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# One dimension photochemical models in global mean conditions in question: Application to Titan

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1           **One dimension photochemical models in**  
2                   **global mean conditions in question:**  
3                           **application to Titan**

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18 **Please send Editorial Correspondence to:**  
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28 **ABSTRACT**

29 Observational data of Titan's atmosphere composition, gathered in particular  
30 by the Cassini mission, allow accessing latitudinal, longitudinal and temporal  
31 variations of the altitudinal profiles of several species. While 1D models are  
32 a powerful tool to gain insight into the chemistry occurring in Titan's atmo-  
33 sphere, they cannot capture the four-dimensional nature of these processes at  
34 the same time. However, due to the large extent of the atmosphere and the  
35 complexity of chemistry, global 2D and 3D models with the chemical complex-  
36 ity of 1D models do not exist yet. On the way of developing a 2D photochem-  
37 ical model of Titan, including the very complex chemical schemes used in 1D  
38 models and also taking latitudinal variations into account, we developed an ul-  
39 traviolet radiative transfer model to compute the actinic flux in a 2D geometry.  
40 We found that photolysis rates calculated in classical plane-parallel models to  
41 derive the rates in mean conditions give results notably different from a model  
42 that calculates the mean rates with a 2D geometry. We demonstrate that the  
43 introduction of the 2D geometry affects significantly the density profiles on  
44 both neutrals and ions, especially on nitriles. As a consequence, we advocate  
45 using radiative transfer model in 2D geometry from now on to interpret the  
46 wide diversity of observational data about Titan's atmosphere (pending the  
47 emergence of 2D models with complex chemical schemes).

48 *Keywords:* Titan ; Photochemistry ; Atmospheres ; Ionospheres

## 49 1 Introduction

50 The atmosphere of Titan is a very complex system. Photolysis by solar pho-  
51 tons and ionization by Saturn magnetospheric electrons of the two major  
52 compounds, molecular nitrogen ( $N_2$ ) and methane ( $CH_4$ ), are the starting  
53 point of a very rich chemistry, enhanced by the surface-atmosphere interac-  
54 tion, influxes from the Enceladus torus (Hartogh et al., 2011; Moreno et al.,  
55 2012; Dobrijevic et al., 2014; Lara et al., 2014; Teanby et al., 2018) and in-  
56 terplanetary dust particles (Moses and Poppe, 2017). This efficient chemistry  
57 produces aerosols as the end products, which sediment down to the surface,  
58 contributing to the radiative budget of the atmosphere and serving as nu-  
59 cleation particles in the lower stratosphere. Modeling Titan’s atmosphere is  
60 very challenging. In particular, from the chemical point of view, it is nec-  
61 essary to include numerous species and reactions in atmospheric models to  
62 study the coupling of neutral, cationic and anionic species composed of vari-  
63 ous elements like carbon, hydrogen, oxygen, nitrogen and sulfur, throughout  
64 the extended atmosphere (see for instance the recent models of Krasnopolsky  
65 (2014), Hickson et al. (2014), Mukundan and Bhardwaj (2018), Loison et al.  
66 (2019) and Vuitton et al. (2019)). Continuous detections of new molecules,  
67 like ethyl cyanide ( $C_2H_5CN$ , Cordiner et al. (2015)), vinyl cyanide ( $C_2H_3CN$ ,  
68 Palmer et al. (2017)), and even isomers like propadiene ( $CH_2CCH_2$ , Lom-  
69 bardo et al. (2019)) and cyclopropenylidene ( $c-C_3H_2$ , Nixon et al. (2020)),  
70 force modelers to constantly improve the chemical scheme they use, render-  
71 ing codes more and more time consuming. The study of isotopologues (Liang  
72 et al., 2007; Mandt et al., 2009; Krasnopolsky, 2016; Loison et al., 2017; Dobri-  
73 jevic and Loison, 2018) also requires to increase drastically the complexity of  
74 the chemical scheme: hundreds of species are necessary to encompass the en-  
75 tire chemical system of Titan’s atmosphere in current photochemical models.  
76 Two directions can then be taken to model Titan’s atmosphere: (1) include  
77 limited chemistry to focus on dynamics with 2D or 3D models using some  
78 assumptions (for instance: few species, fixed neutral background atmosphere,  
79 no cations, no anions, uncoupled chemistry between hydrocarbons and oxygen  
80 species, and so on); (2) expand the chemical scheme in 1D models to focus  
81 on chemical processes assuming mean conditions with neither latitudinal nor  
82 longitudinal transport.

83 Due to this remarkable chemical complexity, one-dimensional photochemical  
84 models are still a powerful tool and used internationally by several teams.  
85 However, more and more observational data, in particular those gathered by  
86 the Cassini mission, allow accessing latitudinal, longitudinal and temporal  
87 variations of the altitudinal profiles of several species (see for instance Vinatier  
88 et al. (2010, 2015); Sylvestre et al. (2020)). It is then important to improve  
89 these models with the objective to develop 2D photochemical models. As a first  
90 step, we advocate to use a 2D geometry to calculate the solar flux available

91 for photolysis instead of a plane-parallel approximation in 1D photochemical  
92 models.

93 In the present paper, we compare two types of 1D photochemical models used  
94 in mean conditions. In the first model, the photolysis rates are computed  
95 by a classic plane-parallel ultraviolet radiative transfer model. In the second  
96 model, the ultraviolet radiative transfer model is based on a 2D geometry. In  
97 the following, we first present our 1D photochemical model (Section 2) and  
98 the two radiative transfer models (Section 3). In Section 4, we compare the  
99 photolysis rates calculated in 1D mean conditions and those derived from our  
100 2D model. We then present the impact of the 2D photolysis rates on the mole  
101 fraction profiles (Section 5) and we conclude in Section 6.

## 102 2 Description of the 1D photochemical model

103 The present 1D photochemical model is based on the one presented in Loison  
104 et al. (2019) and Dobrijevic et al. (2016). We summarize the main character-  
105 istics in the following.

106 We use a non-uniform altitudinal grid composed of 138 levels from the surface  
107 (altitude  $z_0 = 0$  km) up to the top of the atmosphere ( $z_{top} = 1500$  km) with  
108 intervals  $\Delta_z$  calculated on the basis of value of the atmospheric scale height  
109 such as  $\Delta_z = H_a/5$ . Consequently, two consecutive altitudes are separated  
110 by 4 km near the surface and 17 km near the top of the atmosphere. The  
111 temperature profile is the same as in Loison et al. (2015).

112 The mole fractions of  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{CO}$  and  $\text{Ar}$  are fixed at the lower boundary  
113 (surface of Titan):  $y_{\text{CH}_4} = 1.48 \times 10^{-2}$ ,  $y_{\text{H}_2} = 3.0 \times 10^{-3}$ ,  $y_{\text{CO}} = 5.1 \times 10^{-5}$   
114 and  $y_{\text{Ar}} = 3.39 \times 10^{-5}$  (Loison et al. (2015) and references therein). The  
115 mole fraction of  $\text{N}_2$  is simply given by  $y_{\text{N}_2} = 1 - (y_{\text{CH}_4} + y_{\text{H}_2} + y_{\text{Ar}} + y_{\text{CO}})$ .  
116 At the upper boundary, we use an external flux of  $\text{O}(^3\text{P})$  and a production  
117 of  $\text{H}_2\text{O}$  from micrometeoritic ablation equal respectively to  $1.6 \times 10^6$  and  
118  $5.2 \times 10^5 \text{ cm}^{-2} \text{ s}^{-1}$  (values referred to the surface, see Dobrijevic et al. (2014)  
119 for details). We assumed a zero flux as an upper boundary condition for all  
120 the other species, except for atomic hydrogen ( $\text{H}$ ) and molecular hydrogen  
121 ( $\text{H}_2$ ), which were allowed to escape with velocities following Jean's thermal  
122 escape mechanism (this mechanism is negligible for other species). We do not  
123 consider sulfur species in the present study since no sulfur species have been  
124 detected yet (see Hickson et al. (2014) for model prediction of sulfur-bearing  
125 species abundances).

126 The eddy diffusion coefficient profile is constrained in the present model using  
127 argon ( $\text{Ar}$ ) and methane ( $\text{CH}_4$ ) in the higher atmosphere and water ( $\text{H}_2\text{O}$ ) and

128 hydrogen cyanide (HCN) in the lower atmosphere (see Loison et al. (2019) for  
129 details).

130 The chemical scheme is the same as in Loison et al. (2019) but using recent  
131 measurements of the rate constants at low temperatures of N(<sup>2</sup>D) with CH<sub>4</sub>,  
132 C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> (Nunez-Reyes et al., 2019a) and N(<sup>2</sup>D) with C<sub>2</sub>H<sub>2</sub> (Nunez-  
133 Reyes et al., 2019b). Magnetospheric electrons are not taken into account to  
134 focus on the effect of photolysis. Our model contains 99 neutral species and  
135 83 ion species (including electron). The chemical scheme has been published  
136 in Loison et al. (2019) and modifications are available upon request.

### 137 **3 UV radiative transfer model**

#### 138 *3.1 Actinic flux in a plane-parallel model*

139 The actinic flux is the quantity of light available to molecules at a particu-  
140 lar point in the atmosphere and which, on absorption and ionisation, drives  
141 photochemical processes in the atmosphere. This quantity is one of the terms  
142 required in the calculation of photolysis rates (photodissociation and pho-  
143 toionisation rates).

144 In the present study, we compute the actinic flux as a function of altitude in  
145 the classic approximation of a plane parallel atmosphere. Attenuation of the  
146 solar flux is calculated using the Beer-Lambert law and takes the cosine of the  
147 Solar Zenith Angle (SZA) into account.

148 The actinic flux  $I(\lambda, z)$  is the number of solar photons of wavelength  $\lambda$  at  
149 altitude  $z$  per unit of wavelength. It is calculated as:

$$150 \quad I(\lambda, z) = I_0(\lambda)e^{-\tau(\lambda, z)} \quad (1)$$

151 where  $I_0(\lambda)$  is the number of solar photons of wavelength  $\lambda$  at the top of the  
152 atmosphere per unit of wavelength. The total optical depth at wavelength  $\lambda$   
153 and altitude  $z$  is given by:

$$154 \quad \tau(\lambda, z) = \frac{1}{\cos(\theta)} \sum_i \sigma_i(\lambda) \int_z^\infty n_i(z') dz' \quad (2)$$

155 where  $\sigma_i(\lambda)$  is the photoabsorption cross section of the species  $i$  at wavelength  
156  $\lambda$ ,  $n_i(z)$  the density of species  $i$  at altitude  $z$  and  $\theta$  the SZA.

