Electronic and Rovibrational Quantum Chemical Analysis of $C_3P^-$: The Next Interstellar Anion?

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ABSTRACT

$C_3P^-$ is analogous to the known interstellar anion $C_3N^-$ with phosphorus replacing the nitrogen in a simple step down the periodic table. In this work, it is shown that $C_3P^-$ is likely to possess a dipole-bound excited state. It has been hypothesized and observationally supported that dipole-bound excited states are an avenue through which anions could be formed in the interstellar medium. Additionally, $C_3P^-$ has a valence excited state that may lead to further stabilization of this molecule, and $C_3P^-$ has a larger dipole moment than neutral $C_3P$ ($\sim 6$ D vs. $\sim 4$ D). As such, $C_3P^-$ is probably a more detectable astromolecule than even its corresponding neutral radical. Highly-accurate quantum chemical quartic force fields are also applied to $C_3P$ and its singly $^{13}$C substituted isotopologues in order to provide structures, vibrational frequencies, and spectroscopic constants that may aid in its detection.

1 INTRODUCTION

It is currently uncertain as to why anions are found in the interstellar medium (ISM) with six known to date: $C_2H^-$, $C_4H^-$, $C_2H^-$, CN$^-$, $C_2N^-$, and $C_3N^-$ ($Cernicharo et al.$, 2007; $Br\"unken et al.$, 2007; $Remijan et al.$, 2007; $Thaddeus et al.$, 2008; $Cernicharo et al.$, 2008; $Fortenberry et al.$, 2013a). Since all of the known anions are closed-shell and, as a result, valence in nature, one of the leading theories about their existence comes from the presence of a dipole-bound excited state $Ag\"endez et al.$, 2008). If a neutral molecule possesses a large enough dipole moment (somewhere in excess of 2.0–2.5 D), it can bind an additional electron in a highly diffuse s-type orbital $Ferri \& Teller$, 1945; $Conson \& Walmsley$, 1967; $Gutsev \& Adamowicz$, 1995b; $Compton et al.$, 1996; $Jordan \& Wang$, 2003; $Simons$, 2008; $Cordiner et al.$, 2011). These loosely bound excited states $Hammer et al.$, 2003) can relax to a lower energy valence state if the molecule can support the additional electron in its valence electron cloud. This phenomenon is known for some small anions $Lykke et al.$, 1987; $Mullin et al.$, 1992, 1993), and its reverse for electronic excitation has even been hypothesized as a potential explanation $Sarr$, 2000; $Cordiner \& Sarr$, 2007; $Fortenberry, Crawford \& Lee$, 2013) for at least one of the diffuse interstellar bands, the series of visible to near-infrared absorption features largely uniformly observed towards many stellar objects $Sarr$, 2000) whose carriers have only very recently come into focus $Campbell et al.$, 2013). As such, it is currently hypothesized that the large dipole moment of the neutral-radical captures an incident electron whereby the dipole-bound anion then decays down to the stable, valence ground electronic state $Ag\"endez et al.$, 2008; $Fortenberry et al.$, 2013a).

All of the known interstellar anions possess large enough dipole moments to undergo this process save for $CN^-$ which is likely formed by collisional or chemical processes $Larsson, Genpert \& Nyman$, 2012; $Carelli et al.$, 2014). The greater $[C_6H^-]/[C_6H]$ ratio as compared to the significantly smaller $[C_4H^-]/[C_4H]$ ratio is most elegantly explained by the dipole-bound formation hypothesis $Ag\"endez et al.$, 2008) especially since $C_6H$ is more abundant than $C_6H^-$, but $C_4H^-$ is more abundant than $C_4H^-$. $C_6H$ must be excited into its low-lying $^2\Pi$ excited state in order to have a dipole moment large enough to capture the additional electron. $C_6H$ is $^2\Pi$ and strongly dipolar in its ground state meaning that capture of the dipole-bound electron is much more likely for the longer hydrocarbon chain. Additionally, $C_6H^-$ has not been detected. Its corresponding neutral-radical is very abundant $Heikkil\"a, Johansson \& Olofsson$, 1994), but the dipole moment of the unchanged species is not large enough to support a dipole-bound state. Finally, all of the corresponding neutral-radicals are known to exist in the ISM for each of the closed-shell anions detected $McCarthy \& Thaddeus$, 2001).

