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M. Dobrijevic, J.C. Loison, V. Hue, T. Cavalié. One dimension photochemical models in global mean conditions in question: Application to Titan. Icarus, 2021, 364, pp.114477. 10.1016/j.icarus.2021.114477. hal-03358182

HAL Id: hal-03358182 https://hal.science/hal-03358182v1

Submitted on 6 Oct 2021

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

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¹³ Number of pages: 31

1

2

3

4

- ¹⁴ Number of tables: 2
- ¹⁵ Number of figures: 14

Preprint submitted to Icarus

¹⁶ Proposed Running Head:

17 Photochemical model in global mean conditions

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28 ABSTRACT

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

48 Keywords: Titan; Photochemistry; Atmospheres; Ionospheres

49 **1** Introduction

The atmosphere of Titan is a very complex system. Photolysis by solar pho-50 tons and ionization by Saturn magnetospheric electrons of the two major 51 compounds, molecular nitrogen (N_2) and methane (CH_4) , are the starting 52 point of a very rich chemistry, enhanced by the surface-atmosphere interac-53 tion, influxes from the Enceladus torus (Hartogh et al., 2011; Moreno et al., 54 2012; Dobrijevic et al., 2014; Lara et al., 2014; Teanby et al., 2018) and in-55 terplanetary dust particles (Moses and Poppe, 2017). This efficient chemistry 56 produces aerosols as the end products, which sediment down to the surface, 57 contributing to the radiative budget of the atmosphere and serving as nu-58 cleation particles in the lower stratosphere. Modeling Titan's atmosphere is 59 very challenging. In particular, from the chemical point of view, it is nec-60 essary to include numerous species and reactions in atmospheric models to 61 study the coupling of neutral, cationic and anionic species composed of vari-62 ous elements like carbon, hydrogen, oxygen, nitrogen and sulfur, throughout 63 the extended atmosphere (see for instance the recent models of Krasnopolsky 64 (2014), Hickson et al. (2014), Mukundan and Bhardwaj (2018), Loison et al. 65 (2019) and Vuitton et al. (2019)). Continuous detections of new molecules, 66 like ethyl cyanide (C_2H_5CN , Cordiner et al. (2015)), vinyl cyanide (C_2H_3CN , 67 Palmer et al. (2017)), and even isomers like propadiene (CH₂CCH₂, Lom-68 bardo et al. (2019)) and cyclopropenylidene (c-C₃H₂, Nixon et al. (2020)), 69 force modelers to constantly improve the chemical scheme they use, render-70 ing codes more and more time consuming. The study of isotopologues (Liang 71 et al., 2007; Mandt et al., 2009; Krasnopolsky, 2016; Loison et al., 2017; Dobri-72 jevic and Loison, 2018) also requires to increase drastically the complexity of 73 the chemical scheme: hundreds of species are necessary to encompass the en-74 tire chemical system of Titan's atmosphere in current photochemical models. 75 Two directions can then be taken to model Titan's atmosphere: (1) include 76 limited chemistry to focus on dynamics with 2D or 3D models using some 77 assumptions (for instance: few species, fixed neutral background atmosphere, 78 no cations, no anions, uncoupled chemistry between hydrocarbons and oxygen 79 species, and so on); (2) expand the chemical scheme in 1D models to focus 80 on chemical processes assuming mean conditions with neither latitudinal nor 81 longitudinal transport. 82

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

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

₉₂ models.

In the present paper, we compare two types of 1D photochemical models used 93 in mean conditions. In the first model, the photolysis rates are computed 94 by a classic plane-parallel ultraviolet radiative transfer model. In the second 95 model, the ultraviolet radiative transfer model is based on a 2D geometry. In 96 the following, we first present our 1D photochemical model (Section 2) and 97 the two radiative transfer models (Section 3). In Section 4, we compare the 98 photolysis rates calculated in 1D mean conditions and those derived from our 90 2D model. We then present the impact of the 2D photolysis rates on the mole 100 fraction profiles (Section 5) and we conclude in Section 6. 101

¹⁰² 2 Description of the 1D photochemical model

The present 1D photochemical model is based on the one presented in Loison et al. (2019) and Dobrijevic et al. (2016). We summarize the main characteristics in the following.

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

The mole fractions of CH_4 , H_2 , CO and Ar are fixed at the lower boundary 112 (surface of Titan): $y_{CH_4} = 1.48 \times 10^{-2}$, $y_{H_2} = 3.0 \times 10^{-3}$, $y_{CO} = 5.1 \times 10^{-5}$ and $y_{Ar} = 3.39 \times 10^{-5}$ (Loison et al. (2015) and references therein). The 113 114 mole fraction of N₂ is simply given by $y_{N_2} = 1 - (y_{CH_4} + y_{H_2} + y_{Ar} + y_{CO})$. 115 At the upper boundary, we use an external flux of $O(^{3}P)$ and a production 116 of H₂O from micrometeoritic ablation equal respectively to 1.6×10^6 and 117 5.2×10^5 cm⁻² s⁻¹ (values referred to the surface, see Dobrijevic et al. (2014) 118 for details). We assumed a zero flux as an upper boundary condition for all 119 the other species, except for atomic hydrogen (H) and molecular hydrogen 120 (H_2) , which were allowed to escape with velocities following Jean's thermal 121 escape mechanism (this mechanism is negligible for other species). We do not 122 consider sulfur species in the present study since no sulfur species have been 123 detected yet (see Hickson et al. (2014) for model prediction of sulfur-bearing 124 species abundances). 125

The eddy diffusion coefficient profile is constrained in the present model using argon (Ar) and methane (CH₄) in the higher atmosphere and water (H₂O) and hydrogen cyanide (HCN) in the lower atmosphere (see Loison et al. (2019) for details).

