2006

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Recommended Citation

Ingels, Justin B.; Turney, Justin M.; Richardson, Nancy A.; Yamaguchi, Yukio; and Schaefer III, Henry F., "Characterization of Singlet Ground and Low-Lying Electronic Excited States of Phosphaethyne and Isophosphaethyne" (2006). *Faculty Publications and Presentations*. 69.
https://digitalcommons.liberty.edu/bio_chem_fac_pubs/69

THE JOURNAL OF CHEMICAL PHYSICS **125**, 104306 (2006)

Characterization of singlet ground and low-lying electronic excited states of phosphaethyne and isophosphaethyne

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(Received 17 November 2005; accepted 19 June 2006; published online 8 September 2006)

The singlet ground ($\tilde{X}\ ^1\Sigma^+$) and excited ($^1\Sigma^-, ^1\Delta$) states of HCP and HPC have been systematically investigated using *ab initio* molecular electronic structure theory. For the ground state, geometries of the two linear stationary points have been optimized and physical properties have been predicted utilizing restricted self-consistent field theory, coupled cluster theory with single and double excitations (CCSD), CCSD with perturbative triple corrections [CCSD(T)], and CCSD with partial iterative triple excitations (CCSDT-3 and CC3). Physical properties computed for the global minimum ($\tilde{X}\ ^1\Sigma^+$HCP) include harmonic vibrational frequencies with the cc-pV5Z CCSD(T) method of $\omega_1 = 3344$ cm^{-1}, $\omega_2 = 689$ cm^{-1}, and $\omega_3 = 1298$ cm^{-1}. Linear HPC, a stationary point of Hessian index 2, is predicted to lie 75.2 kcal mol^{-1} above the global minimum HCP. The dissociation energy $D_0[\mathrm{HCP}(\tilde{X}\ ^1\Sigma^+) \rightarrow \mathrm{H}(^2S) + \mathrm{CP}(X\ ^2\Sigma^+)]$ of HCP is predicted to be 119.0 kcal mol^{-1}, which is very close to the experimental lower limit of 119.1 kcal mol^{-1}. Eight singlet excited states were examined and their physical properties were determined employing three equation-of-motion coupled cluster methods (EOM-CCSD, EOM-CCSDT-3, and EOM-CC3). Four stationary points were located on the lowest-lying excited state potential energy surface, $^1\Sigma^- \rightarrow {}^1A''$, with excitation energies T_e of 101.4 kcal mol^{-1}($^1A''$ HCP), 104.6 kcal mol^{-1}($^1\Sigma^-$ HCP), 122.3 kcal mol^{-1}($^1A''$ HPC), and 171.6 kcal mol^{-1}($^1\Sigma^-$ HPC) at the cc-pVQZ EOM-CCSDT-3 level of theory. The physical properties of the $^1A''$ state with a predicted bond angle of 129.5° compare well with the experimentally reported first singlet state ($\tilde{A}\ ^1A''$). The excitation energy predicted for this excitation is $T_0 = 99.4$ kcal mol^{-1}(34 800 cm^{-1}, 4.31 eV), in essentially perfect agreement with the experimental value of $T_0 = 99.3$ kcal mol^{-1}(34 746 cm^{-1}, 4.308 eV). For the second lowest-lying excited singlet surface, $^1\Delta \rightarrow {}^1A'$, four stationary points were found with T_e values of 111.2 kcal mol^{-1} ($2^1A'$ HCP), 112.4 kcal mol^{-1} ($^1\Delta$ HPC), 125.6 kcal mol^{-1}($2\ ^1A'$ HCP), and 177.8 kcal mol^{-1}($^1\Delta$ HPC). The predicted CP bond length and frequencies of the $2\ ^1A'$ state with a bond angle of 89.8° (1.707 Å, 666 and 979 cm^{-1}) compare reasonably well with those for the experimentally reported $\tilde{C}\ ^1A'$ state (1.69 Å, 615 and 969 cm^{-1}). However, the excitation energy and bond angle do not agree well: theoretical values of 108.7 kcal mol^{-1} and 89.8° versus experimental values of 115.1 kcal mol^{-1} and 113°. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2222356]

I. INTRODUCTION

The successful synthesis of phosphaethyne or methinophosphide (HCP) in 1961 by Gier was the first report of a molecule containing a multiple bond between phosphorus and carbon.[1] Gier observed bands in the infrared (IR) absorption spectrum that compared favorably to assumed C–H stretching frequencies and H–C–X bending frequencies. Failing to see any band in the region corresponding to a H–P bend, Gier concluded that the molecule was linear HCP and not HPC. In 1964, Tyler[2] reported the microwave spectrum of HCP and concurred with the conclusion of Gier.[1] The dipole moment (0.39 polarity $^+$HCP$^-$) and bond lengths (1.067 and 1.542 Å) of the ground state ($^1\Sigma^+$) were determined by Tyler. HCP is of astrophysical interest owing to its presence in the interstellar medium and the atmosphere of Saturn.[3–5]

The ultraviolet (UV) spectrum of HCP was first reported in an extensive spectroscopic study by Johns *et al.* in 1969.[6] They deduced ground state information using their own rovibronic analysis along with data from Tyler's earlier microwave study.[2] Fundamental vibrational frequencies for the symmetric and asymmetric stretching and the bending modes were reported as 3217 cm^{-1}(ν_1), 1278 cm^{-1}(ν_3), and 675 cm^{-1}(ν_2), respectively. Also, the CP bond length was reported as 1.542 Å, in agreement with that of Tyler. Seven excited electronic states were identified, including three singlet states of interest, with electronic excitation energies (T_0) of 34 750 cm^{-1} (99.3 kcal mol^{-1}) for $\tilde{A}\ ^1A''$, 35 930 cm^{-1} (102.7 kcal mol^{-1}) for $\tilde{B}\ ^1\Pi$, and 40 250 cm^{-1} (115.1 kcal mol^{-1}) for $\tilde{C}\ ^1A'$, as well as four triplet states. For the $\tilde{A}$ and

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$\tilde{C}$ states, values of ν_2 were found to be 567 and 615 cm^{-1} and values of ν_3 to be 954 and 969 cm^{-1}, respectively.

The second singlet excited state ($\tilde{B}$), considered by Johns *et al.*[6] to be a $^1\Pi$ state, was reexamined in 1972 by Moehlmann *et al.*[7] in a study exploiting the Zeeman effect. The group found that the Zeeman splitting for the $\tilde{B}$ state increased as the rotational quantum number J increases. This sort of behavior is not expected of a $^1\Pi$ state, and Moehlmann *et al.* concluded that the excited state described as $\tilde{B}$ was actually a $^3\Delta$ state. Later that year the same group, utilizing the Stark effect, determined the dipole moment of the first $^1A''$ state of HCP to be 0.44 ± 0.06 D (polarity not determined). In 1973 Frost *et al.*[8] measured the photoelectron spectrum of HCP and determined the energy required to remove an electron from the HOMO (2π) to be 10.8 eV. In 1999 Ishikawa *et al.*[9] reported results of an IR-UV double resonance spectroscopy study on HCP. They established a C–H stretching frequency of 2930 cm^{-1} for the $\tilde{A}\ ^1A''$ state.

