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ABSTRACT

The photochemical processes at work in the atmosphere of Titan are very complex and lead to a great variety of compounds with aerosols as an end-product. One of the most complex molecules detected so far is benzene (C_6H_6). In the present work, we have updated and improved the chemistry of aromatics in order to better understand the main chemical pathways leading to the production of benzene and determine what other aromatics could be produced efficiently in the atmosphere. This new chemical scheme has been incorporated in our 1D photochemical model corresponding to mean conditions. We confirm the importance of ionic chemistry for benzene production in the upper atmosphere and we have found that excited benzene is an important intermediate in benzene production due to the exothermicity of many production reactions. Among the 24 aromatics included in the model, neutral aromatics like toluene ($C_6H_5CH_3$) and ethylbenzene ($C_6H_5C_2H_5$) are relatively abundant, suggesting in particular that toluene could be detectable in the infrared, and eventually microwave wavelength ranges. However, we obtained large uncertainties on model results highlighting the need for more experiments and theoretical studies to improve the chemistry of aromatics.

Keywords: Titan ; Photochemistry ; Atmospheres ; Ionospheres

1 Introduction

The atmosphere of Titan, the largest moon of Saturn, is a factory for organic molecules on a planetary scale. Dissociation and ionisation of the major constituents, N_2 and CH_4, by solar photons, magnetospheric electrons and galactic cosmic rays lead to the production of radicals and ions that initiate a very active and complex chemistry. A diverse range of species are produced: hydrocarbons, amines, imines, oxygen compounds, etc, with aerosols as an end-product, which form haze layers in the atmosphere. A variety of molecules have been detected so far from ground-based observatories and interplanetary probes. Among these, the benzene molecule, C_6H_6, deserves a particular mention for two main reasons: (1) Benzene is one of the more complex molecules to be detected so far. Consequently, it provides a good constraint to test photochemical models and better understand the chemical pathways producing complex molecules in Titan's atmosphere (Wilson and Atreya, 2003; Vuitton et al., 2009; Krasnopolsky, 2009, 2012, 2014; Loison et al., 2015; Frankland et al., 2016). (2) Benzene, and other aromatics, are also considered to be key compounds in the formation of larger molecules such as polycyclic aromatic hydrocarbons (PAHs) or polycyclic aromatic nitrogen heterocycles (PANHs). They are also suspected to contribute to the production of aerosols (Lebonnois et al., 2002; Waite et al., 2007; Delitsky and McKay, 2010; Mahjoub et al., 2016; Gautier et al., 2017).

In the present paper, we extend the chemical schemes presented previously (Dobrijevic et al., 2016b; Loison et al., 2015) to study the production of some aromatic molecules. Several new species are added in order to better understand the production of complex molecules and to determine which aromatics could be present in sufficiently high abundances to be detected in the future and could serve, as suggested by other studies, as precursors of aerosols. In Section 2, we present the photochemical model and the updated version of the chemical scheme. Emphasis is placed on the chemistry of aromatic species (photolyses and reactions). The model results are presented in Section 3 and the main points are discussed in Section 4.

2 Model

2.1 Eddy diffusion

The eddy diffusion coefficient $K(z)$ is a free parameter of photochemical models that can be constrained in principle by comparison between the observed mole fractions of atmospheric species and the corresponding model results.

In order to constrain the altitudinal profile of $K(z)$, it is preferable to use inert species or species involved in a well known chemical sub-scheme with low chemical uncertainties. The altitudinal profiles of these species have to be determined by observations.

In the high atmosphere, above the argon (Ar) homopause around 930 km, molecular diffusion drives the profile of Ar. The Ar profile derived from INMS/Cassini data (Waite et al., 2013) gives a quite strong constraint on the altitude level of the homopause. Methane (CH_4) is also interesting to constrain the eddy coefficient since its molecular mass is lower than the one of N_2 (contrary to Ar).

Below this altitude, eddy diffusion is the dominant vertical transport in 1D photochemical models and it could be constrained in principle using species with well known altitudinal profiles. Here, we used water (H_2O) and hydrogen cyanide (HCN) for that purpose. Their altitudinal profiles have been inferred by observations with relatively low uncertainties and the chemical processes that drive their composition are expected to be simple. Also, uncertainties on chemical parameters give rise to low model result uncertainties for these species (Dobrijevic et al., 2016b). In addition, their chemical lifetimes are greater than their dynamical lifetimes (dominated by eddy diffusion) and the abundance profiles of these species are therefore driven by diffusion (note that in a narrow altitudinal region around 200 km, chemical and dynamical lifetimes are about the same). We use in the present study the eddy profile used in Dobrijevic et al. (2016b). It gives abundance profiles for these species in good agreement with observations (see Fig. 1 for H_2O and HCN and Dobrijevic et al. (2016b) for Ar and CH_4).

Acetylene (C_2H_2) has also been proposed as a tracer species of vertical diffusion (Li et al., 2014). Li et al. (2014) obtained a non-monotonic $K(z)$ in the stratosphere. A comparison between models is presented and discussed briefly in Dobrijevic et al. (2016a) showing that a given eddy profile does not give model results in agreement with observations for all species. In particular, the eddy profile of Li et al. (2014) gives a HCN abundance in disagreement with observations. Concerning C_2H_2, it is noteworthy to clarify that the branching ratios of C_2H_2 photolysis are not well-known. Loison et al. (2015) discussed that point and showed that the abundances of both C_2H_2 and C_2H_6 depend on that parameter. Moreover, in a recent study made by Douglas et al. (2018), the kinetics of the reactions of the first excited state of methylene, $^1CH_2$, with N_2, H_2 and CH_4 have been measured over the temperature range 43-160 K. Using a photochemical model including only neutral species, they studied the impact of the new measurements for Titan's atmosphere, obtaining a significant decrease ($\approx 40\%$) in the mixing ratio of ethane (C_2H_6) and a smaller increase in the mixing ratio of C_2H_2 between 800 and 1550 km. In addition, the abundance profile of C_2H_6 above 800 km depends on the radiative association

reactions. We found that by turning on all these reactions in our model, the C_2H_6 mole fraction increases by a factor of 2 in the ionosphere (see Section 2.2 for more details on radiative association reactions). On the other hand, H_2O and HCN are not affected by radiative association reactions. Consequently, the C_2H_2 and C_2H_6 profiles calculated from photochemical models might be more uncertain that currently suspected (see also Dobrijevic et al. (2018)).

Ethylene (C_2H_4) is currently not a good candidate for constraining $K(z)$. C_2H_4 is known to be a species that has a calculated profile from various photochemical models in disagreement with observations in the lower stratosphere (see for instance Krasnopolsky (2009); Dobrijevic et al. (2016b)). For the moment, the other photochemical products have too strong uncertainties to be used as tracers of eddy mixing.

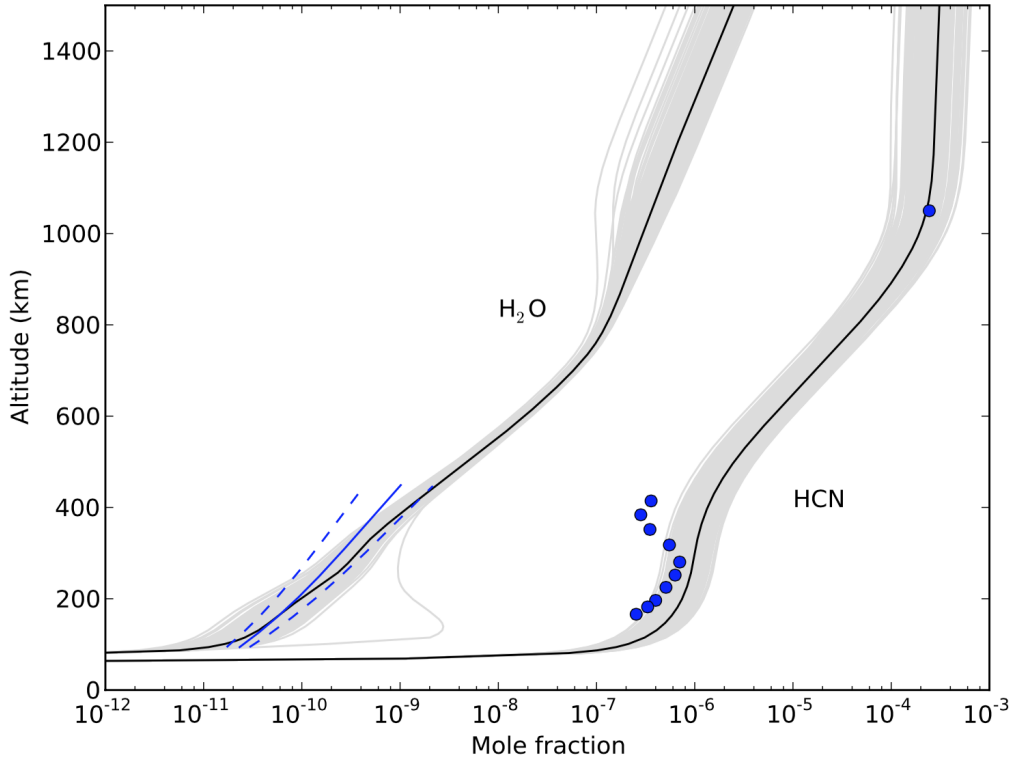

Fig. 1. Abundance profiles of H_2O and HCN in the nominal model (see text). Nominal profiles are in black and 200 Monte-Carlo runs in grey (see section 3.6 for an explanation of these runs). Observations of HCN in the upper atmosphere: Cassini Ion and Neutral Mass Spectrometer (INMS) measurements by Magee et al. (2009). HCN in the lower atmosphere: analysis of Cassini-CIRS mid infrared limb spectra corresponding to 15°S latitude (Vinatier et al., 2007). Observations of H_2O from Moreno et al. (2012) (solid lines for mean and dashed lines for 1-σ uncertainty).

