



Spectroscopic Characterization of Key Aromatic and Heterocyclic Molecules: A Route toward the Origin of Life

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Abstract

To gain information on the abiotic synthesis of the building blocks of life from simple molecules, and their subsequent chemical evolution to biological systems, the starting point is the identification of target species in Titan-like planets; i.e., planets that resemble the primitive Earth, as well as in Earth-like planets in the habitable zone of their star, namely planets where life can be already originated. In this scenario, molecular spectroscopy plays a crucial role because spectroscopic signatures are at the basis of an unequivocal proof for the presence of these target molecules. Thanks to advances in many different techniques and NASA’s successful *Kepler* exoplanet transit mission, thousands of diverse planets outside of our solar system have been discovered. The *James Webb Space Telescope (JWST)*, scheduled to be launched in 2018, will be very helpful in the identification of biosignature gases in Earth-like planets’ atmospheres and prebiotic molecule signatures in Titan-like atmospheres, by observing their absorption during transits. Although the search for key-target molecules in exoplanet atmospheres can be carried out by the *JWST* Transit Spectroscopy in the infrared (IR) region (0.6–29 μm wavelength range), opportunities for their detection in protostellar cores, protoplanetary disks, and on Titan are also offered by interferometric high spectral and spatial resolution observations using the Atacama Large Millimeter/submillimeter Array. In the present work, target molecules have been selected, and their spectroscopic characterization presented in view of supporting their infrared and complementary millimeter/submillimeter-wave spectral observations. In detail, the selected target molecules include: (1) the three-membered oxygen-containing heterocycles, oxirane and protonated oxirane; (2) the cyclopropenyl cation and its methyl derivative; (3) two examples of ortho- and peri-fused tri-cyclic aromatic rings, i.e., the phenalenyl cation ($\text{C}_{13}\text{H}_9^+$) and anion ($\text{C}_{13}\text{H}_9^-$); and (4) uracil, a specific RNA base.

Key words: ISM: molecules – line: identification – methods: data analysis – molecular data – planets and satellites: atmospheres

1. Introduction

The observation of an abiological organic synthesis on Titan by the Cassini–Huygens Mission is a major breakthrough, and by far the largest “surprise” in terms of planetary chemistry in our solar system (Ali et al. 2013, 2015). The observed organics on Titan, i.e., hydrocarbons, their derivatives, and ions (carbocations and carbanions), show a structural complexity similar to that of the terrestrial prebiotic molecules. The chemical pathway begins in Titan’s upper atmosphere, with the conversion of methane to methonium ion CH_5^+ , and proceeds toward molecular complexity. The abiotic organic synthesis is thus a direct consequence of Olah’s related two-electron three-center (2e, 3c) bound penta- or tetracoordinated nonclassical carbonium ion chemistry (Olah 1972, 1995; Ali et al. 2013, 2015; Olah et al. 2016a, 2016b). In two recent pioneering articles, Olah et al. (2016a, 2016b) posited that the abiotic carbon chemistry on Titan (Ali et al. 2015) is intimately linked with chemistry in the interstellar medium (ISM). Both methane and its derivative methanol are among the most abundant molecular species in the observable galaxies. Olah et al. (2016a, 2016b) proposed a feasible new pathway in which the dense cores of interstellar molecular clouds of methanol ices undergo transformations similar to that pointed out by Cassini’s mass spectrometry on Titan for hydrocarbons and their derivatives, under the influence of either high-energy cosmic

rays or ultraviolet photolysis (Ali et al. 2013, 2015). A possible connection between interstellar grain catalysis in solid state and methonium ion-based gas-phase chemistry on Titan is discussed. The authors (Olah et al. 2016a, 2016b) carried out quantum-chemical calculations of structures, energies, and frequencies at the coupled-cluster level, also accounting for zero-point energy correction (CCSD(T)/cc-pVTZ + ZPE), and showed feasible interconversion pathways for the CH_5^+ and CH_3OH_2^+ carbocations. No one has stated this more boldly than the chemistry Nobel Laureate George Andrew Olah (in Olah et al. 2016a): “Of particular interest to us is the remarkable detection of varied carbocations and their similarity with their terrestrial analogues. The proven similarity with our terrestrial studied chemistry provides the first scientific evidence that our Earth is not a unique celestial body for producing the chemical building blocks.”

The key point in the theme of origin of life is that biological macromolecules like proteins, ribonucleic acid (RNA), and deoxyribonucleic acid (DNA) are built from smaller precursors such as amino acids, nucleobases, sugars, and phosphates. The fact that various aromatic molecules and heterocycles (Ali et al. 2013, 2015) exist in Titan’s atmosphere is remarkable to the RNA-based world hypothesis, which implies that life is “built” from ribose (a cyclic, five-membered, ring-structure sugar molecule), the pyrimidine and purine nucleobases, and

phosphates. Both purine and pyrimidine are aromatic organic compounds belonging to the class of nitrogen-containing heterocyclic molecules. Of interest to the present study is that three of the five nucleobases, namely, cytosine, thymine, and uracil, are derivatives of pyrimidine. A potential precursor for prebiotic aromatic species, which can also be considered a precursor of pentoses, is ethylene oxide (also known as oxirane, $c\text{-C}_2\text{H}_4\text{O}$) that is a cyclic three-membered ring consisting of one oxygen and two carbon atoms. Raulin and coworkers (Bernard et al. 2003) detected oxirane as the most abundant (by about one order of magnitude) O-containing species in an experimental simulation of Titan's atmosphere, including CO at a 100 ppm level in $\text{N}_2\text{-CH}_4$ mixtures. However, the formation of aromatic cyclic compounds, as well as of the N-containing counterparts in space environment, is a long-standing problem. As a first step toward the understanding of how aromaticity (including the formation of heterocycles) was achieved in the atmosphere of primitive Earth, in two recent publications (Ali et al. 2013, 2015), some of us pointed out how the molecular structure and reactivity of the carbocations detected by Cassini instruments (also including Olah's "nonclassical carbonium" ions) can lead to the formation of aromatic species. In Ali et al. (2015), the composition, molecular structures, and chemistry at the basis of the growth of the complex macromolecules observed by the Cassini CAPS spectrometers were investigated. Plausible reaction routes from simple aromatic molecules to complex polyaromatic compounds were proposed, and the phenalenyl cation $\text{C}_{13}\text{H}_9^+$ and its corresponding anion $\text{C}_{13}\text{H}_9^-$ were identified as important intermediates in the process of molecular growth.

