

IR band intensities of DC₃N and HC₃¹⁵N: Implication for observations of Titan's atmosphere

Yves Bénilan^{a,*}, Antoine Jolly^a, Francois Raulin^a, Jean-Claude Guillemin^b

^aLaboratoire Interuniversitaire des Systèmes Atmosphériques, UMR 7583 du CNRS, Universités Paris XII-Val de Marne et Paris VII, 94010 Créteil, France

^bLaboratoire de Synthèse et Activation de Biomolécules, UMR CNRS 6052, Institut de Chimie de Rennes, ENSCR, 35700 Rennes, France

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Abstract

We have obtained the infrared spectra and the corresponding absolute band intensities for two HC₃N isotopomers: DC₃N and HC₃¹⁵N. Our results for DC₃N are in good agreement with previous measurements except for the ν_2 and ν_3 stretching modes. For HC₃¹⁵N, this study is the first including intensity measurements.

We have also studied the possible detection of these isotopomers in Titan's atmosphere using the CIRS spectrograph onboard the Cassini spacecraft. Our simulation of the expected spectra shows that for a signal-to-noise ratio better than 100, the ¹⁵N isotopomer of HC₃N could be detected. But, further study of HC₃N hot bands are needed since some of them overlap the HC₃¹⁵N Q-branch.

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1. Introduction

The IRIS instruments on the Voyager spacecraft have shown the presence of many organic compounds in Titan's atmosphere and among them, nitriles (Hanel et al., 1981; Kunde et al., 1981). One of the most intriguing is propynenitrile (also named cyanoacetylene, with chemical formula HC₃N) because this compound shows a high enhancement from the equator to the north pole at the time of Voyager measurements (Coustenis and Bezard, 1995). Furthermore, HC₃N is the first member of the cyanopolyne's family predicted by photochemical models to be one of the main links between the gas phase and the photochemical haze seen at high altitudes.

One of the key questions on Titan's atmosphere concerns its origin. The other one is the evolution of the organic mater in this environment. Most recent models on the origin of this dense atmosphere are based on isotopic observations. Mainly, D/H ratio and ¹⁵N/¹⁴N are used to construct a scenario of the origin and evolution of the atmosphere

(Owen, 2000; Coustenis, 2005). However, until very recently those ratios have been measured on only two species namely, CH₃D and HC¹⁵N. Hence, to differentiate between primordial escape phenomena and photochemical fractionation, it would be interesting to study those isotopic ratio on other molecules especially the ones implied in the complex chemistry that leads to the photochemical haze.

The detection and determination of the mean abundance of such species by spectroscopy are conditioned by the knowledge of band intensities of the expected species. However, there is a general lack of appropriate experimental absorption data. It is specially true for HC₃N isotopomers which are thermally unstable and difficult to synthesize in the laboratory with high purity. For that reason we have studied the infrared spectra of HC₃N isotopomers.

In the next section we briefly review the experimental conditions and the data reduction procedure. We then present the spectra and the absolute band intensities for both isotopomers DC₃N and HC₃¹⁵N. Finally, we discuss the possible detection of these isotopomers in Titan's atmosphere using the CIRS spectrograph onboard the Cassini spacecraft.

*Corresponding author. Fax: +33 145171564.

E-mail address: benilan@lisa.univ-paris12.fr (Y. Bénilan).

2. Experimental

2.1. Synthesis

Cyanoacetylene (also named propynenitrile) was prepared according to the procedure of Moureu and Bongrand (1920) as modified by Miller and Lemmon (1967). The final product, stored in a glass container within a cold nitrogen bath, exhibited a 99.5% minimum purity measured through gas chromatography.

