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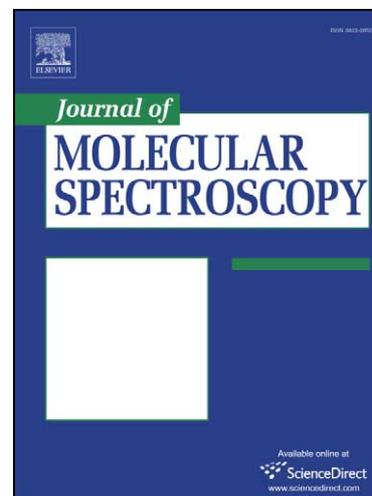
PII: S0022-2852(07)00205-6  
DOI: [10.1016/j.jms.2007.07.006](https://doi.org/10.1016/j.jms.2007.07.006)  
Reference: YJMSP 9566

To appear in: *Journal of Molecular Spectroscopy*

Received Date: 3 July 2007  
Revised Date: 19 July 2007  
Accepted Date: 26 July 2007

Please cite this article as: Y. Bénilan, A. Jolly, Y. Trolez, F. Raulin, J-C. Guillemin, Infrared band intensities of cyanobutadiyne ( $\text{HC}_5\text{N}$ ) between 400 and 4000  $\text{cm}^{-1}$ , *Journal of Molecular Spectroscopy* (2007), doi: [10.1016/j.jms.2007.07.006](https://doi.org/10.1016/j.jms.2007.07.006)

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**Infrared band intensities of cyanobutadiyne (HC<sub>5</sub>N) between 400 and 4000 cm<sup>-1</sup>**

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Submitted 3 July 2007

Revised 19 July 2007

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**Abstract**

We report the first infrared spectra of pure gaseous cyanobutadiyne between 400 and 4000  $\text{cm}^{-1}$ . A great care has been taken to obtain a pure sample so that, for the first time, intensities could be determined for all the main bands in the studied domain. The results are compared with available theoretical works. A sample containing a mixture of  $\text{HC}_5\text{N}$  and  $\text{DC}_5\text{N}$  was also studied in the same wavenumber range. The data obtained in this study should be very useful to identify those compounds by IR spectroscopy and will allow the quantification of cyanobutadiyne in various environments.

## 1. Introduction

Cyanobutadiyne ( $\text{HC}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CN}$ , also called 2,4-pentadiynenitrile or cyanodiacetylene) was observed in space for the first time in the molecular cloud Sgr B2 by Avery *et al.* [1]. In the following years, its presence was acknowledged in numerous environments from dark molecular clouds to the envelop of dying carbon stars. Since its abundance is high enough to be observed in numerous environments, cyanobutadiyne is a good probe to compare the different physical conditions of those environments [2]. As an example, the recent study by Pardo *et al.* [3] analysed the rotational lines to deduce the physical and chemical structure of the envelop of the proto planetary nebula CRL618. In 1981, using rotational transitions, the deuterated specie ( $\text{DC}_5\text{N}$ ) was observed in TMC 1 [4]. Its abundance compared to  $\text{HC}_5\text{N}$  is of the order of 1%.

In a totally different environment, results from simulation experiments of Titan's atmospheric chemistry also suggested the presence of  $\text{HC}_5\text{N}$  in the atmosphere of this satellite of Saturn [5]. However, the attempts to detect it using millimeter observations were up-to-now unsuccessful [6].

The first spectroscopic study of cyanobutadiyne was reported by Alexander *et al.* [7], 30 years ago. In this study, they obtained the spectrum of a typical linear molecule in the ground state. From their data they derived bond lengths, rotational constants and a large permanent dipole moment. They also observed the presence of numerous satellite lines for each fundamental rotational transition corresponding to transitions from excited vibrational states. The strongest lines came from the  $\nu_{11}$ , the lowest bending mode [8].

In 1981, Yamada and Winnewisser [9] observed in the laboratory for the first time in the infrared a vibrational band of  $\text{HC}_5\text{N}$ : the fundamental CN stretching mode  $\nu_2$  at  $2256.124\text{ cm}^{-1}$ . The presence of very low-lying bending modes was also confirmed experimentally in this study [10]. Haas *et al.* [11] reported the infrared spectra of cyanobutadiyne between  $500$  and  $4000\text{ cm}^{-1}$  at low resolution. The product was obtained from a mixture of  $\text{HC}_3\text{N}$  and acetylene submitted to a dc discharge. The spectra of the distilled products showed large amount of hexatriyne ( $\text{C}_6\text{H}_2$ ) that precluded the identification of all the main bands. Consequently, they focused their analysis on  $\nu_7$ , the most intense bending mode. In this study they reported the presence of a lot of accompanying hot bands arising from the presence of very low lying bending modes.