A series of IR studies[10–13] were conducted that appear to give fundamental stretching vibrational frequencies to greater precision than those reported by Johns *et al.*[6] Kalasinsky and Pechsiri[14] recorded the Raman spectrum in 1985 and determined the fundamental vibrational frequencies, $\nu_1=3218$ cm^{-1} and $\nu_3=1277$ cm^{-1}. Mason and Lehman[15] in 1993 measured the laser-induced fluorescence spectrum of HCP and found a sharp decrease in intensity at 41 680 cm^{-1}. They assigned this decrease in intensity to the coupling of excited vibrational levels with the dissociative continuum of the ground state. From their data they placed a lower limit on the dissociation energy at 41 650 cm^{-1} (119.1 kcal mol^{-1}).

A number of studies have been conducted with the intention of determining accurate structural parameters for the ground state of HCP. Using results obtained for HCN as constraints, Strey and Mills[16] in 1973 used vibration-rotation constants determined by Johns *et al.*[6] to deduce an anharmonic force field for HCP. From this data they determined $r_e(\mathrm{HC})=1.0692(8)$ Å and $r_e(\mathrm{CP})=1.5398(2)$ Å. In 1996, Dréan *et al.*[17] remeasured the rotational spectrum, determining zero-point rotational constants and values for $r_0(\mathrm{HC})=1.0652$ Å and $r_0(\mathrm{CP})=1.5442$ Å. Dréan *et al.* used rotational constants to extrapolate to equilibrium rotational constants yielding $r_e(\mathrm{HC})=1.0670$ Å and $r_e(\mathrm{CP})=1.5402$ Å. Ishikawa *et al.*[18] performed an algebraic analysis of intensities from the emission spectrum of HCP. From their study, Ishikawa *et al.* reported $r_e(\mathrm{HC})=1.067$ Å and $r_e(\mathrm{CP})=1.642$ Å and a bond angle of 122.1° for the first excited $\tilde{A}\ ^1A''$ state.

Numerous theoretical studies have also been reported regarding the ground state parameters of HCP.[19–38] There have been three configuration interaction (CI) studies of the excited states of HCP. First, in 1990, Karna *et al.*[39] studied a number of singlet, triplet, and quintet and linear and bent excited states using the multireference configuration interaction single and double excitation (MRCISD) method including energy extrapolation. The linear singlet states of interest to the present study, with T_e in eV, are $^1\Sigma^-$ (4.57) and $^1\Delta$ (4.95). In accord with other groups, Karna *et al.* did not find a $^1\Pi$ state where Johns *et al.*[6] had reported. The bent structures Karna *et al.* characterized include the $^1A''$ (4.42) and $^1A'$ (4.9) states with a H–C–P bond angle of 131° and 140°, respectively. In 1993 Sannigrahi and Grein[40] described results of multireference double excitation configuration interaction (MRD-CI) calculations on the three lowest $^1A'$ and $^1A''$ states at a fixed CH distance of 1.071 Å. The three lowest $^1A'$ states corresponded (approximate T_e values in eV and bond angles) to $^1\Sigma^+$ (0.0, 180.0°), $^1\Delta$ (4.60, 93°), and $^1\Sigma^+$ (6.25, 105.0°) and the three lowest $^1A''$ states to $^1\Sigma^-$ (4.45, 126.0°), $^1\Delta$ (5.00, 180.0°), and $^1\Delta$ (7.10, 116.0°). The third CI study was performed by Nanbu *et al.*[41] in 2000, utilizing DZP and aug-cc-pVDZ basis sets with MRCISD based on a complete active space self-consistent field (CASSCF) reference wave function. The latter group was the first to characterize excited states that more closely resemble HPC than HCP. They distinguished two $^1A''$ states arising from $^1\Sigma^-$ and $^1\Delta$, plus three $^1A'$ minima and one $^1A''$ minimum. The group found that even though the ground state does not exhibit any stable linear minima on the HPC side, both the $^1\Sigma^-$ and $^1\Delta$ states lead to bent minima resembling HPC.

One other theoretical study of interest concerning HCP singlet excited states was reported in 1993 with work by Goldstein *et al.*[42] Geometries were optimized with Møller-Plesset second-order perturbation theory (MP2) for the ground state while CASSCF was utilized to study the excited states. The study of Goldstein *et al.* reported that linear HCP and linear HPC are minima with a bent transition state occurring near $\theta(\mathrm{HPC})=136°$ with respect to the HPC angle. The only singlet state discussed in their study was the aforementioned $^1A''$ state derived from linear $^1\Sigma^-$ at 4.80 eV (with their largest basis, TZV++, and CASSCF configuration space, ten electrons in ten molecular orbitals).

Early experimental studies do not mention the possibility that linear HPC exists.[1,2,6,8,10–14] A later study by Lehmann *et al.*[43] in 1985 found that a fit of vibrational levels of the ground state gives a description of the bending potential from 0° (linear HCP) to 100°. The fit gives no indication that a turnover will occur causing a minimum for HPC. There was much controversy by early theoretical investigations regarding the true nature of HPC. It was previously mentioned that Goldstein *et al.*[42] determined linear HPC to be a local minimum through the use of MP2 theory. The potential energy surface of the ground state was once again studied in 1993 by Ma *et al.*,[44] who found MP2 and MP4 to give local minima while MP3 found a saddle point for the linear HPC conformation. Hong and Cave[45] in 1994 concluded that HPC has considerably more multireference character than HCP. The results of CASSCF and CCSD wave functions both reveal linear HPC to be a saddle point with the use of a small basis set (6–311G). The MRCI method was utilized by Beck *et al.*[46] to determine a potential energy surface for the ground state, leading to the conclusion that HPC is an energetic maximum with respect to bending. Much of what has been stated about the HPC→HCP isomerization has been reviewed in an important paper by Ishikawa *et al.*[47]

The goals of the present study are twofold. Potential energy surfaces of the ground and low-lying singlet excited states of HCP will be constructed as an aid to uncovering minima and saddle points. The ground state energies, geometries, dipole moments, and harmonic vibrational frequencies will be determined for both the linear HCP and HPC configurations in the ground state. These two conformations, from previous work, likely constitute the global minimum and a local maximum, respectively. Secondly, the low-lying singlet excited states of both linear and bent geometries will be explored using a variety of equation-of-motion (EOM) coupled cluster techniques. This will be conducted for states arising from both the HCP and HPC regions of the potential energy surface. The results will be compared to previous experimental and theoretical studies.

