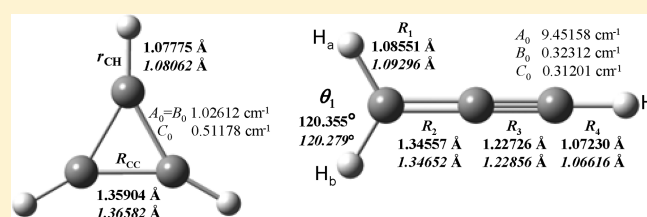


Highly Accurate Quartic Force Fields, Vibrational Frequencies,
and Spectroscopic Constants for Cyclic and Linear $C_3H_3^+$ Xinchuan Huang,^{†,‡} Peter R. Taylor,^{§,||} and Timothy J. Lee^{*,⊥}[†]SETI Institute, 189 Bernardo Avenue, Suite 100, Mountain View, California 94043, United States[§]Victorian Life Sciences Computation Initiative and Department of Chemistry, University of Melbourne, Victoria 3010, Australia[⊥]NASA Ames Research Center, Moffett Field, California 94035-1000, United States

ABSTRACT: High levels of theory have been used to compute quartic force fields (QFFs) for the cyclic and linear forms of the $C_3H_3^+$ molecular cation, referred to as $c-C_3H_3^+$ and $l-C_3H_3^+$. Specifically, the singles and doubles coupled-cluster method that includes a perturbational estimate of connected triple excitations, CCSD(T), has been used in conjunction with extrapolation to the one-particle basis set limit, and corrections for scalar relativity and core correlation have been included. The QFFs have been used to compute highly accurate fundamental vibrational frequencies and other spectroscopic constants by use of both vibrational second-order perturbation theory and variational methods to solve the nuclear Schrödinger equation. Agreement between our best computed fundamental vibrational frequencies and recent infrared photodissociation experiments is reasonable for most bands, but there are a few exceptions. Possible sources for the discrepancies are discussed. We determine the energy difference between the cyclic and linear forms of $C_3H_3^+$, obtaining 27.9 kcal/mol at 0 K, which should be the most reliable available. It is expected that the fundamental vibrational frequencies and spectroscopic constants presented here for $c-C_3H_3^+$ and $l-C_3H_3^+$ are the most reliable available for the free gas-phase species, and it is hoped that these will be useful in the assignment of future high-resolution laboratory experiments or astronomical observations.



1. INTRODUCTION

The two lowest energy forms of $C_3H_3^+$ are cyclopropenyl cation and propargyl cation, though the energy difference between these is large, with the cyclic form being approximately 26 kcal/mol lower in energy.¹ Cyclopropenyl cation is the smallest aromatic carbocation, which explains its stability, but it should be noted that even with this large energy difference, it is common to find both isomers when they are produced in the gas phase, suggesting that they form via different mechanisms. There has been considerable experimental and theoretical work on both isomers, and we refer the interested reader to refs 1–9 and references therein. Here, we discuss a few of the earlier works that relate to this study, but first we note that for convenience we shall refer to cyclopropenyl cation (cyclic form) as $c-C_3H_3^+$ and to propargyl cation (linear form) as $l-C_3H_3^+$, and when referring to both isomers we use $C_3H_3^+$.

Our interest in $c-C_3H_3^+$ stems from astrochemistry. Cyclopropenylidene, $c-C_3H_2$, which possesses a large dipole moment, has been shown to be ubiquitous in the interstellar medium (ISM),^{10–12} and its main formation pathway has been proposed to be due to dissociative recombination of an electron with $c-C_3H_3^+$.^{13,14} Hence there has been considerable interest in detecting $c-C_3H_3^+$ in the ISM for more than two decades. However, $c-C_3H_3^+$ possesses D_{3h} symmetry, resulting in no permanent dipole moment, and thus is not detectable via microwave (rotational) spectroscopy. Furthermore, there is no

experimental high-resolution rovibrational spectrum available to analyze astronomical observations. In fact, until recently there was no gas-phase spectrum of its vibrational frequencies, but instead only matrix isolation spectra or spectra from salts.^{15,16} That changed in 2002 when Dopfer and co-workers^{2–4} used infrared photodissociation (IRPD) experiments to observe the C–H stretching region of $C_3H_3^+$ complexed with various ligands. In 2010, Ricks et al.⁵ improved upon these experiments by measuring the gas-phase infrared (IR) spectrum of the isomers of $C_3H_3^+$ that were associated with one Ar atom. The results of these latter two studies are generally consistent with the matrix isolation experiments, though many more bands were assigned in the Ricks et al. IRPD experiment, going down to approximately 1100 cm^{-1} . One inconsistency that was noted by Ricks et al., however, was that the assignment for the doubly degenerate CH stretching mode, $\nu_4(e')$, at 3182 cm^{-1} was about 44 cm^{-1} higher than theory. They attributed this to problems in scaling factors for the theoretical calculations and suggested that further theoretical work was needed. Thus one of the purposes of the present study was to provide theoretical predictions of the fundamental vibrational frequencies of both $C_3H_3^+$ wherein scaling is not required.

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Determination of an anharmonic force field and fundamental vibrational frequencies has actually been reported for $c\text{-C}_3\text{H}_3^+$ in two 1989 studies by Lee et al.⁶ and by Xie and Boggs.⁷ Lee et al. computed a full quartic force field (QFF) at the Hartree–Fock level of theory to determine anharmonic corrections via second-order rovibrational perturbation theory, which they then appended to harmonic frequencies computed at the second-order Møller–Plesset (MP2) perturbation level of theory. They reported an array of spectroscopic constants from their anharmonic analysis including anharmonic constants, vibration–rotation interaction constants, and quartic and sextic centrifugal distortion constants for $c\text{-C}_3\text{H}_3^+$ and its deuterated isotopologues. One interesting issue they uncovered was the fact that the standard formula used to compute the spectroscopic constants for symmetric top molecules^{17–19} can be incorrect when there is a non-totally-symmetric, nondegenerate vibrational mode, as there is for $c\text{-C}_3\text{H}_3^+$. The issue was discussed in some detail, and Lee et al.⁶ confirmed the modifications they made to the standard symmetric top formula by slightly perturbing the mass of one atom, thereby slightly breaking the D_{3h} symmetry and forcing the SPECTRO program²⁰ to use an asymmetric top analysis. Xie and Boggs⁷ used the MP4(SDQ) level of theory (fourth-order Møller–Plesset perturbation theory including single, double, and quadruple excitations but excluding the more expensive triple excitations) to construct a partial potential energy surface that included diagonal force constants through sixth-order, but only second-order off-diagonal force constants (in a local internal coordinate system). They then used an approximate variational approach to solve the nuclear Schrödinger equation. A detailed comparison of the two studies was presented by Lee et al.⁶ In short, for the levels of theory used, both studies gave reasonable agreement with the matrix isolation experiments available at the time and with each other, though it is interesting to note that Lee et al. obtained 3178 cm^{-1} for $\nu_4(e')$ while Xie and Boggs obtained 3149 cm^{-1} .

The higher energy isomer, $l\text{-C}_3\text{H}_3^+$, has also received considerable attention from both theory and experiment. It was observed in both of the IRPD experiments mentioned above,^{2–5} and it has also been studied recently at high levels of theory by Botschwina and Oswald.⁸ Botschwina and Oswald used an explicitly correlated method, CCSD(T)-F12x ($x = a, b$),^{21,22} which is based on the singles and doubles coupled-cluster method that includes a perturbational correction for triple excitations, denoted CCSD(T).²³ They computed a five-dimensional potential energy function, involving the totally symmetric modes, which included up through sixth-order diagonal constants and up through fourth-order off-diagonal force constants, and they solved the nuclear Schrödinger equation variationally. The five dimensions included symmetric CH_2 stretch, free acetylenic CH stretch, CH_2 scissor mode, and the two CC stretching modes (a correction was applied to the antisymmetric CH_2 fundamental to account for the neglect of anharmonic coupling). Botschwina and Oswald⁸ found generally good agreement with the IRPD experiment of Ricks et al.⁵

More recently, Botschwina and Oswald⁹ used the CCSD(T)-F12x ($x = a, b$) levels of theory to examine the equilibrium structure and harmonic vibrational frequencies of Ar complexes of both $c\text{-C}_3\text{H}_3^+$ and $l\text{-C}_3\text{H}_3^+$. They located three distinct minima for Ar complexes of both isomers, though one of the C_s minima for $l\text{-C}_3\text{H}_3^+$ was noticeably lower in

energy than the other two minima. For the $c\text{-C}_3\text{H}_3^+$ isomer, all three minima were relatively close in energy. The results of this latter study reaffirmed the assignment by Botschwina and Oswald⁸ of the 3238 cm^{-1} band in the IRPD experiments of Ricks et al.⁵ to the acetylenic CH stretch vibration in $l\text{-C}_3\text{H}_3^+$.

The accuracy of state-of-the-art ab initio predictions for fundamental vibrational frequencies has improved considerably in the last 20 years, and it is common now to determine fundamental vibrational frequencies to within a few wavenumbers (cm^{-1}) of high-resolution experiments (for example, see refs 24–27). To this end, theoretical spectroscopists predicted more than a decade ago²⁸ that state-of-the-art ab initio predictions were becoming reliable enough that it should be possible to assign an astronomical spectrum by use of only ab initio predictions and without high-resolution laboratory experimental data for difficult species, such as small molecular anions and cations. This has now occurred only a few years ago when Cernicharo et al.²⁹ reported detecting the small molecular anion C_5N^- in the C-rich star IRC+10216 and based their assignment on the ab initio calculations of Aoki³⁰ and Botschwina and Oswald.³¹

Thus our goal in the present study is to compute highly accurate QFFs for the $c\text{-C}_3\text{H}_3^+$ and $l\text{-C}_3\text{H}_3^+$ molecules and to predict their rovibrational spectroscopic constants to very high accuracy. These data are of interest to astronomers now more than ever, given that the Herschel Space Observatory is in operation and collecting high-resolution data, the NASA Stratospheric Observatory for Infrared Astronomy (SOFIA) has begun its series of initial science flights, and the James Webb Space Telescope (JWST), often referred to as the replacement for the Hubble Space Telescope, will launch later in this decade. Furthermore, the Atacama Large Millimeter Array (ALMA) is set to start early science operations in late 2011. Some of the instruments for these telescopes operate at longer wavelengths and thus are not useful for rovibrational spectroscopy of $c\text{-C}_3\text{H}_3^+$, but they may be able to detect deuterium and ^{13}C isotopologues due to their increased sensitivity, which is especially interesting for isotopologues of $c\text{-C}_3\text{H}_3^+$. The parent isotopologue has no permanent dipole moment, and hence it cannot be observed via rotational spectroscopy, but isotopologues that do not retain D_{3h} symmetry will exhibit a small permanent dipole moment since the center of nuclear charge and center of mass of the molecule will no longer be the same (and the molecule rotates about its center of mass). For $l\text{-C}_3\text{H}_3^+$, the lowest energy vibration may be within range for instruments on all of the above telescopes, but since $l\text{-C}_3\text{H}_3^+$ possesses a permanent dipole moment, the parent isotopologue as well as all deuterium and ^{13}C isotopologues may be detectable. However, a full spectroscopic analysis of all deuterium and ^{13}C isotopologues of $c\text{-C}_3\text{H}_3^+$ and $l\text{-C}_3\text{H}_3^+$ is beyond the scope of the present study and will be reported separately.³²

2. THEORETICAL APPROACH

A. Details of Electronic Structure Methods. We first describe details of the electronic structure calculations, including details of the corrections that have been included. In general, we follow the approach we have developed in recent years,^{33,34} in which we extrapolate CCSD(T) energies to the one-particle basis set limit,³⁵ followed by addition of corrections for scalar

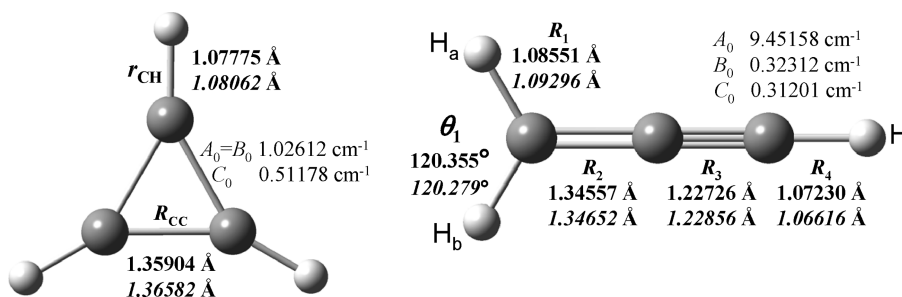


Figure 1. Equilibrium structures, vibrationally averaged structures (numbers in italic type), and rotational constants of $c\text{-C}_3\text{H}_3^+$ and $l\text{-C}_3\text{H}_3^+$, determined from our best QFF. See text for details.

