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The microwave spectrum of a new phosphorus-bearing radical $CH_2P(^2B_2)$

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The microwave spectrum of the CH_2P radical in its $^2B_2$ ground electronic state was detected for the first time using a source-modulated spectrometer equipped with a free-space cell. The CH_2P radical was generated in the cell by a dc-glow discharge in a mixture of PH_3, CH_4, and He, and its isotopic species, CD_2P, in a mixture containing CD_4 instead of CH_4. Forty four *a*-type *R*-branch rotational transitions of CH_2P were measured for the transitions $N=8-7$ to $N=12-11$ with $K_a=0$ to 5 in the frequency region of 260–400 GHz, for which fine and hyperfine structures due to the phosphorus and hydrogen nuclei were resolved. For CD_2P, 39 rotational transitions from $N=9-8$ to $N=13-12$ with $K_a=0$ to 4 were measured in the 240–355 GHz with fine structure and phosphorus hyperfine structure. Molecular constants of CH_2P, including the fine structure constants and hyperfine coupling constants due to both the nuclei of P and H, were precisely determined by least-squares methods from 158 observed spectral lines. Those of CD_2P were similarly obtained from 70 observed spectral lines. The rotational constants of both species were used to derive the molecular structural parameters for CH_2P: $r_0(CP)=1.6576(28)$ Å, $r_0(CH)=1.0912(61)$ Å, and $\angle HCH=115.96(96)^\circ$. The spin densities of unpaired electrons on the P and H nuclei were estimated from the hyperfine coupling constants, and found to be consistent with the molecular structure determined.

INTRODUCTION

Many simple and fundamental phosphorus-bearing molecules, composed of hydrogen, carbon, and/or oxygen, have been postulated to exist in the gas phase, because of the multi-valence feature of phosphorus. However, many of them are unknown spectroscopically as well as chemically, and their chemical and physical properties have been uncharacterized.

Recently we studied two such examples, H_3PO (Ref. 1) and H_2PO,[2] by microwave spectroscopy. Both molecules had previously not been studied in the gas phase by any high-resolution spectroscopic methods. For the H_3OP chemical system several high-level and sophisticated *ab initio* calculations had predicted that *cis* and *trans* H_2POH (separated by a small energy difference of 0.3 kcal/mol) are the most stable isomers and the third form, H_3PO, is located at an energy of 6.5 kcal/mol above the *cis* H_2POH form.[3] However, we found that the most stable form for the chemical system of H_3OP is a symmetric top form, H_3PO,[1] which was efficiently generated in a discharge mixture of PH_3, CO_2, and H_2. We also found that a new stable H_2PO radical exists in the discharged PH_3 and CO_2 gas mixture. From the rotational constants for the $H_2P^{16}O$ and $H_2P^{18}O$ species the PO bond length was determined to be 1.4875(4) $Å^2$. This result was in contrast with with sophisticated quantum chemical calculations which predicted the optimized PO bond length of $H_2PO(\tilde{X}\,^2A')$ and were found to differ significantly at the various level of calculations used: a single PO bond length of 1.589 Å was calculated at the HF/6–31G** level and a double PO bond length of 1.495 Å at UMP2/6–31G^{**}.[4] A structural difference among HPO, H_2PO, and H_3PO was explained by the fact that the PO bond in HPO is a typical double bond made up of one p_σ bond and one p_π bond, whereas the PO bond in H_2PO and H_3PO is a resonance hybrid between a single and triple bond structure or a dative single bond augmented by π back donation to the vacant *d* orbital of P from the O lone pairs.[1] A full characterization of H_3PO and H_2PO has been substantiated by high-resolution microwave spectroscopy.

Furthermore very few spectroscopic and theoretical studies have been caried out made on transient CP-bond-bearing molecules. We also studied two such examples HCCP (Ref. 5) and CH_2CP (Ref. 6) by microwave spectroscopy. Based on the spin densities of HCCP derived from its observed hyperfine coupling constants, we concluded that the molecular structure of HCCP could be explained by a linear combination of two canonical configurations of phospho-allene and phosphorene forms with an approximate weight of three to one. The molecular structure of HCCP is quite different from that of the corresponding nitrogen-bearing radical HCCN, for which was suggested a canonical form composed of allene and carbene with a weight of two to one.[7] Similarly the molecular structure of CH_2CP was found to have a C–C double bond and a relatively long C–P triple bond.[6] Molecular structural characterization of HCCP and CH_2CP has been also demonstrated by microwave spectroscopy.

