1 **Climatology of CH₄, HCN and C₂H₂ in Titan**
2 **upper atmosphere from Cassini/VIMS**
3 **observations**

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15 **ABSTRACT**

16 The Visual and Infrared Mapping Spectrometer (VIMS) measurements of non-
17 LTE emissions of CH₄, HCN and C₂H₂ in the near-infrared represent a dataset
18 with unique coverage to study Titan's upper atmosphere in the altitude range
19 from 500 to 1000 km. This region is the key to a better understanding of the
20 middle atmosphere circulation. The assessment of the latitudinal and seasonal
21 variations in the distributions of HCN and C₂H₂ could give important hints

22 about it and complement the Composite InfraRed Spectrometer (CIRS) obser-
 23 vations, that target the atmosphere below 500 km. The measurement of CH₄
 24 and HCN above 900 km can also help in understanding the Ion and Neutral
 25 Mass Spectrometer (INMS) observations near and above 1000 km. We have
 26 analysed the VIMS daytime spectra in the 2.9-3.4 μ m region measured from
 27 2004 to 2012 that span from the mid-northern winter through mid-northern
 28 spring Titan seasons. The measurements exhibit very strong non-LTE emis-
 29 sions of CH₄, HCN and C₂H₂. Non-LTE vibrational temperatures have been
 30 calculated for the emitting levels of the three molecules, and have been used
 31 in the inversion of their abundances in the 500-1100 km region. The retrieved
 32 abundances have been averaged in latitudinal bins and in two seasons: north
 33 hemisphere winter (2004-2009) and north hemisphere early spring (2010-2012).
 34 The C₂H₂ average profile, retrieved for the first time from VIMS measure-
 35 ments, shows good agreement with UltraViolet Imaging Spectrograph (UVIS)
 36 measurements below 850 km, while higher values are found above that alti-
 37 tude. The HCN volume mixing ratio (VMR) shows an enhancement at the
 38 North pole during winter at all altitudes (from $\sim$ 700 km up to near 1000 km)
 39 and at the North and South poles during spring below 900 km. Also, the aver-
 40 age C₂H₂ abundance is larger at both poles during spring below 800 km, while
 41 no significant variation is seen during winter. For CH₄ we found enhancements
 42 above 800 km at the North pole during winter and at both poles during spring.
 43 Our results suggest that the middle atmosphere circulation on Titan extends
 44 well above the 500 km level, up to 750-800 km or even higher if we assume
 45 that the CH₄ concentration above 800 km is mainly controlled by the circu-
 46 lation. The behavior of CH₄ at the winter pole above 800 km is in line with
 47 the strong zonal winds suggested to explain INMS observations, although it
 48 can also be explained by the slower photo-dissociation occurring during polar
 49 winter. Despite the poor statistic at the polar regions, our results represent
 50 an unique dataset that could help to improve our understanding of Titan's
 51 atmosphere above 500 km.

52 1 Introduction

53 The Cassini mission produced an unprecedented advance in the understanding
54 of Titan’s atmosphere. His heritage is an enormous amount of measurements,
55 still to be fully exploited, covering about half of a Titan’s year. Titan, like
56 the Earth, shows seasonal variations in its atmospheric structure and climate
57 (Hourdin et al., 2004; Lebonnois et al., 2012; Vinatier et al., 2015). Therefore
58 Cassini measurements can be used to monitor the seasonal evolution of Titan’s
59 atmosphere.

60 One of the key instruments for the study of the thermal structure and com-
61 position of Titan’s middle atmosphere has been CIRS (Composite InfraRed
62 Spectrometer), a mid and far infrared spectrometer (Flasar et al., 2004; Jen-
63 nings et al., 2017). CIRS observations focused on Titan’s stratosphere, up
64 to about 450-500 km, and produced detailed latitude/pressure maps of Ti-
65 tan’s atmospheric thermal structure and composition; monitoring also their
66 time evolution (Achterberg et al., 2008, 2011; Vinatier et al., 2015; Coustenis
67 et al., 2016; Coustenis et al., 2018).

68 During Titan’s northern winter (before 2009), colder temperatures were ob-
69 served in the northern polar troposphere/lower stratosphere and warmer in
70 the corresponding upper stratosphere and mesosphere. These observations
71 can be interpreted as a signature of the subsidence of air above the winter
72 pole, accompanied by the formation of a polar vortex (Flasar et al., 2014;
73 Teanby et al., 2012, 2008, 2009). In late 2009 and 2010, soon after the North-
74 ern spring equinox, CIRS temperatures revealed the disruption of the vortex
75 at the North pole and the reversal of the meridional circulation. The same be-
76 havior was confirmed by CIRS measurements of dynamical tracers like HCN
77 and C_2H_2 , that showed enhanced concentrations at the winter polar strato-
78 sphere (Teanby et al., 2009, 2012, 2010, 2008; Vinatier et al., 2015). CIRS
79 data have also shown the formation of haze and ice clouds, some of which are

80 based on nitrile and hydrocarbons aerosols (Coustenis et al., 2016; Coustenis
81 et al., 2018). Recently, Teanby et al. (2017) reported CIRS observations of the
82 winter polar vortex formation at the South pole below 500 km. They observed
83 a mesospheric hot-spot in conjunction with extreme enrichment of trace gases
84 in 2010-2011, followed by a rapid mesospheric cooling beginning on 2012. The
85 recent work of Coustenis et al. (2018), still focused below 500 km, reports
86 a strong temperature decrease and a dramatic enhancement of several trace
87 species in Titan’s south pole beginning on 2012 while the concentration of
88 most molecules in the northern hemisphere shows a clear depletion only since
89 2015.

90 Current Global Circulation Models (GCMs) of Titan’s middle atmosphere
91 predict the existence of a single meridional cell that goes from the summer
92 hemisphere to the winter pole, with ascending motions in the former and
93 subsidence in the latter (Rannou et al., 2004; Lebonnois et al., 2012). This
94 circulation reverses within 2 years after the northern spring equinox, and in
95 the reversal process the single cell breaks (Vinatier et al., 2015). These predic-
96 tions are in good agreement with CIRS observations, even though a complete
97 description of the atmospheric processes involved is still missing (Teanby et al.,
98 2012; Vinatier et al., 2015).

99 Both, CIRS measurements and current GCMs, describe Titan’s atmosphere
100 only below 500 km. However, in order to explain the observed trace gases
101 enrichment, Teanby et al. (2012) estimated that the middle atmosphere cir-
102 culation has to be extended up to at least 600 km, inside the photochemical
103 source region of these species. However, Titan’s atmosphere above 500 km still
104 remains to be well characterized. A direct measurement of the temperature in
105 the whole atmosphere was provided by Huygens Atmosphere Structure Instru-
106 ment (HASI), showing high variability especially above 500 km (Fulchignoni
107 et al., 2005). More extensive data, from about 600 to 1000 km, have been pro-
108 vided by the UltraViolet Imaging Spectrograph (UVIS) (Esposito et al., 2004).

