

**Spectroscopic Constants and Vibrational Frequencies for  $l$ -C<sub>3</sub>H<sup>+</sup>  
and Isotopologues from Highly-Accurate Quartic Force Fields:  
The Detection of  $l$ -C<sub>3</sub>H<sup>+</sup> in the Horsehead Nebula PDR  
Questioned**

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## ABSTRACT

Very recently, molecular rotational transitions observed in the photon-dominated region of the Horsehead nebula have been attributed to  $l\text{-C}_3\text{H}^+$ . In an effort to corroborate this finding, we employed state-of-the art and proven high-accuracy quantum chemical techniques to compute spectroscopic constants for this cation and its isotopologues. Even though the  $B$  rotational constant from the fit of the observed spectrum and our computations agree to within 20 MHz, a typical level of accuracy, the  $D$  rotational constant differs by more than 40%, while the  $H$  rotational constant differs by three orders of magnitude. With the likely errors in the rotational transition energies resulting from this difference in  $D$  on the order of 1 MHz for the lowest observed transition ( $J = 4 \rightarrow 3$ ) and growing as  $J$  increases, the assignment of the observed rotational lines from the Horsehead nebula to  $l\text{-C}_3\text{H}^+$  is questionable.

**Keywords:** astrochemistry – ISM: individual objects: Horsehead nebula – ISM: lines and bands – ISM: molecules – molecular data – radio lines: ISM

## 1. Introduction

Within the past months,  $l\text{-C}_3\text{H}^+$  has been attributed as the source of several rotational lines observed in the Horsehead nebula photon-dominated region (PDR) (Pety et al. 2012). In order for the observed spectral features to be linked to a single molecular carrier, the molecule must be linear with a  $^1\Sigma$  ground state and a lone ( $B$ -type) rotational constant close to 11.24 GHz. However, only standard quantum chemical computations of  $l\text{-C}_3\text{H}^+$  have given qualitative corroborating evidence for the rotational constants, and no quantitative, high-accuracy reference data, either from computation or laboratory experiment, exists for

$l$ -C<sub>3</sub>H<sup>+</sup>. The corresponding C<sub>3</sub>H radical has long been known to exist in the interstellar medium (ISM) (Thaddeus et al. 1985) and was confirmed with concurrently generated laboratory reference data (Gottlieb et al. 1985). Although laboratory studies of known interstellar molecules in simulated interstellar environments have often produced what is believed to be C<sub>3</sub>H<sup>+</sup> (Bohme et al. 1983; Schwell et al. 2012) with theory providing further insights (Radom et al. 1976; Ikuta 1996; Wang et al. 2007), neither high-accuracy rotational nor vibrational spectroscopic data has yet been generated for  $l$ -C<sub>3</sub>H<sup>+</sup>.

Recently, we have employed state-of-the art *ab initio* quartic force fields (QFFs) and perturbation theory at second order (Papousek & Aliev 1982) to compute rotational constants that are within 20 MHz or better of experiment (Fortenberry et al. 2011a,b, 2012b,a) for similar tetra-atomic systems. The use of QFFs has also been applied to other molecules of interstellar relevance in order to compute accurately their spectroscopic constants in addition to their fundamental vibrational frequencies and even some overtones and combination bands (Huang & Lee 2008; Lee et al. 2009; Huang & Lee 2009; Inostroza et al. 2011; Huang et al. 2011; Huang & Lee 2011; Fortenberry et al. 2012a, 2013b). Since high-accuracy reference data is currently not available for  $l$ -C<sub>3</sub>H<sup>+</sup>, the methods utilized previously are employed here in order to assist in confirmation for the detection of this cation in the Horsehead nebula. Additionally, we will also supply spectroscopic constants and vibrational frequencies for the deuterated form and for each of the three <sup>13</sup>C singly-substituted isotopologues.

