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## **Infrared spectroscopy of astrophysically relevant hydrocarbons**

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## HIGH-RESOLUTION INFRARED SPECTRUM OF THE $\nu_4$ FUNDAMENTAL BAND OF CYCLOPROPENYL CATION

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The cyclopropenyl cation ( $c\text{-C}_3\text{H}_3^+$ ) is the smallest aromatic hydrocarbon molecule and considered to be a pivotal intermediate in ion-molecule reactions in space. An astronomical identification has been prohibited so far, because of a lack of gas-phase data. Here we report the first high resolution infrared laboratory gas-phase spectrum of the  $\nu_4$  (C-H asymmetric stretching) fundamental band of  $c\text{-C}_3\text{H}_3^+$ . The  $c\text{-C}_3\text{H}_3^+$  cations are generated in supersonically expanding planar plasma by discharging a propyne/helium gas pulse, yielding a rotational temperature of  $\sim 35$  K. The absorption spectrum is recorded in the  $3.19\ \mu\text{m}$  region using sensitive continuous-wave cavity ring-down spectroscopy. The analysis of about 130 ro-vibrational transitions results in precise spectroscopic parameters. These constants allow for an accurate comparison with high-level theoretical predictions, and provide the relevant information needed to search for this astrochemically relevant carbo-cation in space.

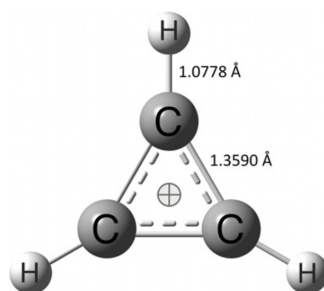
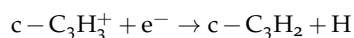


Figure 7.1: Equilibrium geometry of  $c\text{-C}_3\text{H}_3^+$ . The type of CC bond is an intermediate between a typical double bond and single bond. Bond lengths are *ab initio* calculated values by Huang et al. (2011).

## 7.1 INTRODUCTION

The cyclopropenyl cation ( $c\text{-C}_3\text{H}_3^+$ ), a centro-symmetric molecule with  $D_{3h}$  symmetry (Figure 7.1), is the smallest aromatic carbo-cation of high chemical relevance for which accurate spectroscopic data are still incomplete. Astrochemical models consider  $c\text{-C}_3\text{H}_3^+$  as a key intermediate in reaction networks explaining the presence of other hydrocarbons in the interstellar medium (ISM; (Smith, 1992; Agúndez & Wakelam, 2013)). The main formation pathway of cyclopropenyliene ( $c\text{-C}_3\text{H}_2$ ), for example, which is ubiquitous in both diffuse interstellar clouds and dark cloud cores (Cox et al., 1988; Madden et al., 1989), is expected to follow dissociative electron recombination:



The two delocalized  $\pi$  electrons stabilize the aromatic three-member ring structure (Lee et al., 1989), and  $c\text{-C}_3\text{H}_3^+$  is therefore expected to be abundantly present in space. It is also relevant in ion-molecule reactions, driving gas-phase chemistry in the ISM (Smith, 1992) as well as in Titan's atmosphere (Ali et al., 2013), but, contrary to more than 20 cations and anions detected so far in space, an observational identification of  $c\text{-C}_3\text{H}_3^+$  is still pending. The  $c\text{-C}_3\text{H}_3^+$  molecule has no permanent dipole moment, making a radio-astronomical detection through its microwave spectrum impossible. There has been a lack of infrared (IR) gas-phase data of  $c\text{-C}_3\text{H}_3^+$  up to now, prohibiting an astronomical identification through its ro-vibrational spectrum. Instead, in the laboratory, the focus over the past few decades has been on a structural characterization of this cation by IR spectroscopy in the solution of salts and in neon matrices (Craig et al., 1986; Wyss et al., 2001). Vibrational IR predissociation spectra have been reported for weakly bonded complexes of  $c\text{-C}_3\text{H}_3^+$  with various ligands (Dopfer et al., 2002; Roth & Dopfer, 2002). Because of the ligand effect (Botschwina, 2011b) on the molecular geometry of the chromophore, and lower spectral resolution typical for such experiments, these spectra did not allow the deduction of accurate spectroscopic parameters for free, *i.e.*, uncomplexed,  $c\text{-C}_3\text{H}_3^+$ . Such data, however, are available from high-level theory-based *ab initio* calculations of quartic force fields (QFFs), for both  $c\text{-C}_3\text{H}_3^+$  and its  $^{13}\text{C}$ - and D-substituted isotopologues (Huang et al., 2011; Huang & Lee, 2011). These calculated parameters are useful to simulate the expected spectra, as will be demonstrated here, and to guide high resolution laboratory studies, but also hold the potential to guide future astronomical surveys, as will be discussed.