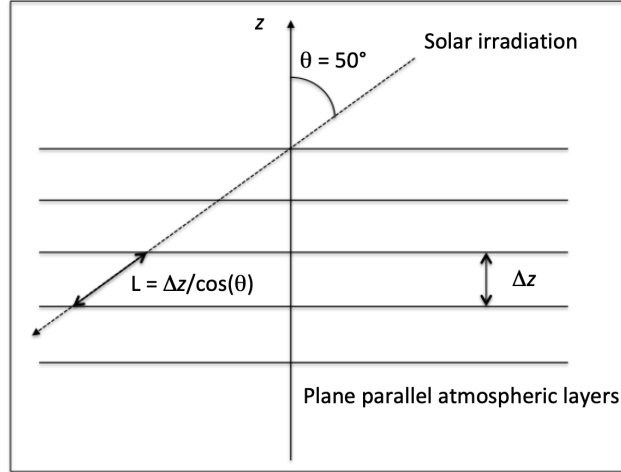


Fig. 1. Model A. The atmosphere of Titan is divided in 137 plane-parallel layers in altitude from the ground  $z_0 = 0$  up to the top of the atmospheric model  $z_{top} = 1500$  km. The altitude grid is non-uniform (i.e. the thickness  $\Delta z$  is not constant with altitude). We use a Solar Zenith Angle  $\theta = 50^\circ$  corresponding to the mean SZA over a day at equinox.

157 The photolysis rate  $J_i^j(z)$  of a species  $i$  and branching path  $j$  at altitude  $z$  is  
 158 given by:

$$159 \quad J_i^j(z) = \int q_i^j(\lambda) \sigma_j(\lambda) I(\lambda, z) d\lambda \quad (3)$$

160 where  $\sigma_j(\lambda)$  is the absorption (or ionisation) cross section and  $q_i^j(\lambda)$  the  
 161 branching ratio for path  $j$ . The total photolysis rate  $J_i(z)$  for species  $i$  is  
 162 then given by:

$$163 \quad J_i(z) = \sum_{j=0}^{N_j} J_i^j(z) \quad (4)$$

164 where  $N_j$  is the number of paths for the photolysis process in question.

165 To reproduce global mean conditions, all photolysis rates are calculated for  
 166 a SZA of  $50^\circ$  (this angle is the mean SZA during the day at the equinox)  
 167 and the solar flux at the top of the atmosphere is divided by 2 for day/night  
 168 averaging. This approximation is also used in many other previous models  
 169 but with slightly different SZA values (see for instance Hörst et al. (2008),  
 170 Krasnopolsky (2009), Dobrijevic et al. (2014), Vuitton et al. (2019)). This  
 171 model is called Model A in the following.

172 The solar irradiance at the top of the atmosphere comes from Dobrijevic et al.  
 173 (2016). We consider a wavelength range from 0 to 730 nm with a spectral  
 174 resolution of 0.001 nm in order to take into account the high resolution cross



175 sections of many species ( $N_2$ ,  $H_2$ ,  $CO$ , etc.). The model takes into account  
 176 absorption, ionization, and Rayleigh scattering by  $N_2$ ,  $H_2$  and attenuation by  
 177 aerosols in the lower stratosphere.

### 178 3.2 Actinic flux in a 2D geometry

179 We now present the model to compute the actinic flux in a 2D geometry. For  
 180 that, we use a classical spatial discretization. The latitudinal discretization is  
 181 based on a regular grid with  $10^\circ$  separation as illustrated in Figure 2. The  
 182 origin of latitudes is associated with the sub-solar point (or sub-solar latitude  
 183  $0^\circ$ , SSL0 in the following) . The atmosphere is then divided in 19 sections of  
 184  $10^\circ$  from  $-5^\circ$  to  $185^\circ$  sub-solar latitude (SSL). Taking both the altitudinal grid  
 185 into account and latitudinal sections, the atmosphere is divided in  $19 \times 138 =$   
 186 2622 cells.

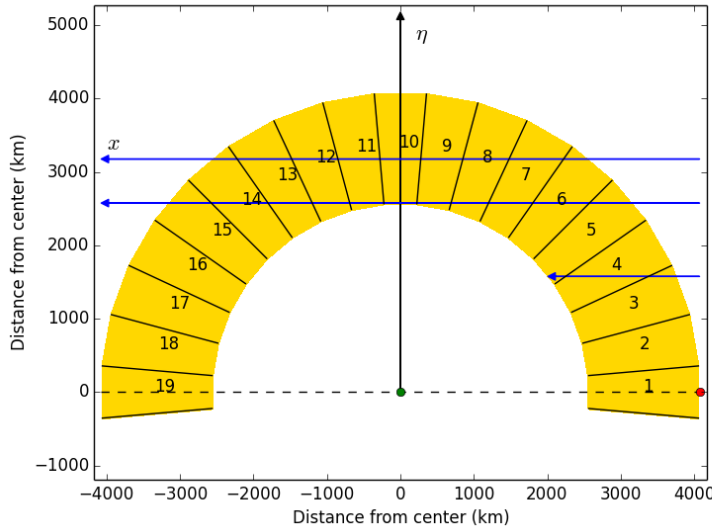


Fig. 2. Model B. The atmosphere of Titan (in yellow) is divided in 19 latitude sections from  $-5^\circ$  to  $185^\circ$ . Each section corresponds to a latitudinal range of  $10^\circ$ . The red point corresponds to a sub-solar latitude of  $0^\circ$  (SSL0). Section #1 is the sub-solar section and section #10 corresponds to SSL90. The green point corresponds to the center of Titan. The radius of Titan is 2575 km and the top level of altitude is 1500 km from the surface. The altitude grid is not depicted. The blue lines correspond to some solar rays coming from the right of the picture and going through the atmosphere.

187 The atmospheric vertical structure (temperature-pressure profile) and the alti-  
 188 tudinal abundance profiles of each species are considered to be the same in  
 189 all latitudinal sections.

190 We used a ray-tracing based method to compute the actinic flux in each lati-

191 tudinal section. For a given wavelength, each solar ray goes through the atmo-  
 192 sphere (like the ones represented by a blue line in Figure 1) and is attenuated  
 193 depending on the abundance of the various absorbing species and the length  
 194 of the optical path in each cell.

195 The actinic flux  $I(\lambda, \eta, x)$  is the number of solar photons of wavelength  $\lambda$  per  
 196 unit of wavelength at the impact parameter  $\eta$  and  $x$  is the abscissa along the  
 197 path of the solar ray. It is calculated as:

$$198 \quad I(\lambda, \eta, x) = I_0(\lambda)e^{-\tau(\lambda, \eta, x)} \quad (5)$$

199 where  $I_0(\lambda)$  is the solar flux at the top of the atmosphere at wavelength  $\lambda$  per  
 200 unit of wavelength. The total optical depth at wavelength  $\lambda$  and altitude  $z$  is  
 201 given by:

$$202 \quad \tau(\lambda, \eta) = \sum_i \sigma_i(\lambda) \int_0^\infty n_i(x) dx \quad (6)$$

203 where  $\sigma_i(\lambda)$  is the absorption cross section of the species  $i$  at wavelength  $\lambda$   
 204 and  $n_i(x)$  the density of species  $i$  at the abscisse  $x$ .

205 We used a non-uniform grid for the impact parameter  $\eta$  (distance from the  
 206 center of Titan to the top of the atmosphere corresponding to SSL90) with  
 207 a constant interval of 5 km from the center of Titan to a distance of the  
 208 impact parameter corresponding to 2500 km (a little bit lower than 2575 km  
 209 that corresponds to the radius of Titan). From 2500 km up to the top of  
 210 the atmosphere (4075 km), we used a constant interval of 1 km to ensure  
 211 that each cell at the terminator is crossed by several solar rays to compute  
 212 meaningful mean photolysis rates (with a minimum of 4 rays near the surface,  
 213 since  $\Delta_z = 4$  km at the lower boundary). This gives a total of 2575 levels of  
 214 the impact parameter (or 2575 solar rays from SSL0 to SSL90).

215 For a given wavelength and impact parameter, we compute the length of the  
 216 optical path of the corresponding solar ray in each cell of the different sections  
 217 it goes through. From this length and the concentration of each species (given  
 218 by the 1D photochemical model), we compute the optical depth in each cell.  
 219 We repeat that for all impact parameters and wavelengths. With an interval  
 220 of 5 km or 1 km for the impact parameter (depending on the distance from  
 221 the center of Titan to the top of the atmosphere), a given cell can be crossed  
 222 by several solar rays and the number of times each cell is crossed varies from  
 223 one another depending on the geometry. As a consequence, the optical depth  
 224 has to be normalized. We normalized the total optical depth in each cell (the  
 225 sum of optical depth) by the number of times it has been crossed by a solar  
 226 ray.

227 Finally, after calculating the actinic flux in each cell ( $z,s$ ) where  $z$  is the  
 228 latitude and  $s$  the section number, we introduce a specific photolysis rate  
 229  $J_i(z, s)$ , which corresponds to the photolysis rate as a function of altitude for  
 230 each section numbers ( $\#s$ ). This model is called Model B in the following.

### 231 3.3 Coupling of the UV transfer models and the photochemical model

232 The first step of our calculations (step #1 in Figure 3) is to compute the  
 233 photolysis rates for Model A and the mole fraction profiles at the steady state  
 234 with the 1D photochemical model. As a starting point of the Model A, we con-  
 235 sider that the atmosphere is only composed of  $N_2$ ,  $CH_4$ , Ar and  $H_2$  (the initial  
 236 atmosphere). This allows computing the first photolysis rates for all photolysis  
 237 (photodissociation and photoionisation) processes considered. Then, we com-  
 238 pute the relative abundance of each species using the 1D photochemical model  
 239 until we reach a steady state. We then iterate this procedure considering the  
 240 whole set of photolysis processes (see Loison et al. (2019) for information on  
 241 the chemical scheme) until we reach a convergence in the relative abundance  
 242 profiles (in practice, two iterations are sufficient; uncertainties on reaction  
 243 rates render useless obtaining a convergence criteria lower than few percent).