Parallel to this experimental approach, quantum molecular calculations have been performed. The first theoretical study of vibrational levels in HC<sub>5</sub>N molecule was done with the main goal of determining the population of excited levels through infrared pumping [12]. From their *ab initio* calculations, they determined vibrational frequencies and band intensities for the normal modes  $\nu_1$  to  $\nu_{11}$ . Unfortunately, since they were interested mainly in modelling the radiative transfer in relatively cool star envelopes as IRC +10216, they reported the position and intensity only for the bending modes  $\nu_7$  to  $\nu_{11}$  (see Table 1). Nevertheless, they showed that radiative excitation through the  $\nu_7$  band alone is more effective than the collisional excitation because of the large intensity of this absorption band. Since then, numerous theoretical studies have been done and confirmed the low energy  $\nu_{10}$  and  $\nu_{11}$  and the intense  $\nu_7$ -bending mode [13, 14 and references therein].

Finally, only two experimental studies of the infrared spectra of cyanobutadiyne in the gas phase have been reported [9, 10] and only the positions of the  $\nu_2$  and the  $\nu_7$  bands have been firmly confirmed. Furthermore, starting from a mixture of compounds, none of the studies were able to give the absolute intensities of the infrared bands.

The recently reported preparation of cyanobutadiyne allows the isolation of a sample for the first time and opens the way for studies with a pure and thermodynamically stable sample [15]. In the present work we report the first infrared spectra of pure gaseous cyanobutadiyne between 400 and 4000 cm<sup>-1</sup>. A great care has been taken to obtain a pure sample so that, for the first time, intensities could be determined for all the main bands in the studied domain. The results are compared with available theoretical works. A sample containing a mixture of HC<sub>5</sub>N and DC<sub>5</sub>N was also studied in the same wavenumber range.

## 2. Experimental

Cyanobutadiyne was synthesised by the reaction of 1,3-butadiynyltri-n-butylstannane with p-toluenesulfonyl cyanide [15]. The pure sample was selectively trapped at -70°C under vacuum (0.1 mbar) and kept under liquid nitrogen.

Deuterocyanobutadiyne has been prepared by addition of deuterated water (1 mL) and small amounts of potassium carbonate (10 mg) to a solution of cyanobutadiyne (30 mg) in dichloromethane (3 mL). After ten minutes of stirring at room temperature, the aqueous phase was removed and the sequence was repeated two

times. Purification was performed by vaporization of the organic phase in a vacuum line equipped with a tube ( $L = 15$  cm,  $\phi = 30$  mm) containing phosphorus pentoxide in half-section and followed by a selective condensation of deuterocyanobutadiyne in a  $-70$  °C cooled trap (for a similar experiment see [16]). The isotopic purity is of about 80 %.  $^{13}\text{C}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 293 K)  $\delta$  48.9 (C-CN), 65.6 ( $\text{HC}\equiv\text{C}$ ,  $^2J_{\text{CD}} = 7.8$  Hz), 67.2 ( $\text{C}\equiv\text{C-CN}$ ), 72.1 (D-C,  $^1J_{\text{CD}} = 40.5$  Hz), 105.2 (CN).

All spectra were recorded on an IRTF spectrometer (Bruker Equinox 55) equipped with a KBr beamsplitter and a DTGS detector. The spectrometer was flushed with nitrogen at a rate of 3 L/min in order to desaturate and stabilise water vapour and carbon dioxide absorption bands. The spectra were measured at room temperature and at  $0.5$   $\text{cm}^{-1}$  resolution between 400 and  $4000$   $\text{cm}^{-1}$ . The gas samples were placed in a White cell (Specac 10.6 m pathlength) equipped with KBr windows. Sample pressures were measured with two MKS Baratron covering the 1 bar to  $10^{-4}$  mbar pressure range. The gas samples were transferred from the tubes where they were stored in solid phase at liquid nitrogen temperature, to the cell via a vacuum line pumped below  $10^{-7}$  mb with a turbo pump (Pfeiffer TMH 065).