With the exception of aromatic compounds, the basic chemical scheme used in the present study is similar to the model presented in Dobrijevic et al. (2016b) except that we consider neither anions nor radiative association reactions. We performed runs including anions and radiative associations to test their effects on our model results. Anion reactions are responsible for small production fluxes and do not play any role in the production of aromatic species present in our study. Radiative association reactions (derived from statistical theory: see Vuitton et al. (2012); Hébrard et al. (2012); Hébrard et al. (2013)) play a role for small species produced through association reactions (C_2H_6, C_3H_6, C_3H_8, C_4H_6, C_4H_8, C_4H_{10}, C_2H_5CN, C_3H_7CN, CH_3NH_2), increasing their abundance in the upper atmosphere. For large species, such as aromatics, the three body association reactions reach their high pressure limit even at high altitude and the inclusion of radiative association does not change their abundances. Moreover, recent quantum chemistry studies (Douguet et al., 2015; Stoecklin et al., 2018) showed that the radiative association rate constants might be much lower than those obtained by statistical theory, then their effect in Vuitton et al. (2012); Hébrard et al. (2012); Hébrard et al. (2013) might be overestimated.

Some improvements have been made in the chemical scheme presented in Dobrijevic et al. (2016b). In particular, we have removed the very minor reactions. We have also included the new measurements of Douglas et al. (2018) concerning the reactions of $^1CH_2$ with N_2, H_2 and CH_4. We have updated the ionic chemistry, particularly for H^+ and H_3^+ reactions (which have however only a small effect for Titan's atmosphere). We removed the bimolecular exit channel of the H + C_4H_3 $\rightarrow$ C_4H_4 $\rightarrow$ C_2H_2 + C_2H_2 reaction keeping only the termolecular H + C_4H_3 $\rightarrow$ C_4H_4 channel, and also the direct H + C_4H_3 $\rightarrow$ C_4H_2 + H reaction, from our previous studies (Loison et al., 2015; Dobrijevic et al., 2016b). There are no experimental studies of this reaction but it is related to the unimolecular decomposition of C_4H_4 studied by Ghibaudi and Colussi (1988). The bimolecular H_2C_2 (vinylidene) + C_2H_2 production reaction involves a Transition State (TS) slightly above the energy of H + C_4H_3 (Cremer et al., 2006), so it should therefore be inefficient in Titan's atmosphere conditions. It should be noted that inclusion of the bimolecular exit channel leads to a large rate constant for this reaction that strongly decreases the C_4H_2 abundance in the upper atmosphere, a result that is in poor agreement with observations. As the bimolecular exit channel is very uncertain (and probably weak) and as C_4H_2 is involved in aromatic formation through ion-molecule reactions, we do not consider it here and prefer to wait for further experimental or theoretical studies. For the rate constant of this reaction, we adopt the value used by Vuitton et al. (2012).

Table 1
List of aromatics included in the model: 14 neutrals and 14 ions.

Neutrals	C_6H_4, C_6H_5, C_6H_6, $C_6H_5CH_2$, $C_6H_5CH_3$ $C_6H_5C_2H$, $C_6H_5C_2H_5$, C_6H_5N, C_6H_5NH $C_6H_5NH_2$, $C_6H_5NCH_3$, $C_6H_5NHCH_3$, C_6H_5CN, AROM
Ions	$C_6H_5^+$, $C_6H_6^+$, $C_6H_7^+$, $C_7H_7^+$, $C_6H_5CH_2^+$ $C_6H_5CH_3^+$, $C_2H_9^+$, $C_8H_{10}^+$ ($C_6H_5C_2H_5^+$), $C_8H_{11}^+$, $C_6H_5C_2H_2^+$ $C_6H_5NH_3^+$, $C_6H_5CNH^+$, $C_7H_5NH_2CH_3^+$, $AROM^+$

Although this new chemical scheme, which contains 177 species and 1217 reactions, has been improved, it is important to be aware that it is far from complete. In particular, the number of species in the scheme (and the number of reactions) should increase with the number of atoms considered in the species. As shown in Figure 2, this is not the case in the present model. Although it is clear that not all the missing species and reactions will be important, it is possible that crucial species and reactions are absent. Although uncertainty propagation studies are mandatory to determine which reactions should be studied in priority, it is not easy to develop an exhaustive investigation of hundreds of species and thousands of relevant reactions. This is the case in particular when considering aromatic molecules. The list of aromatics included in the present model is given in Table 1. It includes "only" 14 neutrals and 14 ions. Two generic species called AROM and $AROM^+$ are used to limit the number of species. AROM and $AROM^+$ are the sum of all the aromatics produced in the chemical network but not described here (see the list of the 38 reactions producing such species in the Appendix A and Appendix B).

Due to the lack of experimental data, all the aromatics, except for C_6H_4 and C_6H_5 radicals, are assumed in the present study to follow the same saturated vapor pressure expressions as C_6H_6.

2.2.1 Aromatics photolysis

The photolysis of benzene is very important in Titan's atmosphere as it involves very large fluxes. This photolysis is particularly complex as analyzed by Delitsky and McKay (2010). In the present work, we use the recent Capalbo et al. (2016) absorption cross section leading to the photolysis rate presented in Figure 3. The integrated absorption rate constant of benzene leads to about 50% of absorption due to the strong band between 160 and 190 nm, and 50% around 200 nm. The fluorescence quantum yield and direct dissociation rate are very low across the whole excitation wavelength range, whereas highly vibrationally excited benzene is generated with a quantum yield near unity through internal conversion to the ground singlet state of benzene ($C_6H_6^{**}$)

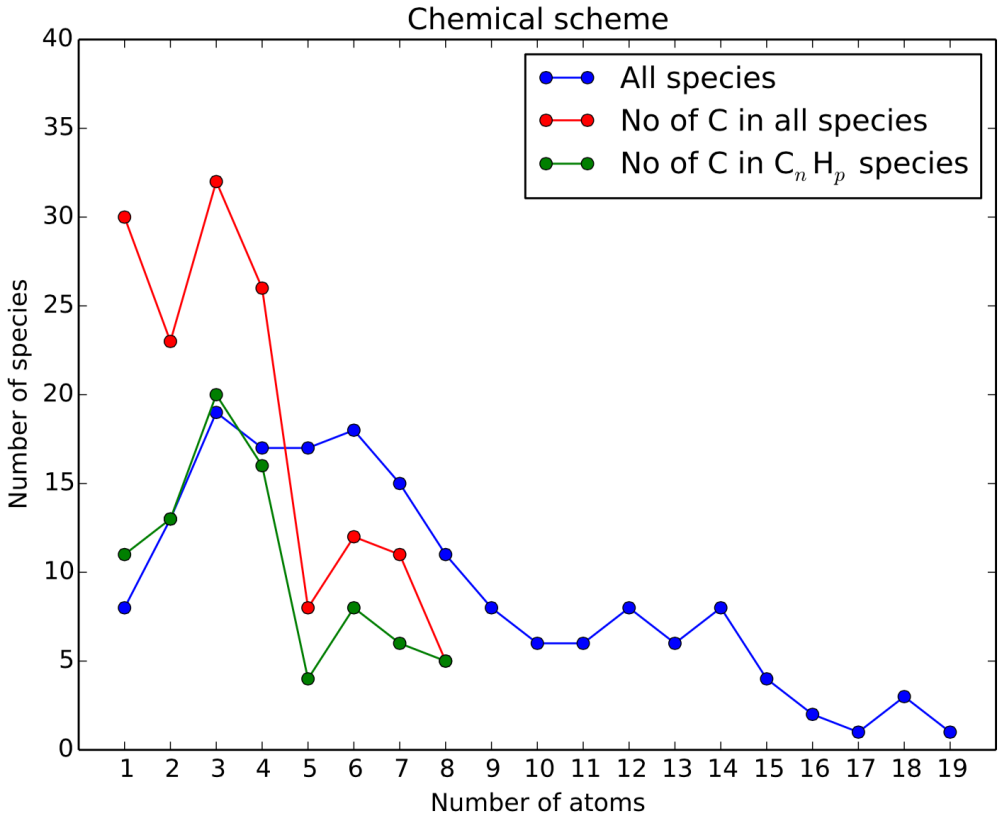

Fig. 2. Analysis of the chemical scheme in the present model, in terms of the number of species as a function of the number of atoms (sum of carbon, nitrogen, hydrogen and oxygen atoms) in blue and the number of carbons in red (whatever the number of other atoms) or green (whatever the number of hydrogen atoms). For instance, there are 15 species with 7 atoms, 11 species with 7 carbon atoms and 6 hydrocarbons (C_nH_p-type species) with 7 carbon atoms.

