.030)
$32_{2\,30}-31_{2\,29}$	346 759.317 (0.050)	346 774.573 (0.002)
$32_{3\,30}-31_{3\,29}$	346 604.664 (0.003)	
32_4-31_4	346 535.384 (−0.021)	346 504.771 (−0.079)[c]
32_5-31_5	346 445.612 (0.081)[c]	
32_6-31_6	346 321.852 (0.005)	346 220.202 (0.004)
$31_{0\,31}-30_{0\,30}$	335 686.462 (0.088)[c]	335 710.156 (−0.032)
$31_{1\,31}-30_{1\,30}$	334 151.059 (−0.029)	334 161.393 (0.012)
$31_{2\,30}-30_{2\,29}$	335 778.943 (0.000)	335 790.002 (0.062)
$31_{2\,29}-30_{2\,28}$	335 923.761 (0.000)	335 937.662 (−0.277)[d]
$31_{3\,29}-30_{3\,28}$	335 781.658 (0.059)	335 774.098 (−0.139)[d]
$31_{3\,28}-30_{3\,27}$	335 782.756 (−0.023)	335 775.437 (−0.023)
31_4-30_4	335 716.201 (0.098)[c]	
31_5-30_5	335 630.721 (0.030)	
31_6-30_6	335 512.614 (−0.090)[c]	335 402.789 (0.038)
$30_{0\,30}-29_{0\,29}$	324 874.240 (0.007)	324 898.307 (0.060)
$30_{1\,30}-29_{1\,29}$	323 381.803 (−0.057)	323 391.883 (−0.054)
$30_{1\,29}-29_{1\,28}$	326 551.158 (−0.164)[d]	326 585.290 (−0.192)[d]
$30_{2\,29}-29_{2\,28}$	324 957.025 (0.017)	324 967.013 (0.023)
$30_{2\,28}-29_{2\,27}$	325 088.295 (0.047)	325 101.320 (0.109)[d]
30_4-29_4	324 896.201 (−0.046)	324 857.719 (−0.044)
$29_{0\,29}-28_{0\,28}$	314 060.325 (−0.111)[d]	314 084.492 (−0.152)[d]
$29_{1\,28}-28_{1\,27}$	315 675.465 (−0.093)[c]	
$29_{2\,28}-28_{2\,27}$	314 134.293 (0.086)[c]	314 143.071 (0.010)
$29_{2\,27}-28_{2\,26}$	314 252.746 (0.007)	314 264.371 (−0.010)
29_4-28_4	314 075.845 (−0.038)	314 032.758 (−0.058)
$28_{0\,28}-27_{0\,27}$	303 244.990 (−0.047)	303 269.455 (0.022)
$28_{1\,28}-27_{1\,27}$	301 840.609 (0.039)	301 850.134 (0.009)
$28_{1\,27}-27_{1\,26}$	304 798.999 (0.183)[d]	
$28_{2\,27}-27_{2\,26}$	303 310.536 (−0.040)	303 318.195 (0.019)
$28_{2\,26}-27_{2\,25}$	303 417.255 (0.012)	303 427.452 (0.009)
28_4-27_4	303 255.082 (−0.018)	303 206.941 (0.020)

[a]The standard deviation of the fit is 35.13 kHz.
[b]$\Delta\nu=\nu_{obs}-\nu_{calc}$. ν_{calc} is obtained from the molecular constants in Table II.
[c]Line weighted to 0.5.
[d]Line weighted to 0.0.
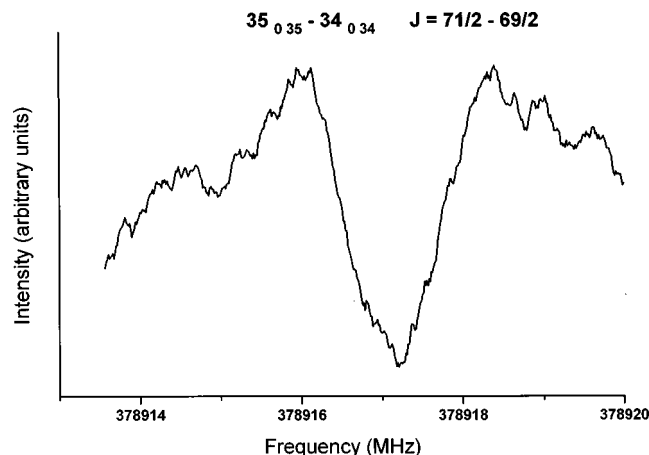[e]Overlapped line.