## 2. Computational Details

Utilizing the MOLPRO 2006.1 suite of quantum chemical programs (Werner et al. 2006), spin-restricted Hartree-Fock (RHF) (Scheiner et al. 1987) coupled cluster theory (Lee & Scuseria 1995; Shavitt & Bartlett 2009; Crawford & Schaefer 2000) at the singles,

doubles, and perturbative triples level [CCSD(T)] (Raghavachari et al. 1989) is employed to compute the reference geometry. This initial geometry is based on a composite approach to give the most accurate bond lengths in this linear molecule. The CCSD(T) bond lengths (denoted as  $R$ ) computed with the cc-pV5Z basis set (Dunning 1989; Peterson & Dunning 1995; Dunning et al. 2001) are corrected for effects from the smaller cc-pVQZ basis set as well as core correlation and scalar relativistic effects (Douglas & Kroll 1974) through the following approach:

$$R = R_{5Z} + (R_{5Z} - R_{QZ}) + (R_{Rel.+Core} - R_{QZ}). \quad (1)$$

The  $R_{Rel.+Core}$  CCSD(T) geometry optimization makes use of the standard cc-pVQZ-DK basis set, which can account for relativistic effects, further augmented to include core correlating  $s$ ,  $p$ ,  $d$ , and  $f$  functions from the standard cc-pCVQZ basis set (Dunning 1989). The last term in Eq. 1 serves to isolate the scalar relativistic and core correlating effects so that they may then enhance the standard cc-pV5Z bond lengths.

From this reference geometry, the quartic force field (QFF) is created from displacements of 0.005 Å and 0.005 radians (Huang et al. 2011), respectively for the three bond lengths and two doubly-degenerate linear bends, and contains 569 points. At each point CCSD(T)/cc-pVTZ, cc-pVQZ, and cc-pV5Z energies are computed and extrapolated to the complete basis set (CBS) limit via a three-point formula (Martin & Lee 1996). The CBS energy is then corrected for scalar relativity (Douglas & Kroll 1974) and core correlation effects from the Martin-Taylor basis set (Martin & Taylor 1994). This results in the CcCR QFF defined previously (Fortenberry et al. 2011a, 2013a). The QFF is then fit with a sum of residual squares of  $5.7 \times 10^{-17}$  a.u.<sup>2</sup> to a Taylor series expansion of the potential and is of the form:

$$V = \frac{1}{2} \sum_{ij} F_{ij} \Delta_i \Delta_j + \frac{1}{6} \sum_{ijk} F_{ikj} \Delta_i \Delta_j \Delta_k + \frac{1}{24} \sum_{ijkl} F_{ikjl} \Delta_i \Delta_j \Delta_k \Delta_l \quad (2)$$

where  $F_{ij\dots}$  are force constants and  $\Delta_i$  are the displacements. This high-symmetry  $C_{\infty v}$  system is most easily represented in the simple-internal coordinate system defined here (with atom numbering from Fig. 1) as:

$$S_1(\Sigma^+) = C_1 - H \quad (3)$$

$$S_2(\Sigma^+) = C_1 - C_2 \quad (4)$$

$$S_3(\Sigma^+) = C_2 - C_3 \quad (5)$$

$$S_4(\Pi_{xz}) = \text{LIN1}(H - C_1 - C_2 - \vec{y}) \quad (6)$$

$$S_5(\Pi_{yz}) = \text{LIN1}(H - C_1 - C_2 - \vec{x}) \quad (7)$$

$$S_6(\Pi_{xz}) = \text{LIN1}(C_1 - C_2 - C_3 - \vec{y}) \quad (8)$$

$$S_7(\Pi_{yz}) = \text{LIN1}(C_1 - C_2 - C_3 - \vec{x}) \quad (9)$$

These coordinate subscripts correspond to the force constants given in Table 1. The  $\vec{x}$  and  $\vec{y}$  quantities are necessary to define the linear bending angles ( $S_4 - S_7$ ) and correspond to a direction perpendicular to the bending plane so that degenerate linear modes may be uniquely specified, since  $\vec{x} \perp \vec{y}$ . Second-order vibrational perturbation theory (VPT2) (Mills 1972; Watson 1977) via the SPECTRO program (Gaw et al. 1996) produces the desired spectroscopic constants and vibrational frequencies. Since the QFF is computed within the Born-Oppenheimer approximation, only the SPECTRO anharmonic analyses differ between the five total isotopologues.

