



# The 3 . 4 $\mu$ m absorption in Titan's stratosphere: Contribution of ethane, propane, butane and complex hydrogenated organics

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- A strong and unexplained absorption at  $3.4\text{ }\mu\text{m}$  in Titan's atmosphere has been revealed by solar occultations by the instrument CASSINI/VIMS
- Several simple molecules (like  $\text{CH}_4$  or  $\text{C}_2\text{H}_6$ ) absorb in this region but their effect is not efficient enough to account for observations
- We show that Polycyclic Aromatic Hydrocarbon (PAH) or Hydrogenated Amorphous Carbons (HAC) could be introduced to reproduce this band

# The 3.4 $\mu\text{m}$ absorption of the Titan's stratosphere: contribution of ethane, propane, butane and complex hydrogenated organics

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## Abstract

The complex organic chemistry harbored by the atmosphere of Titan has been investigated in depth by Cassini observations. Among them, a series of solar occultations performed by the VIMS instrument throughout the 13 years of Cassini revealed a strong absorption centered at  $\sim 3.4 \mu\text{m}$ . Several molecules present in Titan's atmosphere create spectral features in that wavelength region, but their individual contributions are difficult to disentangle. In this work, we quantify the contribution of the various molecular species to the 3.4  $\mu\text{m}$  band using a radiative transfer model. Ethane and propane are a significant component of the band but they are not enough to fit the shape perfectly, then we need something else. Polycyclic Aromatic Hydrocarbons (PAHs) and more complex polyaromatic hydrocarbons like Hydrogenated

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Amorphous Carbons (HACs) are the most plausible candidates because they are rich in C-H bonds. PAHs signature have already been detected above  $\sim 900$  km, and they are recognized as aerosols particles precursors. High similarities between individual spectra impede abundances determinations.

*Keywords:* planets and satellites: individual: Titan – planets and satellites: general – solar system: general

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## 1. Introduction

Titan is an extraordinary object among the planets and satellites of the solar system. Its thick atmosphere, mainly composed of nitrogen and methane, harbors a complex photochemistry producing organic compounds that participate to the formation of haze which produces its typical orange/brown color. Due to its unique and exotic properties, Titan's atmosphere remains a very active field of research in investigating the possible origin and main properties (Johnson *et al.*, 2016; Charnay *et al.*, 2014; Newman *et al.*, 2016). Its composition can be modeled by complex chemical network (Krasnopolsky, 2014; Lavvas *et al.*, 2015), but also by laboratory experiments (Bourgalais *et al.*, 2016; Romanzin *et al.*, 2016) to match the observations made by Cassini's instruments (Vinatier *et al.*, 2015; Coustenis *et al.*, 2016; Bellucci *et al.*, 2009). In Bellucci *et al.* (2009), the authors raised an issue about the CH<sub>4</sub> 3.3  $\mu\text{m}$  band.

In 2006, during Cassini's 10<sup>th</sup> flyby of Titan (T10), Bellucci *et al.* (2009) observed features in CH<sub>4</sub> 3.3  $\mu\text{m}$  band with the Visible and Infrared Mapping Spectrometer (VIMS). VIMS is an imaging spectrometer onboard the Cassini spacecraft. This instrument is composed of a visible channel (0.3 – 1.05  $\mu\text{m}$ ) and an infrared channel (0.89 – 5.1  $\mu\text{m}$ ). The FWHM of the 256 infrared spectral pixels are in the range 13 - 20 nm. VIMS can be used in different observation modes corresponding to nadir, limb and occultation geometry. Our study uses the latter mode. More details can be found in Maltagliati *et al.* (2015). Bellucci *et al.* (2009) tentatively attributed the observed features in CH<sub>4</sub> 3.3  $\mu\text{m}$  band to solid state organic compounds, similar to those observed in the InterStellar Medium (ISM) (Sandford *et al.*, 1991; Pendleton

26 & Allamandola, 2002). However, this interpretation was far to be firm and  
 27 Bellucci *et al.* (2009) concluded that precise comparison of their data with  
 28 laboratory spectrum needed in future work.

29 Interestingly, a similar feature had been observed by VIMS during a stellar  
 30 occultations in Saturn’s atmosphere (Nicholson *et al.*, 2006; Kim *et al.*, 2012).  
 31 Continued by Kim *et al.* (2012), these analysis shown that the optical-depth  
 32 spectra exhibit a broad peak at 3.36-3.41  $\mu\text{m}$  for the observations obtained  
 33 at 12 pressure levels between 0.0150 and 0.0018 mbar in the Saturnian at-  
 34 mosphere. Kim *et al.* (2012), in particular, attributed these 3.4  $\mu\text{m}$  spectral  
 35 features to the aliphatic C–H stretching bands of solid-state hydrocarbons,  
 36 such as  $\text{C}_5\text{H}_{12}$ ,  $\text{C}_6\text{H}_{12}$ ,  $\text{C}_6\text{H}_{14}$  and  $\text{C}_7\text{H}_{14}$ . Kim *et al.* (2011) reached a similar  
 37 conclusion for Titan in analyzing the occultation T10. However, the forma-  
 38 tion of such organic microcrystals in the atmosphere of Titan is questionable  
 39 due to thermodynamic arguments (see Sec. 2).

40 More recently, Maltagliati *et al.* (2015) analyzed an extended set of four  
 41 VIMS solar occultations, performed between January 2006 and September  
 42 2011. In Fig. 1, we reporte an example of transmission data derived from  
 43 Maltagliati *et al.* (2015). Spectra have been normalized by a 3<sup>th</sup> order poly-  
 44 nomial and data have been interpolated at the altitude of 145 km to allow  
 45 easy comparisons. This value offers a good compromise: at lower altitudes,  
 46 the stronger absorptions damp spectral features and at higher altitudes, the  
 47 absorptions are weak and the spectra are more noisy due to a weaker signal.  
 48 Deviations between the four curves plotted in Fig. 1 give an idea of transmit-  
 49 tance uncertainties, and spatial or temporal variations in Titan’s atmosphere.

50

Table 1: Triple points coordinates for the sample of hydrocarbon species considered by Kim *et al.* (2011). The temperatures have all been taken in the NIST database<sup>†</sup>, for CH<sub>3</sub>CN, C<sub>5</sub>H<sub>12</sub> and C<sub>6</sub>H<sub>12</sub>. The pressures are not available in this database, we then estimated their values by using their Antoine’s equation at the triple point temperature.

Species	Chemical formula	$T_{\text{triple}}$ (in K)	$P_{\text{triple}}$ (in bar)
Ethane	C <sub>2</sub> H <sub>6</sub>	91.0	$1.1 \times 10^{-5}$
Methane	CH <sub>4</sub>	90.7	$1.2 \times 10^{-1}$
Methylcyanide	CH <sub>3</sub> CN	229.3	$2.2 \times 10^{-3}$ *
Pentane	C <sub>5</sub> H <sub>12</sub>	143.5	$3.9 \times 10^{-7}$ *
Cyclohexane	C <sub>6</sub> H <sub>12</sub>	279.7	$5.3 \times 10^{-2}$ *

<sup>†</sup><http://webbook.nist.gov/chemistry/>

\* Our estimation

51 In their line-by-line radiative transfer model, Maltagliati *et al.* (2015)  
 52 took into account the absorption caused by 9 molecules : CH<sub>4</sub> , CH<sub>3</sub>D, CO,  
 53 CO<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, HCN and N<sub>2</sub>. In spite of the level of sophistica-  
 54 tion of their approach, Maltagliati *et al.* (2015) found a clear disagreement  
 55 between the observed absorption in the 3.4  $\mu\text{m}$  band and their computed  
 56 spectra. It appears then that the atmosphere of Titan is a more efficient  
 57 absorber than in this model. By comparing the observed residual absorption  
 58 and the ethane cross sections measured by the Pacific Northwest National  
 59 Lab (PNNL - Sharpe *et al.*, 2004), and given the lack of C<sub>2</sub>H<sub>6</sub> spectral lines  
 60 in major databases (HITRAN and GEISA), Maltagliati *et al.* (2015) inter-  
 61 preted the strong absorption band centered at 3.4  $\mu\text{m}$  as the effect of ethane.  
 62 These authors also tentatively attribute the narrow absorption at 3.28  $\mu\text{m}$

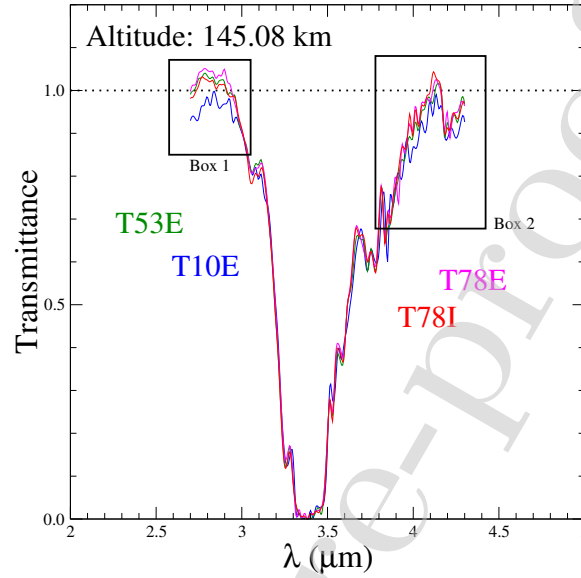


Figure 1: Transmittance curves derived from solar occultations T10E, T53E, T78E and T78I studied by [Maltagliati et al. \(2015\)](#). Altitude interpolations, at 145 km, have been performed to allow easy comparisons. Boxes delineate domains where data are significantly noisy.

63 to the presence of Polycyclic Aromatic Hydrocarbons (PAHs) in the strato-  
 64 sphere. Indeed, a few years before, [López-Puertas et al. \(2013\)](#) identified the  
 65 presence of these aromatic molecules in Titan's upper atmosphere around  
 66 650 km up to  $\sim 1300$  km. Their results rely on the emission near  $3.28 \mu\text{m}$   
 67 detected by VIMS.