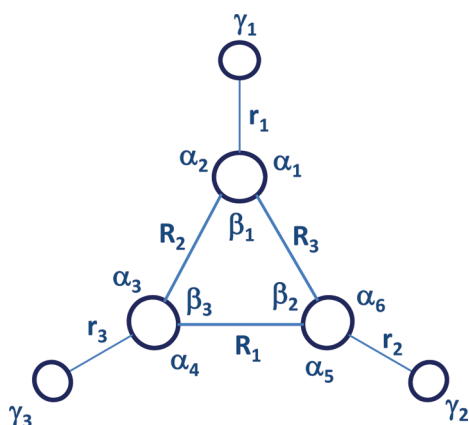


Figure 2. Internal coordinate definitions used for the $c\text{-C}_3\text{H}_3^+$ cation.

relativity³⁶ and core correlation. The valence CCSD(T) calculations were performed in conjunction with Dunning's correlation-consistent basis sets.³⁷ We will denote the cc-pVXZ ($X = \text{T}, \text{Q}$, or S) basis sets as TZ, QZ, or 5Z. A correction for scalar relativity is evaluated at the CCSD(T)/TZ level of theory by use of the Douglas–Kroll approximation.³⁶ As we pointed out previously,³³ the scalar relativity integrals lose precision beyond the TZ basis set, which is problematic for computing QFFs. Core correlation was included as a correction by performing CCSD(T) calculations, with and without the core correlated, with the Martin–Taylor basis set designed for this purpose.³⁸

QFFs have been determined according to the prescription described previously.^{33,34} For both $c\text{-C}_3\text{H}_3^+$ and $l\text{-C}_3\text{H}_3^+$, a reference geometry was determined at the CCSD(T)/5Z level of theory with corrections for core correlation and scalar relativity taken into account. A grid of displacement geometries centered on this reference structure (and based on the symmetry internal coordinates discussed later) was then used for all calculations. The number of unique geometries was 1961 and 2479 for $c\text{-C}_3\text{H}_3^+$ and $l\text{-C}_3\text{H}_3^+$, respectively. As indicated, CCSD(T) energies are extrapolated to the one-particle basis set limit by use of a three-point formula that experience has shown to be reliable.^{33,34,39} The scalar relativity and core-correlation corrections are added, and the energies are used in a least-squares fit of a QFF for each molecule. For $c\text{-C}_3\text{H}_3^+$, the 1961 unique energies were augmented to a redundant set of 3837 energies that was used to fit 460 unique coefficients in the QFF. The sum of the squared residuals was 1.31×10^{-17} a.u.². For $l\text{-C}_3\text{H}_3^+$, the

Table 1. Equilibrium Structure, Rotational Constants, and Harmonic Frequencies for $c\text{-C}_3\text{H}_3^+$ ^a

| Geometry Parameters | | |
|-------------------------------------|--|---------------------------|
| $R(\text{C}-\text{C})$ | | 1.359 036 3 Å |
| $r(\text{C}-\text{H})$ | | 1.077 746 1 Å |
| $A_e = B_e$ | | 1.032 60 cm^{-1} |
| C_e | | 0.51630 cm^{-1} |
| $\angle \text{C}-\text{C}-\text{H}$ | | 150.0° |
| $\angle \text{C}-\text{C}-\text{C}$ | | 60.0° |
| Harmonic Vibrational Frequencies | | |
| mode | symmetry and description | freq (cm^{-1}) |
| ω_1 | a_1' (breathing, C–H str – C–C str) | 3312.3 |
| ω_2 | a_1' (breathing, C–H str + C–C str) | 1650.8 |
| ω_3 | a_2' (in-plane internal torsion) | 1058.2 |
| ω_4 | e' (in-plane deformation) | 3265.1 |
| ω_5 | e' (in-plane wagging) | 1326.7 |
| ω_6 | e' (in-plane scissoring) | 946.0 |
| ω_7 | a_2'' (symmetric out-of-plane bends) | 764.5 |
| ω_8 | e'' (asymmetric out-of-plane bends) | 1023.4 |

^a Determined from our best QFF [CCSD(T)/cc-pV(T,Q,S)Z extrapolation + core-correlation + scalar relativistic corrections]. See text for more details.

2479 unique energies were augmented to a redundant set of 4565 energies that was used to fit 572 unique coefficients in the QFF (sum of the squared residuals = 2.61×10^{-17} a.u.²). The final QFF for each molecule was then obtained by an analytical transformation to the exact minimum (i.e., to where the gradient terms are exactly zero). We note that it has been shown that some molecules with C–C multiple bonds exhibit erratic behavior for bending frequencies, including molecules like acetylene, ethylene, and benzene,^{39–43} although cyclopropenylidene does not show this behavior.⁴⁴ The problem is associated with ensuring that the one-particle basis set is properly balanced with respect to saturation in the lower angular momentum functions (i.e., s and p functions) and inclusion of higher angular momentum functions. Though we report only our best QFF here for both $c\text{-C}_3\text{H}_3^+$ and $l\text{-C}_3\text{H}_3^+$, we have examined in detail several QFFs for both isomers and found that neither suffers from this issue. All electronic structure calculations were performed with the MOLPRO 2006.1 program.⁴⁵

B. Details of Coordinate Systems and Vibrational Methods. For both molecules, the QFFs were determined in symmetry

Table 2. Equilibrium Structure, Rotational Constants, and Harmonic Frequencies for $l\text{-C}_3\text{H}_3^+$ ^a

| Geometry Parameters | | |
|----------------------|--|---------------------------|
| R_1 | | 1.085 506 Å |
| R_2 | | 1.345 571 Å |
| R_3 | | 1.227 265 Å |
| R_4 | | 1.072 298 Å |
| θ_1 | | 120.355° |
| $\angle\text{C-C-H}$ | | 180.0° |
| $\angle\text{C-C-C}$ | | 180.0° |
| A_e | | 9.532 09 cm^{-1} |
| B_e | | 0.323 29 cm^{-1} |
| C_e | | 0.312 69 cm^{-1} |

| mode | Harmonic Vibrational Frequencies symmetry and description | freq (cm^{-1}) |
|---------------|--|---------------------------|
| ω_1 | a_1 (C-H str) | 3367.15 |
| ω_2 | a_1 (CH ₂ sym str) | 3122.73 |
| ω_3 | a_1 (C≡C str) | 2131.15 |
| ω_4 | a_1 (CH ₂ bending) | 1483.44 |
| ω_5 | a_1 (C-C str) | 1137.60 |
| ω_6 | b_1 (CH ₂ antisym str) | 3232.42 |
| ω_7 | b_1 (CH ₂ group rocking) | 1039.76 |
| ω_8 | b_1 (CCH in-plane linear bend) | 631.00 |
| ω_9 | b_1 (CCC in-plane linear bend) | 292.51 |
| ω_{10} | b_2 (CH ₂ out-of-plane wag) | 1120.50 |
| ω_{11} | b_2 (CCH out-of-plane linear bend) | 882.00 |
| ω_{12} | b_2 (CCC out-of-plane linear bend) | 254.71 |

^aDetermined from our best QFF [CCSD(T)/cc-pV(T,Q,S)Z extrapolation + core-correlation + scalar relativistic corrections]. See text and Figure 1 for more details and the definition of R_1 – R_4 and θ_1 .

internal coordinates. For $l\text{-C}_3\text{H}_3^+$, we use the following definition of symmetry internal coordinates:

$$\begin{aligned}
 S_1(A_1) &= R_4(\text{C-H}) \\
 S_2(A_1) &= (R_{1a} + R_{1b})/\sqrt{2} \\
 S_3(A_1) &= (R_2[\text{C=C}] + R_3[\text{C}\equiv\text{C}])/\sqrt{2} \\
 S_4(A_1) &= (R_2[\text{C=C}] - R_3[\text{C}\equiv\text{C}])/\sqrt{2} \\
 S_5(A_1) &= \theta_1(\angle\text{H}_a\text{CH}_b) \\
 S_6(B_1) &= (R_{1a} - R_{1b})/\sqrt{2} \\
 S_7(B_1) &= \text{LIN1}(\text{C-C-C}-\vec{r}_{\text{out}}) \\
 S_8(B_1) &= \text{LIN1}(\text{C-C-H}-\vec{r}_{\text{out}}) \\
 S_9(B_1) &= (\angle\text{H}_a\text{CC} - \angle\text{H}_b\text{CC})/\sqrt{2} \\
 S_{10}(B_2) &= \text{LIN1}(\text{C-C-C}-\vec{r}_{\text{in}}) \\
 S_{11}(B_2) &= \text{LIN1}(\text{C-C-H}-\vec{r}_{\text{in}}) \\
 S_{12}(B_2) &= \tau(\text{H}_a\text{-C-C-H}_b)
 \end{aligned}$$

where the simple internal coordinates for $l\text{-C}_3\text{H}_3^+$ are given in Figure 1. Note that S_7 and S_8 are in-plane bending modes and S_{10} and S_{11} are out-of plane bending modes. The definitions of $\text{LIN1}(\text{a-b-c-d})$ and $\tau(\text{a-b-c-d})$ are taken from the INTDER program:⁴⁶

$$\begin{aligned}
 \text{LIN1}(\text{a-b-c-d}) &= \sin^{-1} [\vec{e}_d (\vec{e}_{bc} \times \vec{e}_{ba})] \\
 \tau(\text{a-b-c-d}) &= \sin^{-1} [\vec{e}_{ba} (\vec{e}_{cb} \times \vec{e}_{cd}) / (\sin \phi_{abc} \sin \phi_{bcd})]
 \end{aligned}$$

where the \vec{e} are unit vectors defined as $\vec{e}_{ab} = \vec{e}_b - \vec{e}_a$. The reference vectors \vec{r}_{in} and \vec{r}_{out} were defined as follows:

$$\begin{aligned}
 \vec{r}_{\text{in}} &= \vec{R}_2 \times (\vec{R}_{1a} \times \vec{R}_{1b}) \\
 \vec{r}_{\text{out}} &= \vec{R}_2 \times \vec{r}_{\text{in}} = \vec{R}_2 \times [\vec{R}_2 \times (\vec{R}_{1a} \times \vec{R}_{1b})]
 \end{aligned}$$

Figure 1 also gives the planar equilibrium and ground-state (GS) vibrationally averaged structures for both $c\text{-C}_3\text{H}_3^+$ and $l\text{-C}_3\text{H}_3^+$, as well as the GS vibrationally averaged rotational