109 The thermal structure measured by UVIS shows an average temperature be-
110 tween 170 and 180 K, with large fluctuations of up to 10-20 K attributed to
111 gravity waves (Koskinen et al., 2011). Unfortunately UVIS observations are
112 mainly in occultation, therefore its sampling is sparse and does not allow to
113 obtain seasonal/latitudinal variations (Capalbo et al., 2015; Koskinen et al.,
114 2011; Yelle et al., 2014).

115 The upper region of Titan’s atmosphere, from about 950 km to 1400 km, has
116 been explored by the Ion and Neutral Mass Spectrometer (INMS) (Waite et al.,
117 2004). INMS has been able to indirectly retrieve temperature profiles (Yelle
118 et al., 2006; Cui et al., 2009; Snowden et al., 2013; Yelle et al., 2014), showing
119 a very large variability. Snowden et al. (2013) concluded that the tempera-
120 ture shows no clear correlation with latitude, longitude, solar zenith angle or
121 local time. Again the sparse coverage of INMS data (only 32 passes in close
122 flybys) does not allow to clearly observe seasonal and latitudinal variations of
123 thermospheric temperatures. Still using INMS observations Cui et al. (2016)
124 derived the HCN abundance at the altitude range from 960 to 1400 km from
125 a large number of Cassini flybys, but no seasonal behaviour has been studied.

126 Overall, the intermediate region between 500 and 1000 km is still poorly known.
127 This work tries to partially fill this gap through the retrievals of CH₄, HCN
128 and C₂H₂ abundances from the Visual and Infrared Mapping Spectrometer
129 (VIMS) observations of their emissions in the 3 μ m spectral region. CH₄,
130 HCN and C₂H₂ are chemically active species in the upper atmosphere of Ti-
131 tan. The photolysis of CH₄, mainly through solar UV photons, initiates a rich
132 hydrocarbon chemistry, which gives rise to the large abundance of trace gases
133 present in Titan’s atmosphere (Wilson and Atreya, 2004; Krasnopolsky, 2009;
134 Vuitton et al., 2014; Dobrijevic et al., 2014; Willacy et al., 2016). The main
135 reaction for the production of acetylene (C₂H₂) takes place in the upper at-
136 mosphere from the primary products of the CH₄ dissociation. C₂H₂ is very
137 important in the photochemistry of Titan’s atmosphere since it is photolized

by lower energies ($h\nu > 5.17$ eV) photons which are not absorbed by CH_4 or N_2 . HCN is produced in the upper atmosphere with reactions that involve atomic nitrogen and products of the CH_4 dissociation (Krasnopolsky, 2014). Cui et al. (2016) argue that the HCN variability may contribute to the large temperature variability observed in Titan’s upper atmosphere.

At Titan’s thermospheric temperatures the thermal emission of CH_4 , HCN and C_2H_2 near $3\text{ }\mu\text{m}$ would be too faint to be detected. In daytime, VIMS measures a significant signal in this region, up to about 1000-1100 km, because the emitting energy levels of these molecules are excited by solar radiation, leading to non-LTE (non-Local Thermodynamic Equilibrium) populations much larger than those expected under LTE conditions. Non-LTE occurs when the rate of collisional adjustment to the population of the energy states of a molecule is smaller than the rate of adjustment due to radiative processes (López-Puertas and Funke, 2015). In daytime, the emitting levels of the three molecules studied here are in non-LTE in practically the whole studied atmospheric region.

HCN and CH_4 abundances in the 500-1000 km region have already been obtained from two Cassini flybys (T34 on 19 July and T35 on 31 August 2007) (Adriani et al., 2011; García-Comas et al., 2011) using a set of VIMS observations. They developed non-LTE models for both molecules and retrieved HCN and CH_4 VMR profiles for the two flybys. Since the emission of C_2H_2 is strongly overlapped to the HCN signal at VIMS spectral resolution, its contribution was only approximately included in the analysis of Adriani et al. (2011). In this work we improve the work of Adriani et al. (2011) by developing an accurate non-LTE model for C_2H_2 which allows both the improvement of the retrieval of HCN and the accurate retrieval of the concentration of C_2H_2 itself. Using the developed non-LTE models, we have performed the retrievals of HCN, C_2H_2 and CH_4 to all Cassini’s flybys in the 2004 to 2012 period. VIMS daytime coverage for the considered time interval is very good both in latitude and time, enabling the study of the seasonal and latitudinal variations

167 of the vertical distribution of these molecules in Titan’s upper atmosphere
168 ($\sim 500\text{--}1000\text{ km}$).

169 **2 Measurements**

170 VIMS, on board the Cassini spacecraft, was an imaging spectrometer that
171 measured the same scene with a 64×64 pixels detector, in 352 separate wave-
172 lengths. The resulting set of images is called a data cube. The angular reso-
173 lution of each pixel varied from $0.17 \times 0.17\text{ mrad}$ in the visual (VIS) channels
174 ($0.35\text{--}1.08\text{ }\mu\text{m}$) to $0.25 \times 0.5\text{ mrad}$ over the infrared (IR) channels ($0.85\text{--}5.2$
175 μm). The infrared spectrum was provided by a single linear array of 256 InSb
176 photo detectors with constant 0.12 mm spacing while a 2D 64×96 equiva-
177 lent pixels CCD was used by the visible channel (Brown et al., 2004). The
178 VIMS optics included a tip/tilt mirror that step-scanned the image plane
179 over the entrance aperture of the IR spectrometer. VIMS data used here have
180 been calibrated radiometrically, using the most recent pipeline RC19 (Clark
181 et al., 2016). The geometry of each pixel (latitude, longitude, distance from
182 the spacecraft, local time, and phase, emission and incidence angles) have
183 been determined with the ad hoc NAIF-SPICE toolkit (Acton, 1996). This
184 takes into account the VIMS navigation parameters reported in each Plane-
185 tary Data System (PDS) header where also instrumental parameters of the
186 specific observation are included.

187 In this work we have used only observations of the atmospheric limb emission
188 of Titan. Given the weakness of the signal, target of our analysis, we have
189 selected VIMS IR images acquired with long integration time ($\geq 600\text{ ms}$).
190 An appropriate selection of the solar phase angles is also crucial as stray-light
191 effects can contaminate the atmospheric signal. A maximum value of 90° has
192 been selected as a good compromise between contamination and number of
193 measurements.

194 The dataset used in this work has been built by extracting from each sin-
 195 gle VIMS cube the spectra corresponding to the pixels observing right out of
 196 the Titan’s disk. Each pixel samples Titan’s atmosphere down to the mini-
 197 mum distance of its line of sight from Titan’s surface (the so-called tangent
 198 altitude). The spectra have been grouped into sub-sets or collections, each
 199 composed by the spectra corresponding to the pixels aligned along a straight
 200 line perpendicular to Titan’s surface (see Fig. 1 in Adriani et al., 2011). The
 201 spectra in each collection have been labeled according to: the tangent altitude,
 202 the geo-location of the origin of the vertical line, the elevation angle of the
 203 Sun at the tangent point (solar zenith angle) and to the corresponding local
 204 time. The projection of the pixel’s size on Titan’s atmosphere (e.g. the vertical
 205 sampling of the tangent height) varies with the Cassini-Titan distance and is
 206 on the range of 50 to 70 km.