68  
 69 It is well accepted that a strong absorption at  $3.2 - 3.5 \mu\text{m}$  is related to  
 70 the C-H stretching bands, but the C-H bonds can be present in icy hydro-  
 71 carbons, in simple molecules, in more complex polyaromatic hydrocarbons



or in aerosols particles. In this paper, we try to disentangle the problematic attribution of this strong absorption around  $3.4\ \mu\text{m}$ . In Fig 1, transmittances corresponding to box 1 and box 2 are clearly too noisy to allow a clear analysis. In this work, we specifically focus our efforts on the highest absorption spectral range, *i.e.* between  $3.3$  and  $3.5\ \mu\text{m}$ . In Sec. 2 we examine, in the light of an advanced thermodynamic model, the possibility of the existence of hydrocarbon ices in the stratosphere of Titan, as proposed by Kim *et al.* (2011). In Sec. 3 and 4 we revisit the absorption of gases in the  $3.4\ \mu\text{m}$  spectral region while in Sec. 5 we discuss the possible presence of PAHs or more complex polyaromatic hydrocarbons like Hydrogenated Amorphous Carbons (HACs). In Sec. 6, we further discuss these issues and present our conclusions.

## 2. Solid-Vapor equilibria in Titan's stratosphere

An explanation for the nature of Titan's  $3.4\ \mu\text{m}$  absorption was put forward by Kim *et al.* (2011) who could reproduce the VIMS solar occultations by using hydrocarbon ices like  $\text{C}_2\text{H}_6$ ,  $\text{CH}_4$ ,  $\text{CH}_3\text{CN}$ ,  $\text{C}_5\text{H}_{12}$  and  $\text{C}_6\text{H}_{12}$  ices. However, the real existence of such ices in the stratosphere of Titan needs to be discussed. Indeed, as mentioned by Kim *et al.* (2011), above  $130\ \text{km}$  (the lowest altitude explored by these authors) the temperature remains in  $160 - 190\ \text{K}$  interval while the pressure decreases below  $5 \times 10^{-3}\ \text{bar}$ . A look at Table 1, in which we have gathered the triple points coordinates of involved species, shows that at least  $\text{C}_2\text{H}_6$ ,  $\text{CH}_4$  and  $\text{C}_5\text{H}_{12}$  should not be in solid form at these relatively high temperatures. In order to investigate more

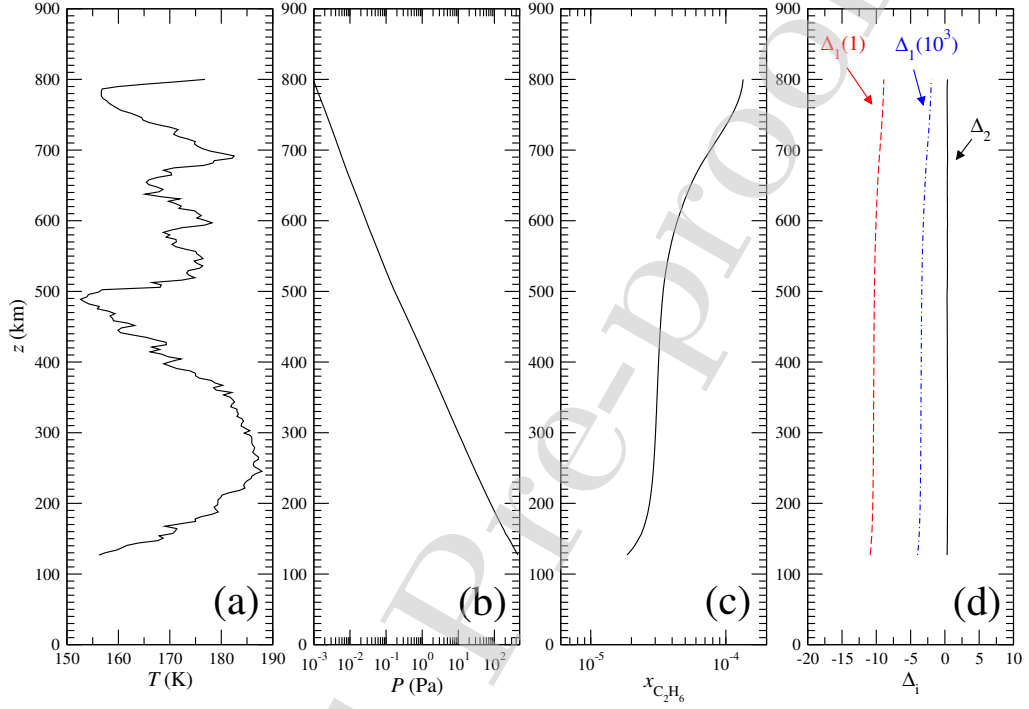


Figure 2: Panels (a) and (b) stand respectively for the temperature and pressure profiles, provided by HASI instruments, between the altitudes 127 km and 800 km in the atmosphere of Titan (Fulchignoni *et al.*, 2005). Panel (c) represents the molar fraction of ethane as computed by Lavvas *et al.* (2008a,b). In panel (d) the thermodynamic quantities  $\Delta_1$  and  $\Delta_2$  (defined in the text by Eq. (1) and Eq. (2)) for ethane. We recall that  $\Delta_1$  and  $\Delta_2$  correspond respectively to the chemical potential, of a given species, in the gas phase and in the solid phase, the coexistence of both is reached when  $\Delta_1 = \Delta_2$  (see Eq. (3)).  $\Delta_1(1)$  corresponds to the abundances found by Lavvas *et al.*'s while  $\Delta_1(10^3)$  has been obtained by multiplying the mole fraction  $x_{C_2H_6}$  by  $10^3$ .

95 deeply the existence of these ices, we introduce two quantities, the first is:

$$\Delta_{1,i} = \ln(\Gamma_i^{\text{vap}} y_i) \quad (1)$$

where  $y_i$  is the mole fraction of the compound  $i$  at equilibrium, in the vapor, and  $\Gamma_i^{\text{vap}}$  is the activity coefficient of the considered species. The second introduced term is written as :

$$\Delta_{2,i} = -\frac{\Delta H_{i,m}}{RT_{i,m}} \left( \frac{T_{i,m}}{T} - 1 \right) \quad (2)$$

The thermodynamic equilibrium between the species  $i$  in the vapor, and its icy counterpart , is reached when the equation :

$$\Delta_{1,i} = \Delta_{2,i} \quad (3)$$

is satisfied (Poling *et al.*, 2007). Eq. (3) correspond to a thermodynamic equilibrium between the considered organic ice  $i$  and the vapor – Eq. (3) is an equality of chemical potential. The activity coefficient  $\Gamma_i^{\text{vap}}$  is given by the Perturbed-Chain Statistical Associating Fluid Theory (PC-SAFT). Originally proposed by Gross & Sadowski (2001), PC-SAFT is now widely employed in the chemical engineering community, due to its very good performances. This theory has been successfully employed in several recent studies of Titan to model liquid-vapor and solid-liquid equilibria (Tan *et al.*, 2013; Luspay-Kuti *et al.*, 2015; Tan *et al.*, 2015; Cordier *et al.*, 2016; Cordier, 2016).

In Eq. (1) the activity coefficient  $\Gamma_i^{\text{vap}}$  quantifies the *degree of ideality* of the considered gas mixture. When  $\Gamma_i^{\text{vap}} \sim 1$  the system has an ideal behavior, *i.e.* all the molecules of the same species and those of different species interact with the same intensity. In our context, for all the molecules listed in Table 1, we found the  $\Gamma_i^{\text{vap}}$ 's very close to unity, whatever the altitude. This indicates an ideal behavior of the gases, which is not a surprise at densities provided by HASI measurements (Fulchignoni *et al.*, 2005). Practically, this means that Eq. (3) can be satisfied only if  $\Delta_{2,i}$  is negative,

118 meaning that the molar fraction  $y_i$  has to be smaller than unity. In the case  
 119 of ethane,  $\Delta_{2,i}$  remains slightly larger than zero (see Fig. 2.d), then, in the  
 120 conditions of pressure and temperature in the Titan's stratosphere, accord-  
 121 ing to the present model,  $\text{C}_2\text{H}_6$  can never form solid particles. For the other  
 122 species, even if  $\Delta_{2,i} < 0$ , the measured or estimated values of their mole  
 123 fractions are order of magnitude too small for Eq. (3) to be satisfied. For  
 124 instance, concerning  $\text{CH}_3\text{CN}$ , [Lara et al. \(1996\)](#) (see their Fig. 10 p. 279) re-  
 125 ported abundances, derived from ground-based millimeter-wave observations  
 126 ([Bézard et al., 1993](#)), between roughly  $10^{-9}$  and  $10^{-7}$  in molar fraction, while  
 127 [Lavvas et al. \(2008a,b\)](#) computed values around  $10^{-8}$ . Our calculations show  
 128 that even in the most favorable case (*i.e.* when the abundances of  $\text{CH}_3\text{CN}$   
 129 is taken equal to  $10^{-7}$ ) the term  $\Delta_{1,i}$  is more than ten orders of magnitude  
 130 smaller than the typical value of  $\Delta_{2,i}$  in stratospheric conditions. As a con-  
 131 sequence, we conclude that the compounds proposed by [Kim et al. \(2011\)](#)  
 132 cannot exhibit solid-vapor equilibria in the stratosphere of Titan. The only  
 133 possibility remaining is the presence of these icy hydrocarbon aerosols in a  
 134 non-equilibrium state, but such a situation seems unlikely.

