Highly Accurate Quartic Force Fields, Vibrational Frequencies, and Spectroscopic Constants for Cyclic and Linear $C_3H_3^+$

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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 using both vibrational 2nd-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 from 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 as c-$C_3H_3^+$ and propargyl cation 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 et al[2-4] used infrared photodissociation (IRDP) 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.

Determination of an anharmonic force field and fundamental vibrational frequencies has actually been reported for c-$C_3H_3^+$ 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) pertubation 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-$C_3H_3^+$ 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, non-degenerate vibrational mode, as there is for c-$C_3H_3^+$. The issue was discussed in some detail and Lee et al 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 program[20] to use an asymmetric top analysis. Xie and Boggs 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 in the Lee et al paper. 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-$C_3H_3^+$, 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 solved the nuclear Schrödinger equation variationally. The five dimensions included the symmetric CH_2 stretch, the free acetylenic CH stretch, the 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 Oswald found generally good agreement with the IRPD experiment of Ricks et al.

More recently Botschwina and Oswald 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-$C_3H_3^+$ and l-$C_3H_3^+$.[9] They located three distinct minima for Ar complexes of both isomers, though one of the C_s minima for l-$C_3H_3^+$ was noticeably lower in energy than the other two minima. For the c-$C_3H_3^+$ isomer, all three minima were relatively close in energy. The results of this latter study reaffirmed Botschwina and Oswald's assignment of the 3238 cm^{-1} band in Ricks et al's IRPD experiments to the acetylenic CH stretch vibration in l-$C_3H_3^+$.

The accuracy of state-of-the art *ab initio* predictions for fundamental vibrational frequencies has improved considerably in the last twenty 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 ago[28] that state-of-the art *ab initio* predictions were becoming reliable enough that it should be possible to assign an astronomical spectrum using 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 Aoki[30] and Botschwina and Oswald.[31]

Thus our goal in the present study is to compute highly accurate QFFs for the c-$C_3H_3^+$ and l-$C_3H_3^+$ 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 to the Hubble Space Telescope, will launch later in this decade. Further, 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-$C_3H_3^+$, 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-$C_3H_3^+$. The parent isotopologue has no permanent dipole moment, 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-$C_3H_3^+$, the lowest energy vibration may be within range for instruments on all of the above telescopes, but since l-$C_3H_3^+$ 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-$C_3H_3^+$ and l-$C_3H_3^+$ is beyond the scope of the present study, and will be reported separately.[32]

The Theoretical Approach is described in the next section, followed by Results and Discussion. Our Conclusions are presented in the final section.

2. Theoretical Approach

A. Details of the 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 relativity[36] 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=T, Q, or 5) basis sets as TZ, QZ, or 5Z. A correction for scalar relativity is evaluated at the CCSD(T)/TZ level of theory using the Douglas-

Kroll approximation.[36] As we pointed out previously,[33] the scalar relativity integrals lose precision when going 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, using 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-$C_3H_3^+$ and l-$C_3H_3^+$, 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-$C_3H_3^+$ and l-$C_3H_3^+$, respectively. As indicated, CCSD(T) energies are extrapolated to the one-particle basis set limit using 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-$C_3H_3^+$, 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-$C_3H_3^+$, the 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-$C_3H_3^+$ and l-$C_3H_3^+$, 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 the Coordinate Systems and the Vibrational Methods

For both molecules, the QFFs were determined in symmetry internal coordinates. For l-$C_3H_3^+$, we use the following definition of symmetry internal coordinates:

$$
\begin{aligned}
&S_1(\mathrm{A}_1) = R_4(C-H);\\
&S_2(\mathrm{A}_1) = (R_{1a}+R_{1b})/\sqrt{2};\\
&S_3(\mathrm{A}_1) = (R_2[C=C]+R_3[C\equiv C])/\sqrt{2};\\
&S_4(\mathrm{A}_1) = (R_2[C=C]-R_3[C\equiv C])/\sqrt{2};\\
&S_5(\mathrm{A}_1) = \theta_1(\angle H_aCH_b);\\
&S_6(\mathrm{B}_1) = (R_{1a}-R_{1b})/\sqrt{2};\\
&S_7(\mathrm{B}_1) = LIN1(C-C-C-\vec{r}_{out});\\
&S_8(\mathrm{B}_1) = LIN1(C-C-H-\vec{r}_{out});\\
&S_9(\mathrm{B}_1) = (\angle H_aCC-\angle H_bCC)/\sqrt{2};\\
&S_{10}(\mathrm{B}_2) = LIN1(C-C-C-\vec{r}_{in});\\
&S_{11}(\mathrm{B}_2) = LIN1(C-C-H-\vec{r}_{in});\\
&S_{12}(\mathrm{B}_2) = \tau(H_a-C-C-H_b)
\end{aligned}
$$

where the simple internal coordinates for l-$C_3H_3^+$ are given in Fig. 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 definition of *LIN1*(*a-b-c-d*) and τ(*a-b-c-d*) are taken from the INTDER program:[46]

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

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

$$\vec{r}_{in} = \vec{R}_2 \times (\vec{R}_{1a} \times \vec{R}_{1b})$$
$$\vec{r}_{out} = \vec{R}_2 \times \vec{r}_{in} = \vec{R}_2 \times (\vec{R}_2 \times (\vec{R}_{1a} \times \vec{R}_{1b}))$$

Fig.1 also gives the planar equilibrium and ground state (GS) vibrationally averaged structures for both c-$C_3H_3^+$ and l-$C_3H_3^+$, as well as the GS vibrationally averaged rotational constants. The vibrationally averaged quantities are the "position average," i.e., r_z, computed from 2nd-order perturbation theory. Symmetry relationships for the quadratic, cubic, and quartic force constants are given later.

For c-$C_3H_3^+$, we use the exact same definition of symmetry internal coordinates as given by Lee et al.[6] They are repeated here for convenience:

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

where the simple internal coordinates R, r, α, β are the bond lengths and bond angles defined in Fig. 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 Fig. 2).