However, no new anions have been detected in the
ISM since 2010 as reported in the literature (Agúndez et al. 2014). Several candidate anions have been studied quantum chemically in order to provide accurate predictions of their rovibrational nature. These include CH$_2$CN$^-$, C$_2$ and l-C$_3$H$^-$, and COCH$^-$ (Fortenberry, Crawford & Lee 2013; Fortenberry et al. 2013a, 2014a; Fortenberry & Lee 2015). Another tantalizing potential interstellar anion is C$_3$P$^−$. It is analogous with the known C$_3$N$^-$ anion, and several phosphorus-containing carbon chains (CP, HCP, and CCP) have been detected in the ISM (Guélin et al. 1990; Agúndez, Cernicharo & Guélin 2007; Halfen, Cernicharo & Ziurys 2008). However, little is known about l-C$_3$P$^−$. The linear neutral-radical is known to be the lowest energy isomer on the [C,C,C,P] potential energy surface and has a strongly dipolar (3.797 D) 2H ground state (del Río, Barrientos & Largo 1994; Maclean et al. 2008).

Hence, this present work sets to provide both electronic as well as high-level rovibrational data on C$_3$P$^−$ in order to assist in its potential detection.

Quantum chemical studies of excited states of anions have recently shown that many anions may possess dipole-bound excited states, and some anion excited states may also be valence in nature (Fortenberry & Crawford 2011b; Fortenberry 2013; Fortenberry, Morgan & Envard 2014; Fortenberry 2014; Theis et al. 2013). Excited states of anions have been experimentally known for many species (Lykke et al. 1987; Mullin et al. 1992; 1993; Grutter, Wyss & Maiel 1999; Pachkov et al. 2001; Pino et al. 2002, 2004). However, the number of dipole-bound excited state candidate anions has increased with the improvement of computational tools. Additionally, high-level rovibrational computations have been able to produce rotational constants to within 15 MHz of experiment and vibrational frequencies to within 1.0 cm$^{-1}$ of laboratory results in some cases (Huang, Taylor & Lee 2011; Inostroza, Huang & Lee 2011; Fortenberry et al. 2012b; Huang, Fortenberry et al. 2013a; Zhao, Donev & Linnartz 2014; Fortenberry et al. 2014b). Consequently, both approaches are applied to C$_3$P$^−$ in this work in order to elucidate more fully the chemical physics of this potentially astrochemically significant anion.

2 COMPUTATIONAL DETAILS

All computations make use of coupled cluster theory at either the singles and doubles (CCSD) or singles, doubles, and perturbative triples (CCSD(T)) levels (Raghavachari et al. 1989; Crawford & Schaefer III 2004; Shavitt & Bartlett 2009) and the correlation-consistent family of basis sets in the cc-pVXZ from Dunning (1989; Peterson & Dunning 1993; Kendall, Dunning & Harrison 1992). The cc-pV(N+d)Z basis sets are used for the phosphorus atom, but this distinction should be understood by the reader to be implied for the remainder of the discussion. Additionally, restricted Hartree-Fock reference wavefunctions (Scheiner et al. 1987) and the PSi4 quantum chemistry software (Turner et al. 2012) are utilized except where noted.

The electronically excited states are computed vertically using the equation of motion (EOM) formalism (Stanton & Bartlett 1993; Krylov 2007) of CCSD and are based on the optimized CCSD(T)/aug-cc-pVTZ geometry. Increasing the diffuseness of the basis set allows one to observe the convergence of the excitation energy. Early convergence in the series indicates a valence excited state while late convergence is a sign that the excited state of interest is dipole-bound. This can them be corroborated by analysis of the orbitals involved from the most diffuse basis set. The double-zeta (n-aug-cc-pVQZ where n = 0 – 3) and triple zeta (m-aug-cc-pVTZ where m = 0 – 2) basis sets are employed. The vertical electron binding energy (eBE), the energy required to removed the electron from the system starting from the ground electronic state, is computed using the ionization potential potential form of EOM: EOMIP-CCSD (Stanton & Gaus 1994). The rovibrational computations utilize the scheme developed previously (Huang & Lee 2008, 2009; Huang, Taylor & Lee 2011) that has met with much success as described above. The optimized CCSD(T)/aug-cc-pV5Z geometry is corrected for core-electron inclusion by adding the differences in the bond lengths between the CCSD(T) and without inclusion of the core electrons: 1$\Sigma^+$ to 1$\Sigma^−$.

