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

4 M. Dobrijevic ^a J.C. Loison ^b V. Hue ^c T. Cavalié ^{a,d}

5 ^a*Laboratoire d'Astrophysique de Bordeaux, Univ. Bordeaux, CNRS, B18N, allée*
6 *Geoffroy Saint-Hilaire, 33615 Pessac, France*

7 ^b*Institut des Sciences Moléculaires (ISM), CNRS, Univ. Bordeaux, 351 cours de la*
8 *Libration, 33400, Talence, France*

9 ^c*Southwest Research Institute, San Antonio, TX 78228, United States.*

10 ^d*LESIA, Observatoire de Paris, Université PSL, CNRS, Sorbonne Université,*
11 *Univ. Paris Diderot, Sorbonne Paris Cité, 5 place Jules Janssen, 92195 Meudon,*
12 *France*

13 Number of pages: 31

14 Number of tables: 2

15 Number of figures: 14

16 **Proposed Running Head:**
17 Photochemical model in global mean conditions

18 **Please send Editorial Correspondence to:**
19

20 Michel Dobrijevic
21 Laboratoire d'Astrophysique de Bordeaux
22 Université de Bordeaux - Bât. B18N
23 Allée Geoffroy Saint-Hilaire
24 CS 50023
25 33615 PESSAC CEDEX, France.
26 Email: michel.dobrijevic@u-bordeaux.fr
27

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

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 ($\text{C}_2\text{H}_5\text{CN}$, Cordiner et al. (2015)), vinyl cyanide ($\text{C}_2\text{H}_3\text{CN}$,
68 Palmer et al. (2017)), and even isomers like propadiene (CH_2CCH_2 , Lom-
69 bardo et al. (2019)) and cyclopropenylidene ($\text{c-C}_3\text{H}_2$, 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 Δ_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 CH_4 , H_2 , CO and 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 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 H_2O from micrometeoritic ablation equal respectively to 1.6×10^6 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 (H) and molecular hydrogen
121 (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 (Ar) and methane (CH_4) in the higher atmosphere and water (H_2O) 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.

3 UV radiative transfer model

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.

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

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

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:

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

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.

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

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

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:

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

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 slightly 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

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° separation as illustrated in Figure 2. The
 182 origin of latitudes is associated with the sub-solar point (or sub-solar latitude
 183 0° , SSL0 in the following) . The atmosphere is then divided in 19 sections of
 184 10° from -5° to 185° 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° 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-

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 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:

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

199 where $I_0(\lambda)$ is the solar flux at the top of the atmosphere at wavelength λ per
 200 unit of wavelength. The total optical depth at wavelength λ 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 λ
 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 η (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

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.

4 Results: photolysis rates

4.1 Photolysis rates

4.1.1 Model A

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

4.1.2 Model B

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

Figure 6 shows an example of photolysis rates as a function of altitude and section for H_2 . Although the first 3 sections do not exhibit strong differences in the photodissociation rates of H_2 (for a given altitude), the rate profiles change more and more strongly in the following sections. The H_2 photodissociation rate decreases more rapidly and occurs at higher altitude as a function of section number toward terminator (SSL90) and beyond. The photolysis of H_2 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 $\bar{J}_i(z)$ is simply given by:

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

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

4.1.3 Validation

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).

the rates obtained with Model A (J_A) considering a $\text{SZA} = 0^\circ$ and Model B (J_B) after the calculation of the SSL0 mean rates obtained with sections #1 and #19. In Model A, the solar flux at the top of the atmosphere is divided by 2 for day/night averaging. In Model B, since the actinic flux is null in section #19, the averaging of sections #1 and #19 corresponds to a division 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 agreement between the two models is perfect. Note that, even for section #1 in Model B, there is a geometry effect that is not taken into account in plane-parallel models (Model A). For N_2 (not shown), the ratio J_B/J_A does not exceed 1.1 above 600 km of altitude (only a fraction of the cross section is at high resolution). On the other hand, for species with high resolution cross sections, there are noticeable differences as a function of altitude. For CO (not shown), the ratio (J_B/J_A) is about 0.7 between 800 and 1000 km. This is due to the fact that at some specific wavelength photons go deeper (or are stopped higher) in the atmosphere and the geometric effect in the 2D model becomes more significant. In Model B, photons tend to be slightly absorbed at higher altitude than in Model A. This difference increases when comparing Model A with the other sections in Model B (sections #2 and #18 for instance). For H_2 , the effect is the opposite, J_A being about 40% greater than J_B at 900 km of altitude (see Figure 7).