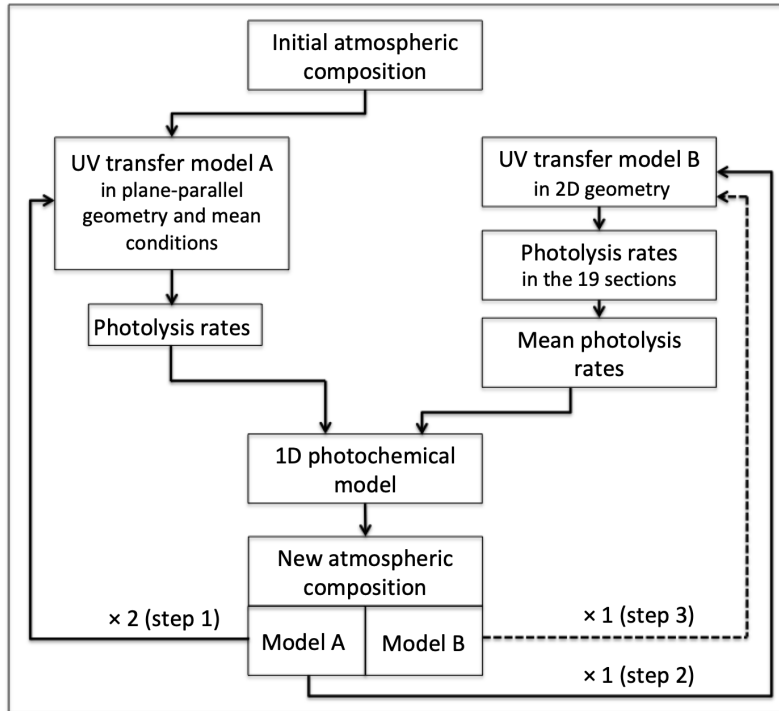


Fig. 3. Schematic diagram showing the two UV transfer models and their use with our 1D photochemical model.

244 In a 2D geometry for calculating the actinic flux, the mean conditions are  
 245 obtained by using the photolysis rates calculated with the Model B and the

246 atmospheric composition obtained with the Model A (end of step #1). This  
247 model computes the photolysis rates for each section. Then, we average them  
248 over all the sections to obtain mean photolysis rates, which correspond to  
249 an average over SZA from 0° to 90° and day/night average. This procedure  
250 corresponds to step #2 in Figure 3.

251 In the following section, we first present the photolysis rate results of these  
252 two approaches and then we compare the mole fraction profiles obtained with  
253 the same 1D photochemical model. A comment on step #3 is given in the  
254 conclusion.

## 255 4 Results: photolysis rates

### 256 4.1 Photolysis rates

#### 257 4.1.1 Model A

258 At the steady state, the depth of penetration of solar photons in the Model  
259 A is shown in Figure 4. This level corresponds to the altitude where the  
260 total optical depth is equal to 1 at a given wavelength (which corresponds  
261 also to the maximum of the photolysis rate). Molecular nitrogen ( $N_2$ ) is the  
262 main absorber in the EUV up to 80 nm. High resolution cross section of  
263  $N_2$  is only known between approximately 80 nm and 100 nm. From 80 to  
264 140 nm, methane ( $CH_4$ ) absorbs with a contribution of molecular hydrogen  
265 ( $H_2$ ) between 100 and 110 nm. Around 150 nm, both carbon monoxide (CO)  
266 and acetylene ( $C_2H_2$ ) contribute to the absorption. Several species absorb at  
267 greater wavelengths with the major contribution of aerosols beyond 200 nm.

#### 268 4.1.2 Model B

269 Figure 5 shows the optical depth as a function of latitude and altitude at two  
270 wavelengths (85 nm and 121.6 nm) where  $N_2$  and  $CH_4$  absorb efficiently. This  
271 figure shows also the night side where photolysis is null. We see the increase of  
272 the altitude level corresponding to the maximum of the photolysis rate (where  
273 the optical depth is equal to 1) from the SSL0 to the SSL90 and beyond. The  
274 depth of penetration of UV is lower at 85 nm than at 121.6 nm. The most  
275 important difference between the 2D and 1D plane parallel models is that a  
276 substantial part of the atmosphere beyond the terminator is photochemically  
277 active, when it is by definition inactive in 1D models. This geometric difference  
278 should enhance the mean photolysis rate over the entire atmosphere.

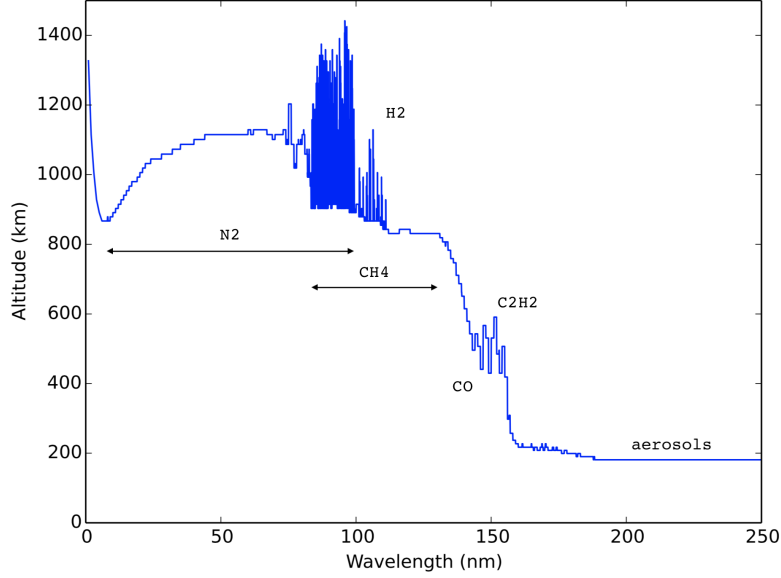


Fig. 4. Depth of penetration of solar photons in the atmosphere of Titan as a function of wavelength. The main contributors to the absorption are depicted.

279 Figure 6 shows an example of photolysis rates as a function of altitude and  
 280 section for  $H_2$ . Although the first 3 sections do not exhibit strong differences in  
 281 the photodissociation rates of  $H_2$  (for a given altitude), the rate profiles change  
 282 more and more strongly in the following sections. The  $H_2$  photodissociation  
 283 rate decreases more rapidly and occurs at higher altitude as a function of  
 284 section number toward terminator (SSL90) and beyond. The photolysis of  $H_2$   
 285 is no more efficient after section #12 (SSL115).

286 Let us write  $J_i(z, s)$  the photolysis rate of species  $i$  at altitude  $z$  and section  
 287 number  $s$ . The global mean photolysis rate over the entire atmosphere  $\bar{J}_i(z)$   
 288 is simply given by:

$$289 \quad \bar{J}_i(z) = \frac{\sum_{s=1}^{N_s} J_i(z, s)}{N_s} \quad (7)$$

290 where  $N_s = 19$  is the number of sections considered in Model B. Figure 6  
 291 shows the mean rate  $\bar{J}_i(z)$  for  $H_2$  obtained from equation 7. The effect of  
 292 day/night mean is clearly visible.

### 293 4.1.3 Validation

294 The photolysis rates are calculated in two different ways in models A and  
 295 B. In order to validate the two radiative transfer models and to highlight  
 296 the geometric effect on the calculation of photolysis rates, we first compared

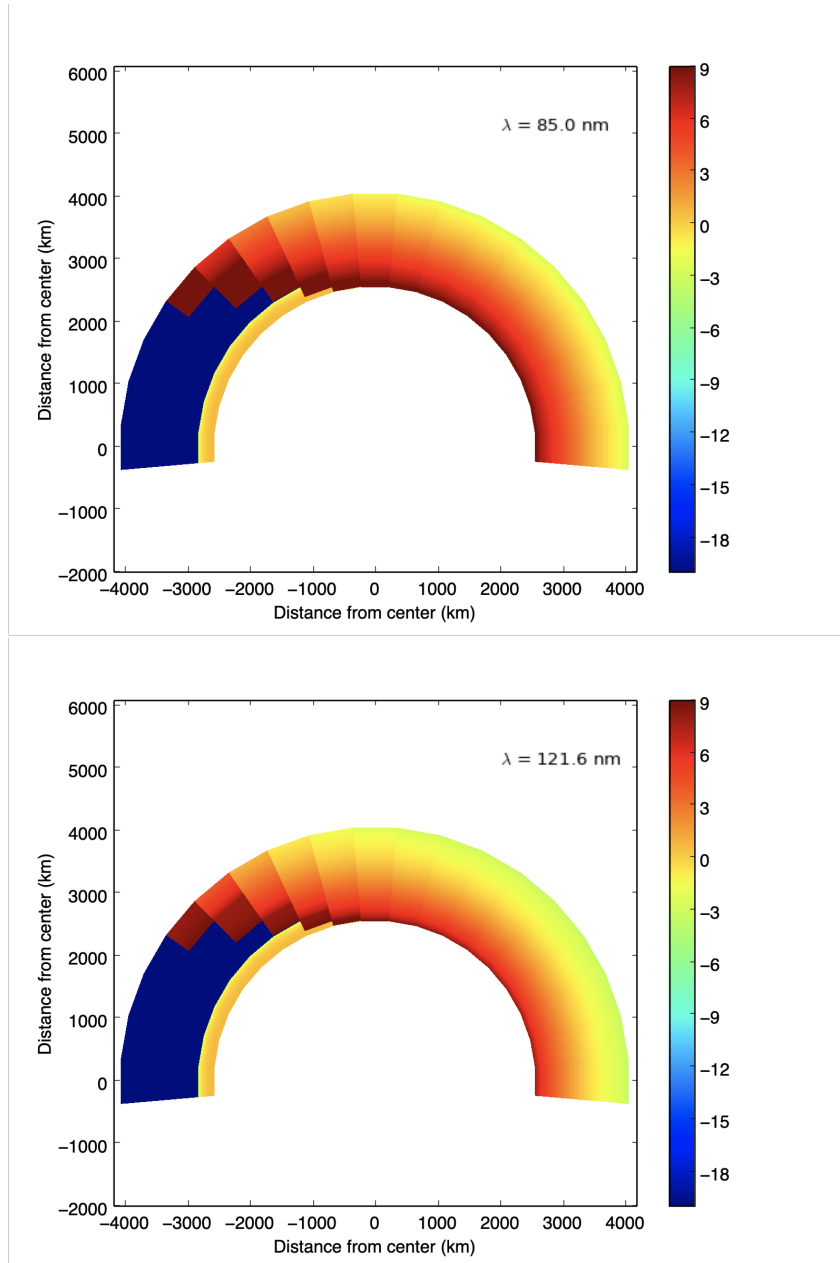


Fig. 5. Logarithm of the total optical depth as a function of altitude and section at two wavelengths (85 nm and 121.6 nm). The maximum of the photolysis rate profile corresponds to the altitude where the total optical depth is equal to 1 (altitude level corresponding to the orange level). The contribution of aerosols extinction to the total optical depth is visible on the night side (but it plays no role on this side).