Table 3. Vibrationally Averaged Structure, Rotational Constants, and Vibrational Fundamental Frequencies for $c\text{-C}_3\text{H}_3^+$ ^a

| Zero-Point Structure and Rotational Constants | | | | | | |
|---|---|--|---------|--|---------------------------|---|
| | $R_c(\text{C-C})$ | | | | 1.365 823 4 Å | |
| | $R_c(\text{C-H})$ | | | | 1.080 620 4 Å | |
| | $A_0 = B_0$ | | | | 1.026 10 cm^{-1} | |
| | C_0 | | | | 0.511 78 cm^{-1} | |
| mode | 2nd-PT | Anharmonic Vibrational Analysis (cm^{-1}) | | | expt ^d | expt |
| | | VCI 4MR | VCI 5MR | | | |
| $\nu_1(a_1')$ | 3176.6, \rightarrow 3171.7 ^b | 3174.8 | 3175.4 | | 3183 | |
| $\nu_2(a_1')$ | 1618.3, \rightarrow 1620.7 ^c | 1622.0 | 1622.1 | | 1626 | |
| $\nu_3(a_2')$ | 1040.3 | 1039.3 | 1040.6 | | (1031) | |
| $\nu_4(e')$ | 3131.7 | 3133.8 | 3134.8 | | 3138 | 3182 ^e , 3125 \pm 4 ^f , 3129 ^g , 3130 ^h |
| $\nu_5(e')$ | 1299.6 | 1295.9 | 1296.2 | | 1290 | 1293 ^e |
| $\nu_6(e')$ | 924.2 | 925.9 | 927.0 | | 927 | |
| $\nu_7(a_2'')$ | 756.6 | 755.6 | 757.1 | | 758 | |
| $\nu_8(e'')$ | 1004.5 | 1000.9 | 1002.0 | | (990) | |
| ZPE | 9841.5 | 9833.2 | 9834.0 | | | |

^aDetermined from our best QFF; second-order perturbation theory (2nd PT) and vibrational variational CI results, where $n\text{MR}$ represents the highest mode coupling level in the potential term expansions, are presented and compared to experiment. See text for more details. ^bFermi type 1 resonance with $2\nu_2$. ^cFermi type 1 resonance with $2\nu_7$. ^dReferences 15 and 16. ^eReference 5 ^fReference 2 ^gReference 3 ^hReference 4

Table 4. α_{st} and g_{it} Anharmonic Constant Matrices for $c\text{-C}_3\text{H}_3^+$ ^a

| mode | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|------|---------|---------|--------|---------|--------|--------|--------|-------|
| 1 | -18.820 | | | | | | | |
| 2 | -2.749 | -3.596 | | | | | | |
| 3 | -6.862 | -3.610 | -1.030 | | | | | |
| 4 | -75.767 | -2.134 | -5.084 | -28.685 | | | | |
| 5 | 1.634 | -12.513 | -6.429 | 0.943 | -6.667 | | | |
| 6 | -7.881 | -2.876 | -1.420 | -6.993 | -3.418 | -1.647 | | |
| 7 | -7.703 | -3.452 | 0.727 | -6.373 | -0.076 | -1.681 | -1.811 | |
| 8 | -7.001 | -2.323 | 3.143 | -5.993 | 1.398 | 1.159 | -1.541 | 0.077 |

| mode | 4 | 5 | 6 | 8 |
|------|--------|--------|--------|-------|
| 4 | 9.532 | | | |
| 5 | -0.684 | 3.384 | | |
| 6 | 0.064 | -0.361 | 0.762 | |
| 8 | -0.073 | -0.287 | -0.182 | 0.578 |

^a Determined from our best QFF. All values are in cm^{-1} . See text for more details.

constants. The vibrationally averaged quantities are the “position average,” that is, r_z , computed from second-order perturbation theory. Symmetry relationships for the quadratic, cubic, and quartic force constants are given later.

For $c\text{-C}_3\text{H}_3^+$, we use the exact same definition of symmetry internal coordinates as given by Lee et al.⁶ They are repeated here for convenience:

$$\begin{aligned}
 S_1(a_1') &= (R_1 + R_2 + R_3)/\sqrt{3} \\
 S_2(a_1') &= (r_1 + r_2 + r_3)/\sqrt{3} \\
 S_3(a_2') &= (\alpha_1 + \alpha_3 + \alpha_5 - \alpha_2 - \alpha_4 - \alpha_6)/\sqrt{6} \\
 S_{4a}(e') &= (2r_1 - r_2 - r_3)/\sqrt{6} \\
 S_{5a}(e') &= (2\beta_1 - \beta_2 - \beta_3)/\sqrt{6} \\
 S_{6a}(e') &= (\alpha_1 + \alpha_2 + \alpha_4 + \alpha_5 - 2\alpha_3 - 2\alpha_6)/\sqrt{12} \\
 S_7(a_2'') &= (\gamma_1 + \gamma_2 + \gamma_3)/\sqrt{3} \\
 S_{8a}(e'') &= (2\gamma_1 - \gamma_2 - \gamma_3)/\sqrt{6} \\
 S_{4b}(e') &= (r_2 - r_3)/\sqrt{2} \\
 S_{5b}(e') &= (\beta_2 - \beta_3)/\sqrt{2} \\
 S_{6b}(e') &= (\alpha_2 + \alpha_5 - \alpha_1 - \alpha_4)/2 \\
 S_{8b}(e'') &= (\gamma_2 - \gamma_3)/\sqrt{2}
 \end{aligned}$$

where the simple internal coordinates R , r , α , and β are the bond lengths and bond angles defined in Figure 2, and γ refers to the out-of-plane bending angle for a given C–H bond with respect to the plane defined by the three C atoms (see Figure 2).

Fundamental vibrational frequencies were computed by use of either a vibrational variational method (VAR) or second-order perturbation theory (PT).^{17–19} The MULTIMODE program⁴⁷ was used for the VAR calculations, while the SPECTRO program²⁰ was used for the PT calculations and for computing other spectroscopic constants. For $l\text{-C}_3\text{H}_3^+$, the QFF was analytically transformed into a simple-internal, Morse-cosine coordinate system for the vibrational variational calculations. The benefits of using Morse coordinates for the stretches when a QFF is used in vibrational variational calculations can be traced back to Meyer et al.⁴⁸ and Carter and Handy⁴⁹ more than 20 years ago. Later, in 1994, Dateo et al.⁵⁰ first defined the Morse β parameter solely on the

computed force constants (i.e., $\beta = -F_{iii}/3F_{ii}$) instead of optimizing it with respect to experimental data. We follow this β definition, which requires that the transformed diagonal cubic force constant for the stretch vanish. For $c\text{-C}_3\text{H}_3^+$, it is necessary to use a symmetry-adapted Morse-cosine coordinate system (for the stretches and bends) because it is a ringed system. In addition, instead of the out-of-plane coordinates (S_7 , S_{8a} , and S_{8b}), we use the sine of these coordinates. Rather than transforming the symmetry internal coordinate QFF into the symmetry-adapted Morse-cosine-sine coordinate system, we refit the QFF. We note that transformation of the QFF into a Morse-cosine coordinate system is important (and in the case of $c\text{-C}_3\text{H}_3^+$, a Morse-cosine-sine coordinate system), otherwise some fundamental vibrational frequencies, in particular stretching frequencies, can be too high by tens of cm^{-1} . As discussed in ref 50, the Morse-cosine coordinate system serves to build in the correct limiting behavior for the potential function.

3. RESULTS AND DISCUSSION

A. Equilibrium Structures and Harmonic Frequencies. The equilibrium structure, equilibrium rotational constants, and harmonic frequencies for $c\text{-C}_3\text{H}_3^+$ and $l\text{-C}_3\text{H}_3^+$ are presented in Tables 1 and 2, respectively. The equilibrium structures obtained in this work have somewhat shorter bond distances relative to those published recently^{8,9} using CCSD(T*)-F12a, and the HCH angle determined here for $l\text{-C}_3\text{H}_3^+$ is about 1° larger. We note that the longer C–C bond in $l\text{-C}_3\text{H}_3^+$, R_2 (see Figure 1), is intermediate between a typical double and single bond length, but it is much closer to that in ethylene rather than ethane. Conversely, the corresponding harmonic frequency ω_4 is intermediate between a typical double bond and a single bond, but its value is closer to that for ethane rather than ethylene. Previous authors have referred to this C–C bond as a “single bond,” so we adopt that terminology here, but we note that it is intermediate between a single and double bond, which also means that there will not be free rotation of the terminal CH_2 group about this bond. The shorter C–C bond is very much like a typical triple bond both in its bond length and harmonic frequency.

The harmonic frequencies obtained here for $l\text{-C}_3\text{H}_3^+$ are in reasonable agreement with those given by Botschwina and Oswald,⁸ though our stretching harmonic frequencies are generally a few cm^{-1} higher, consistent with the shorter bond lengths obtained in the present work. We note that we use a different convention for the symmetry labeling of the modes relative to refs 5 and 8—essentially the B_1 and B_2 labels are reversed. That is, following the convention that Herzberg used for C_{2v} planar molecules, B_1 is used for in-plane antisymmetric modes and B_2 is reserved for out-of-plane vibrations, and that is the convention adopted here. For $c\text{-C}_3\text{H}_3^+$, the harmonic frequencies given in Table 1 are in reasonable agreement with the MP2 values from ref 6 and the MP4(SDQ) values of ref 7, given the differences in levels of theory.

As indicated previously, the energy difference between $c\text{-C}_3\text{H}_3^+$ and $l\text{-C}_3\text{H}_3^+$ is about 26 kcal/mol, but the levels of theory used in the present study should yield a much more definitive value. The energies that we obtain at the minimum are $-115.764\,746\,766\,2E_h$ and $-115.717\,377\,491E_h$ for $c\text{-C}_3\text{H}_3^+$ and $l\text{-C}_3\text{H}_3^+$, respectively. The electronic energy difference is thus $10\,396.4\text{ cm}^{-1}$. The anharmonic zero-point energies given by second-order PT are 9841.5 and 9208.0 cm^{-1} , which includes

Table 5. Vibration–Rotation Interaction Constants and Quartic and Sextic Centrifugal Distortion Constants for $c\text{-C}_3\text{H}_3^+$.^a

| mode | vib–rot constant (MHz) | | distortion constant | | Watson S reduction | | | | | |
|------|---------------------------|------------|------------------------|--------|-----------------------|--------|----------|--------|----------|--------|
| | α^B | α^C | (MHz) | (Hz) | (MHz) | (Hz) | | | | |
| 1 | 92.1 | 45.9 | τ'_{aaaa} | −0.291 | Φ_{aaa} | 0.183 | D_J | 0.073 | H_J | 0.259 |
| 2 | 90.0 | 44.9 | τ'_{bbbb} | −0.291 | Φ_{bbb} | 0.335 | D_{JK} | −0.122 | H_{JK} | −1.119 |
| 3 | −13.8 ^b | 16.6 | τ'_{cccc} | −0.023 | Φ_{ccc} | 0.001 | D_K | 0.055 | H_{KJ} | 1.466 |
| 4 | 85.7 | 42.2 | τ'_{aabb} | −0.291 | Φ_{aab} | 0.956 | d_1 | 0.000 | H_K | −0.605 |
| 5 | −15.2 | 42.1 | τ'_{aacc} | −0.047 | Φ_{abb} | −0.179 | d_2 | 0.000 | h_1 | 0.000 |
| 6 | 137.8 ^b | 21.7 | τ'_{bbcc} | −0.047 | Φ_{aac} | −0.171 | | | h_2 | 0.000 |
| 7 | −109.8 ^b | −10.9 | | | Φ_{acc} | 0.002 | | | h_3 | −0.038 |
| 8 | 23.7 ^b | −26.4 | | | Φ_{bcc} | 0.002 | | | | |
| | | | | | Φ_{bbc} | −0.171 | | | | |
| | | | | | Φ_{abc} | −0.342 | | | | |

^a See text for more details. ^b Modes for which Coriolis resonance has been taken into account.

the E_0 term (the polyatomic equivalent of the a_0 Dunham coefficient for diatomics).⁵¹ The corresponding MULTIMODE zero-point energies are 9834.0 and 9189.1 cm^{-1} , for $c\text{-C}_3\text{H}_3^+$ and $l\text{-C}_3\text{H}_3^+$, respectively. The 0 K energy difference we obtain is 27.9 kcal/mol, which is slightly larger than what has been reported experimentally.¹ While the experimental value is not at 0 K, it also has a few kilocalories per mole uncertainty; see ref 1 and references therein for more details. The 27.9 kcal/mol 0 K value obtained in the present work should be the most reliable available.

