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A high-resolution photoelectron imaging and theoretical study of CP⁻ and C₂P⁻

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The discovery of interstellar anions has been a milestone in astrochemistry. In the search for new interstellar anions, CP⁻ and C₂P⁻ are viable candidates since their corresponding neutrals have already been detected astronomically. However, scarce data exist for these negatively charged species. Here we report the electron affinities of CP and C₂P along with the vibrational frequencies of their anions using high-resolution photoelectron imaging. These results along with previous spectroscopic data of the neutral species are used further to benchmark very accurate quartic force field quantum chemical methods that are applied to CP, CP⁻, C₂P, and two electronic states of C₂P⁻. The predicted electron affinities, vibrational frequencies, and rotational constants are in excellent agreement with the experimental data. The electron affinities of CP (2.8508 ± 0.0007 eV) and C₂P (2.6328 ± 0.0006 eV) are measured accurately and found to be quite high, suggesting that the CP⁻ and C₂P⁻ anions are thermodynamically stable and possibly observable. The current study suggests that the combination of high-resolution photoelectron imaging and quantum chemistry can be used to determine accurate molecular constants for exotic radical species of astronomical interest. *Published by AIP Publishing*. https://doi.org/10.1063/1.5008570

I. INTRODUCTION

The detections of negative ions consisting of carbon chains with a heteroatom (C_nX^- , X = H, and N) represent a major breakthrough in astrochemistry.¹⁻⁶ The observation of neutral CP and C₂P astronomically,^{7,8} along with isovalent CN and C₂N (as well as CN⁻), 6,9,10 suggests the possibility that the corresponding anions CP^- and C_2P^- may also exist in the interstellar medium. The large predicted dipole moments of these two anions¹¹ make them suitable targets for astronomical observations. However, accurate vibrational and rotational data from laboratory measurements are needed in order to assist the assignments of any astronomical data. Furthermore, the electron affinities (EAs) of the neutrals are needed to assess the thermodynamic stability of these anions. In general, accurate spectroscopic data for anions are more challenging to be obtained experimentally. Hence, theoretical methods for accurate prediction of molecular constants are highly valuable both to help interpret the observed data or to provide reliable data when experiments are not feasible. To do so, one must carefully establish benchmarks for these computations, and in order to ensure, reliable predictions are to be made.

Both neutral CP and C₂P radicals have been well characterized experimentally with the CP radical first observed in the laboratory in 1930 by Herzberg.¹² Several studies have been carried out over the past 30 years to analyze the rovibrational

spectra of CP in its ${}^{2}\Sigma^{+}$ ground state. ${}^{13-16}$ The observation and spectroscopic characterization of C₂P have been much more recent by Clouthier and co-workers.^{17–19} The ground state of C_2P was found to be linear in a ${}^2\Pi_{1/2}$ state with a higher spin-orbit state (${}^{2}\Pi_{3/2}$) being 17.49 meV (141 cm⁻¹) higher in energy.¹⁹ The stretching modes and rotational constants of C₂P were determined along with a detailed Renner-Teller analysis.¹⁸ In contrast, very little is known about the corresponding CP⁻ and C₂P⁻ anions. The only experimental data available are the detection of both anions in mass spectrometry using a laser ablation source.²⁰ Larger carbon cluster phosphide anions $(C_n P^-)$ have been studied through collisioninduced dissociation, suggesting they are linear at least up to C₉P^{-.21} The vertical detachment energies and fragmentation energies were calculated for these linear chains as well.²² Recently, the permanent dipole moments for both CP and C₂P anions and neutrals were calculated along with the EA of CP and isomerization energy of C_2P^- from linear to cyclic.¹¹ In particular, C₂P neutral was predicted to have a dipole moment of 3.35 D, which could support a dipole bound state.¹¹ Recent computations have supported the presence of electronically excited states for C_3P^- , the next in the C_nP^- series, and have produced rovibrational spectroscopic constants that could aid in its astronomical detection.^{23,24} However, there has been no experimental spectroscopic information for the smaller members of this family of carbon cluster phosphide anions.

Here we report high-resolution photoelectron (PE) imaging experiments of the two smallest carbon phosphide anions, CP⁻ and C₂P⁻. High-resolution PE imaging has become a

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powerful tool to determine the vibrational and electronic structure of neutral and anionic species.^{25–27} Anion photoelectron spectroscopy (PES) has already been used to determine the vibrational and electronic structure of several heteroatom carbon chains.^{28–32} The current results, along with previous experimental results, are then used to benchmark high level theoretical calculations.