207 During the various Cassini flybys, the VIMS latitude/longitude coverage of
 208 500–1000 km region was rather extensive. Because our work relies on the
 209 stronger daytime emissions, only measurements with SZA lower than 120°
 210 have been used. This threshold ensures that the altitude region above 500 km
 211 is illuminated by the Sun. Except for 2008, when the polar regions could not
 212 be observed due to the spacecraft-planet alignment, all other years show an
 213 almost complete latitudinal coverage. The coverage of the polar latitudes, key
 214 regions for the understanding of Titan’s circulation and seasonal behavior, is
 215 the most problematic, with always high values of the local SZA. In particular,
 216 for the winter polar region (latitudes above 80°) we only have measurements
 217 with SZA higher than 90° .

218 Figure 1 shows a set of average VIMS spectra in the 2900–3500 nm spectral
 219 region at different tangent altitudes. The spectra, with solar zenith angle lower
 220 than 40° , have been averaged in 50 km bins. The spectra show several features:
 221 the signature centered at 3050 nm is produced by the emission of both HCN
 222 and C_2H_2 , not resolved at VIMS resolution. The emission from CH_4 is located

223 between 3200 and 3500 nm, where we can clearly distinguish the Q branch
 224 (strongest signal), and the two less intense P and R branches, at longer and
 225 shorter wavelengths, respectively. We note here, as reported by Adriani et al.
 226 (2011) and Dinelli et al. (2013), that the R branch is stronger than expected,
 227 especially at altitudes above 750 km. This is due to the superimposed signal
 228 of polycyclic aromatic hydrocarbons (PAHs) that have been identified and
 229 studied by Dinelli et al. (2013) and López-Puertas et al. (2013). At altitudes
 230 below 500 km, a continuum like signal due to the aerosol scattering of the
 231 sunlight strongly affects the baseline of the spectra.

232 Figure 2 shows the non-LTE nature of the emission measured by VIMS. Mea-
 233 surements with a tangent altitude of about 600 km have been averaged in solar
 234 zenith angle bins, to show the dependence of the emission on the SZA. The
 235 maximum radiance corresponds to lower SZAs because the stronger solar ra-
 236 diation produces a larger excitation of the molecules. The dependence of the
 237 spectral intensity on the SZA is moderate up to $\sim 80^\circ$, and becomes more pro-
 238 nounced at the terminator (SZA=80–120°). At SZA $> 120^\circ$ the signal is very
 239 weak because of the lack of solar excitation.

240 Out of the complete VIMS dataset a set of 264 collections containing, on av-
 241 erage, about 10 limb sequences of spectra have been selected to study the
 242 latitudinal and seasonal variability of Titan’s upper atmosphere. The used
 243 VIMS data cubes along with their latitudinal coverage and other parameters
 244 are listed in Table 1. Also, the latitude coverage as a function of the year of
 245 the measurement is shown in Fig. 3. As discussed above, they were selected to
 246 satisfy the requirements of long integration time (larger than 600 s), phase an-
 247 gle lower than 90° , and an acceptable signal to noise ratio; i.e., with SZA $< 90^\circ$.
 248 Due to the requirement on the SZA, the coverage at the winter polar latitudes
 249 during the first period (2004–2009) is not optimal.

250 Figure 4 shows the latitudinal distribution of the selected collections as a func-

tion of SZA. The blue symbols are the measurements acquired from 2004 to 2009 (Northern winter) and the red symbols are for those acquired from 2010 to 2012 (early Northern spring). We can see that near the polar regions the SZA is systematically larger. This, in principle, should not pose any problem, since we are appropriately calculating the non-LTE populations at the measured SZA, but it is convenient to have it present in the discussion.

3 Non-LTE modeling

As already mentioned in Section 2, the three molecules under study (CH_4 , HCN and C_2H_2) show a non-LTE behavior. The excitation produced by the absorption of solar radiation is weakly thermalized by molecular collisions, which are infrequent due to the low density in these atmospheric regions, driving the populations of the relevant vibrational levels far away from equilibrium. The non-LTE models for CH_4 and HCN have already been published in García-Comas et al. (2011) and Adriani et al. (2011). Therefore, we only summarize below, in Sections 3.1 and 3.2, their main results. The non-LTE model for C_2H_2 , that has been specifically developed for this study, is thoroughly described in Section 3.3.

3.1 CH_4

The main bands responsible of the emission of CH_4 near $3.3\ \mu\text{m}$ in Titan's upper atmosphere are the $\nu_3 \rightarrow 0$ fundamental band, which dominates at all altitudes, and the hot band $\nu_3 + \nu_4 \rightarrow \nu_4$, which contributes significantly at lower altitudes. The main processes controlling their populations are the absorption of solar radiation in the $3.3\ \mu\text{m}$, $2.3\ \mu\text{m}$ and $1.7\ \mu\text{m}$ regions and the collisional relaxation. The vibrational temperatures, T_v , of these CH_4 levels have been calculated for the pressure-temperature and constituents abundances described

276 in Sec. 4 by using the non-LTE model detailed in García-Comas et al. (2011).
 277 Figure 5 shows an example of the vibrational temperatures calculated for the
 278 pressure-temperature profile of the equatorial latitude, a SZA of 30° , and the
 279 Sun-Titan distance of 2006. The ν_3 level is in LTE up to about 400 km, where it
 280 gradually starts departing from the collisional equilibrium in the 400-800 km
 281 region. From 800 km upwards, the vibrational temperature is very close to
 282 266 K. Higher energy levels, containing one ν_3 quanta and one or two ν_2 or
 283 ν_4 quanta, or the second excited ν_3 level, are out of equilibrium in the whole
 284 atmosphere, being their vibrational temperatures fairly constant above about
 285 800 km and decreasing almost linearly below. The CH_4 vibrational tempera-
 286 tures depend very much on the SZA (see, e.g., Fig. 4 in García-Comas et al.,
 287 2011). Thus, they have been computed in the inversion of the limb sequence
 288 of spectra by using the actual SZA.

289 García-Comas et al. (2011) estimated the systematic errors affecting the CH_4
 290 vibrational temperatures. The largest errors arise from the uncertainty in the
 291 non-LTE parameters and the uncertainties in the assumed pressure tempera-
 292 ture profile. These lead to vibrational temperature errors in the ν_3 and $\nu_3 + \nu_4$
 293 levels of up to 8 K and 5 K for the former uncertainties, and 5 K and 2 K for
 294 the latter, respectively. These translate into retrieved CH_4 overall errors of
 295 60% at 650 km, 25% at 850 km and 7% at 1050 km.