B. Fundamental Vibrational Frequencies and Spectroscopic Constants. The GS vibrationally averaged structure and rotational constants, and the fundamental vibrational frequencies obtained for $c\text{-C}_3\text{H}_3^+$ in the present work are presented in Table 3. Other spectroscopic constants obtained from second-order perturbation theory are presented in Table 4 (anharmonic constants) and Table 5 (vibration–rotation interaction constants, and quartic and sextic centrifugal distortion constants). For the variational calculations, we used four-mode and five-mode coupling in order to demonstrate the convergence. Comparison of the fundamental vibrational frequencies for the two columns labeled VCI 4MR and VCI 5MR shows that indeed there is excellent convergence, with the largest difference being only 1.5 cm^{-1} for ν_7 . 4MR/5MR refer to the number of modes coupled in the potential energy expansion formula, while four-mode coupling was adopted in all Coriolis integrations. For most vibrational modes, the difference is 1.1 cm^{-1} or less, and for three of the modes the difference is less than 1 cm^{-1} . On the basis of these comparisons and experience, we would estimate that the variational fundamentals are converged to better than 1.0 cm^{-1} for the VCI 5MR values. Comparison of the VCI 5MR results with the fundamentals obtained from second-order perturbation theory shows good agreement between the two approaches, with the differences being consistent with what we usually find for tightly bound molecules that do not possess a large-amplitude motion. Specifically, the largest difference is 3.8 cm^{-1} for ν_2 , but this mode is affected by a Fermi type 1 resonance with $2\nu_7$. For most of the vibrational modes the difference is less than 3 cm^{-1} , again showing that second-order perturbation theory is a good approximation for solving the nuclear Schrödinger equation for a tightly bound molecule.

Our best results should be the VCI 5MR fundamentals. Comparison of these to the available experimental data shows

Table 6. Vibrationally Averaged Structure, Rotational Constants, and Vibrational Fundamental Frequencies for $l\text{-C}_3\text{H}_3^+$.^a

| Zero-Point Structure and Rotational Constants | | | | |
|--|----------------|----------------|---------------------------|--|
| R_1 | 1.095 770 Å | θ_1 | 120.284° | |
| R_2 | 1.353 993 Å | A_0 | 9.403 57 cm^{-1} | |
| R_3 | 1.236 271 Å | B_0 | 0.319 56 cm^{-1} | |
| R_4 | 1.068 242 Å | C_0 | 0.308 61 cm^{-1} | |
| Anharmonic Vibrational Analysis (cm^{-1}) | | | | |
| | 2nd PT | Variational CI | | |
| | | 4MR | 5MR | expt ^e |
| $\nu_1 (A_1)$ | 3228.7 | 3238.9 | 3239.0 | 3138, 3139 ^f |
| $\nu_2^b (A_1)$ | 2997.0 | 2999.2 | 2998.7 | 3004 |
| $\nu_3 (A_1)$ | 2084.0 | 2082.2 | 2082.2 | 2077 |
| $\nu_4 (A_1)$ | 1429.8 | 1433.7 | 1434.4 | 1445 |
| $\nu_5^c (A_1)$ | 1128.5 | 1131.9 | 1131.8 | 1222 |
| $\nu_6^d (B_1)$ | 3061.9, 3097.6 | 3070.8, 3104.5 | 3071.0, 3105.0 | 3093, 3113 ^g |
| $\nu_7 (B_1)$ | 998.0 | 999.8 | 1000.6 | |
| $\nu_8 (B_1)$ | 598.0 | 607.8 | 607.7 | |
| $\nu_9 (B_1)$ | 294.0 | 294.2 | 294.8 | |
| $\nu_{10} (B_2)$ | 1054.6 | 1057.9 | 1058.1 | 1111 |
| $\nu_{11} (B_2)$ | 859.7 | 861.8 | 861.9 | |
| $\nu_{12} (B_2)$ | 249.3 | 251.8 | 251.7 | |
| $2\nu_4$ | 2836.9 | 2856.8 | 2857.8 | 2878 |
| $\nu_{12} + \nu_4$ | 1676.4 | 1695.2 | 1695.5 | 1755 |
| $\nu_5 + \nu_3$ | 3193.4 | 3202.0 | 3201.8 | 3191/3243 ^g , 3184/3238 ^h |

^a Determined from our best QFF. Second-order perturbation theory (2nd PT) and vibrational variational CI results, where n MR represents the highest mode coupling level in the potential term expansions, are presented and compared to experiment. See text for more details and Figure 1 for coordinate definition. ^b Fermi resonance type 1 with $2\nu_4$. ^c Fermi resonance type 2 with $\nu_{11} + \nu_{12}$. ^d Fermi resonance type 2 with $\nu_3 + \nu_7$. ^e Reference 5. ^f Reference 2. ^g Reference 3. ^h Reference 4.

reasonable agreement for the matrix isolation values where we might expect differences of up to 20 cm^{-1} or so due to a matrix shift. In fact, the largest differences between the matrix isolation

Table 7. Matrix of Anharmonic Constants α_{st} for $\text{l-C}_3\text{H}_3^+$ ^a

| mode | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|------|---------|----------|---------|---------|--------|---------|--------|---------|--------|---------|--------|--------|
| 1 | -54.889 | | | | | | | | | | | |
| 2 | -0.146 | -27.831 | | | | | | | | | | |
| 3 | -5.779 | -1.751 | -8.478 | | | | | | | | | |
| 4 | -1.230 | -31.736 | -3.781 | -2.102 | | | | | | | | |
| 5 | 1.635 | -2.248 | -15.680 | -3.110 | -0.881 | | | | | | | |
| 6 | -0.335 | -113.563 | -0.901 | -21.757 | -1.314 | -32.215 | | | | | | |
| 7 | -1.719 | -11.150 | -2.502 | -17.450 | -2.595 | -11.681 | -3.844 | | | | | |
| 8 | -20.642 | -2.628 | -11.108 | -6.735 | -2.675 | -2.796 | -8.808 | -5.238 | | | | |
| 9 | -2.301 | -0.575 | -8.408 | -2.241 | 3.420 | -0.498 | -1.749 | -2.636 | -0.679 | | | |
| 10 | -3.339 | -10.399 | -6.230 | -5.004 | -3.113 | -20.36 | -4.794 | -16.356 | -2.625 | -9.210 | | |
| 11 | -20.948 | -1.829 | 0.992 | -2.515 | -3.018 | -1.529 | -3.121 | 27.704 | 1.906 | -13.415 | -6.040 | |
| 12 | -2.493 | -1.797 | -5.193 | -3.296 | 7.240 | -1.374 | -2.602 | 1.710 | 21.446 | -9.393 | -4.744 | -2.569 |

^a Determined from our best QFF. All values are in cm^{-1} . See text for more details.

Table 8. Vibration–Rotation Interaction Constants and Quartic and Sextic Centrifugal Distorsion Constants for $\text{l-C}_3\text{H}_3^+$ ^a

| mode | vib–rot constants (MHz) | | | distorsion constants | | | Watson S reduction | | | | |
|------|-------------------------|----------------------|----------------------|----------------------|---------|--------------|--------------------|----------|--------|----------|-----------|
| | α^A | α^B | α^C | (MHz) | (Hz) | (MHz) | (Hz) | (MHz) | (Hz) | | |
| 1 | -21.277 | 25.909 | 24.454 | τ'_{aaaa} | -85.377 | Φ_{aaa} | 4809.680 | D_J | 0.003 | H_J | -0.001 |
| 2 | 4879.106 | 6.846 | 11.688 | τ'_{bbbb} | -0.012 | Φ_{bbb} | 0.000 | D_{JK} | 0.479 | H_{JK} | 4.988 |
| 3 | 151.243 | 55.273 | 51.836 | τ'_{cccc} | -0.010 | Φ_{ccc} | 0.000 | D_{Kc} | 20.862 | H_{Kc} | -2267.423 |
| 4 | -3188.803 | 3.755 ^b | 11.156 | τ'_{aabb} | -1.931 | Φ_{aab} | -742.911 | d_1 | -0.000 | H_K | 7072.116 |
| 5 | 225.856 | 23.754 ^b | 24.150 ^b | τ'_{aacc} | -0.007 | Φ_{abb} | 5.534 | d_2 | -0.000 | h_1 | -0.000 |
| 6 | 3052.329 | 8.691 | 9.786 | τ'_{bbcc} | -0.011 | Φ_{aac} | -1515.360 | | | h_2 | 0.001 |
| 7 | -3310.921 ^b | -8.912 | 6.571 ^b | | | Φ_{acc} | -0.059 | | | h_3 | 0.000 |
| 8 | 336.274 ^b | -12.094 | -0.485 | | | Φ_{bcc} | 0.000 | | | | |
| 9 | -2468.800 ^b | -54.337 | -24.327 ^b | | | Φ_{bbc} | -0.001 | | | | |
| 10 | 3490.356 ^b | 0.795 ^b | -5.110 | | | Φ_{abc} | 5.962 | | | | |
| 11 | 403.182 ^b | 2.727 | -6.288 | | | | | | | | |
| 12 | 1278.499 ^b | -42.247 ^b | -62.886 | | | | | | | | |

^a See text for more details. ^b Modes for which Coriolis resonance has been taken into account.

Table 9. Complete Set of Non-Zero Quadratic and Cubic Force Constants for $\text{c-C}_3\text{H}_3^+$ in a Symmetry Internal Coordinate System^a

| | | | | | |
|---------------------|------------|--|----------|-------------------------------------|---------|
| F_{11} | 7.217 432 | $F_{441} = F_{4b4b1}$ | -0.1448 | $F_{655} = -F_{6sb5b} = -F_{6bs5b}$ | -0.4172 |
| F_{21} | -0.098 532 | $F_{442} = F_{4b4b2}$ | -19.1998 | $F_{65b3} = -F_{6bs3}$ | 0.3817 |
| F_{22} | 5.798 770 | $F_{444} = -F_{44b4b}$ | -13.5720 | | |
| F_{33} | 0.262 156 | $F_{541} = F_{5b4b1}$ | 0.2160 | $F_{661} = F_{6b6b1}$ | -0.1679 |
| $F_{44} = F_{4b4b}$ | 5.800 512 | $F_{542} = F_{5b4b2}$ | -0.1399 | $F_{662} = F_{6b6b2}$ | -0.0729 |
| $F_{54} = F_{5b4b}$ | -0.009 810 | $F_{544} = -F_{54b4b} = -F_{5b44b}$ | -0.0774 | $F_{664} = -F_{6b64b} = -F_{6b6b4}$ | 0.0495 |
| $F_{55} = F_{5b5b}$ | 5.316 006 | $F_{54b3} = -F_{5b43}$ | -0.1386 | $F_{665} = -F_{6b65b} = -F_{6b6b5}$ | -0.2352 |
| $F_{64} = F_{6b4b}$ | 0.017 754 | $F_{551} = F_{5b5b1}$ | -13.225 | $F_{666} = -F_{6b6b6}$ | 0.0959 |
| $F_{65} = F_{6b5b}$ | 0.298 226 | $F_{552} = F_{5b5b2}$ | -0.2622 | F_{771} | -0.2385 |
| $F_{66} = F_{6b6b}$ | 0.414 829 | $F_{554} = -F_{5b54b} = -F_{5b5b4}$ | -0.1110 | F_{772} | -0.0827 |
| F_{77} | 0.371 862 | $F_{555} = -F_{5b5b5}$ | -18.9961 | $F_{874} = F_{8b74b}$ | -0.0760 |
| $F_{88} = F_{8b8b}$ | 0.490 412 | $F_{641} = F_{6b4b1}$ | -0.0146 | $F_{875} = F_{8b75b}$ | 0.3281 |
| F_{111} | -22.5615 | $F_{642} = F_{6b4b2}$ | -0.0009 | $F_{876} = F_{8b76b}$ | 0.2836 |
| F_{211} | -0.1640 | $F_{644} = -F_{64b4b} = -F_{6b4b4}$ | 0.0073 | $F_{881} = F_{8b8b1}$ | -0.4132 |
| F_{221} | 0.1680 | $F_{64b3} = -F_{6b43}$ | -0.0602 | $F_{882} = F_{8b8b2}$ | -0.1193 |
| F_{222} | -19.2136 | $F_{651} = F_{6b5b1}$ | -0.1032 | $F_{884} = -F_{8b84b} = -F_{8b8b4}$ | -0.0776 |
| F_{331} | -0.2589 | $F_{652} = F_{6b5b2}$ | -0.1790 | $F_{885} = -F_{8b85b} = -F_{8b8b5}$ | 0.3106 |
| F_{332} | -0.0596 | $F_{654} = -F_{6b5b4} = -F_{6b5b4b} = -F_{6b5b4b}$ | 0.1160 | $F_{886} = -F_{8b86b} = -F_{8b8b6}$ | 0.2418 |

^a See text for more details. Units of force constants are $\text{mdyn}/\text{\AA}^n \cdot \text{rad}^m$ appropriate for an energy unit of $\text{mdyn} \cdot \text{\AA}$ ($1 \text{mdyn} \cdot \text{\AA} \equiv 1 \text{ aJ}$).