We report the gas-phase identification of free  $c\text{-C}_3\text{H}_3^+$  using high resolution IR absorption spectroscopy. The motivation of this work is a full characterization of the IR spectroscopic properties of  $c\text{-C}_3\text{H}_3^+$  and to make this molecule accessible to astronomers. In parallel, this work allows an independent examination of the applicability of *ab initio* QFF-predictions by Huang et al. (2011) and Huang & Lee (2011) for astronomical use.

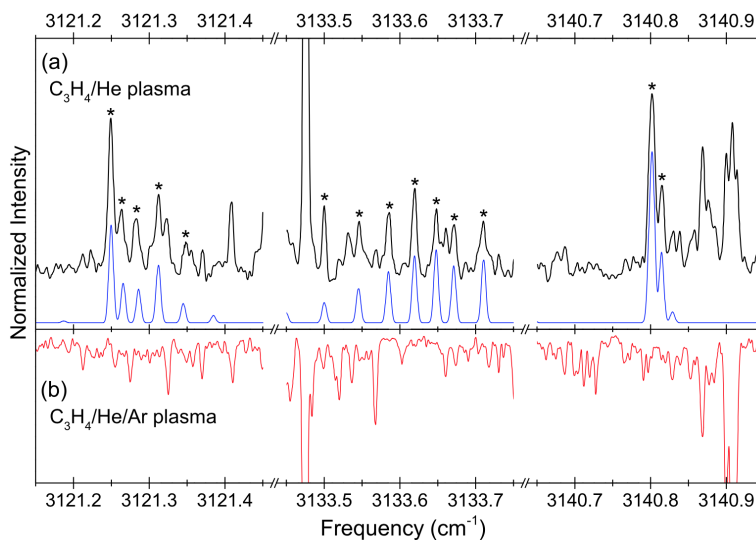


Figure 7.2: Three parts of the experimental spectra recorded in the C<sub>3</sub>H<sub>4</sub>/He (a, upper trace) and C<sub>3</sub>H<sub>4</sub>/He/Ar (b) plasma. The latter spectrum is inverted and illustrates absorption features due to other plasma products that also show up in the upper trace of (a). The simulated spectra using the derived spectroscopic parameters (as listed in Table 7.1) are shown in the lower trace of (a). Absorption lines unambiguously identified as ro-vibrational transitions of c-C<sub>3</sub>H<sub>3</sub><sup>+</sup> are marked by asterisks.

## 7.2 EXPERIMENTAL METHOD

The experimental setup is described in detail by Zhao et al. (2013, 2014a). In brief, the c-C<sub>3</sub>H<sub>3</sub><sup>+</sup> cations are generated by discharging a propyne (C<sub>3</sub>H<sub>4</sub>):He ~1:200 gas mixture in a multi-layer slit discharge nozzle (Motylewski & Linnartz, 1999) in combination with a pulsed valve (General Valve, Series 9, 2 mm orifice). The gas mixture is expanded with a backing pressure of ~7 bar through a 300 μm × 3 cm slit into a vacuum chamber. A pulsed negative high voltage (-600 V/300 mA) with a ~600 μs duration is found to be optimum for c-C<sub>3</sub>H<sub>3</sub><sup>+</sup> production, is applied to the expanding gas mixture, and is set to coincide with the expanding gas pulse (~800 μs).

Continuous-wave cavity ring-down spectroscopy (cw-CRDS) is used to record spectra in direct absorption. The axis of the optical cavity is aligned parallel to and ~2 mm downstream of the slit nozzle throat. A single-mode cw optical parametric oscillator (Aculight), operating at ~3.15 μm with a bandwidth < 5 × 10<sup>-5</sup> cm<sup>-1</sup>, is employed as tunable IR light source. A hardware-based (boxcar integrator) multi-trigger and timing scheme recently reported by Zhao et al. (2013) is used to apply cw-CRDS to the pulsed plasma. In the present experiment, typical ring-down time values are ~8 - 10 μs, corresponding to a detection sensitivity, *i.e.*, noise equivalent absorption, of up to ~2 × 10<sup>-7</sup> per centimeter for the 3 cm long plasma jet.