II. ELECTRONIC STRUCTURE CONSIDERATIONS

The electronic configurations of the linear $\tilde{X}\,{}^1\Sigma^+$ ground states of HCP and HPC are qualitatively described as

$$[\text{core}](5\sigma)^2(6\sigma)^2(7\sigma)^2(2\pi)^4\tilde{X}\,{}^1\Sigma^+, \tag{1}$$

where [core] denotes the carbon $1s$-like molecular orbital and the phosphorus $1s$-, $2s$-, and $2p$-like orbitals. Let π_x and π_y be π molecular orbitals (MOs) in real coordinates, denoting the π components in the xz plane and yz plane (the z axis is assigned to the molecular axis). Configuration (1) may be written in real orbital form

$$[\text{core}](5\sigma)^2(6\sigma)^2(7\sigma)^2(2\pi_x)^2(2\pi_y)^2\,\tilde{X}\,{}^1\Sigma^+. \tag{2}$$

The lowest-lying excited electronic states for HCP/HPC are obtained conceptually by exciting an electron from the bonding 2π [highest occupied molecular orbital (HOMO)] orbital to the antibonding 3π [lowest unoccupied molecular orbital (LUMO)] orbital. This gives rise to three excited singlet states of HCP and HPC for linear geometries,

$$[\text{core}](5\sigma)^2(6\sigma)^2(7\sigma)^2(2\pi)^3(3\pi)\;{}^1\Sigma^+,{}^1\Sigma^-,{}^1\Delta. \tag{3}$$

The electronic configuration of the ${}^1\Delta$ state requires four Slater determinants in real MO notation. Assuming the molecule lies on the z axis, the two ${}^1\Delta$ components (${}^1A_1$ and ${}^1A_2$ in C_{2v} subgroup, respectively) are

$$\begin{aligned}&[\text{core}](5\sigma)^2(6\sigma)^2(7\sigma)^2[(2\pi_x\alpha)(2\pi_y)^2(3\pi_x\beta)\\&\quad+(2\pi_x)^2(2\pi_y\beta)(3\pi_y\alpha)-(2\pi_x\beta)(2\pi_y)^2(3\pi_x\alpha)\\&\quad-(2\pi_x)^2(2\pi_y\alpha)(3\pi_y\beta)]\end{aligned} \tag{4}$$

and

$$\begin{aligned}&[\text{core}](5\sigma)^2(6\sigma)^2(7\sigma)^2[(2\pi_x\alpha)(2\pi_y)^2(3\pi_y\beta)\\&\quad+(2\pi_x)^2(2\pi_y\alpha)(3\pi_x\beta)-(2\pi_x\beta)(2\pi_y)^2(3\pi_y\alpha)\\&\quad-(2\pi_x)^2(2\pi_y\beta)(3\pi_x\alpha)].\end{aligned} \tag{5}$$

The open-shell part of the ${}^1\Sigma^-$ state also requires four Slater determinants in real MO notation,

$$\begin{aligned}&[\text{core}](5\sigma)^2(6\sigma)^2(7\sigma)^2[(2\pi_x\alpha)(2\pi_y)^2(3\pi_y\beta)\\&\quad+(2\pi_x)^2(2\pi_y\beta)(3\pi_x\alpha)-(2\pi_x\beta)(2\pi_y)^2(3\pi_y\alpha)\\&\quad-(2\pi_x)^2(2\pi_y\alpha)(3\pi_x\beta)]\end{aligned} \tag{6}$$

III. THEORETICAL METHODS

Five correlation-consistent polarized-valence basis sets developed by Dunning and co-workers,[48–50] cc-pVXZ (X $=$T,Q,5) and aug-cc-pVXZ (X=T,Q), were utilized in this study. The largest basis set, cc-pV5Z, consisted of 241 contracted Gaussian functions. Geometries were optimized with each basis set and level of theory. Harmonic vibrational frequencies were determined using analytic methods when available and otherwise through finite differences of analytic gradients or numerical differentiation of total energies.

The zeroth-order description of the ground state was obtained using restricted Hartree-Fock (RHF) self-consistent field theory (SCF). The effects of electron correlation were then included for the ground state molecules using coupled cluster (CC) theory with single and double excitations (CCSD),[51,52] the inclusion of perturbative triple excitations [CCSD(T)],[53,54] and with two methods for partial iterative triples [CCSDT-3 (Ref. 55) and CC3 (Ref. 56)]. To investigate the excited electronic states, three equation-of-motion coupled cluster[57,58] (EOM-CC) methods were utilized (EOM-CCSD, EOM-CCSDT-3, and EOM-CC3). For these correlated methods, six core orbitals were frozen, namely, the $1s$-like orbital of carbon and the $1s$-, $2s$-, and $2p$-like orbitals of phosphorus. The *ab initio* quantum chemistry packages utilized in this study include ACESII (Ref. 59) and MOLPRO.[60]

IV. RESULTS

In Fig. 1 the stationary points optimized are schematically depicted using excitation energies (T_e) determined with the cc-pVQZ basis set at the CCSDT-3 level of theory for the ground state and EOM-CCSDT-3 for the excited states. For the $\tilde{X}\,{}^1\Sigma^+$ states of HCP and HPC, the total energies, frequencies, and dipole moments can be found in Tables S1 and S2 (see supplementary material[61]) and the bond lengths in Figs. S1 and S2 (see supplementary material), respectively. Energy differences between the two ground state isomers and dissociation energies are reported in Table S3. For the ${}^1\Sigma^-$ states, the total energies, bond lengths, and excitation energies are summarized in Tables I and II. The total energy and harmonic vibrational frequencies of the HCP and HPC ${}^1A''$ states arising from ${}^1\Sigma^-$ are given in Tables III and IV, with optimized geometries and angles in Figs. 2 and 3. For the ${}^1\Delta$ states, the energy, bond lengths, and excitation energies are summarized in Tables V and VI. The total energy and harmonic vibrational frequencies of the HCP and HPC ${}^1A'$ states arising from ${}^1\Delta$ are given in Tables VII and VIII with optimized geometries in Figs. 4 and 5.

