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## **CCSD(T)-F<sub>12</sub> calculations of the IR spectrum of cyanoacetylene HC<sub>3</sub>N beyond the harmonic approximation.**

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### **Abstract**

The high-resolution infrared spectrum of HC<sub>3</sub>N has been the subject of numerous experimental studies. However, none of these studies has been based on high-quality theoretical work. On the basis of an anharmonic potential CCSD(T)-F<sub>12</sub>/aug-cc-pVTZ and the use of a pure variational method (VCI) the IR spectrum of HC<sub>3</sub>N was calculated between 200 and 4800 cm<sup>-1</sup>. These calculations make it possible, on the basis of the positioning of the bands and the calculation of their intensity, to revisit the entire IR spectrum and to assign a large part of it, overtones, combinations bands and hot bands to the experimental observations.

Keywords: Ab-initio CCSD(T) and CCSD(T)-F<sub>12</sub> calculations- cyanoacetylene molecule- IR spectroscopy

### **1. Introduction**

Cyanopolyynes, linear molecules of the raw formula H-(CC)<sub>n</sub>-CN, are among the most common species found in astronomical environments. The first members of this series have been detected and identified in the interstellar medium (ISM) since the 1970s [1] and have been the subject of Voyager [2] and Cassini [3] missions in Titan's atmosphere.

The simplest of these cyanopolyynes, propynenitrile, more commonly known as cyanoacetylene, detected in 1971 by Turner [1] was quickly the subject of great interest and its presence noticed in various astrophysical objects (Milky way, starless cores, solar-type protostar, comets, protoplanetary disks, external galaxies...), as recently reported in the article by Bizzochi et al. [4], has stimulated a large number of laboratory experiments. Among these experiments, we can note the numerous investigations to better understand the rotational [5-7], vibrational [8-12] and ro-vibrational [4] spectra and more precisely to understand the positions and intensity of the IR bands with the work of Uyemura et al. [8], Khlifi et al. [9-10], Jolly et al. [11-12] and more recently the work of Bizzochi et al. [4] exploring between 450 and 1350 cm<sup>-1</sup> the ro-vibrational spectrum by an exhaustive study using a high resolution IR spectra recording. Despite the importance of these experimental works, few theoretical calculations on the vibrational spectrum of this molecule have been undertaken, often limited to a simple harmonic approach [13] or not taking into account at the anharmonic level

the totality of the potential by limiting the study only to the four stretching modes treated without coupling with the bending vibrations [14,15]. Very recently C. Pouchan [16] published the theoretical modelling of the HC<sub>3</sub>N vibrational spectrum by comparing a DFT molecular dynamics (DFT/MD) approach with a static anharmonic approach under the assumption of a vibrational second order perturbative treatment (VPT2). This study, limited to fundamental frequencies only, showed that the DFT harmonic calculations from a B3LYP functional [17] associated with a 6-31+G (d,p) base did not reflect, unlike many other systems previously studied [18-25], the harmonic results obtained at the CCSD(T)[26]/aug-cc-pVTZ [27] level, and that the potential function limited to the order 4 did not allow to give accurate VPT2 anharmonic wavenumbers to reproduce the first harmonic bands of the lowest frequencies and their combinations.

It seemed interesting under these conditions to revisit the IR spectrum modelling by considering a new CCSD(T) approach in combination with a basis set of triple or quadruple zeta quality with adaptive accurate multidimensional potential energy surfaces followed by a vibrational analysis using a vibrational configuration interaction method (VCI). The bottleneck of this procedure remains the accurate calculation of extended areas of the potential energy surface by high-level ab-initio method that is a very time consuming task.

The major objectives of the theoretical work presented here to describe and predict the vibrational spectrum of HC<sub>3</sub>N are threefold and consist of:

- on the one hand to give a computational contribution to the experimental works carried out for the fundamental modes on the positioning and intensity of IR bands.
- on the other hand to analyse and assign by quantum calculation the combinations and hot bands recently identified by Bizzochi et al.[4] between 450 and 1350 cm<sup>-1</sup>
- finally, to predict for regions not fully studied experimentally the active bands expected to help in their future identification.

