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Emmanuel Arzoumanian, T. Ferradaz, Et Es-Sebbar, Jean-Claude Guillemin

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Temperature-dependent photoabsorption cross section of cyanodiacetylene in the vacuum UV

N. Fray,¹ Y. Bénilan,¹ M.-C. Gazeau,¹ A. Jolly,¹ M. Schwell,¹ E. Arzoumanian,¹ T. Ferradaz,¹ Et. Es-Sebbar,¹ and J.-C. Guillemin^{2,3}

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[1] Using synchrotron radiation as a tunable VUV light source, we have measured, for the first time, the absolute photoabsorption cross sections of HC₅N with a spectral resolution of 0.05 nm in the region between 80 and 205 nm from 233 to 298 K. The measured cross sections are used to predict the HC₅N photodestruction rate in the solar system and to model a transmission spectrum in Titan's atmosphere. Comparing the latter with that acquired by the Ultraviolet Imaging Spectrograph on board the Cassini spacecraft, we have determined an upper limit of 2.7×10^{-5} on the HC₅N abundance at 1100 km.

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1. Introduction

[2] Cyanobutadiyne (H-C≡C-C≡C-N, also called 2, 4-pentadiynenitrile or cyanodiacetylene) is the simplest cyanopolyne. Numerous members of the (H-(C≡C)_n-C≡N) family, up to $n = 5$, have been detected in dark clouds [Bell *et al.*, 1997]. HC₅N was detected for the first time in the molecular cloud Sgr B2 by Avery *et al.* [1976]. Since then, it has also been observed in numerous cold dark clouds [Suzuki *et al.*, 1992] and in hot circumstellar environments such as CRL 618 [Cernicharo *et al.*, 2001; Pardo *et al.*, 2005]. We also note that the isotopologues DC₅N [MacLeod *et al.*, 1981], HC¹³CCCCN, as well as HCCCC¹³CN [Takano *et al.*, 1998] have been detected in Taurus Molecular Cloud 1 (TMC-1).

[3] In the cometary environment, a very low upper limit on the production rate of HC₅N has been determined [Crovisier *et al.*, 2004]. The upper limit on the relative abundance ratio of [HC₅N]/[HCN] is thus <0.012, which is lower than that in CRL 618 (0.1 [see Cernicharo *et al.*, 2001]) and in TMC-1 (0.14 [see Irvine *et al.*, 1987]). HC₅N has been found to be a product of laboratory simulations of Titan's atmosphere [de Vanssay *et al.*, 1995; Coll *et al.*, 1995]. Traces of HC₅N have also been observed after the irradiation of a mixture of cyanoacetylene (HC₃N) and acetylene (C₂H₂) as well as a mixture of dicyanoacetylene (C₄N₂) and acetylene (C₂H₂) [Trolez and Guillemin, 2005].

Recently, HC₅N has been predicted to be present at an altitude of 1100 km with an abundance of 10^{-6} by Vuitton *et al.* [2007]. Attempts to detect this molecule in Titan's atmosphere were unsuccessful in the submillimeter range [Marten *et al.*, 2002], and no detection or upper limits have been reported using infrared or in the UV range.

[4] Until recently, quantitative spectroscopic studies were hindered by the lack of an efficient method to form pure samples of HC₅N. This situation has changed recently with the development of a new chemical synthesis by Trolez and Guillemin [2005] that allows the isolation of very pure samples. This approach enabled Bénilan *et al.* [2007] to measure the vibrational band intensities in the mid-IR range (from 3500 to 400 cm⁻¹) and Coupeaud *et al.* [2007] to record relative cross sections of HC₅N in the 200–320 nm spectral range.

[5] In this article we present, for the first time, the absolute photoabsorption cross sections of HC₅N in the VUV spectral range from 80 to 205 nm and with a temperature dependence between 233 and 298 K. This information enables us to calculate the photodestruction rate, which is an essential parameter to constrain photochemical models of planetary atmospheres. Our cross sections can also be used to determine an upper limit of HC₅N abundance in Titan's upper atmosphere by using the data recorded in the VUV range by the Ultraviolet Imaging Spectrograph (UVIS) on board the Cassini spacecraft.