A. $\tilde{X}\,{}^1\Sigma^+$ ground states of HCP and HPC

HCP in Fig. S1 and HPC in Fig. S2 exhibit elongation of the two bonds upon augmentation of the basis set and a decrease in bond length with increases in the size of the basis set. More advanced treatments of correlation effects induce a lengthening of both bond distances for each ground state isomer. Overall, smaller changes are found for the CH and PH bonds than the CP bond upon increasing the size of the

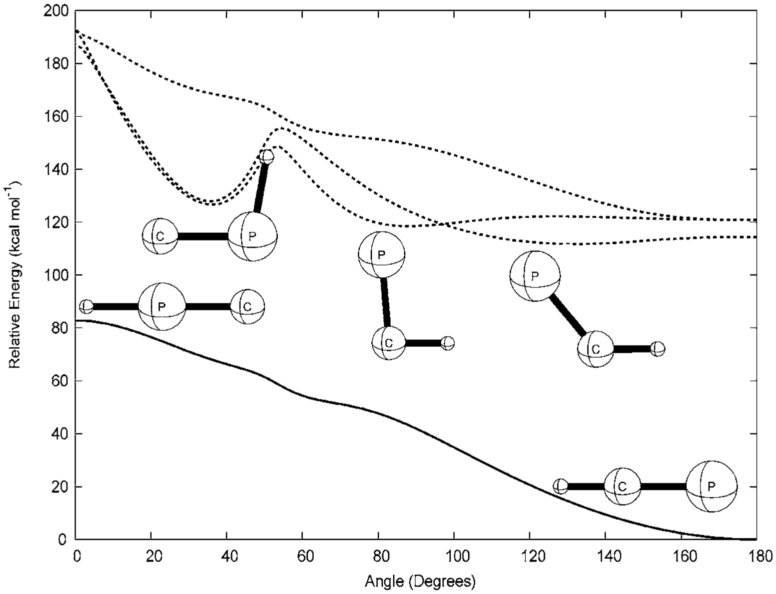

FIG. 1. Ten stationary points determined in this study. Energies reported in diagram are with the cc-pVQZ basis set utilizing CCSD level of theory for the ground state and EOM-CCSD level of theory for the excited states. There is no attempt to depict barriers in this figure.

basis. As bond lengths decrease, the vibrational frequency will tend to increase, which is consistent with Badger's rule[62,63] that the larger force constant (higher vibrational frequency) may be associated with the shorter bond length. The vibrational frequencies generally decrease with the inclusion of diffuse functions, increase when changing the basis from triple to quadruple zeta, and decrease with increasing sophistication in the treatment of electron correlation. The magnitude of the dipole moment (direction $^{+}$HCP^{-}) tends to decrease with the basis set size and increase with electron correlation with the opposite effect occurring for the IR intensities.

The present theoretical predictions provide excellent agreement with the equilibrium values of the bond lengths reported in previous experimental studies.[16–18] The CCSD(T) CH bond length differs by 0.003 Å from the equilibrium bond lengths determined from the experimental anharmonic force field of Strey and Mills.[16] There is a larger distinction for the CP bond lengths; for example, SCF with the cc-pV5Z basis still differs by roughly 0.04 Å but only by 0.004 Å from experiment with cc-pV5Z CCSD(T). Excellent agreement was also obtained for the cc-pV5Z values of ω_2 and ω_3 for HCP, which agree with the experimental fundamentals to within 20 cm^{-1}. The calculated value of ω_1 agrees with experiment to within 130 cm^{-1} at the highest level of theory, but this sort of discrepancy is expected as we are comparing harmonic to fundamental vibrational frequencies.

As mentioned previously, HPC has never been realized experimentally. This is nicely explained by the rearrangement of HCP to HPC being a monotonically uphill process with HPC serving as a stationary point of Hessian index 2. Table S2 summarizes the theoretical results for HPC. The second-order saddle point can be seen from the degenerate imaginary frequencies for the bending mode, denoted $\omega_2(\pi)$. The CP bond lengthens by nearly a tenth of an angstrom in going from HCP to HPC. The two stretching frequencies, ω_1 and ω_3, are lower for HPC than for HCP due to the weakening and subsequent lengthening of the two bonds. HPC has an imaginary bending frequency roughly half the magnitude of the real bending frequency for HCP. There is a considerable increase in the dipole moment (direction $^{+}$HCP^{-}) for HPC owing mainly to the greater electronegativity of the carbon atom now situated at the end of the molecule.

The relative energy differences between HCP and HPC and the dissociation energies defined by HCP ($\tilde{X}\,^1\Sigma^+$) $\rightarrow \mathrm{H}(^2S)+\mathrm{CP}(X\,^2\Sigma^+)$ are found in Table S3. At the highest level of theory, the energy differences between HCP and HPC with and without zero-point vibrational energy (ZPVE)

TABLE I. Total energies (in hartree), bond lengths (in Å), and electronic excitation energies T_e (in kcal mol^{-1}) for the linear 1 $^1\Sigma^-$ state of HCP.

Level of theory	Total energy	r_e (HC)	r_e (CP)	T_e
cc-pVTZ EOM-CCSD	−379.292 778	1.6593	1.0702	107.3
aug-cc-pVTZ EOM-CCSD	−379.299 339	1.6597	1.0711	105.9
cc-pVQZ EOM-CCSD	−379.315 206	1.6522	1.0694	106.9
cc-pVTZ EOM-CCSDT-3	−379.315 449	1.6771	1.0726	105.0
aug-cc-pVTZ EOM-CCSDT-3	−379.322 783	1.6776	1.0737	103.6
cc-pVQZ EOM-CCSDT-3	−379.339 608	1.6695	1.0720	104.6
cc-pVTZ EOM-CC3	−379.317 836	1.6809	1.0733	105.0
aug-cc-pVTZ EOM-CC3	−379.325 255	1.6814	1.0745	103.5
cc-pVQZ EOM-CC3	−379.342 023	1.6731	1.0727	104.5
MRD-CI (Ref. 39)		1.677	1.079	105

TABLE II. Total energies (in hartree), bond lengths (in Å), and electronic excitation energy T_e (in kcal mol^{-1}) for the linear 1 $^1\Sigma^-$ state of HPC.

Level of theory	Total energy	r_e (HP)	r_e (CP)	T_e
cc-pVTZ EOM-CCSD	−379.180 927	1.4051	1.7781	177.5
aug-cc-pVTZ EOM-CCSD	−379.187 769	1.4067	1.7744	175.9
cc-pVQZ EOM-CCSD	−379.202 072	1.4039	1.7669	177.9
cc-pVTZ EOM-CCSDT-3	−379.209 798	1.4140	1.8133	171.3
aug-cc-pVTZ EOM-CCSDT-3	−379.217 489	1.4158	1.8101	169.6
cc-pVQZ EOM-CCSDT-3	−379.232 781	1.4130	1.8014	171.6
cc-pVTZ EOM-CC3	−379.214 370	1.4168	1.8270	169.9
aug-cc-pVTZ EOM-CC3	−379.222 192	1.4188	1.8237	168.2
cc-pVQZ EOM-CC3	−379.237 398	1.4158	1.8142	170.2

TABLE III. HCP total energies (in hartree), harmonic vibrational frequencies (in cm^{-1}), zero-point vibrational energies (ZPVE) (in kcal mol^{-1}), and electronic excitation energies T_e and T_0 (in kcal mol^{-1}) for the bent $^1A''(^1\Sigma^-)$ state.