The chemical scheme is the same as in Loison et al. (2019) but using recent measurements of the rate constants at low temperatures of $N(^2D)$ with CH_4 , C_2H_6 and C_3H_8 (Nunez-Reyes et al., 2019a) and $N(^2D)$ with C_2H_2 (Nunez-Reyes et al., 2019b). Magnetospheric electrons are not taken into account to focus on the effect of photolysis. Our model contains 99 neutral species and 83 ion species (including electron). The chemical scheme has been published 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

The actinic flux is the quantity of light available to molecules at a particular point in the atmosphere and which, on absorption and ionisation, drives photochemical processes in the atmosphere. This quantity is one of the terms required in the calculation of photolysis rates (photodissociation and photoionisation rates).

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

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

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

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

$$\tau(\lambda, z) = \frac{1}{\cos(\theta)} \sum_{i} \sigma_i(\lambda) \int_{z}^{\infty} n_i(z') dz'$$
(2)

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

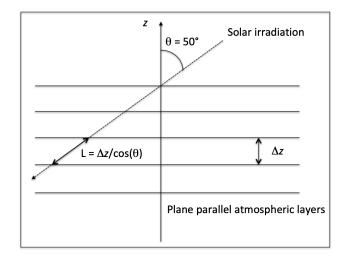


Fig. 1. Model A. The atmosphere of Titan is divided in 137 plane-parallel layers in altitude from the ground $z_0 = 0$ up to the top of the atmospheric model $z_{top} = 1500$ km. The altitude grid is non-uniform (i.e. the thickness Δz is not constant with altitude). We use a Solar Zenith Angle $\theta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

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

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

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

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

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

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

The solar irradiance at the top of the atmosphere comes from Dobrijevic et al. (2016). We consider a wavelength range from 0 to 730 nm with a spectral resolution of 0.001 nm in order to take into account the high resolution cross sections of many species (N_2 , H_2 , CO, etc.). The model takes into account absorption, ionization, and Rayleigh scattering by N_2 , H_2 and attenuation by aerosols in the lower stratosphere.

178 3.2 Actinic flux in a 2D geometry

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

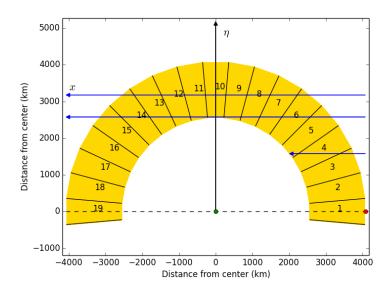


Fig. 2. Model B. The atmosphere of Titan (in yellow) is divided in 19 latitude sections from -5° to 185° . Each section corresponds to a latitudinal range of 10° . The red point corresponds to a sub-solar latitude of 0° (SSL0). Section #1 is the sub-solar section and section #10 corresponds to SSL90. 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 al-¹⁸⁸ titudinal 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-

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

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

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

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

$$\tau(\lambda,\eta) = \sum_{i} \sigma_i(\lambda) \int_0^\infty n_i(x) dx$$
(6)

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

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

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

Finally, after calculating the actinic flux in each cell (z,s) where z is the latitude and s the section number, we introduce a specific photolysis rate $J_i(z,s)$, which corresponds to the photolysis rate as a function of altitude for 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

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

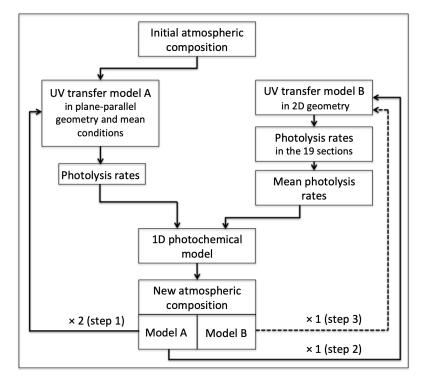


Fig. 3. Schematic diagram showing the two UV transfer models and their use with our 1D photochemical model.

In a 2D geometry for calculating the actinic flux, the mean conditions are obtained by using the photolysis rates calculated with the Model B and the atmospheric composition obtained with the Model A (end of step #1). This model computes the photolysis rates for each section. Then, we average them over all the sections to obtain mean photolysis rates, which correspond to an average over SZA from 0° to 90° and day/night average. This procedure corresponds to step #2 in Figure 3.

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

255 4 Results: photolysis rates

256 4.1 Photolysis rates

257 4.1.1 Model A

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

268 4.1.2 Model B

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

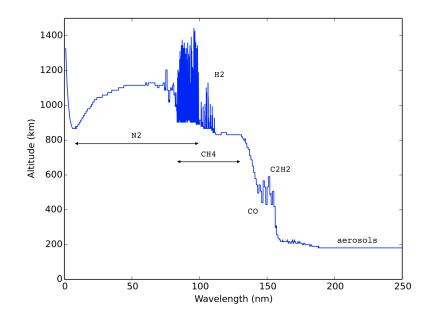


Fig. 4. Depth of penetration of solar photons in the atmosphere of Titan as a function of wavelength. The main contributors to the absorption are depicted.

Figure 6 shows an example of photolysis rates as a function of altitude and section for H₂. Although the first 3 sections do not exhibit strong differences in the photodissociation rates of H₂ (for a given altitude), the rate profiles change more and more strongly in the following sections. The H₂ photodissociation rate decreases more rapidly and occurs at higher altitude as a function of section number toward terminator (SSL90) and beyond. The photolysis of H₂ is no more efficient after section #12 (SSL115).