2. Experimental Methods and Procedures

[6] The samples of HC₅N have been prepared by the reaction of 1, 3-butadiynyltri-*n*-butylstannane with *p*-toluenesulfonyl cyanide [Trolez and Guillemin, 2005]. They were distilled at low temperature and this process was monitored using IR spectrometry. At the end of the distillation, no band of any impurities was seen in the IR spectra. The

¹Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR 7583 du CNRS, Universités Paris 7 et 12, Créteil, France.

²École Nationale Supérieure de Chimie de Rennes, UMR 6226, CNRS, Rennes, France.

³Also at Université européenne de Bretagne, Rennes, France.

resulting pure samples were stored in solid form at liquid nitrogen temperature to avoid any polymerization.

[7] As all the details of the experimental methods and procedures have already been described by *Ferradaz et al.* [2009], we give only a brief summary of the experimental protocols. To measure the VUV spectra of HC₅N, we used two spectroscopic cells. The first has a very short optical path length (10 cm) and is enclosed by a MgF₂ window at the entrance and by a VUV photomultiplier at the exit. The second cell is longer (120 cm) and the entrance window has been replaced by a microchannel plate (MCP), which allows photons of short wavelengths (in principle, down to 50 nm) to penetrate into the cell and thus provides precise knowledge of the optical path length. The exit window was covered with sodium salicylate on the inside, transforming VUV light into visible light to be detected by a visible photomultiplier.

[8] Both cells have double walls allowing the flow of liquid nitrogen, which is controlled through a cryogenic valve at the entrance. A standard proportional, integral, and derivative control loop is used to stabilize the temperature within ± 1 K. Although the cell can, in principle, reach liquid nitrogen temperature (77 K), no experiments could be performed below 220 K because the vapor pressure of HC₅N drops below the detection limit of our pressure measurement system at that point.

[9] Tunable VUV light is obtained from the synchrotron radiation facility in Berlin (BESSY). A first set of measurements was obtained at the U125/2 undulator beamline equipped with a 10 m focal length normal incidence monochromator (NIM). This undulator allows us to overcome problems associated with high-order radiation from the grating, and the stepwise system in the monochromator provides spectra that are self-calibrated in wavelength [Reichardt et al., 2001a]. During this first campaign, we used the long cell equipped with the MCP to record spectra below the cutoff of MgF₂ windows. With this setup, spectra were acquired in the 80–180 nm spectral region at a resolution of 0.3 nm. A second set of measurements was performed at the DIP 12-1B dipole magnet beamline equipped with a 3 m focal length NIM [Reichardt et al., 2001b]. The short cell, closed by MgF₂ windows that allowed high-order the radiation of the grating to be cut off, was used to record spectra in the 115–205 nm spectral range, at a resolution of 0.05 nm. We calibrated wavelength by using the first self-calibrated set of measurements as a reference.

[10] For each recorded spectrum, the solid sample of HC₅N was vaporized to the desired pressure, which was monitored by an MKS Baratron capacitance manometer (range 10^{-4} to 1 mbar). Most spectra were taken for at least at three different pressures in the 2–200 μ bar range to check the reproducibility of our measurements. Comparing all the spectra we have acquired, we restricted the influence of the stray light by selecting only spectra that were free from any saturation and had low absorption.

[11] To account for the steady decrease of the incident VUV light intensity, which is caused by the decay of BESSY's storage ring current, two “empty-cell” spectra were recorded just before and right after each HC₅N spectrum. A synthetic empty-cell spectrum was then interpolated by considering a linear decrease of the incident light intensity. Comparing the spectra we have acquired at different pressures, we estimate that this procedure leads to an

uncertainty of 10% on the absorption cross section and that this error dominates all other sources of errors.

3. Results and Discussion

3.1. Photoabsorption Cross Section at Room Temperature

[12] Figure 1 shows the absolute photoabsorption coefficient of HC₅N in the 80–300 nm range measured at room temperature (298 K). The spectral resolution of our measurements (80–205 nm) is 0.3 nm below 115 nm and 0.05 nm for wavelengths between 115 and 205 nm (see Table 1). In the 115–205 nm spectral region, at least three spectra have been taken with different pressures between 2 and 200 μ bar. The uncertainty on the absorption cross sections is about 10% (see section 2). For wavelengths lower than 115 nm, this uncertainty is estimated to be about 40% because only one spectrum has been taken in this spectral range.