FIG. 1. The F_1 component of the $35_{0\,35}-34_{0\,34}$ transitions of CH$_2$CP ($^2B_1$), observed by dc glow discharge of a mixture of phosphine (22 mTorr) and acetylene (26 mTorr) gases.

tional constants, centrifugal distortion constants, and spin-rotation coupling constants could be determined for CH$_2$CP and are given in Table II. A value of 22.52 MHz for the centrifugal distortion constant Δ_K was adopted from the *ab initio* calculations (see below), as this particular constant cannot be deduced from *a*-type rotational transitions only. In addition to the four quartic centrifugal distortion constants, it was essential to include the sextic and octic distortion terms in the analysis to obtain a better fit to the spectral lines. These higher order terms appear to be well determined.

From the rotational constants, the ground-state inertial defect was calculated to be $\Delta_0 = 0.087\,66(106)\ u\text{Å}^2$ which is indicative of a planar equilibrium structure for CH$_2$CP. The Δ_0 value for CH$_2$CP is comparable in magnitude to those obtained for similar planar molecules like CH$_2$CS (Ref. 24) or CH$_2$CO.[25]

III. *AB INITIO* CALCULATIONS

Partially spin-adapted coupled cluster theory involving single and double excitation operators (RCCSD) (Ref. 26)

TABLE II. Experimental values for molecular constants of CH$_2$CP (MHz).

Constant	Present study (MW)[a]
A	288 810 (85)
B	5 472.319 0 (141)
C	5 365.571 0 (132)
Δ_N	0.001 090 08 (101)
Δ_{NK}	0.151 51 (33)
Δ_K	22.52(fixed)[b]
δ_N	0.000 025 35 (173)
δ_K	0.120 3 (52)
Φ_{NK}	0.000 000 892 (94)
Φ_{KN}	−0.000 275 (20)
L_{KKN}	−0.000 011 61 (38)
ϵ_{aa}	−3 268.44 (196)
ϵ_{bb}	−51.116 (114)
ϵ_{cc}	−2.874 (102)

[a]Values in parentheses denote three times the standard deviation and apply to the last digits of the constants.
[b]*Ab initio* value (see the text).

was employed in a study of the electronic ground state of CH$_2$CP. In addition, connected triple substitutions were taken perturbationally into account by variants RCCSD-T and RCCSD(T).[27] Throughout, all valence electrons were correlated in the coupled cluster calculations most of which made use of the correlation consistent polarized valence quadruple-zeta (cc-pVQZ) basis set.[28,29] It comprises 229 contracted Gaussian-type orbitals (cGTOs), with real spherical harmonics being employed for the angular parts of the *d*, *f*, and *g* functions. All electronic structure calculations of this work were carried out with the MOLPRO suite of programs.[30]

Calculated equilibrium geometries and equilibrium rotational constants are listed in Table III. As expected, the differences between the RCCSD-T and RCCSD(T) results are very minor. Valence electron correlation effects are most pronounced for the CC equilibrium bond length which is elongated by as much as 0.0415 Å. 25% of this difference between RCCSD(T) and RHF values is due to connected triple substitutions. On the other hand, valence electron correlation effects hardly influence the CP equilibrium bond length, which is actually slightly shortened upon inclusion of valence correlation. The CH equilibrium bond length is elongated by 0.0088 Å. It is only slightly longer (by 0.0007 Å) than in ethylene [cf. Ref. 31 for analogous CCSD(T) calculations]. Electron correlation slightly increases the HCH equilibrium angle by 0.28°.