296 3.2 *HCN*

297 The main HCN band emitting at $3\ \mu\text{m}$ is the fundamental $\nu_3 \rightarrow 0$, with the
 298 hot bands $2\nu_3 \rightarrow \nu_3$ and $\nu_2 + \nu_3 \rightarrow \nu_2$ contributing to some extent at lower
 299 altitudes. The absorption of solar radiation in the ν_3 fundamental and hot
 300 bands of HCN, as well as in the higher energy overtone ($2\nu_3$) and combination
 301 bands ($\nu_2 + \nu_3$), constitute the main excitation for the population of these
 302 levels. The collisional relaxation with N_2 and the quasi-resonant energy trans-

303 fer from $\text{HCN}(\nu_3)$ to $\text{CH}_4(\nu_3)$ are the major de-activation processes (Adriani
304 et al., 2011).

305 The HCN vibrational temperatures used in the inversion have been calculated
306 for the pressure-temperature and constituents abundances discussed in Sec. 4
307 by using the non-LTE model described in Adriani et al. (2011). This model
308 has been slightly improved here. In particular, the radiative transfer in the
309 major HCN bands is now performed using the the lambda-iteration scheme
310 instead of the Curtis Matrix (Funke et al., 2012). This leads to a reduction
311 in the T_v of the $\text{HCN}(001)$ level of 1.5 K above ~ 400 km. We also included
312 the overlapping of HCN and C_2H_2 bands in the $3.0\ \mu\text{m}$ region (see Sec. 3.3
313 below), although we found that it is negligible for the HCN levels from the top
314 of the atmosphere down to ~ 100 km. Typical vibrational temperatures of the
315 HCN levels are shown in Fig. 6. The ν_3 level is in LTE up to ~ 450 km, then
316 its vibrational temperature steadily increases reaching a value of 232 K near
317 1000 km. The second excited, $2\nu_3$, is fully in non-LTE in the whole atmosphere
318 and its vibrational temperature reaches 314 K above 1000 km and declines
319 below, but it is always larger than the kinetic temperature.

320 The vibrational temperatures of the HCN ν_3 levels also depend largely on
321 SZA (see, e.g., Fig. 8 in Adriani et al., 2011). The effects can be as large as
322 20 K differences in the vibrational temperatures for large SZAs, and expand
323 over the whole region from 1000 km down to 200 km. This explains the large
324 variation of the radiance near $3.0\ \mu\text{m}$ shown in Fig. 2, and evidences that this
325 dependency has to be taken into account in the retrieval.

326 Adriani et al. (2011) already studied the major errors affecting the non-LTE
327 populations of the HCN vibrational levels. They found that the error in the re-
328 trieved HCN caused by the uncertainty in its VMR is about 10%. Adriani et al.
329 (2011) also found that the T_v 's changes due to likely pressure/temperature
330 profiles are negligible, less than 0.5 K above 400 km. Furthermore, they also

331 reported that the errors incurred in the retrieved HCN by the uncertainties in
332 the collisional parameters are $\sim 10\%$ at 600–800 km and $\sim 5\%$ above.

333 3.3 C_2H_2

334 C_2H_2 also contributes with a significant non-LTE emission in the $3.0\ \mu\text{m}$ re-
335 gion in Titan during daytime conditions. As for CH_4 and HCN, the absorp-
336 tion of solar radiation is the major excitation mechanism. Thus, in order to
337 retrieve the C_2H_2 concentration from this emission, it also requires the mod-
338 eling of the non-LTE populations of its emitting energy levels. Here we have
339 used the Generic RAdiative traNsfer AnD non-LTE population Algorithm
340 (GRANADA) (Funke et al., 2012) adapted to the Titan’s atmosphere as de-
341 scribed by Adriani et al. (2011) and García-Comas et al. (2011), to compute
342 C_2H_2 non-LTE populations. We included the coupled v_3 and $v_2 + v_4 + v_5$ en-
343 ergy levels and their corresponding bands arising from the ground vibrational
344 state. These two levels are nearly resonant with energies of 3294.8401 and
345 $3281.8999\ \text{cm}^{-1}$, respectively, and are the most important levels emitting in
346 the $3.0\ \mu\text{m}$ region. Both bands were considered with full radiative transfer and
347 using the lambda iteration option (Funke et al., 2012). This includes a line-by-
348 line calculation of the upwelling tropospheric flux given by the temperature
349 of the lower boundary (Titan’s surface) and the solar flux at the top of the
350 atmosphere. As these bands are partially overlapped with those of HCN, the
351 overlapping was taken into account when calculating the absorption of the
352 solar radiation.

353 The spectroscopic data for these bands were taken from the HITRAN 2008
354 compilation (Rothman et al., 2009). The solar flux in this spectral region
355 has been taken from the SOLAR2000 compilation (Tobiska et al., 2000) and
356 adapted to the appropriate Sun-Titan distance for the different years.

357 About the collisional processes, we have included thermal relaxation of both
 358 vibrational levels in collisions with N_2 . Häger et al. (1981) found that the v_3
 359 and $v_2+v_4+v_5$ coupled levels rapidly deactivate via the relaxation of the v_5 and
 360 v_2 levels at rates of $4.26 \pm 0.51 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ and $3.09 \pm 0.43 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, re-
 361 spectively. In our calculations we have taken a deactivation rate of $4 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$
 362 for each of the v_3 and $v_2+v_4+v_5$ levels. Note that the total deactivation rate
 363 of $v_2+v_4+v_5$ might be larger if we assume that the relaxation can take place
 364 simultaneously by the deactivation of the v_5 and v_2 modes. However, the v_3
 365 would have to re-arrange its v_3 vibrational mode to those of the $v_2+v_4+v_5$
 366 level (Häger et al., 1980). Hence, for this v_3 state, the relaxation might be
 367 slower. Moreover, these measurements were taken at room temperatures and
 368 hence values at the cold Titan temperatures might be smaller. According to
 369 the classical gas kinetic theory, the rate depends on the square root of temper-
 370 ature. Hence for the typical stratospheric Titan temperatures of 170 K, those
 371 rates could be smaller by a factor of ~ 0.75 . Taken into account these consid-
 372 erations we estimate errors of about $\pm 50\%$ in these rates. Their effects are
 373 shown below.

374 In the computation of the non-LTE populations of the C_2H_2 energy levels
 375 we used the pressure-temperature and constituents abundances described in
 376 Sec. 4. The vibrational temperatures of the C_2H_2 v_3 and $v_2+v_4+v_5$ levels are
 377 very similar. They are dominated by the solar pumping and are nearly constant
 378 with altitude down to ~ 500 km where the collisional deactivation in collisions
 379 with N_2 starts being important (see Figs. 7 and 8). As solar pumping is the
 380 major excitation of these levels, they show a large dependence on the solar
 381 illumination (see Fig. 7). As for HCN, this variation is very important, having
 382 a weaker dependence at small SZAs and increasing towards larger SZAs. This
 383 dependence is taken into account in the retrieval of C_2H_2 . The effects of the
 384 estimated uncertainties of the collisional deactivation rates on the vibrational
 385 temperature of $\text{C}_2\text{H}_2(v_3)$ are shown in Fig. 8. This uncertainty induces very

386 small errors on its vibrational temperatures above ~ 500 km. Since we retrieve
 387 C_2H_2 abundance only down to that altitude, the errors of C_2H_2 abundance
 388 due this uncertainty are then negligible.