A similar coordinate setup has been utilized previously on the structurally-related l-C$_3$H$^+$ cation (Huang, Fortenberry & Lee 2013b). The step sizes for the bond length displacements are 0.005 Å and 0.005 radians for the bends.

625 total displacements are needed to describe the C$_3$P$^−$ QFF. At each displacement, seven quantum chemical computations are undertaken at the CCSD(T) level. Extrapolation of the aug-cc-pVTZ, aug-cc-pVQZ, and aug-cc-pV5Z energies to the complete basis set (CBS) limit via a three-point formula (Martin & Lee 1996) provides the reference energy for each point. Differences between the MT computed energies including and not including core electrons are added to the CBS energy. Furthermore, Douglas-Kroll scalar relativistic corrections (Douglas & Kroll 1974) available in the MOLPRO 2010.1 quantum chemistry program (Werner et al. 2014) are also added to the CBS en-
ergy. The CcCR QFF [Fortenberry et al. 2011] is created from this approach where the CBS energy (“C”), core correlation (“cC”), and relativistic terms (“R”) provide for a very detailed description of the molecular potential energy surface.

The energy points are fitted to the force constants via a least-squares formula. Refitting the surface provides the CcCR minimum equilibrium geometry as well as the proper force constants including zero value gradients. Transformation of the force constants into Cartesian coordinates is accomplished via the INTDER [Allen & coworkers 2005] program. Rotational [Mills 1972; Watson 1977] and vibrational [Papousek & Al? 1982] perturbation theory computations at second order (VPT2) produce spectroscopic constants and anharmonic vibrational frequencies, respectively, through the SPECTRO program [Gaw et al. 1991]. A 2ν = ν2 type-1 Fermi resonance is included in SPECTRO’s VPT2 computations. Møller-Plesset second-order electron perturbation theory (MP2) computations with the 6-31+G∗ basis set [Møller & Plesset 1934; Hehre, Ditchfield & Pople 1972] in the Gaussian09 program [Frisch et al. 2009] provide the vibrational intensities.

3 RESULTS AND DISCUSSION

3.1 Electronically Excited States

The ground electronic state C3P has a X 2Π term and a (core)σ2π2s2p2σ10ε2s1ε3ε3σ3 electronic configuration (del Rio, Barrientos & Larg? 1996). The anion’s additional electron occupies the 3σ orbital to complete the shell and give a valence X 1Σ+ ground state term. The 3σ highest occupied molecular orbital (HOMO) is significant for the electronic properties of the anion. Computations of the first two vertically excited states of C3P− are given in Table 1. Both excitations are out of the 3σ HOMO. The 2 1Σ+ state involves excitations into the 4π∗ orbital, while the 1 1Π state is produced by exciting the electron into a diffuse s-type orbital.

The 1 1Π state is a candidate for classification as a dipole-bound excited state. The excitation energy decreases significantly as the spatial extent of the orbitals increases, the excitations are, again, into high-diffuse orbitals as is necessary for a dipole-bound state [Skurski, Gutowski & Simons 2000; Morgan & Fortenberry 2013], and the eBE and dipole-bound excitation energy are nearly coincident. Since the eBEs of dipole-bound states are known to be on the order of ~ 0.01 eV [Hammer et al. 2003; Diken, Hammer & Johnson 2004], the latter point is a clear marker of dipole-bound behavior. Additionally, the dipole moment of the C3P X 2Π state at the anion geometry is computed here by CCSD(T)/aug-cc-pVTZ to be 4.20 D, in line with previous computations [Maclean et al. 2008] and large enough to support a dipole-bound state.