The paper is structured as follows: Sec. 2 summarizes the computational methods applied and the details of our calculations, the outline of the theory being given in more details in related papers [28-30].

Sec. 3 provides the results obtained to describe, assign, and predict in spectral region not fully explored, the IR spectrum of propynenitrile HC<sub>3</sub>N in vacuo. All the results will be discussed and compared, when possible, with experimental data.

## **2- Methods and computational details.**

### **2-1 Methods for calculating PES and VCI calculations**

The calculation of extended areas of potential energy surface (PES) for a polyatomic linear system by coupled-cluster methods is a great challenge in quantum chemistry and needs very time-consuming resources. Different techniques and algorithms developed in our lab and reported in literature [30-32] offer an accurate representation of PES. They remain however a little limited to deal with the

case of linear molecules and so we preferred to use the formalism developed by Rauhut et al. [28-30] reporting an algorithm for an efficient and fully automatic generation of PES around an equilibrium structure. This method uses an incremental scheme of difference potentials ( $V_i$ ,  $V_{ij}$ ,  $V_{ijk}$ ...called respectively 1D, 2D, 3D...terms) spanned by the normal coordinates  $q_i$  of the system as originally proposed and described by Carter et al.[33-34]. In our case the many body expansion of the PES is truncated after the 3D terms.

$$V(q_1, \dots, q_n) = V_0 + \sum_i V_i(q_i) + \sum_{i < j} V_{ij}(q_i, q_j) + \sum_{i < j < k} V_{ijk}(q_i, q_j, q_k) + \dots \quad (1)$$

with

$$V_i(q_i) = V_i^0(q_i) - V_0 \quad (2)$$

$$V_{ij}(q_i, q_j) = V_{ij}^0(q_i, q_j) - \sum_{r \in \{i,j\}} V_r(q_r) - V_0 \quad (3)$$

$$V_{ijk}(q_i, q_j, q_k) = V_{ijk}^0(q_i, q_j, q_k) - \sum_{r \in \{i,j,k\}} V_r(q_r) - V_0 \quad (4)$$

$V_0$  represents the total energy at the equilibrium geometry and the quantities with the superscript 0 denote the total energy obtained from the electronic calculations at distorted nuclear configurations.

The calculation of the PES, that can be computed by using different methods for the different increments, needs 9288 grid points resulting in 48 single-point calculations for the 1D terms, 956 energy calculations and 8284 energy determinations respectively for the 2D and the 3D terms contributions in the case of  $\text{HC}_3\text{N}$  treated as belonging to the point group of  $C_{2v}$  symmetry. Taking into account the small size of the system all determinations are made at the highest computational level i.e. CCSD(T).

VCI calculations account for vibrational correlation effects and the use of PES as generated from the SURF program and a basis of VSCF modals in which all modals were generated from 16 distributed Gaussians. VCI calculations include single (S), double (D), triple (T) and quadruple (Q) excitations. All calculations are carried out in  $C_{2v}$  symmetry. For the irreducible representation  $A_1$  27019 configurations (32 S, 504 D, 4820 T and 21662 Q) have been selected while 22387 configurations (9S, 270 D, 3464 T, 18644 Q) are required to describe each irreducible representation  $B_1$  and  $B_2$ .

All calculations presented here have been performed with the MOLPRO suite of ab-initio programs [35]

## 2-2 Computational details.

The CCSD(T) coupled-cluster electronic method is a standard tool to provide reliable values of molecular energies and properties as in our case Infra-red (IR) spectra. Associated at large number of orbital basis functions it gives chemically useful accuracy. To improve this method, explicitly-correlated  $R_{12}$  approach that use additional two-particles basis functions depending explicitly on the inter-electronic distance has been proposed increasing the accuracy of reliable properties predictions [36-37]. This method including correlated geminal is known as the CCSD(T)  $R_{12}$  model [37] or the