II. EXPERIMENTAL METHODS

The experiments were carried out using a high-resolution PE imaging apparatus equipped with a laser vaporization supersonic cluster source, details of which have been described elsewhere.^{33,34} Briefly, the second harmonic of an Nd:YAG laser (532 nm) was focused onto a disk target compressed from a mixed powder of graphite, red phosphorus, and bismuth with a 1:1:100 ratio by mass. The bismuth component served both as a binder and as a source of Bi used as a calibrant. The laserinduced plasma was quenched by a helium carrier gas containing 10% argon to promote cluster formation. Nascent clusters were entrained by the carrier gas and underwent a supersonic expansion to produce cold clusters. Anions from the collimated cluster beam were extracted perpendicularly into a time-of-flight mass spectrometer. The CP⁻ or C₂P⁻ anions of current interest were mass-selected before entering the velocity-map imaging (VMI) detector. Photodetachment was done using the third harmonic of an Nd: YAG laser or a YAGpumped Deyang Tech dye laser. The detached photoelectrons were then focused onto a set of microchannel plate (MCP) detector that is coupled with a phosphor screen and chargecoupled device (CCD) camera. The raw images were inverted and analyzed using the maximum entropy method (MEVIR and MEVELER).³⁵ The VMI lens was calibrated using PE images of Au⁻ and Bi⁻ at various photon energies. The typical resolution of this VMI detector is ~0.6% for high kinetic energy electrons and as low as 1.2 cm⁻¹ for low kinetic energy electrons.³³

Another valuable piece of information available from PE imaging is the photoelectron angular distribution (PAD) of the detached electrons. The PAD is characterized by an anisotropy parameter (β), as defined in the differential cross section,

$$d\sigma/d\Omega = \sigma_{tot}/4\pi \left[1 + \beta P_2(\cos\theta)\right], \tag{1}$$

where σ_{tot} is the total cross section, P₂ is the second-order Legendre polynomial, and θ is the angle of the photoelectron relative to the laser polarization.³⁶ The PAD can be approximated by

$$l(\theta) \sim [1 + \beta P_2(\cos \upsilon)], \tag{2}$$

where β can have any value between -1 and 2. This model works well for single-photon detachment from randomly oriented particles. Because photons carry one unit of angular momentum ($l = \pm 1$), the conservation of momentum dictates that an electron detached from an *s* atomic orbital will result in an outgoing wave with l = 1 (pure *p*-wave) and $\beta = 2$. Molecular orbitals are approximated as linear combinations of atomic orbitals, so interpreting an exact value for β is not a trivial process.³⁷ Nevertheless, it can be used to qualitatively assess the symmetries of the molecular orbitals involved in the photodetachment.

III. COMPUTATIONAL METHODS

Geometry optimization was first done using the coupled cluster^{38,39} singles, doubles, and perturbative triples [CCSD(T)] method⁴⁰ with the aug-cc-pV(5+d)Z basis set,^{41–43} as well as CCSD(T) with the Martin-Taylor (MT) core



FIG. 1. High-resolution photoelectron images (left) and spectra for CP^- at (a) 432.66 nm (2.8656 eV), (b) 409.73 nm (3.0260 eV), and (c) 354.67 nm (3.4958 eV). The vertical lines in (b) and (c) denote the vibrational progressions. The double arrow below the images indicates the laser polarization.

TABLE I. The observed peaks, their binding energies (BEs), shifts (ΔE) relative to the 0–0 transition (peak X), and assignments for the photoelectron spectra of CP⁻. The anisotropy parameter (β) is also given for the main transitions at 3.4958 eV photon energy [Fig. 1(c)].

| Peak | BE (eV) ^a | $\Delta E (cm^{-1})^{a}$ | β | Assignment |
|------|----------------------|--------------------------|-------------------|-----------------|
| hb1 | 2.5740(76) | -2232(61) | | 12 ⁰ |
| hb2 | 2.6095(37) | -1946(30) | | 1_{3}^{1} |
| hb3 | 2.7073(22) | -1157(18) | | 1_1^{0} |
| hb4 | 2.7180(60) | -1071(49) | | 12^{1} |
| Х | 2.8508(7) | 0 | 1.45 ^b | 10^{0} |
| a | 2.8590(5) | 66(7) | | 1_1^{1} |
| b | 3.0029(9) | 1227(9) | 1.36 ^c | 10^{1} |
| с | 3.0097(4) | 1282(6) | | 1_1^2 |
| d | 3.17(1) | 2500(80) | 1.51 | 10^{2} |
| | | | | |

^aThe numbers in the parentheses represent the uncertainty of the last digit(s). ^bThe β value for peak X is 1.61 at 3.0260 eV photon energy [Fig. 1(b)] and 1.10 at 2.8656 eV [Fig. 1(a)].

^cThe β value for peak b is 1.26 at 3.0260 eV [Fig. 1(b)].



FIG. 2. Photoelectron image (left) and spectrum of C_2P^- at 354.67 nm (3.4958 eV). The double arrow below the image indicates the directions of the laser polarization and the vertical lines denote vibrational progressions.

correlating basis set.⁴⁴ The differences in the MT geometries including and excluding the core electrons were added to the 5Z results to create the reference geometry, from which a quartic force field (QFF), a fourth-order Taylor series expansion of the Watson internuclear Hamiltonian potential, was computed. Energy points were defined from 0.005 Å bond length and 0.005 radian bond angle displacements of the symmetry-internal coordinates, where the only bending present was in the degenerate, perpendicular bends of the C₂P radical and



FIG. 3. High-resolution photoelectron images (left) and spectra of C_2P^- at (a) 473.93 nm (2.6161 eV), (b) 470.24 nm (2.6366 eV), (c) 462.46 nm (2.6810 eV), (d) 444.96 nm (2.7864 eV), and (e) 427.16 nm (2.9025 eV). The arrow below the images indicates the directions of the laser polarization.

