

State-of-the-art computation of the rotational and IR spectra of the methyl-cyclopropyl cation: Hints on its detection in space ^{†,‡}

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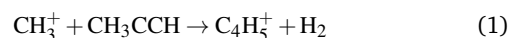
Recent measurements by Cassini Ion Neutral Mass Spectrometer demonstrated the presence of numerous carbocations in Titan's upper atmosphere. In [Ali *et al.*, *Planet. Space Sci.*, 2013, **87**, 96], an analysis of these measurements revealed the formation of the three-membered cyclopropenyl cation and its methyl derivatives. As a starting point of a future coordinated effort of laboratory experiments, quantum-chemical calculations, and astronomical observations, in the present work the molecular structure and spectroscopic properties of the methyl-cyclopropenyl cation have been investigated by means of state-of-the-art computational approaches in order to simulate its rotational and infrared spectra. Rotational parameters have been predicted with an expected accuracy better than 0.1% for rotational constants and on the order of 1-2% for centrifugal-distortion terms. As for the infrared spectrum, despite the challenge of a large amplitude motion, fundamental transitions have been computed to a good accuracy, i.e., the uncertainties are expected to be smaller than 5-10 wavenumbers.

1 Introduction

The recent measurements by instruments on board the Cassini space craft revealed that Titan's upper atmosphere harbors the richest atmospheric organic chemistry in the solar system (see Ref. 1 and references therein). The Cassini Ion and Neutral Mass Spectrometer (INMS) detection of numerous carbocations²⁻⁴ and the detection of heavy negative ions, in particular very large molecular anions (carbanions), by the Cassini CAPS Electron Spectrometer^{5,6} in Titan's thermosphere and ionosphere were two of the highly unexpected findings. Recent studies suggest that these large ions are singly-charged⁷ and that, as shown by Lavvas *et al.*⁸, the mechanism of formation of macromolecules and their growth in Titan's atmosphere is directly related to the ion-neutral chemistry. However, the mechanisms involved in their formation remain largely unclear^{8,9}. As pointed in Refs. 1,10, a deep understanding of the mechanisms of formation and growth of macromolecules and their compositions require studies of the

molecular structure for the individual carbocations and carbanions detected by Cassini instruments.

Based on INMS Cassini observations^{2-4,11} of specific carbocations, such as CH_3^+ , CH_5^+ , C_2H_3^+ , C_2H_5^+ , C_3H_5^+ , and C_3H_7^+ , and on the analysis of previous laboratory crossed molecular beam measurements¹² and theoretical studies (see Ref. 13 and references therein) of the reactions of CH_3^+ with ethylene and acetylene, in Ref. 10 it was inferred that a significant fraction of the C_3H_3^+ composition detected by INMS in Titan's upper atmosphere^{2,4} is the stable cyclopropenyl cation - the simplest Huckel's aromatic system. As a sort of natural consequence, in Ref. 10 another important class of reactions in Titan's upper atmosphere was identified, namely, those of CH_3^+ with methylacetylene and dimethylacetylene. These reactions are supposed to provide an explanation of the observed composition of C_4H_5^+ and C_5H_7^+ in terms of the methyl substituted form of the cyclopropenyl cation and the double-methyl substituted cyclopropenyl cation, respectively^{2,3}. Of interest to this work is the first of these two proposed reactions, i.e.:



However, there are no laboratory studies of the collision complexes involved in this reaction that can provide the dynamical information and product isomer branching ratios. Therefore, one has to resort to an accurate quantum-chemical investigation of the thermochemistry and kinetics of the reaction above, whose

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importance is further stressed by the fact that methylacetylene is an abundant molecule in Titan’s thermosphere and ionosphere⁴.

The study of the reaction above requires as starting point the structural characterization of all reagents and possible reaction products. According to what suggested in Ref. 10 and to the potential energy surface (PES) characteristics of the $\text{CH}_3^+ + \text{HCCH}$ reaction, the attack of CH_3^+ on methylacetylene is expected to form a C_4H_7^+ collision-complex that, via isomeric rearrangement, leads to the delocalized allyl cation where one of the hydrogen atoms in either of the two end carbon atoms is replaced by a methyl group (i.e., $[\text{CH}_2=\text{CH}-\text{CH}(\text{CH}_3)]^+$) and the 2-methylvinyl cation where one hydrogen of the vinyl cation is replaced by a methyl functional group (i.e., $[\text{CH}_3-\text{C}=\text{CH}(\text{CH}_3)]^+$). These reaction intermediates can then evolve into molecular hydrogen plus either the linear (i.e., $[\text{CH}_3\text{CH}=\text{C}\equiv\text{CH}]^+$) or the cyclic (see Figure 1) form of the methyl-propenyl cation, with the latter being expected to be the most stable isomer. While the reactive PES for the reaction (1) as well as the isomerization process between linear and cyclic methyl-propenyl cation are under investigation in our laboratories, the focus of the present work is the spectroscopic characterization of the methyl-cyclopropenyl cation with the final aim of obtaining accurate data that can guide its experimental-laboratory and/or astronomical observation. In this respect, it has to be noted that the detection of the methyl-cyclopropenyl cation in Titan’s atmosphere would confirm that the reaction (1) is actually taking place and, in turn, this would provide important insights on the initial steps of the molecular growth that leads to Titan’s haze formation.