(West et al., 2016). Once formed, $C_6H_6^{**}$ can either dissociate or be relaxed through collision with N_2 leading to ground singlet state benzene in a high vibrational state below the dissociation limit ($C_6H_6^*$). Both mechanisms are internal energy dependent (West et al., 2016) but a simplified treatment can be applied as shown by Nakashima and Yoshihara (1983) following benzene excitation at 193 nm.

The dissociation lifetime of benzene after excitation at 157 nm is equal to 1.4 μs from Hsu et al. (2001) but 0.045 μs from Shimada et al. (1993), and is equal to 10 μs (Hsu et al., 2001; Tsai et al., 2000; Kislov et al., 2004) after excitation at 193 nm. Consequently, benzene excited below 190 nm will be almost entirely dissociated as the relaxation lifetime through collisions with N_2 is longer than the dissociation lifetime for altitudes above 90 km. At 211 nm, the dissociation lifetime is calculated to be equal to 1.7 ms by Mebel et al. (2001) which corresponds to a relaxation lifetime by N_2 at 350 km. We consider

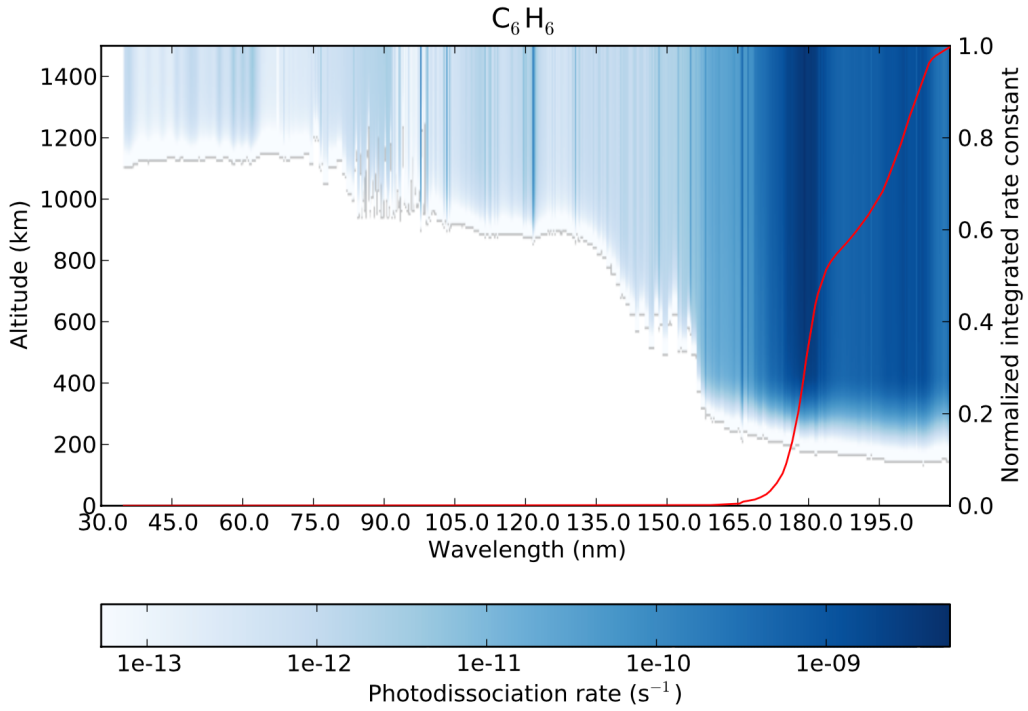

Fig. 3. Map of c-C_6H_6 photolysis rate as a function of altitude and wavelength. The more intense the blue color, the greater the benzene photodissociation rate. The grey line delimits the altitude where the rate tends to zero. For short wavelength (below 135 nm), the photodissociation of benzene is low and occurs in the ionosphere. At longer wavelength (greater than 160 nm) benzene photodissociation occurs in the lower atmosphere down to 200 km. The normalized integrated rate constant is also shown (superimposed red line). This shows that benzene photolysis is efficient only for wavelengths greater than 165 nm up to 220 nm.

then an average value for the hot benzene ($C_6H_6^{**}$) dissociation lifetime of 20 μs, an intermediate figure between the values for benzene excitation at 193 nm and 211 nm. This average dissociation lifetime corresponds to a relaxation lifetime by N_2 at 160 km. Considering the work of Yokoyama et al. (1990); Ni and Lee (2004); Kislov et al. (2004) we consider a fixed dissociation branching ratio for excited $C_6H_6^{**}$ equal to 95% towards C_6H_5 + H and 5% towards C_6H_4 + H_2. The relative branching ratios between the two channels are not critical since C_6H_4 (benzyne) is thought to react quickly with H atoms leading to C_6H_5 (Madden et al., 1997) (there is a very small barrier, equal to 400 K, at the M06-2X/AVTZ level for the H + C_6H_4 → C_6H_5 reaction). As the lifetime of $C_6H_6^{**}$ is short, we can neglect its reactivity and its photolysis.

In contrast to $C_6H_6^{**}$, $C_6H_6^{*}$ has a long lifetime and its photochemistry should be taken into account. $C_6H_6^{*}$ does not react with O_2, benzene or propane (Nakashima and Yoshihara, 1983) and we can neglect its reactivity with closed shell molecules. $C_6H_6^{*}$ may react with H atoms leading to C_6H_7, which should however give back C_6H_6 through reaction with H. We then neglect the reac-

tivity of $C_6H_6^*$ (it should be noted that the apparent reactivity of $C_6H_6^*$ with O_2 (Jain et al., 2012; Kovacs et al., 2009) is due to C_6H_5 produced through photodissociation of hot benzene after absorption of two 248 nm photons). Although we can probably neglect the reactivity of $C_6H_6^*$, we cannot neglect its photodissociation. The absorption cross section of hot benzene produced by an absorbed photon at 248 nm has been measured equal to 1.7×10^{-17} cm^2 at 248 nm (Kovacs et al., 2009) and equal to 3.2×10^{-17} cm^2 at 193 nm (Honjo et al., 2005). We consider a constant absorption cross section of 1.0×10^{-17} cm^2 between 150 and 300 nm leading mainly to C_6H_5 + H and with ring opening photodissociation channels around 20% using Tsai et al. (2001) and Kislov et al. (2004). We also consider a $C_6H_6^*$ photoionization cross section of 1.0×10^{-17} cm^2 between 100 and 250 nm from C_6H_6 photoionization (Cool et al., 2005) and the theoretical model from Koizumi (1991). While $C_6H_6^{**}$ has a very low relative abundance throughout the atmosphere, $C_6H_6^*$ and C_6H_5 are relatively abundant in the ionosphere (see Figure 5).

The photodissociation of substituted benzene (toluene, ethylbenzene, benzonitrile, phenylethyne, ...) involves also the formation of "hot" species followed by dissociation. However, the dissociation lifetime is notably faster than for benzene (850 ns for toluene at 193 nm, Lin et al. (2002)) and we can neglect relaxation through collision with N_2. The photodissociation of substituted benzene leads to various products (see Appendix B), either radical formation through H, CH_3 or CN elimination (toluene ($C_6H_5CH_3$) (Frochtenicht, 1995), ethylbenzene ($C_6H_5C_2H_5$) (Tsai et al., 2001; Huang et al., 2002), aniline ($C_6H_5NH_2$) (Ni et al., 2007), benzonitrile (Park et al., 1989; Hong et al., 2001)) or closed shell molecules formation like C_6H_4 and C_2H_2 from ethynyl benzene ($C_6H_5C_2H$) photodissociation (Sorkhabi et al., 2001) and benzene and C_2H_2 from styrene ($C_6H_5C_2H_3$) photodissociation (Lee et al., 2003). It should be noted that the photodissociation of substituted benzene always preserves the aromatic ring and that C_6H_4 and benzene are among the various products. A key point is the photodissociation of the generic species AROM (AROM being the aromatic compounds produced in our network but not described in detail). Considering the data for photodissociation of various aromatics presented in the Appendix B, there is no doubt that the photodissociation of AROM will preserve the aromatic ring too. Moreover, considering the various species included in AROM ($C_6H_5C_2H_3$, $C_6H_5C_3H_3$, ...) there is also no doubt that some C_6H_4 and benzene would also be among the products of AROM photolysis.