The 2 1Σ+ state is actually valence. Its excitation is not affected by the increase in the diffuseness of the basis set and is well-below the eBE. It is the product of a π → π∗ excitation which is similar to π electron systems in polyunsaturated carbon chains, a commonly-used application of the particle-in-a-box quantum mechanical model system. Hence, C3P− and longer chains of this family will also likely possess a valence excited state. The C3P− 2 1Σ+ excitation energy is well converged to the 3.30 eV level for the double-zeta bases and similarly at 3.24 eV for the triple-zeta bases.

Even though the intensities for the transitions are very small, C3P− is still an excellent candidate for dipole-bound, gas phase synthesis starting from the neutral-radical in the ISM or in circumstellar media. Capture of the electron by the neutral radical can proceed through the dipole-bound excited state producing the valence, closed-shell anion. The valence excited state provides an additional avenue for energy dissipation. This may likely increase its interstellar lifetime giving an exceptionally high [C3P−]/[C3P] ratio, potentially greater than that observed for [C6H]/[C6H]. As a result, C3P− should be more readily observed than its corresponding neutral radical since its electronic properties are more enhanced than the other known interstellar anions. In order to detect C3P−, information regarding the X 1Σ+ valence ground electronic state’s rotational, vibrational, and rovibrational behavior is needed and provided here for the first time from further quantum chemical computations.

3.2 Rovibrational Analysis

The fitting of the force constants needed to define the CcCR QFF and produce the subsequent spectroscopic data of ground state X 1Σ+ C3P− is very tight with a sum of residuals squared on the order of 10−16 a.u.2 The force constants for l-C3P− are given in Table 2 and follow the coordinate labeling given above. For instance, F11 corresponds to the second-derivative of the C1−C2 bond. Additionally, the harmonic, diagonal force constants are proportional to the bond strengths. F11 is the largest of these indicating that the C1−C2 bond is the strongest. This is corroborated by the R0 vibrationally averaged bond lengths given in Table 3. The r0(C1−C2) value is 1.259 055 Å, the shortest bond length given indicating that this is the strongest bond. Interestingly, the C2−C3 bond strength from F22 is roughly equal to the C3−P bond strength from F13. The phosphorus atom creates a longer bond length by default, but these force constants and the bond lengths show that this molecule is neither acetylenic nor cumulenic. It should be thought of as an intermediate between the two classifications with the C1−C2 bond more acetylenic and the rest of the molecule as cumulenic.

In any case, the spectroscopic constants, dipole moment, and vibrational frequencies are given in Table 4 along with the single 13C substituted isotopologues. Phosphorus has only one stable isotope, 31P. C3P− is strongly dipolar with a 6.22 D dipole moment as determined from center-of-mass computations. As a result, its rotational intensities should be brighter than the neutral-radical giving further evidence that the anion may be more easily observed in the ISM than the neutral. The rotational constants are not strongly affected by vibrational averaging with B0 equal to 2798.0 MHz while B1 is only 2.1 MHz greater at 2800.1 MHz. Substitution of the terminal C1 atom with 13C reduces the rotational constants by 102.0 MHz. Substitution of the other carbon atoms is not as significant. The quartic (D) and sextic (H) distortion constants are exceptionally small for this molecule and may only show up in very high-resolution experiments.

While ground-based telescopes such as the Atacama...
Large Millimeter/submillimeter (ALMA) array are excellent for observing molecular rotational spectra, the growth of space-based or airborne infrared telescopes such as the upcoming James Webb Space Telescope or the Stratospheric Observatory for Infrared Spectroscopy (SOFIA), respectively, has enhanced vibrational spectral analysis for astronomical applications. The vibrational frequencies of $C_3P^-$ are given in the middle of Table 3. The descriptions of the fundamental vibrational modes are not as straightforward as one would assume for a $C_{\infty v}$ molecule. The first two modes are defined here as the symmetric and antisymmetric C−C stretches for the three carbon atom portion of the molecule. The last two modes are the internal and external bends. The former mode is dominated by the C2 and C3 atoms moving opposite of one another relative to the central axis. The latter bending vibrational motion is largely described by the C1 and P atoms moving in concert with one another relative to the central axis. The carbon atom, naturally, covers a greater distance in this mode due to its smaller relative mass, but the two atoms are vibrating in concert.