After the introductory considerations above, it is clear that the observational search of key aromatic molecules and heterocycles in planetary and astrophysical objects can help to illuminate the role of the abiological organic synthesis in relation to the origin of life issue. The purpose of the present paper is to provide a state-of-the-art quantum-chemical investigation of the rotational and vibrational spectroscopic features for a few selected aromatic and heterocyclic compounds from a list of prebiotic molecules. The primary goal is to guide astronomical line searches in the infrared and/or millimeter/submillimeter-wave ranges, as well as to direct future laboratory measurements. The selected target molecules include: (1) the three-membered oxygen-containing heterocycles, oxirane and protonated oxirane, to probe oxygen chemistry in space (Puzzarini et al. 2014a, 2014b); (2) cyclopropenyl cation—the simplest Huckel's aromatic molecule—and its cyclic derivative methyl-cyclopropenyl cation, which are key precursor species toward the molecular complexity on Titan; (3) two examples of ortho- and peri-fused tri-cyclic aromatic rings, i.e., the phenalenyl cation ($\text{C}_{13}\text{H}_9^+$) and anion ($\text{C}_{13}\text{H}_9^-$), which are important intermediates in molecular growth; and (4) uracil, a specific RNA base. For the purpose of this study, it is important to point out that, as is well-demonstrated in the literature (see, for example, Puzzarini et al. 2010b, 2014b, 2014c; Puzzarini 2013), high-level quantum-chemical computations with an adequate treatment of electron correlation effects, extrapolation to the basis-set limit, and inclusion of core correlation are able to quantitatively predict spectroscopic parameters. In particular, rotational constants, which are the leading terms in rotational spectroscopy, can be predicted with an accuracy, in relative

terms, of about 0.1% or even better, and their accuracy can be further improved (by about one order of magnitude) by means of empirical scaling procedures based on computed and experimental data available for systems similar to the one under consideration. On the whole, the computed spectroscopic parameters lead to the prediction of rotational transitions with a relative accuracy better than 0.1%, which can be as good as 0.001%. At the same time, vibrational wavenumbers can be calculated with an accuracy well within $5\text{--}15\text{ cm}^{-1}$ with respect to their experimental counterparts. Finally, high-quality computed infrared intensities lead to spectral band-shapes in good agreement with main experimental features, thus allowing the disentanglement of the contributions of low-intensity fundamentals from those of high-intensity overtones and combination bands.

In addition to the characterization of the organic chemistry on Titan, understanding the chemical processes in protoplanetary disks around young stars, the birth sites of planets, can also tell us much about the origin of biological molecules and life in general. There is also a new piece of evidence that nearly all stars have planets around them. Because of the recent discoveries of a vast number of Earth and super-Earth exoplanets, the gap between the chemistry occurring in disks and the resulting chemical composition of exoplanets could be bridged. Therefore, the observation of spectral signatures of key prebiotic compounds in protoplanetary disks and exoplanet atmospheres would provide an important contribution to shed light on the origin of life issue. Young planetary systems are formed from the hard vacuum of interstellar space, in a vast cosmos, over approximately 10^7 years. This evolutionary process in Giant Molecular Clouds begins via gravitational collapse of dense molecular cores with temperatures between 10 and 50 K and densities from 10^3 to 10^6 cm^{-3} to form protostellar cores. Protostellar cores with high-mass protostars are usually referred to as "hot cores," whereas "hot corinos" refers to solar type protostars in star-forming regions. The prebiotic chemistry of hot cores and hot corinos in the interstellar region is very rich and quite complex. There are numerous examples of protostellar cores, such as the low-mass protostar IRAS 16293-2422. Two sources stand out among the known hot cores: one is the nearby object Orion IRC2 massive star-forming region, and the other is the massive proto-cluster SgrB2, with its high abundance of organic species. A key question in the newly flourishing field of astrochemistry is how far abiotic carbon chemistry (the chemical route toward the origin of life) proceeds in the evolution from the protostellar cores to the young planetary systems. Protoplanetary disks (i.e., the T Tauri phase) are just the preceding stages of mature stars and their planetary systems (Sakai et al. 2014a, 2014b). It is therefore critical to unequivocally characterize the primitive abiogenic organic synthesis, occurring via either reactions in the gas phase or surface processes, as a function of the distance in circumstellar disks from the central star. This could actually be achieved using the high sensitivity and wavelength resolution, as well as high spatial resolution capabilities of modern ground- and space-based telescopic observations.

In the era of exoplanet detection and characterization (Seager 2010, 2013; Perryman 2011), astronomers are able to determine some of their physical properties very accurately, such as their mass, orbital period, and distance from the host star. However, the chemical composition of their atmosphere is largely unknown. Probably, the best opportunity to fill this gap will

be provided by the infrared spectroscopy investigation of the atmosphere of exoplanets using the *James Webb Space Telescope (JWST)*. The *JWST* will be launched in 2018 (Gardner et al. 2006), and will most likely characterize the cooler and the smaller exoplanets around M-dwarfs in the solar neighborhood (Ricker et al. 2014). Particular interest is focused upon Titan-like exoplanets, i.e., those characterized by a reducing atmosphere and ultraviolet radiation from the host star. Although much remains to be studied regarding the abiotic synthesis of organic compounds, it is well-accepted that, in planets with highly reducing atmospheres, organic synthesis and prebiological chemistry can take place. Although the search for complex organic molecules in exoplanet atmospheres can be carried out exclusively by the *JWST* transit spectroscopy in the infrared wavelength region (0.6–29 μm wavelength range), opportunities for their detection in protostellar envelopes and protoplanetary disks, as well as on Titan, are also offered by the interferometric high spectral and spatial observations using the ground-based observatory Atacama Large Millimeter/submillimeter Array (ALMA). The complementary infrared spectroscopic detection for these prebiotic compounds can also be undertaken by the high-resolution EXES instrument mounted on the Stratospheric Observatory for Infrared Astronomy in the mid-infrared region.

The present paper is organized as follows: in the following section after this introduction, the computational details of rotational and vibrational spectroscopy of the selected polyatomic prebiotic molecules are discussed in view of guiding their characterization and identification in planetary and astrophysical targets. Finally, in the last section, we offer our concluding remarks on the astrophysical implications of our investigation.

