



HAL
open science

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

T. Cours, D. Cordier, B. Seignovert, L. Maltagliati, Ludovic Biennier

► To cite this version:

T. Cours, D. Cordier, B. Seignovert, L. Maltagliati, Ludovic Biennier. The 3 . 4 μ m absorption in Titan's stratosphere: Contribution of ethane, propane, butane and complex hydrogenated organics. *Icarus*, 2020, 339, pp.113571. 10.1016/j.icarus.2019.113571 . hal-02440192

HAL Id: hal-02440192

<https://hal.science/hal-02440192>

Submitted on 12 Feb 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

- A strong and unexplained absorption at 3.4 μm in Titan's atmosphere has been revealed by solar occultations by the instrument CASSINI/VIMS
- Several simple molecules (like CH_4 or C_2H_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 μm absorption of the Titan's stratosphere: contribution of ethane, propane, butane and complex hydrogenated organics

T. Cours^a, D. Cordier^a, B. Seignovert^{a,b}, L. Maltagliati^c, L. Biennier^d

^a*Université de Reims Champagne Ardenne, CNRS, GSMA UMR 7331, 51097 Reims, France*

^b*Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Dr, MS 183-501, Pasadena, CA 91109, USA*

^c*Nature Astronomy, Springer Nature, 4 Crinan Street, N1 9XW London, UK*

^d*Institut de Physique de Rennes, Département de Physique Moléculaire, Astrophysique de Laboratoire, UMR CNRS 6251, Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex – France*

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 μm 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

Email address: thibaud.cours@univ-reims.fr (T. Cours)

Amorphous Carbons (HACs) are the most plausible candidates because they are rich in C-H bonds. PAHs signature have already been detected above ~ 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

1 **1. Introduction**

2 Titan is an extraordinary object among the planets and satellites of
3 the solar system. Its thick atmosphere, mainly composed of nitrogen and
4 methane, harbors a complex photochemistry producing organic compounds
5 that participate to the formation of haze which produces its typical or-
6 ange/brown color. Due to its unique and exotic properties, Titan's atmo-
7 sphere remains a very active field of research in investigating the possible
8 origin and main properties (Johnson *et al.*, 2016; Charnay *et al.*, 2014; New-
9 man *et al.*, 2016). Its composition can be modeled by complex chemical
10 network (Krasnopolsky, 2014; Lavvas *et al.*, 2015), but also by laboratory
11 experiments (Bourgalais *et al.*, 2016; Romanzin *et al.*, 2016) to match the
12 observations made by Cassini's instruments (Vinatier *et al.*, 2015; Coustenis
13 *et al.*, 2016; Bellucci *et al.*, 2009). In Bellucci *et al.* (2009), the authors raised
14 an issue about the CH₄ 3.3 μm band.

15 In 2006, during Cassini's 10th flyby of Titan (T10), Bellucci *et al.* (2009) ob-
16 served features in CH₄ 3.3 μm band with the Visible and Infrared Mapping
17 Spectrometer (VIMS). VIMS is an imaging spectrometer onboard the Cassini
18 spacecraft. This instrument is composed of a visible channel (0.3 – 1.05 μm)
19 and a infrared channel (0.89 – 5.1 μm). The FWHM of the 256 infrared
20 spectral pixels are in the range 13 - 20 nm. VIMS can be used in different
21 observation modes corresponding to nadir, limb and occultation geometry.
22 Our study use the latter mode. More details can be found in Maltagliati
23 *et al.* (2015). Bellucci *et al.* (2009) tentatively attributed the observed fea-
24 tures in CH₄ 3.3 μm band to solid state organic compounds, similar to those
25 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 μm 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 μm spectral
35 features to the aliphatic C-H stretching bands of solid-state hydrocarbons,
36 such as C_5H_{12} , C_6H_{12} , C_6H_{14} and C_7H_{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 3th 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[†], for CH₃CN, C₅H₁₂ and C₆H₁₂. 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_{triple} (in K)	P_{triple} (in bar)
Ethane	C ₂ H ₆	91.0	1.1×10^{-5}
Methane	CH ₄	90.7	1.2×10^{-1}
Methylcyanide	CH ₃ CN	229.3	2.2×10^{-3} *
Pentane	C ₅ H ₁₂	143.5	3.9×10^{-7} *
Cyclohexane	C ₆ H ₁₂	279.7	5.3×10^{-2} *

[†]<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 : CH₄ , CH₃D, CO,
 53 CO₂, C₂H₂, C₂H₄, C₂H₆, HCN and N₂. 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 μm 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 C₂H₆ spectral lines
 60 in major databases (HITRAN and GEISA), Maltagliati *et al.* (2015) inter-
 61 preted the strong absorption band centered at 3.4 μm as the effect of ethane.
 62 These authors also tentatively attribute the narrow absorption at 3.28 μm