2.2.2 Aromatic chemistry

The main subject of this paper is to describe monocyclic aromatic compounds in Titan's atmosphere. Our photochemical scheme restricted to the major production and loss pathways is shown in Figure 4. The integrated column

rates for each reaction are given in Appendix C.

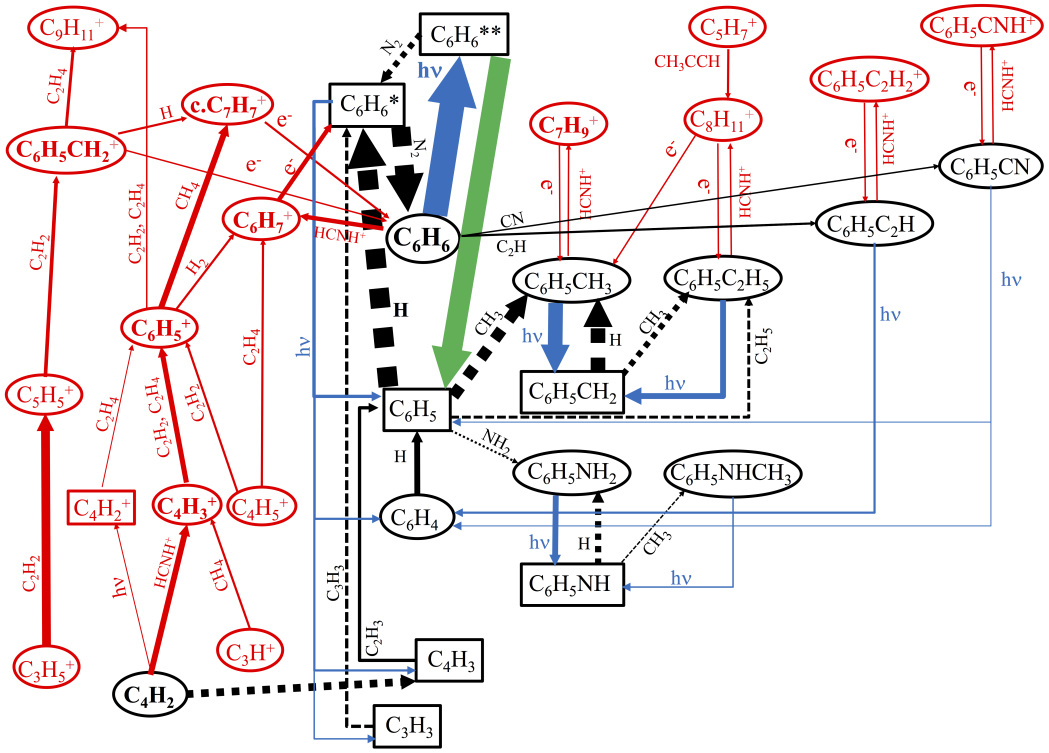

Fig. 4. Schematic diagram highlighting the important neutral (in black) and ionic (in red) pathways for the production of aromatic species. $C_6H_6^{**}$ represents metastable benzene (including all C_6H_6 isomers) excited above the dissociation limit and $C_6H_6^{*}$ represents metastable benzene (including all C_6H_6 isomers) excited below the dissociation limit. Photodissociations are in blue and unimolecular dissociations of $C_6H_6^{**}$ are in green. The thickness of each arrow is proportional to the integral of the total production rate over the atmosphere (see Appendix C). Three body reactions are represented by dashed lines. Radicals are shown in boxes, whereas closed shell compounds are shown in circles. Species observed (C_4H_2, C_6H_6, $C_6H_7^+$, $C_7H_7^+$, $C_7H_9^+$, ...) are in bold.

The first step of aromatic formation in Titan's atmosphere is the production of benzene. The chemical formation pathways of benzene have been studied previously by Vuitton et al. (2008) showing that, in addition to the propargyl recombination reaction $C_3H_3 + C_3H_3 + M$, ionic chemistry is also very important, namely the $C_6H_7^+$ dissociative recombination pathway in their case. We review here the various pathways highlighting the uncertainties due to the large number of isomers potentially involved. A specific point of benzene production in Titan's atmosphere is that most of the formation pathways are very exothermic, leading to C_6H_6 formed with internal energy mostly above the isomerization channels of C_6H_6 (Kislov et al., 2004). We then consider three forms of C_6H_6 for chemical reactions: C_6H_6 which is the usual benzene isomer at thermal equilibrium in Titan's atmosphere, $C_6H_6^*$ which is the sum

of all C_6H_6 isomers with large internal (vibrational) energy but below the dissociation limit, and $C_6H_6^{**}$ which is the excited benzene above its dissociation limit.

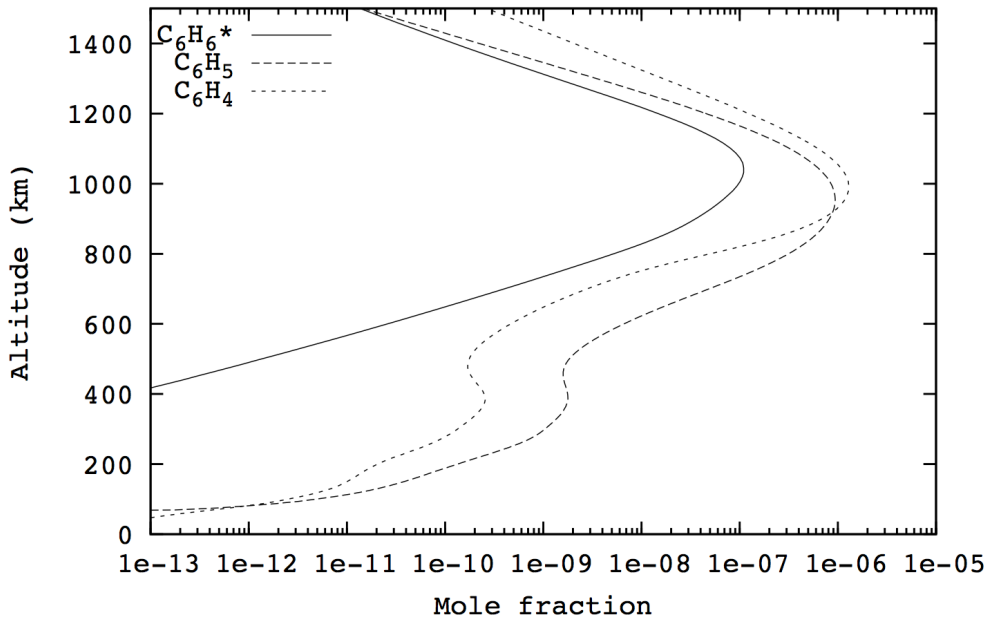

Fig. 5. Mole fraction profiles of $C_6H_6^*$, C_6H_5 and C_6H_4 as a function of altitude for the nominal model. These species play an important role in the production of aromatics in the atmosphere of Titan.

2.2.2.1 $C_6H_7^+$ pathway. (20% of the total, mainly at high altitude around 800-950 km). The Dissociative Recombination (DR) of $C_6H_7^+$ leads almost exclusively to C_6H_6 (Hamberg et al., 2011). It should be noted that considering the exothermicity of this DR reaction, most of the C_6H_6 is produced in an excited vibrational state ($C_6H_6^*$) but below the C_6H_5 + H dissociation limit. There are two main direct sources of $C_6H_7^+$ in the model (direct means not through benzene protonation), the $C_6H_5^+ + H_2 \rightarrow C_6H_7^+ + h\nu$ and the $C_4H_5^+ + C_2H_4 \rightarrow C_6H_7^+ + H_2$ reactions. $C_6H_5^+$ is formed through the $C_4H_2^+ + C_2H_4$ reaction, which leads to the phenyl form of $C_6H_5^+$ (Dheandhanoo et al., 1986; Goebbert et al., 2004; Anicich et al., 2006), and also through $C_4H_3^+ + C_2H_2$ and $C_4H_3^+ + C_2H_4$ (Anicich, 2003; Peverati et al., 2016), which leads also to the phenyl ion. Then $C_6H_5^+ + H_2$ leads mainly to protonated benzene. There are no studies on the nature of $C_6H_7^+$ produced from the $C_4H_5^+ + C_2H_4$ reaction (Anicich et al., 2006), so we assume that protonated benzene is formed.