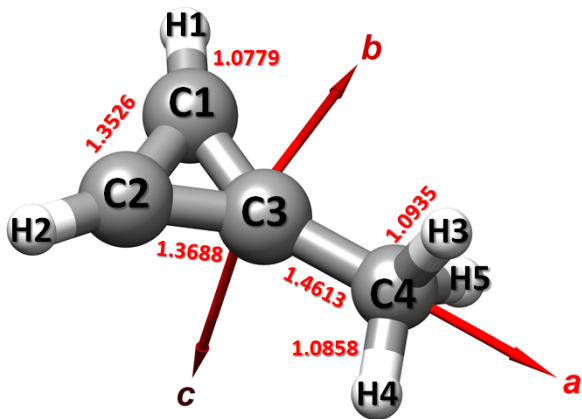


Fig. 1 Methyl-cyclopropenyl cation: atom labeling, inertial axes and selected CCSD(T)/CBS+CV bond distances (values in Å).

The spectroscopic techniques of choice for detecting molecular species in the interstellar medium and/or in planetary atmospheres are rotational and infrared (IR) spectroscopies. Indeed, gas-phase species have been mostly discovered by means of their rotational signatures (with their frequencies ranging from the millimeter-wave region to far-infrared), with the unprecedented resolution and sensitivity of the Atacama Large Millimeter/submillimeter Array (ALMA) offering unique opportunities and already provided the identification of prebiotic molecules in Titan’s atmosphere^{14,15}. However, infrared spectroscopy is

expected to cover an increasingly important role in determining the chemical composition of exoplanets’ atmospheres, which are largely unknown, with the best opportunity to fill this gap being provided in the near future by the James Webb Space Telescope (JWST). In this context, accurate quantum-chemical computations play a key role. Indeed, while the accuracy of state-of-the-art methodologies is usually not yet sufficient to directly guide astronomical searches in the field of rotational spectroscopy, the calculated spectroscopic parameters are the only mean to successfully support the laboratory experiments that in turn can provide the rest transition frequencies with the required accuracy. Different is the situation for infrared spectroscopy for which state-of-the-art quantum-chemical predictions have the accuracy needed for astronomical observations. However, the system under investigation presents an additional challenge because of the large amplitude motion (LAM) related to the internal rotation of the methyl group, which requires a non-standard computational treatment. Furthermore, for cationic species, the accuracy of approximated methods, especially those rooted in the density functional theory (DFT), is not fully assessed for what concerns IR (and Raman) intensities.

The present paper is organized as follows: in the next section after this introduction, the computational details are discussed in view of obtaining an accurate spectroscopic characterization in the framework of rotational and infrared spectroscopies. Subsequently, the results are presented and discussed. Our conclusions are reported in the final section, with particular emphasis given to the possible guidance for the identification of the methyl-cyclopropenyl cation in planetary and astrophysical targets.

2 Methodology

Within the rigid-rotor approximation, rotational signatures only depend on rotational constants, which are straightforwardly derived from equilibrium structure. To improve predictions, centrifugal-distortion and vibrational effects should be accounted for. For a detailed account on the quantum-chemical calculation of spectroscopic parameters for rotational spectroscopy, the reader is referred to Refs.^{16,17}. To ensure high accuracy in equilibrium geometry determinations, the coupled-cluster singles and doubles approximation augmented by a perturbative treatment of triple excitations, CCSD(T)¹⁸, which is considered the “gold standard” in accurate electronic structure calculations, needs to be employed in composite approaches to account for basis-set effects as well as core-correlation contributions. This can be performed by means of the energy-gradient composite scheme introduced in Ref.¹⁹, and implemented in the quantum-chemical package CFOUR²⁰. The contributions considered are: the Hartree-Fock self-consistent-field (HF-SCF) part extrapolated to the complete basis-set (CBS) limit complemented by the valence CCSD(T) correlation energy extrapolated to the CBS limit as well, and the core-valence correlation correction. The resulting energy gradient used in the geometry optimization is thus given by the following

expression:

$$\frac{dE_{\text{CBS+CV}}}{dx} = \frac{dE^{\text{CBS}}(\text{HF-SCF})}{dx} + \frac{d\Delta E^{\text{CBS}}(\text{CCSD(T)})}{dx} + \frac{d\Delta E(\text{CV})}{dx}, \quad (2)$$

where $dE^{\text{CBS}}(\text{HF-SCF})/dx$ and $d\Delta E^{\text{CBS}}(\text{CCSD(T)})/dx$ are the energy-gradient contributions corresponding to the $\exp(-Cn)$ extrapolation scheme for the HF-SCF energy²¹ and to the n^{-3} extrapolation formula for the CCSD(T) correlation contribution,²² respectively. In the expression given above, basis sets with $n=T$, Q and 5 were chosen for the HF-SCF extrapolation, and $n=T$ and Q were used for CCSD(T). The core-correlation energy correction, $\Delta E(\text{CV})$, is obtained as difference of all-electron (all) and frozen-core (fc) CCSD(T) calculations using a core-valence basis set of triple-zeta quality (cc-pCVTZ). In this composite approach, denoted in the following as “CCSD(T)/CBS+CV”, we have made use of Dunning and coworkers correlation-consistent basis sets, cc-p(C)VnZ^{23,24}.