297 the rates obtained with Model A ( $J_A$ ) considering a  $SZA = 0^\circ$  and Model B  
 298 ( $J_B$ ) after the calculation of the SSL0 mean rates obtained with sections #1  
 299 and #19. In Model A, the solar flux at the top of the atmosphere is divided  
 300 by 2 for day/night averaging. In Model B, since the actinic flux is null in  
 301 section #19, the averaging of sections #1 and #19 corresponds to a division  
 302 of the photolysis rates in section #1 by a factor of 2. Results are presented

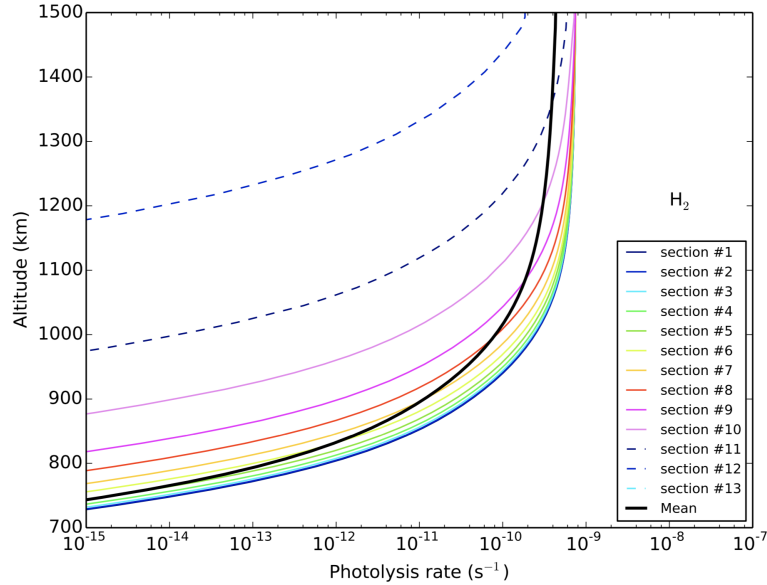


Fig. 6. Photolysis rate of  $\text{H}_2$  as a function of altitude and section number. The rate of section #13 and following sections are too low and does not appear in the figure. The mean photolysis rate computed from all the sections is shown in black for comparison.

303 in Figure 7. For a species like  $\text{CH}_4$  with a low resolution cross section, the  
 304 agreement between the two models is perfect. Note that, even for section #1  
 305 in Model B, there is a geometry effect that is not taken into account in plane-  
 306 parallel models (Model A). For  $\text{N}_2$  (not shown), the ratio  $J_B/J_A$  does not  
 307 exceed 1.1 above 600 km of altitude (only a fraction of the cross section is  
 308 at high resolution). On the other hand, for species with high resolution cross  
 309 sections, there are noticeable differences as a function of altitude. For  $\text{CO}$  (not  
 310 shown), the ratio ( $J_B/J_A$ ) is about 0.7 between 800 and 1000 km. This is due  
 311 to the fact that at some specific wavelength photons go deeper (or are stopped  
 312 higher) in the atmosphere and the geometric effect in the 2D model becomes  
 313 more significant. In Model B, photons tend to be slightly absorbed at higher  
 314 altitude than in Model A. This difference increases when comparing Model A  
 315 with the other sections in Model B (sections #2 and #18 for instance). For  
 316  $\text{H}_2$ , the effect is the opposite,  $J_A$  being about 40% greater than  $J_B$  at 900 km  
 317 of altitude (see Figure 7).

318 Due to the geometry of the 2D model, the best agreement between the 1D  
 319 model at mean conditions (Model A) and the 2D model with day/night av-  
 320 eraged rates (Model B) is obtained when considering section #7 (between  
 321 SSL55 and SSL65) and section #13 (which is the symmetric of section #7  
 322 with respect to the terminator). This result is in agreement with the use of a  
 323 SZA equal to  $60^\circ$  in 1D photochemical models in global mean conditions.

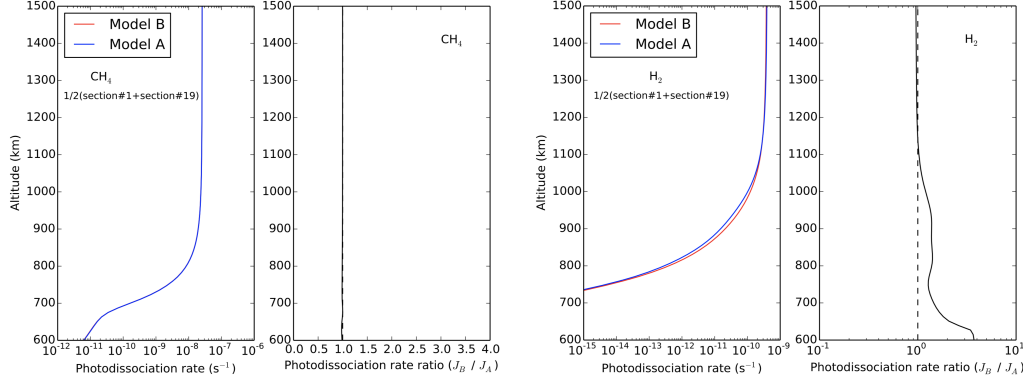


Fig. 7. Left sub-panels: Photolysis rate of  $\text{CH}_4$  and  $\text{H}_2$  for a  $\text{SZA} = 0^\circ$  ( $J_A$ , Model A) and for the mean of sections #1 and #19 ( $J_B$ , Model B). Right sub-panels: Ratios of the photolysis rates ( $J_B/J_A$ ).

#### 4.1.4 Comparison between Model A and Model B

We present in Figure 8 the global mean photolysis rates of the two major compounds in the photochemistry of Titan's atmosphere. The maximum of methane photolysis occurs around an altitude of 800 km (see Figure 4). At this altitude, the ratio  $J_B/J_A$  is around 1.3 and increases up to 2.7 at 735 km. For  $\text{N}_2$ , the ratio  $J_B/J_A$  is between 1.1 and 1.5 in the altitudinal range [1100, 900] km where  $\text{N}_2$  is efficiently photolyzed. As a consequence, the two precursor mechanisms of chemical complexity are increased in Model B compared to Model A. We see in the next section that this has a noticeable effect on the production of organic compounds in the atmosphere.

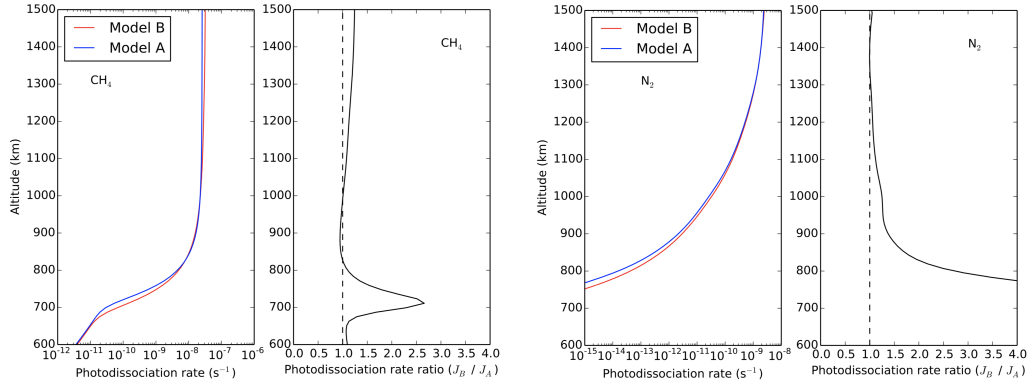


Fig. 8. Global mean photolysis rate of  $\text{CH}_4$  and  $\text{N}_2$  for Model A ( $J_A$ ) and for Model B ( $J_B$ ). Right sub-panels: Ratios of the photolysis rates ( $J_B/J_A$ ).

We can also compare the partial photolysis rates for the various path of photodissociation of a given species. For instance, in Figure 9, we present the total photolysis rates of  $\text{C}_2\text{H}_6$  for the two models. We see that these rates are quite identical throughout the atmosphere. However, the ratios  $J_B(i)/J_A(i)$  for the different pathways of photodissociation are very different above 800



339 km. Paths 1 and 3 (to a lesser extent) are the major contributors to the total  
 340 photodissociation rate. Their ratios are counterbalanced by the ones of paths  
 341 2, 4 and 5. This example shows that partial rates of paths 1 and 3 are favored  
 342 in Model B in contrast to paths 2, 4 and 5.