389 In our previous studies of HCN and CH_4 (García-Comas et al., 2011; Adri-
 390 ani et al., 2011), we found that the vibrational temperatures of their levels
 391 significantly depend on their respective concentrations. This is due to the ra-
 392 diative transfer and exchange of photons between layers, once the molecules
 393 are excited by absorption of solar radiation. We have estimated the effect of
 394 the C_2H_2 abundance on the population of the v_3 level (see Fig. 9). The effects
 395 on the $v_2+v_4+v_5$ level is very similar. The major effects are larger vibrational
 396 temperatures below about 500 km for the smaller C_2H_2 abundances. Note that
 397 the differences in the concentrations at the upper altitudes, above ~ 800 km
 398 have very little effects. The changes in the populations in the region of in-
 399 terest, ~ 500 -1000 km, is small, only of 2–3 K. We should remark than a 2 K
 400 uncertainty in the $\text{C}_2\text{H}_2(v_3)$ T_v induces, at the most (i.e., under optically thin
 401 conditions), a change of only $\sim 10\%$ in the retrieved C_2H_2 concentration.

402 4 Retrieval

403 4.1 Method

404 To obtain the vertical distribution of the target molecules (CH_4 , HCN and
 405 C_2H_2) we have used the same retrieval method described in Adriani et al.
 406 (2011) and García-Comas et al. (2011). Here we briefly recall the major de-
 407 tails. The observations of each collection have been analysed simultaneously
 408 using the global fit method (Carlotti, 1988) with a Bayesian approach (opti-
 409 mal estimation). We fit the vertical profile of the VMR of the target species
 410 to the observations keeping the vibrational temperatures at the values esti-

411 mated with the non-LTE models described in the previous section. The fit
 412 is performed with an iterative procedure to minimize the cost function (χ^2)
 413 using the Levenberg-Marquardt algorithm (Levenberg, 1944). The iterations
 414 are stopped when the χ^2 (that is the square of the differences between the
 415 simulated and observed spectra weighted by the measurement noise) does not
 416 vary for more than 1%.

417 The spectra have been simulated with GBB (Adriani et al., 2011; García-
 418 Comas et al., 2011), a line-by-line radiative transfer code that takes into ac-
 419 count the emission and absorption processes along the line of sight of the
 420 instrument. The simulations include the non-LTE emissions of CH_4 , $^{13}\text{CH}_4$,
 421 HCN , and C_2H_2 . Despite the fact that their contributions are negligible, LTE
 422 emissions of C_2H_6 , C_2H_4 and CH_3D have been included in the simulations.
 423 The spectroscopic data have been taken from the HITRAN 2008 compilation
 424 (Rothman et al., 2009). For CH_4 , additional spectroscopic data relative to the
 425 $2\nu_3 \rightarrow \nu_3$, $\nu_3 + 2\nu_4 \rightarrow 2\nu_4$ and $\nu_2 + \nu_3 + \nu_4 \rightarrow \nu_2 + \nu_4$ bands (Boudon et al.,
 426 2003) have been added to the HITRAN 2008 line list. For HCN , the $2\nu_3 \rightarrow \nu_3$
 427 and $\nu_2 + \nu_3 \rightarrow \nu_2$ bands, which are not included in the HITRAN database,
 428 have also been taken into account (Harris et al., 2002). In order to properly
 429 model the narrow line shape at the low pressures of Titan’s upper atmosphere,
 430 the spectra have been simulated on a wavenumber grid of 0.0005 cm^{-1} .

431 The forward model assumes the atmosphere perfectly stratified, that is, homo-
 432 geneous in the horizontal direction of the plane that contains the instrument
 433 LOS and the vertical to Titan’s surface and vertically inhomogeneous. The
 434 atmosphere has been divided into layers of 20 km vertical extension. All the
 435 retrieved atmospheric quantities have then been referred to the average geolo-
 436 cation of the tangent points of the limb sequences and to the average SZA at
 437 the tangent points.

439 Since our aim is to study the seasonal variations in Titan’s mesosphere, we
 440 have accounted for the potential seasonal changes of all the variables fixed
 441 in the retrieval procedure. In the vibrational temperatures computation with
 442 the models described in section 3, we have used the correct Sun-Titan dis-
 443 tance at the time of each observation and a different pressure-temperature
 444 (p-T) profile for each latitude and year of the analysed limb sequences. The
 445 kinetic temperatures have been taken from the co-located temperature pro-
 446 files measured by CIRS (Achterberg et al., 2011, 2008) and extended upwards
 447 with the temperature profile used in our previous studies (see, García-Comas
 448 et al., 2011; Adriani et al., 2011). This results in an invariant temperature field
 449 above 700 km both in latitude and time of the measurements. We know from
 450 the measurements of HASI (Fulchignoni et al., 2005) that the mesospheric
 451 temperature is affected by strong altitude variations due to gravity waves
 452 (Lorenz et al., 2014). However, so far there are no reliable models for the tem-
 453 perature variations in this altitude range. The model of Müller-Wodarg et al.
 454 (2008) predicted a latitude/altitude variation of temperature of the order of
 455 1 K, much smaller than the amplitude of the gravity waves. On the other hand,
 456 the vibrational temperatures of the considered molecules in this altitude range
 457 deviates so much from the kinetic temperature that they very weakly depend
 458 on the latter. Computed vibrational temperatures with the expected different
 459 kinetic temperature profiles have negligible differences for HCN and C₂H₂ and
 460 rather small for CH₄ (see Sec. 3). Therefore, we may safely assume that our
 461 results have a weak dependence from the kinetic temperature above ~600 km,
 462 and we can assume it as constant on average. Pressures, however, have been
 463 calculated consistently assuming hydrostatic equilibrium and using the CIRS
 464 temperatures along the whole altitude range from very close to the surface
 465 (lower CIRS limit for temperature measurements) up to the uppermost al-
 466 titude in our calculations. These pressure-temperature profiles together with

the corresponding SZA have been injected into the non-LTE models described in Sec. 3.3 to obtain the vibrational temperatures for each of the analysed collections. Subsequently, these vibrational temperatures have also been used together with the corresponding p-T profile in the inversion of the measured spectra.

For each collection two separate inversions were performed: one for the 2900–3100 nm region, where HCN and C₂H₂ were simultaneously retrieved, and another for the 3200–3500 nm region, where the methane abundance was retrieved using the signal from its Q and P branches. The spectral region corresponding to CH₄ R branch ($\lambda < 3290$ nm) has been masked out because of the interfering signal of PAHs identified by Dinelli et al. (2013) and assigned by López-Puertas et al. (2013). For each molecule, the retrieved quantity was a vertical profile of the VMR, discretized with a piecewise linear curve on a vertical grid at 100 km steps. The vertical range of the retrieval of CH₄ was from 450 km to 1050 km. For HCN and C₂H₂, because of the contamination of the lowermost spectra by scattered sunlight, the inversion was performed in the 550–1050 km range. Despite the latest VIMS calibration pipeline takes into account a time dependent drift of the wavelength of each spectral channel, we have fitted, along with the VMR retrieval, a frequency shift to all the spectra in each limb sequence. Separate values were retrieved for each of the two spectral regions. A posterior checks showed that both spectral regions produce consistent frequency shifts.