Level of theory	Total energy	$\omega_1(a')$	$\omega_2(a')$	$\omega_3(a')$	ZPVE	T_e	T_0
cc-pVTZ EOM-CCSD	−379.297 481	3102	569	989	6.66	104.3	102.2
aug-cc-pVTZ EOM-CCSD	−379.303 644	3103	557	984	6.64	103.2	101.1
cc-pVQZ EOM-CCSD	−379.319 188	3120	564	1002	6.70	104.4	102.3
cc-pVTZ EOM-CCSDT-3	−379.321 328	3063	636	968	6.67	101.4	99.5
aug-cc-pVTZ EOM-CCSDT-3	−379.328 149	3062	624	963	6.65	100.2	98.3
cc-pVQZ EOM-CCSDT-3	−379.344 735	3076	628	977	6.69	101.4	99.4
cc-pVTZ EOM-CC3	−379.323 862	3051	645	957	6.65	101.2	99.3
aug-cc-pVTZ EOM-CC3	−379.330 838	3050	633	952	6.63	100.0	98.1
cc-pVQZ EOM-CC3	−379.347 380	3064	636	966	6.67	101.2	99.3
MRD-CI (Ref. 39)			669			101	
CASSCF/TZV++ (Ref. 42)		2885	688	894		110	
MRD-CI (Ref. 40)						99	
MRCI/aug-cc-pVDZ (Ref. 41)						102	
	Total energy	ν_1	ν_2	ν_3	ZPVE	T_e	T_0
Experiment (Ref. 9)		2930					
Experiment (Ref. 6)			566.6	953.9			99.3

corrections are 78.9 and 75.2 kcal mol^{-1}, respectively. The best previous theoretical energy separation[45] is 79.1 kcal mol^{-1}, in good agreement with our value. The previous MPn calculations, with small basis sets, do a mediocre job of describing this energy difference.

The experimental dissociation energy of 119.1 kcal mol^{-1} by Mason and Lehmann[15] was candidly reported as uncertain. Our ZPVE corrected value of 119.0 kcal mol^{-1} at the cc-pV5Z CCSD(T) level of theory provides strong support for their result. The SCF method underestimates the experimental value by 18 kcal mol^{-1}, but the inclusion of electron correlation with the CC methods apparently provides a very good estimation of the experimental value.

B. Excited states

1. Lowest $^1\Sigma^-$ state of HCP

Three low-lying excited singlet states arise from the excitation of an electron from the 2π to 3π orbital [Eq. (3) above]. The lowest energy state arising from this promotion is a $^1\Sigma^-$ electronic state. The linear HCP conformation of this excitation is found to be a stationary point of Hessian index 2. The CH bond length in Table I changes by no more than 0.001 Å for this electronic state, while the CP bond length increases by more than 0.1 Å relative to the ground state of HCP at each level of theory. This trend can be explained by the fact that the 2π orbital is composed of π bonding and the 3π orbital of π-antibonding character between the carbon and phosphorus atoms, leading to little change in the CH bond distance but a considerable lengthening of the CP bond. The $^1\Sigma^-$ state is predicted to lie 104.6 kcal mol^{-1} above $\tilde{X}\,^1\Sigma^+$ HCP at the cc-pVQZ EOM-CCSDT-3 level of theory. A previous theoretical study by Karna *et al.*[39] gave excitation energies similar to our values. Their CP bond length is longer (0.005 Å) than our value, while the values of the CH bond length are very close.

2. Lowest $^1A''$ state of HCP

With only planar (C_s) symmetry, the $^1\Sigma^-$ state becomes $^1A''$ upon bending. The excitation corresponding to this $^1A''$

TABLE IV. HPC total energies (in hartree), harmonic vibrational frequencies (in cm^{-1}), zero-point vibrational energies (ZPVE) (in kcal mol^{-1}), and T_e and T_0 (in kcal mol^{-1}) for the $^1A''(^1\Sigma^-)$ state of HPC relative to $\tilde{X}\,^1\Sigma^+$ HCP.

Level of theory	Total energy	$\omega_1(a')$	$\omega_2(a')$	$\omega_3(a')$	ZPVE	T_e	T_0
cc-pVTZ EOM-CCSD	−379.268 779	2252	809	741	5.44	122.3	119.0
aug-cc-pVTZ EOM-CCSD	−379.274 496	2251	809	743	5.44	121.5	118.2
cc-pVQZ EOM-CCSD	−379.289 791	2259	819	751	5.48	122.8	119.5
cc-pVTZ EOM-CCSDT-3	−379.288 885	2227	770	690	5.27	121.7	118.4
aug-cc-pVTZ EOM-CCSDT-3	−379.295 187	2224	770	692	5.27	120.9	117.6
cc-pVQZ EOM-CCSDT-3	−379.311 340	2216	762	683	5.23	122.3	117.5
cc-pVTZ EOM-CC3	−379.291 088	2220	763	680	5.24	121.8	118.5
aug-cc-pVTZ EOM-CC3	−379.297 458	2216	762	683	5.23	120.9	117.6
cc-pVQZ EOM-CC3	−379.313 586	2225	770	690	5.27	122.4	119.1
MRCI/aug-cc-pVDZ (Ref. 41)						125	

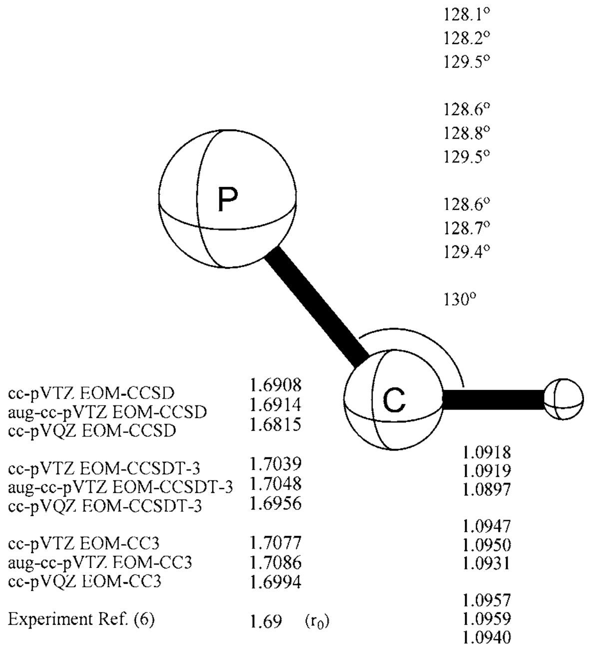

FIG. 2. Predicted geometries of the $^1A''(^1\Sigma^-)$ state of HCP. Bond lengths are in Å. The experimental structure was deduced assuming $r(\text{C–H}) = 1.0667$ Å.

TABLE V. Total energies (in hartree), bond lengths (in Å), and T_e (in kcal mol^{-1}) for the linear 1 $^1\Delta$ state of HCP.