[13] Between 150 and 205 nm, the absorption spectrum of HC₅N exhibits a very large and intense band structure (Figure 1). We assign this structure to the transition from the ground state to the first symmetry-allowed electronic state ($^1\Sigma^+ \leftarrow ^1\Sigma^+$ transition), in agreement with the semiempirical calculation of electronic absorption of cyanopolynes performed by *Scemama et al.* [2002]. Indeed, the wavelength of this transition has been predicted at 175.45 nm [Scemama et al., 2002] and we observe a maximum of absorption at 175.24 nm. Note that this agreement between the theoretical prediction and our subsequent experimental measurement is remarkably good. In this range, the spectrum exhibits numerous local maxima. These substructures, spaced by about 650 and 2300 cm^{-1} , can tentatively be assigned to the ν_7 and ν_2 vibrational modes, which are very intense in the infrared range [Bénilan et al., 2007].

[14] Between 115 and 150 nm, numerous sharp and intense bands are observed (Figure 1). They are presumably due to Rydberg series and seem to converge toward a broad structure located between 114 and 116 nm. Unfortunately, the first ionization energy of HC₅N has never been measured, so we do not know exactly where the Rydberg series should converge. The individual bands of the series are therefore difficult to identify properly. For wavelengths shorter than 115 nm, an intense continuum is observed with some weak superimposed bands.

[15] The spectrum of HC₅N between 200 and 300 nm has been measured by *Coupeaud et al.* [2007] in the gas phase (Figure 1). These authors tentatively assigned the observed bands to the $B^1\Delta \leftarrow X^1\Sigma^+$ transition. Since *Coupeaud et al.* [2007] measured only optical densities, we used our absolute cross sections in the 200–205 nm range to calibrate the intensity of their spectrum.

3.2. Temperature Dependence of the Absorption Coefficient

[16] The VUV spectrum of HC₅N has been measured at 233, 250, and 298 K to study the temperature dependence of the absorption coefficient (Figure 2). At 233 and 250 K, at least three spectra have been recorded at different pressures ranging from 2 to 90 μ bars. The resolution of both spectra varies between 0.05 and 0.1 nm (Table 1).

[17] Significant differences are observed between the spectra obtained at the three different temperatures. First, the