Another important CP bond-bearing molecule is the CH_2P radical which has not been studied in either the gas or solid phase by any spectroscopic methods. Only one *ab initio* calculation study[8] was reported on this radical, predicting that $r(CP)=1.707$ Å, $r(CH)=1.079$ Å, and $\angle HCP=122.1°$ at the MP4SDTQ/6–31G(d,p) level of theory. The nitrogen analog of CH_2P, CH_2N, was studied by microwave spectroscopy, and concluded to have a structure with a relatively short CN bond intermediate between a double C═N bond and a triple C≡N bond, which is consistent with spin densities on H and N derived from its hyperfine coupling constants.[9] Later, CH_2N was found to exist in a cold dark molecular cloud TMC-1 (Cyanopolyyne Peak) on observation of its lowest a-type R-branch transition $1_{01}-0_{00}$ with the 12 m Kitt Peak telescope of NRAO.[10] The fractional abundance was derived to be very small in space (1.5×10^{-11}) relative to that of hydrogen.

This paper presents the first gas-phase identification and characterization of CH_2P by microwave spectroscopy. Molecular constants of CH_2P and CD_2P were determined with high precision, and were used to derive the molecular structure and spin density of CH_2P.

EXPERIMENT

Spectral lines of CH_2P were first measured by using a frequency-modulated microwave spectrometer at Nagoya University,[11] and later at the Institute for Molecular Science.[12] The chemical system used was a dc-glow discharge (200 mA) of a mixture of PH_3 (10 mTorr), CH_4 (15 mTorr), and He(5 mTorr) in a 2 m-free space cell maintained at about −180 °C. A set of fine and hyperfine-structure resolved spectral lines appeared at about every 33 GHz and showed a typical K structure feature of a-type R-branch rotational transitions. The K_a= odd transitions showed a doublet pattern for a fine structure component, whereas the K_a= even transitions showed a complicated pattern composed of several lines. The spectral line pattern and the chemical behavior made us conclude that the observed lines originated from a new phosphorus-bearing radical, CH_2P. The ground electronic state of CH_2P was considered to have $^2B_2$ symmetry, as implied by the ground electronic state of CH_2N,[9] so that the hyperfine structures observed for the K_a= even and odd transitions were well explained by the coupling scheme of $J=N+S$, $F_1=J+I(P)$, $I(H)=I(H_1)+I(H_2)$, and $F=F_1+I(H)$. An example of the observed spectral pattern is shown in Fig. 1.

When CD_4 was used instead of CH_4 in the gas mixture, most of the CD_2P rotational lines did not show hyperfine structure due to the deuterium nuclei. Only $K_a=1$ and 2 components of the $N=9-8$ transition showed broadened and unsymmetrical line shapes, and high K_a components revealed partially resolved features which were too weak to be measured precisely. An example of such line shapes is shown in Fig. 2.

ANALYSIS

The observed spectral lines were analyzed using the following Hamiltonian for an asymmetric top radical in a doublet electronic state:[13]

$$H=H_{rot}+H_{sr}+H_{mhf}(P)+H_{mhf}(H\text{ or }D), \qquad (1)$$

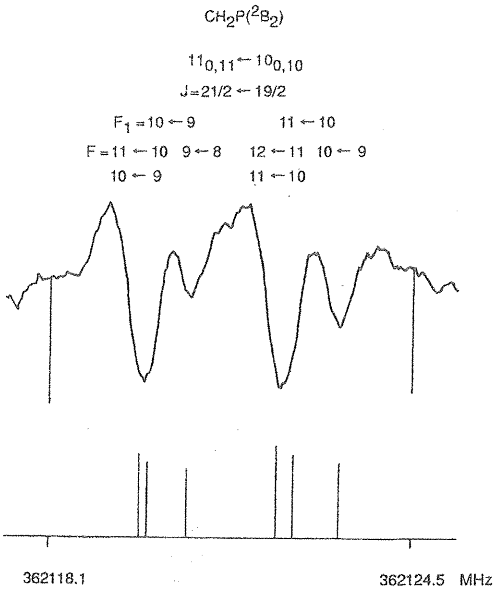

FIG. 1. The observed phosphorus and hydrogen hyperfine structure of the $K_a=0$ rotational transition of CH_2P: $11_{0,11}-10_{0,10}$, $J=21/2-19/2$. The lower stick diagram shows calculated hyperfine structure with relative intensity. CH_2P was produced by a 200 mA dc-glow discharge in a mixture of PH_3 (10 mTorr), CH_4 (15 mTorr), and He (5 mTorr). The integration time was 20 s.