Fundamental vibrational frequencies were computed using either a vibrational variational method (VAR) or second-order perturbation theory (PT).[17-19] The MULTIMODE program[47] was used for the VAR calculations, while the SPECTRO program[20] was used for the PT calculations, and for computing other spectroscopic constants. For l-$C_3H_3^+$, 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 using a QFF in vibrational variational calculations can be traced back to Meyer et al[48] and Carter and Handy[49] 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-$C_3H_3^+$, 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}, 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-$C_3H_3^+$, 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-$C_3H_3^+$ and l-$C_3H_3^+$ 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-$C_3H_3^+$ is about 1°

larger. We note that the longer C-C bond in l-$C_3H_3^+$, R_2 (see Fig. 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-$C_3H_3^+$ 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-$C_3H_3^+$, 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-$C_3H_3^+$ and l-$C_3H_3^+$ is about 26 kcal/mol, but the levels of theory used in the present study should yield a much more definitive value. The energy that we obtain at the minimum is -115.7647467662 E_h and -115.717377491 E_h for c-$C_3H_3^+$ and l-$C_3H_3^+$, respectively. The electronic energy difference is thus 10,396.4 cm^{-1}. The anharmonic zero-point energies given by 2nd-order PT are 9841.5 cm^{-1} and 9208.0 cm^{-1}, which includes the E_0 term (the polyatomic equivalent of the a_0 Dunham coefficient for diatomics).[51] The corresponding MULTIMODE zero-point energies are 9823.7 cm^{-1} and 9189.1

cm^{-1}, for c-$C_3H_3^+$ and l-$C_3H_3^+$, 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 kcal/mol uncertainty – see Ref. 1 and references therein for more details. The 27.9 kcal/mol 0K 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-$C_3H_3^+$ in the present work are presented in Table 3. Other spectroscopic constants obtained from 2nd 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 coupling 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 4-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}. Based on 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 2nd-order perturbation theory shows good agreement with the two approaches, with the differences being consistent to 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 2nd-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 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 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 et al.[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 2nd-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 is either not representative of the free gas-phase spectrum for c-$C_3H_3^+$ or it 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 c-$C_3H_3^+$ or l-$C_3H_3^+$, 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 c-$C_3H_3^+$ in Tables 4 and 5 should be highly accurate, and it is hoped 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 the fundamental vibrational frequencies obtained for l-$C_3H_3^+$ in the present work are presented in Table 6. These are "position averaged" values (i.e., r_z) computed with 2nd-order perturbation theory. Other spectroscopic constants obtained from 2nd 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 c-$C_3H_3^+$. In fact, the largest difference is only 0.8 cm^{-1} for ν_7. Comparison of the VCI 5MR and 2nd-order perturbation theory fundamental vibrational frequencies for l-$C_3H_3^+$ shows reasonable agreement, though not as good as found for c-$C_3H_3^+$. 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 2nd-order perturbation theory and VCI 5MR (35.7 versus 34.0 cm^{-1}). Differences between 2nd-order perturbation theory and VCI 5MR for the other fundamental vibrational frequencies are more in line with the differences we found for c-$C_3H_3^+$. Interestingly, the agreement between 2nd-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.

Agreement between our best VCI 5MR fundamental vibrational frequencies and those obtained by Botschwina and Oswald[8] 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 5MR results with the experiments of Ricks et al 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 Oswald[9] 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 $2\nu_4$ 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 Oswald[8] have already questioned the reliability of the assignment for the totally symmetric mode ν_5. Given that the lowest energy structure found for l-$C_3H_3^+$ • 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 and our VCI 5MR results can reasonably be attributed to shifts in the vibrational frequencies as a result of complexation for l-$C_3H_3^+$.

For *l*-$C_3H_3^+$, the effects of scalar relativistic corrections are small: ~ -5E-5 Å on the C-H bond lengths and ~-3E-4 Å on the CC bonds; less than or equal to 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 (-1.3E-3 Å for the CH bonds and -3E-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 *c*-$C_3H_3^+$, the effects of scalar relativity corrections are smaller than found for *l*-$C_3H_3^+$: -2.1E-4 Å for R_{CC}; -5.5E-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: -5.4E-3 Å for R_{CC}; -1.4E-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 l-$C_3H_3^+$ in Tables 7 and 8 should be highly accurate, and it is hoped 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 c-$C_3H_3^+$. Table 11 contains the quadratic and cubic force constants and Table 12 the quartic force constants for l-$C_3H_3^+$. 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 l-$C_3H_3^+$, 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 c-$C_3H_3^+$ and l-$C_3H_3^+$ 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 2nd-order perturbation theory and fundamental vibrational frequencies have been evaluated from 2nd-order perturbation theory and from variational calculations. Agreement between 2nd-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 experiment[5] to ν_4 for c-$C_3H_3^+$ does not agree well with our calculations where we obtain 3134.8 cm^{-1} (VCI 5MR), 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 l-$C_3H_3^+$, 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* study[9] that explored the potential energy surface of l-$C_3H_3^+$ 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 c-$C_3H_3^+$ and l-$C_3H_3^+$ 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 the c-$C_3H_3^+$ and l-$C_3H_3^+$, obtaining a value of 27.9 kcal/mol at 0 K.

Acknowledgments

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References

(1) Burgess, P. C.; Holmes, J. L.; Mommers, A. A.; Szulejko, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 521.

(2) Dopfer, O.; Roth, D.; Maier, J. P. *J. Am. Chem. Soc.* **2002**, *124*, 494.

(3) Dopfer, O.; Roth, D.; Maier, J. P. *Int. J. Mass Spectrom.* **2002**, *218*, 281.

(4) Roth, D.; Dopfer, O.; Roth, D. *Phys. Chem. Chem. Phys.* **2002**, *4*, 4855.

(5) Ricks, A. M.; Douberly, G. E.; Schleyer, P. v. R.; Duncan, M. A. *J. Chem. Phys.* **2010**, *132*, 051101.

(6) Lee, T. J.; Willetts, A.; Gaw, J. F.; Handy, N. C. *J. Chem. Phys.* **1989**, *90*, 4330.

(7) Xie, Y.; Boggs, J. E. *J. Chem. Phys.* **1989**, *90*, 4320.

(8) Botschwina, P.; Oswald, R. *Chem. Phys.* **2010**, *378*, 4.