anion structures. For the CP molecules, the bond stretch is the only coordinate. For the C₂P molecules, coordinate 1 is the C-C stretch, coordinate 2 is the C-P stretch, and coordinates 3 and 4 are the bends. CCSD(T)/aug-cc-pV(X+d)Z (X = T, O, 5) energies were extrapolated to the one-particle complete basis set (CBS) limit⁴⁵ energy at each point. Core correlation and scalar relativistic corrections^{46,47} were included to define the CcCR QFF from the CBS ("C"), core correlation ("cC"), and relativity ("R") energies. The QFF was fit with a least-squares approach to give the CcCR equilibrium geometry. With the exception of the C₂P radical, all of the QFFs exhibit a sum of squared residuals on the order of 10^{-17} a.u.² A refitting produced zero gradients and the quartic, cubic, and quadratic force constants. The coordinates were transformed with the INTDER program⁴⁸ into Cartesian coordinates for the SPECTRO⁴⁹ program to run vibrational second-order perturbation theory (VPT2) or rotational perturbation theory calculations.^{50–52} The fitting of the C₂P radical is much greater and could not produce useful cubic and quartic force constants due to degeneracies in the energy computations; the anharmonic force constants of triplet C_2P^- are utilized as approximations. The triplet form of C_2P^- exhibits a $2v_3 = v_2$ type-1 Fermi resonance, while the singlet form has no resonances. Computationally, the C₂P radical also has $2v_3 = v_2$ and $2v_2 = v_1$ type-1 Fermi resonances included in the analysis for completeness, even though the estimated perturbations are less than 1.0 cm^{-1} .

The CcCR method⁵³⁻⁵⁶ has produced experimentally comparable vibrational frequencies to better than 1.0 cm⁻¹ of

TABLE II. The observed peaks, their binding energies (BEs), shifts (ΔE) relative to the 0–0 transition (peak X), and assignments for the photoelectron spectra of C₂P⁻. The anisotropy parameter (β) is also given for the main transitions at 2.9025 eV photon energy [Fig. 3(e)].

| | | | | Assignment | |
|------|----------------------|--------------------------|--------------------|---|----------------|
| Peak | BE (eV) ^a | $\Delta E (cm^{-1})^{a}$ | β | Electronic | Vibrational |
| hb1 | 2.5385(20) | -761(8) | | $^{2}\Pi_{1/2} \leftarrow ^{3}\Sigma^{+}$ | 210 |
| hb2 | 2.5978(8) | -282(4) | | $^{2}\Pi_{1/2} \leftarrow ^{3}\Sigma^{+}$ | 3_1^{0} |
| hb3 | 2.6145(14) | -148(6) | | $^{2}\Pi_{1/2} \leftarrow ^{3}\Sigma^{+}$ | 3_1^{1} |
| Х | 2.6328(6) | 0 | -0.38 ^b | ${}^{2}\Pi_{1/2} \leftarrow {}^{3}\Sigma^{+}$ | 0_0^{0} |
| a | 2.6507(18) | 144(8) | -0.35 ^c | $^{2}\Pi_{3/2} \leftarrow ^{3}\Sigma^{+}$ | 000 |
| b | 2.6685(11) | 288(5) | | $^{2}\Pi_{1/2} \leftarrow ^{3}\Sigma^{+}$ | 30^{2} |
| с | 2.6720(11) | 309(5) | | $^{2}\Pi_{3/2} \leftarrow ^{3}\Sigma^{+}$ | 30^{2} |
| d | 2.7228(19) | 726(8) | | ${}^{2}\Pi_{1/2} \leftarrow {}^{3}\Sigma^{+}$ | $2_0^1 3_1^1$ |
| e | 2.7369(19) | 840(8) | -0.31 ^d | $^{2}\Pi_{1/2} \leftarrow ^{3}\Sigma^{+}$ | 20^{1} |
| f | 2.7535(10) | 974(5) | -0.36 ^e | $^{2}\Pi_{3/2} \leftarrow ^{3}\Sigma^{+}$ | 20^{1} |
| g | 2.7755(10) | 1151(5) | | $^{2}\Pi_{1/2} \leftarrow ^{3}\Sigma^{+}$ | $20^{1}30^{2}$ |
| h | 2.7783(10) | 1174(5) | | ${}^{2}\Pi_{3/2} \leftarrow {}^{3}\Sigma^{+}$ | $20^{1}30^{2}$ |
| i | 2.8208(42) | 1516(17) | | $^{2}\Pi_{1/2} \leftarrow ^{3}\Sigma^{+}$ | $1_0^1 3_1^1$ |
| j | 2.8376(24) | 1652(10) | -0.25 | $^{2}\Pi_{1/2} \leftarrow ^{3}\Sigma^{+}$ | 10^{1} |
| k | 2.8544(23) | 1787(10) | -0.41 | $^{2}\Pi_{3/2} \leftarrow ^{3}\Sigma^{+}$ | 10^{1} |
| 1 | 2.8714(26) | 1924(11) | | $^{2}\Pi_{1/2} \leftarrow ^{3}\Sigma^{+}$ | $10^{1}30^{2}$ |
| m | 2.8756(21) | 1958(9) | | $^{2}\Pi_{3/2} \leftarrow ^{3}\Sigma^{+}$ | $10^{1}30^{2}$ |

^aThe numbers in the parentheses represent the uncertainty of the last digit(s). ^bThe β value for peak X is -0.26 at 2.7864 eV photon energy [Fig. 3(d)], -0.36 at 2.6810 eV photon energy [Fig. 3(c)], and -0.14 at 2.6366 eV [Fig. 3(b)].