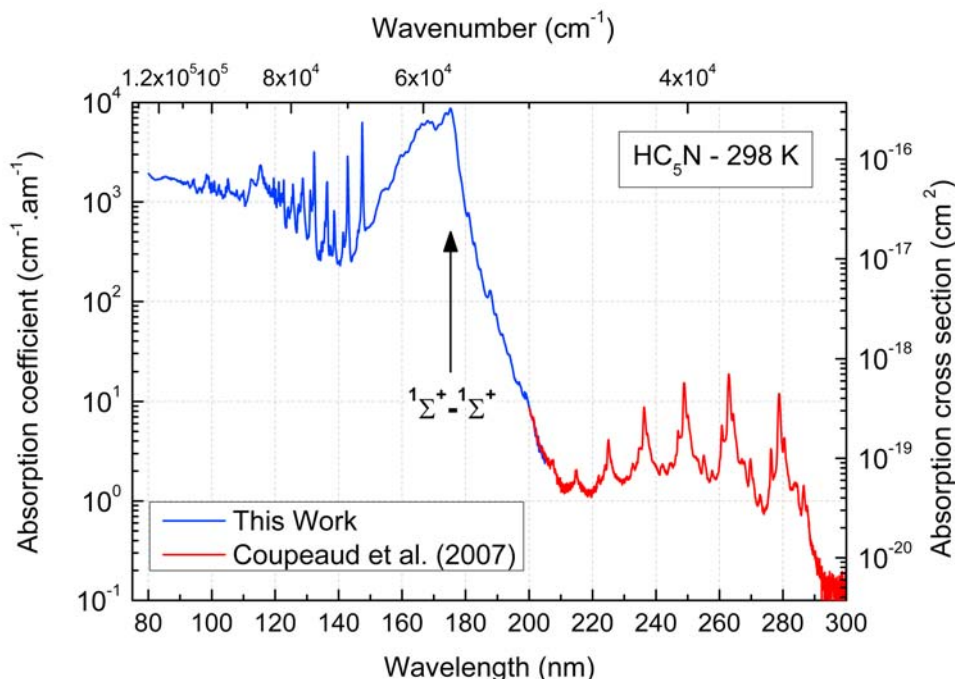


Figure 1. Absolute photoabsorption coefficient of HC₅N between 80 and 300 nm at room temperature. Our measurement at 298 K, in blue, ranges from 80 to 205 nm; for longer wavelengths, the spectrum of *Coupeaud et al.* [2007] is shown in red. The origin of the $^1\Sigma^+ \leftarrow ^1\Sigma^+$ electronic transition is indicated.

absorption coefficient of the transition $^1\Sigma^+ \leftarrow ^1\Sigma^+$ shows an increase of 25% when the temperature decreases from 298 to 233 K. Second, as can be seen in the inset of Figure 2, some of the sharpest bands show typical temperature effects. The band maximum increases and the full width at half maximum decreases when the temperature decreases from 298 to 233 K, as already observed for C₄N₂ and C₂H₂ in the mid-UV range [Bénilan *et al.*, 1996, 2000]. These effects are due to the change in the population distribution that favors the low J rotational levels when the gas temperature is reduced.

4. Astrophysical Implications

4.1. Photodestruction Rate

[18] Very few photolysis studies of HC₅N exist. In the gas phase, attempts to detect products of HC₅N photolysis at 254 nm have been unsuccessful, but dust attributed to the formation of oligomeric compounds was observed [Guillemin *et al.*, 2008]. In an Ar matrix at 10 K, *Coupeaud et al.* [2007] demonstrated that photolysis at 267 nm of HC₅N leads to the formation of isocyanodiacetylene (H-C≡C-C≡C-N=C) with no other products being observed.

[19] The photodestruction rate, denoted J (in s⁻¹), determines the lifetime of molecules in environments subject to solar UV radiation. Knowledge of its value is a requisite for predicting molecular abundances from chemical modeling of atmospheres. This important parameter can be calculated using the following formula:

$$J = \int_{\lambda_1}^{\lambda_2} \Phi(\lambda) \sigma(\lambda) S(\lambda) d\lambda,$$

where $\Phi(\lambda)$, $\sigma(\lambda)$, and $S(\lambda)$ are the photodestruction quantum yield, the absorption cross section (in cm²), and the solar irradiance spectra (in photons cm⁻² s⁻¹ nm⁻¹), respectively. Because the exact dissociation limit is unknown, we have chosen to include all wavelengths up to 290 nm for calculating J , using the spectrum of *Coupeaud et al.* [2007] (see section 3.1). The wavelength of 290 nm corresponds to the origin of the absorption system observed in their study (included here in Figure 1). Another important assumption concerns the photodestruction quantum yield Φ taken as equal to unity for all the wavelengths, in the absence of any further information. Given these hypotheses, the values of J calculated have to be considered upper limits.

[20] We have further considered two solar irradiance reference spectra, ATLAS 1 and ATLAS 3, which have been measured during moderately high and low activity levels, respectively, of the Sun [Thuillier *et al.*, 2004a, 2004b]. If we consider that the photodestruction of HC₅N occurs for wavelengths ranging from 80 to 290 nm, the HC₅N photodestruction rate at 1 AU from the Sun is equal to $(4.2 \pm 0.4) \times 10^{-4}$ and $(4.0 \pm 0.4) \times 10^{-4}$ s⁻¹ for moderately high and low solar activity levels, respectively. Note that the variation

Table 1. Experimental Details of the HC₅N Spectra

	Spectral Range (nm)	Resolution (nm)	Sampling (nm)	Uncertainty (%)
298 K	80–115	0.3	0.1	40
	115–205	0.05	0.015	10
250 K	115–150	0.05	0.015	10
	150–181.5	0.1	0.015	10
233 K	115–184	0.05	0.015	10