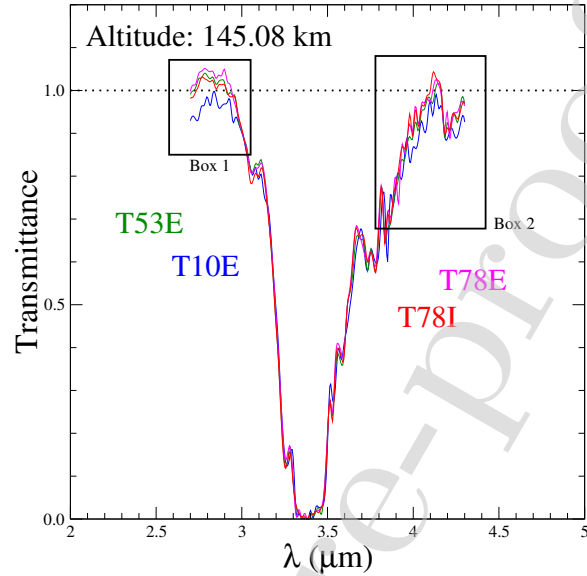


Figure 1: Transmittance curves derived from solar occultations T10E, T53E, T78E and T78I studied by [Maltagliati *et al.* \(2015\)](#). Altitude interpolations, at 145 km, have been performed to allow easy comparisons. Boxes delineate domains where data are significantly noisy.

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 ~ 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

72 or in aerosols particles. In this paper, we try to disentangle the problematic
73 attribution of this strong absorption around $3.4 \mu\text{m}$. In Fig 1, transmittances
74 corresponding to box 1 and box 2 are clearly too noisy to allow a clear anal-
75 ysis. In this work, we specifically focus our efforts on the highest absorption
76 spectral range, *i.e.* between 3.3 and $3.5 \mu\text{m}$. In Sec. 2 we examine, in the
77 light of an advanced thermodynamic model, the possibility of the existence
78 of hydrocarbon ices in the stratosphere of Titan, as proposed by Kim *et al.*
79 (2011). In Sec. 3 and 4 we revisit the absorption of gases in the $3.4 \mu\text{m}$
80 spectral region while in Sec. 5 we discuss the possible presence of PAHs
81 or more complex polyaromatic hydrocarbons like Hydrogenated Amorphous
82 Carbons (HACs). In Sec. 6, we further discuss these issues and present our
83 conclusions.

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

85 An explanation for the nature of Titan's $3.4 \mu\text{m}$ absorption was put for-
86 ward by Kim *et al.* (2011) who could reproduce the VIMS solar occultations
87 by using hydrocarbon ices like C_2H_6 , CH_4 , CH_3CN , C_5H_{12} and C_6H_{12} ices.
88 However, the real existence of such ices in the stratosphere of Titan needs
89 to be discussed. Indeed, as mentioned by Kim *et al.* (2011), above 130 km
90 (the lowest altitude explored by these authors) the temperature remains in
91 $160 - 190 \text{ K}$ interval while the pressure decreases below $5 \times 10^{-3} \text{ bar}$. A
92 look at Table 1, in which we have gathered the triple points coordinates of
93 involved species, shows that at least C_2H_6 , CH_4 and C_5H_{12} should not be in
94 solid form at these relatively high temperatures. In order to investigate more

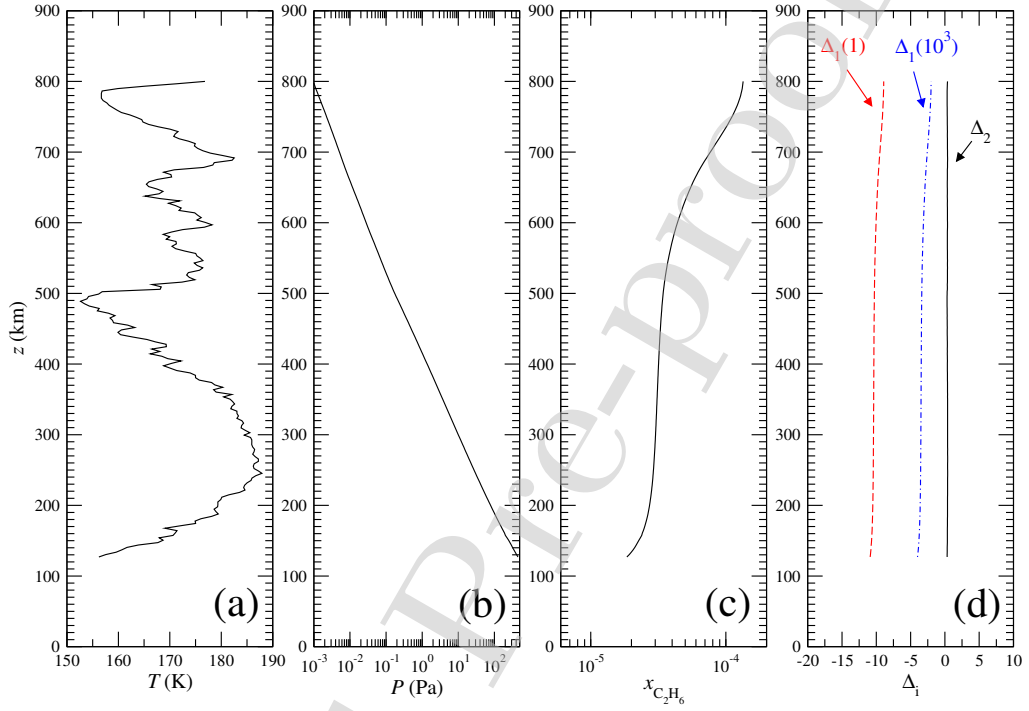


Figure 2: Panels (a) and (b) stand respectively for the temperature and pressure profiles, provided by HASI instruments, between the altitudes 127 km and 800 km in the atmosphere of Titan (Fulchignoni *et al.*, 2005). Panel (c) represents the molar fraction of ethane as computed by Lavvas *et al.* (2008a,b). In panel (d) the thermodynamic quantities Δ_1 and Δ_2 (defined in the text by Eq. (1) and Eq. (2)) for ethane. We recall that Δ_1 and Δ_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:

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

96 where y_i is the mole fraction of the compound i at equilibrium, in the vapor,
 97 and Γ_i^{vap} is the activity coefficient of the considered species. The second
 98 introduced term is written as :

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

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

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

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

110 In Eq. (1) the activity coefficient Γ_i^{vap} quantifies the *degree of ideality*
 111 of the considered gas mixture. When $\Gamma_i^{\text{vap}} \sim 1$ the system has an ideal
 112 behavior, *i.e.* all the molecules of the same species and those of different
 113 species interact with the same intensity. In our context, for all the molecules
 114 listed in Table 1, we found the Γ_i^{vap} 's very close to unity, whatever the alti-
 115 tude. This indicates an ideal behavior of the gases, which is not a surprise at
 116 densities provided by HASI measurements (Fulchignoni *et al.*, 2005). Prac-
 117 tically, 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, C_2H_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 CH_3CN , Lara *et al.* (1996) (see their Fig. 10 p. 279) re-
125 ported abundances, derived from ground-based millimeter-wave observations
126 (Bézar *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 CH_3CN
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 μm 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 λ 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 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

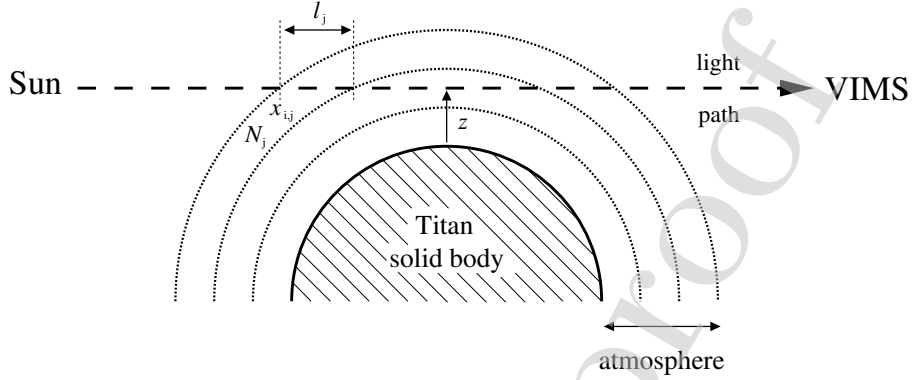


Figure 3: A schematic representation of our “onion-skin” radiative transfer model, used in this paper and suitable for the analysis of Titan’s solar occultations data published by [Maltagliati *et al.* \(2015\)](#). In the text, the term *altitude* refers to the parameter called “*z*” in this figure. 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 : CH_4 , CH_3D , CO , C_2H_2 , C_2H_4 ,
 167 C_2H_6 , H_2O , C_6H_6 and 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 CH_4 , C_2H_2 , C_2H_4 ,
 173 C_2H_6 , C_6H_6 and HCN vertical mixing ratio profiles come from photochemical
 174 models developed by [Krasnopolsky \(2014\)](#). The abundance of deuterated

175 methane (CH_3D) with respect to the methane has been kept constant with
 176 a $\text{CH}_3\text{D}/\text{CH}_4$ ratio of about 5.3×10^{-4} (Bézard *et al.*, 2007). Concerning
 177 water, we performed tests including molar fractions corresponding to the
 178 highest value given by Coustenis *et al.* (1998). Finally, the abundance of CO
 179 has been taken from Flasar *et al.* (2005).

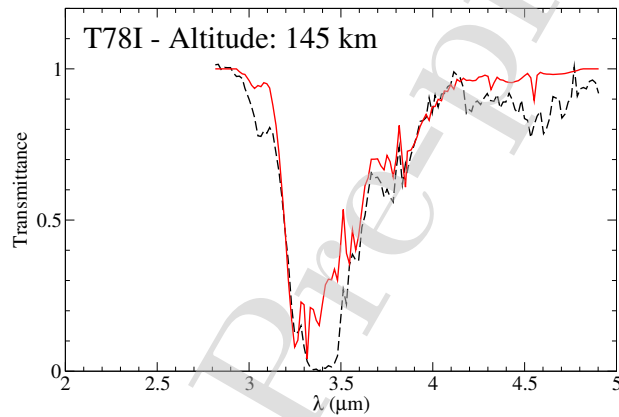


Figure 4: Comparison between observed transmittance (dashed line) acquired during occultation T78I at the altitude of 145 km (Maltagliati *et al.*, 2015), and the computed transmittance due to our FG composition: with only CH_4 , CH_3D , CO, C_2H_2 , C_2H_4 , C_2H_6 , H_2O , C_6H_6 and HCN. For C_2H_6 , only spectral lines provided by HITRAN have been taken into account.