### 3. Discussion

The  $l\text{-C}_3\text{H}^+$  and isotopologue bond lengths, rotational constants, quartic and sextic centrifugal distortion constants, and center-of-mass dipole moments are given in Table 2, and the fundamental vibrational frequencies are listed in Table 3. The relevant data are in fairly good agreement with the full-dimensional PES computed previously given the

much lower level of theory used (Wang et al. 2007). The inclusion of the scalar relativity correction is necessary since, for example,  $B_0$  for standard  $l\text{-C}_3\text{H}^+$  computed with only the CBS-energy-including QFF is 11 209.78 MHz, while the CR QFF (which additionally includes the relativistic terms, see Fortenberry et al. (2011a)) raises this value to 11 213.99 MHz. Similarly but more importantly, core correlation is also necessary as the rotational constant for the CcC QFF, which is the CBS plus core correlation QFF, puts  $B_0$  at 11 258.41 MHz. The total CcCR QFF  $B_0$ , listed in Table 2, is thus 11 262.68 MHz. This value differs by 17.73 MHz from that (11 244.947 4 MHz) obtained in the fitting by Pety et al. (2012) to assign the observed lines in the Horsehead nebula to  $l\text{-C}_3\text{H}^+$ . This represents similar accuracy as that noted previously for the *cis*- and *trans*-HOCO radicals (Fortenberry et al. 2011a,b), *trans*-HOCO<sup>+</sup> (Fortenberry et al. 2012b), and *trans*-HOCS<sup>+</sup> (Fortenberry et al. 2012a), as well as many other examples.

However, the correspondence between theory and experiment for the  $D$ -type constant is not as good. The CcCR  $D_e$  value is 4.248 kHz while the  $D$  value obtained by Pety et al. (2012) in their second-order fit is 7.652 kHz and 7.766 kHz for their third-order fit. This represents a difference of 3.404 kHz or 44.5% between theory and experiment for the second-order fit  $D$  and is larger still for the third-order fit. Though this is a comparison of  $D_e$  to  $D_0$ , i.e., vibrational averaging is not included in the theoretical value, the percentage change between the computed  $B_0$  and  $B_e$  values for this same molecule is only 0.77%. Further, various QFFs have been formulated to examine this system (33 in all) ranging from those that are state-of-the art and have been proven to yield highly-accurate spectroscopic constants including  $D$ , such as the given CcCR QFF, to those that use more modest levels of theory, such as CCSD(T)/cc-pVTZ, and the range in  $D_e$  values for these QFFs is only 0.053 kHz, which conclusively shows that the *ab initio*  $D_e$  value is converged to an extent that rules out a value near 7.6-7.8 kHz.

Additionally, other linear systems have been studied using similar theoretical approaches. For instance, the percentage error between the computed  $D_e$  (84.135 kHz) and the experimental  $D$  [87.22 kHz from Winnewisser et al. (1971)] is 3.5% for HCN computed with a CCSD(T)/ANO1 QFF (Lee et al. 1993). The  $D/D_e$  error for CCH<sup>-</sup> is 2.1% as computed with a CcCRE QFF (with corrections for higher-order electron correlation effects: “E”) in the same second order perturbational approach utilized here, where  $D_e$  is 94.3 kHz (Huang & Lee 2009), and the experimental  $D$  is 96.97 kHz (Brünken et al. 2007). Furthermore, the error for acetylene is only 2.27% between a  $D_e$  of 47.673 kHz (Martin et al. 1998) and a  $D$  of 48.780 kHz (Kabbadj et al. 1991). Perhaps a more relevant example for the current case is given for C<sub>3</sub>N<sup>-</sup> where  $D_0$  has been experimentally determined to be 0.68 578 kHz and a CCSD(T)/aug-cc-pVQZ QFF yields a  $D_e$  of 0.627 kHz (Thaddeus et al. 2008; McCarthy & Thaddeus 2008). The 8.57% error is still much less than the 44.5% discrepancy for C<sub>3</sub>H<sup>+</sup> and is probably somewhat larger than the other examples because of using lower levels of theory to compute the QFF, and because it is well known that small molecular anions are harder to describe accurately. Hence, the known errors for these systems are an order of magnitude smaller than that which is present for  $D_e$  and  $D$  in  $l$ -C<sub>3</sub>H<sup>+</sup>. As a result, we cannot attribute the substantial disagreement between the computed  $D_e$  for  $l$ -C<sub>3</sub>H<sup>+</sup> and the  $D$  value obtained by Pety et al. (2012) merely to errors in the theoretical approach. Thus, it is doubtful that the series of lines observed in the Horsehead nebula actually correspond to  $l$ -C<sub>3</sub>H<sup>+</sup>.