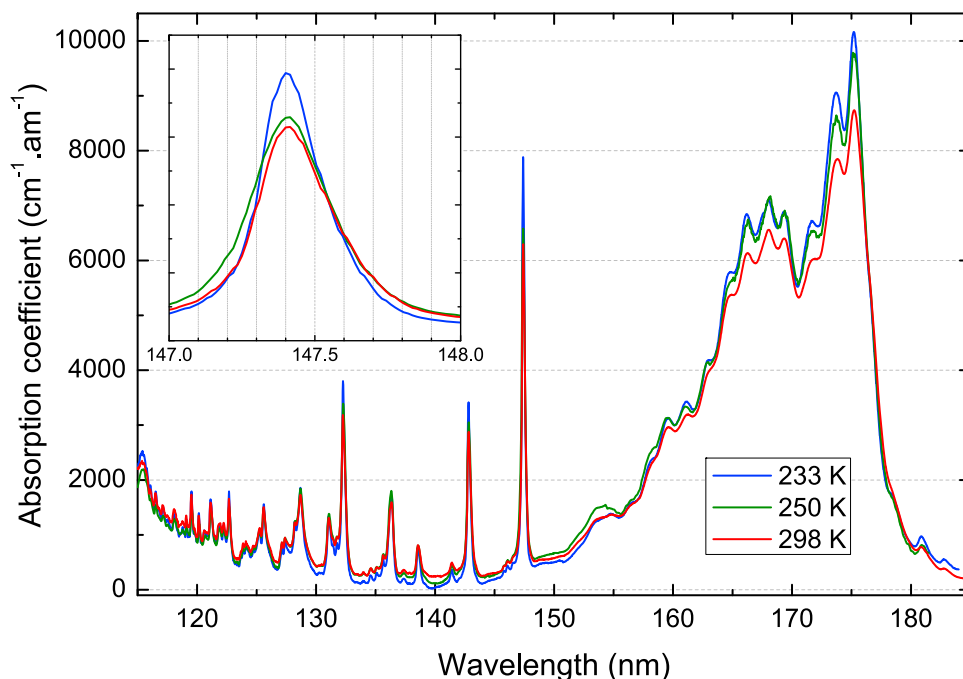


Figure 2. Absolute photoabsorption coefficient of HC₅N between 115 and 185 nm at 233, 250, and 298 K. A magnification of the sharp band located at 147.4 nm is shown in the inset.

attributable to the solar cycle is lower than the uncertainties of the absorption spectrum.

[21] Because of the very low solar flux in this domain, the 80–115 nm spectral range accounts for less than 1% of the HC₅N photodestruction rate. In contrast, the 115–180 nm spectral range accounts for 70% of the J value, which emphasizes the importance of our measurements in this spectral region. The 180–290 nm spectral range, despite its very low absorption cross section, accounts for about 30% of the photodestruction rate of HC₅N. The solar flux in this domain is quite high and perhaps is overestimated since we suppose $\Phi = 1$.

[22] The J calculations were performed for the spectra at 233, 250, and 298 K. Because the absorption cross sections are slightly higher for $T = 233$ and 250 K than for 298 K, the photodestruction rate increases by about 5% when the gas temperature decreases. Thus, the temperature dependence is not significant in comparison with the uncertainties of our spectra.

[23] Comparing our J value with those for HCN ($1.5 \times 10^{-5} \text{ s}^{-1}$) and HC₃N ($6.6 \times 10^{-5} \text{ s}^{-1}$) given by Crovisier [1994], we can conclude that the lifetime of HC₅N is about 25 and 6 times shorter than HCN and HC₃N, respectively. We note that the abundances of these three molecules in comets and in Titan's atmosphere decrease when the photodissociation rate increases [Crovisier et al., 2004; Vuitton et al., 2007].

[24] In Krasnopolsky's [2009] photochemical model of Titan's upper atmosphere, the photodestruction rate of HC₅N was considered to be equal to that of HC₃N. Our preceding result suggests that the HC₅N rate may be significantly higher than that for HC₃N.