As mentioned above, to provide accurate predictions of rotational transitions it is mandatory to go beyond the rigid-rotor approximation, thus accounting for centrifugal-distortion and vibrational effects. To incorporate the latter, vibrational corrections (ΔB_{vib}) are added to the best-estimated equilibrium rotational constants (B_e), straightforwardly derived from the equilibrium structure, thus leading to the vibrational ground-state rotational constants (B_0):

$$B_0^i = B_e^i + \Delta B_{\text{vib}}^i = B_e^i - \frac{1}{2} \sum_r \alpha_r^i, \quad (3)$$

with i denoting the inertial axis ($i = a, b, c$; that is, for instance, $B_0^a = A_0$). Within second-order vibrational perturbation theory (VPT2)^{25,26}, the vibrational corrections are expressed in terms of the vibration-rotation interaction constants α_r^i , with the summation in eq. (3) running over the vibrational normal modes. The evaluation of the α_r^i 's requires a cubic force field (see e.g. Ref.¹⁶). This has been computed using the double-hybrid B2PLYP functional²⁷ in conjunction with the maug-cc-pVTZ-dH basis set, with the GAUSSIAN package²⁸. The maug-cc-pVTZ-dH set has been obtained from the maug-cc-pVTZ basis set²⁹ by removing d functions on hydrogen atoms³⁰. All B2PLYP calculations have been corrected for dispersion effects according to Grimme's DFT-D3³¹ scheme employing the Becke-Johnson damping function³².

Finally, to account for centrifugal distortion, the computation of the corresponding parameters is required. The quartic centrifugal-distortion constants are obtained as a byproduct of harmonic force field computations¹⁶. For the latter, we resorted to a composite approach, denoted as “cheap” to point out the reduced computational cost with respect to a full CCSD(T) additive scheme^{33,34}. This is based on correcting the CCSD(T)/cc-pVTZ harmonic frequencies ($\omega(\text{CCSD(T)}/\text{VTZ})$) in a normal coordinate representation for the contributions due to the extrapolation to the complete basis set (CBS) limit ($\Delta\omega(\text{CBS})$) and core-valence correlation effects ($\Delta\omega(\text{CV})$), both computed at the second-order Møller-Plesset perturbation theory (MP2)³⁵. Overall, the com-

posite scheme can be expressed as:

$$\omega(\text{best}) = \omega(\text{CCSD(T)}/\text{VTZ}) + \Delta\omega(\text{CBS}) + \Delta\omega(\text{CV}) + \Delta\omega(\text{aug}). \quad (4)$$

The CBS limit has been evaluated using the cc-pVTZ and cc-pVQZ basis sets ($n = T$ and Q) and by applying the n^{-3} extrapolation formula²², while the CV correction, obtained from the difference of all electron and frozen-core calculation, has been determined with the cc-pCVTZ set. The “aug” term appearing in Eq. (4) denotes the correction due to the inclusion of diffuse functions in the basis set, which is an important corrective term to recover the overestimation of the extrapolation to the CBS limit due to the use of rather small sets, and it is given by the difference MP2/aug-cc-pVTZ³⁶ - MP2/cc-pVTZ. This composite harmonic force field has been used to derive the quartic centrifugal-distortion constants, there employing Watson S-reduction Hamiltonian in the I' representation³⁷. An analogous composite scheme has been used for evaluating the best estimate of the equilibrium dipole moment components.

To fully characterize the vibrational spectrum, anharmonic force field calculations are first of all required. These have been carried out at the B2PLYP/maug-cc-pVTZ-dH level, with the cubic and semi-diagonal quartic force constants and up to the third derivatives of the electric dipole moment being determined by numerical differentiations of analytic second derivatives of the energy and first derivatives of the electric dipole moment. To further improve the description of the anharmonic force field, a hybrid model has been employed, which assumes that the differences between vibrational frequencies computed at two different levels of theory are mainly due to the harmonic terms. The hybrid force field has been obtained in a normal-coordinate representation by adding the cubic and semi-diagonal quartic B2PLYP/maug-cc-pVTZ-dH force constants to the best-estimated harmonic frequencies (Eq. (4)); in the following, this has been denoted as “CC/B2”.

The computation of the infrared spectrum beyond the double-harmonic approximation has been performed within the VPT2 approach^{25,26,38-42} developed and implemented in the GAUSSIAN suite of programs²⁸. VPT2 calculations have been carried out using both the B2PLYP/maug-cc-pVTZ-dH and the hybrid “CC/B2” anharmonic force fields. To overcome the problem of singularities (known as resonances) impacting the VPT2 approach, the GVPT2 scheme has been used, where the nearly-resonant contributions are removed from the perturbative treatment (leading to the deperturbed model, DVPT2) and variationally treated in a second step^{38,42-44}. Furthermore, the LAM associated to the methyl internal rotation has been treated separately by means of a 1D discrete variable representation (DVR) anharmonic approach, with the couplings between the LAM and the small amplitude orthogonal motions being neglected in the VPT2 treatment. In detail, the large amplitude torsion has been described as the distance (in mass weighted cartesian coordinates) between structures obtained from a rigid scan around the methyl dihedral angle (every 10 degrees over 36 points) and oriented in order to minimize the angular momentum between pairs of successive structures. Next, additional points along the path are generated using a cubic B-spline interpolation and the one-dimensional problem has been

Table 1 Equilibrium structure (distances in Å, angles in degrees)^a, rotational constants (in MHz), and electric dipole moment components (in debye) of the methyl-cyclopropenyl cation.