### 135 3. Radiative transfer modeling of the $3.4\ \mu\text{m}$ absorption

136 In order to simulate the properties of the flux of photons that emerges  
 137 from the Titan's atmosphere during a solar occultation, we have built a sim-  
 138 ple radiative transfer model. On one hand, the structure of the atmosphere  
 139 is represented by a set of concentric spherical shells; on the other hand, the  
 140 solar radiations are assumed to follow a straight optical path through the  
 141 atmosphere. The refraction is neglected in our entire approach, this approx-

142 imation is relevant due to the low density probed in these explored regions.  
 143 For a given altitude  $z$ , the transmittance  $T(\lambda, z)$  of the atmosphere at the  
 144 wavelength  $\lambda$  is estimated using

$$T(\lambda, z) = \exp\left(-\sum_{i,j,k} N_j x_{i,j} \sigma_{i,k} l_j\right) \quad (4)$$

145 where the indexes  $i$ ,  $j$  and  $k$  denote respectively the chemical species, the  
 146 atmospheric layers and the spectral lines. The cross-sections are  $\sigma_{i,k}$ ,  $N_j$   
 147 represents the total number of molecules (per units of volume) in layer  $j$ ,  
 148 while  $x_{i,j}$  is the molar fraction of species  $i$  in the same layer. Finally  $l_j$   
 149 stands for the distance travelled by photons in the layer  $j$  (see Fig. 3). Doing  
 150 several tests on the number of layers, we found  $N_{\text{layers}} = 70$  to be a suffi-  
 151 cient total number of shells, linearly distributed between the ground and a  
 152 maximum altitude of 700 km. The pressure and temperature profiles come  
 153 from HASI measurements (Fulchignoni *et al.*, 2005). The cross-section  $\sigma_{i,k}$   
 154 (in  $\text{cm}^2/\text{molecule}$ ) are written as

$$\sigma_{i,k}(\tilde{\nu}) = I_{i,k}(\tilde{\nu}_{i,k}) f(\tilde{\nu} - \tilde{\nu}_{i,k}) \quad (5)$$

155 where  $f$  is a Voigt profile,  $\tilde{\nu}$  and  $\tilde{\nu}_{i,k}$  are respectively the wavenumber (in  
 156  $\text{cm}^{-1}$ ) and the spectral line  $k$  wavenumber of the chemical species  $i$ ,  $I_{i,k}$  are  
 157 the intensities (in  $\text{cm}/\text{molecule}$ ) of the spectral line  $k$  of the chemical species  
 158  $i$ . In the cases where high resolution spectral data are available, the cross-  
 159 section  $\sigma_{i,k}$  are computed using  $k$ -correlated coefficient method (Arking &  
 160 Grossman, 1972; Chou & Arking, 1980; Fu & Liou, 1992). When only low  
 161 resolution spectral data are available in the literature or when the lines are  
 162 wider than the spectral resolution of VIMS (16-20 nm), the  $k$ -correlated

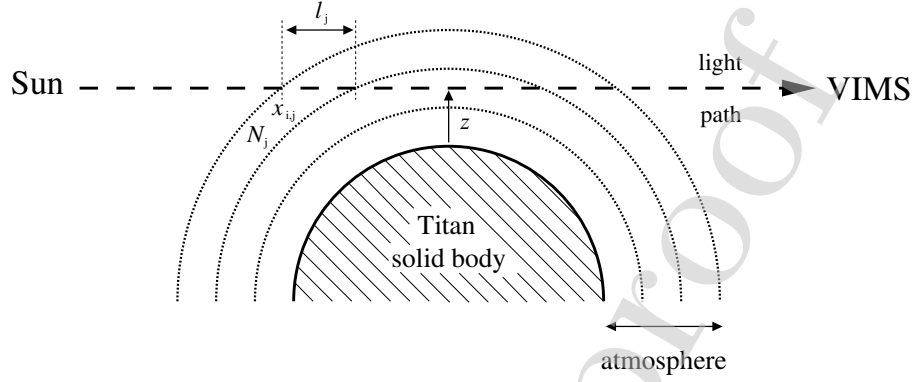


Figure 3: A schematic representation of our “onion-skin” radiative transfer model, used in this paper and suitable for the analysis of Titan’s solar occultations data published by [Maltagliati \*et al.\* \(2015\)](#). In the text, the term *altitude* refers to the parameter called “ $z$ ” in this figure. After tests with different numbers of layers, a total number  $N_{\text{layers}} = 70$  of atmospheric layers was found sufficient to describe the atmosphere. Layers have been linearly distributed between the ground and 700 km.

163 coefficient method is not necessary to compute cross-section and therefore a  
 164 Gauss profile has been proved to be sufficient.

165 Our initial composition is based on the one published by [Maltagliati \*et al.\*](#)  
 166 (2015) and include the following molecules :  $\text{CH}_4$ ,  $\text{CH}_3\text{D}$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  
 167  $\text{C}_2\text{H}_6$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_6$  and  $\text{HCN}$ . In this entire paper, we adopt this list of species  
 168 as our First Guess composition (hereafter FG composition), the influence  
 169 of other compounds will be made by comparing what it is obtained using  
 170 this FG composition. Nitrogen is voluntarily omitted since it is extremely  
 171 poor absorbant in the domain of interest. Moreover, the collision-induced  
 172 effects are negligible within the band  $3.3 - 3.5 \mu\text{m}$ . The  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  
 173  $\text{C}_2\text{H}_6$ ,  $\text{C}_6\text{H}_6$  and  $\text{HCN}$  vertical mixing ratio profiles come from photochemical  
 174 models developed by [Krasnopolsky \(2014\)](#). The abundance of deuterated

methane ( $\text{CH}_3\text{D}$ ) with respect to the methane has been kept constant with  
a  $\text{CH}_3\text{D}/\text{CH}_4$  ratio of about  $5.3 \times 10^{-4}$  (Bézard *et al.*, 2007). Concerning  
water, we performed tests including molar fractions corresponding to the  
highest value given by Coustenis *et al.* (1998). Finally, the abundance of CO  
has been taken from Flasar *et al.* (2005).

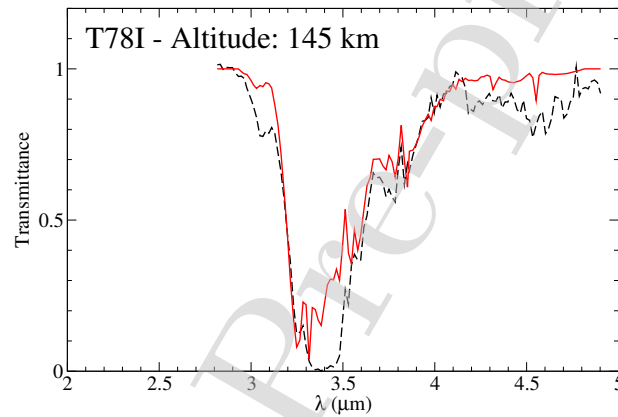


Figure 4: Comparison between observed transmittance (dashed line) acquired during occultation T78I at the altitude of 145 km (Maltagliati *et al.*, 2015), and the computed transmittance due to our FG composition: with only  $\text{CH}_4$ ,  $\text{CH}_3\text{D}$ , CO,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_6$  and HCN. For  $\text{C}_2\text{H}_6$ , only spectral lines provided by HITRAN have been taken into account.

The spectral data of CO,  $\text{C}_2\text{H}_2$ ,  $\text{H}_2\text{O}$  and HCN were mainly taken in HITRAN<sup>1</sup> (Rothman *et al.*, 2013) and GEISA<sup>2</sup> (Jacquinet-Husson *et al.*, 2008). For  $\text{CH}_4$ ,  $\text{CH}_3\text{D}$  and  $\text{C}_2\text{H}_4$  we used the up-to-date theoretical line lists computed by Rey *et al.* (2016) and available at the Theoretical Reims-Tomsk

<sup>1</sup><http://hitran.org/>

<sup>2</sup><http://www.pole-ether.fr/geisa/>

184 Spectral database<sup>3</sup>. For benzene, due to the lack of data in these database,  
 185 we performed *ab initio* computations of its absorption frequencies and their  
 186 respective intensities. Based on the MP2/6-311G\*\* level of the theory, devel-  
 187 oped by Moller & Plesset (1934), we obtained frequencies, which were scaled  
 188 by 0.95, according to that is the recommended in such a situation. The only  
 189 none zero intensities near the 3.4  $\mu\text{m}$  band are for the frequencies 3064.0917  
 190  $\text{cm}^{-1}$  (3.26  $\mu\text{m}$ ) and 3064.0949  $\text{cm}^{-1}$  (3.26  $\mu\text{m}$ ) (including the scaling factor  
 191 of 0.95) corresponding to two C-H asymmetric stretching normal modes. The  
 192 intensities were found quite low with values of 32.63 km/mole for both tran-  
 193 sitions. Considering the vertical profile of  $\text{C}_6\text{H}_6$ , we find that the benzene is  
 194 a minor absorber around 3.26  $\mu\text{m}$ .

195 Maltagliati *et al.* (2015) selected a set of four occultations data, T10  
 196 Egress (T10E), T53 Egress (T53E), T78 Egress (T78E) and T78 Ingress  
 197 (T78I) acquired during three flybys, T10, T53 and T78 respectively. For  
 198 each occultation, the altitude ranges between  $\sim 50$  km and  $\sim 690$  km. We  
 199 provide, in supplementary material, four cube's name lists used in our analy-  
 200 sis, one name list by occultation. The name lists are in Excel cvs format and  
 201 can be downloaded from the pds-rings site<sup>4</sup>. For all these occultations, the  
 202 retrieved transmittance curves, at a given altitude, are extremely similar (see  
 203 for instance Fig. 11 of Maltagliati *et al.*, 2015). In order to facilitate com-  
 204 parison between our theoretical output, and observational determinations,  
 205 we have chosen the Ingress occultation T78 (T78I) as a typical case. We also  
 206 selected the altitude of 145 km because it offers a good compromise between

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<sup>3</sup><http://theorets.tsu.ru>

<sup>4</sup><https://pds-rings.seti.org/cassini/vims/>



high altitudes data for which the transmittance curves are pretty flat, and low altitudes measurements presenting a global strong absorption that masks or damps spectral features.

A first model-observation comparison can be seen in Fig. 4, the disagreement is clear, particularly around  $3.4\ \mu\text{m}$  our domain of interest. This nicely confirms the findings by [Maltagliati \*et al.\* \(2015\)](#).

#### 4. The possible absorption of ethane, propane and butane around $3.4\ \mu\text{m}$

##### 4.1. Ethane

As already mentioned, the C-H stretching bands produce a strong absorption at  $3.2 - 3.5\ \mu\text{m}$ , this is why any compound containing one or several C-H bonds can potentially contribute to the observed  $3.4\ \mu\text{m}$  absorption. In this context, ethane, quantitatively the main product of Titan's photochemistry ([Lavvas \*et al.\*, 2008a,b](#); [Krasnopolsky, 2014](#)), should be the object of our first intentions. The presence of ethane in the Titan's atmosphere is firmly established by previous observations, *e.g.* it has been detected by Cassini's instruments: UVIS ([Koskinen \*et al.\*, 2011](#)), INMS ([Cui \*et al.\*, 2009](#)) and CIRS ([Vinatier \*et al.\*, 2010](#)). Unfortunately, in HITRAN and GEISA databases, ethane spectral lines in the band of interest are pretty scarce. Surprisingly, the absorption spectrum of the C-H stretching region of ethane, measured by [Pine & Lafferty \(1982\)](#) (hereafter PL82) at  $T = 119\ \text{K}$ , is not available in these compilations. Then, we included the  $\sim 3000$  lines provided by PL82 data in our model; 1614 entries specify wavenumbers, intensities and the lower state energies whereas for 1426 other entries the lower state energy is

not available. Thus, in the latter case, we have neglected the temperature corrections of the intensities. The contribution to the absorption around 3.4  $\mu\text{m}$ , of ethane alone, is plotted in Fig. 5(a).