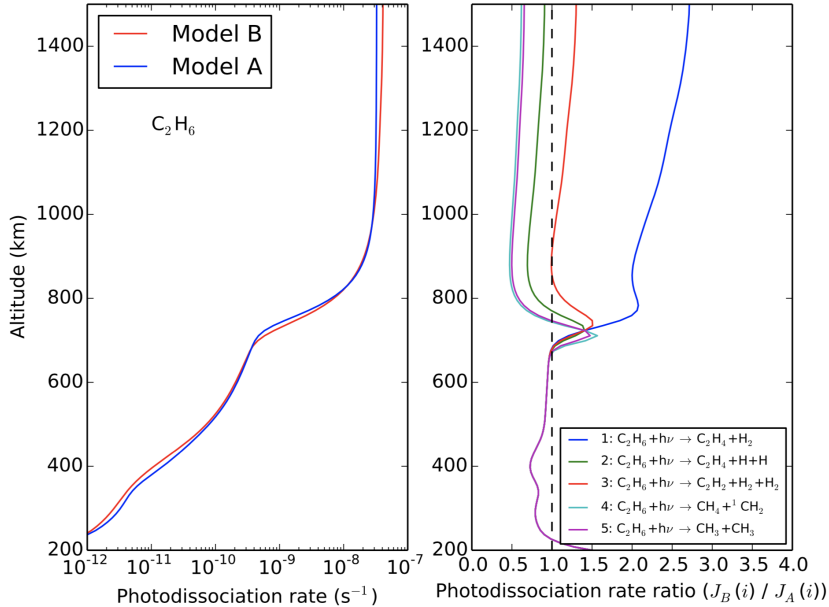


Fig. 9. Left: Photolysis rates of  $C_2H_6$  for Models A and B. Right: Photolysis rate ratios for the five photodissociation pathways.

343 In order to give an overview of the impact of the 2D geometry on the calcu-  
 344 lation of photolysis rates, we compare the two models in Tables 1 and 2 for  
 345 each photolysis process included in our model. In these tables, we selected the  
 346 following quantities:

- 347 • The number of compounds that are photodissociated (or photoionised)  $P_i(z)$   
 348 at altitude  $z$  (in  $cm^{-3}s^{-1}$ ) is given by:

$$349 \quad P_i(z) = n_i(z) \times J_i(z) \quad (8)$$

350 where  $n_i(z)$  is the density of compound  $i$  (in  $cm^{-3}$ ) and  $J_i(z)$  its photodisso-  
 351 ciation (or photoionisation) rate (in  $s^{-1}$ ) at altitude  $z$ . This quantity reaches  
 352 a maximum  $P_i(z_m)$  at altitude  $z_m$ . For instance, the maximum of methane  
 353 photodissociation occurs around an altitude of 830 km with 42.42 molecules  
 354 dissociated per  $cm^3$  and per second. In the tables, the subscripts A and B  
 355 correspond to Model A and Model B respectively.

- 356 • The ratio  $P_B(z_{m,B})/P_A(z_{m,A})$  is given for the altitude corresponding the  
 357 maximum of  $P_i(z)$ ,  $z_{m,A}$  in Model A and  $z_{m,B}$  in Model B. We see in the  
 358 tables that  $z_{m,B}$  can be at the same altitude than in Model A but in gen-  
 359 eral, it is at lower altitude, and sometimes at higher altitude (like for  $C_2H_4$ ).  
 360 The precision on  $z_{m,A}$  and  $z_{m,B}$  is limited by the discretization of our alti-

361 tude grid. For instance, around 900 km of altitude the interval between two  
 362 consecutive altitude levels is 12 km and 10 km around 220 km of altitude.

363 For some processes, the peak of dissociation is quite pronounced and the ra-  
 364 tio  $P_B(z_{m,B})/P_A(z_{m,A})$  is rather representative of the difference between the  
 365 two models. For others processes, the dissociation occurs in a larger part of  
 366 the atmosphere and it is therefore instructive to define the column-integrated  
 367 production rate, such as:

$$368 \quad \tilde{P}_i = \int_0^{z_{top}} P_i(z) dz \quad (9)$$

369 The integration is done from the surface to the top of our atmospheric model.  
 370 For instance, the ratio  $\tilde{P}_B/\tilde{P}_A$  is 1.12 for  $C_2H_2$  and only 1.01 for  $P_B(z_{m,B}) /$   
 371  $P_A(z_{m,A})$ .

372 The general trend is the following. With very few exceptions (see  $C_2H_6$ ,  
 373  $CH_3C_3N$  and  $CO$ ), the photodissociation rates are enhanced in Model B com-  
 374 pared to Model A. The enhancement is between 10% and 30%. There is no  
 375 systematic correlation between this quantity and the altitude of the peak of  
 376 photodissociation. The most affected rate is the one of  $HCO$  for which the peak  
 377 of photodissociation is very low in the stratosphere (around 120-140 km) with  
 378 an enhancement factor of 2.4 at the peak. Also, there is no clear correlation  
 379 between the value of the ratio  $\tilde{P}_B / \tilde{P}_A$  and the value of  $\tilde{P}_A$ .

380 Results for photoionisation rates are presented in Table 2. They are signifi-  
 381 cantly different from the one obtained for photodissociation rates. For some  
 382 species, the photoionisation rates are lower in Model B (this is the case for  
 383  $H$  and  $C_4H_2$ ), quite identical in both models, or even enhanced in Model B  
 384 (for  $C_6H_6^*$ ,  $CO_2$  and  $CO$ ). In general, the peak of photolysis occurs at lower  
 385 altitudes in Model B.

## 386 5 Results: abundance profiles

387 We have seen in the previous section that the geometric effects alter both the  
 388 magnitude of the rates, the relative importance of the branching paths and  
 389 the location of the peak of photolysis. We now present how these differences in  
 390 photolysis rate profiles affect the abundances of the various species calculated  
 391 from the two models. It is not possible to show the abundance profiles of  
 392 the 182 species present in our model so we focus our presentation on some  
 393 particular species, especially some of those that have been detected.

Table 1

Report of photodissociation rate results for Models A and B.  $P_A(z_{m,A})$  is the maximum of the number of compounds that are photodissociated in  $\text{cm}^{-3}\text{s}^{-1}$  at altitude  $z_{m,A}$  for Model A.  $\tilde{P}_A$  is the column-integrated production rate for Model A in  $\text{cm}^{-2}\text{s}^{-1}$ .

Compound	$P_A(z_{m,A})$ ( $\text{cm}^{-3}\text{s}^{-1}$ )	$z_{m,A}$ (km)	$z_{m,B}$ (km)	$P_B(z_{m,B})/P_A(z_{m,A})$	$\tilde{P}_A$ ( $\text{cm}^{-2}\text{s}^{-1}$ )	$\tilde{P}_B/\tilde{P}_A$
H <sub>2</sub>	$4.12 \times 10^{-3}$	1019	980	1.36	$1.15 \times 10^5$	1.30
CH <sub>3</sub>	$1.11 \times 10^1$	807	807	1.13	$3.75 \times 10^8$	1.10
CH <sub>4</sub>	$4.24 \times 10^1$	831	819	1.00	$8.25 \times 10^8$	1.08
C <sub>2</sub> H <sub>2</sub>	$2.34 \times 10^2$	227	217	1.01	$3.39 \times 10^9$	1.12
C <sub>2</sub> H <sub>3</sub>	$4.36 \times 10^{-1}$	227	227	1.03	$5.28 \times 10^6$	1.12
C <sub>2</sub> H <sub>4</sub>	$1.78 \times 10^1$	227	651	0.95	$9.45 \times 10^8$	1.00
C <sub>2</sub> H <sub>6</sub>	$1.68 \times 10^{-1}$	257	247	0.83	$6.87 \times 10^6$	0.94
C <sub>3</sub>	$8.57 \times 10^{-4}$	1059	1073	1.17	$2.04 \times 10^4$	1.16
cC <sub>3</sub> H <sub>2</sub>	$9.70 \times 10^{-1}$	891	891	1.32	$3.37 \times 10^7$	1.33
C <sub>3</sub> H <sub>3</sub>	$1.16 \times 10^0$	208	199	1.29	$3.29 \times 10^7$	1.36
CH <sub>3</sub> C <sub>2</sub> H	$5.10 \times 10^0$	208	199	1.08	$6.17 \times 10^7$	1.18
CH <sub>2</sub> CCH <sub>2</sub>	$3.06 \times 10^0$	217	208	1.05	$5.21 \times 10^7$	1.17
C <sub>3</sub> H <sub>6</sub>	$1.45 \times 10^1$	217	199	1.06	$1.59 \times 10^8$	1.18
C <sub>3</sub> H <sub>8</sub>	$8.98 \times 10^{-1}$	237	237	0.94	$1.33 \times 10^7$	0.99
C <sub>4</sub> H <sub>2</sub>	$1.86 \times 10^1$	217	208	1.15	$2.89 \times 10^8$	1.27
C <sub>4</sub> H <sub>4</sub>	$4.13 \times 10^0$	227	227	1.07	$7.29 \times 10^7$	1.19
C <sub>4</sub> H <sub>6</sub>	$1.15 \times 10^1$	190	181	1.32	$1.23 \times 10^8$	1.40
C <sub>4</sub> H <sub>8</sub>	$1.03 \times 10^1$	208	190	1.15	$1.08 \times 10^8$	1.25
C <sub>4</sub> H <sub>10</sub>	$1.46 \times 10^0$	237	227	0.97	$1.97 \times 10^7$	1.04
C <sub>6</sub> H <sub>6</sub>	$2.69 \times 10^1$	267	277	1.04	$8.91 \times 10^8$	1.21
C <sub>6</sub> H <sub>6</sub> *	$2.68 \times 10^{-1}$	891	891	1.32	$8.24 \times 10^6$	1.32
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	$2.78 \times 10^1$	247	247	1.05	$4.48 \times 10^8$	1.16
C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H	$1.51 \times 10^{-2}$	639	651	1.26	$7.79 \times 10^5$	1.27
C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	$6.27 \times 10^0$	217	208	1.12	$8.07 \times 10^7$	1.25
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	$2.60 \times 10^{-2}$	419	419	1.19	$1.07 \times 10^6$	1.25
C <sub>6</sub> H <sub>5</sub> NHCH <sub>3</sub>	$2.37 \times 10^{-3}$	993	993	1.32	$5.93 \times 10^4$	1.29
C <sub>6</sub> H <sub>5</sub> CN	$4.99 \times 10^{-4}$	855	855	1.35	$1.80 \times 10^4$	1.29
AROM	$3.71 \times 10^0$	199	181	1.33	$4.46 \times 10^7$	1.4
NH <sub>2</sub>	$1.17 \times 10^{-3}$	639	639	1.15	$4.55 \times 10^4$	1.17
NH <sub>3</sub>	$9.86 \times 10^{-3}$	879	879	1.30	$3.94 \times 10^5$	1.29
N <sub>2</sub>	$6.77 \times 10^{-1}$	1087	1073	1.14	$2.42 \times 10^7$	1.14
HCN	$2.22 \times 10^0$	227	217	1.06	$3.33 \times 10^7$	1.16
HNC	$1.04 \times 10^{-2}$	967	967	0.99	$2.41 \times 10^5$	1.02
CH <sub>2</sub> NH	$1.28 \times 10^{-1}$	831	831	1.34	$5.28 \times 10^6$	1.33
CH <sub>3</sub> NH <sub>2</sub>	$8.38 \times 10^{-2}$	485	485	1.20	$1.98 \times 10^6$	1.20
CH <sub>3</sub> CN	$1.15 \times 10^{-1}$	227	217	1.05	$1.75 \times 10^6$	1.14
HC <sub>3</sub> N	$5.57 \times 10^{-2}$	639	639	1.20	$2.63 \times 10^6$	1.20
HC <sub>5</sub> N	$1.48 \times 10^{-2}$	867	867	1.18	$3.68 \times 10^5$	1.17
C <sub>2</sub> H <sub>3</sub> CN	$2.72 \times 10^{-1}$	519	519	1.22	$1.41 \times 10^7$	1.24
C <sub>2</sub> H <sub>5</sub> CN	$6.18 \times 10^{-2}$	227	217	1.05	$1.03 \times 10^6$	1.13
C <sub>3</sub> H <sub>7</sub> CN	$1.68 \times 10^{-3}$	227	217	1.00	$2.25 \times 10^4$	1.10
CH <sub>3</sub> C <sub>3</sub> N	$6.65 \times 10^{-2}$	843	855	0.92	$1.67 \times 10^6$	0.92
C <sub>2</sub> N <sub>2</sub>	$7.67 \times 10^{-3}$	247	247	0.95	$2.47 \times 10^5$	1.06
C <sub>4</sub> N <sub>2</sub>	$1.63 \times 10^{-3}$	795	795	1.12	$6.51 \times 10^4$	1.12
H <sub>2</sub> O	$4.05 \times 10^{-2}$	247	247	0.98	$1.02 \times 10^6$	1.10
CO	$2.80 \times 10^{-3}$	891	879	0.79	$6.29 \times 10^4$	0.85
HCO	$3.47 \times 10^0$	147	123	2.44	$3.83 \times 10^7$	2.25
H <sub>2</sub> CO	$1.12 \times 10^{-2}$	855	855	1.35	$5.32 \times 10^5$	1.34
CO <sub>2</sub>	$4.02 \times 10^{-3}$	227	217	1.08	$5.30 \times 10^4$	1.18