The first infrared spectra of  $\text{HC}_5\text{N}$  showed the presence of some impurities in the sample. Butadiyne was easily identified impurity and a distillation under vacuum at  $-70^\circ\text{C}$  allowed to get rid of it. Another remaining impurity was not clearly identified. We suspected intermediate chlorine compound formed in the synthesis of the stannane precursor. Such compounds were already observed as residue in the synthesis of polyynes [17, 18]. The purification procedure was performed by warming the sample at temperature around  $-50^\circ\text{C}$  up to a pressure of 0.1 mbar in the 2.5 l volume of our apparatus. The spectrum was recorded and checked to detect the presence of impurities. The sample was then pumped out and the procedure was repeated until the mixing ratio of the impurity was observed to be less than 0.04. This mixing ratio was checked afterward since the spectrum of the unidentified impurity can be obtained from the difference of highly polluted sample to purified ones.

For  $\text{DC}_5\text{N}$ , the sample purity was difficult to establish because of the limited amount of product. The sample showed the presence of both the chlorine residue and  $\text{HC}_5\text{N}$ . We grossly determined that 15% of  $\text{HC}_5\text{N}$  was present in the sample. We did not achieve the total purification of the sample and we estimated to 5% the amount of chlorine compound left in the sample. The  $\text{DC}_5\text{N}$  spectrum presented in Figure 1 has been

obtained after subtraction of the HC<sub>5</sub>N spectrum and the unidentified impurity. No absolute intensities could be determined.

### 3. Spectral results

#### 3.1. Bands position and relative intensities

HC<sub>5</sub>N is an unsymmetrical linear molecule with seven atoms. It has six fundamental stretching vibrational modes and five degenerate bending modes. The most recent theoretical determination of the frequency of those fundamental bands and some of their combination [13] indicates that the first two fundamental stretching modes ( $\nu_1$  and  $\nu_2$ ) are in fact dyads with the combination  $\nu_3+\nu_5$  and the overtone  $2\nu_5$  respectively. Those are clearly identified on our spectra (Figure 1, 2). As we will see later, the  $\nu_5$  band was too weak to be observed. Thus, the observed  $\nu_3+\nu_5$  and  $2\nu_5$  bands must be due to intensity borrowing through the Fermi resonance from the  $\nu_1$  and  $\nu_2$  bands, respectively.

The combination band  $\nu_3+\nu_5$  strongly overlaps the  $\nu_1$  CH stretching mode so that the intensity is determined for the two bands together. Nevertheless, by comparing the maximum of the R branch of  $\nu_1$  at  $3333\text{ cm}^{-1}$  and the maximum of the P branch of  $\nu_3+\nu_5$  at  $3310\text{ cm}^{-1}$  the fundamental stretching  $\nu_1$  can be estimated to be at least two times more intense than the combination  $\nu_3+\nu_5$ . In the DC<sub>5</sub>N spectrum, since the  $\nu_1$  stretching mode shifts to lower energies ( $2599\text{ cm}^{-1}$ ), there is no Fermi resonance with the combination band which is not observed but predicted at higher energies. The next stretching vibration  $\nu_2$  can be identified at  $2253\text{ cm}^{-1}$  for HC<sub>5</sub>N and  $2251\text{ cm}^{-1}$  for DC<sub>5</sub>N, as the lower component of the dyad. Its intensity is four times that of the overtone  $2\nu_5$  observed at  $2334\text{ cm}^{-1}$  for HC<sub>5</sub>N and  $2321\text{ cm}^{-1}$  for DC<sub>5</sub>N. The  $\nu_3$  stretching mode is also clearly observed as it already was in Hass *et al.* [11] low-resolution spectrum of HC<sub>5</sub>N. The intensity of  $\nu_3$  is approximately equal to that of the  $2\nu_5$  overtone for both molecules.