2. Rotational and Vibrational Spectroscopy of Prebiotic Molecules

Among the selected molecules, only oxirane, uracil, and the cyclopropenyl cation have been investigated experimentally. For all other species, we must rely on quantum-chemical computations of the required spectroscopic parameters. Because high accuracy is required, state-of-the-art quantum-chemical methods are employed, in conjunction with composite approaches. However, experimental data for oxirane, uracil, and the cyclopropenyl cation allow us to confirm the accuracy obtainable with the computational approaches employed.

2.1. Rotational Spectroscopy of Three-membered Ring Compounds

2.1.1. Three-membered Oxygen-containing Heterocyclic Compounds: Oxirane and Protonated Oxirane

Recent measurements revealed that Titan’s atmosphere is characterized by a rich and complex organic chemistry (see Ali et al. 2015 and references therein). Furthermore, oxirane and protonated oxirane have been suggested as potential prebiotic species present in Titan’s atmosphere (Puzzarini et al. 2014a, 2014b). Although the rotational and infrared spectra of the former have been well-characterized experimentally, a spectroscopic study of the latter was completely missing. For oxirane and protonated oxirane, in Puzzarini et al. (2014a, 2014b), a thorough investigation has been carried out by means of a state-of-the-art computational approach, with the experimental data

of the former molecule being used to assess the accuracy of the spectroscopic parameters.

To determine accurate equilibrium structures, we used the coupled-cluster singles and doubles method, augmented by a perturbative treatment of triple excitations (CCSD(T); Raghavachari et al. 1989), in conjunction with a composite scheme based on the additivity approximation applied at the energy-gradient level (Heckert et al. 2005, 2006), as implemented in the CFOUR package (Stanton et al. 2009). Within this approach, the contributions considered are the extrapolation to the complete basis set (CBS) limit and the core-valence (CV) correlation correction. The equilibrium geometries obtained in this way are denoted as CCSD(T)/CBS+CV. From knowledge of the equilibrium structure, the equilibrium rotational constants B_e are straightforwardly derived (Gordy & Cook 1984). By correcting them for vibrational effects, estimates of the vibrational ground-state rotational constants B_0 are obtained (Puzzarini et al. 2010b; Puzzarini 2013). The vibrational corrections require cubic force constants to be computed. To this end, a hybrid force field (denoted “Best/CC (VTZ)”) was employed in Puzzarini et al. (2014a, 2014b). The hybrid force field was obtained by combining a best-estimated harmonic force field (at the CCSD(T)/CBS+CV level) with cubic and semi-diagonal quartic force constants at the CCSD(T)/cc-pVTZ level (see Puzzarini et al. 2014a, 2014b for all details). As a byproduct of the force field calculations, centrifugal-distortion constants are also obtained.

While we refer interested readers to Puzzarini et al. (2014a, 2014b) for a complete account, Figure 1 shows a portion of the simulated spectra for oxirane, based on computed and experimental values, as well as for protonated oxirane in the ALMA band 3. Despite very good agreement in relative terms, absolute deviations larger than 1–2 MHz make the predictions unsuitable for guiding astronomical searches, albeit sufficient to support laboratory measurements. To further improve the predictive capabilities of the computed spectroscopic parameters (i.e., rotational and centrifugal-distortion constants), an empirical scaling procedure can be employed. Considering a generic parameter X , the procedure is based on multiplying the computed value of X for protonated oxirane (denoted by the superscript oxiH^+) by the corresponding experiment/theory ratio for a reference compound, oxirane in the present case (denoted by the superscript oxi):

$$X_{\text{scal}}^{\text{oxiH}^+} = X_{\text{calc}}^{\text{oxiH}^+} \times \left(\frac{X_{\text{exp}}^{\text{oxi}}}{X_{\text{cal}}^{\text{oxi}}} \right), \quad (1)$$

where scal , exp , and calc denote the scaled, experimental, and quantum-chemically calculated values for X , respectively. This approach is extensively used in the field of rotational spectroscopy. Figure 2 compares the simulated spectrum of protonated oxirane in ALMA band 3 via the computed parameters and the scaled values. From the inset, it is evident that the differences can be as small as a few MHz, but also as large as about 100 MHz. Based on the literature (see, for example, Puzzarini et al. 2014c; Cazzoli et al. 2014; Puzzarini et al. 2014b), the scaling procedure is able to improve the spectroscopic parameters to such an extent that the rotational transitions can be predicted with an accuracy of 1 MHz or better. The scaled spectroscopic parameters, based on the data reported in Puzzarini et al. (2014a), are collected in Table 1.

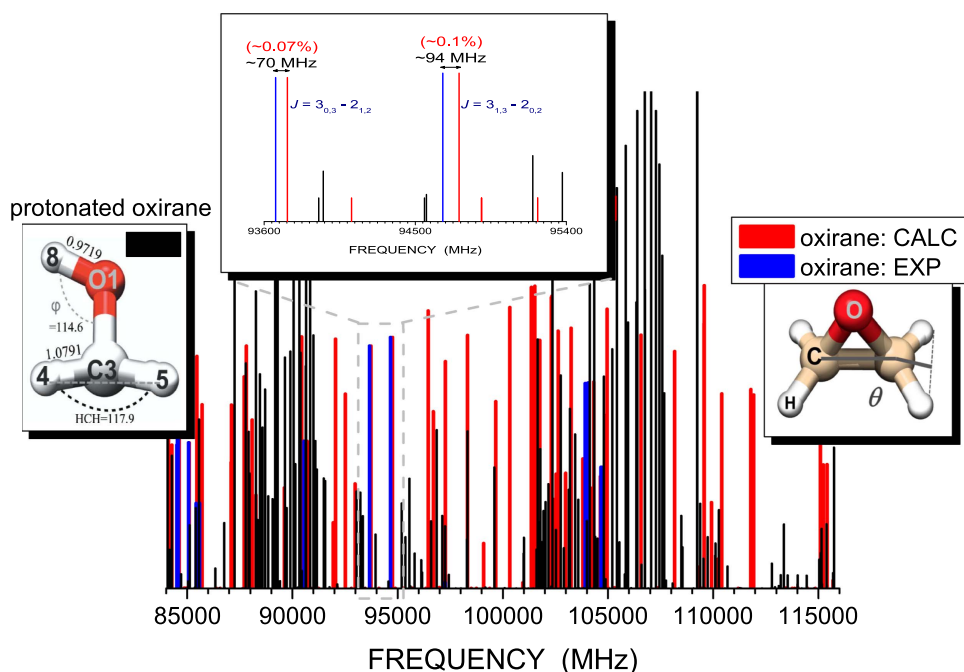


Figure 1. Rotational stick spectra of oxirane and protonated oxirane in the ALMA band 3 frequency range. For details, see text. Intensities are in arbitrary units.