^cThe β value for peak *a* is -0.42 at 2.7864 eV photon energy [Fig. 3(d)] and -0.36 at 2.6810 eV photon energy [Fig. 3(c)].

^dThe β value for peak *e* is -0.44 at 2.7864 eV photon energy [Fig. 3(d)].

^eThe β value for peak f is -0.10 at 2.7864 eV photon energy [Fig. 3(d)].

experiment in some cases with rotational constants as good as within 30 MHz.^{55,57–62} The MOLPRO 2015.1 quantum chemistry package⁶³ was used for all quantum chemical computations. The CcCR adiabatic excitation energies and EAs were computed as the difference in minima from each QFF with the anharmonic zero-point energies included.

IV. EXPERIMENTAL RESULTS

A. High-resolution PE images of CP⁻

The high-resolution PE images and spectra of CP- at several wavelengths are shown in Fig. 1. The left column shows the inverted images, while the right column presents the PE spectra obtained from the imaging data. The binding energies of all peaks and their assignments are summarized in Table I. An intense peak labeled X is observed at 2.8508 ± 0.0007 eV in Fig. 1(a). This peak is identified as the 0-0 transition and defines the most accurate EA for CP. A very weak peak (labeled a) is observed at a slightly higher binding energy, as shown more clearly in the inset of Fig. 1(a). Several other weak features are also observed at lower binding energies than the 0-0 transition (hb1-hb4) and they come from vibrational hot bands of CP-. Frank-Condon simulations (vide infra) yielded a very high vibrational temperature of ~2000 K for CP-, consistent with the fact that small cluster anions, in particular diatomic and triatomic cluster anions, are difficult to be cooled in our

laser vaporization cluster source than larger clusters.^{64–68} The hb3 and hb4 peaks at around 2.71 eV heavily overlap and their binding energies are obtained by fitting two Gaussian functions to the asymmetric peak.

Using a slightly higher photon energy of 3.0260 eV [Fig. 1(b)], we observe two more weak peaks (labeled *b* and *c*) in the PE spectrum (shown more clearly in the inset). The spacing between peaks *b* and *c* is nearly identical to the spacing between peaks X and *a*. The same features at lower binding energies (hb1–hb4) are also observed, albeit with slightly different intensities. At an even higher photon energy [3.4958 eV in Fig. 1(c)], one additional peak (labeled *d*) was resolved approximately 2500 cm⁻¹ above peak X. In addition, the β values for the PAD of the most intense peaks are obtained and also given in Table I. Qualitatively, a *p*-wave-like distribution is observed for all peaks with β values being greater than 1.

B. High-resolution PE images of C₂P⁻

A lower-resolution survey PE image and spectrum of C_2P^- is presented in Fig. 2 at a detachment photon energy of 3.4958 eV. An intense and relatively broad peak (X) was observed ~2.63 eV, followed by two vibrational progressions. A series of high-resolution images and spectra are shown in Fig. 3 at lower photon energies, revealing numerous fine peaks and complicated spectral features. The peak X labeled

TABLE III. Calculated and measured molecular constants and vibrational frequencies for the ground states of CP and CP⁻.

| | $CP(^{2}\Sigma^{+})$ | | $CP^{-}(^{1}\Sigma^{+})$ | |
|-------------------------------------|----------------------|--------------------------------|--------------------------|-----------------------|
| | Theoretical | Experimental | Theoretical | Experimental |
| EA (eV) | 2.867 | 2.8508(7) ^a | | |
| $r_0(C-P)$ (Å) | 1.559 | 1.561 978 0(2) ^b | 1.601 | 1.60(2) ^a |
| $r_{\rm e}({\rm C-P})$ (Å) | 1.560 | | 1.600 | |
| BDE (kJ mol ⁻¹) | | 658(50) | | 585(75) ^a |
| $B_{\rm e}$ (MHz) | 24 011.3 | | 22 783.0 | |
| B_0 (MHz) | 23 989.4 | 23 859.930(0.065) ^b | 22 809.8 | |
| | | 23 859.955(0.066) ^c | | |
| | | 23 859.915 21(28) ^d | | |
| D _e (kHz) ^e | 39.296 | | 37.860 | |
| $D_0 (\mathrm{kHz})^{\mathrm{e}}$ | | 39.793(25) ^b | | |
| | | 39.8107(9) ^c | | |
| | | 39.814 0(19) ^d | | |
| $H_{\rm e}$ (mHz) | 6.917 | | 9.479 | |
| $\omega_1 (\mathrm{cm}^{-1})$ | 1252.3 | 1239.807 6(5) ^b | 1179.2 | |
| | | 1239.799 24(8) ^c | | |
| $\omega_e X_e \ (\mathrm{cm}^{-1})$ | | 6.840 2(3) ^b | | |
| | | 6.833 769(46) ^c | | |
| $v_1 ({\rm cm}^{-1})$ | 1244.3 | 1227(9) ^a | 1171.2 | 1157(18) ^a |
| | | 1226.127 3(2) ^b | | |
| | | 1226.127 26(21) ^c | | |
| $2v_1 (\mathrm{cm}^{-1})$ | 2488.5 | 2500(80) ^a | 2342.4 | 2232(61) ^a |
| | | 2438.574 3(3) ^b | | |
| | | 2438.574 59(20)° | | |

^aCurrent experiments.