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

289

$$\overline{J}_i(z) = \frac{\sum\limits_{s=1}^{\infty} J_i(z,s)}{N_s}$$
(7)

where $N_s = 19$ is the number of sections considered in Model B. Figure 6 shows the mean rate $\overline{J}_i(z)$ for H₂ obtained from equation 7. The effect of day/night mean is clearly visible.

293 4.1.3 Validation

 N_s

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

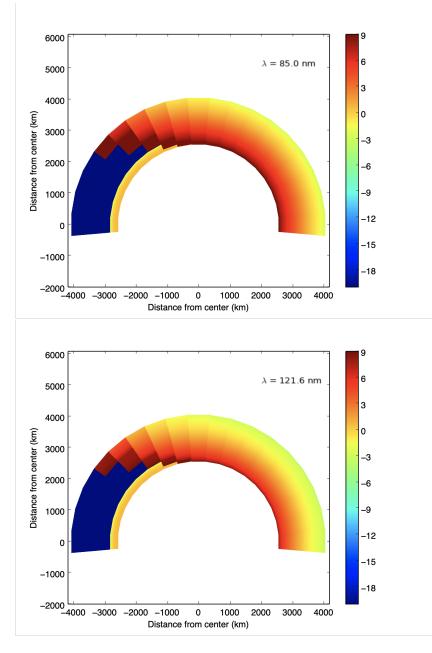


Fig. 5. Logarithm of the total optical depth as a function of altitude and section at two wavelengths (85 nm and 121.6 nm). The maximum of the photolysis rate profile corresponds to the altitude where the total optical depth is equal to 1 (altitude level corresponding to the orange level). The contribution 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° 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

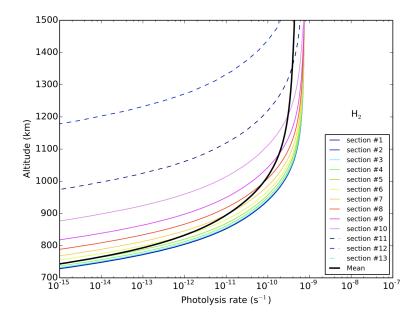


Fig. 6. Photolysis rate of H_2 as a function of altitude and section number. The rate of section #13 and following sections are too low and does not appear in the figure. The mean photolysis rate computed from all the sections is shown in black for comparison.

in Figure 7. For a species like CH_4 with a low resolution cross section, the 303 agreement between the two models is perfect. Note that, even for section #1304 in Model B, there is a geometry effect that is not taken into account in plane-305 parallel models (Model A). For N₂ (not shown), the ratio J_B/J_A does not 306 exceed 1.1 above 600 km of altitude (only a fraction of the cross section is 307 at high resolution). On the other hand, for species with high resolution cross 308 sections, there are noticeable differences as a function of altitude. For CO (not 309 shown), the ratio (J_B/J_A) is about 0.7 between 800 and 1000 km. This is due 310 to the fact that at some specific wavelength photons go deeper (or are stopped 311 higher) in the atmosphere and the geometric effect in the 2D model becomes 312 more significant. In Model B, photons tend to be slightly absorbed at higher 313 altitude than in Model A. This difference increases when comparing Model A 314 with the other sections in Model B (sections #2 and #18 for instance). For 315 H_2 , the effect is the opposite, J_A being about 40% greater than J_B at 900 km 316 of altitude (see Figure 7). 317

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 #7³²² with respect to the terminator). This result is in agreement with the use of a ³²³ SZA equal to 60° in 1D photochemical models in global mean conditions.

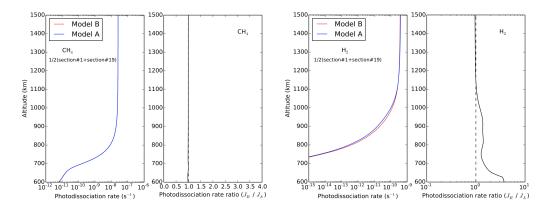


Fig. 7. Left sub-panels: Photolysis rate of CH₄ and H₂ for a SZA = 0° (J_A , Model A) and for the mean of sections #1 and #19 (J_B , Model B). Right sub-panels: Ratios of the photolysis rates (J_B/J_A).

324 4.1.4 Comparison between Model A and Model B

We present in Figure 8 the global mean photolysis rates of the two major 325 compounds in the photochemistry of Titan's atmosphere. The maximum of 326 methane photolysis occurs around an altitude of 800 km (see Figure 4). At this 327 altitude, the ratio J_B/J_A is around 1.3 and increases up to 2.7 at 735 km. For 328 N_2 , the ratio J_B/J_A is between 1.1 and 1.5 in the altitudinal range [1100, 900] 329 km where N_2 is efficiently photolyzed. As a consequence, the two precursor 330 mechanisms of chemical complexity are increased in Model B compared to 331 Model A. We see in the next section that this has a noticeable effect on the 332 production of organic compounds in the atmosphere. 333

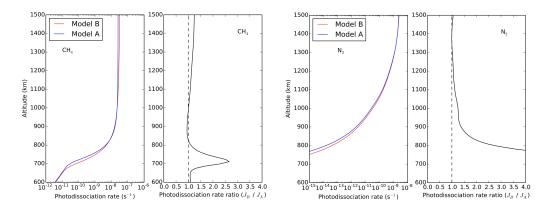


Fig. 8. Global mean photolysis rate of CH₄ and N₂ for Model A (J_A) and for Model B (J_B) . Right sub-panels: Ratios of the photolysis rates (J_B/J_A) .