The use of a Bayesian approach implies the use of a-priori knowledge of the retrieved quantities, that is, the a-priori profile of each VMR and its error. For the whole analysis we have used the same a-priori values and errors. For C₂H₂ and HCN we have used as a-priori the VMR reported by Koskinen et al. (2011), which was derived from the analysis of UVIS observations in 2008. For CH₄ we have used the profile reported in García-Comas et al. (2011). The a-priori errors for all the three molecules were set to 100% of the a-priori

profile plus a constant value of 300, 100, and 1.5×10^4 ppmv for HCN, C_2H_2 and CH_4 , respectively, in order to avoid the too strong constraint that results from the small a-priori values at certain altitudes. The quality of the retrieved VMR values has been assessed through the individual information gain, the quantity q_j described in Adriani et al. (2011), that measures the improvement produced by the measurement to the a-priori.

5 Results

The average VMR profiles for HCN and CH_4 from the analysis of their non-LTE emission in VIMS spectra acquired during Titan's encounters TA, T34 and T35 (19 July and 31 August 2007) have been published in previous works (Adriani et al., 2011; García-Comas et al., 2011). The value found for HCN concentration for those encounters was not in agreement with the average value of Cui et al. (2016). They report an HCN density of $8 \times 10^6 \text{ cm}^{-3}$ derived from INMS measurements at 1000 km for the T41 flyby, in agreement with what reported by Koskinen et al. (2011). For the same flyby we now find at 1050 km an average value of $8.2 \times 10^6 \text{ cm}^{-3}$ with a standard deviation of the mean of $5 \times 10^6 \text{ cm}^{-3}$. Considering that the vertical resolution of our retrievals is about the same as the vertical retrieval step (100 km), we may consider our data in agreement with Cui et al. (2016).

Despite in Adriani et al. (2011) the VMR of C_2H_2 was retrieved simultaneously with HCN, this was done only to account for the spectral shape of the emission, without a non-LTE model. Therefore, this is the first time that we retrieve C_2H_2 VMR in Titan's mesosphere by using an accurate non-LTE model (see Sec. 3.3). In Figure 10 we report the average C_2H_2 VMR profile obtained from the analysis of the spectra acquired during the same encounters analysed by Adriani et al. (2011). The error bars reported in the figure are the standard deviation of the mean. The profile is compared to the values obtained by

523 Koskinen et al. (2011) at the same altitudes. While our retrieved VMRs are in
524 agreement (within our error bar) with their results from 550 km to 850 km, we
525 find higher VMRs above 900 km. Indeed, when using the values of Koskinen
526 et al. (2011) for both HCN and C₂H₂ in our simulations, the modeled spectral
527 signature was always lower than the VIMS measured signal.

528 The retrieved CH₄, HCN and C₂H₂ VMR profiles for the 264 collections have
529 been averaged in 20° latitudinal bins from pole to pole, and have been divided
530 into two periods: 2004 to 2009 (or Northern winter) and 2010 to 2012 (or
531 early Northern spring). Only data with information gain higher than 0.5 (that
532 implies that the a-priori error has been improved by a factor of 2) have been
533 included in the averages. The latitude-altitude maps for the retrieved HCN,
534 C₂H₂ and CH₄ are shown in Figures 11, 12, and 13, respectively. Left and
535 right panels represent, respectively, the average VMR maps in the Northern
536 winter season and early spring.

537 The inversion program retrieves VMRs even if in the radiative transfer calcula-
538 tion the VMR is translated into number density through the assumed pressure
539 and temperature profiles. Hence, one can then argue that the results should be
540 represented as maps of number densities instead of VMR. However, plotting
541 the results in VMRs enables an easier interpretation of their distributions in
542 terms of the meridional circulation and the seasonal effects. Systematic errors
543 due to the imperfect knowledge of the vibrational temperatures of the con-
544 sidered gases affect all the retrieved profiles in the same way, therefore our
545 conclusions on seasonality and latitudinal dependence should not be affected
546 by them.

547 The interpretation of the results is difficult due to the high variability of
548 the retrieved profiles caused by the measurement noise (we use weak signals)
549 and the rather poor coverage in key polar regions. We first comment the
550 major features in the figures and then consider the significance of the observed

551 patterns on the basis of the variability and coverage.

552 5.1 HCN

553 The top panel of Figure 11 (northern winter) shows a positive gradient in
554 the HCN VMR towards the North pole at altitudes above ~ 650 km. We also
555 notice a minimum around the Equator, slightly shifted toward the southern
556 hemisphere at altitudes from 550 to 650 km. The polar enrichment suggests
557 that the middle atmosphere circulation, which drives the observed polar en-
558 hancement of HCN below 500 km (Vinatier et al., 2015; Teanby et al., 2008,
559 2009, 2012), extends up to higher altitudes. This is further suggested by the
560 behavior of the HCN VMR during the northern spring (bottom panel), which
561 shows an almost symmetrical pattern with a pronounced enhancement at both
562 the north and south poles up to 800 km. This can be interpreted as a signature
563 of the reversal of the circulation, with subsidence starting in the southern po-
564 lar upper mesosphere and lower thermosphere and still with a residual winter
565 enrichment in the northern polar region.

566 5.2 C_2H_2

567 The bottom panel of Figure 12 shows strong enhancements at both poles up
568 to ~ 800 km for C_2H_2 during the northern spring. On the other hand, the
569 northern winter map (top panel) shows no clear latitudinal variations. This is
570 in contrast to the pattern exhibited by the HCN field. A pattern similar to
571 that of HCN in both seasons would have strengthened the suggestion of the
572 meridional circulation being extended up to higher altitudes. Nevertheless,
573 it worth to note that Vinatier et al. (2015) also observed differences in the
574 response of these two molecules to the subsidence and enrichment processes.

576 The pattern for CH_4 below ~ 750 km is different to the of HCN and C_2H_2 ones.
 577 No significant latitudinal gradient is seen below ~ 750 km in both winter and
 578 spring (see Fig. 13). This is in agreement with the photochemical models,
 579 since CH_4 is expected to be well mixed up to its homopause that is situated
 580 at ~ 800 km (Koskinen et al., 2011). At altitudes above 800 km we see an
 581 enhancement at the northern winter polar region and a weaker enhancement
 582 at both poles during spring. This behavior is compatible with a summer-to-
 583 winter meridional circulation at altitudes above 800 km, with an increase in the
 584 polar winter region. Seemingly, when spring begins, we see a residual maximum
 585 in the North due to the winter circulation and the start of the enhancement
 586 in the other polar region (South), due to the reversal of the circulation.