^bReference 13.

^cReference 14.

^dReference 15.

^eHere, D_e and D_0 represent the quartic distortion constants.

in Fig. 2 is resolved into four peaks in the high-resolution data in Fig. 3 (X, a-c). The spectrum at 2.6366 eV [Fig. 3(b)] gives the best-resolved peak X at a binding energy of 2.6328 \pm 0.0006 eV, which is identified as the 0–0 detachment transition for C_2P^- and defines the EA of C_2P neutral. Three weak features are observed at lower binding energies (hb1hb3) than the 0–0 transition in Fig. 3 due to vibrational hot bands of C_2P^- . The spectrum in Fig. 3(a) was taken with a photon energy of 2.6161 eV, which was less than the EA of C₂P, and the spectrum is entirely due to hot band transitions. The data in Fig. 3 show that in some spectra, the vibrational cooling was much better than others. In general, the vibrational cooling was improved for C_2P^- relative to CP⁻, consistent with our experience that diatomic anions are most difficult to cool in our laser vaporization source.⁶⁴⁻⁶⁸ We have shown that for tetramers or larger cluster anions, we can achieve optimal cooling. For example, we were able to completely eliminate vibrational hot bands in Au₄⁻ and other larger cluster anions,^{32,68–71} whereas extensive hot bands were observed for Au₂⁻ in our previous high-resolution PE imaging study.72

The spectrum taken at 2.6810 eV [Fig. 3(c)] resolved three more peaks (labeled *a*, *b*, *c*) within 310 cm⁻¹ of the 0– 0 transition. At a slightly higher photon energy of 2.7864 eV [Fig. 3(d)], five more peaks are observed and identified as d-h. Peaks *e* and *f* are relatively strong, while *d*, *g*, and *h* are quite weak. Finally, the spectrum taken with 2.9025 eV [Fig. 3(e)] also revealed five additional peaks *i*–*m*, which exhibit a nearly identical spectral pattern as peaks *d*–*h*. The PADs were accurately fit for the intense peaks using the images in Figs. 3(b)–3(e). The β values were slightly negative, indicating an *s*+*d* wave detachment. The binding energies of all the observed peaks and the β values are summarized in Table II, along with their assignments.

V. COMPUTATIONAL RESULTS

A. CP and CP⁻

The optimized bond lengths, vibrational frequencies, and molecular constants for CP and CP⁻ are given in Table III. The ground state of the CP radical is an open-shell with a valence electron configuration of $4\sigma^2 5\sigma^2 3\pi^4 6\sigma^1$ and a ${}^{2}\Sigma^+$ term symbol, which is isovalent with the CN radical. In the anion, the extra electron enters the 6 σ orbital to give a closedshell CP⁻ with the ${}^{1}\Sigma^+$ ground state. The adiabatic EA of CP was predicted to be 2.867 eV. The 6 σ orbital is primarily a lone pair orbital with a slight antibonding character, as inferred from the increased bond length and decreased vibrational frequency of the anion. There is very little anharmonicity between the first and second vibrational quanta for both the anion and neutral radical, as expected in low frequency transitions of heavy atom stretching, especially for a more massive thirdrow atom in this case. The CcCR force constants for the anion