Parameters	B2PLYP/ maug-cc-pVTZ-dH	CCSD(T) cc-pVTZ	CCSD(T)/ CBS+CV
Bonds			
C ₁ -C ₂	1.3534	1.3616	1.3526
C ₁ -C ₃	1.3713	1.3770	1.3688
C ₃ -C ₄	1.4602	1.4693	1.4613
C ₁ -H ₁	1.0779	1.0880	1.0779
C ₄ -H ₃	1.0944	1.0960	1.0935
C ₄ -H ₄	1.0861	1.0884	1.0858
Angles			
H ₁ -C ₁ -C ₂	150.00	148.62	150.01
C ₂ -C ₁ -C ₃	60.43	60.37	60.58
H ₃ -C ₄ -C ₃	107.18	106.96	107.03
H ₄ -C ₄ -C ₃	110.95	110.60	110.74
Dihedrals			
H ₁ -C ₁ -C ₃ -C ₄	0.00	0.00	0.00
H ₃ -C ₄ -C ₃ -C ₂	90.00	90.00	90.00
H ₄ -C ₄ -C ₃ -C ₂	27.64	27.83	27.76
Rotational constants			
A _e	26120.83	25801.35	26075.71
B _e	6655.24	6599.82	6673.22
C _e	5482.57	5432.09	5492.69
Dipole moments			
μ _a ^b	1.14	1.21	1.18 ^c
μ _c ^b	0.11	0.10	0.10 ^c

^a Atom labeling according to Figure 1.

^b μ_b is null by symmetry and thus omitted. For the definition of the inertial axes, see Figure 1.

^c Evaluated by means of the “cheap” composite scheme (see text).

solved by the variational DVR approach using the sine basis functions introduced by Colbert and Miller⁴⁵, as described in Ref. 46.

3 Results and Discussion

The molecular structure of the methyl-cyclopropenyl cation evaluated at different levels of theory is presented in Table 1, following the atom labelling provided in Figure 1. According to the literature on this topic (see, for example, Refs. 47–49), the CCSD(T)/CBS+CV composite model provides bond lengths with an accuracy of 0.001-0.002 Å and valence angles accurate to 0.05-0.1 degrees. Table 1 further confirms the good performance of the B2PLYP functional in conjunction with a triple-zeta quality basis set, as previously pointed out (see, for examples, Refs. 34,48,49). Indeed, the B2PLYP/maug-cc-pVTZ-dH level provides C-C distances that are only 0.001 Å longer than the CCSD(T)/CBS+CV ones and, for the C-H bond lengths, the discrepancies reduce to even less. A very good agreement is also noted for bond angles, the deviations being on the order of 0.1-0.2 degrees. Furthermore, despite the lower computational cost, it is interesting to note that the B2PLYP/maug-cc-pVTZ-dH level of theory yields significantly better results than CCSD(T)/cc-pVTZ. Therefore, B2PLYP/maug-cc-pVTZ-dH represents a very good compromise between computational cost and accuracy, thus providing an additional support to our choice of computing the anharmonic force field at this level of theory.

3.1 Rotational Spectroscopy

The rotational parameters, computed as described in the Methodology section, are collected in Table 2. According to the results

Table 2 Rotational parameters^a of the methyl-cyclopropenyl cation.

Parameter	Best values ^b	Scaled ^c
A ₀ / MHz	25370.326	25362.71
B ₀ / MHz	6623.636	6621.65
C ₀ / MHz	5449.221	5447.59
D _J / kHz	11.259	
D _{JK} / kHz	4.310	
D _K / kHz	22.242	
d ₁ / kHz	-0.291	
d ₂ / kHz	4.804	

^a Watson S-reduction.

^b Equilibrium rotational constants from CCSD(T)/CBS+CV equilibrium structure augmented by vibrational corrections at the B2PLYP/maug-cc-pVTZ-dH level (ΔA₀ = -705.382 MHz, ΔB₀ = -49.586 MHz, ΔC₀ = -43.470 MHz). Quartic centrifugal-distortion constants from the best-estimated “cheap” harmonic force field (Eq. 4). See text.