The next two stretching modes could not be unambiguously identified in HC<sub>5</sub>N. Their predicted intensities are at least ten times less than the previous ones [13]. So, they could be easily mixed up with combination bands or absorption of the impurity. Nevertheless for DC<sub>5</sub>N, the stretching vibration  $\nu_4$  was predicted with intensity almost equal to that of stretching vibration  $\nu_3$  [13]. It is observed in fact at  $1960\text{ cm}^{-1}$ . The next band to be observed in HC<sub>5</sub>N is the  $2\nu_7$  overtone at  $1272\text{ cm}^{-1}$ . It has an intensity ratio compared to the

fundamental  $\nu_7$  CCH bending mode which is about one third, approximately the same as the one observed between the equivalent  $\nu_5$  fundamental CCH bending mode and its  $2\nu_5$  overtone for  $\text{HC}_3\text{N}$  [19]. In addition to the strong  $\nu_7$  bending mode at  $642\text{ cm}^{-1}$ , we also observe two more bending modes,  $\nu_8$  at  $501\text{ cm}^{-1}$  and  $\nu_9$  at  $461\text{ cm}^{-1}$  (Figure 2). Their intensities are respectively one order and two orders of magnitude weaker than  $\nu_7$ . We also observe the  $2\nu_7$  overtone at  $1005\text{ cm}^{-1}$  for  $\text{DC}_5\text{N}$ . Its intensity is one third of the total intensity of the  $\nu_7$  and  $\nu_8$  bending modes respectively at  $508\text{ cm}^{-1}$  and  $500\text{ cm}^{-1}$ . The proximity of those two modes leads to large interactions. Finally, two bands with low intensities and parallel band profiles are present both in  $\text{HC}_5\text{N}$  and  $\text{DC}_5\text{N}$ . The first one is observed around  $700\text{ cm}^{-1}$  and is assigned to a combination between the  $\nu_9$  and the  $\nu_{10}$  modes. The second one is seen around  $600\text{ cm}^{-1}$  and is assigned to the fundamental  $\nu_6$  stretching vibration. Finally,  $\text{HC}_5\text{N}$  has two more bending modes expected at  $254$  and  $106.8\text{ cm}^{-1}$  which are out of reach of our instrumental apparatus.

### 3.2. Absolute band intensities

All spectra correspond to the sum of two hundred scans. Eight different pressures, with column densities from  $5 \cdot 10^{-3}$  to  $0.5\text{ cm}\cdot\text{atm}$ , have been used to determine the integrated intensities for the main bands. For the highest column densities used here, one bar of nitrogen was added to the sample to check for saturation effect. Nevertheless, no variation was observed. Band intensities  $S_{band}$  in  $\text{atm}^{-1}\text{ cm}^{-2}$  were calculated as follows ( $\nu$  is in  $\text{cm}^{-1}$ )

$$S_{band} = \frac{1}{pl_{band}} \int \ln\left(\frac{I_0}{I}\right) d\nu, \quad (1)$$

where  $I_0$  is the incident intensity,  $I$  the transmitted intensity with the sample at the pressure  $p$  (in atm) and  $l$  is the pathlength (in cm). The results are reported in Table 1 for  $\text{HC}_5\text{N}$ . For each spectrum, the pressure is corrected from the presence of the impurity. This correction is only of a few percent since the purity of the sample varies from 96 to 98 %. The mean error on the final intensities is determined from the  $1\sigma$  standard deviation on the data. It is generally less than 3% except for the  $2\nu_5$  overtone, which is overlapped by  $\text{CO}_2$  absorption, and for the  $\nu_9$ , which has a very low intensity. Since for  $\text{DC}_5\text{N}$ , we only have one sample and no

possibility to estimate the purity, we report in Table 2 the relative intensities integrated for each band after subtraction of the HC<sub>5</sub>N spectrum.