If the computed  $D_e$  value closely represents the actual  $D$  for  $l$ -C<sub>3</sub>H<sup>+</sup> and assuming the  $B_0$  value reported by Pety et al. (2012), the  $J = 4 \rightarrow 3$  transition will differ from that reported by Pety et al. (2012) by 0.9 MHz. The  $J = 5 \rightarrow 4$  transition will differ by 1.7 MHz,  $J = 6 \rightarrow 5$  by about 3.0 MHz, and these differences will continue to increase up to 23.4 MHz as  $J$  increases to the  $J = 12 \rightarrow 11$  transition. For high-resolution rotational spectroscopy, these large discrepancies are well outside of the precision present in most

spectrometers utilized in the laboratory and for observation of the ISM, and well outside the errors expected from state-of-the art *ab initio* calculations. For example, Brites & Jutier (2012) computed the rotational transitions of HCNH<sup>+</sup> with a six-dimensional PES from a CCSD(T)-F12A/cc-pCVTZ-F12 QFF for  $J = 1 \rightarrow 0$  up to  $J = 10 \rightarrow 9$  with errors ranging from 0.6 MHz to 4.84 MHz compared to experimental work (Amano et al. 2006). This comparison of theory and experiment again strongly supports our assertion that the assignment of the observations in the Horsehead Nebula PDR to  $l$ -C<sub>3</sub>H<sup>+</sup> are incorrect.

Similarly, the computed  $H_e$  value for  $l$ -C<sub>3</sub>H<sup>+</sup> is 0.375 mHz, while the third-order fit  $H$  obtained by Pety et al. (2012) is 0.56 Hz or 560 mHz. This represents three orders of magnitude difference between the two values. There are not as many comparisons in the literature between theoretical  $H_e$  values and experimental  $H$  values, but for acetylene,  $H_e$  has been computed to be 0.0380 Hz (Martin et al. 1998), while  $H$  has been experimentally determined to be 0.0480 Hz (Kabbadj et al. 1991), an error of 20.8%. Even if the computed  $H_e$  for  $l$ -C<sub>3</sub>H<sup>+</sup> is in error from the proper physical value by as much as 40%, this is only a minute step towards the value necessary to fit the lines observed. Admittedly, comparison of computed  $H_e$  values to experimental  $H$  constants has not been as common making the error range for the computed value less certain, but the substantially large difference between values here should be well-beyond the potential accuracy range for the computed  $H_e$ . This difference in the  $H$  constant casts further doubt on  $l$ -C<sub>3</sub>H<sup>+</sup> as the carrier of the observed transitions in the Horsehead nebula PDR.

Since the energy points necessary to define the QFF are computed within the Born-Oppenheimer approximation, the same QFF can also be used to produce VPT2 spectroscopic constants and vibrational frequencies for the isotopologues, as well. Thus, the spectroscopic constants of C<sub>3</sub>D<sup>+</sup>, <sup>13</sup>CCCH<sup>+</sup>, C<sup>13</sup>CCH<sup>+</sup>, and CC<sup>13</sup>CH<sup>+</sup> are listed in Table 2, and the fundamental vibrational frequencies are given in Table 3. These reference data



should aid in the analysis of further laboratory studies of interstellar reactions that create  $l\text{-C}_3\text{H}^+$ .