Cyanoacetylene-d. Cyanoacetylene (3 g, 59 mmol), deuterated water (3 mL) and potassium carbonate (50 mg) were introduced under nitrogen in a Schlenk flask equipped with a stirring bar and the biphasic mixture was then energetically stirred for 20 min. The Schlenk flask was adapted to a vacuum line (10^{-1} mbar) equipped with two traps. The water was condensed in the first trap cooled at -50°C and the cyanoacetylene was condensed in the second one cooled at 77 K. The sequence was repeated three times by addition of D_2O and potassium carbonate to the partially deuterated cyanoacetylene. The cell containing the cyanoacetylene was then fitted to a vacuum line equipped with a short tube (ϕ : 3 cm, L : 15 cm) containing in half-section P_4O_{10} (20 g) and a trap. Residual water was removed by P_4O_{10} and the deuterocycanoacetylene was condensed in the trap cooled at -120°C . A pure and dry sample (2.0 g, 40 mmol) was thus obtained (Yield 67%, isotopic purity >98%). ^{13}C NMR (CD_2Cl_2): δ 57.2 (t, $^2J_{\text{CD}} = 8.0$ Hz, C–CN); 73.3 (t, $^1J_{\text{CD}} = 41.0$ Hz, D–C); 104.8 (s, CN).

Cyanoacetylene- ^{15}N : The reaction was performed in a two-step sequence starting from methyl propiolate and ammonia ($^{15}\text{NH}_3$) and followed by dehydration of the formed propiolamide- ^{15}N . Methyl propiolate (3 g, 36 mmol) was introduced in a one-necked flask equipped with a stirring bar. The flask was fitted on a vacuum line, cooled at 77 K and degassed. The vacuum line was disconnected by a stopcock. Gaseous ammonia ($^{15}\text{NH}_3$, 42 mmol) was introduced in the apparatus and condensed in the flask cooled at 77 K. The flask was allowed to warm to 220 K and the mixture was stirred for 2 h. The whole volume was small enough to maintain a pressure of about 300–500 mbar of ammonia. The flask was then allowed to warm to room temperature and the gaseous components were removed in vacuum. Propiolamide- ^{15}N (2.1 g, 26 mmol) was thus obtained in pure form in a 71% yield. Cyanoacetylene- ^{15}N was then synthesized by dehydration of propiolamide- ^{15}N by P_4O_{10} in sea sand. ^{13}C NMR (CDCl_3): δ 57.2 (C–CN) ; 73.0 (H–C) ; 104.2 (s, $^1J_{\text{CN}} = 20.9$ Hz, CN).

2.2. Infrared spectroscopy

All spectra were recorded on an IRTF spectrometer (Brucker Equinox 55) equipped with a KBr beamsplitter. The spectrometer was flushed with nitrogen at a rate of 3 L/min in order to desaturate and stabilize water vapour and

carbon dioxide absorption bands. The spectra were measured at ambient temperature and at 0.5cm^{-1} resolution between 400 and 4000cm^{-1} . The gas samples were placed in a White cell (Specac Sirocco 10 m variable pathlength) equipped with CsI 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 are stored in solid phase at liquid nitrogen temperature, to the cell via a vacuum line pumped below 10^{-7} mbar with a turbo pump (Pfeiffer TMH 065). Band intensities S_{band} in $\text{atm}^{-1}\text{cm}^{-2}$ are calculated as the integral over ν (the wavenumber in cm^{-1})

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

where I_0 is the incident intensity, I is the transmitted intensity with the sample at the pressure p (in atm) and l is the pathlength (in cm). All spectra correspond to the sum of one hundred scans.

3. Spectral results

DC_3N has been measured with an optical path length of 105 cm for 8 different gas sample pressures between 0.049 and 6.6 mbar resulting in a column density range between 5×10^{-3} and 6×10^{-1} cm atm. At each pressure, the spectra of the pure sample and of the mixture with 1 bar of nitrogen have been measured. A typical spectrum is presented in Fig. 1.

The absolute intensity of the stretching and overtone bands has been obtained by averaging 14 independent measurements only excluding our lowest pressure where the signal to noise ratio is too low for those relatively weak bands. More overtone and combination bands have been detected but none of them has an intensity above $5\text{atm}^{-1}\text{cm}^{-2}$. For the two strong bending modes ν_5 and ν_6 , we have also averaged 14 results excluding both spectra, i.e. with and without 1 bar of nitrogen added, at 6.6 mbar since a deviation to linearity above 10% was observed. The reason is that the two spectra at 6.6 mbar are saturated. So, 1.5 mbar was the highest pressure available to measure the intensities of those bending modes. The saturation for the pure samples is naturally stronger and it can be already observed at 1.5 mbar but the deviation does not reach 10%. Although the stretching mode ν_1 has almost the same strength as the bending modes, the particular shape of the band, with a low intensity Q branch, makes it less subject to saturation. All the results are gathered in Table 1. The error bars indicated in this table have been obtained by calculating the standard deviation of the measured values. Uncertainties between 5 and 10% have been obtained.