(9) Botschwina, P.; Oswald, R. *J. Chem. Phys.* **2011**, *134*, 044305.

(10) Thaddeus, P.; Vrtilek, J. M.; Gottlieb, C. A. *Astrophys. J.* **1985**, *299*, L63.

(11) Bell, M. B.; Feldman, P. A.; Matthews, H. E.; Avery, L. W. *Astrophys. J.* **1986**, *311*, 1989.

(12) Oike, T.; Kawaguchi, K.; Takano, S.; Nakai, N. *Pub. Astron. Soc. Japan* **2004**, *56*, 4310.

(13) Kamata, H.; Yamamoto, S.; Saito, S. *Chem. Phys. Lett.* **1987**, *140*, 221. and references therein.

(14) Smith. D. *Chem. Rev. (Washington, D.C.)* **1992**, *92*, 1473.

(15) Breslow, R.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 984.

(16) Wyss. M.; Riaplov, E.; Maier, J. P. *J. Chem. Phys.* **2001**, *114*, 10355; Craig, N. C.; Pranata, J.; Reinganum, S. J.; Sprague, J. R.; Stevens, P. S. *J. Am. Chem. Soc.* **1986**, *108*, 4378.

(17) Mills, I. M. in *Molecular Spectroscopy – Modern Research*, ed. by K. N. Rao and C. W. Mathews (Academic Press, New York, 1972).

(18) Papousek, D.; Aliev, M. R. *Molecular Vibrational-Rotational Spectra* (Elsevier, Amsterdam, 1982).

(19) Watson, J. K. G; in *Vibrational Spectra and Structure*, edited by Durig, J. R. (Elsevier, Amsterdam, 1977), *Vol. 6*, pp. 1-89.

(20) SPECTRO program, version 3.0 (1996), written by Gaw, J. F.; Willets, A.; Green, W. H.; Handy, N. C.

(21) Adler, T. B.; Knizia, G.; Werner, H.-J. *J. Chem. Phys.* **2007**, *127*, 221106.

(22) Knizia, G.; Adler, T. B.; Werner, H.-J. *J. Chem. Phys.* **2009**, *130*, 054104.

(23) K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479.

(24) Martin, J. M. L.; Lee, T. J. *Chem. Phys. Lett.* **1992**, *200*, 502.

(25) Wong, A. T.; Bacskay, G. B. *Mol. Phys.* **1993**, *79*, 819.

(26) Martin, J. M. L.; Lee, T. J.; Taylor, P. R. *J. Chem. Phys.* **1998**, *108*, 676.

(27) Martin, J. M. L.; Lee, T. J.; Taylor, P. R.; Francios, J.-P. *J. Chem. Phys.* **1995**, *103*, 2589.

(28) Lee T. J.; Dateo, C. E. *Spectrochim. Acta.* **1999**, *55A*, 739.

(29) Cernicharo, J.; Guelin, M.; Agundez, M.; McCarthy, M. C.; Thaddeus, P. *Astrophys. J.* **2008**, *688*, L83.

(30) Aoki, K. *Chem. Phys. Lett.* **2000**, *323*, 55.

(31) Botschwina, P.; Oswald, R. *J. Chem. Phys.* **2008**, *129*, 044305.

(32) Huang, X.; Lee, T. J. *Astrophys. J.* **2011**, to be submitted.

(33) Huang, X.; Lee, T. J. *J. Chem. Phys.* **2008**, *129*, 044312.

(34) Huang, X.; Lee, T. J. *J. Chem. Phys.* **2009**, *131*, 104301.

(35) Martin, J. M. L.; Lee, T. J. *Chem. Phys. Lett.* **1996**, *258*, 136.

(36) Douglas, M.; Kroll, N. M. *Ann. Phys.* **1974**, *82*, 89; Hess, B. A. *Phys. Rev. A* **1985**, *32*,756; **1986**, *33*, 3742.

(37) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.

(38) Martin, J. M. L.; Taylor, P. R. *Chem. Phys. Lett.* **1994**, *225*, 473.

(39) Huang, X.; Valeev, E. F.; Lee, T. J. *J. Chem. Phys.* **2010**, *133*, 244108.

(40) Lee, T. J.; Allen, W. D.; Schaefer, H. F. *J. Chem. Phys.* **1987**, *87*, 7062.

(41) Simandiras, E. D.; Rice, J. E.; Lee, T. J.; Amos, R. D.; Handy, N. C. *J. Chem. Phys.* **1988**, *88*, 3187.

(42) Martin, J. M. L.; Taylor, P. R.; Lee, T. J., *Chem. Phys. Lett.* **1997**, *275*, 414.

(43) Moran, D.; Simmonett, A. C.; Leach, F. E.; Allen, W. D.; Schleyer, P. v. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **2006**, *128*, 9342.

(44) Lee, T. J.; Huang, X.; Dateo, C. E. *Mol. Phys.* **2009**, *107*, 1139.

(45) Werner, H.-J. et al. *MOLPRO*, version 2006.1, a package of *ab initio* programs; 2006; see http://www.molpro.net.

(46) INTDER 2005 is a general program written by W. D. Allen and co-workers, which performs vibrational analysis and higher order nonlinear transformations, 2005.

(47) Carter, S.; Bowman, J. M.; Handy, N. C. *Theor. Chem. Acc.* **1998**, *100*, 191; Bowman, J. M.; Carter, S.; Huang, X. *Int. Rev. Phys. Chem.* **2003**, *22*, 533.

(48) Meyer, W.; Botschwina, P.; Burton, P. *J. Chem. Phys.* **1986**, *84*, 891.

(49) Carter, S.; Handy, N. C. *J. Chem. Phys.* **1987**, *87*, 4294.

(50) Dateo, C. E.; Lee, T. J.; Schwenke, D. W. *J. Chem. Phys.* **1994**, *101*, 5853.

(51) Truhlar, D. G.; Isaacson, A. D. *J. Chem. Phys.* **1991**, *94*, 357, and references therein.

Figures and Tables

Figure 1. Equilibrium structures, and vibrationally averaged structures (italic numbers) and rotational constants of c-$C_3H_3^+$ and l-$C_3H_3^+$ determined from our best QFF. See text for details.