The CcCR QFF frequencies are not strongly anharmonic. While anharmonic corrections are necessary for accurate descriptions of the vibrational modes, they do not shift as greatly from the harmonic values as is typical. Most of this behavior is probably due to the increased mass of the system largely from the phosphorus atom, but it is also from the tight bonding present in $C_3P^-$. Anions are not often thought to be tightly bound due to the increased electron-electron repulsion and likely increase in antibonding-character, but $C_3P^-$ appears to be so bound from the data given. In fact, the C−C stretching frequencies in $C_3P^-$ are of the same order as their counterparts in $C_3H^+$ (Huang, Fortenberry & Les 2013). As a result, the vibrational frequencies provided here should be very good representations of physical reality. The frequencies fit SOFIA’s range very well, and the $v_1$ frequency at 1939.7 cm$^{-1}$ should be very bright since the double-harmonic MP2 intensity is 483 km/mol. It is also worth mentioning that the MP2/6-31+G* harmonic frequency agree well with the CcCR harmonics. MP2 is known to give Pauling points for $C_3P^-$, but this correlation ($<5.1$ cm$^{-1}$) is largely unprecedented but nicely coincidental for the significantly lower-level MP2 computations.

In the age of ALMA, unidentified lines (or “U-lines”) are becoming even more of an issue. Many of these are likely to be caused by rotational transitions of known molecules in vibrationally excited states. As a result, the vibrationally-averaged rotational constants of $C_3P^-$ are also provided at the bottom of Table 3 for each fundamental mode. Vibrationally-excited modes associated with the bending frequencies increase the $B$ values, while the stretching vibrational modes decrease them. $^{13}$C substitution largely affects

### Table 1. The $C_3P^-$ Vertical Excitation Energies (in eV), Ground State eBEs$^a$ (in eV), and Oscillator Strengths.$^b$

| Transition | pVDZ | apVDZ | dapVDZ | tapVDZ | eBE | $f$ | pVTZ | apVTZ | dapVTZ |
|------------|------|-------|--------|--------|-----|-----|-------|--------|--------|
| $2 \ 1\Sigma^+ \rightarrow 1 \ 1\Sigma^+$ | 3.52 | 3.31 | 3.30 | 3.30 | $2 \times 10^{-4}$ | 3.35 | 3.23 | 3.24 |
| $1 \ 1\Pi \rightarrow 1 \ 1\Sigma^+$ | 8.23 | 5.04 | 3.98 | 3.81 | 8 $\times 10^{-3}$ | 7.03 | 4.89 | 4.09 |

$^a$Computed with EOMIP-CCSD/t-aug-cc-pVDZ.

$^b$The $f$ values are for EOM-CCSD/d-aug-cc-pVTZ.