### 3.3. Comparison with theoretical studies reported in the literature

The most recent theoretical studies used large-scale coupled cluster calculation of CCSD(T) type with cc-pVTZ basis set [13] or cc-pVQZ [14], in order to predict harmonic vibrational wavenumbers. Anharmonic perturbations were predicted by Botschwina *et al.* [13] for the two dyads ( $\nu_1$ ,  $\nu_3+\nu_5$ ) and ( $\nu_2$ ,  $2\nu_5$ ) and for the  $\nu_3$  stretching mode. The measured positions of the bands are generally in good agreement with the anharmonic calculations. However, systematic differences persist between theoretical and experimental positions. They are about 20 cm<sup>-1</sup> for  $\nu_1$  and  $\nu_3+\nu_5$ , and 10 cm<sup>-1</sup> for  $\nu_2$  and  $\nu_3$ . The observed band at 2335 cm<sup>-1</sup> assigned to  $2\nu_5$  shows a shift of -15 cm<sup>-1</sup> which can be explained by strong anharmonic interaction with  $\nu_2$ . The use of cc-pVQZ basis set [14] does not change much the conclusions since the calculated harmonic frequency for the  $\nu_1$  to  $\nu_3$  stretching mode are not much different. Concerning the intensities, *ab initio* calculations are less efficient to predict accurate values. The intensities of the two dyads are overestimated by 30% and the intensity of  $\nu_3$  is underestimated by about the same amount. The same authors have also calculated the harmonic positions of the bending modes. Here again, the positions are efficiently estimated. Since the anharmonicity decreases for the low energy modes, harmonic calculations using cc-pVQZ basis set [14], are able to predict the position of  $\nu_8$  and  $\nu_9$  with a precision of 1 or 2 cm<sup>-1</sup>. Consequently, the position of  $\nu_{10}$  and  $\nu_{11}$ , which we could not verify, calculated by the same authors at respectively 254 and 106.8 cm<sup>-1</sup>, are certainly accurate values. Intensities of the five bending modes were determined by Uyemura [20] using semi empirical calculations and more recently by Scemama *et al.* [21] using B3LYP/cc-pVQZ method. The first study overestimates the intensity of  $\nu_7$  by 30 % whereas the second underestimates it by the same amount. The errors are even greater when looking at  $\nu_8$  and  $\nu_9$ . Nevertheless, one can notice that the results given by those theoretical methods always bracket the measured value. One would then predict that the intensity of the  $\nu_{10}$  and  $\nu_{11}$  mode should be respectively around 35 and 0.6 cm<sup>-2</sup> atm<sup>-1</sup> with an uncertainty of the order of 30 %.

#### 4. Conclusion

In this experimental study, we have obtained for the first time the spectra of isolated cyanobutadiyne and its deuterated isotopomer ( $\text{DC}_5\text{N}$ ), in the 400 to 4000  $\text{cm}^{-1}$  wavenumber range. The preparation of the  $\text{HC}_5\text{N}$  sample allowed obtaining purity better than 97%. This opens the way to the determination of the position and the intensity of the fundamental vibrational modes present in the studied wavenumber range. The  $\nu_1$ ,  $\nu_2$ ,  $\nu_3$  and  $\nu_6$  stretching modes could be identified and their intensities determined. The missing modes  $\nu_4$  and  $\nu_5$  have too low intensities to be observed. The  $\nu_7$ ,  $\nu_8$  and  $\nu_9$  bending modes were studied and their intensities determined. Beside those fundamental modes, we have also identified two overtones, namely  $2\nu_5$  and  $2\nu_7$ , and two combination bands:  $\nu_3+\nu_5$  and  $\nu_9+\nu_{10}$ . The  $\nu_{10}$  and  $\nu_{11}$  were out of the energy range studied here. For  $\text{DC}_5\text{N}$  we obtained a sample with purity better than 80%. This allowed us to subtract the contribution of  $\text{HC}_5\text{N}$  from the spectra and thus to identify most of the fundamental modes present in the studied wavenumber range. Only the  $\nu_5$  mode is missing. Nevertheless, we observed the two same overtones and combination bands as in  $\text{HC}_5\text{N}$ .

The comparison of our experimental study with previous theoretical predictions lead to the conclusion that for such molecule, high level *ab initio* method like couple cluster calculations are able to predict band positions with an error less than 1%. On the other hand, we found differences as large as 30% between experimental determinations and theoretical predictions concerning the band intensities.

The data obtained in this study should be very useful to identify  $\text{HC}_5\text{N}$  by IR spectroscopy. As an example, a recent study of Coupeaud et al. [22] already used those data to confirm their identification of  $\text{HC}_5\text{N}$  in the irradiation of  $\text{C}_2\text{H}_2/\text{HC}_3\text{N}$  or  $\text{C}_2\text{H}_2/\text{C}_4\text{N}_2$  mixture in cryogenic matrix. The determination of band intensities also opens the way to the quantification of this compound. As an example, Cernicharo et al. [23] used the intensity values of Deguchi and Uyemura [12] to determine the abundance of  $\text{HC}_5\text{N}$  in the spectra of CRL618 proto planetary nebula obtained with ISO. Since the values derived by Deguchi and Uyeruma [12] for the  $\nu_7$  are 30% too high, the derived column densities are underestimated by the same amount. This could have some implication for the modelled photochemistry in this environment.