| | $C_2 P(^2 \Pi_r)$ | $(^{2}\Pi_{1/2})$ | $C_2 P^{-} (^3 \Sigma^{+})$ | | $C_2 P^- (^1 \Sigma^+)$ |
|-----------------------------------|-------------------|----------------------------|-----------------------------|---------------------|-------------------------|
| | Theoretical | Experimental | Theoretical | Experimental | Theoretical |
| EA (eV) | 2.676 | 2.6328(6) ^a | | | |
| $\Delta E (eV)$ | | | 0.000 | | 0.716 |
| $r_0(C-P)$ (Å) | 1.609 | 1.615(2) ^b | 1.672 | | 1.666 |
| $r_{\rm e}({\rm C-P})$ (Å) | 1.608 | | 1.670 | | 1.665 |
| $r_0(C-C)$ (Å) | 1.308 | 1.291(2) ^b | 1.280 | | 1.287 |
| <i>r</i> _e (C–C) (Å) | 1.306 | | 1.280 | | 1.284 |
| $B_{\rm e}$ (MHz) | 6366.9 | | 6160.6 | | 6163.4 |
| B_0 (MHz) | 6359.8 | 6392.4138(26) ^b | 6155.3 | | 6171.0 |
| B_1 (MHz) | 6326.7 | | 6122.0 | | 6135.1 |
| B_2 (MHz) | 6348.1 | | 6131.0 | | 6147.9 |
| B_3 (MHz) | 6375.1 | | 6178.7 | | 6208.1 |
| D _e (kHz) ^c | 1.467 | 2.2595(22) ^b | 1.747 | | 1.721 |
| $H_{\rm e}$ (mHz) | 0.237 | | -0.203 | | -0.151 |
| $\omega_1 (\mathrm{cm}^{-1})$ | 1837.2 | 1646.36(58) ^d | 1722.7 | | 1741.1 |
| $\omega_2 (\mathrm{cm}^{-1})$ | 877.3 | 837.75(44) ^d | 756.9 | | 765.8 |
| $\omega_3 (\mathrm{cm}^{-1})$ | ^e | 211.34(91) ^d | 289 | | 217.3 |
| $v_1 (\text{cm}^{-1})$ | 1809.2 | 1652(10) ^a | 1691.5 | | 1711.6 |
| | | 1644.3 ^d | | | |
| $v_2 ({\rm cm}^{-1})$ | 845.2 | 840(8) ^a | 759.5 | 761(8) ^a | 766.6 |
| | | 834.8 ^d | | | |
| $v_3 (\text{cm}^{-1})$ | ^e | 134(10) ^f | 291.2 | 282(4) ^a | 205.7 |

TABLE IV. Calculated and measured molecular constants and vibrational frequencies for the ground states of C_2P and C_2P^- and the first excited state of C_2P^- .

^aCurrent experiments.

^bReference 19.

^cHere, D_e represents the quartic distortion constant.

^dReference 18.

^fThis is a tentative assignment of the $^{2}\Sigma$ vibronic coupled state that was not observed in Ref. 18.

^eThe bending mode in the computations could not be uniquely defined for neutral C_2P .

and neutral are provided in Table S1 in the supplementary material.

B. C₂P and C₂P⁻

The optimized bond lengths, vibrational frequencies, and molecular constants for C₂P and two electronic states of C₂P⁻ are shown in Table IV. Although there is an even number of electrons, the anion ground state is predicted to be open-shell with a $4\sigma^2 5\sigma^2 6\sigma^2 2\pi^4 7\sigma^2 3\pi^2$ valence electron configuration and a ${}^{3}\Sigma^{+}$ ground state. The corresponding ${}^{1}\Sigma^{+}$ state is calculated adiabatically to be 0.716 eV higher in energy. In the neutral C₂P ground state, one electron is detached from the 3π orbital, yielding a $^{2}\Pi$ state with two spin-orbit components, ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$. The ${}^{2}\Pi_{1/2}$ state is the ground state, but spinorbit coupling was not considered computationally. The C-C bond becomes shorter and the C-P bond becomes longer in both anion states relative to the neutral, indicating that the 3π orbital is bonding between the carbons and anti-bonding to the phosphorus. There is a large change in the vibrational frequencies between the anions and the neutral, particularly for the C-C stretch. The bending mode for the neutral radical could not be uniquely defined leading to erroneous and non-physical values, due to the Renner-Teller effects for the degenerate state $(^{2}\Pi)$ and vibronic couplings. As a result, the C₂P radical values should be treated as initial approximations and not robust computational descriptions as was done in treating the Jahn-Teller-affected modes in c-C₃H.⁷³ However, the anion ground state $({}^{3}\Sigma^{+})$ does not suffer from these issues because it is non-degenerate and should be well described. The CcCR force constants for the neutral both anion states are provided in Table S2 in the supplementary material.

VI. DISCUSSION

A. The assignment of the CP⁻ PE spectra

The strong peak X observed in the PE spectra of CP-(Fig. 1) is due to the detachment transition from the ground vibrational state of CP⁻ to that of the neutral CP. The measured binding energy of this peak at 2.8508 eV represents the adiabatic detachment energy (ADE) of the anion, as well as the EA of neutral CP. The spectrum taken at 3.4958 eV [Fig. 1(c)] displays a short vibrational progression, indicating a small bond length change between the anion and neutral ground electronic state. At lower photon energies, the peaks X and b are much better resolved, yielding a fundamental vibrational frequency for the ground state of CP at 1227 ± 9 cm⁻¹. This is in excellent agreement with the previous experimental results for the CP vibrational frequency.^{13–16} The weak peak d in Fig. 1(c) represents the v = 2 vibrational level of CP, but it was not well resolved due to its high kinetic energy and weak relative intensity.

All the peaks at lower binding energies than X and the weak peaks *a* and *c* are due to hot band transitions. Peaks hb3 and hb1 are due to detachment transitions from the v = 1 and 2 levels of CP⁻ to the v = 0 level of the neutral, i.e., 1_1^0 and 1_2^0 , respectively (Table I), resulting in a vibrational frequency of 1157 ± 18 cm⁻¹ for CP⁻ measured for the first time (Table III). Peaks hb2, hb4, *a*, and *c* are all due to detachment transitions from vibrational hot bands of CP⁻ to different vibrational levels

of CP (Table I). The β parameters obtained from the PAD of the three main vibrational transitions (X, b, d) are all greater than 1 (Table I), indicating an outgoing *p*-wave. These results are consistent with the detachment of a 3σ electron from CP⁻.