The IR laser frequency is calibrated using a wavelength meter (Bristol Instruments, 621A-IR) and is independently checked by recording H<sub>2</sub>O trace gas absorption lines in the vacuum chamber, resulting in a wavelength precision better than 0.001 cm<sup>-1</sup>. The Doppler width in the absorption spectrum of C<sub>3</sub>H<sub>4</sub>/He plasma is ~0.007 cm<sup>-1</sup>. The absolute frequency accuracy of the measured positions of absorption lines is better than 0.003 cm<sup>-1</sup>.

## 7.3 RESULTS AND ANALYSIS

The  $c\text{-C}_3\text{H}_3^+$  molecule has four IR-active vibrational modes:  $\nu_4$  (C-H asymmetric stretching),  $\nu_5$  (in-plane wagging),  $\nu_6$  (in-plane scissoring), and  $\nu_7$  (symmetric out-of-plane bending), corresponding to ro-vibrational transition bands centered around  $3135\text{ cm}^{-1}$  ( $3.19\text{ }\mu\text{m}$ ),  $1300\text{ cm}^{-1}$  ( $7.69\text{ }\mu\text{m}$ ),  $925\text{ cm}^{-1}$  ( $10.8\text{ }\mu\text{m}$ ), and  $757\text{ cm}^{-1}$  ( $13.2\text{ }\mu\text{m}$ ), respectively (Lee et al., 1989). In our experiment, the most intense IR band, *i.e.*, the  $\nu_4$  fundamental band, is searched for in the  $3110 - 3160\text{ cm}^{-1}$  range. Parts of the experimental spectrum recorded in the  $\text{C}_3\text{H}_4/\text{He}$  plasma are shown in Figure 7.2a.

The initial step in the assignment of hundreds of observed lines is to simulate the  $c\text{-C}_3\text{H}_3^+$  spectrum using the *ab initio* results (Huang et al., 2011). This simulated spectrum is compared to the experimental spectrum. Since CRDS lacks mass selectivity, absorption features of other plasma-produced species (neutrals, cat- and anions) are also recorded, resulting in additional transitions, partially overlapping and hindering a straight forward interpretation of the experimental spectrum. Nevertheless, by shifting the calculated spectrum by  $-0.55\text{ cm}^{-1}$ , a remarkably small value, a reasonable first match between theoretical and experimental data is obtained. In addition, contrastive experiments with a different gas mixture ( $\text{C}_3\text{H}_4:\text{He}:\text{Ar} \sim 1:100:100$ ) under similar discharge conditions are performed. An example is shown in Figure 7.2b. It is found that all transitions that can be assigned to  $c\text{-C}_3\text{H}_3^+$  become nearly non-detectable in the  $\text{C}_3\text{H}_4/\text{He}/\text{Ar}$  plasma. This allows us to discriminate between transitions from  $c\text{-C}_3\text{H}_3^+$  and other species that clearly do not share a common chemical history, and makes it possible to assign even weaker absorption lines to  $c\text{-C}_3\text{H}_3^+$ , not directly assignable in the initial step, as these can be labeled just following the plasma settings.

In total, about 130 adjacent lines observed in the experimental spectrum have been assigned to the perpendicular  $\nu_4$  fundamental band of  $c\text{-C}_3\text{H}_3^+$ , with an overall band profile corresponding to a rotational temperature of  $\sim 35\text{ K}$ . The wavenumbers of the observed ro-vibrational transitions are given in the **supplementary material**. Least-squares fits of the observed ro-vibrational transition lines are performed in the PGOPHER software (Western, 2014), using an effective Hamiltonian for symmetric top rotators as discussed by Crofton et al. (1988). In the ground state of  $c\text{-C}_3\text{H}_3^+$ , the rotational level energies can be described by