Table 10. Complete Set of Non-Zero Quartic Force Constants for $c\text{-C}_3\text{H}_3^+$ in a Symmetry Internal Coordinate System^a

| | | | | | |
|-----------------------------|-------|----------------------------|-------|---|-------|
| F_{1111} | 59.44 | $F_{6654} = F_{6b6b5b4b}$ | -0.02 | $F_{875b3} = -F_{8b753}$ | -0.11 |
| F_{2111} | 0.20 | $F_{6655} = F_{6b6b5b5b}$ | 0.07 | $F_{876b3} = -F_{8b763}$ | -0.79 |
| F_{2211} | -0.45 | $F_{665b4b} = F_{6b6b54}$ | -0.14 | $F_{8887} = -F_{8b8b87}$ | 0.57 |
| F_{2221} | -0.35 | $F_{665b5b} = F_{6b6b55}$ | 0.06 | $F_{4444} = F_{4b4b4b4b} = 3F_{4b4b44}$ | 85.18 |
| F_{2222} | 56.66 | $F_{7744} = F_{774b4b}$ | -0.11 | $F_{5555} = F_{5b5b5b5b} = 3F_{5b5b55}$ | 92.62 |
| F_{3311} | 0.02 | $F_{7754} = F_{775b4b}$ | -0.04 | $F_{6666} = F_{6b6b6b6b} = 3F_{6b6b66}$ | -0.16 |
| F_{3321} | 0.11 | $F_{7755} = F_{775b5b}$ | -0.02 | $F_{8888} = F_{8b8b8b8b} = 3F_{8b8b88}$ | 0.43 |
| F_{3322} | -0.00 | $F_{7764} = F_{776b4b}$ | 0.03 | $F_{5444} = F_{5b4b4b4b} = 3F_{5b4b44} = 3F_{54b4b4}$ | 0.55 |
| F_{3333} | 0.04 | $F_{7765} = F_{776b5b}$ | 0.03 | $F_{5554} = F_{5b5b5b4b} = 3F_{5b5b54} = 3F_{5b554b}$ | -0.50 |
| F_{7711} | -0.11 | $F_{7766} = F_{776b6b}$ | 0.94 | $F_{6444} = F_{6b4b4b4b} = 3F_{64b4b4} = 3F_{6b4b44}$ | 0.05 |
| F_{7721} | 0.15 | $F_{8741} = F_{8b74b1}$ | 0.15 | $F_{6555} = F_{6b5b5b5b} = 3F_{6b5b55} = 3F_{6b5b55}$ | 0.55 |
| F_{7722} | -0.10 | $F_{8742} = F_{8b74b2}$ | -0.09 | $F_{6664} = F_{6b6b6b4b} = 3F_{64b6b4} = 3F_{6b6b4b}$ | 0.19 |
| F_{7733} | 0.67 | $F_{8751} = F_{8b75b1}$ | -0.18 | $F_{6665} = F_{6b6b6b5b} = 3F_{64b6b5} = 3F_{6b6b65}$ | 0.19 |
| F_{774b3} | -0.02 | $F_{8752} = F_{8b75b2}$ | -0.10 | $F_{5441} = -F_{54b4b1} = -F_{5b4b41}$ | 0.09 |
| F_{775b3} | 0.01 | $F_{8761} = F_{8b76b1}$ | -0.11 | $F_{5442} = -F_{54b4b2} = -F_{5b4b42}$ | 0.21 |
| F_{776b3} | 0.04 | $F_{8762} = F_{8b76b2}$ | -0.08 | $F_{54b43} = F_{5b443} = -F_{5b4b43}$ | 0.04 |
| F_{7777} | 0.09 | $F_{8811} = F_{8b8b11}$ | -0.08 | $F_{5541} = -F_{5b5b41} = -F_{5b54b1}$ | 0.14 |
| $F_{4411} = F_{4b4b11}$ | -0.37 | $F_{8821} = F_{8b8b21}$ | 0.26 | $F_{5542} = -F_{5b5b42} = -F_{5b542}$ | 0.02 |
| $F_{4421} = F_{4b4b21}$ | -0.42 | $F_{8822} = F_{8b8b22}$ | -0.11 | $F_{554b3} = F_{5b543} = -F_{5b5b4b3}$ | 0.28 |
| $F_{4422} = F_{4b4b22}$ | 56.74 | $F_{8833} = F_{8b8b33}$ | 0.62 | $F_{6441} = -F_{64b4b1} = -F_{6b4b41}$ | -0.01 |
| $F_{4433} = F_{4b4b33}$ | -0.00 | $F_{8844} = F_{8b8b4b4b}$ | -0.14 | $F_{6442} = -F_{64b4b2} = -F_{6b4b42}$ | 0.03 |
| $F_{5411} = F_{5b4b11}$ | -0.26 | $F_{884b4b} = F_{8b8b44}$ | -0.01 | $F_{64b43} = F_{6b443} = -F_{6b4b4b3}$ | 0.05 |
| $F_{5421} = F_{5b4b21}$ | 0.18 | $F_{8854} = F_{8b8b5b4b}$ | 0.03 | $F_{6551} = -F_{6b5b5b1} = -F_{6b5b51}$ | -0.10 |
| $F_{5422} = F_{5b4b22}$ | 0.35 | $F_{8855} = F_{8b8b5b5b}$ | -0.45 | $F_{6552} = -F_{6b5b5b2} = -F_{6b5b52}$ | 0.26 |
| $F_{5433} = F_{5b4b33}$ | -0.02 | $F_{885b4b} = F_{8b8b54}$ | -0.11 | $F_{65b53} = F_{6b5b53} = -F_{6b5b5b3}$ | 0.24 |
| $F_{5511} = F_{5b5b11}$ | 20.59 | $F_{885b5b} = F_{8b8b55}$ | 0.55 | $F_{6641} = -F_{6b6b41} = -F_{6b64b1}$ | -0.04 |
| $F_{5521} = F_{5b5b21}$ | 0.50 | $F_{8864} = F_{8b8b6b4b}$ | -0.03 | $F_{6642} = -F_{6b6b42} = -F_{6b64b2}$ | 0.11 |
| $F_{5522} = F_{5b5b22}$ | -0.34 | $F_{8865} = F_{8b8b6b5b}$ | -0.20 | $F_{664b3} = F_{6b643} = -F_{6b6b4b3}$ | -0.02 |
| $F_{5533} = F_{5b5b33}$ | -0.14 | $F_{8866} = F_{8b8b6b6b}$ | 0.43 | $F_{6651} = -F_{6b6b5b1} = -F_{6b6b51}$ | 0.01 |
| $F_{5544} = F_{5b5b44}$ | -0.33 | $F_{886b4b} = F_{8b8b64}$ | -0.00 | $F_{6652} = -F_{6b6b5b2} = -F_{6b6b52}$ | 0.06 |
| $F_{554b4b} = F_{5b5b4b4b}$ | -0.34 | $F_{886b5b} = F_{8b8b65}$ | 0.22 | $F_{665b3} = F_{6b653} = -F_{6b6b5b3}$ | 0.08 |
| $F_{6411} = F_{6b4b11}$ | 0.05 | $F_{886b6b} = F_{8b8b66}$ | 1.39 | $F_{8744} = -F_{874b4b} = -F_{8b74b4}$ | -0.05 |
| $F_{6421} = F_{6b4b21}$ | 0.02 | $F_{8877} = F_{8b8b77}$ | 0.47 | $F_{8755} = -F_{875b5b} = -F_{8b75b5}$ | -0.76 |
| $F_{6422} = F_{6b4b22}$ | 0.05 | $F_{4441} = -F_{4b4b41}$ | -0.30 | $F_{8766} = -F_{876b6b} = -F_{8b76b6}$ | -0.68 |
| $F_{6433} = F_{6b4b33}$ | 0.01 | $F_{4442} = -F_{4b4b42}$ | 40.12 | $F_{8841} = -F_{8b84b1} = -F_{8b8b41}$ | 0.12 |
| $F_{6511} = F_{6b5b11}$ | -0.22 | $F_{4b443} = -F_{4b4b4b3}$ | 0.00 | $F_{8842} = -F_{8b84b2} = -F_{8b8b42}$ | -0.06 |
| $F_{6521} = F_{6b5b21}$ | 0.03 | $F_{54b31} = -F_{5b431}$ | 0.14 | $F_{884b3} = F_{8b843} = -F_{8b8b4b3}$ | -0.03 |
| $F_{6522} = F_{6b5b22}$ | -0.16 | $F_{54b32} = -F_{5b432}$ | -0.08 | $F_{8851} = -F_{8b85b1} = -F_{8b8b51}$ | -0.41 |
| $F_{6533} = F_{6b5b33}$ | 0.04 | $F_{5551} = -F_{5b5b51}$ | 38.85 | $F_{8852} = -F_{8b85b2} = -F_{8b8b52}$ | -0.40 |
| $F_{6544} = F_{6b5b4b4b}$ | -0.10 | $F_{5552} = -F_{5b5b52}$ | 0.06 | $F_{885b3} = F_{8b853} = -F_{8b8b5b3}$ | -0.22 |
| $F_{654b4b} = F_{6b5b44}$ | -0.13 | $F_{5b553} = -F_{5b5b5b3}$ | -0.18 | $F_{8861} = -F_{8b86b1} = -F_{8b8b61}$ | -0.02 |
| $F_{6554} = F_{6b5b5b4b}$ | -0.13 | $F_{64b31} = -F_{6b431}$ | 0.10 | $F_{8862} = -F_{8b86b2} = -F_{8b8b62}$ | -0.09 |
| $F_{65b5b4} = F_{6b5b54b}$ | 0.05 | $F_{64b32} = -F_{6b432}$ | -0.03 | $F_{886b3} = F_{8b863} = -F_{8b8b6b3}$ | -0.53 |
| $F_{6611} = F_{6b6b11}$ | 0.03 | $F_{65b31} = -F_{6b531}$ | -0.06 | $F_{6541} = -F_{6b54b1} = -F_{6b54b1} = -F_{6b5b41}$ | -0.06 |
| $F_{6621} = F_{6b6b21}$ | 0.24 | $F_{65b32} = -F_{6b532}$ | -0.12 | $F_{6542} = -F_{6b54b2} = -F_{6b54b2} = -F_{6b5b42}$ | 0.07 |
| $F_{6622} = F_{6b6b22}$ | -0.11 | $F_{6661} = -F_{6b6b61}$ | 0.06 | $F_{654b3} = F_{6b543} = F_{6b543} = -F_{6b5b4b3}$ | 0.08 |
| $F_{6633} = F_{6b6b33}$ | 0.09 | $F_{6662} = -F_{6b6b62}$ | -0.08 | $F_{8754} = -F_{875b4b} = -F_{8b754b} = -F_{8b75b4}$ | 0.02 |
| $F_{6644} = F_{6b6b4b4b}$ | -0.09 | $F_{6b663} = -F_{6b6b6b3}$ | 0.01 | $F_{8764} = -F_{876b4b} = -F_{8b764b} = -F_{8b76b4}$ | 0.03 |
| $F_{664b4b} = F_{6b6b44}$ | -0.12 | $F_{874b3} = -F_{8b743}$ | -0.04 | $F_{8765} = -F_{876b5b} = -F_{8b765b} = -F_{8b76b5}$ | -0.68 |

12 Non-Symmetry-Unique Constants

| | | | | | |
|--|-------|---|-------|---|-------|
| $F_{7654} = (F_{6644} - F_{6655})/2$ | 0.00 | $F_{9854} = (F_{8844} - F_{8855})/2$ | 0.01 | $F_{9876} = (F_{8866} - F_{8877})/2$ | 0.00 |
| $F_{65b4b4} = F_{6b54b4} = (F_{6544} - F_{654b4b})/2$ | 0.02 | $F_{65b54b} = F_{6b5b54} = (F_{6554} - F_{65b5b4})/2$ | -0.09 | $F_{6b65b4} = F_{6b654b} = (F_{6654} - F_{665b4b})/2$ | 0.06 |
| $F_{8b84b4} = (F_{8844} - F_{884b4b})/2$ | -0.07 | $F_{8b85b5} = (F_{8855} - F_{885b5b})/2$ | -0.50 | $F_{8b86b6} = (F_{8866} - F_{886b6b})/2$ | -0.48 |
| $F_{8b85b4b} = F_{8b85b4} = (F_{8854} - F_{885b4b})/2$ | 0.07 | $F_{8b864b} = F_{8b86b4} = (F_{8864} - F_{886b4b})/2$ | -0.01 | $F_{8b865b} = F_{8b86b5} = (F_{8865} - F_{886b5b})/2$ | -0.21 |

^a See text for more details. Units of force constants are $\text{mdyn}/\text{\AA}^n \cdot \text{rad}^m$ appropriate for an energy unit of $\text{mdyn} \cdot \text{\AA}$ ($1 \text{mdyn} \cdot \text{\AA} \equiv 1 \text{ aJ}$).