CCSD(T)- $F_{12x}$  model [38] in which the linear  $r_{12}$  correlation factor is replaced by a short range non-linear function  $F_{12}(r_{12})$  that leads to much better results and numerical stability. We will adopt this latter model in accordance with the MOLPRO software used in our calculations. In the case of  $\text{HC}_3\text{N}$  all calculations are carried out at the CCSD(T)- $F_{12}$  level associated with an aug-cc-pVTZ basis set to compute structural parameters and vibrational frequencies. Details of the VCI calculations to obtain anharmonic wavenumbers are given above while the intensities are calculated from dipole surfaces at MP2/aug-cc-pVTZ quality level.

### 3- Results and Discussions

We report in figure 1 the atomic numbering adopted to describe the propynenitrile molecule. The structural parameters as well as the main assignments of the modes reported in tables 1 and 2 refer to this figure.

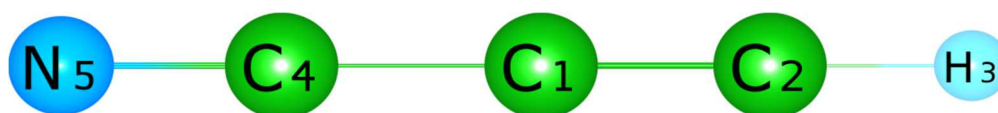


Fig 1: Propynenitrile atomic numbering

#### 3-1 Structural parameters and harmonic wavenumbers

We report in table 1 the geometries obtained at different levels of CCSD(T) theory. As expected we can observe for all distances the remarkable agreement between the values obtained at levels CCSD(T)- $F_{12}$ /aug-cc-pVTZ and CCSD(T)/aug-cc-pVQZ. In all cases the distances calculated at these two levels are 0.002 to 0.004 angstroms shorter than those obtained at the CCSD(T)/aug-cc-pVTZ level often used to correctly deal with the geometrical structure of larger molecular systems.

Table 2 reports the harmonic vibrational wavenumbers obtained at the same different levels. The main assignments are also described for the description of the modes. Although not directly comparable, the experimental values are also recorded in the same table because of their expected low anharmonicity.

As for the structural parameters, the same behaviour can be observed for the calculation of the harmonic frequencies, with the CCSD(T)- $F_{12}$ /aug-cc-pVTZ values are closer to those of CCSD(T)/aug-cc-pVQZ. All the frequencies calculated at the highest calculation levels, with the exception of  $\nu_4$ , being on average about ten  $\text{cm}^{-1}$  higher than those calculated at the CCSD(T)/aug-cc-pVTZ level. This

is particularly important for the lowest set of modes where this difference is greater than the expected anharmonicity values.

### 3-2 Anharmonic wavenumbers and IR intensities for the fundamental modes

We report in Table 3 the anharmonic wavenumbers and the IR intensities obtained for the fundamentals. For comparison the results obtained, with the same potential, at VCI and VPT2 levels are compared too with the experimental values. Looking at the table 3, even though the VPT2 values are of very good quality, it appears that the wave numbers calculated at the VCI level remarkably reflect all the experimental values. The mean deviation between the VCI values and the experiment is less than  $2\text{ cm}^{-1}$  ( $1.6\text{ cm}^{-1}$ ) with a maximum deviation of  $3\text{ cm}^{-1}$  for the frequency  $\nu_2$ . Concerning the IR intensities it is important to note that the most intense bands experimentally are also the most intense in the calculation, that their values are very close to the measured quantities except for the  $\nu_2$  mode for which the VCI and the VPT2 determinations are overestimated with respect to the experimental value.

Considering the quality of the results obtained at the VCI level on the fundamental modes, it seemed interesting to us to propose a complete theoretical analysis of the IR spectrum of  $\text{HC}_3\text{N}$  between 200 and  $4600\text{ cm}^{-1}$ . This analysis will be carried out both on the calculation of frequencies and intensities and will be as far as possible compared to the experimentally observed values.