Due to the geometry of the 2D model, the best agreement between the 1D model at mean conditions (Model A) and the 2D model with day/night averaged rates (Model B) is obtained when considering section #7 (between SSL55 and SSL65) and section #13 (which is the symmetric of section #7 with respect to the terminator). This result is in agreement with the use of a SZA equal to 60° in 1D photochemical models in global mean conditions.

Fig. 7. Left sub-panels: Photolysis rate of CH_4 and 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 N_2 , the ratio J_B/J_A is between 1.1 and 1.5 in the altitudinal range [1100, 900] km where 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 CH_4 and 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 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

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 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 ₂ H 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 ₂ H 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 ₃ H 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 ₆ H ₅ C ₂ H	1.51×10^{-2}	639	651	1.26	7.79×10^5	1.27
C ₆ H ₅ C ₂ H 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
NH ₂	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
N ₂	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	7.67×10^{-3}	247	247	0.95	2.47×10^5	1.06
C ₄ N ₂	1.63×10^{-3}	795	795	1.12	6.51×10^4	1.12
H ₂ O	4.05×10^{-2}	247	247	0.98	1.02×10^6	1.10
CO	2.80×10^{-3}	891	879	0.79	6.29×10^4	0.85
HCO	3.47×10^0	147	123	2.44	3.83×10^7	2.25
H ₂ CO	1.12×10^{-2}	855	855	1.35	5.32×10^5	1.34
CO ₂	4.02×10^{-3}	227	217	1.08	5.30×10^4	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	9.60×10^{-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 ₃ H ₂	7.14×10^{-4}	980	993	1.00	1.95×10^4	1.02
CH ₃ C ₂ H	1.84×10^{-3}	928	915	0.91	4.42×10^4	0.95
CH ₂ CCH ₂	1.12×10^{-3}	954	941	0.89	2.70×10^4	0.94
C ₄ H ₂	2.29×10^{-2}	879	879	0.5	4.37×10^5	0.53
C ₆ H ₆	1.84×10^{-3}	855	843	0.98	3.20×10^4	1.04
C ₆ H ₆ [*]	1.61×10^{-2}	891	891	1.34	4.95×10^5	1.33
C ₆ H ₅ CH ₃	1.58×10^{-3}	879	879	0.95	2.81×10^4	1.00
C ₆ H ₅ C ₂ H ₅	1.99×10^{-4}	903	903	0.95	3.36×10^3	0.99
H ₂ O	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

5.1 Global view

We first present a global view on the differences between Model A and Model B. Figure 10 shows the ratio, at an altitude of 1000 km, of the mole fraction obtained with the Model B over the one of the Model A for the most abundant species (with mole fractions greater than 10^{-12} in the Model B). For clarity, only a few points are labeled in the figure, those corresponding to the extreme values of the ratio. The most important result is that most of the species have a ratio significantly greater than 1, meaning that Model A gives abundances notably smaller than model B. Many species have a ratio greater than 2 (a factor of 3.2 for HCN and 3.4 for C₂H₃CN for instance) and for several species the ratio exceeds a factor of 5 (a factor of 6.7 for C₂N₂ and 13.6 for C₄N₂ for instance). In particular, among the species that have densities significantly enhanced, many of them are nitrogen species.

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)).

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

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

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).

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 HC_3N (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 C_2N_2 (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 $\text{C}_2\text{H}_3\text{CN}$ and $\text{C}_2\text{H}_5\text{CN}$. The mole fraction profiles of $\text{C}_2\text{H}_3\text{CN}$ and $\text{C}_2\text{H}_5\text{CN}$ 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

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.

in polar region might contribute to this discrepancy.

- The two isomers of C_3H_4 (Figure 12) have been detected recently by the Texas Echelle Cross Echelle Spectrograph on the NASA Infrared Telescope Facility (TEXES), i.e. propadiene (or allene, CH_2CCH_2) and propyne (or methylacetylene, CH_3C_2H), see Lombardo et al. (2019). There is no signifi-

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 • CH_3CN (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 HCNH^+ , HC_3NH^+ , NH_2^+
 488 and CH_2NH_2^+ the density is enhanced in Model B compared to Model A. In
 489 the case of C_2H_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 HC_3NH^+ ,
 493 there is a very good agreement between Model B and Cassini/INMS data,
 494 while for 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, 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 (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 HCNH^+ , HC_3NH^+ , NH_4^+ , CH_2NH_2^+ , C_2H_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.