Our sample of DC_3N contained a small amount of residual HC_3N which could be quantified by measuring the strong HC_3N ν_1 band at 3326cm^{-1} . The partial HC_3N pressure could then be subtracted from each spectrum to obtain the DC_3N partial pressure. This procedure has

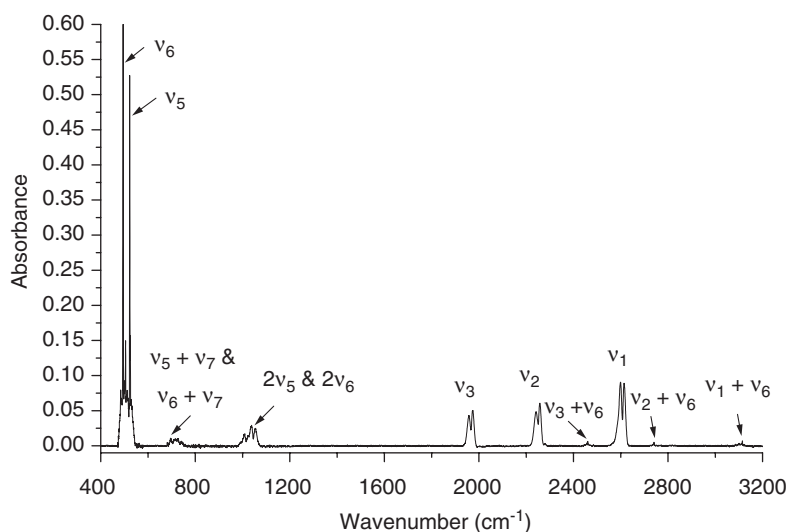


Fig. 1. Typical spectrum of DC₃N measured at ambient temperature, with an optical pathlength of 105 cm, a partial pressure of 0.3 mbar and one bar of nitrogen broadening gas.

Table 1
DC₃N absolute band intensities

Modes	Vibration	Position (cm ⁻¹)	Absolute intensities (atm ⁻¹ cm ⁻²) at 296 K	
			This work (2005)	Uyemura and Maeda (1974), Uyemura et al. (1982)
v ₁	C–D str.	(R) 2614 (P) 2599	81.3 ± 5.7	83.2 ± 12
v ₂	C=C str.	(R) 2257 (P) 2241	50.5 ± 2.4	45.3 ± 6.7
v ₃	C=N str.	(R) 1974 (P) 1958	38.7 ± 4.0	54.8 ± 8
2v ₅ and 2v ₆	Overtones	1015 and 1045	26.6 ± 3.5	—
v ₄	C–C str.	855	—	<0.1
v ₅	Bend.	522.5	83.8 ± 4.7	86.5 ± 12
v ₆	Bend.	494.8	106 ± 8	100.9 ± 15
v ₇	Bend.	213	—	0.89 ± 0.11

proven to be very useful since the ratio between both species evolved from one spectrum to the other. Hydrogen is quite labile and can quickly exchange with deuterium in a deuterium rich environment. This phenomenon was enhanced in the nitrogen mixture compared to the pure sample. Our results show that the ratio evolves between 3 and 9% in the pure sample and between 8 and 19% in the nitrogen mixture. The smallest ratios were obtained for the largest DC₃N pressure. Very similar experimental observation have already been reported, for instance in a study about HCN and DCN intensity measurements (Maki et al., 1995).

Our results shown in Table 1 are in very good agreement with Uyemura's results, particularly for the three strongest bands (Uyemura and Maeda, 1974; Uyemura et al., 1982). This result is especially remarkable for v₅ and v₆ since they appear slightly overlapped in our work at 0.5 cm⁻¹ but were much more difficult to distinguish at 1.6 cm⁻¹ in Uyemura's work. Surprisingly, the largest discrepancies

with Uyemura's results appear for v₂ and v₃, the two weaker stretching modes. While v₂ is significantly stronger than v₃ in our work, Uyemura et al. obtain the opposite result. No explanation could be found to account for this difference but one can note that theoretical calculations by Botschwina expect v₂ to be 7% stronger than v₃ (Botschwina et al., 1995).