^c Scaled parameters according to Eq. (5); see text.

and discussion for the cyclopropenyl cation reported in Ref. 50 as well as to the literature on related topics (see, for example, Refs. 17,51–53), the CCSD(T)/CBS+CV level of theory for equilibrium values in combination with vibrational effects treated at a correlated level in conjunction with a triple-zeta quality basis set is able to provide vibrational ground-state rotational constants with a relative accuracy better than 0.1%. A specific example is provided by the cyclopropenyl cation. Using the computations reported in Ref. 50, it is noted that at the CCSD(T)/CBS+CV level the equilibrium rotational constants differ only by 2.2 MHz for B and 1.1 MHz for C with respect to an improved level of theory which accounts for larger basis sets in the extrapolation to the CBS limit (n = 5,6 for CCSD(T)) and in the CV contribution (cc-pCV5Z) as well as for the full treatment of triple and quadruple excitations. The inclusion of vibrational corrections finally leads to computed rotational constants that are overestimated by ~3.8 MHz for B and ~2.2 MHz for C. Overall, the discrepancies from experiment are well below the conservative estimate of 0.1% mentioned above. The quartic centrifugal-distortion constants are expected to be affected by a relative error of the order of 1-2%^{17,33,52}. Overall, rotational transition frequencies are predicted with uncertainties ranging from 1-2 MHz to tens, and even hundreds of MHz, mainly depending on the rotational quantum numbers involved. While this accuracy is suitable for supporting laboratory experiments, it is usually not sufficient for directly guiding astronomical searches. To further improve the predictive capabilities of the computed spectroscopic parameters, an empirical scaling procedure can be employed. This is based on multiplying the computed value for the methyl-cyclopropenyl cation (denoted by the superscript *metcp+*) by the corresponding experiment/theory ratio for the cyclopropenyl cation (denoted by the superscript *cp+*), which has been chosen as a reference compound:

$$B_{\text{scal}}^{\text{metcp}+} = B_{\text{calc}}^{\text{metcp}+} \times (B_{\text{exp}}^{\text{cp}+} / B_{\text{calc}}^{\text{cp}+}), \quad (5)$$

where *scal*, *exp*, and *calc* denote the scaled, experimental, and quantum-chemically calculated values, respectively. The scaling procedure has been applied to the rotational constants because these are the leading terms in rotational spectroscopy and they

have the major impact on the transition line positions. It is worth mentioning that this approach is extensively used in the field of rotational spectroscopy and, based on the available literature (see, for example, Refs. 53–56), 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 a few MHz or even better. The scaled rotational constants are collected in Table 2; these are based on the cyclopropenyl cation, for which the computed equilibrium rotational constants at the CCSD(T)/CBS+CV are taken from Ref. 50 and the vibrational corrections at the B2PLYP/maug-cc-pVTZ-*dH* are calculated in this work. The experimental data of the cyclopropenyl cation have been obtained from the high resolution infrared laboratory gas-phase spectrum of the ν_4 (C-H asymmetric stretching) fundamental band⁵⁷.

Table 1 also reports the equilibrium values of the electric dipole moment components. According to the symmetry of the molecule, the one along the *b* inertial axis is null by symmetry, while μ_a is nearly one order of magnitude larger than μ_c . This means that the rotational spectrum is characterized by strong *a*-type rotational transitions. The simulation at $T = 100$ K of the rotational spectrum of the methyl-cyclopropenyl cation, based on the scaled rotational constants and the “cheap” quartic centrifugal-distortion terms, is depicted in Figure 2, and it has been obtained using the VMS-ROT program⁵⁸. It is noted that at the temperature considered the maximum of intensity is at ~ 270 –280 GHz.

3.2 Infrared Spectroscopy

The results for the harmonic force field are collected in Table 3, where the harmonic wavenumbers and intensities obtained at the CCSD(T)/cc-pVTZ and B2PLYP/maug-cc-pVTZ-*dH* levels of theory and by means of the “cheap” composite scheme are compared. For frequencies, a good agreement with the best estimates, i.e., within a few wavenumbers, is noted for both CCSD(T)/cc-pVTZ and B2PLYP/maug-cc-pVTZ-*dH*, with the latter however being characterized by a strongly reduced computational cost with respect to the former. Even if not reported in Table 3 (see supplementary information: Table S.2), it is interesting to discuss the various contributions of the additive scheme. It is noted that the CV corrections are always positive and range from 1 to 5 cm^{-1} ; the CBS contributions instead can be either positive or negative and they range, in absolute terms, from 0.1 to 7 cm^{-1} ; finally, the diffuse terms are mostly negative and, in relative terms, they range from 0.1% to 0.5%. According to the literature on this topic (see, for example, refs. 34,59–61, we expect that the mean error obtained (with respect to a full CCSD(T) scheme accounting for extrapolation to the CBS limit, CV correction, and high-order terms in the cluster expansion) is of the order of a few wavenumbers: from 3 cm^{-1} to 15 cm^{-1} , where larger errors affect the higher frequency values and/or challenging vibrational modes.

Concerning the IR intensities, a good agreement is observed between the best-estimated and CCSD(T)/cc-pVTZ harmonic values, while B2PLYP/maug-cc-pVTZ-*dH* results show a few significant discrepancies. Additional computations (see supplementary

Table 3 Harmonic wavenumbers (ω , cm^{-1}) and intensities (I , km mol^{-1}) of the methyl-cyclopropenyl cation.