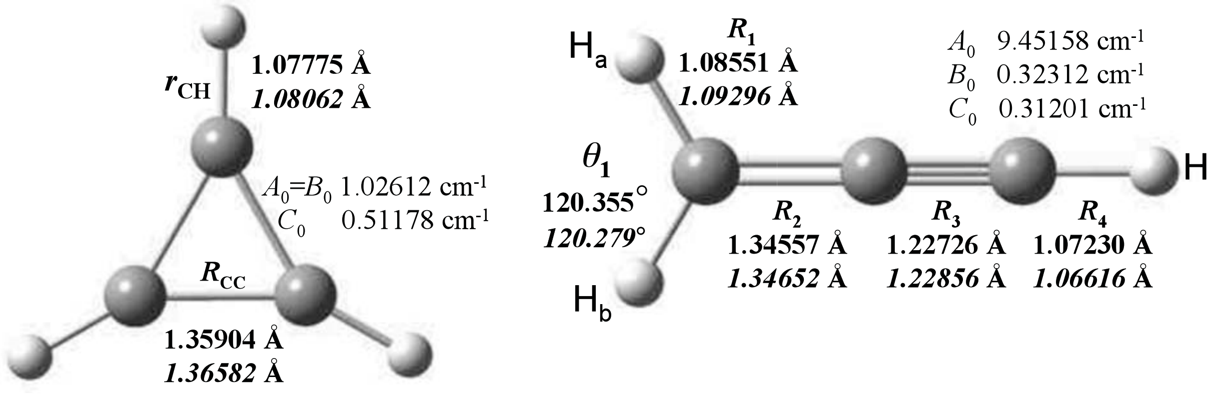


Fig. 2. Internal coordinate definitions used for the c-$C_3H_3^+$ cation.

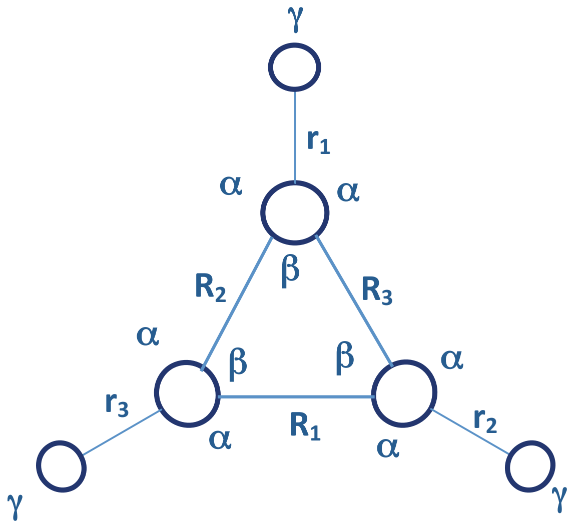


Table 1. Equilibrium structure (Å / deg), rotational constants (cm^{-1}), and harmonic frequencies (cm^{-1}) for c-$C_3H_3^+$, determined from our best QFF (CCSD(T)/cc-pV(T,Q,5)Z extrapolation + core-correlation + scalar relativistic corrections). See text for more details.

Geometry Parameters		Harmonic Vibrational Frequencies Mode	Symmetry and Description	Freq
R(C-C)	1.3590363	ω_1	a_1' (breathing, C-H str – C-C str)	3312.3
r(C-H)	1.0777461	ω_2	a_1' (breathing, C-H str + C-C str)	1650.8
$A_e = B_e$	1.03260	ω_3	a_2' (in-plane internal torsion)	1058.2
C_e	0.51630	ω_4	e' (in-plane deformation)	3265.1
∠C-C-H	150.0	ω_5	e' (in-plane wagging)	1326.7
∠C-C-C	60.0	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

Table 2. Equilibrium structure (Å / deg), rotational constants (cm^{-1}), and harmonic frequencies (cm^{-1}) for *l*-$C_3H_3^+$, determined from our best QFF (CCSD(T)/cc-pV(T,Q,5)Z extrapolation + core-correlation + scalar relativistic corrections). See text and Fig.1 for more details and the definition of R_1-R_4 and θ_1.

Geometry Parameters			Harmonic Vibrational Frequencies	
		Mode	Symmetry and Description	Freq
R_1	1.085506	ω_1	a_1 (C-H str)	3367.15
R_2	1.345571	ω_2	a_1 (CH_2 sym str)	3122.73
R_3	1.227265	ω_3	a_1 (C≡C str)	2131.15
R_4	1.072298	ω_4	a_1 (CH_2 bending)	1483.44
θ_1	120.355	ω_5	a_1 (C-C str)	1137.60
∠C-C-H	180.0	ω_6	b_1 (CH_2 anti-sym str)	3232.42
∠C-C-C	180.0	ω_7	b_1 CH_2 group rocking	1039.76
		ω_8	b_1 (CCH in-plane linear bend)	631.00
A_e	9.53209	ω_9	b_1 (CCC in-plane linear bend)	292.51
B_e	0.32329	ω_{10}	b_2 (CH_2 out-of-plane wag)	1120.50
C_e	0.31269	ω_{11}	b_2 (CCH out-of-plane linear bend)	882.00
		ω_{12}	b_2 (CCC out-of-plane linear bend)	254.71

Table 3. Vibrationally averaged structure (Å / deg), rotational constants (cm^{-1}), and vibrational fundamental frequencies (cm^{-1}) for c-C$_3$H$_3^+$, determined from our best QFF. 2nd-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.

Zero-Point Structure and Rotational Constants			
R$_z$(C-C)	1.3658234	$A_0 = B_0$	1.02610
R$_z$(C-H)	1.0806204	C_0	0.51178

Anharmonic Vibrational Analysis

Mode	2nd-PT	VCI 4MR	VCI 5MR	Exp[c]	Exp[d]	Exp
$\nu_1(a_1')$	3176.6 ->3171.7[a]	3174.8	3175.4	3183		
$\nu_2(a_1')$	1618.3 ->1620.7[b]	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	3125±4[e] 3129[f] 3130[g]
$\nu_5(e')$	1299.6	1295.9	1296.2	1290	1293	
$\nu_6(e')$	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			

[a] Fermi type 1 resonance with 2ν_2

[b] Fermi type 1 resonance with 2ν_7

[c] Refs. 15 and 16.