180 The spectral data of CO, C_2H_2 , H_2O and HCN were mainly taken in HI-
 181 TRAN¹ (Rothman *et al.*, 2013) and GEISA² (Jacquinet-Husson *et al.*, 2008).
 182 For CH_4 , CH_3D and C_2H_4 we used the up-to-date theoretical line lists com-
 183 puted by Rey *et al.* (2016) and available at the Theoretical Reims-Tomsk

¹<http://hitran.org/>

²<http://www.pole-ether.fr/geisa/>

184 Spectral database³. 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 μm band are for the frequencies 3064.0917
190 cm^{-1} (3.26 μm) and 3064.0949 cm^{-1} (3.26 μm) (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 C_6H_6 , we find that the benzene is
194 a minor absorber around 3.26 μm .

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 ~ 50 km and ~ 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 site⁴. 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

³<http://theorets.tsu.ru>

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

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

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

213 4. The possible absorption of ethane, propane and butane around 214 $3.4 \mu\text{m}$

215 4.1. Ethane

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

231 not available. Thus, in the latter case, we have neglected the temperature
232 corrections of the intensities. The contribution to the absorption around 3.4
233 μm , of ethane alone, is plotted in Fig. 5(a).

234 Unfortunately, Pine & Lafferty (1982) did not include ethane PQ-branches
235 which should have a non-negligible contribution in the domaine of interest.
236 To tackle the issue, we used an empirical pseudo-line list **based on the cross-**
237 **section measurements** developed by Harrison *et al.* (2010) (hereafter H10
238 dataset) and freely available on the web⁵. Compared to the absorption ob-
239 tained with PL82 spectral lines, the effect of ethane is significantly enhanced
240 by the use of this more comprehensive list (Fig. 5.b). If both, the PL82
241 and H10 spectral data, are simultaneously included in our model (Fig. 5.c),
242 the actual effect of PL82 is not noticeable. Finally, if we merge PL82 and
243 H10 spectral lines sets, with those employed for our FG composition model,
244 the disagreement with Cassini/VIMS observations is considerably reduced
245 (Fig. 5.d). This clearly demonstrates the prominent role of ethane, as an
246 absorber, at wavelengths around 3.4 μm . Nonetheless, the simulated trans-
247 mittance remains significantly above the observed one. This fact suggests
248 the presence of other absorbers, possibility which we discuss further in next
249 paragraphs.

250 4.2. Propane

251 According to photochemical models (Lavvas *et al.*, 2008a,b; Krasnopol-
252 sky, 2014), propane should also be produced in Titan's upper-atmosphere.
253 This C_3 hydrocarbon has been detected by several Cassini's instruments:

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

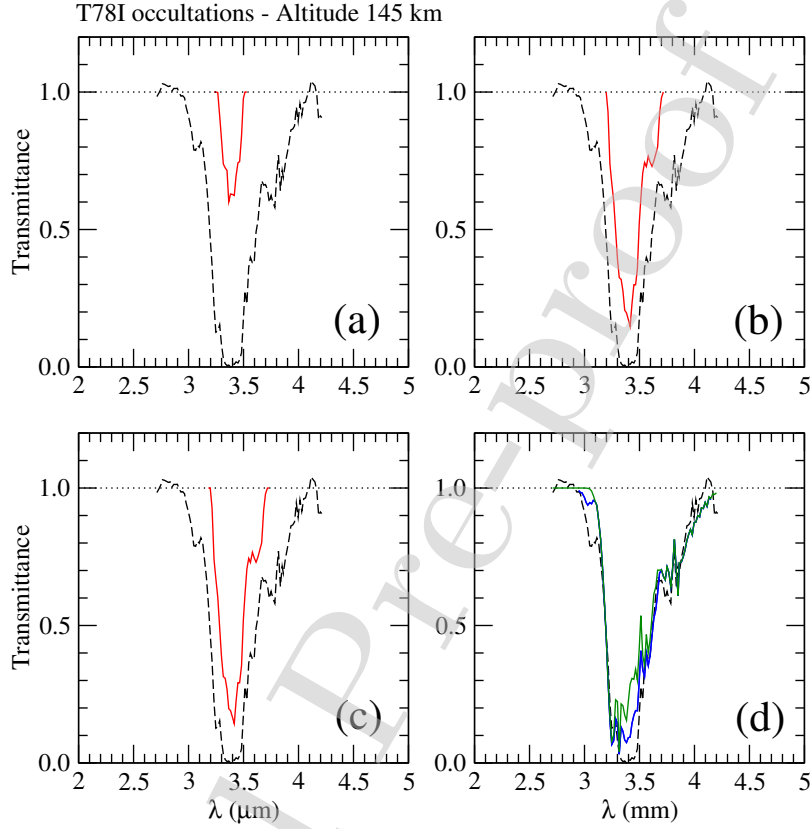


Figure 5: Comparison between simulated transmittances and VIMS for the T78I occultation data (Maltagliati *et al.*, 2015). Observational data are in dashed line, the altitude is 145 km. This figure shows the transmittance of C_2H_6 using: (a) only Pine & Lafferty (1982) spectral lines (red), (b) only 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).