Unfortunately, Pine & Lafferty (1982) did not include ethane PQ-branches which should have a non-negligible contribution in the domaine of interest. To tackle the issue, we used an empirical pseudo-line list based on the cross-section measurements developed by Harrison *et al.* (2010) (hereafter H10 dataset) and freely available on the web<sup>5</sup>. Compared to the absorption obtained with PL82 spectral lines, the effect of ethane is significantly enhanced by the use of this more comprehensive list (Fig. 5.b). If both, the PL82 and H10 spectral data, are simultaneously included in our model (Fig. 5.c), the actual effect of PL82 is not noticeable. Finally, if we merge PL82 and H10 spectral lines sets, with those employed for our FG composition model, the disagreement with Cassini/VIMS observations is considerably reduced (Fig. 5.d). This clearly demonstrates the prominent role of ethane, as an absorber, at wavelengths around 3.4  $\mu\text{m}$ . Nonetheless, the simulated transmittance remains significantly above the observed one. This fact suggests the presence of other absorbers, possibility which we discuss further in next paragraphs.

#### 4.2. Propane

According to photochemical models (Lavvas *et al.*, 2008a,b; Krasnopol-sky, 2014), propane should also be produced in Titan's upper-atmosphere. This  $\text{C}_3$  hydrocarbon has been detected by several Cassini's instruments:

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<sup>5</sup><http://mark4sun.jpl.nasa.gov/pseudo.html>

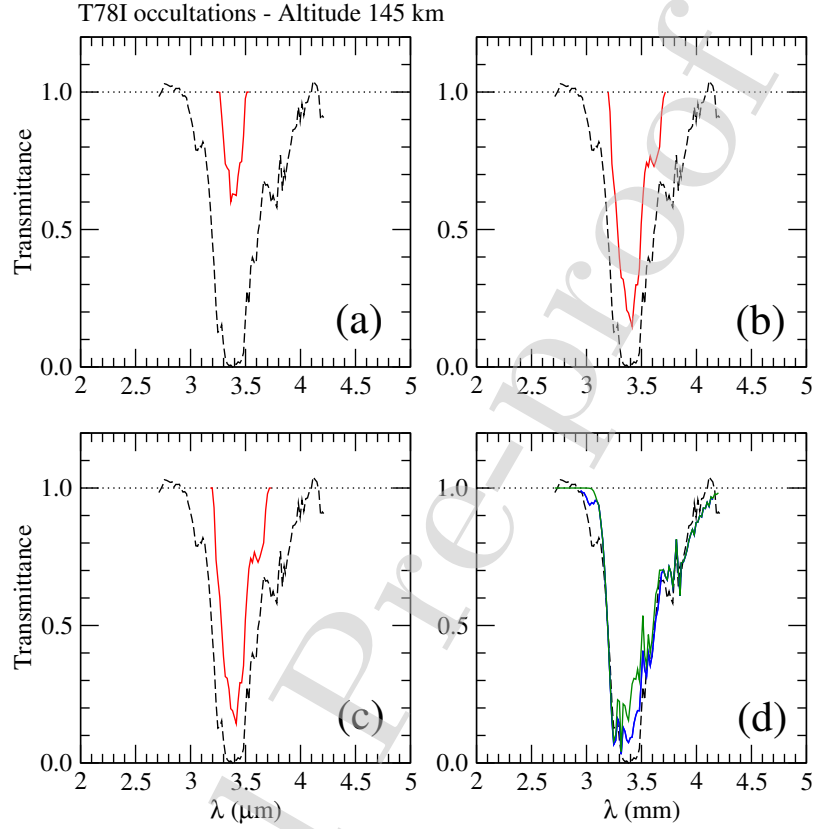


Figure 5: Comparison between simulated transmittances and VIMS for the T78I occultation data (Maltagliati *et al.*, 2015). Observational data are in dashed line, the altitude is 145 km. This figure shows the transmittance of  $\text{C}_2\text{H}_6$  using: (a) only Pine & Lafferty (1982) spectral lines (red), (b) only pseudo-lines lists based on the cross-section measurements (Harrison *et al.*, 2010) (red), (c) the combination of PL82 and H10 spectral data (red), (d) the combination of our FG composition model with PL82 and H10 (blue), the absorption computed with our FG composition is also plotted for comparison (green solid line).

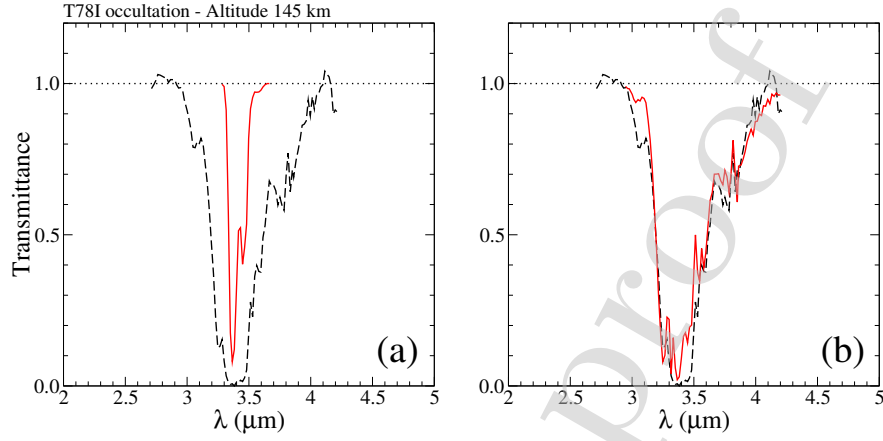


Figure 6: Occultation T78I at 145 km (observed transmittance in dash line) : (a) Absorption due to propane alone, (b) computed absorption using our FG composition complemented by propane (ethane is not taken into account).

254 Nixon *et al.* (2013) determined its mixing ratio using CIRS, while Cui *et al.*  
 255 (2009) and Magee *et al.* (2009) retrieved abundances from INMS measure-  
 256 ments. Similarly to the ethane case, HITRAN and GEISA are very poor in  
 257 spectral data around 3.4  $\mu\text{m}$  for this molecule. Then, we used the propane  
 258 pseudo-lines list based on the cross-section measurements of Harrison &  
 259 Bernath (2010) (freely available on the web<sup>6</sup>). Taking into account the  
 260 propane abundance profil predicted by Krasnopolsky (2014), we have esti-  
 261 mated the corresponding absorption in our domain of interest: in Fig. (6) we  
 262 have displayed the absorption of propane alone a), the effet of this molecule  
 263 is combined with that of our FG composition sample b), clearly the con-  
 264 tribution of propane is comparable to that of ethane, even is propane is

<sup>6</sup><http://mark4sun.jpl.nasa.gov/pseudo.html>

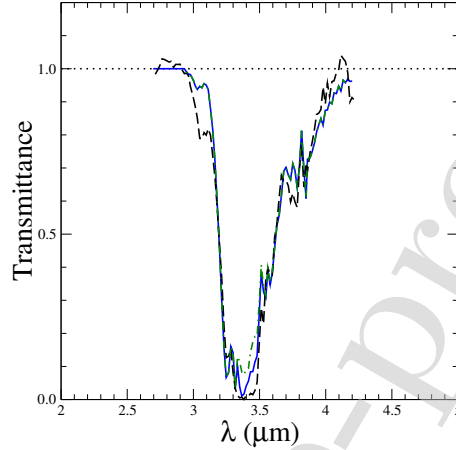


Figure 7: Dashed line : T87I observations, dot-dashed line: our computation taking into account gases of our FG composition and ethane (including pseudo-lines and Lafferty data), solid line: the same simulation including propane pseudo-lines list **based on the cross-section measurements of Harrison & Bernath (2010)**.

approximately one order of magnitude less abundant than ethane. In fact, due to its larger numbers of C-H, propane is an absorber roughly one order of magnitude more efficient than ethane.

#### 4.3. Butane

Butane has not yet been detected, in the atmosphere of Titan. The presence of butane is predicted by photochemical models (Krasnopolsky, 2009, 2010, 2014). The quantity of butane should be lower than what it is measured and computed for propane. Available models indicate a butane mixing ratio about four order of magnitude smaller than what Krasnopolsky (2014) obtained for propane. Since no data concerning butane were found in HITRAN

and GEISA databases, we used cross-sections provided by the NIST<sup>7</sup>. According to this approach and taking vertical profile provided by Krasnopolsky (2014), we have checked that butane has no detectable influence on the 3.4  $\mu\text{m}$  atmospheric transmittance.

#### 4.4. Conclusion about ethane, propane, butane and others linear hydrocarbon

We have summarized our simulations results in Fig. 7, clearly the addition of propane to our set of considered gaseous species reduced the disagreement between theoretical output and solar occultation data. However, the situation is far from satisfactory, and there is room for other efficient absorbers around 3.4 microns. It is likely that other larger linear hydrocarbons are present in the atmosphere, but they are not yet retrievable from the occultation data. Moreover, their molar fractions could be very small in comparison with the molar fraction of butane. Thus, no additional linear hydrocarbon larger than butane was considered in our model.