$$E(J, K) = BJ(J+1) + (C-B)K^2 - D_J J^2(J+1) - D_{JK}J(J+1)K^2 - D_K K^4 \quad (7.1)$$

where  $B$  and  $C$  are rotational constants, and  $D_J$ ,  $D_{JK}$ , and  $D_K$  are the quartic centrifugal distortion constants. For the degenerate  $\nu_4$  vibrational mode Coriolis coupling takes place, *i.e.*, interaction between the two components ( $l = +1$ , and  $-1$ ) of the degenerated pair of  $\nu_4$ . This results in a splitting of the degenerated vibrational levels which can be described by  $-\zeta_4 lC$ , where  $\zeta_4$  is the first-order Coriolis coupling constant. By analyzing the two vibrational components, it is concluded that the Coriolis coupling effect in  $\nu_4$  must be very small. The QFF- predicted Coriolis coupling constant  $|\zeta_4| = 0.0092$  by Huang et al. (2011) confirms this interpretation. In addition, there is an unusual  $l$ -type doubling effect for the  $K = l = 1$  level (Crofton et al., 1988). In PGOPHER, this  $l$ -type doubling is described by  $\pm (q_4/2)J(J+1)$  for levels with  $A_1(+)$  and  $A_2(-)$  symmetries, where  $q_4$  is the  $l$ -type doubling constant. In the present work, other higher-order terms, such as sextic and octic centrifugal distortion, are not included in the analysis because the rotational temperature is rather low, and nearly no high- $J, K$  ( $> 10$ ) transitions are observed. The ro-vibrational transition selection rules of the perpendicular  $\nu_4$  fundamental band are:  $\Delta J^p = 0, \pm 1$ ;  $\Delta K = \pm 1$ ;  $\Delta l = \pm 1$ , and  $\Delta|K - l| = 0$ . Moreover, the symmetry of the ground-state wave function and the rotational energy diagram is the same as for  $\text{CH}_3^+$  (Crofton et al., 1988), which also has  $D_{3h}$  symmetry. Therefore, due to the nuclear spin statistics of the three symmetric hydrogen atoms, the weight of the ground state populations in ( $A_1', A_1''$ ), ( $A_2', A_2''$ ), and ( $E', E''$ ) rotational levels amounts to 0, 2, and 1, respectively.

A least-squares fit including all parameters may suffer from possible correlations between the constants of ground and excited  $\nu_4$  states. Therefore, the 38 combination differences for ground-

state rotational levels that can be derived from the observed ro-vibrational transitions are fitted as a first step. This yields three independently determined ground-state constants (in  $\text{cm}^{-1}$ ):

$$B_0 = 1.02583(10) \quad D_{J,0} = 3.5(12) \times 10^{-6} \quad D_{JK,0} = -4.5(37) \times 10^{-6}$$

In the second step, a global fit of all observed ro-vibrational transitions is made. It is found that it is not possible to determine the  $C_0$  and  $D_{K,0}$  constants from the  $\nu_4$  spectrum, similar as in the case of the ground state combination difference fit. Therefore,  $C_0$  is fixed to a value of  $0.511\ 65\ \text{cm}^{-1}$  that is derived from the constant  $B_0$  (determined from the ground state combination difference fit) and the QFF-predicted value of  $(1/C_0 - 2/B_0 = 0.004\ 837)$ . This interpretation is based on the assumption that the QFF-predicted inertia defect,

$$\Delta_0 = I_c - I_a - I_b = \left( \frac{h}{8\pi^2 c} \right) \left( \frac{1}{C_0} - \frac{2}{B_0} \right) \quad (7.2)$$

where  $I_c$  and  $I_a = I_b$  are the three rotational moments of inertia, has a comparable error as that for the rotational constant  $B_0$ . For  $D_{K,0}$ , the QFF-predicted value is used and fixed in the fit.

The resulting spectroscopic constants are summarized in Table 7.1. The overall rms of the fit is less than  $0.002\ \text{cm}^{-1}$ , *i.e.*, substantially smaller than the spectral resolution in our experiment. The derived ground state constants  $B_0$ ,  $D_{J,0}$ , and  $D_{JK,0}$  are consistent with the corresponding values derived from the combination difference fit. This is indicative for nearly negligible correlations between the derived ground and  $\nu_4$  excited state constants. The high-level QFF-predicted spectroscopic constants by Huang et al. (2011) are also listed in Table 7.1. A comparison with the experimentally determined values shows excellent agreement; the difference in the calculated rotational constants  $B_0$  and  $B_4$  is only  $\sim 0.03\%$ . The  $\nu_4$  anharmonic vibrational frequency computed by second-order perturbation theory shows a remarkable small offset deviation of  $\sim 0.55\ \text{cm}^{-1}$ , substantially smaller than the typical error (several  $\text{cm}^{-1}$ ) for the used level of theory. The QFF predicted centrifugal distortion constants  $D_J$  and  $D_{JK}$  (for the equilibrium structure) are also very close to the experimentally determined values in the zero-point ground state. These comparisons confirm that the *ab initio* QFF calculations for the tightly bounded  $c\text{-C}_3\text{H}_3^+$  by Huang et al. (2011) are highly accurate and can be used in assisting the assignment of high resolution experimental spectra.