On the basis of the present RCCSD(T) calculations, an accurate equilibrium geometry of CH$_2$CP is obtained in the following way: the errors in the CH and CC equilibrium bond lengths are assumed to be the same as for ethylene.[31] Therefore, the RCCSD(T) values are reduced by 0.0014 and 0.0035 Å, respectively. The CP equilibrium bond length and the quadratic CP stretching force constant are intermediate between the corresponding values for the $^2\Sigma$ and $^2\Pi$ states of CP. Analogous RCCSD(T) calculations yield $R_e = 1.5692$ Å and 1.6624 Å for the $^2\Sigma$ and $^2\Pi$ state, to be compared with the experimental values[5] of 1.5620 and 1.6544 Å, respectively. We use the arithmetic means of the errors of 0.0076 Å to correct the RCCSD(T) value for the CP equilibrium bond length of CH$_2$CP. Since CCSD(T) calculations with the cc-pVQZ basis set yield excellent agreement with the best available value for the HCH equilibrium angle (α_e) of ethylene,[31] the RCCSD(T) value for α_e (CH$_2$CP) is left uncorrected. The final recommended equilibrium structure of CH$_2$CP ($\tilde{X}\ ^2B_1$) is thus r_e(CH) = 1.0816(5) Å, α_e(HCH) = 118.22(5)°, R_{1e}(CC) = 1.3418(10) Å, and R_{2e}(CP) = 1.5889(10) Å, with estimated error bars in terms of the last digit given in parentheses. The corresponding equilibrium rotational constants A_e, B_e, and C_e are larger than the experimental ground-state values A_0, B_0, and C_0 (see Table II), by 0.77%, 0.38%, and 0.48%. These differences appear to be quite reasonable for a semirigid molecule without shallow bending potentials (see below).

The complete quadratic force field of CH$_2$CP has been calculated by RCCSD(T) using the cc-pVQZ basis set. The

TABLE III. Calculated equilibrium geometries and equilibrium rotational constants for CH_2CP ($\tilde{X}\ ^2B_1$).[a]

Method	r_e (Å)	α_e (°)	R_{1e} (Å)	R_{2e} (Å)	A_e (MHz)	B_e (MHz)	C_e (MHz)
RHF	1.0742	117.94	1.3040	1.5973	295 920	5583.8	5480.4
RCCSD	1.0810	118.11	1.3350	1.5925	291 678	5500.4	5398.6
RCCSD-T	1.0830	118.22	1.3454	1.5960	290 291	5453.1	5352.6
RCCSD(T)	1.0830	118.22	1.3454	1.5965	290 268	5451.2	5350.7
corr.	1.0816	118.22	1.3418	1.5889	291 030	5493.1	5391.3

[a]Basis set, cc-pVQZ (229 cGTOs). The valence electrons are correlated in the coupled cluster calculations.

following symmetry coordinates are employed:

(a) A_1 species:

$$S_1 = 1/\sqrt{2}(\Delta r_1 + \Delta r_2),$$

$$S_2 = 1/\sqrt{6}(\Delta \beta_1 + \Delta \beta_2 - 2\Delta \alpha),$$

$$S_3 = \Delta R_1(CC) \quad \text{and} \quad S_4 = \Delta R_2(CP);$$

(b) B_1 species:

$$S_5 = \Theta_1(CH_2 \text{ wagging}),$$

$$S_6 = \Theta_2(CCP \text{ out-of-plane});$$

(c) B_2 species:

$$S_7 = 1/\sqrt{2}(\Delta r_1 - \Delta r_2)$$

$$S_8 = 1/\sqrt{2}(\Delta \beta_1 - \Delta \beta_2) \quad \text{and} \quad S_9 = \Theta_3(\text{in-plane CCP}).$$

The numerical values of the force constants are listed in Table IV. The symmetric and asymmetric CH stretching force constants F_{11} and F_{77} are only slightly smaller than the corresponding values for ethylene.[31] The present RCCSD(T) value for the CC stretching force constant F_{33} is smaller than the corresponding value for ethylene by 23%. Together with the rather short equilibrium bond length, we may safely classify the CC bond in CH_2CP as a weak double bond. The CP stretching force constant is larger than the CCSD(T)/cc-pVQZ value for CH_2PH by 29%. Compared to the corresponding RCCSD(T) values for the $^2\Sigma$ and $^2\Pi$ states of CP it is smaller and larger by 19% and 10%, respectively. It is still smaller by 31% compared to HCP, a typical CP triple bond system.[32] We would thus like to talk of a strong CP double bond in the case of CH_2CP.