### 5. The absorption due to Polycyclic Aromatic Hydrocarbons and Hydrogenated Amorphous Carbons

As mentioned in the introduction, PAHs or more complex polyaromatic hydrocarbons like HACs (Dartois *et al.*, 2004, 2005, 2007), considered as organic compounds in solid state, are detected in the ISM (Sandford *et al.*, 1991; Pendleton & Allamandola, 2002). For instance in Dartois *et al.* (2004) the features observed in the ISM spectra fitted very well with those observed in

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<sup>7</sup><http://webbook.nist.gov>

296 spectra of HACs produced in laboratory (Dartois *et al.*, 2004, 2005). Further-  
 297 more, PAHs are detected on the Iapetus' and Phoebe's surface (Cruikshank  
 298 *et al.*, 2008), in micro-meteorites in Antarctic (Becker *et al.*, 1997) and in the  
 299 meteorite Allende (Becker & Bunch, 1997). Observations of comets reveal  
 300 the presence of PAHs (Li, 2009) and in addition they were considered in Ti-  
 301 tan's upper atmosphere to explain an unidentified emission at  $3.3\ \mu\text{m}$  (Dinelli  
 302 *et al.*, 2013; López-Puertas *et al.*, 2013). According to Bellucci *et al.* (2009)  
 303 for Titan's atmosphere and Dartois *et al.* (2004, 2005, 2007); Sandford *et al.*  
 304 (1991); Pendleton & Allamandola (2002) for the ISM, the features observed  
 305 between  $3.38\ \mu\text{m}$  and  $3.48\ \mu\text{m}$  are due to the symmetric and asymmetric  
 306 stretching of the C-H bond in  $-\text{CH}_2$  and  $-\text{CH}_3$  groups of the aliphatic chains.  
 307 Likewise the features around  $3.3\ \mu\text{m}$  are signatures of stretching of aromatic  
 308 C-H bond (Bellucci *et al.*, 2009; Dartois *et al.*, 2004, 2005, 2007). These  
 309 latter signatures emphasize the presence of aromatic compounds like PAHs  
 310 and the signatures at  $3.38\ \mu\text{m}$  and  $3.48\ \mu\text{m}$  together with the signatures of  
 311 aromatic C-H stretching show the presence of complex particles containing  
 312 aromatic cycles and aliphatic chains as it would expect in HACs. In Dartois  
 313 *et al.* (2005), possible structures of HACs compatible with the ISM spectra  
 314 were simulated with a neuronal network simulation: The resulting structure  
 315 shows aromatic cycles and aliphatic chains as expected.  
 316 Thus, to clarify the observed transmission in the  $3.3 - 3.5\ \mu\text{m}$  spectral region  
 317 we considered PAHs and HACs compounds in our model.

### 318 5.1. Polycyclic Aromatic Hydrocarbons

319 The information on PAHs's transition intensities come from the NASA  
 320 Ames PAHs IR Spectroscopic Database <sup>8</sup>. In our calculations the line widths  
 321 were fixed to a reasonable value of  $30\text{ cm}^{-1}$ . This value is approximatively  
 322 comparable to the different values used for HACs (Dartois *et al.*, 2007). we  
 323 introduce a correction factor  $\alpha_{i,k}$  for the intensities  $I_{i,k}$ , with the same mean-  
 324 ing for index  $i$  and  $k$  than the index in Eq. (4), to account for two sources  
 325 of uncertainty : (1) the temperature dependence of the intensities  $I_{i,k}$ , (2)  
 326 the uncertainties on the  $I_{i,k}$ 's themselves. Indeed, the spectral data provided  
 327 by the Ames Database are valid for a temperature of 296 K while the actual  
 328 temperature in Titan's stratosphere is substantially lower (see for instance  
 329 Fig. 2a). In the spectral window of interest (*i.e.*  $2700\text{ cm}^{-1}$ – $3570\text{ cm}^{-1}$ ), for  
 330 the 716 species reported in the Ames database, we counted a total of 11,307  
 331 calculated spectral lines against only 127 coming from an experimental de-  
 332 termination. Even if some overlaps are present, we see that the majority of  
 333 available spectral data are calculated theoretically. This rises the question of  
 334 the degree of confidence that can be placed in these computed data. In this  
 335 context, we have searched for theoretical and experimental spectral lines that  
 336 coincide in terms of wavelength, adopting a given tolerance, respectively:  $1\text{ cm}^{-1}$ ,  
 337  $2\text{ cm}^{-1}$  and  $3\text{ cm}^{-1}$ . This way, we identified 52 lines that correspond to  
 338 both theoretical and laboratory determinations with a tolerance of  $1\text{ cm}^{-1}$ ,  
 339 108 when is increased to  $2\text{ cm}^{-1}$  and 144 when the tolerance is increased to  
 340  $3\text{ cm}^{-1}$ . Consequently, we formed the log ratio  $I_{\text{th}}/I_{\text{exp}}$  for each identified

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<sup>8</sup><http://www.astrochem.org/pahdb/>



couple of lines, with  $I_{\text{th}}$  the theoretical intensity and  $I_{\text{exp}}$  the correspond-  
 ing laboratory measurement. The histograms of log ratio  $I_{\text{th}}/I_{\text{exp}}$  values is  
 plotted in Fig. 8. This figure shows clearly that the theoretical intensities  
 tend to be underestimated, compared to their experimental counterparts, by  
 a factor up to two orders of magnitude. Then, these results motivated our  
 introduction of a factor  $\alpha_{i,k}$  that represents the uncertainties that affect the  
 spectral lines intensities available in the Ames database. In this manner, the  
 intensity  $I_{i,k}$  in Eq. (5) is replaced by the product  $\alpha_{i,k}I_{i,k}$ . Finally, if we  
 combine Eq. (4) with Eq. (5), the product  $\beta_{i,j,k} = x_{i,j}\alpha_{i,k}$ , with the same  
 meaning for index  $j$  than the index in Eq. (4), appears in the expression  
 of the transmission. In first approach, we considered that the correction  
 factors  $\alpha_{i,k}$  are independent of the spectral lines. Therefore,  $\beta_{i,j,k} = x_{i,j}\alpha_{i,k}$   
 becomes  $\beta_{i,j} = x_{i,j}\alpha_i$ . We took 118 neutral and charged PAHs in the Ames  
 database. We have chosen PAHs with less than 100 carbon atoms, free of Fe,  
 Mg, Si (not relevant for Titan's atmosphere) and for which the intensities  
 are significant in the  $3.3 - 3.5 \mu\text{m}$  band.

## 5.2. Hydrogenated Amorphous Carbons

The HACs (sometimes noted a-C:H or a-C:H:N if the HACs contain nitro-  
 gen), are considered as smallest haze particle and precursor of more complex  
 haze particle (called tholins) Lavvas *et al.* (2011) (and p. 304 of Müller-  
 Wodarg *et al.* (2014)). In Dartois *et al.* (2004, 2005, 2007) no identified  
 structure was given but just different vibration modes together with their vi-  
 brational frequencies or wavelengths. Analyzing the spectrum of the galaxy  
 named IRAS 08572+3915, Dartois *et al.* (2007) fitted the intensities, wave-  
 lengths and widths of the lines for these vibration modes. Then, we use

spectrum parameters given in Table 1 of Dartois *et al.* (2007). We do not consider HACs with nitrogen (a-C:H:N) because the vibrational modes containing N are not present in 3.3 – 3.5  $\mu\text{m}$  band (Dartois *et al.*, 2005). As with PAHs, we also introduce a correction factor  $\alpha_{i,k}$  on the intensities  $I_{i,k}$ , with the same meaning for index  $i$  and  $k$  than the index in Eq. (4), taking into account for an uncertainty source: the temperature dependence of the intensities  $I_{i,k}$ . Indeed, the intensities coming from the study of IRAS 08572+3915 spectrum the temperature must be different than that in Titan's stratosphere. In Dartois *et al.* (2007) no distinction was made between the different HACs but just between the vibration modes. Consequently, in our model for HACs we omit index  $i$ . Thus, our correction factor  $\alpha_{i,k}$  becomes  $\alpha_k$  and the intensities are  $I_k$ . In first approach, as with PAHs, the correction factors  $\alpha_k$  are independent of the spectral lines. Consequently, we define a product  $\beta_j = x_j \alpha$ .

### 5.3. Results

For PAHs,  $x_{i,j}$  is the molar fraction of PAHs number  $i$  with respect to the  $\text{C}_6\text{H}_6$  abundance profile in layer  $j$ . As a first approximation, the vertical profile of this molar fraction of PAHs number  $i$  vs the  $\text{C}_6\text{H}_6$  (used as proxy) abundance and the vertical profile of the molar fraction of HACs were kept constant. Thus for PAHs and HACs respectively,  $\beta_{i,j} = x_{i,j} \alpha_i$  turns into  $\beta_i = x_i \alpha_i$  and  $\beta_j = x_j \alpha$  turns into  $\beta = x \alpha$ . Considering the uncertainties on PAHs and HACs intensities, we have fitted, respectively, the product  $\beta_i = x_i \alpha_i$  and not  $x_i$  alone, and  $\beta = x \alpha$  and not  $x$ , to get the best fit to occultation data. However, the resulting values do not provide information about the actual abundances of these PAHs and HACs because the problem

391 is degenerated: the correction coefficient to apply remains unknown. Taking  
 392 into account the log ratio  $I_{\text{th}}/I_{\text{exp}}$  and according to the PAHs number  $i$ , we  
 393 obtain as best fit for  $\beta_i$ , values in the range of  $(4.75 \times 10^{-4} - 3.32) \times \text{molar}$   
 394 fraction of  $\text{C}_6\text{H}_6$ . Concerning the HACs, the best fit for  $\beta$  is found for the  
 395 value  $10^{-7}$ .

396 Fig. 9 shows that the combination of all gases, plus the 118 PAHs and HACs  
 397 allow a satisfactory modelization of the observed transmittance at 145 km.

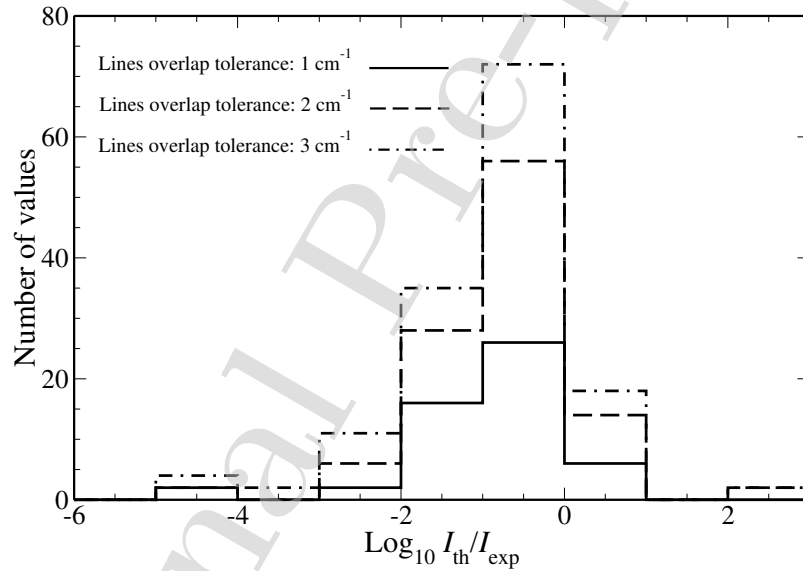


Figure 8: Histograms of the log ratios  $I_{\text{th}}/I_{\text{exp}}$  for the Ames database PAHs for which theoretical and experimental spectral lines features determinations are available. We have considered 3 cases: (1) the wavelengths of theoretical and experimental match with a maximum tolerance of  $1 \text{ cm}^{-1}$ , (2) the same with  $2 \text{ cm}^{-1}$  and finally  $3 \text{ cm}^{-1}$ .