Symmetry	Mode	Best ^a		CCSD(T) ^b		B2PLYP ^c	
		ω	I	ω	I	ω	I
A'	ω_1	3282	49.7	3290	49.1	3295	38.6
	ω_2	3131	6.7	3128	5.7	3133	6.0
	ω_3	3043	26.9	3043	22.8	3050	30.9
	ω_4	1765	56.7	1752	55.7	1763	30.7
	ω_5	1491	9.4	1486	9.6	1493	10.4
	ω_6	1420	110.6	1409	110.1	1415	90.1
	ω_7	1399	5.4	1395	3.3	1402	10.3
	ω_8	1046	34.7	1046	34.5	1047	23.1
	ω_9	977	38.9	982	38.4	983	17.7
	ω_{10}	832	49.4	830	57.0	840	24.6
	ω_{11}	770	1.8	765	2.1	774	4.5
	ω_{12}	384	4.0	387	4.9	396	12.2
A''	ω_{13}	3254	104.2	3254	102.9	3263	72.7
	ω_{14}	3181	4.7	3177	3.9	3185	4.5
	ω_{15}	1463	21.4	1461	21.5	1463	26.5
	ω_{16}	1304	3.4	1293	3.7	1297	13.3
	ω_{17}	1087	18.8	1086	18.8	1095	16.3
	ω_{18}	1013	0.3	1006	0.5	1023	0.1
	ω_{19}	972	9.0	975	8.7	979	0.4
	ω_{20}	354	1.8	355	1.7	359	2.4
	ω_{21}	36	0.8	38	1.0	43	1.7

^a “cheap” composite scheme. See text.

^b cc-pVTZ basis set.

^c maug-cc-pVTZ-*dH* basis set.

information: Table S.3) reveal that the MP2 values are in line with their CCSD(T) counterparts, whereas HF-SCF results are very different. These discrepancies are possibly due to an unbalanced description of the charge polarization in cationic systems. As a consequence, we can infer that DFT values inherit the wrong behavior of HF-SCF due to the fraction of Hartree-Fock exchange contribution included in hybrid and double-hybrid functionals and/or they are plagued by an overestimation of the conjugation effects in local and semi-local functionals.

The anharmonic frequencies and intensities obtained for the methyl-cyclopropenyl cation at both the B2PLYP/maug-cc-pVTZ-*dH* and “CC/B2” levels are reported in Table 4. Before discussing in details this Table, it should be pointed out that the hybrid force field approach is well tested for a large variety of systems ranging from small open-shell species to medium-sized molecular systems (see, for instance, Refs. Refs. 34,62–65) and it is expected to provide an accuracy, in terms of mean average error, of 5–10 cm^{-1} . As mentioned in the Methodology section, the IR spectrum has been computed by using the GVPT2 model coupled to a fourth-order representation of the potential energy surface. While this approach is well suited to treat semi-rigid molecules, it can fail when dealing with large amplitude vibrations. This is the case of the ν_{21} normal mode, corresponding to the torsion of the CH_3 group (see Figure S.1 in the supplementary information). In fact, the anharmonic correction obtained from the full GVPT2 treatment of the semi-diagonal quartic force field results unusually large, thus leading to an unphysical negative wavenumber (-37 cm^{-1}) for this vibration. Clearly, the periodic torsional motion is poorly described by a 4th-order polynomial expansion, but the negative value is due to a large and unphysical cubic force constant coupling the torsion and the CH stretching, and it is re-

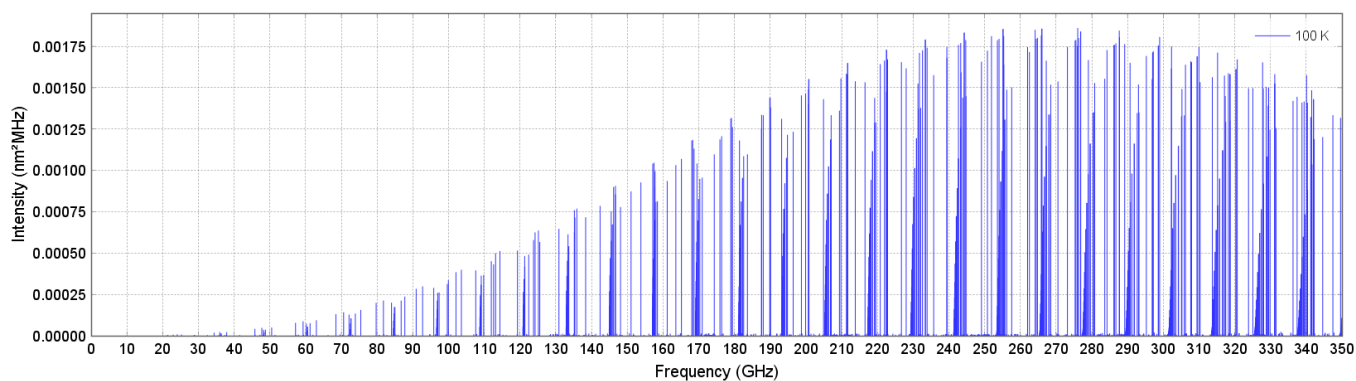


Fig. 2 Simulation of the rotational spectrum of the methyl-cyclopropenyl cation at $T = 100$ K.

Table 4 Anharmonic wavenumbers (ω , cm^{-1}) and intensities (I , km mol^{-1}) of the methyl-cyclopropenyl cation.