Table 2

Report of photoionisation rate results for Models A and B.  $P_A(z_{m,A})$  is the maximum of the number of compounds that are photoionised in  $\text{cm}^{-3}\text{s}^{-1}$  at altitude  $z_{m,A}$  for Model A.  $\tilde{P}_A$  is the column-integrated production rate for Model A in  $\text{cm}^{-2}\text{s}^{-1}$ .

Compound	$P_A(z_{m,A})$ ( $\text{cm}^{-3}\text{s}^{-1}$ )	$z_{m,A}$ (km)	$z_{m,B}$ (km)	$P_B(z_{m,B})/P_A(z_{m,A})$	$\tilde{P}_A$ ( $\text{cm}^{-2}\text{s}^{-1}$ )	$\tilde{P}_B/\tilde{P}_A$
H	$9.60 \times 10^{-4}$	954	928	0.70	$2.09 \times 10^4$	0.79
H <sub>2</sub>	$1.87 \times 10^{-3}$	1101	1087	1.06	$4.66 \times 10^4$	1.12
N <sub>2</sub>	$3.40 \times 10^0$	1073	1059	1.02	$7.98 \times 10^7$	1.07
CH <sub>3</sub>	$2.20 \times 10^{-2}$	879	879	0.89	$4.90 \times 10^5$	0.94
CH <sub>4</sub>	$7.75 \times 10^{-1}$	954	915	0.83	$2.27 \times 10^7$	0.95
cC <sub>3</sub> H <sub>2</sub>	$7.14 \times 10^{-4}$	980	993	1.00	$1.95 \times 10^4$	1.02
CH <sub>3</sub> C <sub>2</sub> H	$1.84 \times 10^{-3}$	928	915	0.91	$4.42 \times 10^4$	0.95
CH <sub>2</sub> CCH <sub>2</sub>	$1.12 \times 10^{-3}$	954	941	0.89	$2.70 \times 10^4$	0.94
C <sub>4</sub> H <sub>2</sub>	$2.29 \times 10^{-2}$	879	879	0.5	$4.37 \times 10^5$	0.53
C <sub>6</sub> H <sub>6</sub>	$1.84 \times 10^{-3}$	855	843	0.98	$3.20 \times 10^4$	1.04
C <sub>6</sub> H <sub>6</sub> *	$1.61 \times 10^{-2}$	891	891	1.34	$4.95 \times 10^5$	1.33
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	$1.58 \times 10^{-3}$	879	879	0.95	$2.81 \times 10^4$	1.00
C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	$1.99 \times 10^{-4}$	903	903	0.95	$3.36 \times 10^3$	0.99
H <sub>2</sub> O	$1.92 \times 10^{-6}$	954	941	0.98	$7.18 \times 10^1$	1.04
CO <sub>2</sub>	$5.43 \times 10^{-8}$	915	891	1.39	$1.04 \times 10^0$	1.40
CO	$5.92 \times 10^{-4}$	928	915	1.21	$1.64 \times 10^4$	1.20

### 394 5.1 Global view

395 We first present a global view on the differences between Model A and Model  
 396 B. Figure 10 shows the ratio, at an altitude of 1000 km, of the mole fraction  
 397 obtained with the Model B over the one of the Model A for the most abundant  
 398 species (with mole fractions greater than  $10^{-12}$  in the Model B). For clarity,  
 399 only a few points are labeled in the figure, those corresponding to the extreme  
 400 values of the ratio. The most important result is that most of the species have  
 401 a ratio significantly greater than 1, meaning that Model A gives abundances  
 402 notably smaller than model B. Many species have a ratio greater than 2 (a  
 403 factor of 3.2 for HCN and 3.4 for C<sub>2</sub>H<sub>3</sub>CN for instance) and for several species  
 404 the ratio exceeds a factor of 5 (a factor of 6.7 for C<sub>2</sub>N<sub>2</sub> and 13.6 for C<sub>4</sub>N<sub>2</sub>  
 405 for instance). In particular, among the species that have densities significantly  
 406 enhanced, many of them are nitrogen species.

407 We see also that in general, the lower the relative abundance of species, the  
 408 greater the number of species that show a strong disagreement between the two  
 409 models. This trend is limited however by the fact that the chemical scheme is  
 410 far from being complete for heavy species. Indeed, due to the lack of available  
 411 information in the literature, the number of reactions in our chemical scheme  
 412 is not proportional to the mass of species, as it should theoretically be (see  
 413 for instance Fig. 4 in Dobrijevic and Dutour (2007)).

414 In the lower atmosphere, below 800 km, abundances of ions are too low to  
 415 give relevant ratios. At 500 km, nitrogen species densities are the ones that  
 416 are the most enhanced in Model B. The effect of 2D geometry on the calcu-  
 417 lation on photolysis rates has no noticeable effect on many hydrocarbons, in

418 particular  $C_2H_2$  and  $C_2H_6$ . As observed at an altitude of 1000 km, a general  
419 trend can be inferred at 500 km, the heavier the species, the greater the im-  
420 pact of 2D geometry on its abundance. This behavior might be connected to  
421 the increasing coupling between more and more species as the mass of species  
422 increases. This is the same behavior we observed when studying the propaga-  
423 tion of uncertainties in photochemical models (see for instance Hébrard et al.  
424 (2009)).

## 425 5.2 Focus on some species

426 We have seen in the previous section that nitriles are the species that present  
427 the larger enhancement in their densities at two specific altitudes. We now  
428 present the model fraction profiles of several species to point out how large  
429 this enhancement as a function of altitude is and to compare the results of  
430 Model B with various recent observations, especially on nitriles (see Figures  
431 11, 12, 13 and 14).

### 432 5.2.1 Neutral species

- 433 • For HCN (Figure 11), the enhancement factor from Model A to Model B is  
434 greater than 2 in the major part of the atmosphere. Model B seems to be  
435 in a better agreement with observations from Cassini/CIRS (Vinatier et al.  
436 (2010)) and Cassini/INMS (Magee et al. (2009)) than Model A.
- 437 • For  $HC_3N$  (Figure 11), the enhancement factor is equal to or greater than 3  
438 from the ionosphere to the stratosphere with a factor of 4 around 400 km.  
439 Model B is in slightly better agreement with both Cassini/CIRS (Vinatier  
440 et al. (2010)) and ALMA observations (Cordiner et al. (2019)), but also  
441 with INMS data from Cui et al. (2009), which is about 20 times greater  
442 than the value inferred by Magee et al. (2009).
- 443 • For  $C_2N_2$  (Figure 11), the enhancement factor is relatively high with a value  
444 between 5 and 6 from the top of the atmosphere down to 200 km. Model B  
445 seems to be in better agreement with Cassini/CIRS observations (Sylvestre  
446 et al. (2020)) and in good agreement with Cassini/INMS data retrieved by  
447 Magee et al. (2009) but not with Cui et al. (2009).
- 448 • For  $C_4N_2$  (Figure 11), the enhancement factor reaches a factor 10 in the  
449 mesosphere and stratosphere. There is no direct detection of this species for  
450 the moment.
- 451 • We obtain also an enhancement factor greater than 2 for  $C_2H_3CN$  and  
452  $C_2H_5CN$ . The mole fraction profiles of  $C_2H_3CN$  and  $C_2H_5CN$  derived from  
453 Model B seem to be in better agreement with ALMA observation (Cordiner  
454 et al. (2019)) but the abundances are still too low at all altitudes. Contri-  
455 bution of the limbs in ALMA data and the increase of nitrile mole fractions



461 cant difference between Model A and Model B. Our model is in quite good  
462 agreement with observations.