Another environment in which cyanobutadiene might be observed using infrared spectroscopy is Titan's atmosphere where an active photochemistry of nitrogen and methane is producing complex molecules. In fact, HC<sub>5</sub>N has been observed in simulation experiments of such environment [5]. Even if the attempts to detect it using millimetre observations were unsuccessful [6], the Cassini-Huygens mission and its CIRS (Composite InfraRed Spectrometer) instrument are presently accumulating data in which the signature of HC<sub>5</sub>N might raise from the noise level in a near future.

### Acknowledgement

This work was financially supported by the CNES (Centre National d'Etudes Spatiales).

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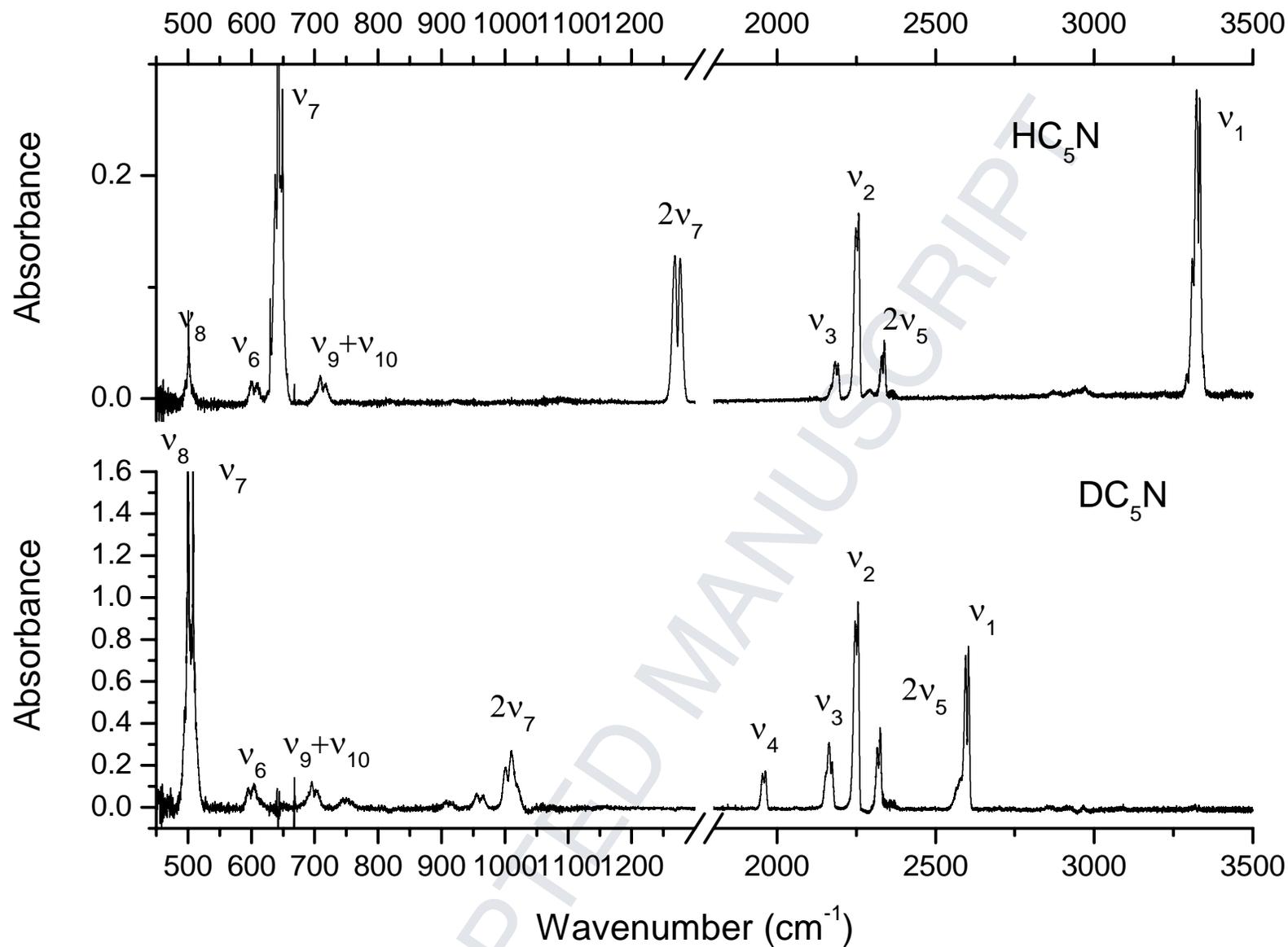
Figure 1: Comparison between HC<sub>5</sub>N and DC<sub>5</sub>N spectra at 295 K and 0.5 cm<sup>-1</sup> resolution, between 450 and 3500 cm<sup>-1</sup>