Compared to HC₃N, the strongest differences are observed for the D–C stretching mode v₁ and for the v₅ bending mode with 720 and 140 cm⁻¹ shifts, respectively. Hot band features accompanying v₆ and v₅ in DC₃N are observed and are comparable in intensity to the ones seen for HC₃N (see Fig. 2). In particular, the separation between Σ and Δ sublevels of the 2v₆ state is large and can be observed in the 2v₆–v₆ subband transition at 505.4 cm⁻¹. This shift which is due to a Fermi resonance between v₆ = 2 and v₄ = 1 is smaller than the 15 cm⁻¹ shift observed for HC₃N (Jolly et al., in preparation). Accompanying the v₅ transition, the main hot band feature is

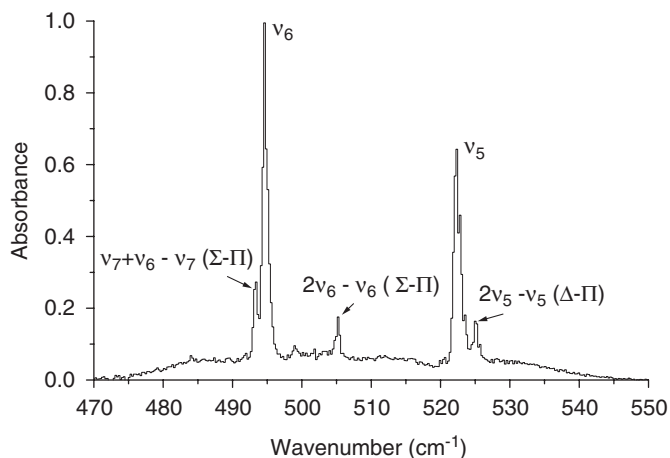


Fig. 2. DC₃N bending modes and accompanying main hot bands.

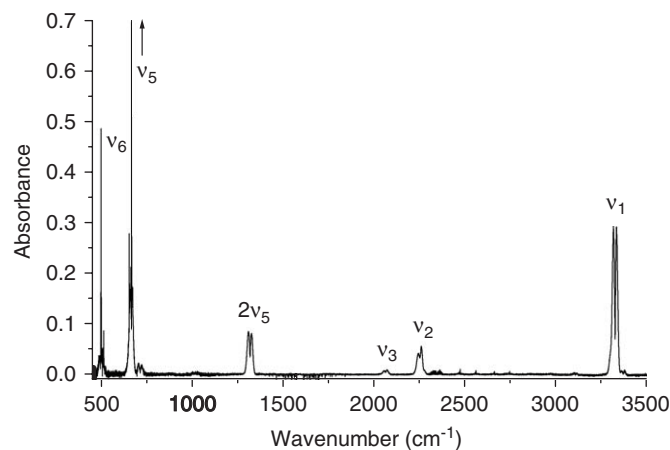


Fig. 3. Typical spectrum of HC₃¹⁵N measured at ambient temperature, with a optical pathlength of 318 cm and a partial pressure of 0.155 mbar.

Table 2
HC₃N¹⁵ absolute band intensities

Modes	Vibration	Position (cm ⁻¹)	This work (2005)
v ₁	C–H str.	(R) 3334 (P) 3317	185.6 ± 5.8
v ₂	C=C str.	(R) 2262 (P) 2245	34.4 ± 2.4
v ₃	C=N str.	(R) 2074 (P) 2059	5.3 ± 0.8
2v ₅	Overtone	1314	54.4 ± 3.6
v ₄	C–C str.	852.4	<0.2
v ₅	Bend.	663.2	180.3 ± 2.8
v ₆	Bend.	497.5	33.1 ± 0.3
v ₇	Bend.	220.8	—

observed at 525.3 cm⁻¹ and corresponds to the 2v₅-v₅ transition. Only one subband can be observed for DC₃N and the shift seems less important than for HC₃N.