2.2.2.2 $C_7H_7^+$ pathway. (18% of the total (with large uncertainty), mainly at high altitude around 800-950 km). In our model, we consider that DR of

$C_7H_7^+$ leads to some C_6H_5 and C_6H_6 production. There are two main isomers for the $C_7H_7^+$ ion: benzylium (C_6H_5-CH_2^+) and tropylium (7 atoms cycle), the tropylium form being slightly more stable. The isomerization barrier from the benzylium cation toward the tropylium cation is located at 272.6 kJ/mol at the G3 level of calculation (Fridgen et al., 2004), so both isomers should coexist in Titan's atmosphere. The isomerization process can also be induced by reactions with H and CH_3 as both are calculated to occur without a barrier (Ausloos, 1982; Fridgen et al., 2004), which will favor tropylium production (for these reactions, there is a competition between isomerization of the benzylium cation toward the tropylium cation and the association reaction leading to $C_6H_5CH_3^+$ and $C_6H_5C_2H_5^+$ ions, in that case the most stable ions are the benzene derivative one's). In Titan's atmosphere, $C_7H_7^+$ will be formed by the $C_5H_5^+ + C_2H_2$ and $C_6H_5^+ + CH_4$ reactions. There are various $C_5H_5^+$ isomers, but all react with acetylene at similar rates (Ozturk et al., 1989), the products being likely both the benzylium and the tropylium ions. In the case of the $C_6H_5^+ + CH_4$ reaction, the major product is the tropylium ion (Ausloos et al., 1989). The DR rate of $C_7H_7^+$ has been studied experimentally (Rebrion-Rowe et al., 2000; Fournier et al., 2013), the rate for the benzylium form being notably larger. However, the products of these DR reactions are unknown. There are various exothermic exit channels for the DR of $C_7H_7^+$, the most important ones are:

		ΔH_r in kJ/mol (benzylium/tropylium)
$C_7H_7 + e^- \rightarrow$	$C_6H_6 + CH$	-239/-208
	$C_6H_5 + CH_2$	-209/-178
	C_2H_2 + c-C_5H_5	-419/-388
	$C_3H_3 + C_4H_4$	-249/-218
	$CH_2CCHCHCHCCH + H$	-225/-194

It is difficult to estimate the products for the DR of $C_7H_7^+$, but the DR of $C_6H_6^+$ and $C_6H_7^+$ preserve the aromatic ring by more than 90% in both cases. We consider that both $C_7H_7^+$ isomers have branching ratios equal to 20% towards C_6H_6 + CH and 20% towards $C_6H_5 + CH_2$, the remaining 60% being ring opening and the cyclopentadienyl radical. The tropylium and the benzylium ions have quite different chemistry, the tropylium being less reactive (Ausloos et al., 1980; Ausloos, 1982). So, we consider both isomers for $C_7H_7^+$ in our model. As there is little doubt that C_6H_6 and/or C_6H_5 are produced through the DR of $C_7H_7^+$, there is also little doubt than the DR of $C_7H_7^+$ is an efficient direct or indirect (through C_6H_5 and C_6H_4) benzene production pathway. It should be noted that c-$C_7H_7^+$ reaches a relatively large abundance in our model

(see figure 9) and is thought to be responsible for the $m/z = 91$ peak observed in INMS spectra.

2.2.2.3 $C_8H_{11}^+$ pathway. (18% of the total (with large uncertainty), mainly at high altitude around 800-950 km). The DR of $C_8H_{11}^+$ is another ionic aromatic formation mechanism in our model. $C_8H_{11}^+$ is produced through the $C_5H_7^+$ + CH_3CCH reaction leading to $C_8H_{11}^+$ (Anicich et al., 2006). There is no information on the isomer(s) produced but, in contrast to $C_7H_7^+$, the most stable isomer is the protonated ethyl benzene form (Fridgen et al., 2004) which is therefore likely to be among the reaction products. In our model we consider that the DR of $C_8H_{11}^+$ leads to ethylbenzene, toluene and benzene.

2.2.2.4 C_3H_3 + C_3H_3 pathway. (20% of the total, mainly at low altitude around 200-300 km). Apart from the ionic pathways for benzene formation, there are also neutral ones. Among them the C_3H_3 + C_3H_3 recombination is important. The rate constant of this reaction has been studied in detail over a large range of temperature and pressure (Miller and Klippenstein, 2001, 2003; Georgievskii et al., 2007; Atkinson and Hudgens, 1999) but not at the low pressures and temperatures characteristic of Titan's middle and upper atmosphere. The product branching ratios are not well known, the first step of the reaction being the formation of linear C_6H_6 with high internal excitation energy which is in fact an isomer of $C_6H_6^{**}$. Above 300 K and above 27 mbar, the main experimental products are 1,5-hexadiyne and 1,2-hexadiene-5-yne (Fahr and Nayak, 2000; Alkemade and Homann, 1989; Howe and Fahr, 2003). However, in Titan's atmosphere the C_3H_3 + C_3H_3 reaction is efficient above 200 km for a pressure below 1 mbar. In that case, the theoretical work of Miller and Klippenstein (2003) suggests that the main products are benzene, fulvene and 2-ethynyl-1,3-butadiene (it should be noted that the H + C_6H_5 production may be favored at very low pressure). However, there is no need to introduce the various C_6H_6 isomers produced by the C_3H_3 + C_3H_3 reaction in Titan's atmosphere. Indeed, the various C_6H_6 isomers will be efficiently photodissociated into C_6H_5 + H similar to benzene (fulvene absorbs strongly above 200 nm (Negri and Zgierski, 1995; Shindo and Lipsky, 1966; Honjo et al., 2005), and likely also 2-ethynyl-1,3-butadiene, leading to $C_6H_6^{**}$). However, in contrast to benzene, the other C_6H_6 isomers are not thought to be produced through the H + C_6H_5 reaction (Miller and Klippenstein, 2003; Mebel et al., 1997; Kislov et al., 2004). As the flux of the H + C_6H_5 reaction is 200 times more important than the C_3H_3 + C_3H_3 flux, the fulvene and 2-ethynyl-1,3-butadiene abundances will be low. Moreover, the H + fulvene and H + 2-ethynyl-1,3-butadiene reactions should be relatively fast (around 1.0×10^{-12} cm^3 $molecule^{-1}s^{-1}$ even at 150-200 K), the barrier for the H + fulvene reaction being calculated equal to 7.0 kJ/mol at the M06-2X/AVTZ level (this work) in good agreement with the recent study of H + butadiene by Li et al. (2017).

The reactions of H atoms with C_6H_6 isomers lead to either adduct stabilisation (C_6H_7) or benzene + H. The fast isomerization of C_6H_6 isomers into benzene through photodissociation and eventually by H atom reactions, explain why no IR transitions of any benzene isomers, apart from benzene itself, have been observed in Titan's atmosphere.

2.2.2.5 $C_2H_3 + C_4H_3$ pathway. (22% of the total, at low altitude around 200 km). Apart from the $C_3H_3 + C_3H_3$ recombination, the $C_2H_3 + C_4H_3$ reaction is also an important neutral pathway for aromatic production in Titan's atmosphere as both C_2H_3 and C_4H_3 are efficiently produced through H atom addition to C_2H_2 and C_4H_2 in the lower atmosphere. There are very few previous studies of this reaction (Duran et al., 1988) but there is no doubt that the first step is the formation of 1,2-hexadiene-5-yne and 1,3-hexadien-5-yne, species which are also produced in the $C_3H_3 + C_3H_3$ reaction. Considering the very large amount of energy in the $C_6H_6^{**}$ produced by the $C_2H_3 + C_4H_3$ reaction, (750 kJ/mol, corresponding to an excitation of C_6H_6 at 159 nm), we consider that all the $C_6H_6^{**}$ formed with such a high internal energy will dissociate into $C_6H_5 + H$.

The few percent remaining production of C_6H_6 is through various minor ionic pathways ending with DR, which are efficient at high altitude around 800-950 km. In this work, we neglect most of the reactions of H and CH_3 with ions (particularly aromatic ions). All these reactions will not change (or very little) the amount of aromatic compounds but may change the relative proportions between benzene and substituted benzenes. However, their importance is notably lower than the other reactions included in the present chemical scheme so that no drastic changes are expected for the most abundant aromatics presented in this study, particularly benzene.

2.2.2.6 Secondary chemistry. Once formed, benzene can accumulate because it is unreactive with the main compounds in Titan's atmosphere and its photochemistry leads mainly back to benzene. However it can react with highly reactive radicals and atoms: C (Bergeat and Loison, 2001; McKee et al., 2014), CH (Berman et al., 1982), C_2H (Woon, 2006), CN (Woon, 2006; Trevitt et al., 2009) and $N(^2D)$ (Balucani et al., 2018), all these reaction involving however relatively small fluxes. Among these reactions, the ones with CN and C_2H lead to closed shell molecules, benzonitrile and phenylethyne, which are included in the chemical scheme and fully described.

Apart from the reaction with benzene, the C_6H_5 radical is also at the origin of a rich production of aromatics through neutral reactions with CH_3 and NH_2. In our model C_6H_5 reaches a large abundance (see Figure 5) but much smaller than in Vuitton et al. (2008). The very large C_6H_5 abundance in Vuitton et al.