587 6 Discussion

588 Figure 14 shows the number of retrieved profiles (top panel) and the average
 589 SZA of the retrieved profiles (bottom panel) for all latitudinal bins and for
 590 the two seasons. As shown in the top panel, the used dataset has a poor
 591 coverage at the north pole during the winter season (only one profile above
 592 $70^\circ N$ and 3 between $50^\circ N$ and $70^\circ N$) and a sparse coverage at the south pole
 593 during spring (only 2 collections south of $70^\circ S$ and 3 between $50^\circ S$ and $70^\circ S$).
 594 Moreover, those regions have the largest SZA, close to 90° (see bottom panel of
 595 Fig. 14). The limited coverage is a direct consequence of the observed seasons
 596 and the use of Non-LTE emissions, present only in sun lit observations

597 Below we will discuss the results in two different regions: the upper mesosphere
 598 and lower thermosphere (UMLT, 450–800 km) and the thermosphere (800–
 599 1100 km). The lower region, from 450 km up to the CH_4 homopause situated

600 near 800 km, is most probably influenced by the global circulation observed
 601 below 450 km (Achterberg et al., 2008, 2011; Vinatier et al., 2015). We have
 602 compared the retrieved HCN and C₂H₂ VMRs at the lowest altitude, 550 km,
 603 with the results of Vinatier et al. (2015) obtained at their highest altitude
 604 (500 km) (see Figs. 8 to 13 in Vinatier et al. (2015)). Both datasets generally
 605 agree within 2σ for all different latitudes. Some significant differences can be
 606 observed at high northern latitudes during the spring season for HCN, being
 607 our values significantly larger (see Fig. 13 in Vinatier et al., 2015). However,
 608 CIRS values show a strong variability in this region and season, with the
 609 2010 and 2011 HCN profiles differing by almost one order of magnitude at
 610 this altitude. We should also note that our retrieved quantities have a vertical
 611 resolution of about ~ 100 km (the vertical step of our retrieval grid), that is, our
 612 values at 550 km are representative for the 500–600 km region. This, together
 613 with the fact that HCN and C₂H₂ increase with altitude, systematically
 614 produces larger VMR values at 550 km than the ones at 500 km.

615 Teanby et al. (2012) suggested that, in order to explain the observed enhance-
 616 ments in trace gases and the adiabatic heating in the polar mesosphere, the top
 617 of the middle atmosphere circulation should extend up to 600 km or higher.
 618 Our data suggests an extension of the middle atmospheric cell up to 750–
 619 800 km, or even higher if we assume that the CH₄ abundance above 800 km is
 620 mainly controlled by the meridional circulation. Figure 15 shows the latitudi-
 621 nal variation of HCN and C₂H₂ VMRs at 550 km. The error bars are the
 622 standard error of the mean, except for the north pole during winter (80°N)
 623 where it represents the retrieval error (only one measurement is available). The
 624 observed latitudinal gradient of HCN is significant in the spring season; we also
 625 see an enhancement at the north in winter, although the large error affecting
 626 the peak makes our results also consistent with a non-enhancement. C₂H₂ also
 627 shows an enhancement in the polar regions during the spring season, though
 628 not as large as HCN. However, we do not find a significant enhancement in

629 the polar winter.

630 Teanby et al. (2012) suggested that, in order to explain the observed enhance-
631 ments in trace gases and the adiabatic heating in the polar mesosphere, the top
632 of the middle atmosphere circulation should extend up to 600 km or higher.
633 Our results, especially the behaviour of HCN and C₂H₂ in spring, suggest an
634 extension of the middle atmospheric cell up to 750–800 km, or even higher if
635 we attribute the CH₄ abundance above 800 km to the same circulation. The
636 HCN latitudinal distribution in winter supports this conclusion. However, the
637 behaviour of C₂H₂ in winter does not confirm this result, in agreement with
638 Vinatier et al. (2015) that found different behaviour of HCN and C₂H₂ in this
639 altitude region. However, a larger statistics would be needed to support our
640 conclusion, especially at the northern polar and sub-polar latitudes during
641 winter and for the southern polar and sub-polar during spring.

642 INMS has shown that the upper thermosphere, above 950 km, is highly vari-
643 able (Snowden et al., 2013; Yelle et al., 2014). This then hampers the de-
644 tection of latitudinal and seasonal variations. Yelle et al. (2006) and Müller-
645 Wodarg et al. (2008) developed an empirical model for analyzing a first set
646 of INMS measurements acquired before 2007 and found some latitudinal pat-
647 terns in Titan’s upper atmosphere. In particular, their model predicted strong
648 meridional winds in the winter thermosphere and a pronounced oblateness of
649 the atmosphere (with lower pressures at the poles for a given altitude) that
650 would produce an accumulation of CH₄ at the winter pole (Müller-Wodarg
651 et al., 2008). Figure 16 shows the latitudinal distribution of the CH₄ VMR
652 at 1050 km, with the errors calculated as for HCN and C₂H₂ in Figure 15.
653 The positive gradient of the CH₄ VMR towards the North pole during winter
654 is significant, despite the low statistics. The CH₄ spring distribution shows a
655 residual enhancement at the northern sub-polar latitudes (at the 1 σ level) and
656 a larger enhancement at the South pole (experiencing autumn) close to the
657 2 σ level. The enhancement at the poles due to winter/autumn conditions is in

658 line with the prediction of the empirical model of Müller-Wodarg et al. (2008).
 659 However, the analysis of Müller-Wodarg et al. (2008) has been questioned by
 660 a subsequent reanalysis of a more complete INMS dataset by Snowden et al.
 661 (2013), who found no clear correlation of their retrieved temperatures with
 662 latitude or SZA. They pointed out that the most remarkable feature observed
 663 is an extreme variability of the thermospheric environment, which is thought
 664 to be due to gravity waves propagating from below. However, VIMS measure-
 665 ments contain information at different locations along the instrument line of
 666 sight, possibly smoothing the effect of gravity waves, while INMS data were
 667 collected *in situ* and therefore reflect the local composition of the atmosphere.
 668 The CH₄ enhancement that we observe at the winter pole might also be caused
 669 by the larger SZA (fainter illumination) of the winter/autumn polar region.
 670 This would be in line with the model of Westlake et al. (2014) that predicts
 671 larger CH₄ abundances for smaller EUV (Extreme UltraViolet) fluxes, due to
 672 diminished photo-dissociation of CH₄.

673 **7 Conclusions**

674 VIMS measurements of daytime non-LTE emissions from CH₄, HCN and C₂H₂
 675 in the 2900–3500 nm spectral region represent a unique dataset to study Ti-
 676 tan’s upper atmosphere in the altitude region from 500 to 1000 km. This region
 677 is the key to a better understanding of the middle atmosphere circulation, and
 678 the assessment of the latitudinal and seasonal variations in the distributions
 679 of HCN and C₂H₂ could give important hints about it and complement to
 680 CIRS observations taken below 500 km. The inversion of CH₄ and HCN at the
 681 highest altitudes can also help in understanding of the complex environment
 682 observed by INMS above 1000 km.