Level of theory	Total energy	R_e (CP)	R_e (HC)	T_e
cc-pVTZ EOM-CCSD	−379.280 183	1.6502	1.0705	115.2
aug-cc-pVTZ EOM-CCSD	−379.287 009	1.6597	1.0711	113.6
cc-pVQZ EOM-CCSD	−379.303 092	1.6428	1.0697	114.5
cc-pVTZ EOM-CCSDT-3	−379.302 519	1.6678	1.0730	113.2
aug-cc-pVTZ EOM-CCSDT-3	−379.310 119	1.6776	1.0737	111.5
cc-pVQZ EOM-CCSDT-3	−379.327 105	1.6598	1.0725	112.4
cc-pVTZ EOM-CC3	−379.305 009	1.6718	1.0737	113.0
aug-cc-pVTZ EOM-CC3	−379.312 671	1.6814	1.0745	111.4
cc-pVQZ EOM-CC3	−379.329 596	1.6636	1.0732	112.3
MRD-CI (Ref. 39)		1.672	1.079	114
MRD-CI (Ref. 40)		1.675		115
MRCI/aug-cc-pVDZ (Ref. 41)		1.662	1.080	123

state is $2a'' \rightarrow 10a'$. According to Walsh's diagram for HAB molecules,[64] an electron added to the $10a'$ orbital of HCP will cause a decrease in energy upon bending. The behavior reported in this study is consistent with Walsh's rules. The $^1A''$ state total energies and vibrational frequencies are summarized in Table III, with geometrical parameters given in Fig. 2. Upon bending ($^1\Sigma^- \rightarrow {}^1A''$), the two bond lengths increase by 0.020 Å (CH) and 0.026 Å (CP) relative to the linear ($^1\Sigma^-$) stationary point. At the best level of theory, $T_e = 101.4$ kcal mol^{-1} and $T_0 = 99.4$ kcal mol^{-1} are predicted, in excellent agreement with an experimental observation of $T_0 = 99.3$ kcal mol^{-1}(34 746 cm^{-1}) by Johns *et al.*[6] for the $\tilde{A}\ {}^1A''$ state. Excellent agreement occurs between the theoretical ω_3 and the experimentally reported ν_3 vibrational modes, while the value of ω_1 is lower by roughly 130 cm^{-1} due to anharmonic effects. With the exception of ω_1, our theoretical frequencies are in better agreement with experimental values than those reported in previous theoretical studies.[39,42]

3. Lowest $^1A''$ state of HPC

Further bending of the $^1A''$ state leads to another stable minimum at a HPC bond angle of approximately 98°. The barrier between this and the lowest $^1A''$ state of HCP lies 40.8 kcal mol^{-1} above the HCP minimum and 22.4 kcal mol^{-1} above the HPC minimum at the cc-pVQZ EOM-CCSD level of theory. Inspection of Fig. 3 shows CP bond lengthening of nearly 0.1 Å with respect to the HCP minimum on this $^1A''$ surface. The $^1A''$ state of HPC is located at $T_e = 120.9$ and $T_0 = 117.5$ kcal mol^{-1} relative to the ground state HCP. Thus we see that this $^1A''$ HPC structure lies approximately 20 kcal mol^{-1} above the analogous HCP structure. This state has been characterized by the previous theoretical study by Nanbu *et al.*[41] whose excitation energy is 3–5 kcal mol^{-1} higher than reported in this study, as seen

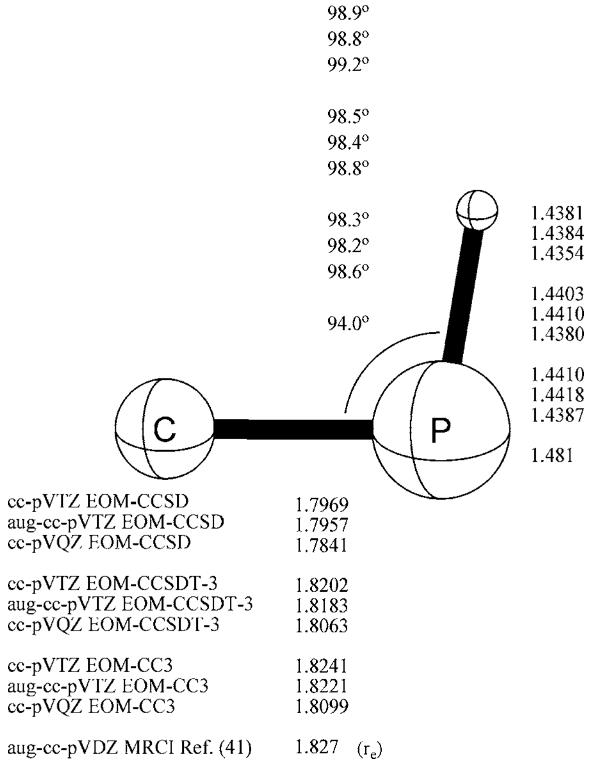

FIG. 3. Predicted geometries of the $^1A''(^1\Sigma^-)$ state of HPC. Bond lengths are in Å.

TABLE VI. Total energies (in hartree), bond lengths (in Å), and T_e (in kcal mol^{-1}) for the linear 1 $^1\Delta$ state of HPC.

Level of theory	Total energy	R_e (HP)	R_e (CP)	T_e
cc-pVTZ EOM-CCSD	−379.171 918	1.4018	1.7784	183.1
aug-cc-pVTZ EOM-CCSD	−379.178 807	1.4039	1.7736	181.5
cc-pVQZ EOM-CCSD	−379.193 158	1.4010	1.7659	183.5
cc-pVTZ EOM-CCSDT-3	−379.199 866	1.4107	1.8120	177.6
aug-cc-pVTZ EOM-CCSDT-3	−379.207 597	1.4129	1.8075	175.9
cc-pVQZ EOM-CCSDT-3	−379.222 941	1.4101	1.7987	177.8
cc-pVTZ EOM-CC3	−379.204 264	1.4137	1.8230	176.3
aug-cc-pVTZ EOM-CC3	−379.212 126	1.4161	1.8186	174.5
cc-pVQZ EOM-CC3	−379.227 389	1.4131	1.8091	176.5

TABLE VII. Total energies (in hartree), harmonic vibrational frequencies (in cm^{-1}), ZPVE (in $\mathrm{kcal\,mol}^{-1}$), and T_e and T_0 values (in $\mathrm{kcal\,mol}^{-1}$) for the bent $2\,^1A'(^1\Delta)$ state of HCP.