[d] Ref. 5.

[e] Ref. 2.

[f] Ref. 3.

[g] Ref. 4.

Table 4. The x_{st} and $g_{tt'}$ anharmonic constant matrices for c-$C_3H_3^+$ determined from our best QFF. All values are in cm^{-1}. See text for more details.

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

Table 5. Vibration-rotation interaction constants and quartic and sextic centrifugal distorsion constants for c-$C_3H_3^+$. See text for more details.

Vib-rot Constant (MHz)			Distortion Constant				Watson *S* reduction			
Mode	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[a]	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[a]	21.7	τ'_{bbcc}	-0.047	Φ_{aac}	-0.171			h_2	0.000
7	-109.8[a]	-10.9			Φ_{acc}	0.002			h_3	-0.038
8	23.7[a]	-26.4			Φ_{bcc}	0.002				
					Φ_{bbc}	-0.171				
					Φ_{abc}	-0.342				

[a] Modes for which Coriolis resonance has been taken into account.

Table 6. Vibrationally averaged structure (Å / deg), rotational constants (cm^{-1}), and vibrational fundamental frequencies (cm^{-1}) for l-$C_3H_3^+$, determined from our best QFF. 2nd-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 Fig. 1 for coordinate definition.

Zero-Point Structure and Rotational Constants			
R_1	1.095770	θ_1	120.284
R_2	1.353993	A_0	9.40357
R_3	1.236271	B_0	0.31956
R_4	1.068242	C_0	0.30861

	Anharmonic Vibrational Analysis			
	2nd PT	Variational CI		Exp [d]
		4MR	5MR	
ν_1 (A_1)	3228.7	3238.9	3239.0	3238 3139[e]
ν_2[a] (A_1)	2997.0	2999.2	2998.7	3004
ν_3 (A_1)	2084.0	2082.2	2082.2	2077
ν_4 (A_1)	1429.8	1433.7	1434.4	1445
ν_5[b](A_1)	1128.5	1131.9	1131.8	1222
ν_6[c] (B_1)	3061.9 3097.6	3070.8 3104.5	3071.0 3105.0	3093 3113[f]
ν_7 (B_1)	998.0	999.8	1000.6	
ν_8 (B_1)	598.0	607.8	607.7	
ν_9 (B_1)	294.0	294.2	294.8	
ν_{10} (B_2)	1054.6	1057.9	1058.1	1111
ν_{11} (B_2)	859.7	861.8	861.9	
ν_{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[f] 3184/3238[g]

[a] Fermi resonance Type 1 with $2\nu_4$

[b] Fermi resonance Type 2 with $\nu_{11}+\nu_{12}$

[c] Fermi resonance Type 2 with $\nu_3+\nu_7$

[d] Ref. 5.

[e] Ref. 2.

[f] Ref. 3.

[g] Ref. 4.

Table 7. The matrix of anharmonic constants x_{st} for l-$C_3H_3^+$, determined from our best QFF. All values are in cm^{-1}. See text for more details.

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

Table 8. Vibration-rotation interaction constants and quartic and sextic centrifugal distorsion constants for l-$C_3H_3^+$. See text for more details.

	Vib-rot constants (MHz)			Distortion Constant				Watson S reduction			
Mode	α^A	α^B	α^C		(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_K	20.862	H_{KJ}	-2267.423
4	-3188.803	3.755[a]	11.156	τ'_{aabb}	-1.931	Φ_{aab}	-742.911	d_1	-0.000	H_K	7072.116
5	225.856	23.754[a]	24.150[a]	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[a]	-8.912	6.571[a]			Φ_{acc}	-0.059			h_3	0.000
8	336.274[a]	-12.094	-0.485			Φ_{bcc}	0.000				
9	-2468.800[a]	-54.337	-24.327[a]			Φ_{bbc}	-0.001				
10	3490.356[a]	0.795[a]	-5.110			Φ_{abc}	5.962				
11	403.182[a]	2.727	-6.288								
12	1278.499[a]	-42.247[a]	-62.886								

[a] Modes for which Coriolis resonance has been taken into account.

Table 9. Complete set of non-zero quadratic and cubic force constants for c-$C_3H_3^+$ in a symmetry internal coordinate system. See text for more details. Units of force constants are mdyn/Å^n.rad^m appropriate for an energy unit of mdyn Å (1 mdyn Å ≡ 1 aJ).

Quadratic and Cubic Force Constants					
F_{11}	7.217432	$F_{441}=F_{4b4b1}$	-0.1448	$F_{655}=-F_{65b5b}=-F_{6b5b5}$	-0.4172
F_{21}	-0.098532	$F_{442}=F_{4b4b2}$	-19.1998	$F_{65b3}=-F_{6b53}$	0.3817
F_{22}	5.798770	$F_{444}=-F_{44b4b}$	-13.5720	$F_{65b4b}=F_{6b54b}$	-0.1160
F_{33}	0.262156	$F_{541}=F_{5b4b1}$	0.2160	$F_{661}=F_{6b6b1}$	-0.1679
$F_{44}=F_{4b4b}$	5.800512	$F_{542}=F_{5b4b2}$	-0.1399	$F_{662}=F_{6b6b2}$	-0.0729
$F_{54}=F_{5b4b}$	-0.009810	$F_{544}=-F_{54b4b}=-F_{5b44b}$	-0.0774	$F_{664}=-F_{6b64b}=-F_{6b6b4}$	0.0495
$F_{55}=F_{5b5b}$	5.316006	$F_{54b3}=-F_{5b43}$	-0.1386	$F_{665}=-F_{6b65b}=-F_{6b6b5}$	-0.2352
$F_{64}=F_{6b4b}$	0.017754	$F_{551}=F_{5b5b1}$	-13.225	$F_{666}=-F_{6b6b6}$	0.0959
$F_{65}=F_{6b5b}$	0.298226	$F_{552}=F_{5b5b2}$	-0.2622	F_{771}	-0.2385
$F_{66}=F_{6b6b}$	0.414829	$F_{554}=-F_{5b54b}=-F_{5b5b4}$	-0.1110	F_{772}	-0.0827
F_{77}	0.371862	$F_{555}=-F_{5b5b5}$	-18.9961	$F_{874}=F_{8b74b}$	-0.0760
$F_{88}=F_{8b8b}$	0.490412	$F_{641}=F_{6b4b1}$	-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	$F_{654}=F_{6b5b4}$	0.1160	$F_{886}=-F_{8b86b}=-F_{8b8b6}$	0.2418

Table 10. Complete set of non-zero quartic force constants for c-$C_3H_3^+$ in a symmetry internal coordinate system. See text for more details. Units of force constants are mdyn/$Å^n$.rad^m appropriate for an energy unit of mdyn Å (1 mdyn Å ≡ 1 aJ).