#### 4. Conclusions

Even though the CcCR VPT2 computed  $B_0$  rotational constant for  $l\text{-C}_3\text{H}^+$  differs by less than 20 MHz from that obtained by Pety et al. (2012) to assign lines in the Horsehead nebula PDR to this cation, the more substantial differences between the  $D$  and  $H$  constants strongly questions the assignment of  $l\text{-C}_3\text{H}^+$  to the observed lines. These large discrepancies, especially for the  $D$  constant, will alter the rotational spectrum of  $\tilde{X}^1\Sigma^+$   $\text{C}_3\text{H}^+$  by nearly 1 MHz for the lowest observed rotational transition,  $J = 4 \rightarrow 3$ , and by more than 23 MHz for the highest,  $J = 12 \rightarrow 11$ . Hence, the astronomical lines observed cannot be conclusively linked to this cation as the carrier.

It is hoped that the reference data provided here should assist in laboratory studies that can conclusively determine the rotational spectrum of  $l\text{-C}_3\text{H}^+$ . Additionally, the data are extended to the deuterated and  $^{13}\text{C}$  singly-substituted isotopologues as well.  $\text{C}_3\text{H}^+$  has long been hypothesized to exist in the ISM and is of significance in the carbon chemistry of space (Turner et al. 2000; Wakelam et al. 2010). There is little doubt that it should be present in ISM, but the attribution of the observed lines by Pety et al. (2012) to  $l\text{-C}_3\text{H}^+$  is questionable.

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Table 1: The simple-internal C<sub>3</sub>H<sup>+</sup> CcCR QFF Force Constants (in mdyn/Å<sup>n</sup>·rad<sup>m</sup>).