- 463 • Using ALMA, Thelen et al. (2020) obtained the first spectroscopic detection  
464 of  $\text{CH}_3\text{C}_3\text{N}$  (methylcyanoacetylene or cyanopropyne) in Titan's atmosphere  
465 (Figure 12). It might be interesting to test our profile with a radiative  
466 transfert code to better compare our profile with ALMA observations.
- 467 • For  $\text{c-C}_3\text{H}_2$ , there is no significant difference between Model A and Model  
468 B. The mole fraction ratio reaches a factor of about 2 in an altitudinal  
469 region where the mole fractions are very low. It might be also required to  
470 use a radiative transfert code to better compare our profile with ALMA  
471 observations.
- 472 •  $\text{CH}_3\text{CN}$  (methyl cyanide) has been also detected by ALMA (see Thelen et al.  
473 (2019) and references therein). There is a factor of about 2 between Model  
474 A and Model B (Figure 12). Observations seem to slightly favor Model A.

### 475 5.2.2 Ions

476 An important constraint for ionospheric models is the electron density. Figure  
477 13 shows the electron density profiles obtained with Model A and Model B and  
478 a comparison with observations inferred from Shebanits et al. (2013) based  
479 on data from 47 flybys of the Cassini spacecraft Radio and Plasma Wave  
480 Science Langmuir Probe (RPWS-LP). Model B is in good agreement with the  
481 observed density value at the peak around 1000 km of altitude. Higher in the  
482 ionosphere, the difference between the two models is not significant. According  
483 to our results, Model B predicts a much higher electron density in the lower  
484 ionosphere (below 800km).

485 As we can see in Figure 10, many ions have densities significantly different in  
486 Model B compared to Model A. We present in Figure 14 the density profiles  
487 of six of them with opposite behaviors. In the case of  $\text{HCNH}^+$ ,  $\text{HC}_3\text{NH}^+$ ,  $\text{NH}_2^+$   
488 and  $\text{CH}_2\text{NH}_2^+$  the density is enhanced in Model B compared to Model A. In  
489 the case of  $\text{C}_2\text{H}_7^+$  and  $\text{C}_2\text{H}_5\text{CNH}^+$ , the density is lower in Model B in the  
490 ionosphere (above the peak of density). Below about 800 km of altitude, the  
491 density in Model B becomes much higher. For the moment, comparison with  
492 observations is not conclusive and cannot favor either model. For  $\text{HC}_3\text{NH}^+$ ,  
493 there is a very good agreement between Model B and Cassini/INMS data,  
494 while for  $\text{NH}_2^+$ , Model A seems to be in better agreement. These differences  
495 reflect in part uncertainties in the chemical rates (see Dobrijevic et al. (2016))  
496 and for an another part to incomplete description of the chemical scheme  
497 (important reaction may be missing or products poorly known).

498 In our methodology presented in Figure 3, the next step (step #3) is to  
499 compute the photolysis rates from the atmospheric composition derived from  
500 Model B (step #2), i.e. the density profiles of Model B we used in the present

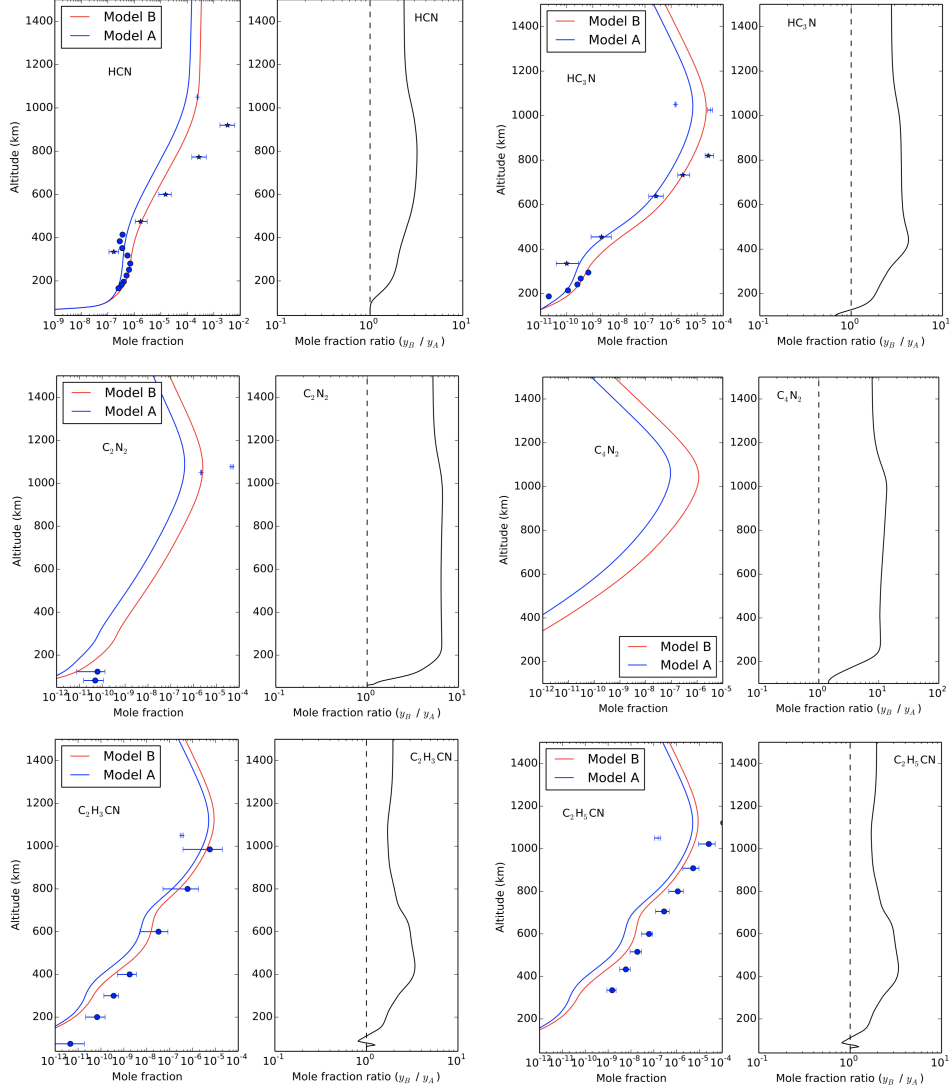


Fig. 11. Mole fraction profiles  $y_i$  of HCN, HC<sub>3</sub>N, C<sub>2</sub>N<sub>2</sub>, C<sub>4</sub>N<sub>2</sub>, C<sub>2</sub>H<sub>3</sub>CN and C<sub>2</sub>H<sub>5</sub>CN for the two models A and B and their ratio  $y_i(\text{B})/y_i(\text{A})$ . Observations come from Cassini/CIRS (HCN and HC<sub>3</sub>N from Vinatier et al. (2010) and C<sub>2</sub>N<sub>2</sub> from Sylvestre et al. (2020)), Cassini/INMS (Magee et al., 2009; Cui et al., 2009) and ALMA (HCN, HC<sub>3</sub>N and C<sub>2</sub>H<sub>5</sub>CN from Cordiner et al. (2019) and C<sub>2</sub>H<sub>3</sub>CN from Palmer et al. (2017)).

501 study. At step #3, we obtained density profiles similar to the ones obtained at  
 502 step #2 meaning that both photolysis rates and density profiles were already  
 503 at the steady state.

504 The next step, after step #3, will be to develop a pseudo-2D model including  
 505 rotation, in which density profiles will depend also on section (i.e. latitude).  
 506 Such a model has been developed by De La Haye et al. (2008) using a simple  
 507 chemical scheme coupling ion and neutral species. They showed that many  
 508 species, especially ions, have chemical life time much shorter than the rotation



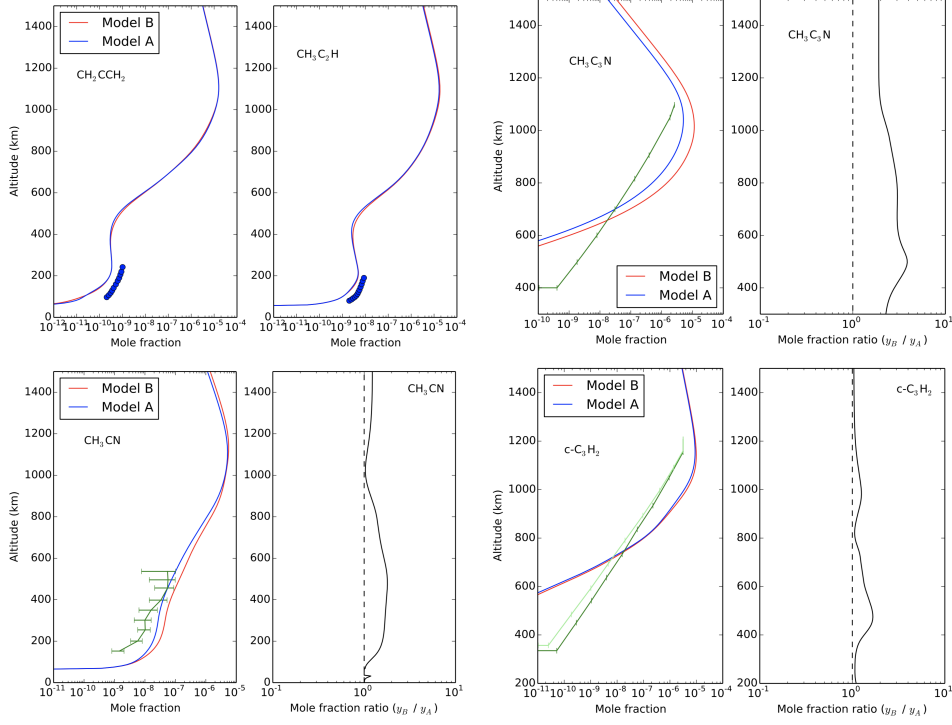


Fig. 12. Mole fraction profiles  $y_i$  of two isomers of  $C_3H_4$  ( $CH_2CCH_2$  and  $CH_3C_2H$ ),  $CH_3C_3N$ ,  $CH_3CN$  and  $c-C_3H_2$  for the two models A and B and their ratio  $y_i(B)/y_i(A)$  (except for  $C_3H_4$ ). Observations come from TEXES (Lombardo et al. (2019)) for  $C_3H_4$  and ALMA ( $CH_3C_3N$  from Thelen et al. (2020),  $CH_3CN$  from Thelen et al. (2019) and  $c-C_3H_2$  from Nixon et al. (2020)). For  $c-C_3H_2$ , observations gathered in two different spectral bands are shown.