TABLE IV. RCCSD(T) quadratic force field for CH_2CP ($\tilde{X}\ ^2B_1$).[a]

Force constant	Value (aJ Å^{-n})[b]	Force constant	Value (aJ Å^{-n})[b]
A_1 species		B_1 species	
F_{11} (s. CH_2)	5.6054	F_{55} (CH_2 wag.)	0.1810
F_{22} (s. bend)	0.4402	F_{66} (CCP out)	0.3308
F_{33} (CC)	7.2814	F_{56}	0.0371
F_{44} (CP)	6.3155	B_2 species	
F_{12}	−0.0792	F_{77} (as. CH_2)	5.5572
F_{13}	0.1890	F_{88} (as. bend)	0.4674
F_{14}	−0.0423	F_{99} (CCP in)	0.3575
F_{23}	0.2198	F_{78}	0.1485
F_{24}	0.0332	F_{79}	0.0179
F_{34}	1.4307	F_{89}	0.0577

[a]Basis, cc-pVQZ.
[b]n is the number of stretching coordinates involved in the partial differential quotient $(\partial^2 V/\partial S_i \partial S_j)_e$.

The equilibrium structure of CH_2CP differs markedly from that of the CH_2CN radical ($\tilde{X}\ ^2B_1$) for which an accurate equilibrium structure was established recently;[33] $r_e(CH) = 1.0769(5)$ Å, $\alpha_e(HCH) = 120.47(5)°$, $R_{1e} = 1.3903(5)$ Å, and $R_{2e} = 1.1670(5)$ Å. In particular, the CC equilibrium bond length in CH_2CP is shorter by as much as 0.0485 Å and the corresponding CC stretching force constant is larger by 20%. On the other hand, the CN bond in CH_2CN is clearly a triple bond which is shorter than the CN equilibrium bond length of the $^2\Sigma$ ground state of the cyano radical[34] by 0.0048 Å and only larger by 0.0138 Å compared with HCN.[35]

The CH_2 wagging force constant F_{55} has a relatively large value of 0.181 aJ. It is considerably larger than the RCCSD(T) value of 0.105 aJ calculated for CH_2CN.[32] Out-of-plane and in-plane CCP bending force constants F_{66} and F_{99} have rather similar values. Among the coupling force constants, F_{34} (CC/CP) has clearly the largest value. It is comparable in magnitude to the CO/CO coupling constant in CO_2.[36]

Calculated harmonic vibrational wavenumbers for CH_2CP and CD_2CP are listed in Table V. As expected, the harmonic wavenumber of the CH_2 wagging vibration in CH_2CP is considerably higher than in CH_3 [ω_2(RCCSD(T)) $= 505$ cm^{-1} and ν_2(expt) $= 606.5$ cm^{-1} (Ref. 13)], and CH_2CN [$\omega_5 = 644$ cm^{-1} (Ref. 33) and ν_5(expt) $= 663.8$ cm^{-1} (Ref. 37)]. The calculated harmonic value of $\omega_5(CH_2CP) = 811$ cm^{-1} should also be a good estimate for the experimental anharmonic value since anharmonicity effects are expected to be smaller than for CH_3 and CH_2CN.

A comparison of RCCSD(T)/cc-pVQZ CH_2 wagging potentials for CH_2CP, CH_2CN, and CH_3 is made in Fig. 2. The remaining geometrical parameters are fixed at their CCSD(T) equilibrium values. While the potentials of CH_3 and CH_2CN

TABLE V. Harmonic vibrational wavenumbers (in cm^{-1}) for CH_2CP and CD_2CP ($\tilde{X}\ ^2B_1$).[a]

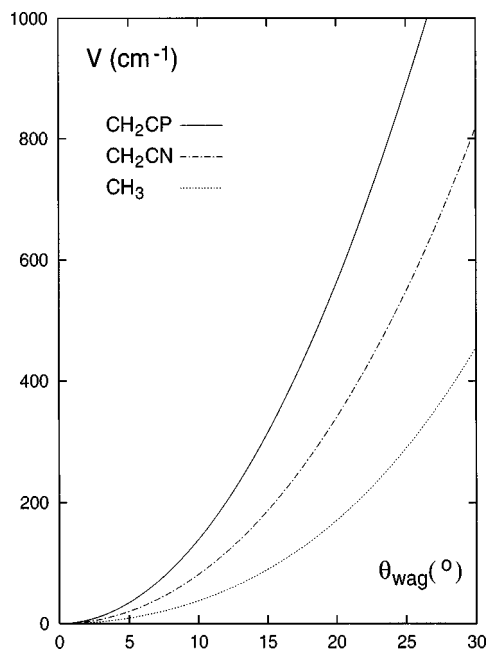|	CH_2CP	CD_2CP
$\omega_1(a_1)$	3137	2276
$\omega_2(a_1)$	1502	1451
$\omega_3(a_1)$	1392	1076
$\omega_4(a_1)$	813	763
$\omega_5(b_1)$	811	648
$\omega_6(b_1)$	325	310
$\omega_7(b_2)$	3233	2408
$\omega_8(b_2)$	996	810
$\omega_9(b_2)$	306	274