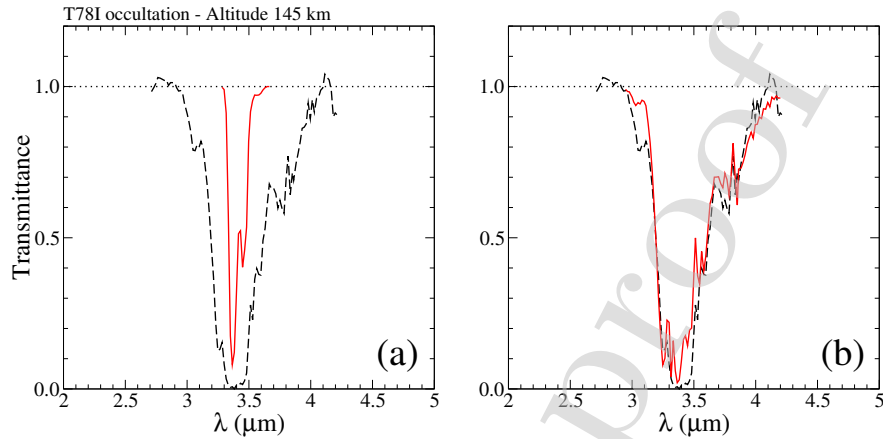


Figure 6: Occultation T78I at 145 km (observed transmittance in dash line) : (a) Absorption due to propane alone, (b) computed absorption using our FG composition complemented by propane (ethane is not taken into account).

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 μm 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 web⁶). 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

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

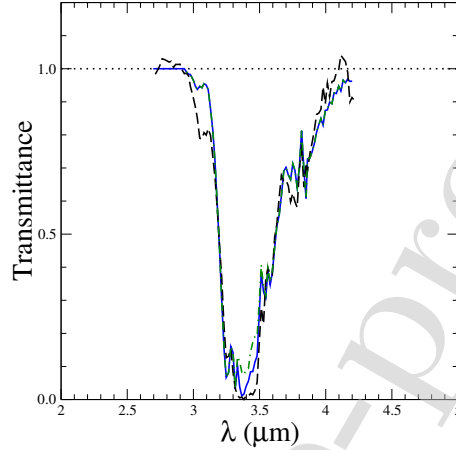


Figure 7: Dashed line : T87I observations, dot-dashed line: our computation taking into account gases of our FG composition and ethane (including pseudo-lines and Lafferty data), solid line: the same simulation including propane pseudo-lines list **based on the cross-section measurements of Harrison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

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

268 4.3. Butane

269 Butane has not yet been detected, in the atmosphere of Titan. The pres-
 270 ence of butane is predicted by photochemical models (Krasnopolsky, 2009,
 271 2010, 2014). The quantity of butane should be lower than what it is measured
 272 and computed for propane. Available models indicate a butane mixing ratio
 273 about four order of magnitude smaller than what Krasnopolsky (2014) ob-
 274 tained for propane. Since no data concerning butane were found in HITRAN

275 and GEISA databases, we used cross-sections provided by the NIST⁷. Ac-
276 cording to this approach and taking vertical profile provided by Krasnopolsky
277 (2014), we have checked that butane has no detectable influence on the 3.4
278 μm atmospheric transmittance.

279 4.4. Conclusion about ethane, propane, butane and others linear hydrocarbon

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

289 5. The absorption due to Polycyclic Aromatic Hydrocarbons and 290 Hydrogenated Amorphous Carbons

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

⁷<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 ⁸. In our calculations the line widths
321 were fixed to a reasonable value of 30 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 cm^{-1} – 3570 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
337 cm^{-1} , 2 cm^{-1} and 3 cm^{-1} . This way, we identified 52 lines that correspond to
338 both theoretical and laboratory determinations with a tolerance of 1 cm^{-1} ,
339 108 when is increased to 2 cm^{-1} and 144 when the tolerance is increased to
340 3 cm^{-1} . Consequently, we formed the log ratio $I_{\text{th}}/I_{\text{exp}}$ for each identified

⁸<http://www.astrochem.org/pahdb/>

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

357 5.2. Hydrogenated Amorphous Carbons

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

366 spectrum parameters given in Table 1 of [Dartois *et al.* \(2007\)](#). We do not
 367 consider HACs with nitrogen (a-C:H:N) because the vibrational modes con-
 368 taining N are not present in 3.3 – 3.5 μm band ([Dartois *et al.*, 2005](#)). As
 369 with PAHs, we also introduce a correction factor $\alpha_{i,k}$ on the intensities $I_{i,k}$,
 370 with the same meaning for index i and k than the index in Eq. (4), tak-
 371 ing into account for an uncertainty source: the temperature dependence of
 372 the intensities $I_{i,k}$. Indeed, the intensities coming from the study of IRAS
 373 08572+3915 spectrum the temperature must be different than that in Titan’s
 374 stratosphere. In [Dartois *et al.* \(2007\)](#) no distinction was made between the
 375 different HACs but just between the vibration modes. Consequently, in our
 376 model for HACs we omit index i . Thus, our correction factor $\alpha_{i,k}$ becomes
 377 α_k and the intensities are I_k . In first approach, as with PAHs, the correction
 378 factors α_k are independent of the spectral lines. Consequently, we define a
 379 product $\beta_j = x_j\alpha$.