### 3-3 Analysis of the IR spectrum between 200 to $4600\text{ cm}^{-1}$

We have reported in Table 4 the complete IR spectrum of  $\text{HC}_3\text{N}$  from the values of IR wavenumbers and intensities calculated at the VCI level. The spectrum thus calculated allows the assignment of all the bands (fundamentals, overtones, combinations, hot bands) expected in the region from 200 to  $4600\text{ cm}^{-1}$ . This calculation is therefore an essential tool for the identification of all the bands observed experimentally. It therefore complements the IR analysis we will do by spectral region since these have either been carefully experimentally studied or partially or not studied at all. In order to propose an assignment to the observed bands, these are shown in Table 4 in correspondence with the theoretical values on the basis of the calculated wavenumbers and intensities.

The analysis of our calculations will be carried out in four spectral regions:

- the first one between 200 and  $1350\text{ cm}^{-1}$  which has been well studied experimentally,
- the second between 1400 and  $2800\text{ cm}^{-1}$ , less well studied experimentally than the first one, and which presents combination bands of not negligible intensity,
- the third between 2900 and  $4000\text{ cm}^{-1}$  where, in addition to the intense band characteristic of the CH valence mode, other weak absorption bands appear.

- the fourth one finally beyond  $4000\text{ cm}^{-1}$  never studied experimentally.

### 3-3-1 Region $200\text{-}1350\text{ cm}^{-1}$

With the exception of the lowest low-intensity band  $\nu_7$  ( $222\text{ cm}^{-1}$ ), this region has been particularly well studied experimentally, in particular the  $\nu_6$  and  $\nu_5$  modes with high and medium intensities respectively centred around  $499$  and  $663\text{ cm}^{-1}$ . Our calculations remarkably reproduce these three bending modes  $\nu_7$ ,  $\nu_6$  and  $\nu_5$  at  $222$ ,  $496$  and  $662\text{ cm}^{-1}$  with intensities of  $0.02$ ,  $12.2$  and  $95.1\text{ km/mol}$  respectively in good agreement with the experimental values of Jolly et al [12]. In this region recently studied by Bizzochi et al. [4] our calculations show the existence of  $2\nu_7$  and  $3\nu_7$  overtones at  $451$  and  $676\text{ cm}^{-1}$  respectively with mean intensities and that correspond to the vibration-rotation bands observed around  $443$  and  $633\text{ cm}^{-1}$ , this latter very close to the fundamental band  $\nu_5$  and which therefore borrows from it a part of the IR intensity. Around these bands our calculations also predict the existence of the hot bands  $\nu_7 \rightarrow \nu_6 + \nu_7$  and  $\nu_6 \rightarrow 2\nu_6$  located at  $495.4$  and  $497.9\text{ cm}^{-1}$  and  $\nu_5 \rightarrow 2\nu_5$  and  $\nu_7 \rightarrow \nu_5 + \nu_7$  calculated at  $649.2$  and  $689.7\text{ cm}^{-1}$  respectively. These bands could correspond to the bands of the spectrum simulated by Jolly et al. respectively at ( $497.9$  and  $514.4\text{ cm}^{-1}$ ) and ( $649.8$  and  $669.8\text{ cm}^{-1}$ ). The  $\nu_6 + \nu_7$  combination band calculated at  $721\text{ cm}^{-1}$  with an intensity of  $8.5\text{ km/mol}$ . corresponds to that observed at  $720\text{ cm}^{-1}$  with a lower intensity of the order of  $3\text{ km/mol}$ . Below  $1000\text{ cm}^{-1}$ , in addition to the fundamental band  $\nu_4$  associated with the  $\nu_{(C-C)}$  valence mode, very well described by our calculations ( $860\text{ cm}^{-1}$ ;  $0.16\text{ km/mol}$  vs.  $862\text{ cm}^{-1}$ ;  $0.17\text{ km/mol}$  experimentally), we also propose the band of mean intensity attributed to the  $3\nu_7$  overtone at  $676\text{ cm}^{-1}$  and the combination bands  $\nu_5 + \nu_7$  and  $\nu_6 + 2\nu_7$  of near-zero intensity at  $901$  and  $959\text{ cm}^{-1}$  respectively. These three bands could correspond to the three signals observed by Bizzochi et al [4] at  $663$ ,  $885$  and  $946\text{ cm}^{-1}$  respectively. The overtone  $2\nu_6$  calculated at  $994\text{ cm}^{-1}$  with a very low intensity of  $0.02\text{ km/mol}$  could explain the two bands observed respectively at  $1013$  and  $998\text{ cm}^{-1}$  by Jolly et al. [12] and Bizzochi et al. [4]. Above  $1000\text{ cm}^{-1}$ , still in this same spectral area, our calculations confirm the presence of the combination band  $\nu_5 + \nu_6$  and the overtone  $2\nu_5$  respectively calculated at  $1176$  and  $1311\text{ cm}^{-1}$  corresponding to the bands observed at  $1163$  and  $1314\text{ cm}^{-1}$  but with much higher intensities. As for the band observed by Jolly et al. at  $1090\text{ cm}^{-1}$ , it could correspond to one of the two bands calculated at either  $1084$  or  $1095\text{ cm}^{-1}$  and respectively assigned to the  $\nu_5 + 2\nu_7$  or  $\nu_4 + \nu_7$  combination bands, the former being much more intense than the latter. To finish with this first spectral region, our calculations indicate the presence at  $1232\text{ cm}^{-1}$  of a low-intensity  $\nu_7 + 2\nu_6$  combination band, a band not observed by the experimentalists so far because of its very low intensity.