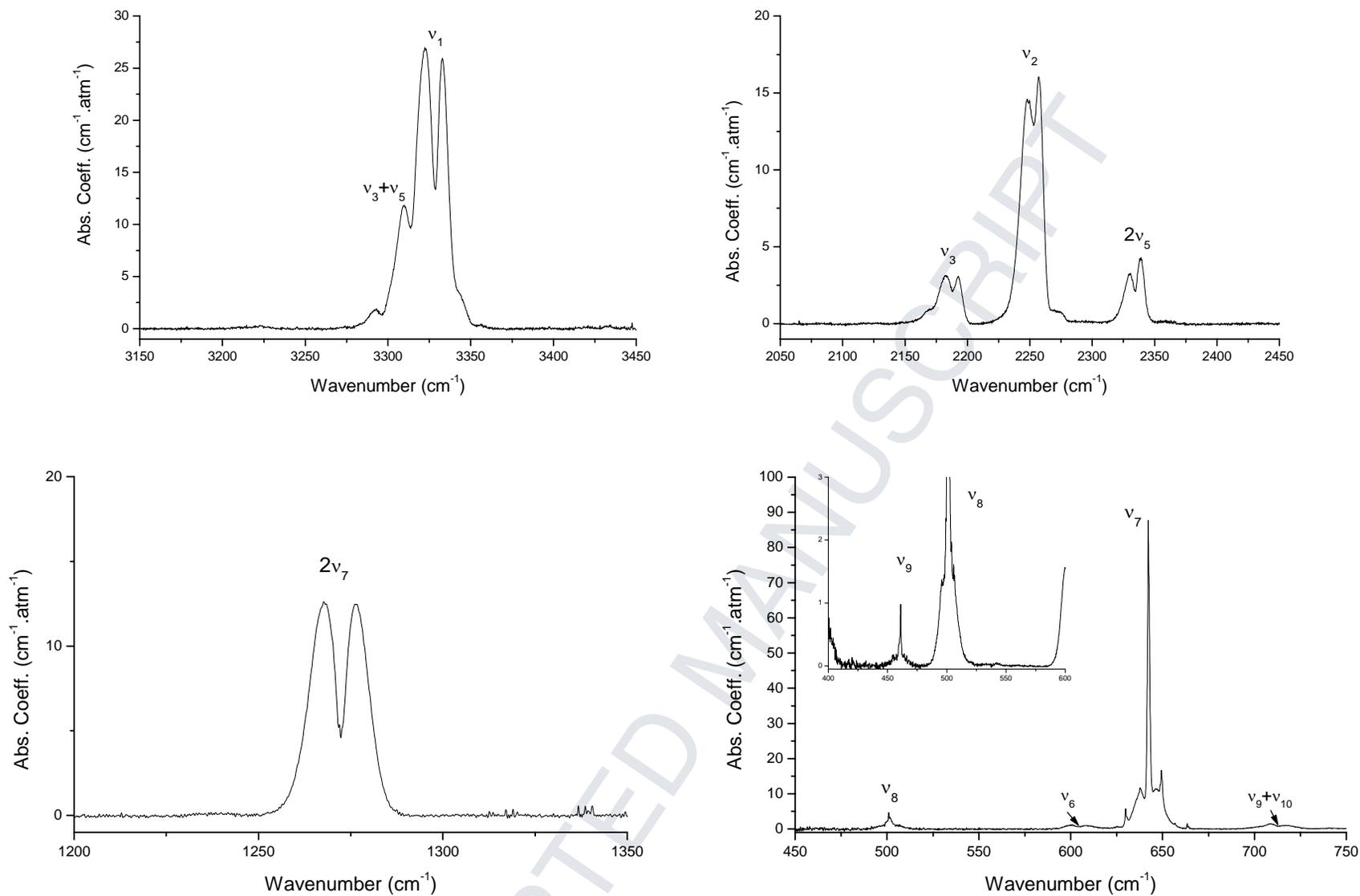
Figure 2: Absolute absorption coefficient of HC<sub>5</sub>N (base e at 295 K) at 0.5 cm<sup>-1</sup> resolution between 450 and 4000 cm<sup>-1</sup>