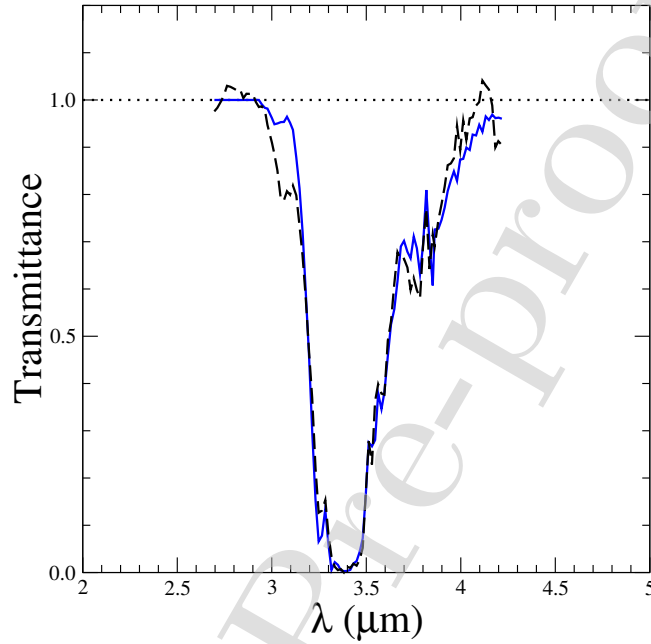


Figure 9: Computed transmittance (solid line) at 145 km during occultation T78I (observed transmittance in dash line), the radiative transfert model takes into account all studied gases plus the best fit of 118 PAHs (from NASA Ames database) and HACs (from [Dartois \*et al.\* \(2007\)](#)).

## 6. Discussion and Conclusion

### 6.1. Discussion

Observations of Saturn's stratospheric auroral regions ([Guerlet \*et al.\*, 2015](#)) seem to underline the remarks made on the features observed in Titan's atmosphere. Indeed, spectral signatures of benzene and aerosols in the range  $680\text{--}900\text{ cm}^{-1}$  and  $1360\text{--}1440\text{ cm}^{-1}$  have been observed with CIRS on

board Cassini, around the 80°S. In particular, vibrational modes in aliphatic and aromatic hydrocarbons were observed revealing the presence of PAHs or HACs in stratosphere of Saturne (Guerlet *et al.*, 2015). Moreover, as mentioned, VIMS observations of Procyon's occultation through Saturn's atmosphere around the 55°N, reported by Nicholson *et al.* (2006) and discussed by Bellucci *et al.* (2009), show similar features in the 3.4  $\mu\text{m}$  band to those observed in our study. Nevertheless, the observations reveal slight differences with the Titan's 3.4  $\mu\text{m}$  band spectra. But these differences could be due to a lower amount of nitrogen compounds in Saturn's atmosphere (Bellucci *et al.*, 2009). Thus, the PAHs and HACs in Titan's atmosphere could be slightly different from those in Saturn's atmosphere.

Our study of 3.4  $\mu\text{m}$  band observed by solar occultation at 145 km of altitude suggests the presence of aromatic molecules like PAHs and more complex like HACs at low altitudes. Some insights can be gained by examining the results from laboratory experiments. Dartois *et al.* (2004, 2005) synthesized HACs (called a-C:H in these references) by ultraviolet photolysis of methane (Dartois *et al.*, 2004) and other hydrocarbons and nitrogen compounds to form a-C:H:N compounds (Dartois *et al.*, 2005) by UV radiation with wavelengths shorter than 120 nm in the EUV domain. Then, they made spectral Infra-Red (IR) analysis of the residues. The aim of these previous studies was to explain the spectral features observed in the ISM. Due to the presence of methane, others hydrocarbons and nitrogen compounds as well as the ultraviolet radiation in EUV domain going down to 600 km (Yoon *et al.*, 2014), the same HACs production process as in the ISM could occur in the Titan's upper atmosphere.

But this explanation is not completely satisfactory, mainly because we should find absorptions in the wavelength range  $3.38\ \mu\text{m}$ – $3.48\ \mu\text{m}$  in high altitude occultation spectra which is not the case (Courtin *et al.*, 2015). In this latter reference, the authors do not observe strong features (in extinction) in this wavelength range above 500 km but rather below 480 km (Courtin *et al.*, 2015, Fig. 2). The authors computed the ratio extinction coefficient at  $3.33\ \mu\text{m}$  / extinction coefficient at  $3.38\ \mu\text{m}$ , the wavelength at  $3.33\ \mu\text{m}$  being characteristic of aromatic C-H stretching and the wavelength at  $3.38\ \mu\text{m}$  characteristic of aliphatic C-H stretching. Thus, this ratio is function of the ratio between the aromatic and aliphatic components in the haze particles. This ratio is about 3 at 700 km and decreases to about 0.5 below 300 km. Then the conclusion of Courtin *et al.* (2015) is a growth of molecules from PAHs to more complex organics by particle-aging and coating process when the altitude decreases. So, even if the explanation in Dartois *et al.* (2004, 2005) about the HACs production in the ISM is not completely relevant for Titan's upper atmosphere, it is possible to have HACs at low altitude, by particle-aging and coating process. This process was also studied in laboratory (Carrasco *et al.*, 2018) by ultraviolet irradiation of analogs of Titan's thermosphere aerosols (and Couturier-Tamburelli *et al.* (2018)). Carrasco *et al.* (2018) analyzed the absorption peaks of residues and their time evolution. They found shifts and modifications of vibrational signatures reflecting aerosols transformation during the irradiation. The observed spectra after 24 h of irradiation appear to tend toward Titan's spectra observed in VIMS spectra at altitude 200 km. The conclusion of Carrasco *et al.* (2018) is that a particle aging process by ultraviolet irradiation occurs in Titan's atmosphere

454 from aerosol embryos in thermosphere to more complex haze particles in low  
 455 altitudes according the following process : (1) aerosol embryos generation,  
 456 (2) sedimentation and (3) chemical evolution by UV irradiation.

457 Other studies were conducted (Gudipati *et al.*, 2013; Yoon *et al.*, 2014).  
 458 In Yoon *et al.* (2014), the authors experimentally studied the role of ben-  
 459 zene photolysis in the PAHs and more complex particles (tholins) produc-  
 460 tion. They stipulated that UV radiation with wavelengths longer than 130  
 461 nm (FUV domain) leads to the photodissociation of benzene. Likewise, in  
 462 the FUV domain the photons could reach low altitudes bringing a benzene  
 463 photolysis in the lower atmosphere. Then this photolysis would lead to the  
 464 production of PAHs and more complex particles. In the same way, Gudipati  
 465 *et al.* (2013); Couturier-Tamburelli *et al.* (2014) proceeded to photochem-  
 466 ical experiments with  $C_4N_2$  ice and photons in FUV domain, reproducing  
 467 the environment of Titan's lower atmosphere and highlighting the fact that  
 468 at low altitudes (below 200 km) the UV flux at 350 nm is comparable to  
 469 the upper radiation field at shorter wavelengths. Their conclusion is that  
 470 photoabsorption by haze particles in this FUV domain would trigger a rich  
 471 solid-state chemistry at low altitudes. In a similar way photolysis of  $HC_5N$  led  
 472 to residues containing aromatic signatures around  $3.3 \mu m$  and C-H stretching  
 473 around  $3.4 \mu m$  (Couturier-Tamburelli *et al.*, 2015). The authors concluded  
 474 that this photolysis drives the formation of more and more complex polymers  
 475 which are precursors of haze particles. These results about the PAHs and  
 476 HACs production at low altitudes are in agreement with our spectral analysis  
 477 of the  $3.4 \mu m$  band for the occultation at 145 km of altitude.

478 Finally, NASA has recently announced the selection of the *Dragonfly*

mission (Turtle *et al.*, 2019) as part of its *New Frontiers* program. This revolutionary quacopter is planned to explore Titan's surface, in the region of Shangri-La dune fields and Selk impact crater, during the mid-2030s. Among onboard instruments, the *Dragonfly Camera Suite* will allow PAH detection via fluorescence, excited by a controlled UV illumination (Lorenz *et al.*, 2018).

## 6.2. Conclusion

To conclude, the present study was to explain the strong absorption around 3.4  $\mu\text{m}$  observed in the occultation spectra by VIMS at low altitudes typically lower than 450 km. We opted for the altitude 145 km which offers a good compromise : at lower altitudes, the stronger absorptions damp spectral features and at higher altitudes, the absorptions are too weak to be extracted from the signal. As a first step in our radiative transfer modeling, we have included 9 molecules following Maltagliati *et al.* (2015) :  $\text{CH}_4$ ,  $\text{CH}_3\text{D}$ ,  $\text{CO}$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_6$  and  $\text{HCN}$ . This composition leads to a poor reproduction of the observed transmittance curve. The disagreement was reduced by including  $\text{C}_2\text{H}_6$  spectroscopic data as the data coming from Pine & Lafferty (1982) or the more exhaustive data, but empirical pseudo-line, coming from Harrison *et al.* (2010). This way, the agreement has been improved, but the simulated transmittance remained above the observed one. The inclusion of propane improved the result but there was still a lack of efficient absorbers around 3.4  $\mu\text{m}$ . Knowing that spectral signatures around 3.4  $\mu\text{m}$  are present in the ISM and identified as PAHs or HACs, we have considered these complex hydrocarbon compounds in our model as possible absorbers in the Titan's atmosphere at about 145 km of altitude. The fit of abundance of PAHs and HACs, taking into account some uncertainty by means of a



correction factor, allowed a rather satisfactory modelization of the observed transmittance at 145 km of altitude. Thus, the model suggests the presence of complex hydrocarbon compounds and precursors of haze particles at low altitudes. This result is also consistent with several laboratory studies showing a complexification of hydrogenated molecules from small hydrocarbons to more complex by UV irradiations (Yoon *et al.*, 2014; Couturier-Tamburelli *et al.*, 2015, 2018; Carrasco *et al.*, 2018).