Level of theory	Total energy	$\omega_1(a')$	$\omega_2(a')$	$\omega_3(a')$	ZPVE	T_e	T_0
cc-pVTZ EOM-CCSD	−379.281 938	2757	555	970	6.12	114.1	111.4
aug-cc-pVTZ EOM-CCSD	−379.287 825	2777	512	950	6.06	113.1	110.5
cc-pVQZ EOM-CCSD	−379.302 800	2779	517	967	6.09	114.7	112.0
cc-pVTZ EOM-CCSDT-3	−379.306 370	2647	683	977	6.16	110.7	108.3
aug-cc-pVTZ EOM-CCSDT-3	−379.312 801	2661	643	957	6.09	109.8	107.4
cc-pVQZ EOM-CCSDT-3	−379.329 048	2662	666	979	6.16	111.2	108.7
cc-pVTZ EOM-CC3	−379.309 787	2612	723	998	6.19	110.0	107.7
aug-cc-pVTZ EOM-CC3	−379.316 288	2624	693	976	6.14	109.1	106.8
cc-pVQZ EOM-CC3	−379.332 549	2626	716	998	6.20	110.5	108.1
MRD-CI (Ref. 39)						113	
MRD-CI (Ref. 40)						106	
MRCI/aug-cc-pVDZ (Ref. 41)						116	
	Total energy	$\omega_1(a')$	ν_1	ν_2	ν_3	T_e	T_0
Experiment (Ref. 6)		615.4	969.4			115.1	

in Table IV. Spectroscopic observation of this state may prove challenging since the only stable minimum on the ground state surface is linear HCP, leading to an excitation that would lead the molecule first to the aforementioned bent $^1A''$ HCP minimum.

4. Lowest $^1\Sigma^-$ state of HPC

When the hydrogen atom is attached to the phosphorus atom and the molecule is linear, the $^1\Sigma^-$ state on the HPC side of the surface should be considered. This state is much higher in energy than any of the states discussed thus far. In fact, it has a T_e value of 172 $\mathrm{kcal\,mol}^{-1}$ relative to the HCP $\tilde{X}\,^1\Sigma^+$ minimum. This excitation energy places it nearly 70 $\mathrm{kcal\,mol}^{-1}$ higher in energy than its $^1\Sigma^-$ HCP counterpart. The excitation energy of this state when compared to the $^1\Sigma^+$ stationary point of HPC is 93 $\mathrm{kcal\,mol}^{-1}$ similar to the T_e value of $^1\Sigma^-$ HCP when compared to $\tilde{X}\,^1\Sigma^+$ HCP (104.6 $\mathrm{kcal\,mol}^{-1}$). The HPC bond lengths for the $^1\Sigma^-$ state are similar for the PH separation, but the CP bond length increases by 0.184 Å in relation to $^1\Sigma^+$ HPC.

5. Lowest $^1\Delta$ state of HCP

For linear structures this electronic state has two degenerate components in C_s symmetry a $^1A'(9a' \rightarrow 10a')$ component and a $^1A''(9a' \rightarrow 3a'')$ component. Upon bending the two states are no longer degenerate, with the $^1A'$ component leading to an energetic minimum and the $^1A''$ component increasing in energy. This behavior is consistent with the Walsh diagram, where an excitation into the $9a'$ orbital lends itself to a bent configuration while an excitation into the $3a''$ orbital lends itself to a linear configuration. As seen in Table V, the CH and CP bond lengths differ by less than 0.01 Å from previous work.[39–41] The energy relative to the $\tilde{X}\,^1\Sigma^+$ state is $T_e = 112.4\ \mathrm{kcal\,mol}^{-1}$ at the cc-pVQZ EOM-CCSDT-3 level of theory. The excitation energies reported at the partial triples levels are as much as 2 $\mathrm{kcal\,mol}^{-1}$ lower in energy than those reported previously by MRD-CI.[39–41]

6. $2\,^1A'$ state of HCP

As stated previously, the $^1A'$ component of the $^1\Delta$ state leads to a minimum (upon bending), occurring near a bond angle of 88°, as described by Fig. 4. The possibility exists

TABLE VIII. Total energies (in hartree), harmonic vibrational frequencies (in cm^{-1}), zero-point vibrational energies (ZPVE) (in $\mathrm{kcal\,mol}^{-1}$), and T_e and T_0 values (in $\mathrm{kcal\,mol}^{-1}$) for the $2\,^1A'(^1\Delta)$ state of HPC relative to $\tilde{X}\,^1\Sigma^+$ HCP.

Level of theory	Total energy	$\omega_1(a')$	$\omega_2(a')$	$\omega_3(a')$	ZPVE	T_e	T_0
cc-pVTZ EOM-CCSD	−379.262 558	2102	896	788	5.41	126.2	122.9
aug-cc-pVTZ EOM-CCSD	−379.268 111	2108	894	786	5.41	125.5	122.2
cc-pVQZ EOM-CCSD	−379.284 580	2114	914	791	5.46	126.1	122.8
cc-pVTZ EOM-CCSDT-3	−379.282 456	2024	832	736	5.14	125.8	122.3
aug-cc-pVTZ EOM-CCSDT-3	−379.288 674	2030	832	733	5.14	125.0	121.6
cc-pVQZ EOM-CCSDT-3	−379.306 055	2030	854	735	5.17	125.6	122.2
cc-pVTZ EOM-CC3	−379.284 939	2003	813	724	5.06	125.6	122.1
aug-cc-pVTZ EOM-CC3	−379.291 267	2009	813	721	5.06	124.8	121.4
cc-pVQZ EOM-CC3	−379.308 609	2008	837	722	5.10	125.5	122.0
MRCI/aug-cc-pVDZ (Ref. 41)						130	

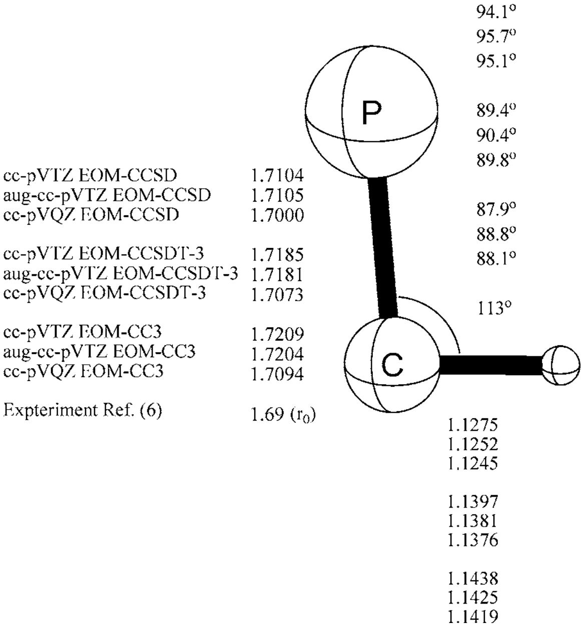

FIG. 4. Predicted geometries of the 2 $^1A'(^1\Delta)$ state of HCP. Bond lengths are in Å. The experimental structure was deduced assuming r(C–H) $=1.0667$ Å.

that this is the state reported by Johns *et al.*[6] as $\tilde{C}\,^1A'$. Inspection of Table VII shows that the agreement between theory and experiment for this state is not as good as for the $\tilde{A}$ state, especially for the excitation energy. The 2 $^1A'$ HCP excitation energy is $T_e=111.2$ and $T_0=108.8$ kcal mol^{-1} at the cc-pVQZ EOM-CCSDT-3 level of theory. The predicted T_0 value is about 6 kcal mol^{-1} below the experimental value;[6] however, there is reasonable agreement in the vibrational frequencies. The angles differ greatly but the CP bond length exhibits excellent agreement with the experimental values. The disagreement also involves the fact that we characterize the 2 $^1A'$ state as arising from the $^1\Delta$ state, whereas experiment concludes that it comes from a $^1\Sigma^+$ state. Other theoretical studies[39–42] agree that this state arises from a $^1\Delta$ rather than a $^1\Sigma^+$ state.