### Table 2. The CcCR $C_3P^-$ Force Constants Given in mdyn/A$^a$-$\text{rad}^m$.$^a$

| Transition | pVDZ | apVDZ | dapVDZ | tapVDZ | eBE | $f$ | pVTZ | apVTZ | dapVTZ |
|------------|------|-------|--------|--------|-----|-----|-------|--------|--------|
| $F_{11}$ | 11.566 227 | -0.4428 | 219.70 | -0.66 | F_{5432} | 0.00 |
| $F_{21}$ | 0.596 174 | -0.5107 | F_{3111} | 0.15 | F_{5433} | 0.23 | F_{7621} | -1.13 |
| $F_{22}$ | 7.708 659 | 0.0197 | F_{3211} | 0.12 | F_{5444} | 0.57 | F_{7622} | 0.77 |
| $F_{31}$ | -0.380 686 | -0.0978 | F_{3221} | -0.38 | F_{5511} | -0.44 | F_{7631} | -0.50 |
| $F_{32}$ | 0.689 835 | 0.0236 | F_{3222} | 0.66 | F_{5521} | 0.65 | F_{7632} | -0.19 |
| $F_{33}$ | 7.655 860 | -0.5050 | F_{3311} | -0.93 | F_{5522} | -0.88 | F_{7633} | 0.25 |
| $F_{44}$ | 0.209 473 | -0.0499 | F_{3321} | 0.31 | F_{5531} | 0.53 | F_{7644} | -2.28 |
| $F_{55}$ | -0.010 817 | -0.4968 | F_{3322} | 0.11 | F_{5532} | 1.80 | F_{7654} | 3.47 |
| $F_{66}$ | 0.401 190 | -0.6287 | F_{3331} | 1.77 | F_{5533} | 0.62 | F_{7655} | 3.32 |
| $F_{77}$ | 0.401 209 | 0.0190 | F_{4411} | 1.46 | F_{5535} | 0.96 | F_{7721} | 0.54 |
| $F_{111}$ | -71.2065 | -0.0952 | F_{4421} | -0.19 | F_{6611} | 1.09 | F_{7722} | -1.29 |
| $F_{211}$ | -0.2476 | 0.0233 | F_{4422} | 0.61 | F_{6621} | -0.42 | F_{7731} | 0.65 |
| $F_{222}$ | -2.4219 | -0.0524 | F_{4431} | 1.39 | F_{6622} | 0.69 | F_{7732} | 1.94 |
| $F_{332}$ | -45.2600 | -0.0492 | F_{4432} | 0.77 | F_{6631} | 1.53 | F_{7733} | -0.61 |
| $F_{311}$ | -0.0455 | -0.4972 | F_{4433} | 0.07 | F_{6632} | 1.31 | F_{7744} | 0.03 |
| $F_{321}$ | 0.7443 | -0.6289 | F_{4444} | -0.15 | F_{6633} | -0.38 | F_{7754} | 2.40 |
| $F_{322}$ | -1.7436 | 349.14 | F_{5411} | -0.05 | F_{6644} | 1.89 | F_{7755} | -0.68 |
| $F_{331}$ | -0.0806 | 0.82 | F_{5421} | -0.66 | F_{6654} | -1.66 | F_{7766} | -0.08 |
| $F_{332}$ | -0.8594 | -3.24 | F_{5422} | -0.07 | F_{6655} | 0.71 | F_{7776} | 0.00 |
| $F_{333}$ | -41.3790 | 4.66 | F_{5431} | 0.64 | F_{6666} | -0.25 | F_{7777} | -0.76 |

$^a1$ mdyn = 10$^{-8}$ N; The $n$ and $m$ values are exponents that correspond to the number of units from the type of modes present in the specific force constant.
the rotational constants in similar ways between isotopologues as it does for \( B_0 \). Finally, a limited line list for the \( J \leq 9 \) rotational transitions of the \( \nu = 0 \) and \( \nu = 1 \) vibrational states is provided in Table 3 in order to assist with further analysis. Previous work (Fortenberry et al. 2013a) has shown that the rotational constants are probably within 10 MHz of experiment putting the anticipated rotational constants within 2\( J \times 10 \) MHz for each line predicted in Table 3 and the relative intensities between the rotational transitions should be very close to experiment.

### 4 CONCLUSIONS

The electronic properties of \( C_3P^- \) are in line with those for the known interstellar anions indicating that it may be a viable molecule waiting to be detected in the ISM. Attachment of an additional electron to the corresponding neutral-radical via the anion’s dipole-bound excited state is a likely creation mechanism for this anion. Additionally, \( C_3P^- \) possesses not only a valence ground electronic state but also a valence excited state. The second excited state should increase the molecule’s lifetime. Since \( [C_6H^-]/[C_6H] > 1 \) (Agúndez et al. 2008), it is likely that \( [C_3P^-]/[C_3P] \) is as well since both radicals possess strongly dipolar ground electronic states available for binding the extra electron leading to the observed valence anion. The valence excited state in \( C_3P^- \) should boost the \( [C_3P^-]/[C_3P] \) ratio further due to the enhanced stability in the phosphorus anion. Furthermore, the anion’s dipole moment is greater than that in the neutral-radical enhancing the anion’s rotational signal. As a result, \( C_3P^- \) may be a better candidate for detection than \( C_3P \).