HC₃¹⁵N has been measured with an optical pathlength of 318 cm for four different pressures between 0.028 and 0.268 mbar resulting in a column density range between 9 × 10⁻³ and 8.5 × 10⁻² cm atm. Due to technical problems, only spectra of the pure sample could be measured. With the exception of v₆, all integrated intensities given in Table 2 are the result of the average of 5 spectra taken at different pressures starting at 0.061 mbar. Results from the lowest pressure spectra at 0.028 mbar were not included because a systematic error was observed on the resulting intensities. Because of stronger noise in the signal around 500 cm⁻¹ and the weakness of v₆, this bending mode could only be accurately measured at 0.155 and 0.268 mbar. No spectra at higher pressures have been measured to avoid saturation of the stronger bands and also because of the small amount of HC₃¹⁵N sample available. Despite a small number of spectra, the accuracy of our results is good since the calculated standard deviation values given in Table 2 do not exceed 3%. The obtained spectrum at 0.155 mbar is presented in Fig. 3.

This study is the first intensity measurement for this isotope. Former studies including a recent complete analysis of the infrared and rotational spectra of HC₃¹⁵N that has been obtained at high resolution did not include intensity measurements (Fayt et al., 2004). Compared to the main isotope HC₃N, we found that all the band intensities of HC₃¹⁵N are smaller by a factor of 15–35%.

4. Implications for future observations of Titan's atmosphere

Because noble gases abundance ratio are so low compared to nitrogen in Titan's atmosphere, its origin must be searched in the planetesimals that either accreted initially from Saturn's subnebula to form the core or, formed in the solar nebula and subsequently impacted on Titan (Coustenis, 2005). The main nitrogen and carbons constituent, N₂ and CH₄, have then been outgassed from the core if the volatiles were initially trapped in the planetesimals or, produced by UV photolysis or shock impact chemistry to form the actual atmosphere. The evolutionary processes that finally led to the present state of the atmosphere can be traced back by studying isotopic ratios in N₂, CH₄ and their photochemical products.

Recent measurements concerning ¹⁴N/¹⁵N ratio in Titan's atmosphere gave a depleted value by a factor of 4.2 with a 7% uncertainty as compared to the Earth (Marten et al., 2002). This ratio was determined from HCN millimetre emission line around 88 and 258 GHz which led to a value of HC¹⁴N/HC¹⁵N = 65. The explanation for such low values was proposed by several authors as being due to the exposition of the atmosphere to very high wind particle outflow from the early sun. Considering non-thermal escape one can calculate that if 30 time the actual atmospheric mass was lost, a 4.5 depletion could be observed (Lunine et al., 1999; Lammer et al., 2000). Nevertheless, one assumption in this model is that no fractionation takes place and that the observed HCN isotope ratio is the same as for N₂. The latest results of Cassini INMS during the first flyby of Titan measured for

N_2 a value of 190 with 10% uncertainty (Waite et al., 2005). This was later confirmed by the GCMS experiment onboard the Huygens probe which found a $^{14}N/^{15}N = 183$ with 3% uncertainty (Niemann et al., 2005). The explanation for such a difference between N_2 and HCN could be the fractionation by photochemical (including ion chemistry) processes but this has still to be demonstrated. It remains that the 1.5 depletion of ^{14}N over ^{15}N found in N_2 in Titan's atmosphere, would imply a loss of 2–10 times the actual atmospheric mass (Niemann et al., 2005).

In another context, from observations of CN violet emission in several comets, Arpigny et al. (2003), Jehin et al. (2004) and Manfroid et al. (2005) derived an anomalously low $^{14}N/^{15}N$ isotopic ratio (about 130). This value is quite different from the $^{14}N/^{15}N$ isotopic ratio determined from the radio lines of HCN, observed in several comets, which is close to the terrestrial ratio. This strongly suggests another source for CN, significantly enriched in ^{15}N compared to HCN and that fractionation takes place in this other source. Could the delivery of this organic matter in early Titan explain the isotopic ratio found in Titan's atmosphere? This has still to be demonstrated.