2.1.2. The Smallest Organic Molecules: Cyclopropenyl and Methyl-cyclopropenyl Cations

In Ali et al. (2013), it was demonstrated that a significant fraction of the $C_3H_3^+$ composition detected by the INMS spectrometer in Titan's upper atmosphere is the stable cyclopropenyl cation ($c-C_3H_3^+$), the simplest Huckel's aromatic molecule. Furthermore, in Ali et al. (2013), the reaction of CH_3^+ with methylacetylene explained the observed composition of $C_4H_5^+$ in terms of the methyl-substituted cyclopropenyl cation ($c-C_3H_2CH_3^+$). To definitively confirm the conclusions drawn in Ali et al. (2013), the spectroscopic features of the cyclopropenyl and methyl-cyclopropenyl cations need to be detected. This first requires an accurate spectroscopic characterization to be carried out.

The computational approach described in the previous section for oxirane and protonated oxirane has been employed for the spectroscopic characterization of the cyclopropenyl and methyl-cyclopropenyl cations. For $c-C_3H_3^+$, the composite approach employed in the geometry optimization also accounted for higher excitations in the cluster expansion (i.e., full treatment of triple (fT) and quadruple (fQ) excitations), thus leading to the CCSD(T)/CBS+CV+fT+fQ level of theory. Readers interested in the methodology are referred to Heckert et al. (2005, 2006) and to Puzzarini et al. (2010b). The molecular structure and the corresponding structural parameters are depicted in Figure 3. Although the methyl-cyclopropenyl cation has a permanent dipole moment, thus ensuring its rotational spectrum to be observable, the high symmetry of $c-C_3H_3^+$ (belonging to the D_{3h} point group) leads to a null dipole moment, thus precluding the use of pure rotational spectroscopy. Therefore, the detection of $c-C_3H_3^+$ is possible only via vibrational or vibro-rotational spectroscopy. On the other hand, isotopic substitution (like deuteration) leads to a small, but sufficient, dipole moment that would allow the observation by means of rotational spectroscopy. The results for the main isotopic and mono-deuterated species of cyclopropenyl cation are collected in Table 2 and compared

to experiment and previous computational data. We note a very good agreement with the experiment, as well as with a previous accurate theoretical work (Huang et al. 2011; Huang & Lee 2011). It is also important to note that rotational constants at the CCSD(T)/CBS+CV level are negligibly worse than the CCSD(T)/CBS+CV+fT+fQ ones.

Zhao et al. (2014) reported the first high-resolution infrared laboratory gas-phase spectrum of the ν_4 (C–H asymmetric stretching) fundamental band of $c-C_3H_3^+$, thus opening the way to its astronomical identification. The ν_4 band lies at 3131.1 cm^{-1} . Another promising vibro-rotational band is ν_5 , which lies at 1293 cm^{-1} and corresponds to the asymmetric CCC ring stretching. In Table 2, our computed rotational constants for the $\nu_4 = 1$ and $\nu_5 = 1$ states are given; those of the former state are compared to the experimental data, showing a very good agreement. The quartic centrifugal-distortion constants of the ground state can be used as a good approximation for simulating the ν_5 vibro-rotational spectrum.

The same accuracy noted for the spectroscopic parameters of $c-C_3H_3^+$ is also expected for the computational results of $c-C_3H_2CH_3^+$, which are summarized in Table 3. To the best of our knowledge, this is the first spectroscopic characterization of this cation, whose importance in Titan's atmosphere has been pointed out in Ali et al. (2013).

2.2. Vibrational (IR) Spectroscopy of Aromatic Compounds

2.2.1. Nucleobasis: Uracil

The informational subunits of RNA or DNA consist of substituted N-heterocyclic compounds that fall into two groups: those based on purine (adenine and guanine) and those based on pyrimidine (uracil, cytosine, and thymine). Although not yet detected in the ISM, N-heterocycles, including uracil, have been confirmed to exist in extraterrestrial meteorites (carbonaceous chondrites; Callahan et al. 2011). Various studies have shown that the irradiation of pyrimidine in ices containing H_2O and/or NH_3 leads to the abiotic production of substituted

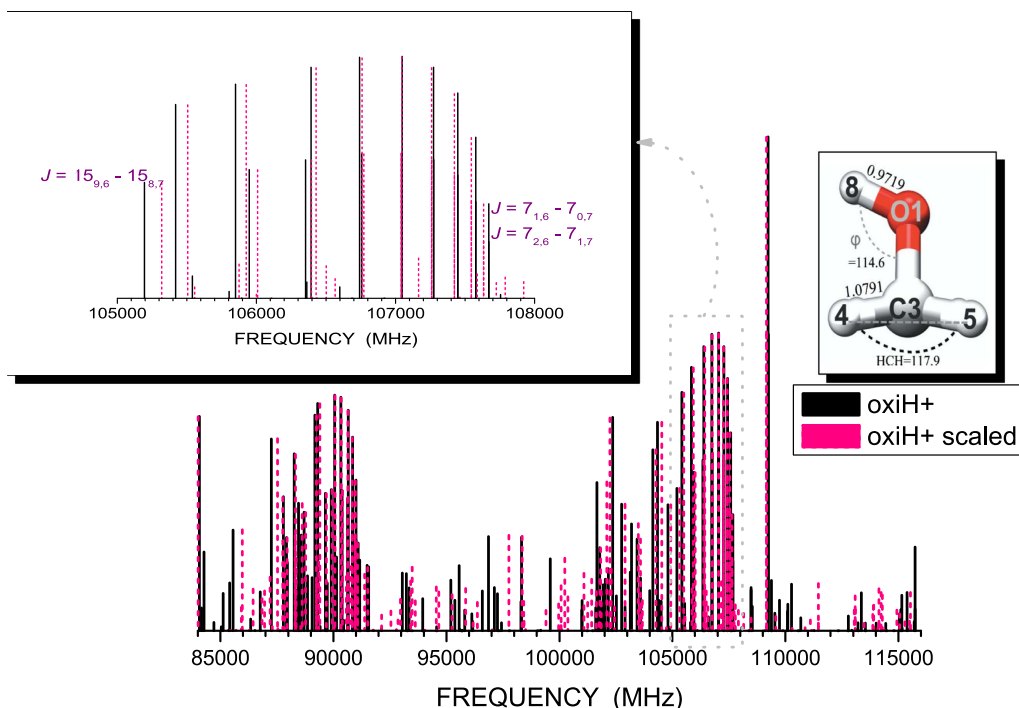


Figure 2. Comparison of the computed and scaled rotational spectra of protonated oxirane in the ALMA band 3 frequency range. For details, see text. Intensities are in arbitrary units.