Table 11. Complete Set of Non-Zero Quadratic and Cubic Force Constants for $\text{l-C}_3\text{H}_3^+$ in a Symmetry Internal Coordinate System^a

| | | | | | | | | | | | |
|----------|------------|-----------|----------|-----------|----------|-----------|---------|-----------|---------|-----------|---------|
| F_{11} | 6.029 788 | F_{xx} | 0.167448 | F_{444} | 15.2311 | F_{765} | -0.0249 | F_{965} | 0.0962 | F_{yx5} | -0.0131 |
| F_{21} | 0.005 712 | F_{yx} | 0.000441 | F_{511} | 0.0002 | F_{771} | -0.0363 | F_{971} | 0.0092 | F_{yy1} | -0.1937 |
| F_{22} | 5.540 738 | F_{yy} | 0.385229 | F_{521} | 0.0047 | F_{772} | 0.0272 | F_{972} | 0.0408 | F_{yy2} | -0.0120 |
| F_{31} | -0.119 775 | F_{zx} | 0.000222 | F_{522} | -0.1527 | F_{773} | -0.9361 | F_{973} | 0.1397 | F_{yy3} | -0.4253 |
| F_{32} | 0.072 319 | F_{zy} | 0.015043 | F_{531} | -0.0050 | F_{774} | 0.1170 | F_{974} | -0.0580 | F_{yy4} | 0.1286 |
| F_{33} | 11.885 630 | F_{zz} | 0.238988 | F_{532} | 0.1349 | F_{775} | 0.0325 | F_{975} | -0.0546 | F_{yy5} | 0.0064 |
| F_{41} | 0.144 706 | F_{111} | -34.5269 | F_{533} | 0.0086 | F_{861} | 0.0002 | F_{981} | 0.0010 | F_{zx1} | -0.0026 |
| F_{42} | 0.074 156 | F_{211} | -0.0010 | F_{541} | -0.0043 | F_{862} | -0.0015 | F_{982} | 0.0095 | F_{zx2} | -0.0063 |
| F_{43} | -2.970 851 | F_{221} | -0.0055 | F_{542} | 0.1028 | F_{863} | 0.0073 | F_{983} | -0.0528 | F_{zx3} | -0.0961 |
| F_{44} | 10.906 522 | F_{222} | -22.3363 | F_{543} | 0.1047 | F_{864} | 0.0128 | F_{984} | 0.0503 | F_{zx4} | 0.0867 |
| F_{51} | 0.001 714 | F_{311} | 0.1236 | F_{544} | 0.2391 | F_{865} | -0.0053 | F_{985} | -0.0134 | F_{zx5} | 0.0082 |
| F_{52} | 0.065 407 | F_{321} | 0.0056 | F_{551} | 0.0024 | F_{871} | -0.0002 | F_{991} | 0.0086 | F_{zy1} | -0.0032 |
| F_{53} | -0.231 773 | F_{322} | 0.0869 | F_{552} | -0.3928 | F_{872} | -0.0025 | F_{992} | -0.2028 | F_{zy2} | -0.0007 |
| F_{54} | -0.173 960 | F_{331} | -0.0602 | F_{553} | -0.1270 | F_{873} | 0.1851 | F_{993} | -0.1762 | F_{zy3} | 0.0332 |
| F_{55} | 0.682 966 | F_{332} | -0.1223 | F_{554} | -0.0076 | F_{874} | -0.2203 | F_{994} | 0.0320 | F_{zy4} | -0.0053 |
| F_{66} | 5.533 706 | F_{333} | -48.6285 | F_{555} | -0.2658 | F_{875} | 0.0052 | F_{995} | 0.3241 | F_{zy5} | 0.0068 |
| F_{76} | -0.002 072 | F_{411} | -0.1359 | F_{661} | -0.0068 | F_{881} | -0.1404 | F_{xx1} | -0.0281 | F_{zz1} | -0.0031 |
| F_{77} | 0.283 223 | F_{421} | -0.0008 | F_{662} | -22.4743 | F_{882} | -0.0192 | F_{xx2} | -0.0185 | F_{zz2} | -0.0768 |
| F_{86} | -0.004 390 | F_{422} | 0.1801 | F_{663} | 0.1739 | F_{883} | -0.6080 | F_{xx3} | -0.3280 | F_{zz3} | -0.2289 |
| F_{87} | 0.109 569 | F_{431} | 0.0147 | F_{664} | 0.3239 | F_{884} | 0.7960 | F_{xx4} | -0.0273 | F_{zz4} | -0.0271 |
| F_{88} | 0.227 801 | F_{432} | -0.2336 | F_{665} | 0.2737 | F_{885} | -0.0047 | F_{xx5} | 0.0040 | F_{zz5} | 0.4596 |
| F_{96} | 0.109 515 | F_{433} | 13.1266 | F_{761} | -0.0003 | F_{961} | -0.0011 | F_{yx1} | 0.0022 | | |
| F_{97} | -0.067 911 | F_{441} | 0.0753 | F_{762} | -0.0023 | F_{962} | 0.0428 | F_{yx2} | 0.0098 | | |
| F_{98} | -0.023 719 | F_{442} | -0.5212 | F_{763} | 0.0911 | F_{963} | -0.2622 | F_{yx3} | 0.1577 | | |
| F_{99} | 0.514 243 | F_{443} | -45.3965 | F_{764} | 0.0117 | F_{964} | -0.3053 | F_{yx4} | 0.0810 | | |

^a See text for more details. Units of force constants are $\text{mdyn}/\text{\AA}^n \cdot \text{rad}^m$ appropriate for an energy unit of $\text{mdyn} \cdot \text{\AA}$ ($1 \text{mdyn} \cdot \text{\AA} \equiv 1 \text{aj}$). x , y , and z represent the 10th, 11th, and 12th internal coordinates, respectively.

results and our VCI 5MR values are only 9.6 and 12.0 cm^{-1} for ν_3 and ν_8 , which are both determined indirectly (see refs 15 and 16 for details). Comparison of the VCI 5MR results to the IRPD values from Ricks et al.⁵ shows very good agreement for ν_5 , but for ν_4 we obtain a value that is 47.2 cm^{-1} lower than their assignment at 3182 cm^{-1} . Thus our best estimate for ν_4 is consistent with previous theory and calls into question their assignment. Further, the value we obtain for ν_4 , 3134.8 cm^{-1} , is more consistent with the assignment from Dopfer and co-workers.²⁻⁴ One of the reasons we performed the variational calculations in the present study was to be certain that we had ν_4 described properly since our second-order perturbation theory results did not agree with the assignment from Ricks et al. Given the levels of theory used in the present study and the fact that we have ruled out any possible resonance issues in solving the vibration problem, we can definitively conclude that the 3182 cm^{-1} band observed by Ricks et al. either is not representative of the free gas-phase spectrum for $\text{c-C}_3\text{H}_3^+$ or is due to a different vibrational mode or species. We have examined the variational CI results for possible combination bands or overtones in the variational calculations that might explain the band at 3182 cm^{-1} , but none appear for either $\text{c-C}_3\text{H}_3^+$ or $\text{l-C}_3\text{H}_3^+$, at least not within 10 cm^{-1} . There is a doubly degenerate band involving three quanta, $2\nu_6 + \nu_5$, that is very close to 3182 cm^{-1} , but this seems unlikely. It may be that the band observed at 3182 cm^{-1} is shifted somewhat due to complexation with the Ar atom, or it may be due to a different species.

Given the levels of theory used in the present study, the spectroscopic constants presented for $\text{c-C}_3\text{H}_3^+$ in Tables 4 and 5 should be highly accurate, and it is hoped that these will be useful

in the future assignment of high-resolution rovibrational spectra from either laboratory experiments or astronomical observations.

The vibrationally averaged structure and rotational constants and fundamental vibrational frequencies obtained for $\text{l-C}_3\text{H}_3^+$ in the present work are presented in Table 6. These are “position-averaged” values (i.e., r_z) computed with second-order perturbation theory. Other spectroscopic constants obtained from second-order perturbation theory are presented in Table 7 (anharmonic constants) and Table 8 (vibration-rotation interaction constants and quartic and sextic centrifugal distortion constants). Comparison of the VCI 4MR and 5MR results contained in Table 6 shows that the variational calculations are converged to better than 1 cm^{-1} , similar to the situation for $\text{c-C}_3\text{H}_3^+$. In fact, the largest difference is only 0.8 cm^{-1} for ν_7 . Comparison of the VCI 5MR and second-order perturbation theory fundamental vibrational frequencies for $\text{l-C}_3\text{H}_3^+$ shows reasonable agreement, though not as good as that found for $\text{c-C}_3\text{H}_3^+$. The largest differences occur for the C-H stretches ν_1 and ν_6 , being 10.3 and 9.1 cm^{-1} , respectively. We note that ν_6 is involved with a significant Fermi type 2 resonance with $\nu_3 + \nu_7$, though the difference between the two components of the resonance is fairly consistent between second-order perturbation theory and VCI 5MR (35.7 versus 34.0 cm^{-1}). Differences between second-order perturbation theory and VCI 5MR for the other fundamental vibrational frequencies are more in line with the differences we found for $\text{c-C}_3\text{H}_3^+$. Interestingly, the agreement between second-order perturbation theory and VCI 5MR for the $2\nu_4$ overtone and the $\nu_{12} + \nu_4$ combination band is not nearly as good, which is expected as one moves into the realm of less pure states and stronger coupling.