683 To study the seasonal effects, we have selected 264 collections (limb sequences
 684 of spectra) measured by VIMS from 2004 to 2012. Non-LTE vibrational tem-

685 peratures for CH_4 , HCN and C_2H_2 have been calculated in Titan's atmo-
 686 sphere. These temperatures have been used in the inversion of the non-LTE
 687 emission to determine the vertical distribution of the CH_4 , HCN and C_2H_2
 688 abundances in the altitude region from 500 to 1100 km. This is the first time
 689 C_2H_2 has been retrieved from VIMS measurements. Our C_2H_2 average profile
 690 shows good agreement with the data reported by Koskinen et al. (2011) below
 691 850 km, while they are higher above that altitude. The VMR profiles inverted
 692 for the three molecules for the whole period have been averaged in latitudinal
 693 bins of 20° and divided into two seasons: Northern winter (2004-2009) and
 694 early Northern spring (2010-2012).

695 The HCN VMRs show an enhancement at the North pole during the winter
 696 at all altitudes, from ~ 700 km up to near 1000 km, and at both the North and
 697 South poles during spring below 900 km. Also the average C_2H_2 abundance is
 698 larger at both poles during spring below 800 km, while no significant variation
 699 is seen for C_2H_2 during winter. For CH_4 we found enhancements above 800 km
 700 at the North pole during winter and at both poles during spring. Our results
 701 support the hypothesis of Teanby et al. (2012) who suggested that the middle
 702 atmosphere circulation extends above the 500 km level. Actually, our data sug-
 703 gest that it extends higher, up to 750-800 km or even higher if we assume that
 704 the CH_4 concentration above 800 km is mainly controlled by the meridional
 705 circulation. This has strong implications in the development of Titan's upper
 706 atmosphere circulation models.

707 The CH_4 behavior that we have observed above 800 km at the winter pole
 708 is in line with the empirical model of Müller-Wodarg et al. (2008), although
 709 that model has been questioned by Snowden et al. (2013). On the other hand,
 710 the observed CH_4 enhancement at the winter pole could also be explained by
 711 the reduction of its photo-dissociation due to lower insolation, as shown by
 712 Westlake et al. (2014).

713 Despite our results suffer for a poor statistic at the polar regions due to the use
714 of Non-LTE emissions, they represent a unique dataset for the study of Titan’s
715 atmosphere above 500 km and could help to improve our understanding of
716 Titan’s upper atmosphere.

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Table 1

List of VIMS cubes used in the analysis. For each cube, its name, the year of the measurement, the mean phase angle (Pha), the average distance of Cassini from Titan and the covered latitude range are listed.

#	Cube	Day-Month-Year	Pha (deg)	Cassini-Titan distance (km)	Lat. range
1	V1477459118	26-10-2004	13	208873	70 S - 40 N
2	V1490948671	31-03-2005	57	241450	80 S - 30 N
3	V1490955139	31-03-2005	57	204450	80 S - 40 N
4	V1530471051	21-07-2006	61	293660	80 S - 70 N
5	V1536397418	07-09-2006	63	257313	70 S - 40 N
6	V1563524168	19-07-2007	60	139000	85 S - 60 S
7	V1563524658	19-07-2007	60	139000	80 S - 55 S
8	V1563525149	19-07-2007	26	139000	70 S - 45 S
9	V1567269485	31-08-2007	26	211820	80 S - 0
10	V1582444145	22-02-2008	66	292796	60 S - 40 N
11	V1590707892	28-05-2008	89	305130	50 S - 30 N
12	V1590616570	28-05-2008	95	228692	50 S - 50 N
13	V1612658738	07-02-2009	70	178137	0 - 40 N
14	V1612664166	07-02-2009	70	146537	0 - 40 N
15	V1649210753	05-04-2010	15	194294	60 S - 60 N
16	V1649227483	05-04-2010	18	287621	50 S - 60 N
17	V1654449711	05-06-2010	31	283383	50 S - 80 N
18	V1676803273	18-02-2011	31	364049	70 S - 60 N
19	V1681937300	19-04-2011	16	299460	50 S - 80 N
20	V1704257066	02-01-2012	58	256027	70 S - 60 N
21	V1706671551	30-01-2012	22	258713	20 S - 80 N

Figure 1. Average spectra acquired by VIMS at SZA lower than 40° and different tangent altitudes. The colours indicate the different tangent altitudes as shown in the figure.

Figure 2. Mean spectra acquired by VIMS at 600 km tangent altitude for different SZAs. The colors indicate the different values of the SZA as shown in the figure.

Figure 3. Distribution of the latitudinal coverage of the analysed VIMS measurements as a function of the year of acquisition.

Figure 4. Distribution of the analysed VIMS measurements versus SZA and latitude at a tangent height of 750 km. The blue color indicates the measurements acquired in the time span 2004-2009 while the red color indicates the 2010-2012 measurements.

Figure 5. Vibrational temperatures of the CH_4 ν_3 vibrational levels, the major contributor to the radiance emitted in the $3\text{ }\mu\text{m}$ region. The calculations are shown for the equatorial latitude, at a SZA of 30° , and using the Sun-Titan distance of 2006. The kinetic temperature, T_k , is also shown and serves as a guidance of the high populations of the levels.

Figure 6. Vibrational temperatures for the ν_3 and higher energy levels (containing ν_3 quanta) of HCN. The kinetic temperature, T_k , is also shown.

Figure 7. Vibrational temperatures for the $\text{C}_2\text{H}_2(v_3)$ level as function of SZA. The kinetic temperature, T_k , is also shown.

Figure 8. The effects of the collisional relaxation uncertainties on the vibrational temperature of the $\text{C}_2\text{H}_2(v_3)$ level. The kinetic temperature, T_k , is also shown.

Figure 9. The effects of the C_2H_2 concentration on the vibrational temperature of the $C_2H_2(v_3)$ level. Upper panel: concentrations of C_2H_2 . Bottom panel: vibrational temperatures of the $C_2H_2 v_3$ level. The kinetic temperature, T_k , is also shown.

Figure 10. Average C_2H_2 VMR profile for T34 and T35 encounters. The red line shows our results with the associated error bars in green. The blue dots are the values reported by Koskinen et al. (2011).

Figure 11. Latitude-altitude maps of the retrieved HCN VMR abundance. Top panel refers to the northern winter, bottom panel to northern early spring.

Figure 12. Latitude-altitude maps of the retrieved C_2H_2 VMR abundance. Top panel refers to the northern winter and bottom panel to northern early spring.

Figure 13. Latitude-altitude maps of the retrieved CH₄ VMR abundance. Top panel refers to the northern winter, bottom panel to early spring.

Figure 14. Number of retrieved profiles for the two seasons (top panel) and mean SZA of the observations (bottom panel) for each latitudinal bin.

Figure 15. Average retrieved VMR at 550 km in each latitudinal bin for HCN (top) and C₂H₂ (bottom). Negative latitudes refer to the southern hemisphere. The error bars represent the standard error, except for the point at +80° in the winter, where it represents the retrieval error.

Figure 16. Average retrieved VMR at 1050 km in each latitudinal bin for CH₄. The error bars represent the standard error, except for the point at +80° in the winter season, where it represents the retrieval error.