Table 1

Computed^a and Scaled Spectroscopic Parameters of Protonated Oxirane

	Computed	Scaled
A_0 /MHz	21501.549	21469.627
B_0 /MHz	20352.458	20357.711
C_0 /MHz	12619.031	12610.080
D_J /kHz	28.469	28.590
D_{JK} /kHz	14.521	13.560
D_K /kHz	-15.930	-16.630
d_J /kHz	10.123	10.290
d_K /kHz	28.073	28.310
H_J /Hz	0.00361	0.00361
H_{JK} /Hz	-0.09846	-0.10373
H_{KJ} /Hz	0.15440	0.16185
H_K /Hz	-0.05451	-0.05714
h_J /Hz	0.01014	0.01216
h_{JK} /Hz	-0.02097	-0.02216
h_K /Hz	0.05577	0.06804

Note.

^a From Puzzarini et al. (2014a): Equilibrium rotational constants at the CCSD(T)/CBS+CV level augmented by vibrational corrections from a hybrid “Best/CC(VTZ)” force field (see text). Quartic and sextic centrifugal-distortion constants computed from the same hybrid force field.

pyrimidines, also including uracil (see Materese et al. 2013 and references therein) and that nucleobases and other prebiotic molecules can be formed in the complex organic aerosols produced in Titan’s atmosphere (see, for example, Hörst et al. 2012).

As already mentioned, Titan’s atmosphere is characterized by a rich and complex organic chemistry (see Ali et al. 2015 and references therein), and is considered to be a model of primitive Earth. Thus, its investigation might provide a unique opportunity to explain terrestrial prebiotic chemistry. Several simulation studies of

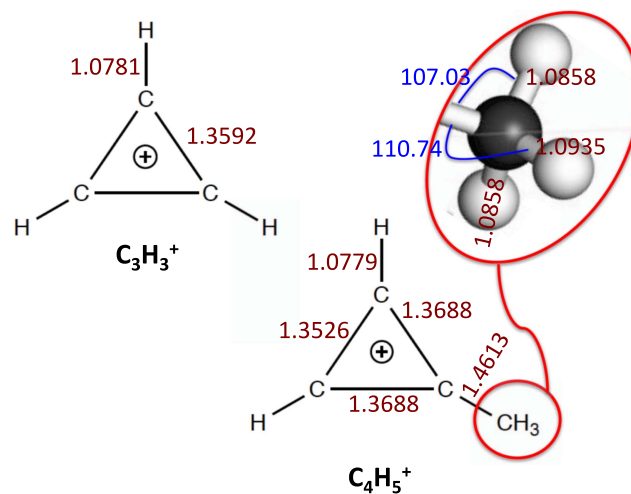


Figure 3. Molecular structures of the cyclopropenyl (at the CCSD(T)/CBS+CV+fT+fQ; the corresponding geometrical parameters at the CCSD(T)/CBS+CV, $r_{\text{CH}} = 1.0782$ Å and $r_{\text{CC}} = 1.3591$ Å) and methyl-cyclopropenyl cations (at the CCSD(T)/CBS+CV).

Titan’s atmosphere have shown the formation of complex organic mixtures known as “tholins” (Cable et al. 2012) that contain prebiotic molecules, particularly N-bearing cyclic compounds such as purines and pyrimidines. Cassini INMS measurements pointed out the presence of large molecules (>100 amu) in Titan’s atmosphere. Thus, the next step to be taken is the astronomical detection of key prebiotic molecules by means of the observation of their spectroscopic, infrared, or millimeter-wave features.

The best-estimated harmonic force field for uracil has been evaluated by means of a composite scheme to account for electron correlation and basis-set effects in the harmonic wavenumbers (ω) evaluation. This approach is based on the assumption of the additivity for various contributions. The

Table 2
Spectroscopic Parameters^a of the Main and Mono-deuterated
Isotopic Species of the Cyclopropenyl Cation

c-C ₃ H ₃ ⁺	This work ^b	Experiment ^c	Huang, Taylor, & Lee ^d
Ground state			
B_0 /MHz	30755.5 (30757.7)	30753.9(1.8)	30761.7
C_0 /MHz	15340.0 (15341.1)	15338.9	15342.8
D_J /MHz	0.069	0.129(18)	0.073
D_{JK} /MHz	-0.119	-0.207(18)	-0.122
D_K /MHz	0.055	0.054	0.055
H_J /Hz	0.249	...	0.259
H_{JK} /Hz	-1.083	...	-1.119
H_{KJ} /Hz	1.422	...	1.466
H_K /Hz	-0.588	...	-0.605
$\nu_4 = 1$ (3131.1 cm ⁻¹)			
B_4 /MHz	30663.9	30668.2(2.1)	30669.6
C_4 /MHz	15294.4	15301.4(6)	15296.9
$\nu_5 = 1$ (1293 cm ⁻¹)			
B_5 /MHz	30791.1	...	30776.9
C_5 /MHz	15299.9	...	15300.7
c-C ₃ H ₂ D ⁺			
	This work ^b		Huang & Lee ^e
Ground state			
A_0 /MHz	30753.7	...	30756.9
B_0 /MHz	25468.2	...	25477.6
C_0 /MHz	13898.4	...	13901.4
D_J /MHz	0.0145	...	0.0145
D_{JK} /MHz	0.0835	...	0.084
D_K /MHz	-0.0254	...	-0.026
d_1 /MHz	-0.0100	...	-0.0100
d_2 /MHz	0.0051	...	-0.0051
H_J /Hz	-0.076	...	-0.018
H_{JK} /Hz	0.335	...	-0.019
H_{KJ} /Hz	1.247	...	1.476
H_K /Hz	-1.333	...	-1.293
$h1$ /Hz	0.011	...	0.012
$h2$ /Hz	0.074	...	0.046
$h3$ /Hz	0.025	...	0.025
μ/D	0.225	...	0.225