Quartic Force Constants					
F_{1111}	59.44	$F_{7744}=F_{774b4b}$	-0.11	$F_{5554}=F_{5b5b5b4b}=3F_{5b5b54}=3F_{5b554b}$	-0.50
F_{2111}	0.20	$F_{7754}=F_{775b4b}$	-0.04	$F_{6444}=F_{6b4b4b4b}=3F_{64b4b4}=3F_{6b4b44}$	0.05
F_{2211}	-0.45	$F_{7755}=F_{775b5b}$	-0.02	$F_{6555}=F_{6b5b5b5b}=3F_{65b5b5}=3F_{6b5b55}$	0.55
F_{2221}	-0.35	$F_{7764}=F_{776b4b}$	0.03	$F_{6664}=F_{6b6b6b4b}=3F_{6b6b64}=3F_{6b664b}$	0.19
F_{2222}	56.66	$F_{7765}=F_{776b5b}$	0.03	$F_{6665}=F_{6b6b6b5b}=3F_{6b6b65}=3F_{6b665b}$	0.19
F_{3311}	0.02	$F_{7766}=F_{776b6b}$	0.94	$F_{5441}=-F_{54b4b1}=-F_{5b4b41}$	0.09
F_{3321}	0.11	$F_{8741}=F_{8b74b1}$	0.15	$F_{5442}=-F_{54b4b2}=-F_{5b4b42}$	0.21
F_{3322}	-0.00	$F_{8742}=F_{8b74b2}$	-0.09	$F_{54b43}=F_{5b443}=-F_{5b4b4b3}$	0.04
F_{3333}	0.04	$F_{8751}=F_{8b75b1}$	-0.18	$F_{5541}=-F_{5b5b41}=-F_{5b54b1}$	0.14
F_{7711}	-0.11	$F_{8752}=F_{8b75b2}$	-0.10	$F_{5542}=-F_{5b5b42}=-F_{5b542}$	0.02
F_{7721}	0.15	$F_{8761}=F_{8b76b1}$	-0.11	$F_{554b3}=F_{5b543}=-F_{5b5b4b3}$	0.28
F_{7722}	-0.10	$F_{8762}=F_{8b76b2}$	-0.08	$F_{6441}=-F_{64b4b1}=-F_{6b4b41}$	-0.01
F_{7733}	0.67	$F_{8811}=F_{8b8b11}$	-0.08	$F_{6442}=-F_{64b4b2}=-F_{6b4b42}$	0.03
F_{774b3}	-0.02	$F_{8821}=F_{8b8b21}$	0.26	$F_{64b43}=F_{6b443}=-F_{6b4b4b3}$	0.05
F_{775b3}	0.01	$F_{8822}=F_{8b8b22}$	-0.11	$F_{6551}=-F_{65b5b1}=-F_{6b5b51}$	-0.10
F_{776b3}	0.04	$F_{8833}=F_{8b8b33}$	0.62	$F_{6552}=-F_{65b5b2}=-F_{6b5b52}$	0.26
F_{7777}	0.09	$F_{8844}=F_{8b8b4b4b}$	-0.14	$F_{65b53}=F_{6b553}=-F_{6b5b5b3}$	0.24
$F_{4411}=F_{4b4b11}$	-0.37	$F_{884b4b}=F_{8b8b44}$	-0.01	$F_{6641}=-F_{6b6b41}=-F_{6b64b1}$	-0.04
$F_{4421}=F_{4b4b21}$	-0.42	$F_{8854}=F_{8b8b5b4b}$	0.03	$F_{6642}=-F_{6b6b42}=-F_{6b64b2}$	0.11
$F_{4422}=F_{4b4b22}$	56.74	$F_{8855}=F_{8b8b5b5b}$	-0.45	$F_{664b3}=F_{6b643}=-F_{6b6b4b3}$	-0.02
$F_{4433}=F_{4b4b33}$	-0.00	$F_{885b4b}=F_{8b8b54}$	-0.11	$F_{6651}=-F_{6b6b51}=-F_{6b65b1}$	0.01
$F_{5411}=F_{5b4b11}$	-0.26	$F_{885b5b}=F_{8b8b55}$	0.55	$F_{6652}=-F_{6b6b52}=-F_{6b65b2}$	0.06
$F_{5421}=F_{5b4b21}$	0.18	$F_{8864}=F_{8b8b6b4b}$	-0.03	$F_{665b3}=F_{6b653}=-F_{6b6b5b3}$	0.08
$F_{5422}=F_{5b4b22}$	0.35	$F_{8865}=F_{8b8b6b5b}$	-0.20	$F_{8744}=-F_{874b4b}=-F_{8b74b4}$	-0.05
$F_{5433}=F_{5b4b33}$	-0.02	$F_{8866}=F_{8b8b6b6b}$	0.43	$F_{8755}=-F_{875b5b}=-F_{8b75b5}$	-0.76
$F_{5511}=F_{5b5b11}$	20.59	$F_{886b4b}=F_{8b8b64}$	-0.00	$F_{8766}=-F_{876b6b}=-F_{8b76b6}$	-0.68
$F_{5521}=F_{5b5b21}$	0.50	$F_{886b5b}=F_{8b8b65}$	0.22	$F_{8841}=-F_{8b84b1}=-F_{8b8b41}$	0.12
$F_{5522}=F_{5b5b22}$	-0.34	$F_{886b6b}=F_{8b8b66}$	1.39	$F_{8842}=-F_{8b84b2}=-F_{8b8b42}$	-0.06
$F_{5533}=F_{5b5b33}$	-0.14	$F_{8877}=F_{8b8b77}$	0.47	$F_{884b3}=F_{8b843}=-F_{8b8b4b3}$	-0.03
$F_{5544}=F_{5b5b44}$	-0.33	$F_{4441}=-F_{4b4b41}$	-0.30	$F_{8851}=-F_{8b85b1}=-F_{8b8b51}$	-0.41
$F_{554b4b}=F_{5b5b4b4b}$	-0.34	$F_{4442}=-F_{4b4b42}$	40.12	$F_{8852}=-F_{8b85b2}=-F_{8b8b52}$	-0.40
$F_{6411}=F_{6b4b11}$	0.05	$F_{4b443}=-F_{4b4b4b3}$	0.00	$F_{885b3}=F_{8b853}=-F_{8b8b5b3}$	-0.22
$F_{6421}=F_{6b4b21}$	0.02	$F_{54b31}=-F_{5b431}$	0.14	$F_{8861}=-F_{8b86b1}=-F_{8b8b61}$	-0.02
$F_{6422}=F_{6b4b22}$	0.05	$F_{54b32}=-F_{5b432}$	-0.08	$F_{8862}=-F_{8b86b2}=-F_{8b8b62}$	-0.09
$F_{6433}=F_{6b4b33}$	0.01	$F_{5551}=-F_{5b5b51}$	38.85	$F_{886b3}=F_{8b863}=-F_{8b8b6b3}$	-0.53
$F_{6511}=F_{6b5b11}$	-0.22	$F_{5552}=-F_{5b5b52}$	0.06	$F_{6541}=-F_{65b4b1}=-F_{6b54b1}=-F_{6b5b41}$	-0.06
$F_{6521}=F_{6b5b21}$	0.03	$F_{5b553}=-F_{5b5b5b3}$	-0.18	$F_{6542}=-F_{65b4b2}=-F_{6b54b2}=-F_{6b5b42}$	0.07
$F_{6522}=F_{6b5b22}$	-0.16	$F_{64b31}=-F_{6b431}$	0.10	$F_{654b3}=F_{65b43}=F_{6b543}=-F_{6b5b4b3}$	0.08
$F_{6533}=F_{6b5b33}$	0.04	$F_{64b32}=-F_{6b432}$	-0.03	$F_{8754}=-F_{875b4b}=-F_{8b754b}=-F_{8b75b4}$	0.02
$F_{6544}=F_{6b5b4b4b}$	-0.10	$F_{65b31}=-F_{6b531}$	-0.06	$F_{8764}=-F_{876b4b}=-F_{8b764b}=-F_{8b76b4}$	0.03
$F_{654b4b}=F_{6b5b44}$	-0.13	$F_{65b32}=-F_{6b532}$	-0.12	$F_{8765}=-F_{876b5b}=-F_{8765b}=-F_{8b76b5}$	-0.68
$F_{6554}=F_{6b5b5b4b}$	-0.13	$F_{6661}=-F_{6b6b61}$	0.06	*12 Non-Symmetry-Unique Constants:*	
$F_{65b5b4}=F_{6b554b}$	0.05	$F_{6662}=-F_{6b6b62}$	-0.08	$F_{7654}=(F_{6644}-F_{6655})/2$	0.00
$F_{6611}=F_{6b6b11}$	0.03	$F_{6b663}=-F_{6b6b6b3}$	0.01	$F_{9854}=(F_{8844}-F_{8855})/2$	0.01