Symmetry	Mode	B2PLYP ^a				CC/B2 ^b	
		ν^c	I^c	ν^d	I^d	ν^d	I^d
A'	ν_1	3167	36.4	3167	38.4	3152	49.5
	ν_2	2987	7.0	3025	7.9	3014	8.6
	ν_3	2939	28.4	2918	28.1	2907	24.1
	ν_4	1711	16.0	1732	16.4	1729	42.4
	ν_5	1446	15.2	1455	9.7	1452	8.7
	ν_6	1395	21.8	1382	33.1	1381	53.6
	ν_7	1346	62.0	1359	59.8	1357	54.9
	ν_8	1029	11.6	1020	25.6	1019	37.2
	ν_9	959	15.6	960	17.2	958	38.4
	ν_{10}	827	25.8	826	23.3	819	48.1
	ν_{11}	755	3.1	752	3.6	741	0.9
	ν_{12}	395	11.4	393	12.7	381	4.5
A''	ν_{13}	3136	69.5	3136	69.5	3125	101.0
	ν_{14}	3043	2.5	3038	3.5	3034	3.7
	ν_{15}	1428	21.0	1416	23.4	1416	18.3
	ν_{16}	1262	10.9	1264	11.7	1273	1.8
	ν_{17}	1068	15.6	1069	17.3	1061	19.8
	ν_{18}	1001	0.1	1004	0.2	993	0.4
	ν_{19}	956	0.5	958	0.5	950	9.1
	ν_{20}	356	2.7	357	2.5	352	1.9
	ν_{21}	-37	2.9	16	0.0	16	0.0

^a maug-cc-pVTZ-*d*H basis set.

^b Hybrid force field. See text.

^c Full GVPT2 treatment.

^d GVPT2 treatment reduced to the normal modes $\nu_1 - \nu_{20}$, while ν_{21} is treated by the 1D DVR anharmonic approach.

lated to the use of rectilinear coordinates. Conversely, by restricting the GVPT2 treatment to the small amplitude vibrations ($\nu_1 - \nu_{20}$) and by treating the LAM by means of a variational DVR treatment⁴⁶, the anharmonic wavenumber of the ν_{21} mode is predicted to be 16 cm^{-1} with a negligible intensity, thus showing how the potential energy profile of the methyl torsion can be effectively described within this framework. It should be recalled that the method is exact at the harmonic level and remarkably accurate whenever the single degree of freedom associated with the LAM shows small anharmonic couplings with the perpendicular small amplitude vibrations⁶⁶. In the present case, this requirement should be fulfilled when using curvilinear internal coordinates, whereas, as mentioned above, couplings between Cartesian-based normal coordinates tend to be overestimated in anharmonic force constants⁶⁷.

Due to the fair agreement between CCSD(T) and B2PLYP harmonic frequencies, B2PLYP anharmonic frequencies are also quite close to the corresponding values from the hybrid “CC/B2” force field, with a mean absolute deviation of only 6 cm^{-1} and a maximum discrepancy of 15 cm^{-1} for the ν_1 normal mode. Concerning intensities, the effects of mechanical and electrical anharmonicity are generally small, ranging between -3 and 2.5 km mol^{-1} , the only exceptions being ν_4 , ν_6 and ν_7 for which the anharmonic corrections to intensity amount to -14 , -57 and $+49 \text{ km mol}^{-1}$, respectively. Among these, the ν_6 and ν_7 normal modes are coupled through a 1-1 Darling-Dennison resonance responsible for an intensity transfer from the stronger ν_6 to the weaker ν_7 band. Overall, we note that these results are reasonable; however, a warning is deserved because a systematic analysis of DFT anharmonic corrections in charged and/or conjugated systems is still missing.

The theoretical IR spectrum of the methyl-cyclopropenyl cation between 350 and 3500 cm^{-1} is reported in Figure 3, where the two top panels compare the computed harmonic and anharmonic spectra. The former is obtained from the “cheap” scheme (Eq. (4)) applied to both wavenumbers and intensities, while the latter has been simulated by using hybrid “CC/B2” anharmonic frequencies and intensities. As it can be seen, anharmonicity has a huge impact on the spectrum shape due to significant shifts of several bands. Finally, the third panel of Figure 3 reports the spectral simulation obtained by convoluting the anharmonic stick spectrum with Gaussian functions having a half width at half maximum of 5 cm^{-1} . It is observed that overtones and combination bands mostly affect the region between 2000 and 3000 cm^{-1} ; however, their intensity is so small that they can be barely seen in Figure 3. As mentioned in the Introduction, the mass spectrometers on board Cassini pointed out the presence of several carbocations in Titan’s atmosphere. It is therefore interesting to compare our prediction of the IR spectrum of the methyl cyclopropenyl cation with those of C_3H_3^+ and other carbocations recorded in Refs. 68,69. Even if intense features are observed in the 1400 - 1600 cm^{-1} range, and around 2800 cm^{-1} and 3200 cm^{-1} , the most intense transitions of the methyl cyclopropenyl cation do not seem to overlap them. However, the calculation of the IR spectra for the best candidates possibly present in Titan’s atmosphere by means of the computational approach used in the present work is