Table 12. Complete Set of Non-Zero Quartic Force Constants for I-C₃H₃⁺ in a Symmetry Internal Coordinate System^a

| | | | | | | | | | | | | | | | | | | | |
|-------------------|--------|-------------------|-------|-------------------|-------|-------------------|-------|-------------------|-------|-------------------|-------|-------------------|-------|-------------------|-------|-------------------|-------|-------------------|-------|
| F ₁₁₁₁ | 177.60 | F ₅₃₃₁ | -0.01 | F ₆₆₅₅ | -0.97 | F ₈₆₄₁ | 0.02 | F ₈₈₅₅ | -0.21 | F ₉₈₂₁ | 0.02 | F ₉₉₉₇ | 0.03 | F _{yx54} | -0.01 | F _{zx21} | -0.02 | F _{zy77} | 0.08 |
| F ₂₁₁₁ | 0.01 | F ₅₃₃₂ | 0.02 | F ₆₆₆₆ | 81.74 | F ₈₆₄₂ | 0.06 | F ₈₈₆₆ | -0.21 | F ₉₈₂₂ | 0.01 | F ₉₉₉₈ | -0.01 | F _{yx55} | -0.13 | F _{zx22} | -0.04 | F _{zy86} | 0.15 |
| F ₂₂₁₁ | -0.14 | F ₅₃₃₃ | -0.35 | F ₇₆₁₁ | 0.02 | F ₈₆₄₃ | 0.02 | F ₈₈₇₆ | 0.02 | F ₉₈₃₁ | 0.03 | F ₉₉₉₉ | -0.34 | F _{yx66} | 0.03 | F _{zx31} | 0.00 | F _{zy87} | -0.10 |
| F ₂₂₂₁ | 0.01 | F ₅₄₁₁ | 0.00 | F ₇₆₂₁ | -0.02 | F ₈₆₄₄ | 0.01 | F ₈₈₇₇ | -0.12 | F ₉₈₃₂ | -0.01 | F _{xx11} | -0.27 | F _{yx76} | -0.18 | F _{zx32} | 0.02 | F _{zy88} | 0.04 |
| F ₂₂₂₂ | 79.45 | F ₅₄₂₁ | 0.01 | F ₇₆₂₂ | 0.10 | F ₈₆₅₁ | -0.01 | F ₈₈₈₆ | 0.09 | F ₉₈₃₃ | 0.00 | F _{xx21} | -0.01 | F _{yx77} | -0.06 | F _{zx33} | -0.07 | F _{zy96} | 0.02 |
| F ₃₁₁₁ | -0.36 | F ₅₄₂₂ | -0.08 | F ₇₆₃₁ | 0.00 | F ₈₆₅₂ | -0.03 | F ₈₈₈₇ | -0.19 | F ₉₈₄₁ | 0.03 | F _{xx22} | -0.32 | F _{yx86} | -0.05 | F _{zx41} | -0.03 | F _{zy97} | -0.05 |
| F ₃₂₁₁ | 0.03 | F ₅₄₃₁ | 0.02 | F ₇₆₃₂ | 0.06 | F ₈₆₅₃ | -0.03 | F ₈₈₈₈ | -0.14 | F ₉₈₄₂ | -0.02 | F _{xx31} | -0.02 | F _{yx87} | -0.30 | F _{zx42} | 0.03 | F _{zy98} | -0.19 |
| F ₃₂₂₁ | -0.03 | F ₅₄₃₂ | -0.05 | F ₇₆₃₃ | -0.33 | F ₈₆₅₄ | -0.01 | F ₉₆₁₁ | -0.02 | F ₉₈₄₃ | 0.03 | F _{xx32} | 0.06 | F _{yx88} | 0.08 | F _{zx43} | -0.15 | F _{zy99} | -0.02 |
| F ₃₂₂₂ | -0.65 | F ₅₄₃₃ | -0.16 | F ₇₆₄₁ | 0.05 | F ₈₆₅₅ | 0.05 | F ₉₆₂₁ | 0.00 | F ₉₈₄₄ | -0.01 | F _{xx33} | -0.56 | F _{yx96} | -0.01 | F _{zx44} | 0.08 | F _{zyxx} | -0.01 |
| F ₃₃₁₁ | -0.50 | F ₅₄₄₁ | 0.02 | F ₇₆₄₂ | 0.01 | F ₈₆₆₆ | 0.07 | F ₉₆₂₂ | -0.31 | F ₉₈₅₁ | -0.02 | F _{xx41} | -0.01 | F _{yx97} | 0.32 | F _{zx51} | -0.01 | F _{zyyx} | -0.02 |
| F ₃₃₂₁ | 0.06 | F ₅₄₄₂ | -0.08 | F ₇₆₄₃ | -0.13 | F ₈₇₁₁ | -0.12 | F ₉₆₃₁ | -0.03 | F ₉₈₅₂ | 0.01 | F _{xx42} | 0.04 | F _{yx98} | 0.26 | F _{zx52} | 0.02 | F _{zyyy} | 0.00 |
| F ₃₃₂₂ | -0.54 | F ₅₄₄₃ | -0.05 | F ₇₆₄₄ | -0.10 | F ₈₇₂₁ | -0.03 | F ₉₆₃₂ | -0.01 | F ₉₈₅₃ | -0.01 | F _{xx43} | 0.17 | F _{yx99} | -0.06 | F _{zx53} | -0.01 | F _{zz11} | -0.21 |
| F ₃₃₃₁ | 0.30 | F ₅₄₄₄ | 0.70 | F ₇₆₅₁ | -0.02 | F ₈₇₂₂ | -0.05 | F ₉₆₃₃ | 0.00 | F ₉₈₅₄ | 0.04 | F _{xx44} | 1.02 | F _{yxxx} | 0.17 | F _{zx54} | 0.04 | F _{zz21} | 0.03 |
| F ₃₃₃₂ | -0.22 | F ₅₅₁₁ | -0.17 | F ₇₆₅₂ | -0.03 | F ₈₇₃₁ | 0.00 | F ₉₆₄₁ | 0.00 | F ₉₈₅₅ | 0.00 | F _{xx51} | -0.04 | F _{yy11} | -0.34 | F _{zx55} | 0.05 | F _{zz22} | -0.24 |
| F ₃₃₃₃ | 163.84 | F ₅₅₂₁ | 0.02 | F ₇₆₅₃ | 0.11 | F ₈₇₃₂ | 0.00 | F ₉₆₄₂ | 0.03 | F ₉₈₆₆ | -0.01 | F _{xx52} | 0.05 | F _{yy21} | 0.00 | F _{zx66} | 0.00 | F _{zz31} | 0.02 |
| F ₄₁₁₁ | 0.31 | F ₅₅₂₂ | -0.09 | F ₇₆₅₄ | -0.01 | F ₈₇₃₃ | -0.07 | F ₉₆₄₃ | 0.26 | F ₉₈₇₆ | -0.01 | F _{xx53} | -0.06 | F _{yy22} | -0.21 | F _{zx76} | -0.09 | F _{zz32} | 0.10 |
| F ₄₂₁₁ | 0.01 | F ₅₅₃₁ | -0.08 | F ₇₆₅₅ | -0.01 | F ₈₇₄₁ | 0.03 | F ₉₆₄₄ | 0.52 | F ₉₈₇₇ | 0.04 | F _{xx54} | -0.08 | F _{yy31} | 0.37 | F _{zx77} | -0.01 | F _{zz33} | -0.33 |
| F ₄₂₂₁ | 0.00 | F ₅₅₃₂ | 0.15 | F ₇₆₆₆ | 0.05 | F ₈₇₄₂ | -0.01 | F ₉₆₅₁ | -0.02 | F ₉₈₈₆ | -0.01 | F _{xx55} | -0.32 | F _{yy32} | 0.00 | F _{zx86} | -0.05 | F _{zz41} | -0.01 |
| F ₄₂₂₂ | -0.67 | F ₅₅₃₃ | -0.26 | F ₇₇₁₁ | -0.21 | F ₈₇₄₃ | 0.02 | F ₉₆₅₂ | 0.05 | F ₉₈₈₇ | 0.01 | F _{xx66} | -0.23 | F _{yy33} | -0.35 | F _{zx87} | -0.05 | F _{zz42} | 0.07 |
| F ₄₃₁₁ | 0.30 | F ₅₅₄₁ | -0.02 | F ₇₇₂₁ | 0.01 | F ₈₇₄₄ | 0.24 | F ₉₆₅₃ | -0.07 | F ₉₈₈₈ | 0.02 | F _{xx76} | 0.01 | F _{yy41} | -0.14 | F _{zx88} | 0.06 | F _{zz43} | -0.06 |
| F ₄₃₂₁ | -0.03 | F ₅₅₄₂ | 0.12 | F ₇₇₂₂ | -0.25 | F ₈₇₅₁ | 0.01 | F ₉₆₅₄ | -0.11 | F ₉₉₁₁ | -0.24 | F _{xx77} | 0.47 | F _{yy42} | 0.00 | F _{zx96} | 0.00 | F _{zz44} | -0.03 |
| F ₄₃₂₂ | -0.43 | F ₅₅₄₃ | -0.32 | F ₇₇₃₁ | 0.08 | F ₈₇₅₂ | -0.04 | F ₉₆₅₅ | 0.12 | F ₉₉₂₁ | 0.00 | F _{xx86} | 0.08 | F _{yy43} | -0.11 | F _{zx97} | -0.04 | F _{zz51} | 0.04 |
| F ₄₃₃₁ | -0.39 | F ₅₅₄₄ | -0.80 | F ₇₇₃₂ | 0.04 | F ₈₇₅₃ | -0.01 | F ₉₆₆₆ | -0.33 | F ₉₉₂₂ | -0.31 | F _{xx87} | -0.41 | F _{yy44} | 0.73 | F _{zx98} | -0.15 | F _{zz52} | -0.16 |
| F ₄₃₃₂ | 0.04 | F ₅₅₅₁ | -0.05 | F ₇₇₃₃ | 0.63 | F ₈₇₅₄ | 0.03 | F ₉₇₁₁ | 0.07 | F ₉₉₃₁ | 0.04 | F _{xx88} | -0.01 | F _{yy51} | 0.00 | F _{zx99} | -0.22 | F _{zz53} | -0.31 |
| F ₄₃₃₃ | -46.59 | F ₅₅₅₂ | 0.26 | F ₇₇₄₁ | 0.03 | F ₈₇₅₅ | -0.02 | F ₉₇₂₁ | 0.01 | F ₉₉₃₂ | 0.21 | F _{xx96} | -0.06 | F _{yy52} | 0.02 | F _{zxxx} | -0.07 | F _{zz54} | -0.09 |
| F ₄₄₁₁ | -0.52 | F ₅₅₅₃ | -0.16 | F ₇₇₄₂ | -0.10 | F ₈₇₆₆ | -0.05 | F ₉₇₂₂ | 0.06 | F ₉₉₃₃ | -0.30 | F _{xx97} | 0.26 | F _{yy53} | 0.09 | F _{zy11} | 0.02 | F _{zz55} | 0.82 |
| F ₄₄₂₁ | 0.02 | F ₅₅₅₄ | -0.29 | F ₇₇₄₃ | 0.70 | F ₈₇₇₆ | 0.06 | F ₉₇₃₁ | -0.02 | F ₉₉₄₁ | -0.03 | F _{xx98} | 0.21 | F _{yy54} | -0.04 | F _{zy21} | 0.00 | F _{zz66} | -0.25 |
| F ₄₄₂₂ | -0.65 | F ₅₅₅₅ | -0.08 | F ₇₇₄₄ | 0.84 | F ₈₇₇₇ | -0.22 | F ₉₇₃₂ | -0.19 | F ₉₉₄₂ | 0.27 | F _{xx99} | -0.23 | F _{yy55} | -0.15 | F _{zy22} | 0.00 | F _{zz76} | -0.01 |
| F ₄₄₃₁ | -0.09 | F ₆₆₁₁ | -0.22 | F ₇₇₅₁ | 0.00 | F ₈₈₁₁ | -0.17 | F ₉₇₃₃ | 0.17 | F ₉₉₄₃ | -0.55 | F _{xxxx} | -0.57 | F _{yy66} | -0.17 | F _{zy31} | 0.01 | F _{zz77} | -0.09 |
| F ₄₄₃₂ | 0.45 | F ₆₆₂₁ | 0.01 | F ₇₇₅₂ | 0.08 | F ₈₈₂₁ | 0.00 | F ₉₇₄₁ | -0.02 | F ₉₉₄₄ | -1.54 | F _{yx11} | -0.09 | F _{yy76} | -0.03 | F _{zy32} | -0.03 | F _{zz86} | 0.05 |
| F ₄₄₃₃ | 161.99 | F ₆₆₂₂ | 81.00 | F ₇₇₅₃ | 0.01 | F ₈₈₂₂ | -0.20 | F ₉₇₄₂ | -0.10 | F ₉₉₅₁ | 0.00 | F _{yx21} | -0.03 | F _{yy77} | 0.15 | F _{zy33} | 0.01 | F _{zz87} | -0.03 |
| F ₄₄₄₁ | -0.16 | F ₆₆₃₁ | 0.12 | F ₇₇₅₄ | -0.09 | F ₈₈₃₁ | 0.32 | F ₉₇₄₃ | 0.13 | F ₉₉₅₂ | -0.11 | F _{yx22} | 0.00 | F _{yy86} | 0.23 | F _{zy41} | -0.01 | F _{zz88} | -0.24 |
| F ₄₄₄₂ | 0.30 | F ₆₆₃₂ | -0.43 | F ₇₇₅₅ | -0.12 | F ₈₈₃₂ | 0.06 | F ₉₇₄₄ | 0.10 | F ₉₉₅₃ | -0.01 | F _{yx31} | -0.27 | F _{yy87} | -0.20 | F _{zy42} | -0.05 | F _{zz96} | 0.04 |
| F ₄₄₄₃ | -52.04 | F ₆₆₃₃ | -0.43 | F ₇₇₆₆ | -0.19 | F ₈₈₃₃ | -0.29 | F ₉₇₅₁ | 0.05 | F ₉₉₅₄ | 0.04 | F _{yx32} | 0.09 | F _{yy88} | 0.53 | F _{zy43} | -0.03 | F _{zz97} | 0.00 |
| F ₄₄₄₄ | 140.77 | F ₆₆₄₁ | 0.01 | F ₇₇₇₆ | -0.12 | F ₈₈₄₁ | -0.30 | F ₉₇₅₂ | 0.05 | F ₉₉₅₅ | -0.22 | F _{yx33} | 0.04 | F _{yy96} | -0.02 | F _{zy44} | -0.07 | F _{zz98} | -0.03 |
| F ₅₁₁₁ | 0.01 | F ₆₆₄₂ | -0.41 | F ₇₇₇₇ | -0.05 | F ₈₈₄₂ | 0.07 | F ₉₇₅₃ | 0.04 | F ₉₉₆₆ | -0.36 | F _{yx41} | -0.01 | F _{yy97} | 0.13 | F _{zy51} | 0.01 | F _{zz99} | -0.24 |
| F ₅₂₁₁ | 0.01 | F ₆₆₄₃ | -0.49 | F ₈₆₁₁ | 0.05 | F ₈₈₄₃ | -0.20 | F ₉₇₅₄ | -0.02 | F ₉₉₇₆ | -0.09 | F _{yx42} | 0.00 | F _{yy98} | -0.15 | F _{zy52} | 0.01 | F _{zzxx} | -0.19 |
| F ₅₂₂₁ | 0.01 | F ₆₆₄₄ | -0.69 | F ₈₆₂₁ | -0.01 | F ₈₈₄₄ | -0.91 | F ₉₇₅₅ | 0.01 | F ₉₉₇₇ | 0.04 | F _{yx43} | -0.12 | F _{yy99} | -0.13 | F _{zy53} | -0.01 | F _{zyyx} | 0.03 |
| F ₅₂₂₂ | 0.11 | F ₆₆₅₁ | 0.00 | F ₈₆₂₂ | 0.09 | F ₈₈₅₁ | -0.01 | F ₉₇₆₆ | 0.06 | F ₉₉₈₆ | 0.03 | F _{yx44} | -0.23 | F _{yyxx} | -0.16 | F _{zy54} | -0.03 | F _{zyyy} | -0.20 |
| F ₅₃₁₁ | -0.03 | F ₆₆₅₂ | -0.19 | F ₈₆₃₁ | 0.00 | F ₈₈₅₂ | 0.01 | F ₉₇₇₆ | -0.11 | F ₉₉₈₇ | -0.01 | F _{yx51} | -0.11 | F _{yyyx} | -0.01 | F _{zy55} | 0.01 | F _{zzxx} | -0.07 |
| F ₅₃₂₁ | 0.01 | F ₆₆₅₃ | 0.02 | F ₈₆₃₂ | -0.01 | F ₈₈₅₃ | 0.09 | F ₉₇₇₇ | 0.21 | F ₉₉₈₈ | -0.27 | F _{yx52} | 0.00 | F _{yyyy} | -0.37 | F _{zy66} | 0.00 | F _{zzyy} | 0.03 |
| F ₅₃₂₂ | 0.04 | F ₆₆₅₄ | -0.16 | F ₈₆₃₃ | 0.13 | F ₈₈₅₄ | 0.02 | F ₉₈₁₁ | 0.00 | F ₉₉₉₆ | 0.27 | F _{yx53} | -0.26 | F _{zx11} | -0.03 | F _{zy76} | -0.01 | F _{zzzz} | 0.91 |