B. The assignment of the C₂P⁻ PE spectra

The high-resolution PE spectra of C_2P^- are complicated because of several factors: the spin-orbit splitting and the Renner-Teller effects in the C₂P final state $(^{2}\Pi)$, as well as the hot band transitions. However, the relatively well-known spectroscopy of neutral C_2P is helpful for our assignments of the PE spectra. The peak X in Fig. 3 is due to the 0-0 transition, which defines an accurate EA for the C_2P radical as 2.6328 ± 0.0006 eV. The peaks X and a have similar intensities and they correspond to the spin-orbit splitting of the ${}^{2}\Pi_{1/2}$ and ${}^{2}\Pi_{3/2}$ states, in agreement with previous reports of the neutral C₂P spectroscopy.^{17–19} Peaks b and c match the measured frequencies for the second quanta of the bending modes of the lower and higher spin-orbit states, respectively. The uneven spacing of this mode in the two spin-orbit states is due to the Renner-Teller effects, as reported previously.^{17–19} Although the anion and neutral are both linear, it is possible to observe transitions from even quanta of the anion to even quanta of the neutral (or odd to odd) because the wavefunctions are not orthogonal. The even-odd or odd-even transitions cannot be observed because the wavefunctions are orthogonal. The 0-0 transitions will have the largest Franck-Condon factor and transitions to higher vibrational quanta will have much smaller Franck-Condon factors (but still non-zero) due to the different curvatures of the potential energy surfaces. At higher binding energies, the peaks e and f are similar to X and a, indicating these two peaks are due to the C-P stretching mode for the two spin-orbit states. This pattern is also repeated by peaks j and k, which are due to the C–C stretching mode of the two spin-orbit states. The weak pairs of peaks g/h and l/m are assigned as combinational modes between the second quanta of the bending mode and the C-P (2_0^1) or C-C (1_0^1) stretch, respectively.

There are three hot band transitions (hb1, hb2, and hb3) observed below peak X. The C₂P⁻ anions could not be cooled effectively to eliminate hb3, which is the only hot band present in every spectrum. This peak is likely due to the 3_1^1 transition. Using the shift of hb3 from peak X, we can tentatively assign the first quanta of the ${}^{2}\Sigma$ vibronic coupled state to be 134 ± 10 cm^{-1} . This is in good agreement with the predicted value of 141 cm⁻¹.¹⁸ This mode also explains peaks d and i, which are due to combinations of the 3_1^1 transition with the C–P (2_0^1) or C–C (1_0^1) stretch, respectively, and yield frequencies of 114 and 136 cm⁻¹ for the ${}^{2}\Sigma$ vibronic state. Both the hb1 and hb2 hot band transitions appear to be photon energy dependent. In fact, hb2 (3_1^0) is forbidden by symmetry in a single photon process and its observation is likely due to autodetachment from an excited anion state close in energy to the neutral. The appearance of the hb1 peak in Figs. 1(b) and 1(e) could be due to a similar autodetachment mechanism or fluctuation of vibrational cooling. We did not observe any hot bands to the ${}^{2}\Pi_{3/2}$ state. The v_3 mode is nearly equal to the spin-orbit splitting so this is likely overlapped with peaks X, e, and j. However, there seems to be some weak signal between peaks X and a

[Fig. 3(c)], *e* and *f* [Fig. 3(d)], and *j* and *k* [Fig. 3(e)] that may be due to hot bands with the 3_1^{11} transition of the ${}^{2}\Pi_{3/2}$ state. Hot bands from the 2_1^{0} and 3_1^{0} transitions to the ${}^{2}\Pi_{3/2}$ state were not observed in Fig. 3(a) or 3(b), which lends credence to the assignment that hb1 and hb2 are due to an autodetachment mechanism that can only autodetach to the ${}^{2}\Pi_{1/2}$ state. The PADs of the most intense peaks were analyzed and found to have negative β values, indicating an *s* + *d* outgoing wave. This result is consistent with the predicted detachment channel from the 3π orbital.

C. Comparison between experiment and theory

1. CP and CP-

All of the spectroscopic data for CP determined from this and previous work are compared to the calculated values in Table III. The calculated equilibrium bond length of CP differs by only 0.002 Å from the experimental bond length. This translates to calculated rotational constants that also are in good agreement with the available data. B_0 is within 130 MHz and D_e is within 1 kHz of D_0 . Here, D_e refers to the equilibrium quartic distortion constant, but D_0 , the corresponding vibrationally averaged value, cannot be determined from the QFF. Even so, the difference between the computed D_e and the experimental value is small. The calculated vibrational frequency for the anion and neutral is within 20 cm⁻¹ of the measured values. The calculated value of the second quanta for neutral CP is in fairly good agreement with the previous experimental data, whereas there is a very large uncertainty for this transition (peak d) in the current experiment.