4.2. Interpretation of Titan's Atmospheric Spectra

[25] A first attempt to detect HC₅N in Titan's atmosphere in the submillimeter wavelength range was unsuccessful and only an upper limit for the mixing ratio (4×10^{-10}) could be determined in the lower stratosphere [Marten et al., 2002]. More recently, Vuitton et al. [2007] predicted an abundance of 1×10^{-6} at 1100 km. At such a high altitude, one way to firmly detect HC₅N is to use the UVIS instrument [Esposito et al., 2004] on board the Cassini spacecraft. From stellar occultations, the Cassini UVIS experiment was able to measure transmission spectra through Titan's atmosphere in the far UV [Shemansky et al., 2005]. Figure 2 of Shemansky et al.'s publication presented a spectrum acquired at a southern latitude of -36° and for a tangent altitude of 868 km; although many compounds could be detected, no signature of HC₅N was observed. At the wavelength of the strongest feature of HC₅N, the optical density of the UVIS spectrum is close to zero with a noise of ± 0.2 . To reproduce this observation, we calculated the logarithm of the transmission, taking into account the cross sections and the column densities for CH₄, C₂H₂, C₂H₄, C₂H₆, C₄H₂, HCN, and HC₃N given in Table 2 and discussed by Ferradaz et al. [2009]. The calculated transmission spectrum has been convoluted by a boxcar function with a width of 0.275 nm to match the UVIS resolution (Figure 3). To determine an upper limit of HC₅N in the upper atmosphere, we considered a noise level of 0.2, which corresponds to a column density of $5 \times 10^{14} \text{ cm}^{-2}$ (Figure 3, bottom).

[26] We recalculated the logarithm of the transmission by including the contribution of HC₅N (Figure 3, top). The strong $^1\Sigma^+ \leftarrow ^1\Sigma^+$ transition around 175 nm appears as a small bump close to a C₂H₄ structure, whereas the sharp peak around 147 nm appears as a subtle shoulder close to a

Table 2. Column Densities and Characteristics of the Spectra Used to Calculate Titan's Transmission Spectra Presented in Figure 3

Species	Column density (cm ⁻²)	Reference used for the column density	Reference VUV spectrum	Temperature of the reference spectrum (K)
CH ₄	1.9×10^{17}	<i>Shemansky et al.</i> [2005]	<i>Chen and Wu</i> [2004]	150
C ₂ H ₂	4.0×10^{15} ^a	<i>Ferradaz et al.</i> [2009]	<i>Wu et al.</i> [2001]	150
C ₂ H ₄	8.2×10^{15}	<i>Shemansky et al.</i> [2005]	<i>Wu et al.</i> [2004]	200
C ₂ H ₆	7.3×10^{15}	<i>Shemansky et al.</i> [2005]	<i>Chen and Wu</i> [2004]	150
HCN	1.9×10^{16}	<i>Shemansky et al.</i> [2005]	<i>Nuth and Glicker</i> [1982]	300
C ₄ H ₂	1.3×10^{15}	<i>Ferradaz et al.</i> [2009]	<i>Ferradaz et al.</i> [2009]	173
HC ₃ N	1.3×10^{15}	<i>Ferradaz et al.</i> [2009]	<i>Ferradaz et al.</i> [2009]	243
HC ₅ N	5.0×10^{14} ^b	This work	This work	233

^aThis value was printed incorrectly as 1.1×10^{16} cm⁻² in the work published by *Ferradaz et al.* [2009].

^bThe HC₅N column density is the upper limit that we have determined from the transmission spectrum published by *Shemansky et al.* [2005].

C₂H₂ band. We conclude that the $^1\Sigma^+ \leftarrow ^1\Sigma^+$ transition is the most favorable structure for the detection of HC₅N in this spectral range.

[27] To convert our HC₅N column density upper limit to abundance takes two assumptions: to suppose that the HC₅N density (cm⁻³) varies exponentially with the altitude, and to consider that the scale height of HC₅N is equal to that of C₄H₂. The scale height of C₄H₂ can be determined from the density measurements of the Ion Neutral Mass Spectrometer (INMS) [*Cui et al.*, 2009] and is close to 40 km. This leads to a maximum density of 1.2×10^4 cm⁻³ at 1100 km. Because the interpolated N₂ density measured by *Cui et al.* [2009] is 1.7×10^9 cm⁻³ at the same altitude, we determine a maximum abundance of 7×10^{-6} for HC₅N at 1100 km. The principal hypothesis of this calculation is the value of the HC₅N scale height. When this value varies between 30 and 50 km, the upper limit of the HC₅N abundance varies between 1.6×10^{-6} and 2.7×10^{-5} . Considering this range

of variation, even if the HC₅N abundance is expected to depend on at least latitude, we note that both our upper limits are consistent with the value of 1×10^{-6} predicted by *Vuitton et al.* [2007] from INMS measurements.