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 C_2H_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 km. Paths 1 and 3 (to a lesser extent) are the major contributors to the total
photodissociation rate. Their ratios are counterbalanced by the ones of paths
2, 4 and 5. This example shows that partial rates of paths 1 and 3 are favored
in Model B in contrast to paths 2, 4 and 5.

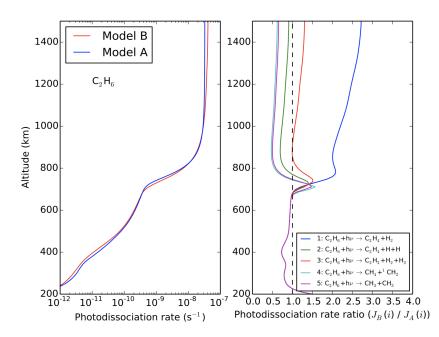


Fig. 9. Left: Photolysis rates of C_2H_6 for Models A and B. Right: Photolysis rate ratios for the five photodissociation pathways.

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

• The number of compounds that are photodissociated (or photoionised) $P_i(z)$ at altitude z (in cm⁻³s⁻¹) is given by:

349

$$P_i(z) = n_i(z) \times J_i(z) \tag{8}$$

where $n_i(z)$ is the density of compound i (in cm⁻³) and $J_i(z)$ its photodissociation (or photoionisation) rate (in s⁻¹) at altitude z. This quantity reaches a maximum $P_i(z_m)$ at altitude z_m . For instance, the maximum of methane photodissociation occurs around an altitude of 830 km with 42.42 molecules dissociated per cm³ and per second. In the tables, the subscripts A and B correspond to Model A and Model B respectively.

• The ratio $P_B(z_{m,B})/P_A(z_{m,A})$ is given for the altitude corresponding the maximum of $P_i(z)$, $z_{m,A}$ in Model A and $z_{m,B}$ in Model B. We see in the tables that $z_{m,B}$ can be at the same altitude than in Model A but in general, it is at lower altitude, and sometimes at higher altitude (like for C₂H₄). The precision on $z_{m,A}$ and $z_{m,B}$ is limited by the discretization of our altitude grid. For instance, around 900 km of altitude the interval between two consecutive altitude levels is 12 km and 10 km around 220 km of altitude.

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

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

The integration is done from the surface to the top of our atmospheric model. For instance, the ratio \tilde{P}_B/\tilde{P}_A is 1.12 for C₂H₂ and only 1.01 for $P_B(z_{m,B})$ / $P_A(z_{m,A})$.