569 **Acknowledgements**

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

572 References

- 573 Cordiner, M. A., Palmer, M. Y., Nixon, C. A., Irwin, P. G. J., Teanby,
574 N. A., Charnley, S. B., Mumma, M. J., Kiesel, Z., Serigano, J., Kuan, Y.-J.,
575 Chuang, Y.-L., Wang, K.-S., Feb. 2015. Ethyl Cyanide On Titan: Spec-
576 troscopic Detection and Mapping Using Alma. *The Astrophysical Journal*
577 *Letters* 800, L14.
- 578 Cordiner, M. A., Teanby, N. A., Nixon, C. A., Vuitton, V., Thelen, A. E.,
579 Charnley, S. B., Aug. 2019. ALMA Spectral Imaging of Titan Contempo-
580 raneous with Cassini’s Grand Finale. *The Astronomical Journal* 158 (2),
581 76.
- 582 Cui, J., Yelle, R. V., Vuitton, V., Waite, J. H., Kasprzak, W. T., Gell, D. A.,
583 Niemann, H. B., Müller-Wodarg, I. C. F., Borggren, N., Fletcher, G. G.,
584 Patrick, E. L., Raaen, E., Magee, B. A., Apr. 2009. Analysis of Titan’s neu-
585 tral upper atmosphere from Cassini Ion Neutral Mass Spectrometer mea-
586 surements. *Icarus* 200, 581–615.
- 587 De La Haye, V., Waite, J. H., Cravens, T. E., Robertson, I. P., Lebonnois,
588 S., Sep. 2008. Coupled ion and neutral rotating model of Titan’s upper
589 atmosphere. *Icarus* 197 (1), 110–136.
- 590 Dobrijevic, M., Dutour, I., Nov. 2007. The distribution of hydrocarbons in
591 Titan’s atmosphere: An evolutionary algorithm-based model. *Planetary and*
592 *Space Science* 55 (14), 2128–2136.
- 593 Dobrijevic, M., Hébrard, E., Loison, J. C., Hickson, K. M., Jan. 2014. Cou-
594 pling of oxygen, nitrogen, and hydrocarbon species in the photochemistry
595 of Titan’s atmosphere. *Icarus* 228, 324–346.
- 596 Dobrijevic, M., Loison, J. C., Jun 2018. The photochemical fractionation of
597 nitrogen isotopologues in Titan’s atmosphere. *Icarus* 307, 371–379.
- 598 Dobrijevic, M., Loison, J. C., Hickson, K. M., Gronoff, G., 2016. 1D-coupled
599 photochemical model of neutrals, cations and anions in the atmosphere of
600 Titan. *Icarus* 268, 313–339.
- 601 Hartogh, P., Lellouch, E., Moreno, R., Bockelée-Morvan, D., Biver, N., Cas-
602 sidy, T., Rengel, M., Jarchow, C., Cavalié, T., Crovisier, J., Helmich, F. P.,
603 Kidger, M., Aug. 2011. Direct detection of the Enceladus water torus with
604 Herschel. *Astronomy and Astrophysics* 532, L2.
- 605 Hébrard, E., Dobrijevic, M., Bénilan, Y., Raulin, F., 2007. Photochemical
606 kinetics uncertainties in modeling Titan’s atmosphere: First consequences.
607 *Planetary and Space Science* 55, 1470–1489.
- 608 Hébrard, E., Dobrijevic, M., Pernot, P., Carrasco, N., Bergeat, A., Hickson,
609 K. M., Canosa, A., Le Picard, S. D., Sims, I. R., 2009. How Measurements
610 of Rate Coefficients at Low Temperature Increase the Predictivity of Pho-
611 tochemical Models of Titan’s Atmosphere. *Journal of Physical Chemistry*
612 113 (42), 11227–11237.
- 613 Hickson, K. M., Loison, J. C., Cavalié, T., Hébrard, E., Dobrijevic, M., Dec.
614 2014. The evolution of infalling sulfur species in Titan’s atmosphere. *As-*
615 *tronomy and Astrophysics* 572, A58.