5. Conclusions

[28] We have determined, for the first time, the absolute absorption coefficient of HC₅N in the 80–205 nm spectral range at ambient temperature with a resolution of 0.05 nm for wavelength longer than 115 nm and of 0.3 nm for shorter wavelengths. We found that the position of the $^1\Sigma^+ \leftarrow ^1\Sigma^+$ transition was predicted accurately by *Scemama et al.* [2002]. For wavelengths ranging from 115 to 180 nm, we recorded three spectra at 233, 250, and 298 K to determine the temperature dependence of the main absorption bands. The intensities of the main absorption bands increased by about 25% and the band profiles narrowed when the temperature decreased from 298 to 233 K.

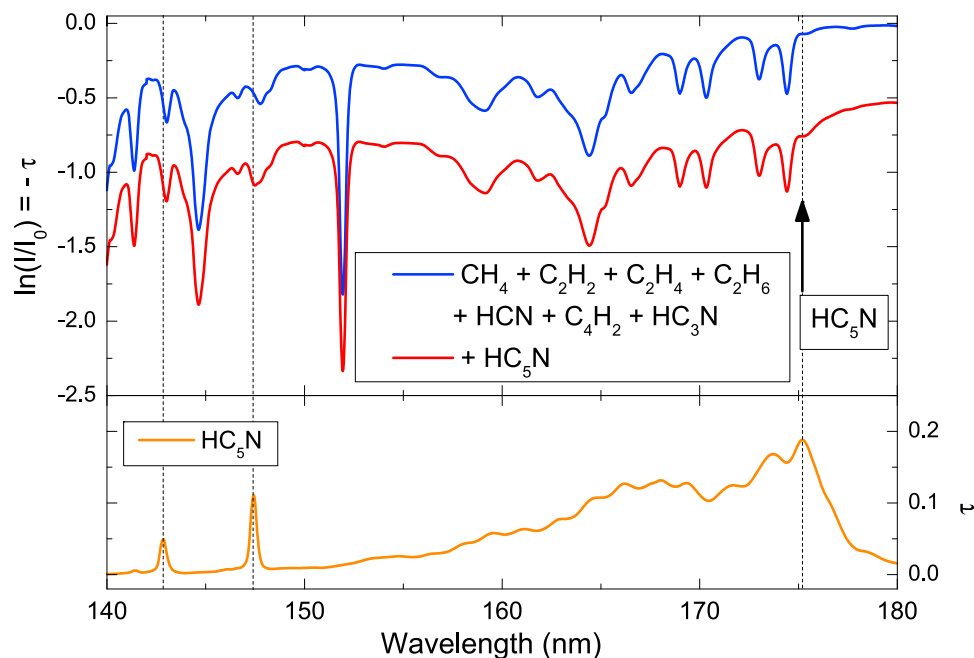


Figure 3. (top) Titan's expected transmission spectra simulated in the 140–180 nm spectral range. The blue line was obtained considering CH₄, C₂H₂, C₂H₄, C₂H₆, C₄H₂, HCN, and HC₃N and the red line (shifted downward by 0.5 for clarity) includes the absorption of HC₅N. (bottom) Optical density of HC₅N assuming a column density of 5×10^{14} cm⁻².

[29] The spectra at room temperature allowed us to calculate the photodestruction rate of HC₅N at 1 AU from the Sun to be $4 \times 10^{-4} \text{ s}^{-1}$, which is 25 and 6 times larger than for HCN and HC₃N, respectively. The intense absorption features of HC₅N between 115 and 180 nm account for 70% of the total photodestruction rate. Finally, we determined an upper limit for HC₅N in the upper atmosphere of Titan, which is higher than the value predicted by Vuitton *et al.* [2007].

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- J.-C. Guillemin, École Nationale Supérieure de Chimie de Rennes, UMR 6226, CNRS, Avenue du Général Leclerc, CS 50837, 35708 Rennes Cedex 7, France.