(2008) was due to large underestimation of the C_6H_5 + H and C_6H_5 + CH_3 rate constants, which were corrected in Vuitton et al. (2012).

Many reactions are not included in the chemical scheme. For instance, we do not describe the chemistry of C_5H_x compounds and many of the C_6H_x and C_7H_x one's, or only as loss reactions. Some of them involve relatively important fluxes, similar to the fluxes of the C_3H_3 + C_3H_3 reaction, and may lead indirectly to benzene or other aromatics. Among them, the reactions leading to linear C_6H_2 (C_2H + C_4H_2, C_4H + C_2H_2, Berteloite et al. (2010)), linear C_6H_4 (C_2H + C_4H_2, C_4H + C_2H_2, Berteloite et al. (2010)) and C_6H_8 isomers including cyclo-hexadiene (C_2H_3 + C_4H_5 and C_2H_5 + C_4H_3) are non negligible and may contribute to indirect benzene formation at similar levels to the C_3H_3 + C_3H_3 and C_2H_3 + C_4H_3 pathways. Moreover, various reactions involving aromatics are included in the chemical scheme as loss reactions but without precise determination of the products. This is the case for the following reactions: C_6H_5 + C_2H_3, C_6H_5 + C_3H_3, C_6H_5 + C_4H_3, $C_6H_5CH_2$ + C_2H_5, $C_6H_5CH_2$ + C_2H_3, C_6H_5 + $C_6H_5CH_2$, $C_6H_5CH_2$ + $C_6H_5CH_2$, all of them involving similar fluxes to the C_3H_3 + C_3H_3 reaction. All these reactions preserve the aromatic ring and photodissociation of their products should also maintain the aromatic ring leading partly to benzene. We introduce a global species called AROM, produced by these reactions, without a precise structure except that it is an aromatic compound. Photodissociation of AROM should very likely preserve the aromatic ring, which would mainly lead to AROM but also to some aromatics present in the network, particularly benzene (see section 2.2.1). A branching fraction as small as 1% for the AROM + $h\nu \rightarrow C_6H_6$ + photodissociation products with an absorption cross section of AROM equal to the one of toluene (which gives fluxes of a similar order of magnitude to the potential amount of benzene produced by the C_5H_x, C_6H_x and C_7H_x reactions that have been neglected) leads to an increase of the total amount of benzene by a factor of 6 in the lower atmosphere (150-200 km) but almost no change in the middle and upper atmosphere. In contrast, the AROM abundance strongly decreases, being divided by 25. This strong effect on the AROM abundance is due to the fact that there are no loss pathways for AROM other than condensation and photodissociation toward benzene. Then, whatever the branching ratio is above 1%, the flux and thus benzene production remains the same. However, the AROM abundance is inversely proportional to the branching ratio. As there is very little doubt that photodissociation of AROM will lead to some benzene (and C_6H_4) production, we consider a branching ratio of 3% in the nominal model. In the present study, we test different models: in the nominal model, the photolysis of AROM is included (with a branching ratio equal to 3% toward benzene and 97% toward AROM) and the chemistry induced by Galactic Cosmic Rays has been turned off. Sensitivity analyses for AROM photolysis, and the effects of GCRs and ionic chemistry on the production of aromatics are considered in section 4.

3 Results

The most abundant aromatic in our model is benzene reaching a relative abundance of 10^{-6} between 800 km and 1000 km as shown in Figure 6. It is in reasonable agreement with observations even if our calculated abundance is slightly below observations. It is worth noting that this large abundance is not due to efficient formation pathways (the ionic and neutral fluxes are rather small) but instead, due to the fact that once formed, the aromatic ring is mostly preserved against photodissociation, DR and other reactions. Then, aromatics can accumulate in the atmosphere, the main loss processes being condensation in the lower atmosphere and photodissociation to the excited benzene $C_6H_6^*$.

3.1 Benzene

The first detection of benzene was reported by Coustenis et al. (2003) from observations performed by the Infrared Space Observatory (ISO). Assuming a constant mole fraction with altitude they obtained a value of $(4 \pm 3) \times 10^{-10}$ in the lower stratosphere (around a pressure level of 9 mbar). A more recent analysis of data recorded by the Composite Infrared Spectrometer (CIRS) aboard the Cassini spacecraft during the Titan flybys T0-T10 (July 2004 - January 2006) by Coustenis et al. (2007) gave a value of $3^{+1.5}_{-2.0} \times 10^{-10}$ near the equator (at 5°S) and $(1.1 \pm 0.5) \times 10^{-9}$ at 50°N between pressure levels of 0.2 and 20 mbar. An analysis of measurements derived from CIRS during a longer period (2006-2012 corresponding to several flybys from T16 to T91) confirmed that the benzene abundance depends strongly on latitude and also demonstrated that it varies significantly with time (Vinatier et al., 2015). At mid-latitude (46°N), the C_6H_6 abundance was about 2.5×10^{-10} between 1 and 5 mbar in July 2006 (this date corresponds approximately to a solar minimum). Cui et al. (2009) obtained the density of C_6H_6 in the ionosphere between 950 and 1200 km based on Cassini/INMS (Ion Neutral Mass Spectrometer) measurements obtained during 15 close flybys of Titan (from T5 to T37, corresponding to the period April 2005 - November 2007). Note that INMS densities have to be corrected according to Teolis et al. (2015). At intermediate altitude (between 400 and 800 km), the abundance of C_6H_6 has been determined from stellar occultation data acquired by the Cassini/UVIS instrument. Koskinen et al. (2011) analyzed such data from two flybys (T41 and T53). Using a new VUV absorption cross section for benzene, Capalbo et al. (2016) reanalyzed UVIS measurements acquired during these stellar occultations of Titan and also added analyses of measurements from the T21 and T41-II flybys. They obtained, around 1000 km, relative abundances in agreement with the values derived from INMS data. Most of these observations are depicted in Figure 6

and compared to our model results. We highlight the relatively good agreement between our model (taking model uncertainties into account) and the observations for benzene despite a slight underestimation of the benzene abundance in our model for the nominal model, not only in the lower atmosphere where the neutral formation mechanism controls benzene chemistry but also in the upper atmosphere where benzene is produced through ionic reactions. The agreement between model and observations is much better in the lower atmosphere when we consider that AROM photodissociation leads to some benzene production.

Our benzene abundance profile is relatively similar to the one of Vuitton et al. (2008) and Krasnopolsky (2009) in the ionosphere, the main reactions producing benzene being relatively similar, although we have introduced new reactions. On the other hand, our profile is quite different in the region between 300 and 500 km.

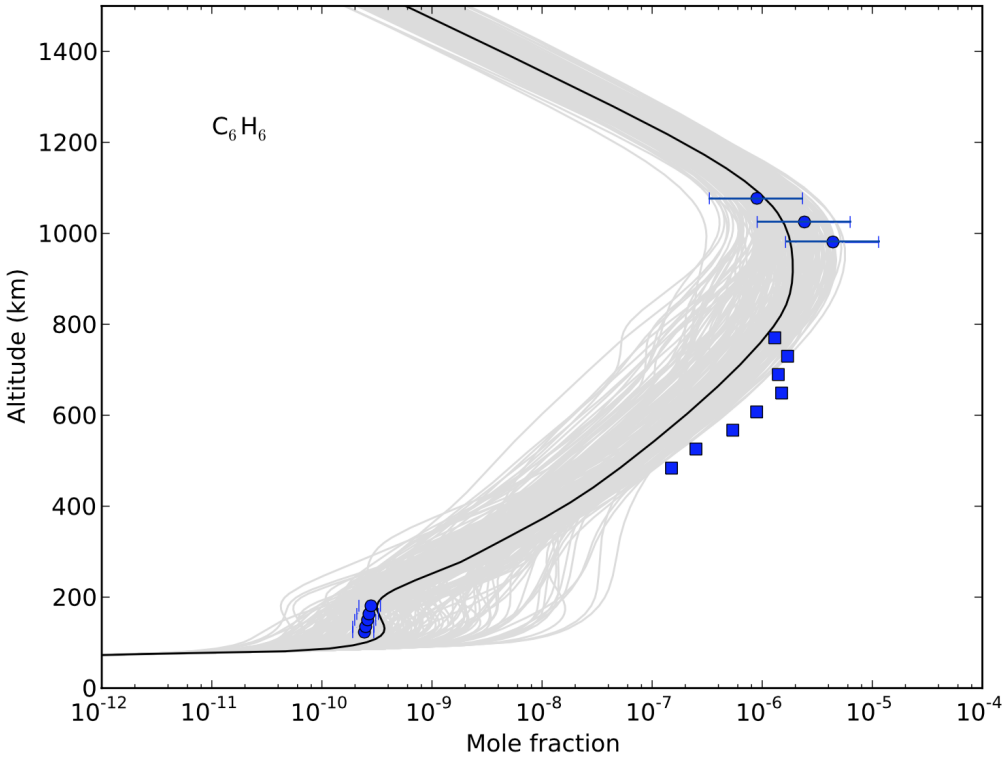

Fig. 6. Mole fraction profiles of benzene in the nominal model (nominal run in black and 200 Monte-Carlo runs in grey, see section 3.6 for an explanation of these runs). Observations are given in blue for comparison. In the ionosphere: INMS data from Cui et al. (2009); In the lower stratosphere: CIRS data from Vinatier et al. (2015) and Coustenis et al. (2007); In the middle atmosphere: UVIS data from Koskinen et al. (2011)).