Notes.^a Watson's S reduction, I' representation.^b Equilibrium rotational constants at the CCSD(T)/CBS+CV+fT+fQ level, augmented by vibrational corrections at the CCSD(T)/cc-pVTZ level (those derived from CCSD(T)/CBS+CV equilibrium rotational constants are given in parentheses). Quartic and sextic centrifugal-distortion constants at the (all)CCSD(T)/aug-cc-pCVQZ and (fc)CCSD(T)/cc-pVTZ levels, respectively, with "all" denoting all electrons being correlated, and "fc" the frozen core approximation. Equilibrium dipole moment at the CCSD(T)/aug-cc-pCVQZ level.^c Zhao et al. (2014). Experimental uncertainties are given in parentheses as figures on the last digits.^d Huang et al. (2011): Spectroscopic parameters derived from a quartic force field evaluated at the CCSD(T)/CBS+CV+SR (SR denotes scalar relativistic corrections).^e Huang & Lee (2011): Spectroscopic parameters derived from a quartic force field evaluated at the CCSD(T)/CBS+CV+SR (SR again denotes scalar relativistic corrections).

starting point is the CCSD(T)/cc-pVTZ level of theory, with second-order Møller–Plesset perturbation theory (MP2) (Møller & Plesset 1934) employed to include the various contributions. For all details, interested readers are referred to

Table 3
Spectroscopic Parameters^a of the Main Isotopic Species
of the Methyl-cyclopropenyl Cation

	Computed Parameters ^b
A_0 /MHz	25904.1
B_0 /MHz	6630.7
C_0 /MHz	5470.6
D_J /kHz	8.562
D_{JK} /kHz	8.512
D_K /kHz	19.867
d_1 /kHz	-0.287
d_2 /kHz	3.536

Notes.^a Watson's S reduction, I' representation.^b Equilibrium rotational constants at the CCSD(T)/CBS+CV level are given in parentheses, augmented by vibrational corrections at the CCSD(T)/cc-pVTZ level. Quartic centrifugal-distortion constants at the CCSD(T)/cc-pVTZ level.

Puzzarini et al. (2011). An analogous composite scheme has also been used to determine best estimates for the infrared intensities within the harmonic approximation. The CFOUR program package has been employed for all computations mentioned. To evaluate accurate anharmonic wavenumbers, a hybrid approach has been used. They have been computed by means of a posteriori corrections to the best-estimated harmonic wavenumbers: $\nu_{\text{hybrid}} = \omega(\text{best}) + \Delta\nu_{\text{DFT}}$. The anharmonic corrections $\Delta\nu_{\text{DFT}}$ have been computed at the density functional theory (DFT) level (B3LYP/N07D) via the Gaussian suite of quantum chemical programs (Barone 2005; Frisch et al. 2009). Figure 4 gives a schematic representation of the vibrational spectrum of uracil. The stick spectrum for fundamentals is predicted based on the hybrid force field described above, and it is reported together with the one computed at the B3LYP/6-31+G(d, p) level (using the results from Ten et al. 2010). Their comparison to experiment (Krasnoshchekov et al. 2015) shows a very good agreement, which proves the suitability of the B3LYP/6-31+G(d, p) level of theory for accurate predictions of vibrational features.

As evident in Figure 4, the vibrational spectrum of uracil shows two characteristic, very strong absorptions at 1706 and 1764 cm⁻¹; unfortunately, these lie above 1400 cm⁻¹, which is the upper limit of the Cassini composite infrared spectrometer (CIRS) observations. Therefore, investigations of Titan's atmosphere in an extended frequency range are required.

2.2.2. Ortho- and Peri-fused Aromatic Compounds: Phenalenyl Cation (C₁₃H₉⁺) and Anion (C₁₃H₉⁻)

In Ali et al. (2015), the composition, molecular structures, and chemistry at the basis of the growth of the complex macromolecules observed by the Cassini CAPS spectrometers are investigated. The focus of the paper is mainly on plausible reaction routes from simple aromatic molecules to complex polyaromatic compounds. In particular, the phenalenyl cation C₁₃H₉⁺ and its corresponding anion C₁₃H₉⁻ are identified as important intermediates in the process of molecular growth.

For both the phenalenyl cation and anion, anharmonic computations have been carried out at the B3LYP/6-31+G(d,p) level, using the Gaussian package (Barone 2005; Bloino & Barone 2012). To simulate the fully anharmonic spectrum (energies and intensities) with a proper account of resonances, the nearest abelian symmetry has been employed by slightly

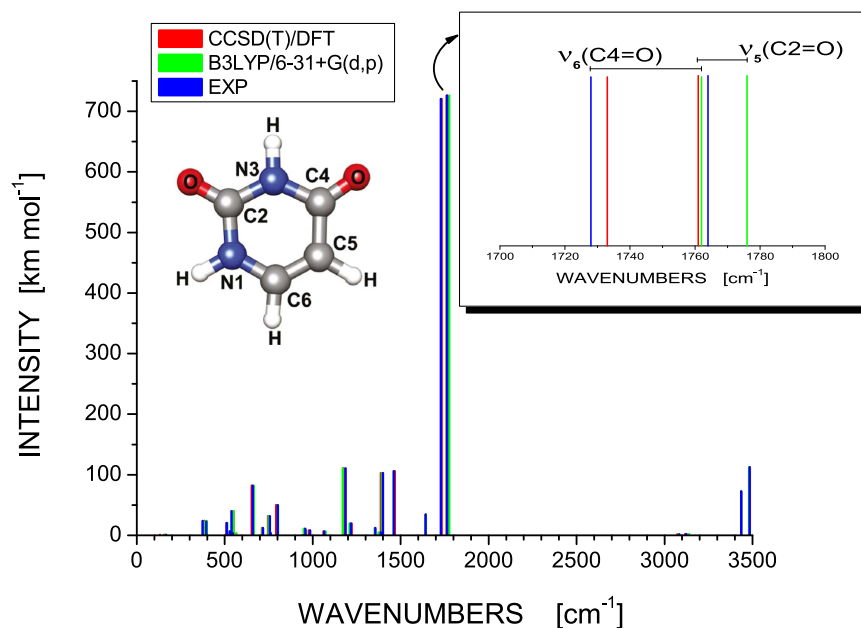


Figure 4. Stick vibrational spectra of uracil, showing only fundamentals. Values from the hybrid CCSD(T)/DFT force field are taken from Puzzarini et al. (2011). Values at the B3LYP/6-31+G(d,p) are from Ten et al. (2010). Experiment is from Krasnoshchekov et al. (2015).

shifting the nuclei. The validity of this approximation has been checked by comparing the resulting fundamental wavenumbers with those of the symmetric top (Piccardo et al. 2015). To the best of our knowledge, this is the first characterization of the IR spectra of the phenalenyl cation and anion.