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

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

386 5 Results: abundance profiles

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

Table 1

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

5^{-1} .						
Compound	$\begin{array}{c} P_A(z_{m,A})\\ (\mathrm{cm}^{-3}\mathrm{s}^{-1}) \end{array}$	$z_{m,A}$ (km)	$z_{m,B}$ (km)	$P_B(z_{m,B})/P_A(z_{m,A})$	$\frac{\widetilde{P}_A}{(\mathrm{cm}^{-2}\mathrm{s}^{-1})}$	$\widetilde{P}_B/\widetilde{P}_A$
H ₂	4.12×10^{-3}	1019	980	1.36	1.15×10^{5}	1.30
CH ₃	1.11×10^{1}	807	807	1.13	3.75×10^{8}	1.10
CH ₄	4.24×10^{1}	831	819	1.00	8.25×10^{8}	1.08
C_2H_2	2.34×10^{2}	227	217	1.01	3.39×10^{9}	1.12
C ₂ H ₃	4.36×10^{-1}	227	227	1.03	5.28×10^{6}	1.12
C_2H_4	1.78×10^{1}	227	651	0.95	9.45×10^{8}	1.00
C ₂ H ₆	1.68×10^{-1}	257	247	0.83	6.87×10^{6}	0.94
C ₃	8.57×10^{-4}	1059	1073	1.17	2.04×10^{4}	1.16
cC_3H_2	9.70×10^{-1}	891	891	1.32	3.37×10^{7}	1.33
C ₃ H ₃	1.16×10^{0}	208	199	1.29	3.29×10^{7}	1.36
CH ₃ C ₂ H	5.10×10^{0}	208	199	1.08	6.17×10^{7}	1.18
CH ₂ CCH ₂	3.06×10^{0}	217	208	1.05	5.21×10^{7}	1.17
C ₃ H ₆	1.45×10^{1}	217	199	1.06	1.59×10^{8}	1.18
C ₃ H ₈	8.98×10^{-1}	237	237	0.94	1.33×10^{7}	0.99
C ₄ H ₂	1.86×10^{1}	217	208	1.15	2.89×10^{8}	1.27
C ₄ H ₄	4.13×10^{0}	227	227	1.07	7.29×10^{7}	1.19
C ₄ H ₆	1.15×10^{1}	190	181	1.32	1.23×10^{8}	1.40
C ₄ H ₈	1.03×10^{1}	208	190	1.15	1.08×10^{8}	1.25
C ₄ H ₁₀	1.46×10^{0}	237	227	0.97	1.97×10^{7}	1.04
C ₆ H ₆	2.69×10^{1}	267	277	1.04	8.91×10^{8}	1.21
C ₆ H [*] ₆	2.68×10^{-1}	891	891	1.32	8.24×10^{6}	1.32
C ₆ H ₅ CH ₃	2.78×10^{1}	247	247	1.05	4.48×10^{8}	1.16
$C_6H_5C_2H$	1.51×10^{-2}	639	651	1.26	7.79×10^{5}	1.27
$C_6H_5C_2H_5$	6.27×10^{0}	217	208	1.12	8.07×10^{7}	1.25
C ₆ H ₅ NH ₂	2.60×10^{-2}	419	419	1.19	1.07×10^{6}	1.25
C ₆ H ₅ NHCH ₃	2.37×10^{-3}	993	993	1.32	5.93×10^4	1.29
C ₆ H ₅ CN	4.99×10^{-4}	855	855	1.35	1.80×10^4	1.29
AROM	3.71×10^{0}	199	181	1.33	4.46×10^{7}	1.4
NH2	1.17×10^{-3}	639	639	1.15	4.55×10^4	1.17
NH ₃	9.86×10^{-3}	879	879	1.30	3.94×10^{5}	1.29
N13 N2	6.77×10^{-1}	1087	1073	1.14	2.42×10^{7}	1.14
HCN	2.22×10^{0}	227	217	1.06	3.33×10^{7}	1.16
HNC	1.04×10^{-2}	967	967	0.99	2.41×10^5	1.02
CH ₂ NH	1.28×10^{-1}	831	831	1.34	5.28×10^{6}	1.33
CH ₃ NH ₂	8.38×10^{-2}	485	485	1.20	1.98×10^{6}	1.20
CH ₃ CN	1.15×10^{-1}	227	217	1.05	1.75×10^{6}	1.14
HC ₃ N	5.57×10^{-2}	639	639	1.20	2.63×10^{6}	1.20
HC ₅ N	1.48×10^{-2}	867	867	1.18	3.68×10^{5}	1.17
C ₂ H ₃ CN	2.72×10^{-1}	519	519	1.22	1.41×10^{7}	1.24
C ₂ H ₅ CN	6.18×10^{-2}	227	217	1.05	1.03×10^{6}	1.13
C ₃ H ₇ CN	1.68×10^{-3}	227	217	1.00	2.25×10^4	1.10
CH ₃ C ₃ N	6.65×10^{-2}	843	855	0.92	1.67×10^{6}	0.92
C ₂ N ₂	0.03×10 7.67×10^{-3}	247	247	0.92	2.47×10^{5}	1.06
C_2N_2 C_4N_2	1.63×10^{-3}	795	795	1.12	2.47×10^{-10} 6.51×10^{4}	1.12
	4.05×10^{-2}	247	247	0.98	1.02×10^{6}	1.12
H ₂ O CO	4.03×10 2.80×10^{-3}	891	879	0.98	6.29×10^4	0.85
нсо	2.80×10^{-4} 3.47×10^{0}	891 147	123	2.44	6.29×10^{-10} 3.83×10^{-7}	0.85 2.25
	3.47×10^{-2} 1.12×10^{-2}				3.83×10^{-5} 5.32×10^{-5}	
H ₂ CO	1.12×10 4.02×10^{-3}	855	855	1.35	5.32×10^{4} 5.30×10^{4}	1.34
CO ₂	4.02×10 5	227	217	1.08	5.30×10-	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 cm ⁻³ s ⁻¹ at altitude $z_{m,A}$ for
Model A, \widetilde{P}_4 is the column-integrated production rate for Model A in cm ⁻² s ⁻¹ .