### 3-3-2 Region $1400\text{-}2800\text{ cm}^{-1}$

In the first half of this spectral region, up to  $2000\text{ cm}^{-1}$ , a single band at  $1970\text{ cm}^{-1}$  of very low intensity was observed. Our calculations place it exactly at  $1970\text{ cm}^{-1}$  with an intensity of  $0.04\text{ km/mole}$  and assign it to the  $3\nu_5$  overtone. Very close, but not active, our calculations predict the presence of the  $2\nu_4+\nu_7$  combination band at  $1962\text{ cm}^{-1}$ . Finally, two other bands not observed so far, are predicted by our calculations at  $1543$  and  $1717\text{ cm}^{-1}$  and are respectively assigned to the  $\nu_4+\nu_5$  combination mode and the  $2\nu_4$  overtone. If the first band of very low intensity could not be observed, it would seem desirable that the second band with a calculated intensity of  $0.29\text{ km/mole}$  could be sought around  $1720\text{ cm}^{-1}$ .

Beyond  $2000\text{ cm}^{-1}$  and up to  $2800\text{ cm}^{-1}$  our calculations predict the existence of ten bands which should be observable whereas only five are observed among that the two fundamental bands  $\nu_3$  and  $\nu_2$  corresponding respectively to the valence modes of the CC and CN triple bonds. Even if the intensities are not perfectly reproduced our calculations locate for  $\nu_3$  and  $\nu_2$  the bands at  $2079$  and  $2277\text{ cm}^{-1}$  in excellent agreement with the experimental observations at  $2079$  and  $2274\text{ cm}^{-1}$ . Excellent agreement can also be noted between the bands observed at  $2494$ ,  $2575$  and  $2766\text{ cm}^{-1}$  with respective intensities of  $0.34$ ,  $0.17$  and  $0.31\text{ km/mole}$  and the bands calculated at  $2505\text{ cm}^{-1}$  ( $0.14\text{ km/mole}$ ) and the two doublets ( $2588$  and  $2569\text{ cm}^{-1}$ ) and ( $2781$  and  $2753\text{ cm}^{-1}$ ) with respective overall intensities of  $0.37$  and  $0.48\text{ km/mole}$ . Thanks to the calculation, these bands can respectively be allocated to the combination  $\nu_2+\nu_7$  for the first one, and to  $(3\nu_4; \nu_3+\nu_6)$  and  $(\nu_3+\nu_5; \nu_2+\nu_6)$  for the two doublets. Finally, not corresponding to any experimentally observed signal, our calculations predict in this region three additional bands at  $2211\text{ cm}^{-1}$  ( $0.44\text{ km/mole}$ ),  $2307\text{ cm}^{-1}$  ( $0.06\text{ km/mole}$ ) and  $2534\text{ cm}^{-1}$  ( $0.06\text{ km/mole}$ ) assigned to the combinations  $\nu_4+2\nu_5$ ,  $\nu_3+\nu_7$  and  $\nu_3+2\nu_7$  respectively.