The accuracy of the B3LYP/6-31+G(d, p) level of theory for the evaluation of the vibrational transition wavenumbers up to two quanta for aromatic compounds can be inspected via comparison of experiment and theory for uracil. This is presented in Figure 4 of this work, as well as in Tables 2 and 3 of Puzzarini et al. (2011). This comparison points out a mean absolute error of 12 cm^{-1} for B3LYP/6-31+G(d,p) wavenumbers, suggesting an accuracy sufficient for guiding astronomical searches of the IR signatures of $\text{C}_{13}\text{H}_9^+$ and $\text{C}_{13}\text{H}_9^-$. Even though this estimated accuracy should be taken with a little caution because of error compensation, some previous benchmark studies tend to confirm it (see, for example, Barone 2004 and Carboniere et al. 2005). In addition to these specific examples, we refer the reader to Barone et al. (2014), Bloino (2015), and Bloino et al. (2016) for other cases demonstrating the suitability of the B3LYP functional, in conjunction with double-zeta quality basis sets, for reliable predictions of vibrational spectra. We further highlight that, as demonstrated by the IR spectrum of uracil discussed above, the replacement of the harmonic part in the full DFT force field with the one obtained by means of composite scheme described above is an effective way to improve the accuracy and obtain quantitative predictions (see, for example, Puzzarini et al. 2010a; Bloino et al. 2012; Barone et al. 2015, and references therein).

The wavenumbers of the fundamental bands and the most intense combination bands and overtones ($>10 \text{ km mol}^{-1}$ for the anion, $>5 \text{ km mol}^{-1}$ for the cation) are collected in Tables 4 and 5, respectively. We note that the transition wavenumbers of the cation and of the anion generally differ by more than $20\text{--}30 \text{ cm}^{-1}$, allowing the two ionic forms to be distinguished without any ambiguity. This is made evident by Figure 5, which shows the simulated infrared spectra in the $0\text{--}3500 \text{ cm}^{-1}$

range for the cationic and anionic species, based on the results collected in Tables 4 and 5. Furthermore, we note that almost all vibrational states of the cation have a higher energy than the corresponding ones of the anion. The differences in position and intensity make the infrared spectra of the cationic and anionic species well distinct.

3. Concluding Remarks

Focusing on the theme of the origin of life and prebiotic chemistry, specific molecular species have been selected as target objectives for which an astronomical detection would either confirm or improve suggested models, and/or would provide key information for further developments. The spectroscopic characterization required to support their infrared and/or millimeter/submillimeter-wave spectral observations have been presented. The target molecular species include (1) the heterocyclic, oxygen-containing, three-membered ring compounds oxirane and protonated oxirane; (2) the cyclopropenyl cation and its methyl derivative; (3) a specific RNA base, uracil; and (4) the polycyclic ortho- and peri-fused aromatic conjugated ionic ring structure perinaphthenyl cation $\text{C}_{13}\text{H}_9^+$ and its corresponding anion $\text{C}_{13}\text{H}_9^-$. The potential astrophysical objects for astronomical line searches span from protostellar envelopes and protoplanetary disks to the atmospheres of exoplanets; they also include planetary targets in our solar system, such as Titan. The latter is particularly important for elucidating the abiological organic synthesis, which has a great relevance in the origin-of-life theme.

Our concluding remarks can be summarized as follows:

1. Oxirane and protonated oxirane have been selected from among the potential prebiotic species present in Titan's atmosphere (Puzzarini et al. 2014a, 2014b). By making use of the experimental data of oxirane, the rotational parameters of protonated oxirane have been derived and improved by means of an empirical scaling procedure. The resulting constants can then be used to predict the

Table 4
Fundamental Wavenumbers^a of C₁₃H₉⁺ and C₁₃H₉⁻

	C ₁₃ H ₉ ⁺		C ₁₃ H ₉ ⁻		Symmetry ^b
	Wavenumber (cm ⁻¹)	Intensity (km mol ⁻¹)	Wavenumber (cm ⁻¹)	Intensity (km mol ⁻¹)	
ν_1	3105.5	0.01	3021.0	2.39	A ₁ '
ν_2	3072.3	0.01	2989.3	10.08	
ν_3	1530.2	0.03	1503.9	0.02	
ν_4	1422.9	0.02	1368.6	1.09	
ν_5	1111.5	0.06	1090.7	0.26	
ν_6	781.5	0.00	774.0	0.01	
ν_7	623.3	0.00	610.2	0.01	
ν_8	942.0	0.00	712.5	2.87	A ₁ ''
ν_9	308.6	0.00	209.9	0.54	
ν_{10}	3072.3	0.01	3009.4	0.61	A ₂ '
ν_{11}	1486.1	0.01	1472.2	0.81	
ν_{12}	1418.6	0.01	1362.2	0.10	
ν_{13}	1211.8	0.02	1179.0	0.12	
ν_{14}	1172.2	0.01	1147.1	0.05	
ν_{15}	565.1	0.00	574.5	0.90	
ν_{16}	1010.4	0.48	917.2	2.10	A ₂ ''
ν_{17}	872.7	83.52	785.4	8.11	
ν_{18}	739.0	43.90	738.6	63.2	
ν_{19}	445.9	7.12	519.9	1.48	
ν_{20}	190.4	11.27	228.1	14.62	
ν_{21}	3100.3	0.42	3007.4	118.52	E'
ν_{22}	3082.3	0.84	3011.6	100.57	
ν_{23}	3065.9	0.15	2965.8	51.19	
ν_{24}	1604.8	79.45	1578.9	18.21	
ν_{25}	1564.4	43.46	1549.6	10.84	
ν_{26}	1431.8	4.25	1404.9	1.00	
ν_{27}	1373.2	45.3	1329.3	99.27	
ν_{28}	1258.3	34.93	1241.1	28.27	
ν_{29}	1209.6	7.43	1170.6	2.43	
ν_{30}	1125.6	25.96	1098.7	12.65	
ν_{31}	1049.4	2.65	1032.7	16.86	
ν_{32}	825.3	1.21	814.4	3.69	
ν_{33}	480.5	5.62	472.2	1.20	
ν_{34}	423.6	0.95	427.7	15.71	
ν_{35}	1015.4	0.03	903.1	0.05	E''
ν_{36}	970.5	0.03	768.6	2.72	
ν_{37}	789.6	0.03	670.2	2.17	
ν_{38}	692.8	0.05	591.1	0.66	
ν_{39}	485.0	0.05	463.0	0.71	
ν_{40}	160.7	0.01	147.9	0.58	

Notes.