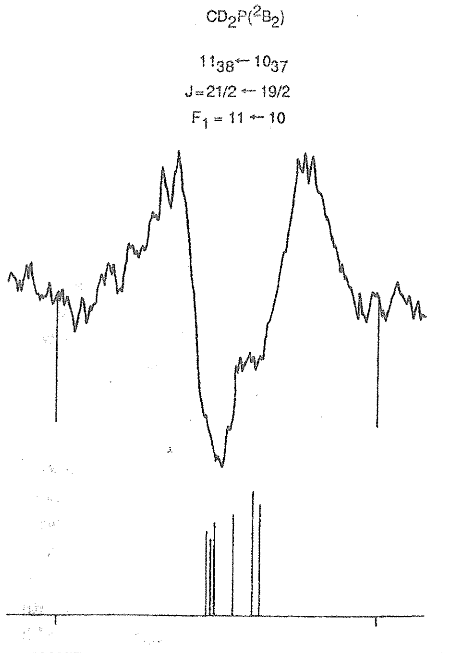

FIG. 2. The observed line shape of the $K_a=3$ rotational transition of CD_2P: $11_{38}-10_{37}$, $J=21/2-19/2$, $F_1=11-10$. The lower stick diagram shows calculated deuterium ($I(D)=0.2$) hyperfine structure with relative intensity. The integration time was 40 s.

TABLE I. Some observed and calculated transition frequencies of CH_2P.[a]

$J'-J$	$F_1'-F_1$	$F'-F$	ν_{obs}	$\Delta\nu$[b]
$N_{KaKc}=11_{0,11}-10_{0,10}$				
23/2–21/2	12–11	13–12	361 948.859	−0.042
		12–11	361 949.663	0.072[c]
		11–10		
	11–10		361 951.299	0.189[c]
21/2–19/2	11–10	12–11	362 122.537	-0.022
		11–10		
		10–9	362 123.533	−0.003
	10–9	11–10	362 120.109	0.070[c]
		10–9		
		9–8	362 120.944	0.090[c]
$11_{1,11}-10_{1,10}$				
23/2–21/2		12–11	357 022.235	0.020
		11–10	357 023.304	−0.028
21/2–19/2		11–10	357 284.146	−0.061
		10–9	357 285.176	0.117[c]
$11_{1,10}-10_{1,9}$				
23/2–21/2		12–11	367 643.180	0.026
		11–10	367 642.374	−0.042
21/2–19/2		11–10	367 761.778	−0.026
		10–9	367 760.248	−0.017
$11_{2,10}-10_{2,9}$				
23/2–21/2	12–11	13–12	362 278.403	−0.012
		12–11	362 217.365	−0.445[c]
		11–10	362 209.135	0.037
	11–10	12–11	362 238.520	0.482[c]
		11–10	362 313.532	0.045
		10–9	362 292.276	0.163[c]
21/2–19/2	11–10	12–11	362 668.692	−0.144[c]
		11–10	362 622.431	−0.110[c]
		10–9	362 564.121	−0.013
	10–9	11–10	362 549.315	−0.018
		10–9	362 559.652	−0.134[c]
		9–8	362 569.756	0.010
$11_{29}-10_{28}$				
23/2–21/2	12–11	13–12	362 829.584	−0.012
		12–11	362 758.149	−0.321[c]
		11–10	362 774.433	−0.106[c]
	11–10	12–11	362 792.924	0.534[c]
		11–10	362 882.501	0.262[c]
		10–9	362 846.059	0.260[c]
21/2–19/2	11–10	12–11	363 201.690	0.282[c]
		11–10		
		10–9	363 089.954	−0.003
	10–9	11–10	363 067.876	−0.128[c]
		10–9	367 086.823	−0.133[c]
		9–8	367 099.549	0.048
$11_{39}-10_{38}$				
23/2–21/2		12–11	362 260.169	−0.036
		11–10	362 257.340	0.015
21/2–19/2		11–10	362 715.725	0.038
		10–9	362 719.449	0.011
$11_{38}-10_{37}$				
23/2–21/2		12–11	362 265.340	−0.030
		11–10	362 262.482	−0.005
21/2–19/2		11–10	362 720.561	0.041
		10–9	362 724.302	−0.006
11_4-10_4				
23/2–21/2	12–11		361 983.137	0.154[c]
	11–10		361 978.155	0.230[c]
21/2–19/2	11–10		362 684.289	0.022
	10–9		362 690.489	0.037
11_5-10_5				
23/2–21/2		12–11	361 646.821	−0.010
		11–10	361 638.884	0.024
21/2–19/2		11–10	362 672.278	0.201[c]

[a] The complete list is deposited at E-PAPS (Ref. 17). Standard deviation of the fit is 25 kHz. Calculated frequencies were obtained from the molecular constants given in Table III.