A. FA is the column-integrated production rate for Model A in chi									
Compound	$P_A(z_{m,A})$	$z_{m,A}$	$z_{m,B}$	$P_B(\boldsymbol{z}_{m,B})/P_A(\boldsymbol{z}_{m,A})$	\widetilde{P}_A	$\widetilde{P}_B/\widetilde{P}_A$			
	$({\rm cm}^{-3}{\rm s}^{-1})$	(km)	(km)		$(cm^{-2}s^{-1})$				
Н	9.60×10^{-4}	954	928	0.70	2.09×10^{4}	0.79]		
H_2	1.87×10^{-3}	1101	1087	1.06	4.66×10^{4}	1.12			
N_2	3.40×10^{0}	1073	1059	1.02	7.98×10^{7}	1.07			
CH_3	2.20×10^{-2}	879	879	0.89	4.90×10^{5}	0.94			
CH_4	7.75×10^{-1}	954	915	0.83	2.27×10^{7}	0.95			
cC_3H_2	7.14×10^{-4}	980	993	1.00	1.95×10^{4}	1.02			
CH_3C_2H	1.84×10^{-3}	928	915	0.91	4.42×10^4	0.95			
CH_2CCH_2	1.12×10^{-3}	954	941	0.89	2.70×10^4	0.94			
C_4H_2	2.29×10^{-2}	879	879	0.5	4.37×10^{5}	0.53			
C_6H_6	1.84×10^{-3}	855	843	0.98	3.20×10^{4}	1.04			
$C_6H_6^*$	1.61×10^{-2}	891	891	1.34	4.95×10^{5}	1.33			
$C_6H_5CH_3$	1.58×10^{-3}	879	879	0.95	2.81×10^{4}	1.00			
$\mathrm{C}_{6}\mathrm{H}_{5}\mathrm{C}_{2}\mathrm{H}_{5}$	1.99×10^{-4}	903	903	0.95	3.36×10^{3}	0.99			
H_2O	1.92×10^{-6}	954	941	0.98	7.18×10^{1}	1.04			
CO_2	5.43×10^{-8}	915	891	1.39	1.04×10^{0}	1.40			
CO	5.92×10^{-4}	928	915	1.21	1.64×10^{4}	1.20			
	$\begin{tabular}{c} Compound \\ H \\ H_2 \\ N_2 \\ CH_3 \\ CH_4 \\ cC_3H_2 \\ CH_3C_2H \\ CH_2CCH_2 \\ C_4H_2 \\ C_6H_6 \\ C_6H_6 \\ C_6H_5CH_3 \\ C_6H_5CH_3 \\ C_6H_5C_2H_5 \\ H_2O \\ CO_2 \\ \end{tabular}$	$\begin{array}{c c} \mbox{Compound} & P_A(z_{m,A}) \\ (cm^{-3}s^{-1}) \\ \mbox{H} & 9.60 \times 10^{-4} \\ \mbox{H}_2 & 1.87 \times 10^{-3} \\ \mbox{N}_2 & 3.40 \times 10^0 \\ \mbox{CH}_3 & 2.20 \times 10^{-2} \\ \mbox{CH}_4 & 7.75 \times 10^{-1} \\ \mbox{cC}_3 \mbox{H}_2 & 7.14 \times 10^{-4} \\ \mbox{CH}_3 \mbox{C}_2 \mbox{H} & 1.84 \times 10^{-3} \\ \mbox{CH}_2 \mbox{CCH}_2 & 1.12 \times 10^{-3} \\ \mbox{C}_4 \mbox{H}_2 & 2.29 \times 10^{-2} \\ \mbox{C}_6 \mbox{H}_6 & 1.61 \times 10^{-2} \\ \mbox{C}_6 \mbox{H}_6 & 1.58 \times 10^{-3} \\ \mbox{C}_6 \mbox{H}_5 \mbox{C}_2 \mbox{H}_5 & 1.99 \times 10^{-4} \\ \mbox{H}_2 \mbox{O} & 1.92 \times 10^{-6} \\ \mbox{CO}_2 & 5.43 \times 10^{-8} \end{array}$	$\begin{array}{c c} \mbox{Compound} & P_A(z_{m,A}) & z_{m,A} \\ (cm^{-3}s^{-1}) & (km) \\ \hline \\ \mbox{H} & 9.60 \times 10^{-4} & 954 \\ \mbox{H}_2 & 1.87 \times 10^{-3} & 1101 \\ \mbox{N}_2 & 3.40 \times 10^0 & 1073 \\ \mbox{CH}_3 & 2.20 \times 10^{-2} & 879 \\ \mbox{CH}_4 & 7.75 \times 10^{-1} & 954 \\ \mbox{cC}_3 \mbox{H}_2 & 7.14 \times 10^{-4} & 980 \\ \mbox{CH}_3 \mbox{C}_2 \mbox{H} & 1.84 \times 10^{-3} & 928 \\ \mbox{CH}_2 \mbox{CC}_2 & 1.12 \times 10^{-3} & 954 \\ \mbox{C}_4 \mbox{H}_2 & 2.29 \times 10^{-2} & 879 \\ \mbox{C}_6 \mbox{H}_6 & 1.84 \times 10^{-3} & 855 \\ \mbox{C}_6 \mbox{H}_6 & 1.58 \times 10^{-3} & 879 \\ \mbox{C}_6 \mbox{H}_5 \mbox{C}_2 \mbox{H}_5 & 1.99 \times 10^{-4} & 903 \\ \mbox{H}_2 \mbox{O} & 1.92 \times 10^{-6} & 954 \\ \mbox{CO}_2 & 5.43 \times 10^{-8} & 915 \\ \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		

394 5.1 Global view

We first present a global view on the differences between Model A and Model 395 B. Figure 10 shows the ratio, at an altitude of 1000 km, of the mole fraction 396 obtained with the Model B over the one of the Model A for the most abundant 397 species (with mole fractions greater than 10^{-12} in the Model B). For clarity, 398 only a few points are labeled in the figure, those corresponding to the extreme 399 values of the ratio. The most important result is that most of the species have 400 a ratio significantly greater than 1, meaning that Model A gives abundances 401 notably smaller than model B. Many species have a ratio greater than 2 (a 402 factor of 3.2 for HCN and 3.4 for C_2H_3CN for instance) and for several species 403 the ratio exceeds a factor of 5 (a factor of 6.7 for C_2N_2 and 13.6 for C_4N_2 404 for instance). In particular, among the species that have densities significantly 405 enhanced, many of them are nitrogen species. 406

We see also that in general, the lower the relative abundance of species, the greater the number of species that show a strong disagreement between the two models. This trend is limited however by the fact that the chemical scheme is far from being complete for heavy species. Indeed, due to the lack of available information in the literature, the number of reactions in our chemical scheme is not proportional to the mass of species, as it should theoretically be (see 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

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

432 5.2.1 Neutral species

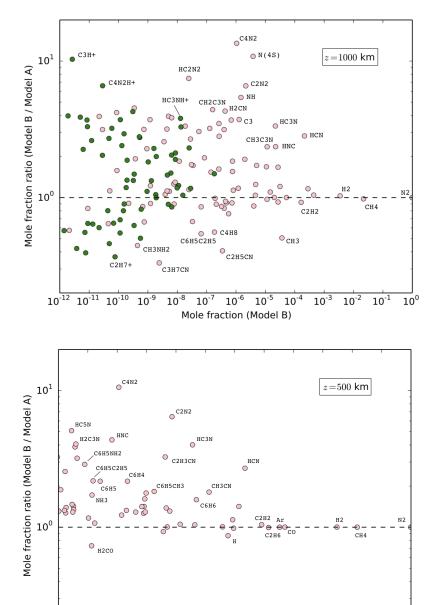
For HCN (Figure 11), the enhancement factor from Model A to Model B is greater than 2 in the major part of the atmosphere. Model B seems to be in a better agreement with observations from Cassini/CIRS (Vinatier et al. (2010)) and Cassini/INMS (Magee et al. (2009)) than Model A.