^a See text for more details. Units of force constants are mdyne/Åⁿ · rad^m appropriate for an energy unit of mdyne · Å (1 mdyne · Å ≡ 1 aJ). x, y, and z represent the 10th, 11th, and 12th internal coordinates, respectively.

Agreement between our best VCI SMR fundamental vibrational frequencies and those obtained by Botschwina and Oswald⁸ using the CCSD(T*)F-12a/VTZ-F12 level of theory is modest. The largest differences occur for ν_1 (15 cm⁻¹) and ν_4 (27 cm⁻¹). There are many possible sources for these differences, with the most significant probably being the use of an approximate (T) contribution by Botschwina and Oswald, their neglect of core correlation, and their neglect of most coupling to non-totally-symmetric vibrational degrees of freedom in solving the variational nuclear Schrödinger equation.

Comparison of our best VCI SMR results with the experiments of Ricks et al.⁵ shows reasonable agreement for most of

the assignments with a few exceptions. Our best value for ν_1 agrees very well, confirming the conclusion by Botschwina and Oswald⁹ that the 3238 cm⁻¹ band observed by Ricks et al. is essentially a free acetylenic C–H stretch. The agreement for ν_2 , ν_3 , and ν_4 is also very good, with differences all less than about 10 cm⁻¹. Agreement for the overtone band 2 ν_4 is reasonable, being about twice the difference for the ν_4 fundamental, and agreement for ν_6 is also reasonable, as the assignment by Ricks et al. falls between the two components of the Fermi type 2 resonance between ν_6 and $\nu_3 + \nu_7$. Agreement for ν_5 , ν_{10} , and the combination band $\nu_{12} + \nu_4$ is more modest, however. Botschwina and Oswald⁸ have

already questioned the reliability of the assignment for the totally symmetric mode ν_5 . Given that the lowest energy structure found for $\text{l-C}_3\text{H}_3^+ \cdot \text{Ar}$ has the Ar atom out of plane and over the C–C single bond, and that this structure is quite a bit lower in energy than the other minima,⁹ it seems plausible that the C–C single bond stretch ν_5 would be significantly impacted in the complex. This same reasoning could be applied to ν_{10} , which is described as a CH_2 out-of plane wag, and to the combination band $\nu_{12} + \nu_4$ since ν_{12} is an out-of plane bending mode that involves the CCC backbone. Thus, the discrepancies found between the assignments of Ricks et al.⁵ and our VCI SMR results can reasonably be attributed to shifts in the vibrational frequencies as a result of complexation for $\text{l-C}_3\text{H}_3^+$.

For $\text{l-C}_3\text{H}_3^+$, the effects of scalar relativistic corrections are small: $\sim -5 \times 10^{-5}$ Å on the C–H bond lengths and $\sim -3 \times 10^{-4}$ Å on the CC bonds, ≤ 0.4 cm^{-1} on harmonic frequencies, and -6 to 0 cm^{-1} for the vibrational fundamentals. As expected from previous experience, core-correlation effects are much larger on the geometry (-1.3×10^{-3} Å for the CH bonds and -3×10^{-3} Å for the CC bonds) and harmonic frequencies ($+2$ to $+7$ cm^{-1}) but only slightly larger for the fundamentals ($+2$ to $+8$ cm^{-1} , except $+10.7$ cm^{-1} for ν_{10}). For $\text{c-C}_3\text{H}_3^+$, the effects of scalar relativity corrections are smaller than found for $\text{l-C}_3\text{H}_3^+$: -2.1×10^{-4} Å for R_{CC} , -5.5×10^{-5} Å for r_{CH} , 0.0 – 0.5 cm^{-1} for harmonic frequencies, and -1 to $+2$ cm^{-1} for fundamentals (except $+8$ cm^{-1} for ν_3). However, core-correlation effects are larger: -5.4×10^{-3} Å for R_{CC} , -1.4×10^{-3} Å for r_{CH} , $+2$ to $+7$ cm^{-1} for harmonic frequencies, and $+3$ to $+9$ cm^{-1} for fundamentals (except $+0.3$ cm^{-1} for ν_6). More details are available upon request.

Given the levels of theory used in the present study, the spectroscopic constants presented for $\text{l-C}_3\text{H}_3^+$ in Tables 7 and 8 should be highly accurate, and it is hoped that these will be useful in the future assignment of high-resolution rovibrational spectra from either laboratory experiments or astronomical observations.

C. Quartic Force Fields. For completeness, the best QFFs computed in this work are given in Tables 9 through 12. Specifically, Table 9 contains the quadratic and cubic force constants and Table 10 the quartic force constants for $\text{c-C}_3\text{H}_3^+$. Table 11 contains the quadratic and cubic force constants and Table 12 the quartic force constants for $\text{l-C}_3\text{H}_3^+$. These are given in symmetry internal coordinates, and symmetry relationships between the force constants are given in the tables. The force constants presented are based on the following quartic expansion:

$$V = \frac{1}{2} \sum_{i,j} F_{ij} \Delta_i \Delta_j + \frac{1}{6} \sum_{i,j,k} F_{ijk} \Delta_i \Delta_j \Delta_k + \frac{1}{24} \sum_{i,j,k,l} F_{ijkl} \Delta_i \Delta_j \Delta_k \Delta_l$$

where the summations are unrestricted. We note that, for the force constant labels for $\text{l-C}_3\text{H}_3^+$, we have labeled modes 10, 11, and 12 as x, y, and z, respectively, in order to avoid confusion. So, for example, the diagonal quadratic force constant for mode 10 is given as F_{xx} .

4. CONCLUSIONS

Accurate CCSD(T) QFFs have been computed for the $\text{c-C}_3\text{H}_3^+$ and $\text{l-C}_3\text{H}_3^+$ molecular cations. Extrapolation to the one-particle basis set limit has been included as well as corrections for scalar relativity and core correlation. Anharmonic spectroscopic constants have been determined from second-order perturbation theory, and fundamental vibrational frequencies have been evaluated from second-order perturbation theory

and from variational calculations. Agreement between second-order perturbation theory and variational CI calculations for the fundamental vibrational frequencies is very good. Agreement between our computed fundamental vibrational frequencies and recent IRPD experiments is good with a few exceptions. The 3182 cm^{-1} band assigned in one recent IRPD experiment⁵ to ν_4 for $\text{c-C}_3\text{H}_3^+$ does not agree well with our calculations, where we obtain 3134.8 cm^{-1} (VCI SMR), but our value does agree well with other recent IRPD experiments.^{2–4} We have examined our VCI calculations for possible combination and overtone bands but can find only one band that could be a reasonable match, and this requires three quanta. Hence we conclude that the 3182 cm^{-1} band may be a combination or overtone band that is perturbed somewhat by the presence of the Ar atom, or it may be due to a different species. For $\text{l-C}_3\text{H}_3^+$, agreement between the IRPD experiments and our variational calculations for the fundamental vibrational frequencies (plus one overtone and one combination band) is reasonable except for ν_5 , ν_{10} , and the combination band $\nu_{12} + \nu_4$. However, a recent ab initio study⁹ that explored the potential energy surface of $\text{l-C}_3\text{H}_3^+$ interacting with an Ar atom shows one minimum quite a bit lower than the others, and this structure would likely exhibit perturbations to ν_5 , ν_{10} , and the combination band $\nu_{12} + \nu_4$, so a plausible explanation for these discrepancies is given.

The fundamental vibrational frequencies and spectroscopic constants presented here for $\text{c-C}_3\text{H}_3^+$ and $\text{l-C}_3\text{H}_3^+$ should be the most reliable available for the free gas-phase species, and it is hoped that they will be useful in the assignment of future high-resolution laboratory experiments or astronomical observations. Finally, we compute what should be the most reliable energy difference between $\text{c-C}_3\text{H}_3^+$ and $\text{l-C}_3\text{H}_3^+$, obtaining a value of 27.9 kcal/mol at 0 K.

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