$F_{6621}=F_{6b6b21}$	0.24	$F_{874b3}=-F_{8b743}$	-0.04	$F_{9876}=(F_{8866}-F_{8877})/2$	0.00
$F_{6622}=F_{6b6b22}$	-0.11	$F_{875b3}=-F_{8b753}$	-0.11	$F_{65b4b4}=F_{6b54b4}=(F_{6544}-F_{654b4b})/2$	0.02
$F_{6633}=F_{6b6b33}$	0.09	$F_{876b3}=-F_{8b763}$	-0.79	$F_{65b54b}=F_{6b5b54}=(F_{6554}-F_{65b5b4})/2$	-0.09
$F_{6644}=F_{6b6b4b4b}$	-0.09	$F_{8887}=-F_{8b8b87}$	0.57	$F_{6b65b4}=F_{6b654b}=(F_{6654}-F_{665b4b})/2$	0.06
$F_{664b4b}=F_{6b6b44}$	-0.12	$F_{4444}=F_{4b4b4b4b}=3F_{4b4b44}$	85.18	$F_{8b84b4}=(F_{8844}-F_{884b4b})/2$	-0.07
$F_{6654}=F_{6b6b5b4b}$	-0.02	$F_{5555}=F_{5b5b5b5b}=3F_{5b5b55}$	92.62	$F_{8b85b5}=(F_{8855}-F_{885b5b})/2$	-0.50
$F_{6655}=F_{6b6b5b5b}$	0.07	$F_{6666}=F_{6b6b6b6b}=3F_{6b6b66}$	-0.16	$F_{8b86b6}=(F_{8866}-F_{886b6b})/2$	-0.48
$F_{665b4b}=F_{6b6b54}$	-0.14	$F_{8888}=F_{8b8b8b8b}=3F_{8b8b88}$	0.43	$F_{8b854b}=F_{8b85b4}=(F_{8854}-F_{885b4b})/2$	0.07
$F_{665b5b}=F_{6b6b55}$	0.06	$F_{5444}=F_{5b4b4b4b}=3F_{5b4b44}=3F_{54b4b4}$	0.55	$F_{8b864b}=F_{8b86b4}=(F_{8864}-F_{886b4b})/2$	-0.01
				$F_{8b865b}=F_{8b86b5}=(F_{8865}-F_{886b5b})/2$	-0.21

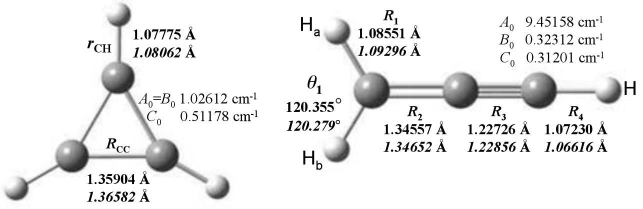
Table 11. Complete set of non-zero quadratic and cubic force constants for l-$C_3H_3^+$ in a symmetry internal coordinate system. See text for more details. Units of force constants are mdyn/Å^n.rad^m appropriate for an energy unit of mdyn Å (1 mdyn Å ≡ 1 aJ). x/y/z represent the 10th, 11th, and 12th internal coordinates, respectively.