For HC₃N (Figure 11), the enhancement factor is equal to or greater than 3 from the ionosphere to the stratosphere with a factor of 4 around 400 km.
Model B is in slightly better agreement with both Cassini/CIRS (Vinatier et al. (2010)) and ALMA observations (Cordiner et al. (2019)), but also with INMS data from Cui et al. (2009), which is about 20 times greater than the value inferred by Magee et al. (2009).

For C₂N₂ (Figure 11), the enhancement factor is relatively high with a value between 5 and 6 from the top of the atmosphere down to 200 km. Model B seems to be in better agreement with Cassini/CIRS observations (Sylvestre et al. (2020)) and in good agreement with Cassini/INMS data retrieved by Magee et al. (2009) but not with Cui et al. (2009).

• For C_4N_2 (Figure 11), the enhancement factor reaches a factor 10 in the mesosphere and stratosphere. There is no direct detection of this species for the moment.

• We obtain also an enhancement factor greater than 2 for C_2H_3CN and C_2H_5CN . The mole fraction profiles of C_2H_3CN and C_2H_5CN derived from Model B seem to be in better agreement with ALMA observation (Cordiner et al. (2019)) but the abundances are still too low at all altitudes. Contribution of the limbs in ALMA data and the increase of nitrile mole fractions



 $10^{-12} \ 10^{-11} \ 10^{-10} \ 10^{-9} \ 10^{-8} \ 10^{-7} \ 10^{-6} \ 10^{-5} \ 10^{-4} \ 10^{-3} \ 10^{-2} \ 10^{-1} \ 10^{0}$ Mole fraction (Model B)

Fig. 10. Ratios of the mole fractions obtained at a given altitude of Model B over Model A. Each point corresponds to a species in the models. Green and pink dots correspond to ions and neutrals respectively. Top: Altitude z equal to 1000 km. Some points with high ratio are labeled. Bottom: Altitude z equal to 500 km. Some particular dots are labeled with the name of the corresponding molecule.

⁴⁵⁶ in polar region might contribute to this discrepancy.

 $_{457}$ • The two isomers of C_3H_4 (Figure 12) have been detected recently by the

458 Texas Echelle Cross Echelle Spectrograph on the NASA Infrared Telescope

⁴⁵⁹ Facility (TEXES), i.e. propadiene (or allene, CH₂CCH₂) and propyne (or

 $_{460}$ methylacetylene, CH₃C₂H), see Lombardo et al. (2019). There is no signifi-

461 cant difference between Model A and Model B. Our model is in quite good462 agreement with observations.

Using ALMA, Thelen et al. (2020) obtained the first spectroscopic detection of CH₃C₃N (methylcyanoacetylene or cyanopropyne) in Titan's atmosphere (Figure 12). It might be interesting to test our profile with a radiative transfert code to better compare our profile with ALMA observations.

• For c-C₃H₂, there is no significant difference between Model A and Model B. The mole fraction ratio reaches a factor of about 2 in an altitudinal region where the mole fractions are very low. It might be also required to use a radiative transfert code to better compare our profile with ALMA observations.

- CH_3CN (methyl cyanide) has been also detected by ALMA (see Thelen et al.
- (2019) and references therein). There is a factor of about 2 between Model
- A and Model B (Figure 12). Observations seem to slightly favor Model A.

475 5.2.2 Ions

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

As we can see in Figure 10, many ions have densities significantly different in 485 Model B compared to Model A. We present in Figure 14 the density profiles 486 of six of them with opposite behaviors. In the case of $HCNH^+$, HC_3NH^+ , NH_2^+ 487 and $CH_2NH_2^+$ the density is enhanced in Model B compared to Model A. In 488 the case of $C_2H_7^+$ and $C_2H_5CNH^+$, the density is lower in Model B in the 489 ionosphere (above the peak of density). Below about 800 km of altitude, the 490 density in Model B becomes much higher. For the moment, comparison with 491 observations is not conclusive and cannot favor either model. For HC₃NH⁺, 492 there is a very good agreement between Model B and Cassini/INMS data, 493 while for NH_2^+ , Model A seems to be in better agreement. These differences 494 reflect in part uncertainties in the chemical rates (see Dobrijevic et al. (2016)) 495 and for an another part to incomplete description of the chemical scheme 496 (important reaction may be missing or products poorly known). 497

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

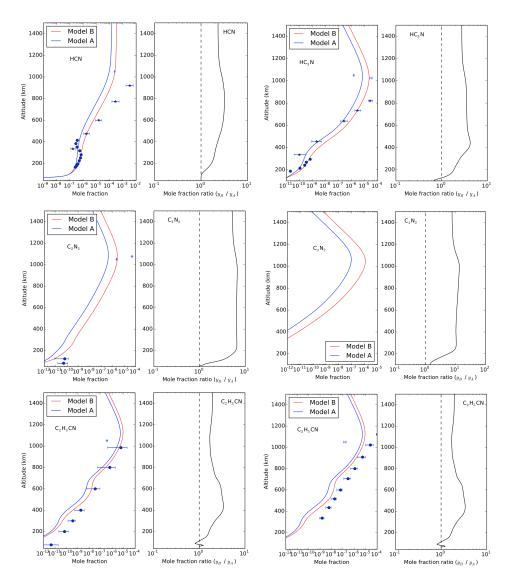


Fig. 11. Mole fraction profiles y_i of HCN, HC₃N, C₂N₂, C₄N₂, C₂H₃CN and C₂H₅CN for the two models A and B and their ratio $y_i(B)/y_i(A)$. Observations come from Cassini/CIRS (HCN and HC₃N from Vinatier et al. (2010) and C₂N₂ from Sylvestre et al. (2020)), Cassini/INMS (Magee et al., 2009; Cui et al., 2009) and ALMA (HCN, HC₃N and C₂H₅CN from Cordiner et al. (2019) and C₂H₃CN from Palmer et al. (2017)).