616 Hörst, S. M., Vuitton, V., Yelle, R. V., Oct. 2008. Origin of oxygen species in
 617 Titan’s atmosphere. *Journal of Geophysical Research (Planets)* 113, 10006.
 618 Krasnopolsky, V. A., May 2009. A photochemical model of Titan’s atmosphere
 619 and ionosphere. *Icarus* 201, 226–256.
 620 Krasnopolsky, V. A., Jul. 2014. Chemical composition of Titan’s atmosphere
 621 and ionosphere: Observations and the photochemical model. *Icarus* 236, 83–
 622 91.
 623 Krasnopolsky, V. A., Dec 2016. Isotopic ratio of nitrogen on Titan: Photo-
 624 chemical interpretation. *Planetary and Space Science* 134, 61–63.
 625 Lara, L. M., Lellouch, E., González, M., Moreno, R., Rengel, M., Jun. 2014. A
 626 time-dependent photochemical model for Titan’s atmosphere and the origin
 627 of H₂O. *Astronomy and Astrophysics* 566, A143.
 628 Liang, M.-C., Heays, A. N., Lewis, B. R., Gibson, S. T., Yung, Y. L., Aug
 629 2007. Source of Nitrogen Isotope Anomaly in HCN in the Atmosphere of
 630 Titan. *The Astrophysical Journal* 664 (2), L115–L118.
 631 Loison, J. C., Dobrijevic, M., Hickson, K. M., Sep 2019. The photochemical
 632 production of aromatics in the atmosphere of Titan. *Icarus* 329, 55–71.
 633 Loison, J. C., Dobrijevic, M., Hickson, K. M., Heays, A. N., Jul. 2017. The
 634 photochemical fractionation of oxygen isotopologues in Titan’s atmosphere.
 635 *Icarus* 291, 17–30.
 636 Loison, J. C., Hébrard, E., Dobrijevic, M., Hickson, K. M., Caralp, F., Hue,
 637 V., Gronoff, G., Venot, O., Bénilan, Y., 2015. The neutral photochemistry of
 638 nitriles, amines and imines in the atmosphere of Titan. *Icarus* 247, 218–247.
 639 Lombardo, N. A., Nixon, C. A., Greathouse, T. K., Bézard, B., Jolly, A.,
 640 Vinatier, S., Teanby, N. A., Richter, M. J., Irwin, P. J. G., Coustenis, A.,
 641 Flasar, F. M., Aug 2019. Detection of Propadiene on Titan. *The Astrophys-
 642 ical Journal Letters* 881 (2), L33.
 643 Magee, B. A., Waite, J. H., Mandt, K. E., Westlake, J., Bell, J., Gell, D. A.,
 644 Dec. 2009. INMS-derived composition of Titan’s upper atmosphere: Analy-
 645 sis methods and model comparison. *Planet. Space Sci.* 57, 1895–1916.
 646 Mandt, K. E., Waite, J. H., Lewis, W., Magee, B., Bell, J., Lunine, J., Mousis,
 647 O., Cordier, D., Dec. 2009. Isotopic evolution of the major constituents of
 648 Titan’s atmosphere based on Cassini data. *Planetary and Space Science*
 649 57 (14-15), 1917–1930.
 650 Moreno, R., Lellouch, E., Lara, L. M., Feuchtgruber, H., Rengel, M., Hartogh,
 651 P., Courtin, R., Nov. 2012. The abundance, vertical distribution and origin
 652 of H₂O in Titan’s atmosphere: Herschel observations and photochemical
 653 modelling. *Icarus* 221, 753–767.
 654 Moses, J. I., Poppe, A. R., Nov. 2017. Dust ablation on the giant planets:
 655 Consequences for stratospheric photochemistry. *Icarus* 297, 33–58.
 656 Mukundan, V., Bhardwaj, A., apr 2018. A model for negative ion chemistry
 657 in titan’s ionosphere. *The Astrophysical Journal* 856 (2), 168.
 658 Nixon, C. A., Thelen, A. E., Cordiner, M. A., Kisiel, Z., Charnley, S. B.,
 659 Molter, E. M., Serigano, J., Irwin, P. G. J., Teanby, N. A., Kuan, Y.-J.,
 660 Nov. 2020. Detection of Cyclopropenylidene on Titan with ALMA. *The*

661 Astronomical Journal 160 (5), 205.

662 Nunez-Reyes, D., Loison, J.-C., Hickson, K. M., Dobrijevic, M., 2019a. A low
663 temperature investigation of the $n(2d) + \text{ch}_4$, c_2h_6 and c_3h_8 reactions.
664 Physical Chemistry Chemical Physics 21 (12), 6574–6581.
665 URL <http://dx.doi.org/10.1039/C9CP00798A>

666 Nunez-Reyes, D., Loison, J.-C., Hickson, K. M., Dobrijevic, M., 2019b. Rate
667 constants for the $n(2d) + c_2h_2$ reaction over the 50296 K temperature range.
668 Physical Chemistry Chemical Physics.