Thus, the situation seems actually really unclear on what could be the relative importance of physical and chemical process on the evolution of this isotopic ratio. One way to try to differentiate between physical and chemical processes would be to study larger photochemical products like HC_3N . But the isotopomers of this molecule first need to be observed.

The possibilities to detect this isotopic component in the infrared range in an astrophysical environment are quite limited. For example, the strongest ν_5 band, at 663.4 cm^{-1} , is only separated from the main isotope by 0.2 cm^{-1} which does not enable Cassini CIRS (resolution: 0.5 cm^{-1}) to detect it separately. The ν_6 bending mode of $HC_3^{15}N$, at 497.5 cm^{-1} , is separated by 1.2 cm^{-1} from HC_3N and more suitable for a low resolution detection but the low band intensity is unfavourable. Fig. 4 shows a simulation of the ν_6 bending region for both isotopes in a cold environment similar to Titan's atmosphere (120 K). We have estimated the lowest detectable isotopic ratio to be around 60 considering a signal-to-noise ratio of 100. The temperature used for the simulation is 120 K and the isotopic ratio 60. For this simulation, we used the GEISA database for HC_3N and the spectroscopic constant from Fayt et al. (2004) for $HC_3^{15}N$ with the integrated intensity from this work. Only the fundamental bands have been taken into account to simulate spectra at 120 K. If the lines belonging to hot bands are not taken away from the GEISA line list, the result of the simulation can be quite surprising since a strong hot band appears at the same wavenumber as the $HC_3^{15}N$ Q-branch.

5. Conclusion

We have obtained the infrared spectra and the corresponding absolute band intensities for two HC_3N iso-

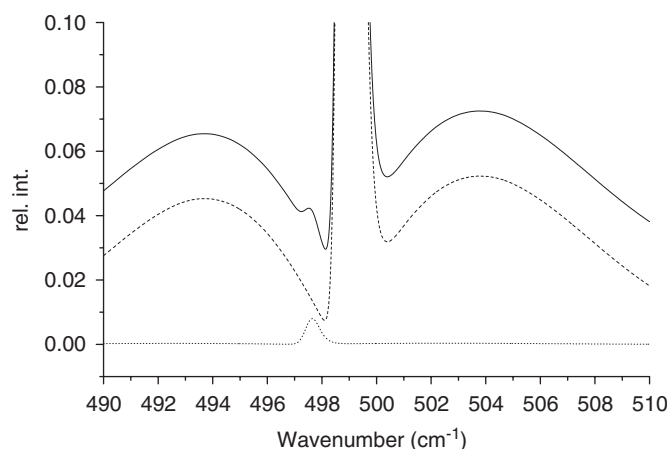


Fig. 4. Simulation of the expected spectrum at 0.5 cm^{-1} resolution with a HC_3N over $HC_3^{15}N$ ratio of 60, in the ν_6 bending region, at a temperature of 120 K. Dotted line $HC_3^{15}N$, dashed line HC_3N and plain line the sum. The spectra are normalized to HC_3N maximum and shifted by 0.05 for the sum.

topomers: DC_3N and $HC_3^{15}N$. Generally our results for DC_3N are in good agreement with Uyemura's results (Uyemura and Maeda, 1974; Uyemura et al., 1982). Nevertheless, large discrepancies appear for the ν_2 and ν_3 stretching modes. No explanation could be found to account for this difference but our results seem more reliable since they agree with theoretical calculation (Botschwina et al., 1995). For $HC_3^{15}N$, this study is the first which includes intensity measurements.

We also studied the possible detection of these isotopomers in Titan's atmosphere using the CIRS spectrograph onboard the Cassini spacecraft. Our simulation of expected spectra shows that for signal-over-noise ratio better than 100, the ^{15}N isotopomer of HC_3N could be detected. Nevertheless, this might be true only for low temperature spectra as those expected in the low equatorial stratosphere of Titan. If the temperature increases as it is expected, for example, at the north pole at the northern winter, the presence of HC_3N hot bands might overlap the $HC_3^{15}N$ Q-branch. Nevertheless, since there is a high increase of abundance at the north pole it might be still there that the detection of $HC_3^{15}N$ could be possible. Further study of HC_3N hot bands will be needed.

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