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

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

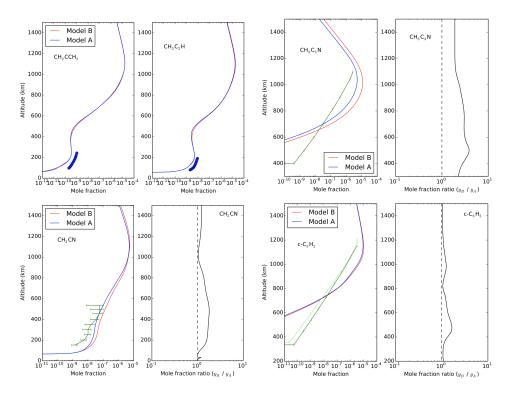


Fig. 12. Mole fraction profiles y_i of two isomers of C_3H_4 (CH₂CCH₂ and CH₃C₂H), CH₃C₃N, CH₃CN and c-C₃H₂ for the two models A and B and their ratio $y_i(B)/y_i(A)$ (except for C₃H₄). Observations come from TEXES (Lombardo et al. (2019) for C₃H₄) and ALMA (CH₃C₃N from Thelen et al. (2020), CH₃CN from Thelen et al. (2019) and c-C₃H₂ from Nixon et al. (2020)). For c-C₃H₂, observations gathered in two different spectral bands are shown.

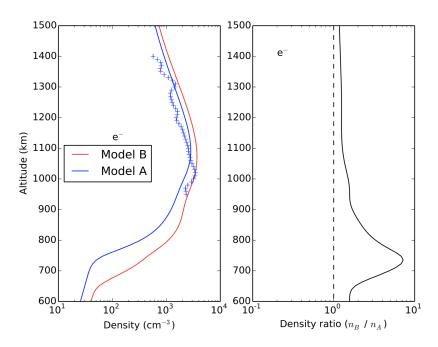


Fig. 13. Density profile of electrons for Model A and Model B.

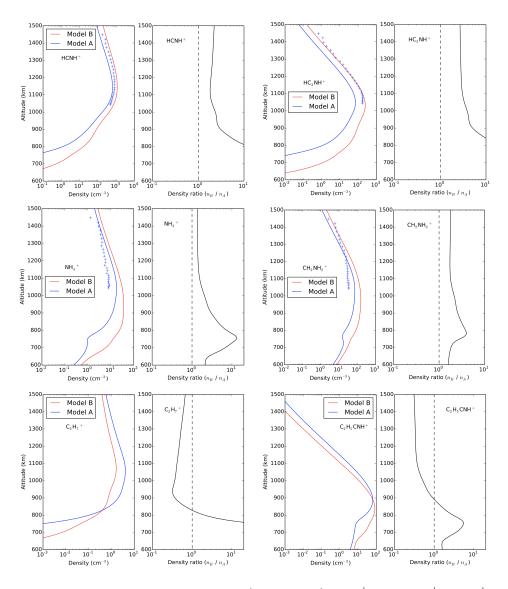


Fig. 14. Density profiles n_i of HCNH⁺, HC₃NH⁺, NH₂⁺, CH₂NH₄⁺, C₂H₇⁺ and C₂H₅CNH⁺ for the two models A and B and their ratio $n_i(B)/n_i(A)$. Observations come from Cassini/INMS (Westlake et al., 2012).

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

515 6 Conclusion

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

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

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

- We found little differences for some light species between the two models, in particular for light hydrocarbons like C₂H₂, C₂H₄ and C₂H₆. This, in fact, validates the use of 1D model in mean conditions for these species compared to a model using 2D geometry for calculating the actinic flux.
- The differences are more marked for many heavier species and especially for nitriles (from C3-hydrocarbons and other nitrogen species, i.e. the ones observers will target with the next generation of observatories). This effect is due to the fact that heavier species depend on several lighter species.

Many density profiles of ions calculated from Model B are significantly dif ferent from the ones obtained with Model A. This concerns major and minor
 species as well.

Note that, for most of the species, uncertainties on model results are important and do not permit to distinguish Model A and Model B profiles for the moment (see Dobrijevic et al. (2016)). Pending a decrease of these uncertainties (as we obtained for light hydrocarbons improving the chemical scheme over the past few years from Hébrard et al. (2007) to Dobrijevic et al. (2016)), it remains that the general tendency is that we obtain an increase in photochemical products from Model A to Model B. Thus, we showed that a 1D photochemical model in which mean photolysis rates are calculated from actinic fluxes derived in 2D geometry gives results significantly different from a classical 1D photochemical model in mean conditions. We then advocate the use of 2D geometry from now on to compute the actinic flux and mean photolysis rates.

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

569 Acknowledgements

We are grateful for the constructive reviews that have significantly improved the manuscript.

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