## References

- Arking A., Grossman K. **1972**. *The Influence of the line Shape and Band Structure on Temperature in Planetary Science*. J Atmos Sci 29:937.
- Becker L., Bunch T.E. **1997**. *Fullerenes, fulleranes and PAHs in the Allende meteorite*. Meteoritics and Planetary Science 32. doi:10.1111/j.1945-5100.1997.tb01292.x.
- Becker L., Glavin D.P., Bada J.L. **1997**. *Polycyclic aromatic hydrocarbons (PAHs) in Antarctic Martian meteorites, carbonaceous chondrites, and polar ice* 61:475–481. doi:10.1016/S0016-7037(96)00400-0.
- Bellucci A., *et al.* **2009**. *Titan solar occultation observed by Cassini/VIMS: Gas absorption and constraints on aerosol composition*. Icarus 201:198–216. doi:10.1016/j.icarus.2008.12.024.
- Bézard B., Marten A., Paubert G. **1993**. *Detection of acetonitrile on Titan*. Bull Am Astron Soc 25:1100.

- 525 Bézard B., Nixon C.A., Kleiner I., Jennings D.E. **2007**. *Detection of  $^{13}\text{CH}_3\text{D}$*   
 526 *on Titan*. Icarus 191:397–400. doi:[10.1016/j.icarus.2007.06.004](https://doi.org/10.1016/j.icarus.2007.06.004).
- 527 Bourgalais J., *et al.* **2016**. *Elusive anion growth in Titan’s atmosphere: Low*  
 528 *temperature kinetics of the  $\text{C}_3\text{N}^- + \text{HC}_3\text{N}$  reaction*. Icarus 271:194–201.  
 529 doi:[10.1016/j.icarus.2016.02.003](https://doi.org/10.1016/j.icarus.2016.02.003).
- 530 Carrasco N., *et al.* **2018**. *The evolution of Titan’s high-altitude*  
 531 *aerosols under ultraviolet irradiation*. Nature Astronomy 2(6):489–494.  
 532 doi:[10.1038/s41550-018-0439-7](https://doi.org/10.1038/s41550-018-0439-7).
- 533 Charnay B., *et al.* **2014**. *Titan’s past and future: 3D modeling of a*  
 534 *pure nitrogen atmosphere and geological implications*. Icarus 241:269–279.  
 535 doi:[10.1016/j.icarus.2014.07.009](https://doi.org/10.1016/j.icarus.2014.07.009). [arXiv:1407.1791](https://arxiv.org/abs/1407.1791).
- 536 Chou M.D., Arking A. **1980**. *Computation of Infrared Cooling Rates in the*  
 537 *Water Vapor Bands*. J Atmos Sci 37:855.
- 538 Cordier D., *et al.* **2016**. *Structure of Titan’s evaporites*. Icarus 270:4156.  
 539 doi:[10.1016/j.icarus.2015.12.034](https://doi.org/10.1016/j.icarus.2015.12.034). [arXiv:1512.07294](https://arxiv.org/abs/1512.07294).
- 540 Cordier D. **2016**. *How speed-of-sound measurements could bring con-*  
 541 *straints on the composition of Titan’s seas*. MNRAS 459:2008–2013.  
 542 doi:[10.1093/mnras/stw732](https://doi.org/10.1093/mnras/stw732). [arXiv:1603.07645](https://arxiv.org/abs/1603.07645).
- 543 Courtin R., Kim S.J., Bar-Nun A. **2015**. *Three-micron extinction of the Ti-*  
 544 *tan haze in the 250–700 km altitude range: Possible evidence of a particle-*  
 545 *aging process*. A&A 573:A21.

- 546 Coustenis A., *et al.* **1998**. *Evidence for water vapor in Titan's atmosphere*  
 547 *from ISO/SWS data*. A&A 336:L85–L89.
- 548 Coustenis A., *et al.* **2016**. *Titan's temporal evolution in strato-*  
 549 *spheric trace gases near the poles*. Icarus 270:409–420.  
 550 doi:[10.1016/j.icarus.2015.08.027](https://doi.org/10.1016/j.icarus.2015.08.027).
- 551 Couturier-Tamburelli I., *et al.* **2014**. *Spectroscopic studies of non-*  
 552 *volatile residue formed by photochemistry of solid C<sub>4</sub>N<sub>2</sub>: A model*  
 553 *of condensed aerosol formation on Titan*. Icarus 234:81–90.  
 554 doi:[10.1016/j.icarus.2014.02.016](https://doi.org/10.1016/j.icarus.2014.02.016).
- 555 Couturier-Tamburelli I., Piétri N., Gudipati M.S. **2015**. *Simulation of Titan's*  
 556 *atmospheric photochemistry. Formation of non-volatile residue from polar*  
 557 *nitrile ices*. A&A 578:A111. doi:[10.1051/0004-6361/201425518](https://doi.org/10.1051/0004-6361/201425518).
- 558 Couturier-Tamburelli I., *et al.* **2018**. *UV-Vis Light-induced Aging of Titan's*  
 559 *Haze and Ice*. ApJ 852:117. doi:[10.3847/1538-4357/aa9e8d](https://doi.org/10.3847/1538-4357/aa9e8d).
- 560 Cruikshank D.P., *et al.* **2008**. *Hydrocarbons on Saturn's satellites Iapetus*  
 561 *and Phoebe*. Icarus 193:334–343. doi:[10.1016/j.icarus.2007.04.036](https://doi.org/10.1016/j.icarus.2007.04.036).
- 562 Cui J., *et al.* **2009**. *Analysis of Titan's neutral upper atmosphere from*  
 563 *Cassini Ion Neutral Mass Spectrometer measurements*. Icarus 200:581–  
 564 615. doi:[10.1016/j.icarus.2008.12.005](https://doi.org/10.1016/j.icarus.2008.12.005).
- 565 Dartois E., Muñoz Caro G.M., Deboffle D., d'Hendecourt L. **2004**. *Diffuse*  
 566 *interstellar medium organic polymers. Photoproduction of the 3.4, 6.85 and*  
 567 *7.25 μm features* 423:L33–L36. doi:[10.1051/0004-6361:200400032](https://doi.org/10.1051/0004-6361:200400032).

- 568 Dartois E., *et al.* **2005.** *Ultraviolet photoproduction of ISM dust. Laboratory characterisation and astrophysical relevance.* A&A 432:895–908.  
569  
570 doi:[10.1051/0004-6361:20042094](https://doi.org/10.1051/0004-6361:20042094).
- 571 Dartois E., *et al.* **2007.** *IRAS 08572+ 3915: constraining the aromatic versus aliphatic content of interstellar HACs.* A&A 463:635–640.  
572  
573 doi:[10.1051/0004-6361:20066572](https://doi.org/10.1051/0004-6361:20066572).
- 574 Dinelli B.M., *et al.* **2013.** *An unidentified emission in Titan’s upper atmosphere.* Geophys. Res. Lett. 40:1489–1493. doi:[10.1002/grl.50332](https://doi.org/10.1002/grl.50332).
- 576 Flasar F.M., *et al.* **2005.** *Titan’s Atmospheric Temperatures, Winds, and Composition.* Science 308:975–978. doi:[10.1126/science.1111150](https://doi.org/10.1126/science.1111150).
- 578 Fu Q., Liou K.N. **1992.** *On the Correlated k-Distribution Method for Radiative Transfert in Nonhomogeneous Atmospheres.* J Atmos Sci 49:2139.  
579
- 580 Fulchignoni M., *et al.* **2005.** *In situ measurements of the physical characteristics of Titan’s environment.* Nature 438:785–791.  
581  
582 doi:[10.1038/nature04314](https://doi.org/10.1038/nature04314).
- 583 Gross J., Sadowski G. **2001.** *Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules.* Ind Eng Chem Res  
584  
585 40:1244–1260. doi:[10.1021/ie0003887](https://doi.org/10.1021/ie0003887).
- 586 Gudipati M.S., *et al.* **2013.** *Photochemical activity of Titans low-altitude condensed haze.* Nat. Commun. 4:1648. doi:[10.1038/ncomms2649](https://doi.org/10.1038/ncomms2649).  
587

- 588 Guerlet S., *et al.* **2015.** *Stratospheric benzene and hydrocar-*  
 589 *bon aerosols detected in Saturn's auroral regions.* A&A 580:A89.  
 590 doi:[10.1051/0004-6361/201424745](https://doi.org/10.1051/0004-6361/201424745).
- 591 Harrison J.J., Bernath P.F. **2010.** *Infrared absorption cross-sections for*  
 592 *propane (C<sub>3</sub>H<sub>8</sub>) in the 3  $\mu$ m region.* JQSRT 111:1282–1288.
- 593 Harrison J.J., Allen N.D.C., Bernath P.F. **2010.** *Infrared absorption cross-*  
 594 *sections for ethane (C<sub>2</sub>H<sub>6</sub>) in the 3  $\mu$ m region.* JQSRT 111:357–363.
- 595 Jacquinet-Husson N., *et al.* **2008.** *The GEISA spectroscopic database:*  
 596 *Current and future archive for Earth and planetary atmosphere*  
 597 *studies.* J Quant Spectrosc Radiat Transfer 109:1043–1059.  
 598 doi:[10.1016/j.jqsrt.2007.12.015](https://doi.org/10.1016/j.jqsrt.2007.12.015).
- 599 Johnson R.E., Tucker O.J., Volkov A.N. **2016.** *Evolution of an early Titan*  
 600 *atmosphere.* Icarus 271:202–206. doi:[10.1016/j.icarus.2016.01.014](https://doi.org/10.1016/j.icarus.2016.01.014).  
 601 [arXiv:1507.08551](https://arxiv.org/abs/1507.08551).
- 602 Kim S.J., *et al.* **2011.** *Retrieval and tentative identification of*  
 603 *the 3  $\mu$ m spectral feature in Titan's haze.* PSS 59:699–704.  
 604 doi:[10.1016/j.pss.2011.02.002](https://doi.org/10.1016/j.pss.2011.02.002).
- 605 Kim S.J., *et al.* **2012.** *The three-micron spectral feature of the Saturnian*  
 606 *haze: Implications for the haze composition and formation process.* PSS  
 607 65:122–129. doi:[10.1016/j.pss.2012.02.013](https://doi.org/10.1016/j.pss.2012.02.013).
- 608 Koskinen T.T., *et al.* **2011.** *The mesosphere and lower thermosphere of*  
 609 *Titan revealed by Cassini/UVIS stellar occultations.* Icarus 216:507–534.  
 610 doi:[10.1016/j.icarus.2011.09.022](https://doi.org/10.1016/j.icarus.2011.09.022).