380 5.3. Results

381 For PAHs, $x_{i,j}$ is the molar fraction of PAHs number i with respect to
 382 the C_6H_6 abundance profile in layer j . As a first approximation, the vertical
 383 profile of this molar fraction of PAHs number i vs the C_6H_6 (used as proxy)
 384 abundance and the vertical profile of the molar fraction of HACs were kept
 385 constant. Thus for PAHs and HACs respectively, $\beta_{i,j} = x_{i,j}\alpha_i$ turns into
 386 $\beta_i = x_i\alpha_i$ and $\beta_j = x_j\alpha$ turns into $\beta = x\alpha$. Considering the uncertainties
 387 on PAHs and HACs intensities, we have fitted, respectively, the product
 388 $\beta_i = x_i\alpha_i$ and not x_i alone, and $\beta = x\alpha$ and not x , to get the best fit to
 389 occultation data. However, the resulting values do not provide information
 390 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 β_i , values in the range of $(4.75 \times 10^{-4} - 3.32) \times$ molar
 394 fraction of C_6H_6 . Concerning the HACs, the best fit for β 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.

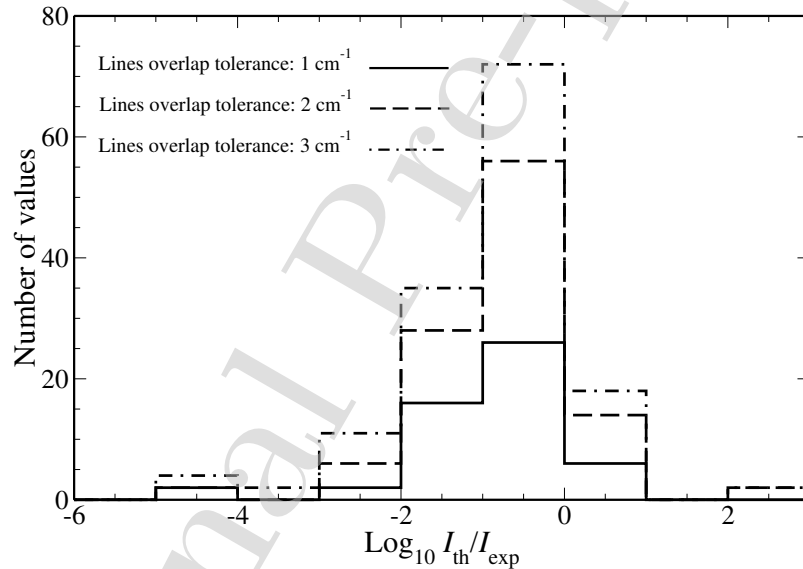


Figure 8: Histograms of the log ratios $I_{\text{th}}/I_{\text{exp}}$ for the Ames database PAHs for which theoretical and experimental spectral lines features determinations are available. We have considered 3 cases: (1) the wavelengths of theoretical and experimental match with a maximum tolerance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

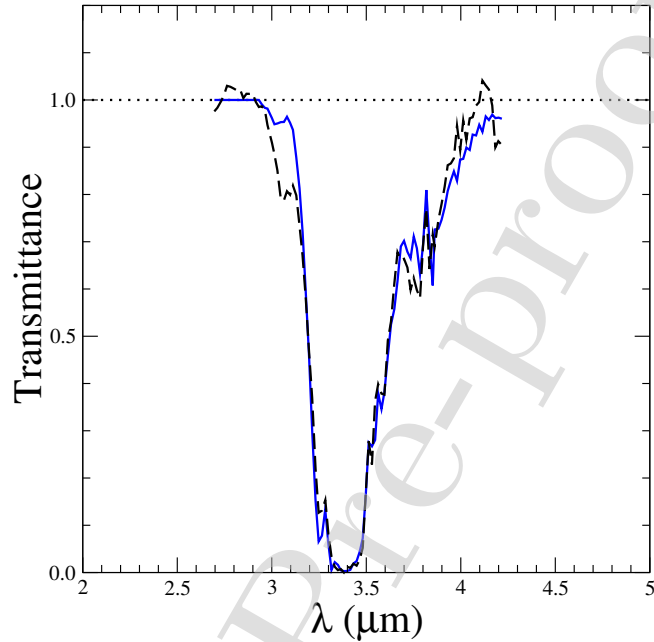


Figure 9: Computed transmittance (solid line) at 145 km during occultation T78I (observed transmittance in dash line), the radiative transfert model takes into account all studied gases plus the best fit of 118 PAHs (from NASA Ames database) and HACs (from [Dartois *et al.* \(2007\)](#)).

398 6. Discussion and Conclusion

399 6.1. Discussion

400 Observations of Saturn's stratospheric auroral regions ([Guerlet *et al.*, 2015](#)) seem to underline the remarks made on the features observed in Ti-
 401 tan's atmosphere. Indeed, spectral signatures of benzene and aerosols in the
 402 range 680-900 cm^{-1} and 1360-1440 cm^{-1} have been observed with CIRS on
 403

404 board Cassini, around the 80°S. In particular, vibrational modes in aliphatic
405 and aromatic hydrocarbons were observed revealing the presence of PAHs or
406 HACs in stratosphere of Saturne (Guerlet *et al.*, 2015). Moreover, as men-
407 tioned, VIMS observations of Procyon’s occultation through Saturn’s atmo-
408 sphere around the 55°N, reported by Nicholson *et al.* (2006) and discussed
409 by Bellucci *et al.* (2009), show similar features in the 3.4 μm band to those
410 observed in our study. Nevertheless, the observations reveal slight differences
411 with the Titan’s 3.4 μm band spectra. But these differences could be due
412 to a lower amount of nitrogen compounds in Saturn’s atmosphere (Bellucci
413 *et al.*, 2009). Thus, the PAHs and HACs in Titan’s atmosphere could be
414 slightly different from those in Saturn’s atmosphere.