### **3-3-3 Region 2900-4000 $\text{cm}^{-1}$**

Except for the fundamental band  $\nu_1$  associated with the very intense CH valence mode ( $61.4\text{ km/mole}$ ) observed at  $3327\text{ cm}^{-1}$ , two other bands of low intensity are reported by Jolly et al.[12] in this region at  $3133$  and  $3549\text{ cm}^{-1}$ . Our calculations locate the fundamental remarkably well at  $3329\text{ cm}^{-1}$  with a high intensity of  $84.1\text{ km/mole}$  and predict for the other two signals the frequencies of  $3151$  and  $3562\text{ cm}^{-1}$  respectively assigned to the combinations  $\nu_2+\nu_4$  and  $\nu_1+\nu_7$  in accordance to the experimental assignments. Five other bands of low and very low intensity proposed by our calculations were not observed. Two of them assigned to the simple combinations  $\nu_3+\nu_4$  and  $\nu_1+\nu_5$  are respectively calculated at  $2952$  and  $3988\text{ cm}^{-1}$  with intensities of  $0.07$  and  $1.60\text{ km/mole}$  respectively. The other three bands are associated with the complex combinations  $\nu_2+\nu_6+\nu_7$ ,  $\nu_2+\nu_5+\nu_7$  and  $\nu_3+\nu_5+\nu_6$  calculated at  $3034$ ,  $3183$  and  $3291\text{ cm}^{-1}$  respectively with very low intensity signals ( $0.32$ ,  $0.21$  and  $0.12\text{ km/mole}$ ).

### **3-3-4 Region 4000-4800 $\text{cm}^{-1}$**

This last region studied theoretically has not been explored experimentally. One can expect to find signals involving the first overtones of the modes associated with the CC and CN triple bonds ( $\nu_3$ ;  $\nu_2$ ) as well as combination bands involving the very intense modes due to the CH valence vibrations ( $\nu_1$ ) and CCH bending deformation ( $\nu_5$ ). The two overtones  $2\nu_3$  and  $2\nu_2$  are respectively calculated at  $4148$



and  $4535\text{ cm}^{-1}$  with intensities of 0.03 and 0.16 km/mole. The most intense combination bands involving the  $\nu_1$  and  $\nu_5$  mode are the complex bands  $\nu_1+\nu_5+\nu_7$  on the one hand and  $2\nu_5+\nu_1$  on the other hand calculated at  $4235$  and  $4636\text{ cm}^{-1}$  with non-negligible respective intensities of 2.02 and 3.80 km/mole. Finally, our calculations predict that two other bands could be observable in this spectral region. These are the complex combination  $\nu_1+\nu_6+\nu_7$  calculated at  $4048\text{ cm}^{-1}$  and the combination band involving the modes associated with the CC and CN triple bonds,  $\nu_2+\nu_3$ , calculated at  $4354\text{ cm}^{-1}$ , the first signal being however much more intense than the second (0.78 km/mole vs 0.01 km/mole).

#### 4- Conclusions

In this study we have carried out, for the first time, accurate theoretical computations concerning the vibrational spectrum of cyanoacetylene  $\text{HC}_3\text{N}$  in the mid-Infrared region. On the basis of CCSD(T)-  $F_{12}/\text{aug-cc-pVTZ}$  potential and by means of a pure variational method we propose a complete ab-initio modelling of the IR spectrum of  $\text{HC}_3\text{N}$  which allows to assign fundamental, combinations, overtones and hot bands between 200 to  $4800\text{ cm}^{-1}$ . Our original results give a new interpretation of the assignments of all the observed bands. We hope that this accurate theoretical work will attract the interest of experimentalists to analyse more precisely the spectrum of  $\text{HC}_3\text{N}$  beyond  $1350\text{ cm}^{-1}$ .