F <sub>11</sub>	5.810 273	F <sub>441</sub>	-0.1688	F <sub>2222</sub>	405.81	F <sub>5532</sub>	-0.16	F <sub>7511</sub>	0.28
F <sub>21</sub>	-0.214 189	F <sub>442</sub>	-0.6565	F <sub>3111</sub>	0.05	F <sub>5533</sub>	0.22	F <sub>7521</sub>	0.94
F <sub>22</sub>	13.840 846	F <sub>443</sub>	-0.1210	F <sub>3211</sub>	0.22	F <sub>5544</sub> <sup>a</sup>	0.41	F <sub>7522</sub>	-0.11
F <sub>31</sub>	0.075 121	F <sub>551</sub>	-0.1688	F <sub>3221</sub>	0.22	F <sub>5555</sub>	1.22	F <sub>7531</sub>	0.01
F <sub>32</sub>	0.116 818	F <sub>552</sub>	-0.6565	F <sub>3222</sub>	2.09	F <sub>6411</sub>	0.28	F <sub>7532</sub>	0.36
F <sub>33</sub>	8.520 119	F <sub>553</sub>	-0.1210	F <sub>3311</sub>	0.15	F <sub>6421</sub>	0.94	F <sub>7533</sub>	-0.35
F <sub>44</sub>	0.330 792	F <sub>641</sub>	-0.0004	F <sub>3321</sub>	0.30	F <sub>6422</sub>	-0.11	F <sub>7544</sub> <sup>a</sup>	-0.04
F <sub>55</sub>	0.330 792	F <sub>642</sub>	0.0412	F <sub>3322</sub>	-1.51	F <sub>6431</sub>	0.01	F <sub>7555</sub>	-0.11
F <sub>64</sub>	0.004 472	F <sub>643</sub>	0.1390	F <sub>3331</sub>	-0.05	F <sub>6432</sub>	0.36	F <sub>7654</sub> <sup>a</sup>	-0.05
F <sub>66</sub>	0.034 854	F <sub>661</sub>	-0.0212	F <sub>3332</sub>	-0.98	F <sub>6433</sub>	-0.35	F <sub>7665</sub> <sup>a</sup>	-0.03
F <sub>75</sub>	0.004 472	F <sub>662</sub>	-0.2630	F <sub>3333</sub>	245.44	F <sub>6444</sub>	-0.11	F <sub>7711</sub>	-0.08
F <sub>77</sub>	0.034 854	F <sub>663</sub>	0.0347	F <sub>4411</sub>	-0.08	F <sub>6554</sub> <sup>a</sup>	-0.04	F <sub>7721</sub>	0.10
F <sub>111</sub>	-33.4159	F <sub>751</sub>	-0.0004	F <sub>4421</sub>	0.45	F <sub>6611</sub>	-0.08	F <sub>7722</sub>	0.18
F <sub>211</sub>	0.1250	F <sub>752</sub>	0.0412	F <sub>4422</sub>	-0.18	F <sub>6621</sub>	0.10	F <sub>7731</sub>	0.11
F <sub>221</sub>	0.0463	F <sub>753</sub>	0.1390	F <sub>4431</sub>	-0.22	F <sub>6622</sub>	0.18	F <sub>7732</sub>	-0.38
F <sub>222</sub>	-82.4686	F <sub>771</sub>	-0.0212	F <sub>4432</sub>	-0.16	F <sub>6631</sub>	0.11	F <sub>7733</sub>	-0.19
F <sub>311</sub>	-0.0121	F <sub>772</sub>	-0.2630	F <sub>4433</sub>	0.22	F <sub>6632</sub>	-0.38	F <sub>7744</sub>	0.00
F <sub>321</sub>	-0.0241	F <sub>773</sub>	0.0347	F <sub>4444</sub>	1.22	F <sub>6633</sub>	-0.19	F <sub>7755</sub>	-0.10
F <sub>322</sub>	-0.7100	F <sub>1111</sub>	172.62	F <sub>5511</sub>	-0.08	F <sub>6644</sub>	-0.10	F <sub>7764</sub> <sup>a</sup>	-0.03
F <sub>331</sub>	-0.1360	F <sub>2111</sub>	0.14	F <sub>5521</sub>	0.45	F <sub>6655</sub>	0.00	F <sub>7766</sub> <sup>a</sup>	0.02
F <sub>332</sub>	-0.4027	F <sub>2211</sub>	-0.69	F <sub>5522</sub>	-0.18	F <sub>6664</sub>	-0.10	F <sub>7775</sub>	-0.10
F <sub>333</sub>	-49.4860	F <sub>2221</sub>	0.98	F <sub>5531</sub>	-0.22	F <sub>6666</sub>	0.06	F <sub>7777</sub>	0.06

<sup>a</sup>These necessary force constants are not symmetry-unique but are defined from relationships of other force constants. See Ref. 60 of Martin et al. (1998).

Table 2: The CcCR QFF Zero-Point ( $R_\alpha$  vibrationally-averaged) and Equilibrium Structures, Rotational Constants, CCSD(T)/aug-cc-pV5Z Dipole Moment, Vibration-Rotation Interaction Constants, and Quartic and Sextic Distortion Constants of linear  $\tilde{X}^1\Sigma^+ C_3H^+$ ,  $C_3D^+$ ,  $^{13}CCCH^+$ ,  $C^{13}CCH^+$ , and  $CC^{13}CH^+$ .