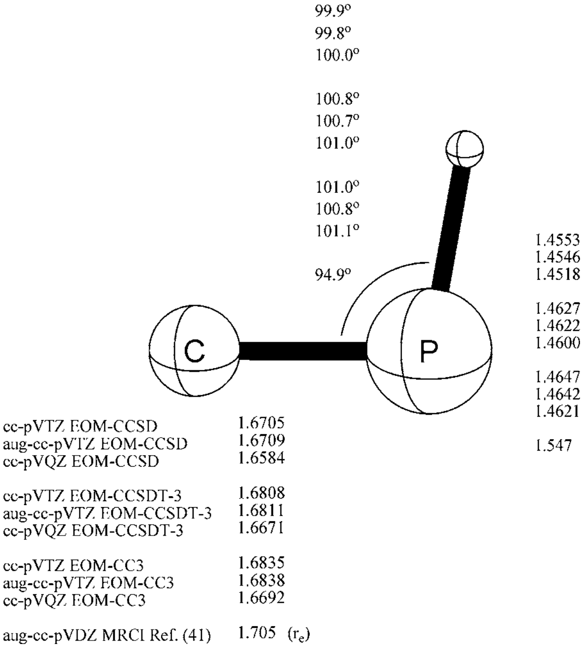

FIG. 5. Predicted geometries of the 2 $^1A'(^1\Delta)$ state of HPC. Bond lengths are in Å.

7. 2 $^1A'$ state of HPC

The next state characterized in this study is seen as the hydrogen atom migrates along this same excited surface to a bent minimum more like HPC. The excitation energy compared to our global minimum is $T_e=125.6$ and $T_0=122.2$ kcal mol^{-1} at the cc-pVQZ EOM-CCSDT-3 level of theory. Our excitation energy for this state, similar to that for the $^1A''$ HPC state, is several kcal mol^{-1} below the theoretical value reported by Nanbu *et al.*[41] As was the case for the ground state isomers, the 2 $^1A'$ state exhibits a lengthening of the bonds as the hydrogen migrates from the carbon atom to the phosphorus atom. This leads to considerable decreases in the theoretical vibrational frequencies. This state should also be challenging to detect experimentally, with the well-characterized linear HCP being the only minimum on the ground state potential energy surface.

8. Lowest $^1\Delta$ state of HPC

The final state characterized in this study occurs for linear HPC. The excitation for this HPC $^1\Delta$ state is $T_e=176.5$ kcal mol^{-1}. Clearly, this electronic state is so far above the H $(^2S)+\mathrm{CP}(X\,^2\Sigma^+)$ dissociation limit to make observation unlikely. The excitation energy of this state relative to $^1\Sigma^+$ HPC is similar to T_e for $^1\Delta$ HCP (99.2 kcal mol^{-1} vs 112.3 kcal mol^{-1}). The bond lengths for this state are remarkably similar to the bond lengths for the $^1\Sigma^-$ state of HPC.

V. CONCLUSIONS

Ten stationary points on the ground and excited singlet state potential energy surfaces of HCP have been characterized. It is confirmed that linear HCP is the only genuine minimum on the ground state surface, with the other stationary point, linear HPC, serving as a stationary point of Hessian index 2. The physical properties determined for linear HCP compare favorably with the available experimental observations. The cc-pV5Z CCSD(T) vibrational frequencies (ω_e) with experimental values[6] (ν_0) in parentheses are 3344 cm^{-1} (3217), 1298 cm^{-1} (1278), and 689 cm^{-1} (675) and the electric dipole moment at the cc-pVQZ CCSD level of theory is 0.373 D [0.390 (Ref. 2)]. The dissociation energy $[\mathrm{HCP}\ (\tilde{X}\,^1\Sigma^+)\rightarrow \mathrm{H}(^2S)+\mathrm{CP}(X\,^2\Sigma^+)]$ is predicted to be 119.0 kcal mol^{-1} which agrees well with the experimentally estimated value of 119.1 kcal mol^{-1}. Eight excited singlet electronic states including four linear stationary points and four bent minimum were considered. The energetic ordering of these states with respect to ground state $\tilde{X}\,^1\Sigma^+$ HCP (in kcal mol^{-1}) is

$$\begin{aligned}
&\tilde{X}\,^1\Sigma^+(\mathrm{HCP},0.0)\\
&\quad < \tilde{X}\,^1\Sigma^+(\mathrm{HPC},78.6)\\
&\quad < {}^1A''(\mathrm{HCP},101.4)\\
&\quad < {}^1\Sigma^-(\mathrm{HCP},104.6)\\
&\quad < 2\,{}^1A'(\mathrm{HCP},111.2)\\
&\quad < {}^1\Delta(\mathrm{HCP},112.4)\\
&\quad < {}^1A''(\mathrm{HPC},122.3)\\
&\quad < {}^1A'(\mathrm{HPC},125.6)\\
&\quad < {}^1\Sigma^-(\mathrm{HPC},171.6)\\
&\quad < {}^1\Delta(\mathrm{HPC},177.8).
\end{aligned} \tag{7}$$

These are the most definitive theoretical results reported to date for the important HCP/HPC system. The present predictions for the lowest $^1A''$ state of HCP compare favorably with the experimental results of Johns *et al.*[6] For the experimentally reported $\tilde{C}\,^1A'$ state, the agreement between theory and experiment leaves much to be desired.

ACKNOWLEDGMENT

This research was supported by the National Science Foundation Grant No. CHE-0451445.

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[60] H.-J. Werner, P. J. Knowles, R. D. Ramos *et al.*, MOLPRO, a package of *ab initio* programs designed, version 2002.1.
[61] See EPAPS Document No. E-JCPSA6-125-309629 for the tables and figures corresponding to the ground state singlet HCP and HPC molecules as well as the isomerization and dissociation energies. This document can be reached via a direct link in the online article's HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).
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