[b] Residuals in the fit. $\Delta\nu=\nu_{obs}-\nu_{calc}$.

[c] Not included in the fit.

TABLE II. Some observed and calculated transition frequencies of CD_2P.[a]

$N'_{KaKc'}-N_{KaKc}$	$J'-J$	$F'-F$	ν_{obs}	$\Delta\nu$[b]
$9_{09}-8_{08}$	19/2–17/2	10–9	244 721.285	0.016
		9–8	244 725.413	0.046
	17/2–15/2	9–8	244 880.845	0.098[c]
		8–7	244 875.377	0.035
$9_{19}-8_{18}$	19/2–17/2	10–9	239 707.660	0.022
		9–8	239 709.880	0.036
	17/2–15/2	9–8	239 923.144	−0.132[c]
		8–7	239 924.581	−0.134[c]
$9_{18}-8_{17}$	17/2–15/2	9–8	251 504.329	0.310[c]
		8–7	251 501.133	−0.181[c]
$9_{28}-8_{27}$	19/2–17/2	10–9	245 598.720	−0.197[c]
		9–8	245 615.570	0.001
	17/2–15/2	9–8	245 812.601	−0.653[c]
		8–7	245 833.546	0.025
$9_{36}-8_{35}$	19/2–17/2	10–9		
$9_{27}-8_{26}$		10–9	246 725.315	−0.260[c]
	17/2–15/2	8–7	246 928.576	−0.288[c]
$9_{37}-8_{36}$	19/2–17/2	10–9	245 813.799	−0.016
	17/2–15/2	9–8	246 167.283	0.007
		8–7	246 174.998	0.014
$9_{36}-8_{35}$	19/2–17/2	9–8	245 828.460	0.194[c]
	17/2–15/2	9–8	246 185.878	−0.138[c]
		8–7	246 193.837	−0.040
9_4-8_4	19/2–17/2	9–8	245 600.529	−0.002
	17/2–15/2	9–8	246 153.683	0.013
		8–7	246 166.274	−0.004

[a] The complete list is deposited at E-PAPS (Ref. 17). Standard deviation of the fit is 36 kHz. Calculated frequencies were obtained from the molecular constants given in Table III.

[b] Residuals in the least-squares fit. $\Delta\nu=\nu_{obs}-\nu_{calc}$.

[c] Not included in the least-squares fit.

where H_{rot} and H_{sr} represent the rotational Hamiltonian and the spin-rotation interaction Hamiltonian including centrifugal distortion effects, respectively. $H_{mhf}(X)$ denotes the Hamiltonian for magnetic dipole–dipole interaction of the nucleus X. The matrix elements of the Hamiltonian were derived by using the standard method[14] with the basis function of $|NKSJI(P)F_1I(H\,\mathrm{or}\,D)FM_F\rangle$ employing the coupling scheme of $J=N+S$, $F_1=J+I(\mathrm{P})$, $I(\mathrm{H\,or\,D})=I(\mathrm{H_1\,or\,D_1})+I(\mathrm{H_2\,or\,D_2})$, and $F=F_1+I(\mathrm{H\,or\,D})$. Least-squares fitting programs were written for the analysis of the observed spectral lines. The program for CH_2P is composed of two subroutines, for $I(\mathrm{H})=0$ and $I(\mathrm{H})=1$, whereas that of CD_2P, three subroutines for $I(\mathrm{D})=0$, $I(\mathrm{D})=1$, and $I(\mathrm{D})=2$.[15] The energy levels were calculated by direct diagonalization of the Hamiltonian matrices. The program was used to determine simultaneously most of the molecular constants related to Eq. (1), regardless of K_a=even or odd.