3.2 Toluene and ethylbenzene

Among the substituted benzene molecules, toluene ($C_6H_5CH_3$) and ethylbenzene ($C_6H_5C_2H_5$) are the most abundant in our model (see Figure 7). Toluene and ethylbenzene are efficiently produced in Titan's atmosphere because C_6H_5 is the main product of benzene photodissociation and C_6H_5 will react mainly with the most abundant radicals, which are H atoms and CH_3 radicals. In fact, considering the values of the k_0 termolecular rate constant, the H + C_6H_5 and CH_3 + C_6H_5 reactions reach their k_∞ values all over the atmosphere and can be considered as bimolecular reactions (Vuitton 2008) (it should be noted that the CH_3 + C_6H_5 → $C_6H_5CH_2$ + H reaction is exothermic by 58 kJ/mol without a TS for the exit channel which slightly decreases the low pressure association rate constant for this reaction). Toluene photodissociation leads mainly to the benzyl radical ($C_6H_5CH_2$, (Frochtenicht, 1995)), which produces ethylbenzene through reaction with CH_3. The growth propagation stops there because photodissociation of ethylbenzene is thought to lead almost exclusively to $C_6H_5CH_2$ + CH_3 and not to $C_6H_5C_2H_4$ + H (Tsai et al., 2001; Huang et al., 2002). Toluene and ethylbenzene have not yet been detected in Titan's lower atmosphere. Both have a small dipole moment around 0.4 Debye and may be detectable with ALMA, and both have active IR transitions well separated from those of benzene. Considering the relative abundance of toluene, around 1/10 of the benzene one, it may be detectable through its IR transitions. An indirect way to estimate the toluene abundance in the upper atmosphere is through the $C_7H_9^+$ ion. Indeed, $C_7H_9^+$ is mainly produced from toluene through proton transfer via reactions with $HCNH^+$ and $C_2H_5^+$, and then the $C_7H_9^+$ mole fraction is proportional to the neutral toluene one.

Our toluene abundance is notably different from Vuitton et al. (2008) and Krasnopolsky (2009, 2012, 2014) mainly due to the fact we use very different rate constants for the reactions C_6H_5 + H and C_6H_5 + CH_3. Moreover the chemical description of toluene in Krasnopolsky (2009) is oversimplified. Ethylbenzene is neither described in Vuitton et al. (2008) nor in Krasnopolsky (2009, 2012, 2014).

3.3 Aniline (C_6H_5-NH_2) and aniline-N-methyl (C_6H_5-$NHCH_3$)

The first step of their formation is addition of NH_2 to the phenyl radical. However, as NH_2 is much less abundant than the methyl radical, aniline is much less abundant than toluene. Aniline-N-methyl is formed through CH_3 addition to C_6H_5-NH produced by the photodissociation of aniline. Considering their relatively low abundances in our model (see Figure 8), both molecules will be difficult to detect through IR spectroscopy. Protonated aniline, $C_6H_5NH_3^+$, is

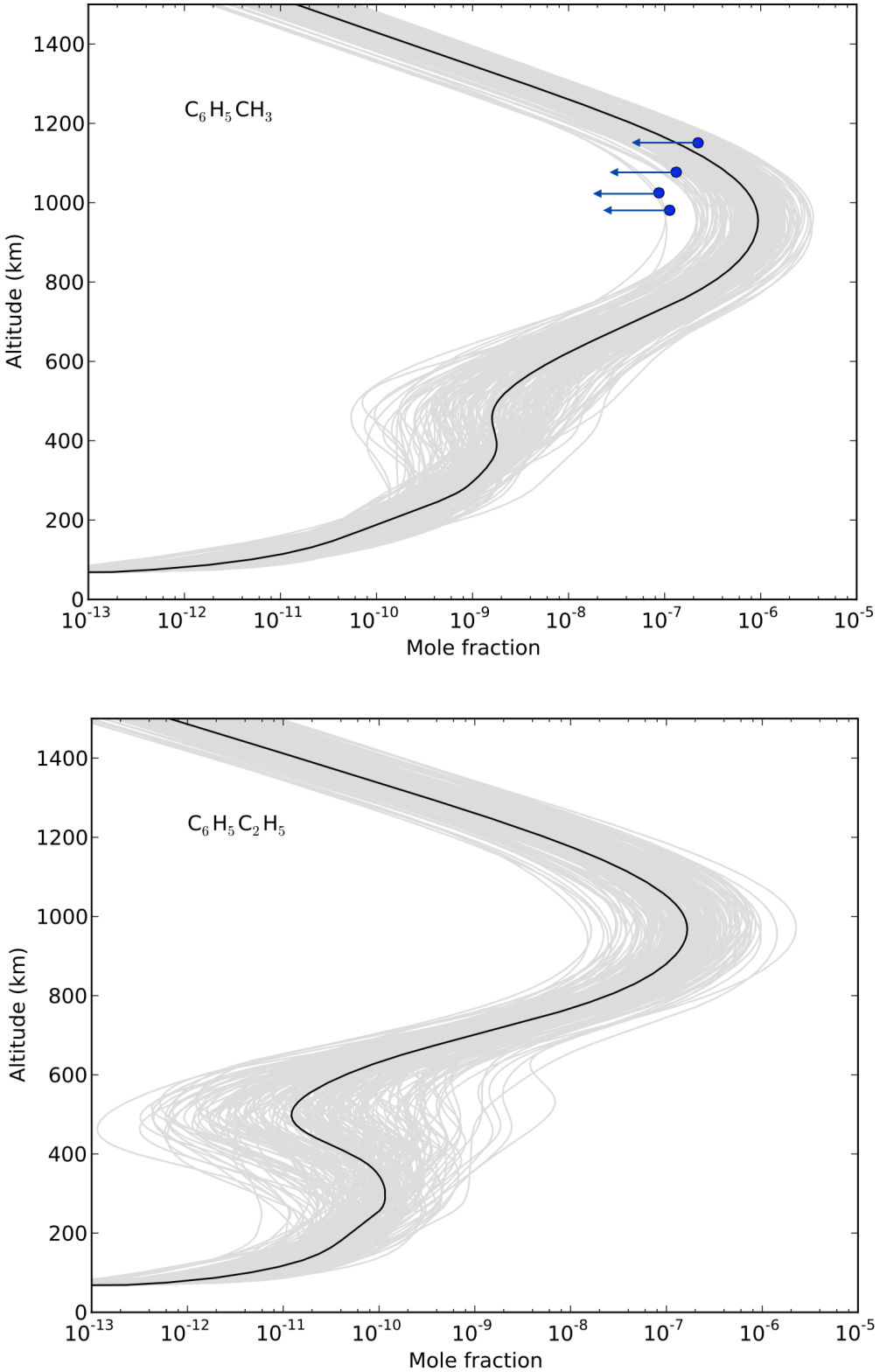

Fig. 7. Top: Mole fraction profiles of toluene ($C_6H_5CH_3$). Upper limits of $C_6H_5CH_3$ from Cui et al. (2009) are given by blue arrows. Bottom: Mole fraction profiles of ethylbenzene ($C_6H_5C_2H_5$). The nominal run is in black and 200 Monte-Carlo runs in grey (see section 3.6 for an explanation of these runs).

only produced from aniline in our model and could be used as a proxy for aniline.

Phenylethyne (C_6H_5-C_2H) and benzonitrile (C_6H_5-CN) are produced through direct bimolecular reactions between C_2H and CN radicals with benzene. Their production in the low atmosphere is weak since C_2H and CN are very efficiently consumed through reaction with CH_4. Their low abundances (see Figure 8) will make their detection in Titan's atmosphere very difficult even though benzonitrile possesses a strong dipole moment (4.7 D), which has allowed its detection in dense molecular cloud TMC-1 (McGuire et al., 2018).

Aniline, aniline-N-methyl, phenylethyne and benzonitrile are not included in previous studies (Vuitton et al., 2008; Krasnopolsky, 2009, 2012, 2014).