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Equilibrium structure	CCSD(T)/ aug-cc- pVTZ	CCSD(T)-F <sub>12</sub> / aug-cc-pVTZ	CCSD(T)/ aug-cc- pVQZ
C <sub>1</sub> -C <sub>4</sub>	1.383	1.381	1.381
C <sub>1</sub> ≡C <sub>2</sub>	1.212	1.208	1.209
C <sub>4</sub> ≡N <sub>5</sub>	1.167	1.163	1.163
C <sub>2</sub> -H <sub>3</sub>	1.065	1.063	1.063

Table 1: Computed geometrical parameters (in Angstroms) for propynenitrile (or cyanoacetylene) in vacuo at different CCSD(T) levels of theory.

Mode	Main Assignment	CCSD(T)/ aug-cc- pVTZ	CCSD(T)- F <sub>12</sub> / Aug-cc- pVTZ	CCSD(T)/ aug-cc- pVQZ	Experimental
		ω	ω	ω	v

$\nu_7$	$\delta(\text{C-CC-N})^a$	218	220	226	222 <sup>c</sup>
$\nu_6$	$\delta(\text{CCN})^a$	487	495	502	504 <sup>d</sup> ; 499 <sup>c</sup> ; 500 <sup>b</sup>
$\nu_5$	$\delta(\text{CCH})^a$	664	675	673	667 <sup>d</sup> ; 663 <sup>c</sup> ; 664 <sup>b</sup>
$\nu_4$	$\nu(\text{C-C})$	875	879	879	862 <sup>c</sup> ; 861 <sup>b</sup>
$\nu_3$	$\nu(\text{C}\equiv\text{C})$	2098	2113	2110	2077 <sup>d</sup> ; 2079 <sup>c</sup>
$\nu_2$	$\nu(\text{C}\equiv\text{N})$	2305	2317	2314	2269 <sup>d</sup> ; 2274 <sup>c</sup>
$\nu_1$	$\nu(\text{CH})$	3445	3452	3451	3316 <sup>d</sup> ; 3327 <sup>c</sup>

Table 2: Computed harmonic wavenumbers (in  $\text{cm}^{-1}$ ) for propynenitrile (or cyanoacetylene) in vacuo at different CCSD(T) levels of theory. Comparison with experimental values

<sup>a</sup> Double degenerated modes

<sup>b</sup> Ref [4]; <sup>c</sup> Ref [12]; <sup>d</sup> Ref [13]

Experimental values			Assignment
	$\nu(\text{VCI})$	$\nu(\text{VPT2})$	
222.4 (0.18)	222 (0.2)	224 (0.4)	$\nu_7$
498.8 (9.6)	496 (12.2)	496 (12.8)	$\nu_6$
663.2 (66.1)	662 (95.0)	672 (88.6)	$\nu_5$
862 (0.17)	860 (0.2)	860 (0.1)	$\nu_4$
2079 (2.0)	2079 (0.1)	2077(0.2)	$\nu_3$
2274 (10.0)	2277 (51.1)	2276 (42.2)	$\nu_2$
3327 (61.4)	3329 (84.0)	3309 (51.2)	$\nu_1$

Table 3: Anharmonic ( $\nu(\text{cm}^{-1})$ ) wavenumbers and IR intensities (in parenthesis) expressed in  $\text{km}/\text{mole}$  calculated for cyanoacetylene at CCSD(T)-  $F_{12}/\text{aug-cc-pVTZ}$  level from VPT2 and VCI methods within an analytical representation. Intensities are calculated within the anharmonic mechanical and electrical scheme. Comparison is made with the experimental work of Jolly and al. [12]