[a]RCCSD(T)/cc-pVQZ.

FIG. 2. Out-of-plane CH_2 bending potentials for CH_2CP, CH_2CN, and CH_3 (CCSD(T)/cc-pVQZ results).

are rather shallow and anharmonic, the CH_2 wagging potential of CH_2CP is much closer to the harmonic limit.

Equilibrium quartic centrifugal distortion constants were calculated from the quadratic force field, RCCSD(T) equilibrium geometry, and atomic masses by standard formulas. The numerical values are listed in Table VI. We note excellent agreement with the experimental ground-state values for Δ_N, Δ_{NK}, and δ_N. The experimental value for δ_K is larger than the theoretical value by 37% which is still reasonable regarding the fact that experimental and theoretical values are not quite the same. The present theoretical value for Δ_K which has been employed in the least-squares fit of the experimental data, is very close to that measured for ketene[25] of 23.5 MHz. This is not surprising at all as this constant is mainly determined by the properties of the CH_2 group which are not very different in ketene compared with CH_2CP.

Making use of two different flexible basis sets, the equilibrium dipole moment of CH_2CP has been calculated at the accurate equilibrium structure from this work. Results are given in Table VII. Virtually identical results are obtained by RCCSD-T and RCCSD(T) which yield $\mu_e = -1.146$ D with the larger basis set. The negative sign means that the negative end of the dipole is located at the phosphorus site. The

TABLE VI. Calculated equilibrium quartic centrifugal distortion constants for CH_2CP and CD_2CP ($\tilde{X}\ ^2B_1$).[a]

	CH_2CP	CD_2CP
Δ_N (kHz)	1.04	0.80
Δ_{NK} (MHz)	0.158	0.109
Δ_K (MHz)	22.52	5.57
δ_N (Hz)	20	30
δ_K (MHz)	0.088	0.064

[a]RCCSD(T)/cc-pVQZ.

TABLE VII. Equilibrium dipole moment (in D) of CH_2CP ($\tilde{X}\ ^2B_1$).[a]

Method	188 cGTO[b]	254 cGTO[c]
RHF	−1.390	−1.372
RCCSD	−1.142	−1.121
RCCSD-T	−1.168	−1.146
RCCSD(T)	−1.168	−1.146

[a]All calculations are carried out at the recommended equilibrium structure from this work.
[b]aug-cc-pVTZ (Refs. 28, 29, and 38).
[c]aug-cc-pVQZ basis set exclusive of g functions at C and P and exclusive of f functions at H.

effect of connected triple substitutions on μ_e is small (0.025 D or 2.2%). The whole correlation contribution amounts to 0.226 D or 16%.

IV. CONCLUSIONS

Making use of microwave spectroscopy in a dc-glow discharge of a mixture of PH_3 and C_2H_2, the phosphorus bearing radical CH_2CP in its $^2B_1$ ground electronic state was observed. According to coupled cluster calculations including the effects of connected triple substitutions, the radical has a planar equilibrium structure with a remarkably short CC equilibrium bond length of 1.342 Å. The out-of-plane CH_2 bending (wagging) potential is much steeper than in CH_2CN or CH_3 and considerably less anharmonic. A rather large value of 811 cm^{-1} is predicted for the harmonic wavenumber of the corresponding normal vibration (ω_5). The equilibrium dipole moment of CH_2CP is calculated to be $\mu_e = -1.15$ D, with the negative end of the dipole at the phosphorus site.