Many line frequencies, partly unresolved for hyperfine structure and for higher K doubling, were included in the fit using calculated frequencies by averaging the component frequencies that were expected to be included. This is because the hidden components were found to give a sizable frequency shift to the calculated line frequency.[16] In the final least-squares fit were included 158 spectral lines from a total of 245 observed lines. The standard deviation of the fit was 25 kHz and residuals between the observed and calculated frequencies are listed in Table I.[17] The determined molecular constants are given in Table III. The centrifugal distortion

TABLE III. Molecular constants of CH_2P and CD_2P in the $^2B_2$ ground electronic state (MHz).[a]

Constant	CH_2P	CD_2P
A_0	296178.1(68)	148439.3(39)
B_0	16967.1024(112)	14312.5948(185)
C_0	16004.0274(110)	13015.1040(151)
Δ_N	0.0200909(67)	0.01352397(180)
Δ_{NK}	0.879592(139)	0.49475(102)
Δ_K	22.85[b]	5.043[c]
δ_N	0.0012308(126)	0.0014339(193)
δ_K	0.6225(48)	0.3504(55)
Φ_{NK}	0.00000708(54)	0.0000076(37)
Φ_{KN}	−0.0001902(35)	−0.000050(54)
ϵ_{aa}	4220.56(24)	2074.27(193)
ϵ_{bb}	−8.334(51)	−7.060(177)
ϵ_{cc}	−295.533(52)	−241.283(157)
Δ_N^s	0.000740(67)	−0.00023(32)
Δ_{KN}^s	−0.0499(26)	−0.017(23)
Δ_K^s	−0.5885(178)	0.199(153)
$a_F(P)$	177.263(58)	173.08(149)
$T_{aa}(P)$	−341.77(21)	−340.2(27)
$T_{bb}(P)$	607.84(189)	601.3(37)
$C_{aa}(P)$	1.116(58)	0.18(48)
$C_{bb}(P)$	0.0[d]	0.0[d]
$C_{cc}(P)$	0.1345(92)	−0.035(61)
$a_F(H)$	104.936(37)	
$T_{aa}(H)$	3.677(176)	
$T_{bb}(H)$	−7.69(135)	

[a] Values in parentheses denote three times the standard deviation and apply to the last digits of the constants.

[b] Centrifugal distortion constant Δ_K from Ref. 18.

[c] Centrifugal distortion constant Δ_K from Refs. 19 and 20.

[d] Fixed.

TABLE IV. Comparison of the structural parameters of CH_2P with those of related molecules.

Molecules	r(CP) (Å)	r(CH) (Å)	∠HCH(°)	Methods
CH_2P				
exp(r_0)	1.6576(28)	1.0912(61)	115.96(96)	MW[a]
ab initio(r_e)	1.707	1.079	115.8	PM4SDTQ/6-31G(d,p)[b]
CH_2PH(r_0)	1.673(2)	1.090(15)	111.2(8)	MW[c]
CH_3PH_2(r_g)	1.858(3)	1.094(8)		ED[d]
CP(r_e)	1.561977(7)			FTIR[e]
HCP(r_e)	1.54020(3)	1.0666(2)		MW[f]
HCCP(r_0)	1.685	1.057		MW[g]
CH_2CP(r_e)	1.5889(10)	1.0816(5)	118.22(5)	*ab initio*[h]

[a] Present study.

[b] Reference 8.

[c] Reference 21.

[d] Reference 24.

[e] Reference 22.

[f] Reference 23.

[g] Reference 5.

[h] Reference 6.

constant Δ_K, which is not determinable from a-type rotational transitions only, was fixed at 22.85 MHz, to a value of a molecule similar in size (CH_2S).[18] In the initial stage of the analysis, three components of the phosphorus nuclear spin rotation coupling constants were included in the fit as determinable parameters, but $C_{bb}(P)$ was found to converge to a very small value around zero. Therefore, C_{bb} was fixed at 0.0 in the later fits. For analysis of the spectral lines of CD_2P, the Δ_K parameter was fixed at 5.043 MHz, to the value for CD_2S.[19,20] Since it was difficult to measure the hyperfine components due to the deuterium nuclei, as described in the Experiment, these were not included in the analysis. In the final fit, 70 spectral lines from 104 observed lines were used. The standard deviation of the fit was 36 kHz and its residuals are listed in Table II.[17] Many unresolved or overlapped lines giving unsymmetrical line shapes for both the species resulted in a large reduction of the line numbers used in the fits as indicated in Tables I and II. The molecular constants determined are given in Table III. The phosphorus nuclear spin rotation coupling constants and the centrifugal distortion terms of the spin rotation coupling constants were included in the analysis of CD_2P, as in the case of CH_2P, but their determined values are marginal as seen in Table III.