Table 1 : Positions and intensities of the major infrared absorption bands of HC<sub>5</sub>N

Mode	Vibration	Position (cm <sup>-1</sup> )		Absolute Intensities (atm <sup>-1</sup> cm <sup>-2</sup> ) at 295 K		
		This work	Theoretical Results	This work		Theoretical Results
				Value	Error	
$\nu_1/\nu_3+\nu_5$	C-H str.	(R) 3333 (P) 3322	3349 <sup>b</sup>	298	5.7	362 <sup>b</sup>
$2\nu_5$	overtone	(R) 2339 (P) 2330	2262 <sup>b</sup>	31.5	2.4	121 <sup>b</sup>
$\nu_2$	CN str.	(R) 2257 (P) 2248	2319 <sup>b</sup>	140	4.0	138 <sup>b</sup>
$\nu_3$	str.	(R) 2192.5 (P) 2182.5	2198 <sup>b</sup>	31.9	0.2	22.5 <sup>b</sup>
$\nu_4$	str.	Not detected	2067 <sup>b</sup>	-	-	0.33 <sup>b</sup>
$2\nu_7$	overtone.	(R) 1276 (P) 1267	-	90.7	1.8	-
$\nu_5$	str.	Not detected	1147 <sup>b</sup>	-	-	0.41 <sup>b</sup>
$\nu_9+\nu_{10}$	combin.	(R) 718 (P) 709	-	16.7	0.6	-
$\nu_7$	bend.	642.2	650.5 <sup>d</sup>	245.1	6.4	177 <sup>c</sup> /318 <sup>a</sup>
$\nu_6$	str.	(R) 609 (P) 600	602 <sup>b</sup>	13.3	0.4	1.4 <sup>b</sup>
$\nu_8$	bend.	500.9	501 <sup>d</sup>	19.3	0.5	7.4 <sup>c</sup> /55 <sup>a</sup>
$\nu_9$	bend.	461.1	462.9 <sup>d</sup>	1.6	0.3	2 <sup>c</sup> /0.8 <sup>a</sup>
$\nu_{10}$	bend.	Out of range	254 <sup>d</sup>	-	-	27 <sup>c</sup> /43 <sup>a</sup>
$\nu_{11}$	bend.	Out of range	106.8 <sup>d</sup>	-	-	0.8 <sup>c</sup> /0.4 <sup>a</sup>

\* converted from km/mol to atm<sup>-1</sup>.cm<sup>-2</sup><sup>a</sup> [12, 20], <sup>b</sup> [13], <sup>c</sup> [21], <sup>d</sup> [14]

**Table 2 : Positions and relative intensities of the major infrared absorption bands of DC<sub>5</sub>N**

Mode	Vibration	Position (cm <sup>-1</sup> )		Relative Intensities	
		This work	<i>Theoretical Results</i>	This work (Uncertainty=10%)	<i>Theoretical Results*</i>
$\nu_1$	C-D str.	(R) 2603 (P) 2595	2617 <sup>b</sup>	0.86	0.66 (124.5) <sup>b</sup>
2 $\nu_5$	overtone	(R) 2325 (P) 2317	2251 <sup>b</sup>	0.30	0.40 (75) <sup>b</sup>
$\nu_2$	CN str.	(R) 2255 (P) 2246	2308 <sup>b</sup>	1	1 (188.5) <sup>b</sup>
$\nu_3$	str.	(R) 2173.5 (P) 2164	2173 <sup>b</sup>	0.35	0.23 (43.5) <sup>b</sup>
$\nu_4$	str.	(R) 1964 (P) 1955	1964 <sup>b</sup>	0.17	0.18 (34) <sup>b</sup>
2 $\nu_7$	overtone	(R) 1010 (P) 1001	-	0.30	-
$\nu_6$	str.	(R) 604 (P) 595	595 <sup>b</sup>	0.11	0.006 (1.1) <sup>b</sup>
$\nu_7$	bend.	508	516.9 <sup>b</sup>	1.05	(168.5) <sup>a</sup> 0.94
$\nu_8$	bend.	500	505.1 <sup>b</sup>		(9.5) <sup>a</sup>

\* relative intensities (absolute intensities converted from km/mol to atm<sup>-1</sup>.cm<sup>-2</sup>)

<sup>a</sup> [12, 20], <sup>b</sup> [13]