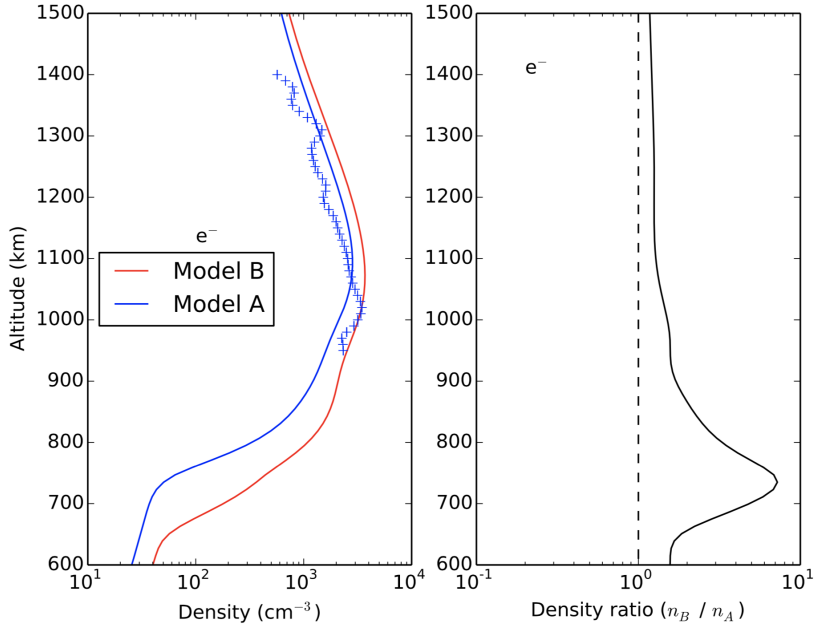


Fig. 13. Density profile of electrons for Model A and Model B.

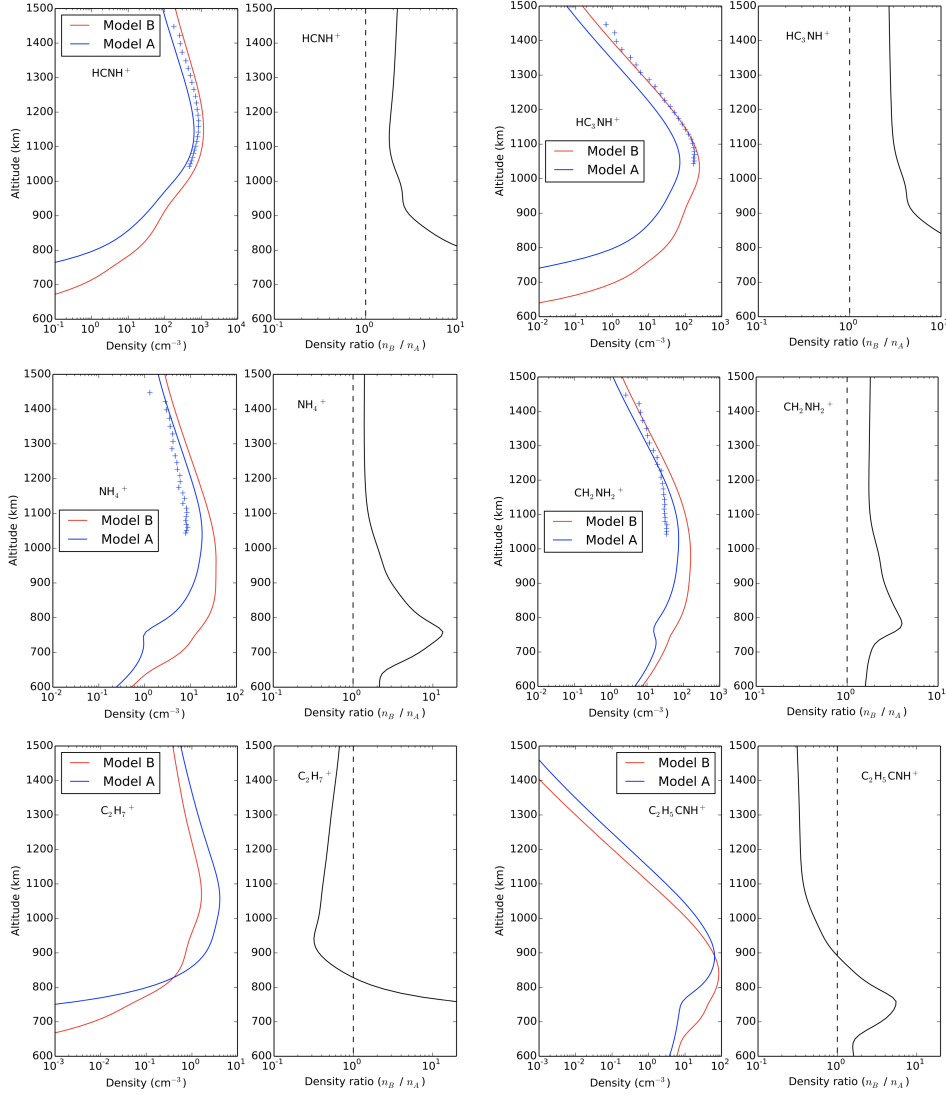


Fig. 14. Density profiles  $n_i$  of  $\text{HCNH}^+$ ,  $\text{HC}_3\text{NH}^+$ ,  $\text{NH}_4^+$ ,  $\text{CH}_2\text{NH}_2^+$ ,  $\text{C}_2\text{H}_7^+$  and  $\text{C}_2\text{H}_5\text{CNH}^+$  for the two models A and B and their ratio  $n_i(\text{B})/n_i(\text{A})$ . Observations come from Cassini/INMS (Westlake et al., 2012).

509 period of Titan. Ions and other species (like HCN) exhibit strong local time-  
 510 dependence. However, they used a rotating technique at constant latitude  
 511 and varying local-time to account for the diurnal variation of solar inputs. We  
 512 intend to improve their model using calculation of actinic flux in 2D geometry.  
 513 Such an extension deserves a dedicated study beyond the scope of the present  
 514 paper.

## 515 6 Conclusion

516 We made a comparison between two types of 1D photochemical models used  
517 in mean conditions. In the first model (Model A), the photolysis rates are  
518 computed by a classic plane-parallel ultraviolet radiative transfer model. In the  
519 second model (Model B), the ultraviolet radiative transfer model is based on a  
520 2D geometry. We first compared the mean photolysis rates for each photolysis  
521 process derived by the two models and found the following results:

- 522 • The mean photodissociation rates obtained with a 2D geometry model are  
523 generally greater than those obtained in a plane-parallel model. For many  
524 species, the enhancement factor is greater than 1.2. For some species, the  
525 enhancement factor reaches 1.4. For photoionisation, the results are more  
526 disparate.
- 527 • Considering the various branching paths of a given photodissociation rate,  
528 we found that the relative rates of each path can be affected differently,  
529 when the 2D geometry is accounted for photolysis, changing the relative  
530 importance of each path in Model B compared to Model A.
- 531 • We also obtained that the location of the photolysis peaks are generally  
532 slightly lower in altitude.

533 All these characteristics sufficiently affect the photochemical processes to give  
534 fraction profiles significantly different in Model B compared to Model A.

- 535 • We found little differences for some light species between the two models, in  
536 particular for light hydrocarbons like  $C_2H_2$ ,  $C_2H_4$  and  $C_2H_6$ . This, in fact,  
537 validates the use of 1D model in mean conditions for these species compared  
538 to a model using 2D geometry for calculating the actinic flux.
- 539 • The differences are more marked for many heavier species and especially  
540 for nitriles (from C3-hydrocarbons and other nitrogen species, i.e. the ones  
541 observers will target with the next generation of observatories). This effect  
542 is due to the fact that heavier species depend on several lighter species.
- 543 • Many density profiles of ions calculated from Model B are significantly dif-  
544 ferent from the ones obtained with Model A. This concerns major and minor  
545 species as well.

546 Note that, for most of the species, uncertainties on model results are important  
547 and do not permit to distinguish Model A and Model B profiles for the moment  
548 (see Dobrijevic et al. (2016)). Pending a decrease of these uncertainties (as we  
549 obtained for light hydrocarbons improving the chemical scheme over the past  
550 few years from Hébrard et al. (2007) to Dobrijevic et al. (2016)), it remains  
551 that the general tendency is that we obtain an increase in photochemical  
552 products from Model A to Model B.

553 Thus, we showed that a 1D photochemical model in which mean photolysis  
554 rates are calculated from actinic fluxes derived in 2D geometry gives results  
555 significantly different from a classical 1D photochemical model in mean con-  
556 ditions. We then advocate the use of 2D geometry from now on to compute  
557 the actinic flux and mean photolysis rates.

558 Additionally, we consider that this procedure is an interesting step to fill the  
559 gap between 1D models with large chemical scheme but limited physics (ra-  
560 diative balance, dynamics, cloud microphysics, etc.) and GCM-type models  
561 with very simplified chemical schemes (if any). This allows the development  
562 of 2D models allowing a better assessment of the effect of photolysis, the  
563 day-night average and putative latitudinal variations of the fluxes of in-falling  
564 species. Such 2D models should be a better tool than 1D models to interpret  
565 the numerous data gathered by the Cassini space probe with the possibility  
566 to better simulate variations with latitude. It would be also a better model  
567 to interpret disk-averaged observations or low spatial resolution observations  
568 obtained from the ground with a global mean approximation.

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