415 Our study of 3.4 μm band observed by solar occultation at 145 km of
416 altitude suggests the presence of aromatic molecules like PAHs and more
417 complex like HACs at low altitudes. Some insights can be gained by exam-
418 ining the results from laboratory experiments. Dartois *et al.* (2004, 2005)
419 synthesized HACs (called a-C:H in these references) by ultraviolet photolysis
420 of methane (Dartois *et al.*, 2004) and other hydrocarbons and nitrogen com-
421 pounds to form a-C:H:N compounds (Dartois *et al.*, 2005) by UV radiation
422 with wavelengths shorter than 120 nm in the EUV domain. Then, they made
423 spectral Infra-Red (IR) analysis of the residues. The aim of these previous
424 studies was to explain the spectral features observed in the ISM. Due to the
425 presence of methane, others hydrocarbons and nitrogen compounds as well
426 as the ultraviolet radiation in EUV domain going down to 600 km (Yoon
427 *et al.*, 2014), the same HACs production process as in the ISM could occur
428 in the Titan’s upper atmosphere.

429 But this explanation is not completely satisfactory, mainly because we
430 should find absorptions in the wavelength range $3.38\ \mu\text{m}$ – $3.48\ \mu\text{m}$ in **high** al-
431 titude occultation spectra which is not the case (Courtin *et al.*, 2015). In this
432 latter reference, the authors do not observe strong features (in extinction)
433 in this wavelength range above 500 km but rather below 480 km (Courtin
434 *et al.*, 2015, Fig. 2). The authors computed the ratio extinction coefficient
435 at $3.33\ \mu\text{m}$ / extinction coefficient at $3.38\ \mu\text{m}$, the wavelength at $3.33\ \mu\text{m}$ be-
436 ing characteristic of aromatic C-H stretching and the wavelength at $3.38\ \mu\text{m}$
437 characteristic of aliphatic C-H stretching. Thus, this ratio is function of the
438 ratio between the aromatic and aliphatic components in the haze particles.
439 This ratio is about 3 at 700 km and decreases to about 0.5 below 300 km.
440 Then the conclusion of Courtin *et al.* (2015) is a growth of molecules from
441 PAHs to more complex organics by particle-aging and coating process when
442 the altitude decreases. So, even if the explanation in Dartois *et al.* (2004,
443 2005) about the HACs production in the ISM is not completely relevant for
444 Titan's upper atmosphere, it is possible to have HACs at low altitude, by
445 particle-aging and coating process. This process was also studied in labora-
446 tory (Carrasco *et al.*, 2018) by ultraviolet irradiation of analogs of Titan's
447 thermosphere aerosols (and Couturier-Tamburelli *et al.* (2018)). Carrasco
448 *et al.* (2018) analyzed the absorption peaks of residues and their time evolu-
449 tion. They found shifts and modifications of vibrational signatures reflecting
450 aerosols transformation during the irradiation. The observed spectra after
451 24 h of irradiation appear to tend toward Titan's spectra observed in VIMS
452 spectra at altitude 200 km. The conclusion of Carrasco *et al.* (2018) is that a
453 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*

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

484 6.2. Conclusion

485 To conclude, the present study was to explain the strong absorption
486 around 3.4 μm observed in the occultation spectra by VIMS at low altitudes
487 typically lower than 450 km. We opted for the altitude 145 km which offers a
488 good compromise : at lower altitudes, the stronger absorptions damp spectral
489 features and at higher altitudes, the absorptions are too weak to be extracted
490 from the signal. As a first step in our radiative transfer modeling, we have
491 included 9 molecules following Maltagliati *et al.* (2015) : CH_4 , CH_3D , CO ,
492 C_2H_2 , C_2H_4 , C_2H_6 , H_2O , C_6H_6 and HCN . This composition leads to a poor
493 reproduction of the observed transmittance curve. The disagreement was re-
494 duced by including C_2H_6 spectroscopic data as the data coming from Pine &
495 Lafferty (1982) or the more exhaustive data, but empirical pseudo-line, com-
496 ing from Harrison *et al.* (2010). This way, the agreement has been improved,
497 but the simulated transmittance remained above the observed one. The in-
498 clusion of propane improved the result but there was still a lack of efficient
499 absorbers around 3.4 μm . Knowing that spectral signatures around 3.4 μm
500 are present in the ISM and identified as PAHs or HACs, we have considered
501 these complex hydrocarbon compounds in our model as possible absorbers
502 in the Titan's atmosphere at about 145 km of altitude. The fit of abundance
503 of PAHs and HACs, taking into account some uncertainty by means of a