^a Anharmonic wavenumbers and IR intensities computed at the B3LYP/6-31+G(d,p) level.

^b For the D_{3h} symmetry, the equivalence with the “shifted” geometry was checked by comparing the anharmonic fundamental wavenumbers with resonances excluded.

rotational spectrum with an accuracy suitable for astronomical searches. The detection of any organic compound containing oxygen in Titan’s atmosphere would have a great impact on understanding how the abiotic synthesis of biological building blocks could proceed.

- In Ali et al. (2013), it was demonstrated that the C₃H₃⁺ and C₄H₅⁺ compositions detected by the INMS spectrometer in Titan’s upper atmosphere can be explained in terms of the cyclopropenyl (c-C₃H₃⁺) and methyl cyclopropenyl (c-C₃H₂CH₃⁺) cations. Although c-C₃H₃⁺ cannot be detected using millimeter-/submillimeter-wave spectroscopy because of its null dipole moment, the situation is different for c-C₃H₂CH₃⁺. Therefore, the spectroscopic characterization carried out for the

cyclopropenyl cation was mostly focused on the prediction of the parameters required to guide vibro-rotational spectroscopic detections, as well as on determining the accuracy of our computations. We then moved to the methyl cyclopropenyl cation, thus providing rotational parameters that we consider suitable for astronomical applications.

- Cassini INMS measurements pointed out the presence of large molecules (>100 μm) in Titan’s atmosphere. Several studies simulating Titan’s atmosphere have demonstrated the formation of complex organic mixtures, known as “tholins” (Cable et al. 2012), that contain prebiotic molecules, such as purines and pyrimidines. Therefore, as pointed out for oxirane and protonated oxirane, their detection would have a great impact on

Table 5
Overtones and Combination Bands^a of $C_{13}H_9^+$ and $C_{13}H_9^-$

	Wavenumber (cm^{-1})	Intensity ($km\ mol^{-1}$)
	$C_{13}H_9^-$	
$\nu_9+\nu_{36}$	975.4	38.73
$\nu_6+\nu_{33}$	1244.7	26.86
$\nu_{37}+\nu_{38}$	1255.8	16.15
$\nu_8+\nu_{37}$	1382.3	14.06
$\nu_8+\nu_{36}$	1481.1	10.28
$2\nu_{36}$	1535.2	69.09
$\nu_{35}+\nu_{37}$	1574.6	70.17
$\nu_{32}+\nu_{36}$	1586.4	53.48
$\nu_{29}+\nu_{34}$	1597.5	19.26
$\nu_{13}+\nu_{34}$	1608.2	14.81
$\nu_{12}+\nu_{28}$	2690.0	12.86
$\nu_{11}+\nu_{25}$	3021.9	12.37
$\nu_3+\nu_{25}$	3061.1	14.88
$\nu_{24}+\nu_{25}$	3129.6	14.90
	$C_{13}H_9^+$	
$\nu_6+\nu_{33}$	1261.7	6.37
$\nu_{37}+\nu_{39}$	1273.6	21.40
$\nu_{15}+\nu_{32}$	1389.8	27.64
$\nu_{37}+\nu_{38}$	1489.3	11.24
$2\nu_{37}$	1578.8	5.55
$\nu_{15}+\nu_{31}$	1617.3	19.54
$\nu_{13}+\nu_{34}$	1636.2	8.82
$\nu_{11}+\nu_{27}$	2788.7	5.24

Note.

^a Anharmonic wavenumbers and IR intensities computed at the B3LYP/6-31+G(d,p) level. Only the bands with intensities $>10\ km\ mol^{-1}$ for the anion and $>5\ km\ mol^{-1}$ for the cation are reported.

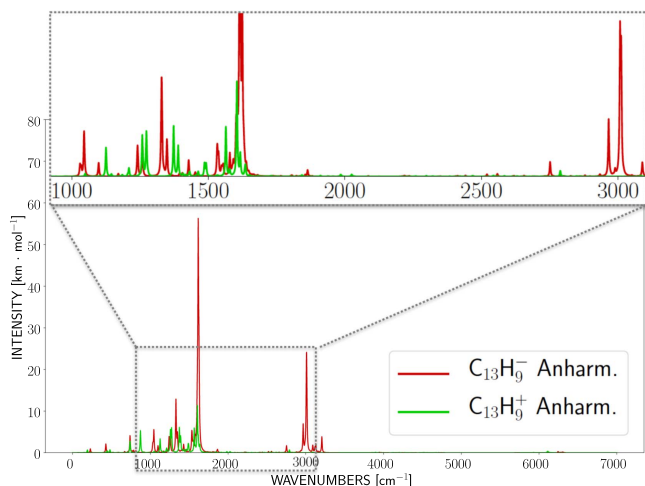


Figure 5. Simulated spectra of $C_{13}H_9^+$ and $C_{13}H_9^-$ in the 0–7000 cm^{-1} range, with anharmonic wavenumbers and anharmonic IR intensities at the B3LYP/6-31+G(d,p) level of theory (see Tables 4 and 5). Stick spectra are convoluted with a Lorentzian line profile (half-width at half-maximum: 5 cm^{-1}). In the inset: the portion of spectra in the 1000–3000 cm^{-1} range is highlighted (half-width at half-maximum: 2 cm^{-1}).

understanding the abiotic synthesis of biological building blocks. In particular, the detection of uracil (a subunit of RNA) in Titan’s atmosphere would be an important step toward understanding and supporting the RNA world hypothesis. Here, the suggested spectroscopic detection is through vibrational spectroscopy: characteristic and strong IR features have been highlighted that deserve future astronomical searches because they lie above the

upper frequency limit of the Cassini CIRS observations. The spectroscopic characterization of uracil also allowed us to point out the accuracy of the computational approach then employed for the $C_{13}H_9^{+/-}$ systems.

- In Ali et al. (2015), the formation of the complex macromolecules observed by the Cassini CAPS spectrometers was investigated in detail, thus identifying the phenalenyl cation ($C_{13}H_9^+$) and its corresponding anion ($C_{13}H_9^-$) as important intermediates in the process of molecular growth. The high symmetry of these molecular species prevents their observation by means of rotational spectroscopy (the corresponding dipole moment being null). However, the investigation of uracil showed that the predicted vibrational features have the proper accuracy to guide astronomical searches. We also pointed out how different the spectra of the cationic and anionic species are, thus ensuring the possibility of distinguishing the two species.

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