Observed frequencies	$\nu(\text{cm}^{-1})$	$I(\text{km/mol})$	Main assignement
	4636	3.80	$2 \nu_5 + \nu_1$
	4535	0.16	$2 \nu_2$
	4354	0.01	$\nu_2 + \nu_3$
	4235	2.02	$\nu_1 + \nu_5 + \nu_7$
	4148	0.03	$2 \nu_3$
	4048	0.78	$\nu_1 + \nu_6 + \nu_7$
	3988	1.60	$\nu_1 + \nu_5$
3549 (0.36)	3562	0.08	$\nu_1 + \nu_7$
3327 (61.4)	3329	84.1	$\nu_1$
	3291	0.12	$\nu_3 + \nu_5 + \nu_6$
	3183	0.21	$\nu_2 + \nu_5 + \nu_7$
3133 (0.64)	3151	1.55	$\nu_2 + \nu_4$

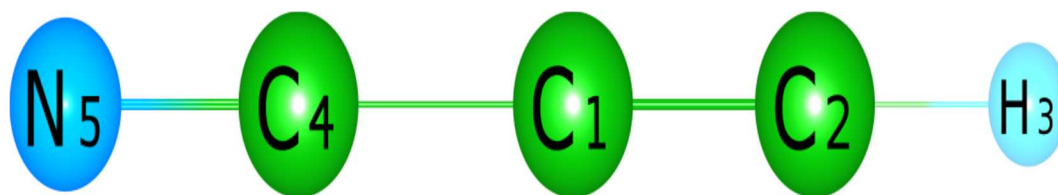
	3034	0.32	$v_2 + v_6 + v_7$
	2952	0.07	$v_3 + v_4$
2766 (0.31)	2781	0.32	$v_2 + v_6$
	2753	0.16	$v_3 + v_5$
2575 (0.17)	2588	0.34	$v_3 + v_6$
	2569	0.03	$3 v_4$
	2534	0.06	$v_3 + 2v_7$
2494 (0.34)	2505	0.14	$v_2 + v_7$
	2307	0.06	$v_3 + v_7$
2274 (10)	2277	51.2	$v_2$
	2211	0.44	$v_4 + 2v_5$
2079 (2.0)	2079	0.21	$v_3$
1970 (0.02)	1970	0.04	$3 v_5$
	1962	0.0	$2v_4 + v_7$
	1717	0.29	$2 v_4$
	1543	0.04	$v_4 + v_5$
1314 (17.4)	1311	41.0	$2 v_5$
	1232	0.04	$v_7 + 2v_6$
1163 (0.03)	1176	0.32	$v_5 + v_6$
1090 (0.08)	1095	0.06	$v_4 + v_7$
	1084	0.36	$v_5 + 2v_7$
1013(0.4)/998	994	0.02	$2v_6$
<i>941</i>	959	0.0	$v_6 + 2v_7$
<i>885</i>	901	0.0	$v_5 + v_7$
862 (0.17)	860	0.16	$v_4$
720 (3.0)	721	8.50	$v_6 + v_7$
<i>663</i>	676	4.20	$3 v_7$
663 (66.1)	662	95.1	$v_5$
498 (9.6)	496	12.2	$v_6$
<i>443</i>	451	2.0	$2 v_7$
222 (0.18)	222	0.02	$v_7$
Hot band	495.4	-	$v_7 \longrightarrow v_6 + v_7$
Hot band	497.9	-	$v_6 \longrightarrow 2 v_6$
Hot band	649.2	-	$v_5 \longrightarrow 2 v_5$
Hot band	689.7	-	$v_7 \longrightarrow v_5 + v_7$

Table 4: Observed and anharmonic ( $v(\text{cm}^{-1})$ ) wavenumbers calculated at CCSD(T)-  $F_{12}/$  aug-cc-pVTZ level from a VCI approach for cyanoacetylene in vacuo. Intensities (km/mol) are calculated within the anharmonic mechanical and electrical scheme. The main assignment is given from the variational method. Observed values are from Jolly et al.[12], values in italic are from Bizzocchi et al.[4]





**Graphical Abstract:**



**Titan**

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