[1] J. F. Nixon, Chem. Rev. **88**, 1327 (1988).
[2] M. Regitz and P. Binger, Angew. Chem. Int. Ed. Engl. **27**, 1484 (1988).
[3] M. Regitz, Chem. Rev. **90**, 191 (1990).
[4] *Multiple Bonds and Low Coordination in Phosphorus Chemistry*, edited by M. Regitz and O. J. Scherer (Thieme, Stuttgart, 1990).
[5] R. S. Ram and P. F. Bernath, J. Mol. Spectrosc. **122**, 282 (1987).
[6] S. Saito, S. Yamamoto, K. Kawaguchi, M. Ohishi, H. Suzuki, S. Ishikawa, and N. Kaifu, Astrophys. J. **341**, 1114 (1989).
[7] I. K. Ahmad, H. Ozeki, and S. Saito, J. Chem. Phys. **107**, 1301 (1997).
[8] M. Guélin, J. Cernicharo, G. Paubert, and B. E. Turner, Astron. Astrophys. **230**, L9 (1990).
[9] L. R. Thorne, V. G. Anicich, S. S. Prasad, and W. T. Huntress, Astrophys. J. **280**, 139 (1984).
[10] T. J. Millar, Astron. Astrophys. **242**, 241 (1991).
[11] S. B. Charnley and T. J. Millar, Mon. Not. R. Astron. Soc. **270**, 570 (1994).
[12] D. Gonbeau and G. Pfister-Guillouzo, Nou. J. de Chim. **9**, 71 (1985).
[13] C. Yamada, E. Hirota, and K. Kawaguchi, J. Chem. Phys. **75**, 5256 (1981).

[14] Y. Endo, C. Yamada, S. Saito, and E. Hirota, J. Chem. Phys. **77**, 3376 (1982).
[15] Y. Endo, C. Yamada, S. Saito, and E. Hirota, J. Chem. Phys. **79**, 1605 (1983).
[16] Y. Endo, S. Saito, and E. Hirota, Can. J. Phys. **62**, 1347 (1984).
[17] N. Inada, K. Saito, M. Hayashi, H. Ozeki, and S. Saito, Chem. Phys. Lett. **284**, 142 (1998).
[18] S. Saito and S. Yamamoto, J. Chem. Phys. **107**, 1732 (1997).
[19] S. Saito and M. Goto, Astrophys. J. **410**, L53 (1993).
[20] Y. Endo, S. Saito, and E. Hirota, J. Mol. Spectrosc. **97**, 204 (1983).
[21] M. Kajita, Y. Endo, and E. Hirota, J. Mol. Spectrosc. **124**, 66 (1987).
[22] W. Gordy and R. L. Cook, *Microwave Molecular Spectra* (Wiley, New York, 1984).
[23] J. M. Brown and T. J. Sears, J. Mol. Spectrosc. **75**, 111 (1979).
[24] M. Winnewisser and E. Schäfer, Z. Naturforsch. A **35**, 483 (1980).
[25] J. W. C. Johns, J. H. R. Stone, and G. Winnewisser, J. Mol. Spectrosc. **42**, 523 (1972).
[26] P. J. Knowles, C. Hampel, and H.-J. Werner, J. Chem. Phys. **99**, 5219 (1993).
[27] M. J. O. Deegan and P. J. Knowles, Chem. Phys. Lett. **227**, 321 (1994), and references therein.
[28] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
[29] D. E. Woon and T. H. Dunning, Jr., J. Chem. Phys. **98**, 1358 (1993).
[30] MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. A. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, R. Lindh, M. E. Mura, and T. Thorsteinsson.
[31] J. M. L. Martin and P. R. Taylor, Chem. Phys. Lett. **248**, 336 (1996).
[32] J. Koput and S. Carter, Spectrochim. Acta A **53**, 1091 (1997).
[33] P. Botschwina (unpublished).
[34] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (von Nostrand Reinhold, New York, 1979).
[35] P. Botschwina, M. Horn, M. Matuschewski, E. Schick, and P. Sebald, J. Mol. Struct.: THEOCHEM **400**, 119 (1997), and references therein.
[36] A. Chédin, J. Mol. Spectrosc. **76**, 430 (1979).
[37] Y. Sumiyoshi, K. Tanaka, and T. Tanaka, J. Chem. Phys. **104**, 1838 (1996).
[38] R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).