DISCUSSION

Small positive values of inertial defects derived from observed moments of inertia for CH_2P and CD_2P clearly show that the CH_2P radical has a planar structure; $\Delta_0 = 0.086\,09(8)\ \mathrm{u\AA^2}$ for CH_2P and $0.115\,49(18)\ \mathrm{u\AA^2}$ for CD_2P. The r_0 structure of CH_2P was determined from the observed rotational constants. Only three of the six moments of inertia are independent because of the planarity condition for the three moments of inertia of each species and the a component of the moments of inertia which is derived only from the H–H distance. The H–H distance was determined to be 1.840 155(42) Å where the figures in parentheses indicate 3σ experimental errors, whereas the D–D distance was calculated to be 1.838 687 8(48) Å. The difference between the H–H and D–D distances originates from rotation-vibration interaction giving an inertial defect. Therefore, three structural parameters of CH_2P were ascertained from the observed moments of inertia of CH_2P and CD_2P by a least-squares fit. The structural parameters determined are $r_0(\mathrm{CP}) = 1.6576(28)$ Å, $r_0(\mathrm{CH}) = 1.0912(61)$ Å, and $\angle\mathrm{HCH} = 115.96(96)°$, where values in parentheses indicate one sigma error, mainly due to the inertial defects of CH_2P and CD_2P, giving $\sigma(\delta I) = 0.0486\ \mathrm{u\AA^2}$, where $\delta I = I_{gg}^{\mathrm{obs}} - I_{gg}^{\mathrm{calc}}$. The determined structure is compared with its theoretically predicted result and also those of related molecules in Table IV. Comparison with theoretical values shows a significant difference in r_0(CP).[8] The CP bond of CH_2P is similar to those in CH_2PH (Ref. 21) and HCCP,[5] but quite different from those in CP,[22] HCP,[23] and CH_2CP (Ref. 6) which have a typical triple C≡P bond and that of CH_3PH_2 (Ref. 24) which has a typical single C–P bond. If CH_2PH is assumed to have a typical CP double bond, a small difference between the CP bond lengths of CH_2P and CH_2PH means that the CP bond of CH_2P has a small contribution from the CP triple bond.

The large Fermi contact term of the hydrogen nucleus could be explained by hyperconjugation of the σ radical, as discussed in the case of CH_2N.[9] The s character of the unpaired electron spin on the P nucleus was derived to be 1.3% from the observed $a_F(P)$ constant, where the atomic value was as given in Ref. 24. Similarly the s character on the hydrogen nuclei was calculated to be 7.3%. The magnetic dipole–dipole coupling constant $T_{bb}(P)$ is almost equal to $-2T_{aa}$ and $-2T_{cc}$. This means that the unpaired electron occupies the p_π orbital that extends to the b principal axis of the molecule. When the T_{bb} constant is compared with the atomic value,[25] the p character at the P nucleus is calculated to be 83.2%. The summation of the spin densities at the P and H nuclei amounts to 99%. The spin density obtained is consistent with the determined molecular structure given above; the CP double bond is somewhat modified by a small contribution of a CP triple bond corresponding to the hyperconjugation form.

There has been no information on the excited electronic states of CH_2P. Semiquantitative information is available from the observed spin-rotation coupling constant.[26] CH_2P has a relatively large value of ϵ_{cc} which is characteristic of the σ radical as exemplified in CH_2N.[9] Since the c component of the angular momentum belongs to B_2 species in C_{2v} symmetry, the ϵ_{cc} constant is mainly responsible for spin–orbit coupling to the excited states with A_1 symmetry. If one electron excitation is applied, the lowest A_1 state is estimated to be 50 000 cm^{-1} above the ground electronic state. Similarly the lowest B_1 state is estimated to lie at 64 000 cm^{-1} from the observed ϵ_{aa} constant.

Finally, the nuclear spin-rotation coupling constant $C_{aa}(P)$ was found to be relatively large, 1.116 MHz, which is comparable to its counterpart in HPO, -1.12 MHz.[27] This $C_{aa}(P)$ constant is related to $a(P)\epsilon_{aa}/A_{SO}$,[28] where $a(P)$ is assumed to be $5T_{bb}/4$ and A_{SO} is calculated to be 229 cm^{-1} from the atomic value of $\zeta(3p^3)$ for the phosphorus atom[29] and the spin density obtained above. The C_{aa} constant is estimated to be 0.468 MHz, which is less than half of the observed value.

In conclusion, the present study has established the existence of a new phosphorus-bearing radical CH_2P in the gas phase for the first time by microwave spectroscopy, and characterized it to be a typical σ radical like CH_2N.

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