- 611 Krasnopolsky V.A. **2009**. *A photochemical model of Titan's atmosphere and*  
 612 *ionosphere*. Icarus 201:226–256. doi:[10.1016/j.icarus.2008.12.038](https://doi.org/10.1016/j.icarus.2008.12.038).
- 613 Krasnopolsky V.A. **2010**. *The photochemical model of Titan's atmosphere*  
 614 *and ionosphere: A version without hydrodynamic escape*. Planet. Space  
 615 Sci. 58:1507–1515. doi:[10.1016/j.pss.2010.07.010](https://doi.org/10.1016/j.pss.2010.07.010).
- 616 Krasnopolsky V.A. **2014**. *Chemical composition of Titan's atmosphere and*  
 617 *ionosphere: Observations and the photochemical model*. Icarus 236:83–91.  
 618 doi:[10.1016/j.icarus.2014.03.041](https://doi.org/10.1016/j.icarus.2014.03.041).
- 619 Lara L.M., Lellouch E., López-Moreno J.J., Rodrigo R. **1996**. *Vertical distri-*  
 620 *bution of Titan's atmospheric neutral constituents*. JGR 101:23261–23283.  
 621 doi:[10.1029/96JE02036](https://doi.org/10.1029/96JE02036).
- 622 Lavvas P., Sander M., Kraft M., Imanaka H. **2011**. *Surface chemistry and*  
 623 *particle shape: Processes for the evolution of aerosol in Titan's atmosphere*.  
 624 ApJ 80:728–739. doi:[10.1088/0004-637X/728/2/80](https://doi.org/10.1088/0004-637X/728/2/80).
- 625 Lavvas P., *et al.* **2015**. *N<sub>2</sub> state population in Titan's atmosphere*. Icarus  
 626 260:29–59. doi:[10.1016/j.icarus.2015.06.033](https://doi.org/10.1016/j.icarus.2015.06.033).
- 627 Lavvas P.P., Coustenis A., Vardavas I.M. **2008a**. *Coupling photochemistry*  
 628 *with haze formation in Titan's atmosphere, Part I: Model description*.  
 629 Planet Space Sci 56:27–66. doi:[10.1016/j.pss.2007.05.026](https://doi.org/10.1016/j.pss.2007.05.026).
- 630 Lavvas P.P., Coustenis A., Vardavas I.M. **2008b**. *Coupling photochem-*  
 631 *istry with haze formation in Titan's atmosphere, Part II: Results and*  
 632 *validation with Cassini/Huygens data*. Planet Space Sci 56:67–99.  
 633 doi:[10.1016/j.pss.2007.05.027](https://doi.org/10.1016/j.pss.2007.05.027).

- Li A. **2009**. Deep Impact as a World Observatory Event: Synergies in Space, Time, and Wavelength: Proceedings of the ESO/VUB Conference held in Brussels, Belgium, 7-10 August 2006; chap. PAHs in Comets: An Overview. Berlin, Heidelberg: Springer Berlin Heidelberg; p. 161–175. doi:[10.1007/978-3-540-76959-0\\_21](https://doi.org/10.1007/978-3-540-76959-0_21).
- López-Puertas M., *et al.* **2013**. *Large Abundances of Polycyclic Aromatic Hydrocarbons in Titan's Upper Atmosphere*. ApJ 770:132. doi:[10.1088/0004-637X/770/2/132](https://doi.org/10.1088/0004-637X/770/2/132).
- Lorenz R.D., *et al.* **2018**. *Dragonfly: A Rotorcraft Lander Concept for Scientific Exploration at Titan*. Tech. Rep. 3; Johns Hopkins APL.
- Luspay-Kuti A., *et al.* **2015**. *Experimental Constraints on the Composition and Dynamics of Titan's Polar Lakes*. EPSL 410C:75–83.
- Magee B.A., *et al.* **2009**. *INMS-derived composition of Titan's upper atmosphere: Analysis methods and model comparison*. Planet. Space Sci. 57:1895–1916. doi:[10.1016/j.pss.2009.06.016](https://doi.org/10.1016/j.pss.2009.06.016).
- Maltagliati L., *et al.* **2015**. *Titan's atmosphere as observed by Cassini/VIMS solar occultations: CH<sub>4</sub>, CO and evidence for C<sub>2</sub>H<sub>6</sub> absorption*. Icarus 248:1–24. doi:[10.1016/j.icarus.2014.10.004](https://doi.org/10.1016/j.icarus.2014.10.004). [arXiv:1405.6324](https://arxiv.org/abs/1405.6324).
- Moller C., Plesset M.S. **1934**. *Note on an approximation treatment for many-electron systems*. Phys Rev 46:618–622.
- Müller-Wodarg I., Griffith C.A., Lellouch E., Cravens T.E. **2014**. Titan. 1st edition ed.; Cambridge Planetary Science.

- 656 Newman C.E., Richardson M.I., Lian Y., Lee C. **2016**. *Simulating Ti-*  
 657 *tan's methane cycle with the TitanWRF General Circulation Model*. *Icarus*  
 658 267:106–134. doi:[10.1016/j.icarus.2015.11.028](https://doi.org/10.1016/j.icarus.2015.11.028).
- 659 Nicholson P.D., Hedman M.M., Gierasch P.J., Cassini VIMS Team. **2006**.  
 660 *Probing Saturn's Atmosphere with Procyon*. In: AAS/Division for Plane-  
 661 tary Sciences Meeting Abstracts #38; vol. 38 of *Bulletin of the American*  
 662 *Astronomical Society*. p. 555.
- 663 Nixon C.A., et al. **2013**. *Detection of Propene in Titan's Stratosphere*. *ApJL*  
 664 776:L14. doi:[10.1088/2041-8205/776/1/L14](https://doi.org/10.1088/2041-8205/776/1/L14). [arXiv:1309.4489](https://arxiv.org/abs/1309.4489).
- 665 Pendleton Y.J., Allamandola L.J. **2002**. *The Organic Refractory Material in*  
 666 *the Diffuse Interstellar Medium: Mid-Infrared Spectroscopic Constraints*.  
 667 *ApJS* 138:75–98. doi:[10.1086/322999](https://doi.org/10.1086/322999).
- 668 Pine A.S., Lafferty W.J. **1982**. *Torsional Splittings and Assignments of the*  
 669 *Doppler-Limited Spectrum of Ethane in the C-H Stretching Region*. *Journal*  
 670 *of Research of the National Bureau of Standards* 87(3):237–256.
- 671 Poling B.E., Prausnitz J.M., O'Connell J. **2007**. *The Properties of Gases*  
 672 *and Liquids*. 5th ed.; Englewood Cliffs: McGraw-Hill Professional.
- 673 Rey M., Nikitin ., Tyuterev V. **2016**. *TheoReTS An information system for*  
 674 *theoretical spectra based on variational predictions from molecular potential*  
 675 *energy and dipole moment surfaces*. *J Mol Spectrosc* 327:138–158.
- 676 Romanzin C., et al. **2016**. *An experimental study of the reactivity of*  
 677 *CN<sup>-</sup> and C<sub>3</sub>N<sup>-</sup> anions with cyanoacetylene (HC<sub>3</sub>N)*. *Icarus* 268:242–252.  
 678 doi:[10.1016/j.icarus.2015.12.001](https://doi.org/10.1016/j.icarus.2015.12.001).



- 679 Rothman L.S., *et al.* **2013.** *The HITRAN2012 molecular spectroscopic database.* J Quant Spectrosc Radiat Transfer 130:4–50.  
680  
681 doi:[10.1016/j.jqsrt.2013.07.002](https://doi.org/10.1016/j.jqsrt.2013.07.002).
- 682 Sandford S.A., *et al.* **1991.** *The interstellar C-H stretching band near 3.4 microns - Constraints on the composition of organic material in the diffuse interstellar medium.* ApJ 371:607–620. doi:[10.1086/169925](https://doi.org/10.1086/169925).  
683  
684
- 685 Sharpe S.W., *et al.* **2004.** *Gas-Phase Databases for Quantitative Infrared Spectroscopy.* Appl Spectrosc 58:1452–1461.  
686  
687 doi:[10.1366/0003702042641281](https://doi.org/10.1366/0003702042641281).
- 688 Tan S.P., Kargel J.S., Marion G.M. **2013.** *Titan's atmosphere and surface liquid: New calculation using Statistical Associating Fluid Theory.* Icarus  
689  
690 222:53–72. doi:[10.1016/j.icarus.2012.10.032](https://doi.org/10.1016/j.icarus.2012.10.032).
- 691 Tan S.P., *et al.* **2015.** *Titans liquids: Exotic behavior and its implications on global fluid circulation.* Icarus 250(0):64 – 75.  
692  
693 doi:<http://dx.doi.org/10.1016/j.icarus.2014.11.029>.
- 694 Turtle E.P., *et al.* **2019.** *Dragonfly: In Situ Exploration of Titan's Organic Chemistry and Habitability.* In: Lunar and Planetary Science Conference.  
695  
696 Lunar and Planetary Science Conference; p. 2888.
- 697 Vinatier S., *et al.* **2010.** *Analysis of Cassini/CIRS limb spectra of Titan acquired during the nominal mission. I. Hydrocarbons, nitriles and CO<sub>2</sub> vertical mixing ratio profiles.* Icarus 205:559–570.  
698  
699  
700 doi:[10.1016/j.icarus.2009.08.013](https://doi.org/10.1016/j.icarus.2009.08.013).

701 Vinatier S., *et al.* **2015**. *Seasonal variations in Titan's middle atmosphere*  
702 *during the northern spring derived from Cassini/CIRS observations*. Icarus  
703 250:95–115. doi:[10.1016/j.icarus.2014.11.019](https://doi.org/10.1016/j.icarus.2014.11.019).

704 Yoon Y.H., *et al.* **2014**. *The role of benzene photolysis in Titan haze forma-*  
705 *tion*. Icarus 233:233–241. doi:[10.1016/j.icarus.2014.02.006](https://doi.org/10.1016/j.icarus.2014.02.006).

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