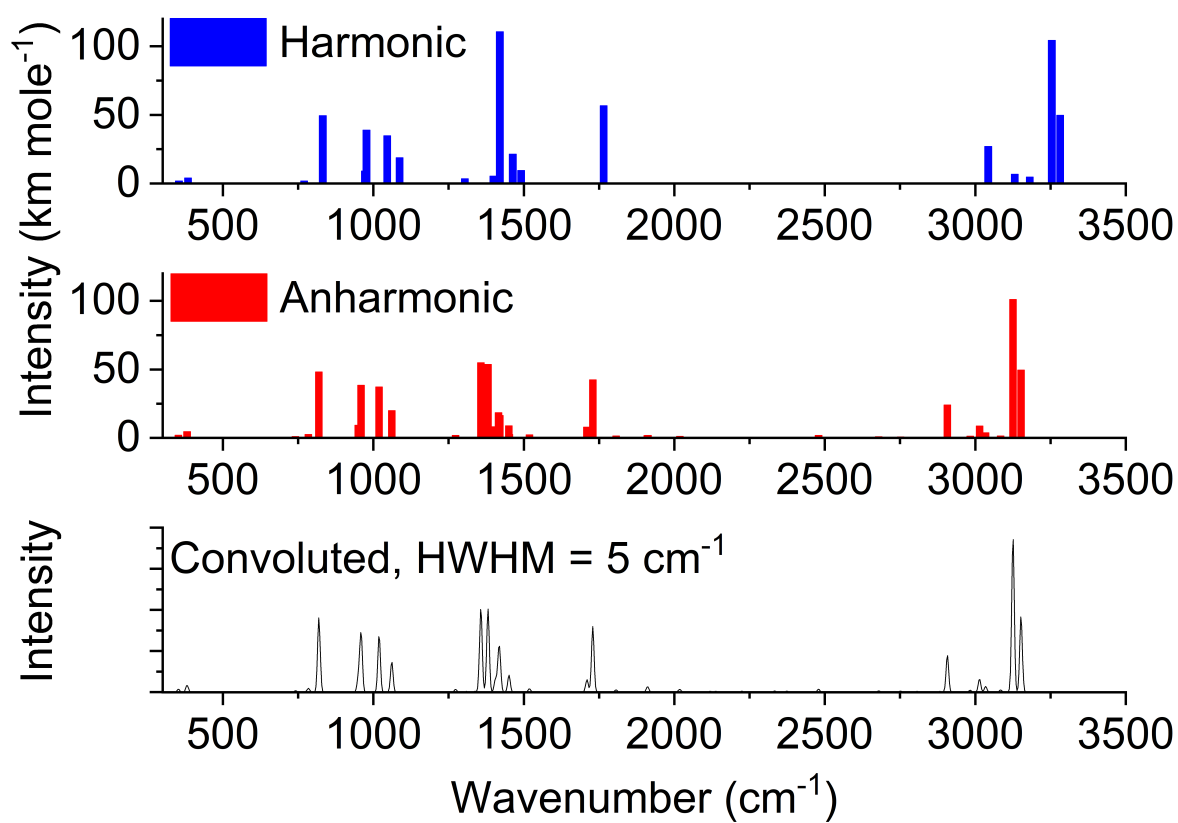


Fig. 3 Simulated IR spectrum of the methyl-cyclopropenyl cation between 300 and 3500 cm⁻¹. Top: stick spectrum reporting harmonic frequencies and intensities obtained from the "cheap" composite scheme. Middle: stick spectrum reporting anharmonic frequencies and intensities obtained from the "CC/B2" hybrid approach. Bottom: "CC/B2" anharmonic spectrum convoluted with a Gaussian function with a half width at half maximum (HWHM) of 5 cm⁻¹.

warranted in order to provide the astronomical community with a more complete overview and it will be the object of future investigations.

4 Conclusions

As far as the rotational spectrum is concerned, nowadays the best opportunity for detecting molecules in the Titan's atmosphere and in the interstellar medium is offered by the ground-based observatory ALMA, whose working frequency range is 31-950 GHz. ALMA combines high sensitivity with high spectral and spatial resolution interferometric observations, thus allowing for unbiased spectral surveys of the astronomical source under consideration. These spectral surveys usually collect a large number of lines and therefore tend to be very crowded; as a consequence, to firmly identify a molecular species, very accurate predictions for rotational transitions are required. While for astronomical observations showing isolated lines an accuracy of a few MHz is well sufficient, in most cases the uncertainties need to be as small as 100 kHz. This means that state-of-the-art quantum-chemical predictions can directly guide astronomical observations only in very limited cases; however, as already mentioned, they play a fundamental role to successfully support the laboratory spectroscopy experiments that will provide the rest frequencies with the required accuracy.

As already pointed out in the Introduction, a great opportunity to investigate Titan's atmosphere by using IR spectroscopy will be provided by the JWST that will cover the 0.6-29 μm wavelength range (i.e., 16667-345 cm^{-1}). In this respect, our predictions of the infrared spectrum should be able to guide the search of the methyl-cyclopropenyl cation in Titan's and other planetary atmospheres. According to our investigation, the most interesting spectral regions are those around 1000 cm^{-1} , 1300-1500 cm^{-1} and 3100 cm^{-1} , where the most intense features lie.

Conflicts of interest

"There are no conflicts to declare".

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