#### 7.4 ASTROPHYSICAL IMPLICATIONS

Since  $c\text{-C}_3\text{H}_3^+$  has no pure rotational transitions, a direct observation of this cation in the ISM is only available via ro-vibrational transitions in the IR. The  $\nu_4$  band is the most intense IR band. Due to the absolute frequency accuracy of our experimental spectrum, the present work provides accurate data that can be directly used for an astronomical search in the  $3.19\ \mu\text{m}$  region. For the other three IR-active fundamental bands ( $\nu_5$  at  $\sim 7.69\ \mu\text{m}$ ,  $\nu_6$  at  $\sim 10.8\ \mu\text{m}$ , and  $\nu_7$  at  $\sim 13.2\ \mu\text{m}$ ), which are not experimentally studied here, spectroscopic constants can be interpreted using the experimentally determined zero-point ground-state constants and the QFF-predicted vibration-rotation interaction constant by Huang et al. (2011). Even without high resolution experimental data for these bands, such interpreted spectroscopic parameters are considered to be of reasonable accuracy to calculate ro-vibrational spectra for astronomical use. It should be noted that due to the level of accuracy of QFF-predicted fundamental vibrational frequencies, a small shift by up to a few  $\text{cm}^{-1}$  might be necessary when applying such calculated spectra to search for  $c\text{-C}_3\text{H}_3^+$  in astronomical IR observations.

The infrared, however, is not the most optimal wavelength domain for high-sensitivity and high resolution studies using ground-based observations. An alternative approach to identify  $c\text{-C}_3\text{H}_3^+$  in space is to search in the radio/millimeter wave-length region for spectral signatures of the (substantially less abundant)  $^{13}\text{C}$  and D mono-substituted isotopologues that have been predicted to possess effective permanent dipole moments (Huang & Lee, 2011). High-level *ab initio* QFF-calculations

Table 7.1: Spectroscopic parameters<sup>a</sup> (in  $\text{cm}^{-1}$ ) of  $c\text{-C}_3\text{H}_3^+$ 

Constants	This work	Huang et al. (2011)
$\nu_4$	3131.1447(5)	3131.7
$B_0$	1.025 84(6)	1.026 10
$C_0^b$	0.511 65	0.511 78
$D_{J,0} (\times 10^6)$	4.3(6)	2.44
$D_{JK,0} (\times 10^6)$	-6.9(6)	-4.07
$D_{K,0}^b (\times 10^6)$	1.8	1.83
$B_4$	1.022 98(7)	1.023 24
$C_4$	0.510 40(2)	0.510 37
$D_{J,4} (\times 10^6)$	3.7(6)	2.44
$D_{JK,4} (\times 10^6)$	-6.3(8)	-4.07
$D_{K,4} (\times 10^6)$	2.2(4)	1.83
$q_4 (\times 10^4)$	1.9(7)	
$\zeta_4 (\times 10^3)$	-7.9(1)	-9.2

a. Numbers in parentheses are one standard deviation in units of the last significant digit.  $\zeta_4$  is dimensionless.

b.  $C_0$  and  $D_{K,0}$  are fixed in the fit (see the text).

on the mono-substituted isotopologues of  $c\text{-C}_3\text{H}_3^+$  have been performed by Huang & Lee (2011). To examine the accuracy, *i.e.*, astronomical applicability of these theoretical predictions, comparisons of the fine rotational structures between the QFF-predicted and simulated experimental spectrum of  $c\text{-C}_3\text{H}_3^+$  are made. It is found that even with an offset of  $-0.55 \text{ cm}^{-1}$  on the QFF-predicted spectrum, discrepancies up to  $\sim 0.03 \text{ cm}^{-1}$  still appear for some strong ro-vibrational transitions, which may be due to small deviations (several MHz) of the QFF predicted rotational constants. This comparison indicates that the QFF predictions by Huang & Lee (2011) for the  $^{13}\text{C}$  and D mono-substituted  $c\text{-C}_3\text{H}_3^+$  isotopologues are useful to guide the data interpretation of a high resolution laboratory-based survey. However, for an astronomical search for  $c\text{-C}_3\text{H}_3^+$  isotopologues in the radio/millimeter wavelength region, these predictions are unfortunately not accurate enough and rest frequencies provided by laboratory experiments will be needed.

## 7.5 CONCLUSIONS

We have presented the first gas-phase detection of  $c\text{-C}_3\text{H}_3^+$  by the high resolution IR spectrum of its  $\nu_4$  band. The accurately determined molecular constants for the ground state and the  $\nu_4$  fundamental vibrational level provide information that is needed to make this molecule accessible to astronomical surveys in the IR.

## 7.6 ACKNOWLEDGEMENTS

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