	$C_3H^+$	$C_3D^+$	$^{13}CCCH^+$	$C^{13}CCH^+$	$CC^{13}CH^+$
$r_0(C_1-H)$	1.069 951 Å	1.072 922 Å	1.067 560 Å	1.070 095 Å	1.069 996 Å
$r_0(C_1-C_2)$	1.230 766 Å	1.231 576 Å	1.230 543 Å	1.230 961 Å	1.230 903 Å
$r_0(C_2-C_3)$	1.332 581 Å	1.331 723 Å	1.332 879 Å	1.332 800 Å	1.332 416 Å
$B_0$	11 262.68 MHz	10 115.99 MHz	10 824.96 MHz	11 258.19 MHz	10 919.88 MHz
$\alpha^B_1$	33.5 MHz	49.0 MHz	31.5 MHz	33.2 MHz	30.6 MHz
$\alpha^B_2$	74.8 MHz	55.0 MHz	71.5 MHz	72.2 MHz	73.4 MHz
$\alpha^B_3$	37.1 MHz	30.1 MHz	35.4 MHz	37.2 MHz	35.1 MHz
$\alpha^B_4$	-2.6 MHz	-10.2 MHz	-2.3 MHz	-2.5 MHz	-1.7 MHz
$\alpha^B_5$	-157.3 MHz	-133.2 MHz	-151.2 MHz	-157.7 MHz	152.7 MHz
$\tau_{aaaa}^a$	-16.992 kHz	-12.991 kHz	-15.803 kHz	-16.988 kHz	-15.966 kHz
$r_e(C_1-H)^b$	1.078 961 Å	–	–	–	–
$r_e(C_1-C_2)$	1.235 360 Å	–	–	–	–
$r_e(C_2-C_3)$	1.339 841 Å	–	–	–	–
$B_e$	11 175.51 MHz	10 039.77 MHz	10 740.68 MHz	11 175.30 MHz	10 834.97 MHz
$D_e$	4.248 kHz	3.248 kHz	3.951 kHz	4.247 kHz	3.992 kHz
$H_e^c$	0.375 mHz	0.315 mHz	0.315 mHz	0.375 mHz	0.361 mHz
$\mu_z^d$	1.20 D	–	–	–	–

<sup>a</sup>Since this is a linear molecule,  $\tau_{aaaa} = \tau_{bbbb} = \tau_{aabb}$  while all other quartic centrifugal distortion constants are 0.0.

<sup>b</sup>The use of the Born-Oppenheimer approximation necessitates that the equilibrium geometry be the same for each isotopologue.

<sup>c</sup> $H_e = \Phi_{aaa} = \Phi_{bbb}$ , and all other sextic centrifugal distortion constants are 0.0.

<sup>d</sup>The  $C_3H^+$  coordinates (in Å with the center-of-mass at the origin) used to generate the Born-Oppenheimer dipole moment component are: H, 0.000000, 0.000000, -2.285175;  $C_1$ , 0.000000, 0.000000, -1.206214;  $C_2$ , 0.000000, 0.000000, 0.029147;  $C_3$ , 0.000000, 0.000000, 1.368989.

Table 3: The VPT2 CcCR QFF harmonic and anharmonic fundamental vibrational frequencies (in  $\text{cm}^{-1}$ ) for  $C_3H^+$ ,  $C_3D^+$ ,  $^{13}CCCH^+$ ,  $C^{13}CCH^+$ , and  $CC^{13}CH^+$ .

Mode	Description	$C_3H^+$		$C_3D^+$		$^{13}CCCH^+$		$C^{13}CCH^+$		$CC^{13}CH^+$	
		Harm.	Anharm.	Harm.	Anharm.	Harm.	Anharm.	Harm.	Anharm.	Harm.	Anharm.
$\nu_1(\sigma)$	$C_1-H$ stretch	3309.7	3167.8*	2580.0	2502.2	3309.7	3166.7*	3308.2	3163.7*	3293.1	3152.0*
$\nu_2(\sigma)$	$C_2-C_3$ stretch	2142.7	2096.3*	2015.5	1972.2	2136.4	2090.4*	2088.4	2044.9*	2126.1	2080.0*
$\nu_3(\sigma)$	$C_1-C_2$ stretch	1189.3	1194.1*	1162.8	1162.2	1161.3	1167.2*	1188.5	1191.2*	1172.7	1178.5*
$\nu_4(\pi)$	$H-C_1-C_2$ bend	805.8	782.3	641.7	625.8*	805.8	782.2	804.3	781.0	799.0	776.0
$\nu_5(\pi)$	$C_1-C_2-C_3$ bend	124.0	114.2	117.8	110.6*	123.2	113.4	121.0	111.2	123.7	114.1

\*Denotes states in Fermi resonance.



Fig. 1.— The CcCR equilibrium geometry of  $\tilde{X}^1\Sigma^+ \text{C}_3\text{H}^+$ .