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

511 References

- 512 Arking A., Grossman K. **1972**. *The Influence of the line Shape and Band*
513 *Structure on Temperature in Planetary Science*. J Atmos Sci 29:937.
- 514 Becker L., Bunch T.E. **1997**. *Fullerenes, fulleranes and PAHs*
515 *in the Allende meteorite*. Meteoritics and Planetary Science 32.
516 doi:[10.1111/j.1945-5100.1997.tb01292.x](https://doi.org/10.1111/j.1945-5100.1997.tb01292.x).
- 517 Becker L., Glavin D.P., Bada J.L. **1997**. *Polycyclic aromatic hydrocarbons*
518 *(PAHs) in Antarctic Martian meteorites, carbonaceous chondrites, and po-*
519 *lar ice* 61:475–481. doi:[10.1016/S0016-7037\(96\)00400-0](https://doi.org/10.1016/S0016-7037(96)00400-0).
- 520 Bellucci A., *et al.* **2009**. *Titan solar occultation observed by Cassini/VIMS:*
521 *Gas absorption and constraints on aerosol composition*. Icarus 201:198–
522 216. doi:[10.1016/j.icarus.2008.12.024](https://doi.org/10.1016/j.icarus.2008.12.024).
- 523 Bézard B., Marten A., Paubert G. **1993**. *Detection of acetonitrile on Titan*.
524 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 C₄N₂: 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. Labo-*
569 *ratory characterisation and astrophysical relevance.* A&A 432:895–908.
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 aro-*
572 *matic versus aliphatic content of interstellar HACs.* A&A 463:635–640.
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 atmo-*
575 *sphere.* 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*
577 *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 Radia-*
579 *tive Transfert in Nonhomogeneous Atmospheres.* J Atmos Sci 49:2139.
- 580 Fulchignoni M., *et al.* **2005.** *In situ measurements of the phys-*
581 *ical characteristics of Titan's environment.* Nature 438:785–791.
582 doi:[10.1038/nature04314](https://doi.org/10.1038/nature04314).
- 583 Gross J., Sadowski G. **2001.** *Perturbed-Chain SAFT: An Equation of State*
584 *Based on a Perturbation Theory for Chain Molecules.* Ind Eng Chem Res
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*
587 *condensed haze.* Nat. Commun. 4:1648. doi:[10.1038/ncomms2649](https://doi.org/10.1038/ncomms2649).

- 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 (C3H8) in the 3 μ 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 (C2H6) in the 3 μ 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 μ 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**. *N₂ 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).

- 634 Li A. **2009**. Deep Impact as a World Observatory Event: Synergies in
635 Space, Time, and Wavelength: Proceedings of the ESO/VUB Conference
636 held in Brussels, Belgium, 7-10 August 2006; chap. PAHs in Comets: An
637 Overview. Berlin, Heidelberg: Springer Berlin Heidelberg; p. 161–175.
638 doi:[10.1007/978-3-540-76959-0_21](https://doi.org/10.1007/978-3-540-76959-0_21).
- 639 López-Puertas M., *et al.* **2013**. *Large Abundances of Polycyclic Aro-*
640 *matic Hydrocarbons in Titan's Upper Atmosphere.* ApJ 770:132.
641 doi:[10.1088/0004-637X/770/2/132](https://doi.org/10.1088/0004-637X/770/2/132).
- 642 Lorenz R.D., *et al.* **2018**. *Dragonfly: A Rotorcraft Lander Concept for Sci-*
643 *entific Exploration at Titan.* Tech. Rep. 3; Johns Hopkins APL.
- 644 Luspay-Kuti A., *et al.* **2015**. *Experimental Constraints on the Composition*
645 *and Dynamics of Titan's Polar Lakes.* EPSL 410C:75–83.
- 646 Magee B.A., *et al.* **2009**. *INMS-derived composition of Titan's upper at-*
647 *mosphere: Analysis methods and model comparison.* Planet. Space Sci.
648 57:1895–1916. doi:[10.1016/j.pss.2009.06.016](https://doi.org/10.1016/j.pss.2009.06.016).
- 649 Maltagliati L., *et al.* **2015**. *Titan's atmosphere as observed by Cassini/VIMS*
650 *solar occultations: CH₄, CO and evidence for C₂H₆ absorption.* Icarus
651 248:1–24. 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).
- 652 Moller C., Plesset M.S. **1934**. *Note on an approximation treatment for many-*
653 *electron systems.* Phys Rev 46:618–622.
- 654 Müller-Wodarg I., Griffith C.A., Lellouch E., Cravens T.E. **2014**. Titan. 1st
655 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⁻ and C₃N⁻ anions with cyanoacetylene (HC₃N)*. *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 222:53–72. doi:[10.1016/j.icarus.2012.10.032](https://doi.org/10.1016/j.icarus.2012.10.032).
689
690
- 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. Lunar and Planetary Science Conference; p. 2888.
695
696
- 697 Vinatier S., *et al.* **2010.** *Analysis of Cassini/CIRS limb spectra of Titan acquired during the nominal mission. I. Hydrocarbons, nitriles and CO₂ 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).

706 **Acknowledgement**

707 We thank Laurence Regalia, Bruno Bézard, Walter Lafferty and Jean
708 Vander Auvera for scientific discussion. We are grateful to Christiaan Boersma
709 for his kind technical help in using the NASA Ames PAH database. Finally,
710 we warmly thank Vladimir Krasnopolsky for providing us with vertical **pro-**
711 **files** of organics.