F_{11}	6.029788	F_{xx}	0.167448	F_{444}	15.2311	F_{765}	-0.0249	F_{965}	0.0962	F_{yx5}	-0.0131
F_{21}	0.005712	F_{yx}	0.000441	F_{511}	0.0002	F_{771}	-0.0363	F_{971}	0.0092	F_{yy1}	-0.1937
F_{22}	5.540738	F_{yy}	0.385229	F_{521}	0.0047	F_{772}	0.0272	F_{972}	0.0408	F_{yy2}	-0.0120
F_{31}	-0.119775	F_{zx}	0.000222	F_{522}	-0.1527	F_{773}	-0.9361	F_{973}	0.1397	F_{yy3}	-0.4253
F_{32}	0.072319	F_{zy}	0.015043	F_{531}	-0.0050	F_{774}	0.1170	F_{974}	-0.0580	F_{yy4}	0.1286
F_{33}	11.885630	F_{zz}	0.238988	F_{532}	0.1349	F_{775}	0.0325	F_{975}	-0.0546	F_{yy5}	0.0064
F_{41}	0.144706	F_{111}	-34.5269	F_{533}	0.0086	F_{861}	0.0002	F_{981}	0.0010	F_{zx1}	-0.0026
F_{42}	0.074156	F_{211}	-0.0010	F_{541}	-0.0043	F_{862}	-0.0015	F_{982}	0.0095	F_{zx2}	-0.0063
F_{43}	-2.970851	F_{221}	-0.0055	F_{542}	0.1028	F_{863}	0.0073	F_{983}	-0.0528	F_{zx3}	-0.0961
F_{44}	10.906522	F_{222}	-22.3363	F_{543}	0.1047	F_{864}	0.0128	F_{984}	0.0503	F_{zx4}	0.0867
F_{51}	0.001714	F_{311}	0.1236	F_{544}	0.2391	F_{865}	-0.0053	F_{985}	-0.0134	F_{zx5}	0.0082
F_{52}	0.065407	F_{321}	0.0056	F_{551}	0.0024	F_{871}	-0.0002	F_{991}	0.0086	F_{zy1}	-0.0032
F_{53}	-0.231773	F_{322}	0.0869	F_{552}	-0.3928	F_{872}	-0.0025	F_{992}	-0.2028	F_{zy2}	-0.0007
F_{54}	-0.173960	F_{331}	-0.0602	F_{553}	-0.1270	F_{873}	0.1851	F_{993}	-0.1762	F_{zy3}	0.0332
F_{55}	0.682966	F_{332}	-0.1223	F_{554}	-0.0076	F_{874}	-0.2203	F_{994}	0.0320	F_{zy4}	-0.0053
F_{66}	5.533706	F_{333}	-48.6285	F_{555}	-0.2658	F_{875}	0.0052	F_{995}	0.3241	F_{zy5}	0.0068
F_{76}	-0.002072	F_{411}	-0.1359	F_{661}	-0.0068	F_{881}	-0.1404	F_{xx1}	-0.0281	F_{zz1}	-0.0031
F_{77}	0.283223	F_{421}	-0.0008	F_{662}	-22.4743	F_{882}	-0.0192	F_{xx2}	-0.0185	F_{zz2}	-0.0768
F_{86}	-0.004390	F_{422}	0.1801	F_{663}	0.1739	F_{883}	-0.6080	F_{xx3}	-0.3280	F_{zz3}	-0.2289
F_{87}	0.109569	F_{431}	0.0147	F_{664}	0.3239	F_{884}	0.7960	F_{xx4}	-0.0273	F_{zz4}	-0.0271
F_{88}	0.227801	F_{432}	-0.2336	F_{665}	0.2737	F_{885}	-0.0047	F_{xx5}	0.0040	F_{zz5}	0.4596
F_{96}	0.109515	F_{433}	13.1266	F_{761}	-0.0003	F_{961}	-0.0011	F_{yx1}	0.0022		
F_{97}	-0.067911	F_{441}	0.0753	F_{762}	-0.0023	F_{962}	0.0428	F_{yx2}	0.0098		
F_{98}	-0.023718	F_{442}	-0.5212	F_{763}	0.0911	F_{963}	-0.2622	F_{yx3}	0.1577		
F_{99}	0.514243	F_{443}	-45.3965	F_{764}	0.0117	F_{964}	-0.3053	F_{yx4}	0.0810		

Table 12. Complete set of non-zero quartic force constants for l-$C_3H_3^+$ in a symmetry internal coordinate system. See text for more details. Units of force constants are mdyn/$Å^n$.rad^m appropriate for an energy unit of mdyn Å (1 mdyn Å ≡ 1 aJ). x/y/z represent the 10th, 11th, and 12th internal coordinates, respectively.

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_{zzyx}	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_{zzyy}	-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_{zzzx}	-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_{zzzy}	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


r_{CH}
1.07775 Å
***1.08062* Å**
A_0=B_0 1.02612 cm-1
C_0 0.51178 cm-1
R_{CC}
1.35904 Å
***1.36582* Å**
$\mathrm{H_a}$
R_1
1.08551 Å
***1.09296* Å**
A_0 9.45158 cm-1
B_0 0.32312 cm-1
C_0 0.31201 cm-1
θ_1
120.355°
120.279°
$\mathrm{H_b}$
R_2
1.34557 Å
***1.34652* Å**
R_3
1.22726 Å
***1.22856* Å**
R_4
1.07230 Å
***1.06616* Å**
H

TOC Graphic