669 URL <http://dx.doi.org/10.1039/C9CP04170B>

670 Palmer, M. Y., Cordiner, M. A., Nixon, C. A., Charnley, S. B., Teanby, N. A.,
671 Kisiel, Z., Irwin, P. G. J., Mumma, M. J., Jul 2017. ALMA detection and
672 astrobiological potential of vinyl cyanide on Titan. Science Advances 3 (7),
673 e1700022.

674 Shebanits, O., Wahlund, J.-E., Mandt, K., Ågren, K., Edberg, N. J. T., Waite,
675 J. H., Aug. 2013. Negative ion densities in the ionosphere of Titan-Cassini
676 RPWS/LP results. Planetary and Space Science 84, 153–162.

677 Sylvestre, M., Teanby, N. A., Dobrijevic, M., Sharkey, J., Irwin, P. G. J.,
678 Oct. 2020. C_2N_2 Vertical Profile in Titan’s Stratosphere. The Astronomical
679 Journal 160 (4), 178.

680 Teanby, N. A., Cordiner, M. A., Nixon, C. A., Irwin, P. G. J., Hörst, S. M.,
681 Sylvestre, M., Serigano, J., Thelen, A. E., Richards, A. M. S., Charnley,
682 S. B., Jun 2018. The Origin of Titan’s External Oxygen: Further Constraints
683 from ALMA Upper Limits on CS and CH_2NH . The Astronomical Journal
684 155 (6), 251.

685 Thelen, A. E., Cordiner, M. A., Nixon, C. A., Vuitton, V., Kisiel, Z., Charnley,
686 S. B., Palmer, M. Y., Teanby, N. A., Irwin, P. G. J., Nov. 2020. Detection
687 of CH_3C_3N in Titan’s Atmosphere. Astrophysical Journal Letters 903 (1),
688 L22.

689 Thelen, A. E., Nixon, C. A., Chanover, N. J., Cordiner, M. A., Molter, E. M.,
690 Teanby, N. A., Irwin, P. G. J., Serigano, J., Charnley, S. B., Feb. 2019.
691 Abundance measurements of Titan’s stratospheric HCN, HC_3N , C_3H_4 , and
692 CH_3CN from ALMA observations. Icarus 319, 417–432.

693 Vinatier, S., Bézard, B., Lebonnois, S., Teanby, N. A., Achterberg, R. K.,
694 Gorius, N., Mamoutkine, A., Guandique, E., Jolly, A., Jennings, D. E.,
695 Flasar, F. M., Apr. 2015. Seasonal variations in Titan’s middle atmosphere
696 during the northern spring derived from Cassini/CIRS observations. Icarus
697 250, 95–115.

698 Vinatier, S., Bézard, B., Nixon, C. A., Mamoutkine, A., Carlson, R. C., Jen-
699 nings, D. E., Guandique, E. A., Teanby, N. A., Bjoraker, G. L., Michael
700 Flasar, F., Kunde, V. G., Feb. 2010. Analysis of Cassini/CIRS limb spectra
701 of Titan acquired during the nominal mission. I. Hydrocarbons, nitriles and
702 CO_2 vertical mixing ratio profiles. Icarus 205 (2), 559–570.

703 Vuitton, V., Yelle, R. V., Klippenstein, S. J., Hörst, S. M., Lavvas, P., May
704 2019. Simulating the density of organic species in the atmosphere of Titan
705 with a coupled ion-neutral photochemical model. Icarus 324, 120–197.

706 Westlake, J. H., Waite, J. H., J., Mandt, K. E., Carrasco, N., Bell, J. M.,
707 Magee, B. A., Wahlund, J. E., Jan. 2012. Titan's ionospheric composition
708 and structure: Photochemical modeling of Cassini INMS data. *Journal of*
709 *Geophysical Research (Planets)* 117 (E1), E01003.