Using the experimentally measured constants for neutral CP, we simulated the PE spectrum using the PESCAL program and the Morse oscillator,⁷³ as shown in Fig. 4(a). The simulation yielded an anion bond length of 1.60 ± 0.02 Å, which is



FIG. 4. Franck-Condon simulations for the 3.4958 eV spectra of (a) CP⁻ [Fig. 1(c)] and (b) C_2P^- (Fig. 2). The red dotted curves are the experimental spectra, the vertical lines are the computed Franck-Condon factors, and the black curves are the simulated spectra.

in good agreement with the calculated value (Table III). The simulation also allowed the estimate of the anion vibrational temperature of ~2000 K. In addition, if the anharmonic constant of the anion is assumed to be the same as the neutral,¹³ we can derive a bond dissociation energy (BDE) of approximately 585 \pm 75 kJ/mol for the anion. Overall, the CcCR method accurately reproduces the molecular constants and EA for the neutral CP radical, landing considerable credence to the calculated molecular constants for the anion.

2. C_2P and C_2P^-

Comparisons between experimental and calculated results of C_2P and the two C_2P^- anion states are shown in Table IV. There is no experimental information available for the ${}^{1}\Sigma^{+}$ anion excited state, and only calculated values are given. The predicted EA of neutral C₂P to the ${}^{3}\Sigma^{+}$ ground state of the anion is 2.676 eV, which is only 0.043 eV higher than the experimental value (2.6328 eV). The computed, zero-point vibrationally averaged bond lengths for neutral C₂P are also within 0.017 Å of the known experimental values.¹⁹ The known experimental B_0 and D_0 constants (6392.4138 ± 26 MHz and 2.2595 \pm 22 kHz)¹⁹ for neutral C₂P are also reproduced accurately from the CcCR calculations within 33 MHz (for B_e) and 1 kHz (for D_{e}). However, the calculated vibrational frequencies for C₂P are not as consistent with experiment as the structural and rotational observables. This discrepancy is due to the difficult nature of treating the ${}^{2}\Pi$ state, which exhibits both strong Renner-Teller effects and spin-orbit coupling. It should be noted that density functional theory also failed to predict the vibrational frequencies for this state.^{17–19}

The excellent agreement for the calculated and measured vibrational frequencies of the ${}^{3}\Sigma^{+}$ ground state of the C₂P⁻ anion confirms that the disagreement of the neutral frequencies is due to the vibronic and spin-orbit couplings in the degenerate neutral ground states. The calculated frequencies for the C–P stretch (759.5 cm⁻¹) and bending mode (291.2 cm⁻¹) of the ${}^{3}\Sigma^{+}$ triplet anion are 2 cm⁻¹ and 9 cm⁻¹ different than the experimental values of 761 ± 8 cm⁻¹ and 282 ± 4 cm⁻¹, respectively.

We also performed Franck-Condon simulations for the PE spectrum of C_2P^- using the PESCAL program⁷⁴ with the Sharp-Rosenstock-Chen method,⁷⁵ which can handle triatomic and larger molecules better than the Morse oscillator. In the simulation, all spectroscopic constants were fixed and only the vibrational temperature was varied. The experimental molecular constants were used in the simulation when available, while computed values were used otherwise (Table IV). The Franck-Condon simulation shown in Fig. 4(b) was done at a 500 K vibrational temperature and is only in semi-quantitative agreement with the lower resolution experimental spectrum at 3.4958 eV. Clearly, the 500 K vibrational temperature was too high, if one compares the calculated Franck-Condon factors with the high-resolution PE spectra in Fig. 3. The vibrational cooling in our cluster source was somewhat difficult to control for small clusters, as mentioned for the CP⁻ anions above. The strong hot band transitions observed in Figs. 3(a), 3(b), and 3(e) are very likely due to autodetachment from near threshold excited anionic state,⁷⁶ or possibly dipole-bound states.77-79

As shown in Table IV, the rotational constants (B_e and B_{0-3}) for the C₂P⁻ ground state are all between 6122.0 and 6178.7 MHz, slightly smaller than those of neutral C₂P, consistent with the small increase in the overall length of the anion. The quartic distortion constant is slightly larger in both anion states, at approximately 1.7 kHz, while the sextic distortion constants are nearly equal but with the opposite sign at -0.203 mHz for the ${}^{3}\Sigma^{+}$ state and -0.151 mHz for the ${}^{1}\Sigma^{+}$ state. Given the great agreement for the EA, bond lengths, and rotational constants, it is expected that any subsequently predicted values of other observables such as the vibrationally excited rotational constants for both anion states of C₂P⁻ should be accurate.

VII. CONCLUSION

High-resolution PE imaging was used to study CP⁻ and C₂P⁻. Accurate EAs of 2.8508 \pm 0.0007 eV and 2.6328 \pm 0.0006 eV were measured for CP and C₂P, respectively, as well vibrational frequencies for both the anionic and neutral species. The computed vibrational frequencies of CP⁻, CP, and C₂P⁻ are in good agreement with the experimental data. Comparison to theoretical results from the CcCR methodology shows that most results, except the vibrational frequencies of the ²Π state of C₂P, agree well with the experimental data, suggesting that the CcCR method should be useful to predict reliable bond lengths, rotational constants, and vibrational frequencies for carbon-containing species of astrochemical interest.

SUPPLEMENTARY MATERIAL

See supplementary material for the CcCR force constants for CP/CP⁻ and C_2P/C_2P^- .

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