In order to assist in potential searches, the spectroscopic constants and vibrational frequencies for \( C_3P^- \) are provided in this work. Ground state \( C_3P^- \) is tightly bound, especially considering that it is an anion, and not strongly anharmonic. Hence, the CcCR approach utilized previously with

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### Table 3. The \( C_3P^- \) and Single \( ^3\)C Isotopologue CcCR Equilibrium and Zero-Point (\( R_o \) vibrationally-averaged) Geometries, Rotational Constants, Vibration-Rotation Interaction Constants, Quartic (D) and Sextic (H) Distortion Constants, CCSD(T)/aug-cc-pVTZ Dipole Moment, and Vibrational Frequencies and Intensities \(^a\)

| \( r_o(C_1-C_2) \) (Å) | \( 1.259 \times 10^5 \) | \( 1.259 \times 10^5 \) | \( 1.259 \times 10^5 \) | \( 1.259 \times 10^5 \) |
| \( r_o(C_2-C_3) \) (Å) | \( 1.345 \times 10^5 \) | \( 1.345 \times 10^5 \) | \( 1.345 \times 10^5 \) | \( 1.345 \times 10^5 \) |
| \( r_o(C_3-P) \) (Å) | \( 1.581 \times 10^6 \) | \( 1.581 \times 10^6 \) | \( 1.581 \times 10^6 \) | \( 1.581 \times 10^6 \) |
| \( B_0 \) (MHz) | \( 2798.0 \) | \( 2696.0 \) | \( 2769.6 \) | \( 2798.0 \) |
| \( \alpha^D_1 \) (MHz) | \( 13.3 \) | \( 13.2 \) | \( 12.8 \) | \( 12.9 \) |
| \( \alpha^D_2 \) (MHz) | \( 12.6 \) | \( 11.8 \) | \( 12.4 \) | \( 12.4 \) |
| \( \alpha^D_3 \) (MHz) | \( 4.3 \) | \( 4.0 \) | \( 4.2 \) | \( 4.3 \) |
| \( \alpha^B_1 \) (MHz) | \( -5.1 \) | \( -4.9 \) | \( -4.9 \) | \( -5.0 \) |
| \( \alpha^B_2 \) (MHz) | \( -7.9 \) | \( -7.7 \) | \( -7.6 \) | \( -7.8 \) |
| \( \omega^b \) Symm. Carbon Stretch (cm\(^{-1}\)) | 1979.2 | 1959.0 | 1930.9 | 1971.8 |
| \( \omega^b \) C\(_2\) Shuttle (cm\(^{-1}\)) | 1481.5 | 1470.5 | 1481.2 | 1439.3 |
| \( \omega^b \) C\(_3-P\) stretch (cm\(^{-1}\)) | 692.0 | 681.7 | 686.6 | 692.0 |
| \( \omega^b \) Internal Bend (cm\(^{-1}\)) | 479.9 | 479.4 | 472.5 | 469.6 |
| \( \omega^b \) External Bend (cm\(^{-1}\)) | 194.8 | 192.3 | 192.4 | 192.6 |
| \( H_e \) (µe) | 1.717 | 1.654 | 1.577 | 1.717 |
| \( \mu_e \) \(^b\) | 6.22 D | – | – | – |
| \( B_1 \) (MHz) | 2784.7 | 2682.8 | 2756.8 | 2785.1 |
| \( B_2 \) (MHz) | 2785.4 | 2684.2 | 2757.1 | 2785.6 |
| \( B_3 \) (MHz) | 2793.7 | 2692.0 | 2765.3 | 2793.8 |
| \( B_4 \) (MHz) | 2803.1 | 2700.9 | 2774.5 | 2803.0 |
| \( B_5 \) (MHz) | 2805.9 | 2703.7 | 2777.2 | 2805.8 |

\(^a\)Given in parentheses in km/mol beside the MP2/6-31+G* harmonic frequencies.

\(^b\)The coordinates used to generate the Born-Oppenheimer dipole moment component (in \( \AA \) with the centre-of-mass at the origin) are: C\(_1\), 0.000000, 0.000000, -2.629136; C\(_2\), 0.000000, 0.000000, -1.367016; C\(_3\), 0.000000, 0.000000, -0.023143; P, 0.000000, 0.000000, 1.557174.
very good results should be similarly accurate in this system. The $\nu_1$ C–C stretch is very bright, and the vibration-rotation interaction constants are small. In summary, C$_3$P$^-$ is an excellent interstellar molecular candidate, and the data provided in this work should assist in spectral searches for this anion whether in the laboratory or in the ISM.

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