3.4 Polyaromatics

Polyaromatics are not included in our model but some production fluxes are taken into account (leading to AROM). Among them, we calculate the fluxes of reactions leading to poly-phenyls. Indeed, neutral reactions between aromatic radicals, mainly phenyl (C_6H_5) and benzyl ($C_6H_5CH_2$), lead to the formation of polyphenyls. Polyphenyls have been suggested to be efficient haze precursors by Delitsky and McKay (2010). In our model we produce some polyphenyls but since the rate constants for the reactions of phenyl and benzyl radicals with hydrogen atoms and methyl radicals are large even at low pressure (Vuitton et al., 2012), and since hydrogen atoms and methyl radicals are much more abundant than phenyl and benzyl radicals, polyphenyl production involves low fluxes. Other neutral reactions may also produce polyaromatics such as $C_6H_5^+ + C_3H_4$ or C_4H_4, which are thought to lead to Polycyclic Aromatic Hydrocarbon formation (PAHs) (Mebel et al., 2017). Another way to produce polyaromatics are ionic reactions between aromatic ions and unsaturated hydrocarbons. Indeed, $C_6H_5CH_2^+$ (benzyl ion) reacts with C_2H_4 leading to $C_9H_{11}^+$ (Ausloos et al., 1980; Anicich et al., 2006) involving a large flux, similar to the ones leading to benzene. The precise form and reactivity of $C_9H_{11}^+$ is unknown but it is clear that ionic reactions could be the source of large ions including polyaromatics as already highlighted by many authors (Anicich et al., 2006; Krasnopolsky, 2009; Westlake et al., 2014). An alternative route for the growth of hydrocarbon molecules in Titan's atmosphere may be the reactions of neutral aromatics with ions such as CH_3^+, $C_2H_5^+$, l-$C_3H_3^+$. Indeed, even if the main channel of the $C_6H_6 + C_2H_5^+$ reaction is proton transfer leading to $C_6H_7^+ + C_2H_4$, termolecular association producing protonated ethylbenzene is also very likely to occur as shown by Žabka et al. (2009). Association could also be important for reactions such as $CH_3^+ + C_6H_6$, $CH_3^+ + C_6H_5CH_3$, l-$C_3H_3^+ + C_6H_6$ and l-$C_3H_3^+ + C_6H_5CH_3$ (Adams 2010). Ionic chemistry is obviously an

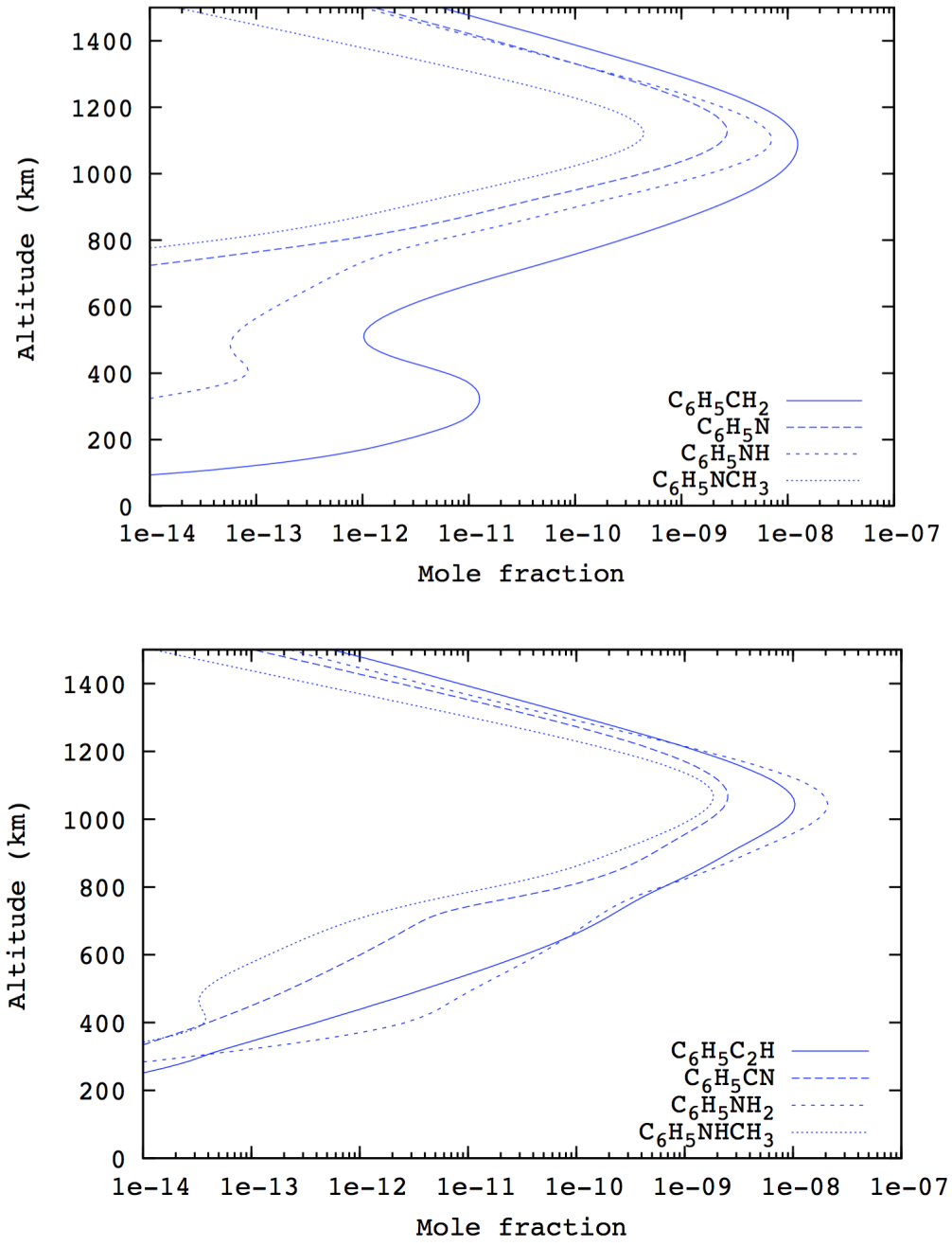

Fig. 8. Mole fraction profiles of aromatic radicals (upper plot) and molecules (lower plot) included in the nominal model (in addition to the ones presented before). They all condense below an altitude of approximately 100 km and have very low relative abundances in the lower atmosphere.

efficient way to increase the molecular complexity in Titan's atmosphere but realistic modeling of such chemistry needs however further experimental and theoretical studies.

3.5 Aromatic related ions

Even if there are direct ionic production pathways of $C_6H_7^+$ (the $C_6H_5^+ + H_2$ and $C_4H_5^+ + C_2H_4$ reactions for example), benzene protonation through the $C_6H_6 + HCNH^+$ and $C_6H_6 + C_2H_5^+$ reactions involve much higher fluxes. Then, the $C_6H_7^+$ mole fraction is proportional to the neutral C_6H_6 one. The density profile of $C_6H_7^+$ derived from INMS observation is depicted in Figure 9 and compared to our model results. The agreement between our model and observations is very good indicating that the benzene and $C_2H_5^+$/$HCNH^+$/electron abundances are likely to be well reproduced. The $C_7H_7^+$ mole fraction is however not very well reproduced, the $m/z = 91$ ion (sum of the benzylium and tropylium ions) is overestimated compared to INMS observations. This could be due to an overestimation of $C_7H_7^+$ production versus $C_6H_5CH_2^+$ and shows that the chemistry of these species should be revisited (particularly the $C_5H_5^+ + C_2H_2$ and $C_6H_5^+ + CH_4$ reactions). The density profiles of $C_6H_7^+$ and $C_7H_7^+$ are in quite close agreement with Krasnopolsky (2012, 2014) except below an altitude of 600 km. This might be due to the fact that we do not consider magnetospheric protons in our model. The density profiles of the other aromatic ions are depicted in Figure 10.

3.6 Uncertainty propagation and sensitivity analysis

It has been demonstrated in several studies that uncertainties on rate constants have noticeable effects on photochemical model results (see for instance Hébrard et al. (2012); Hébrard et al. (2013); Dobrijevic et al. (2014); Loison et al. (2015) for neutrals and Carrasco et al. (2007, 2008); Plessis et al. (2012) for ions). In the present study, we account for the coupling between neutrals and ions to study how uncertainties on rate constants propagate into the model through ion-neutral reactions. Details are given in Dobrijevic et al. (2016b). We performed 200 Monte-Carlo runs to obtain statistically significant results while limiting the computational time. In the following, results are restricted to the nominal model (for which the photolysis of AROM has been included with a branching ratio equal to 3%).

The propagation of uncertainties for C_6H_6 gives a large distribution of mole fraction profiles (see Figure 6) with possible epistemic multi-modality in the lower atmosphere (see Figure 11), which are caused by uncertainties on some key rate coefficients. Such behaviour has already been observed in photochemical models for C_2H_2 and C_2H_4 in the atmosphere of Titan (Dobrijevic et al., 2008), but uncertainties on the rate constants of the key reactions, which were responsible for this behaviour for these two compounds have been reviewed since then, and the earlier bimodalities are no longer present in our model.

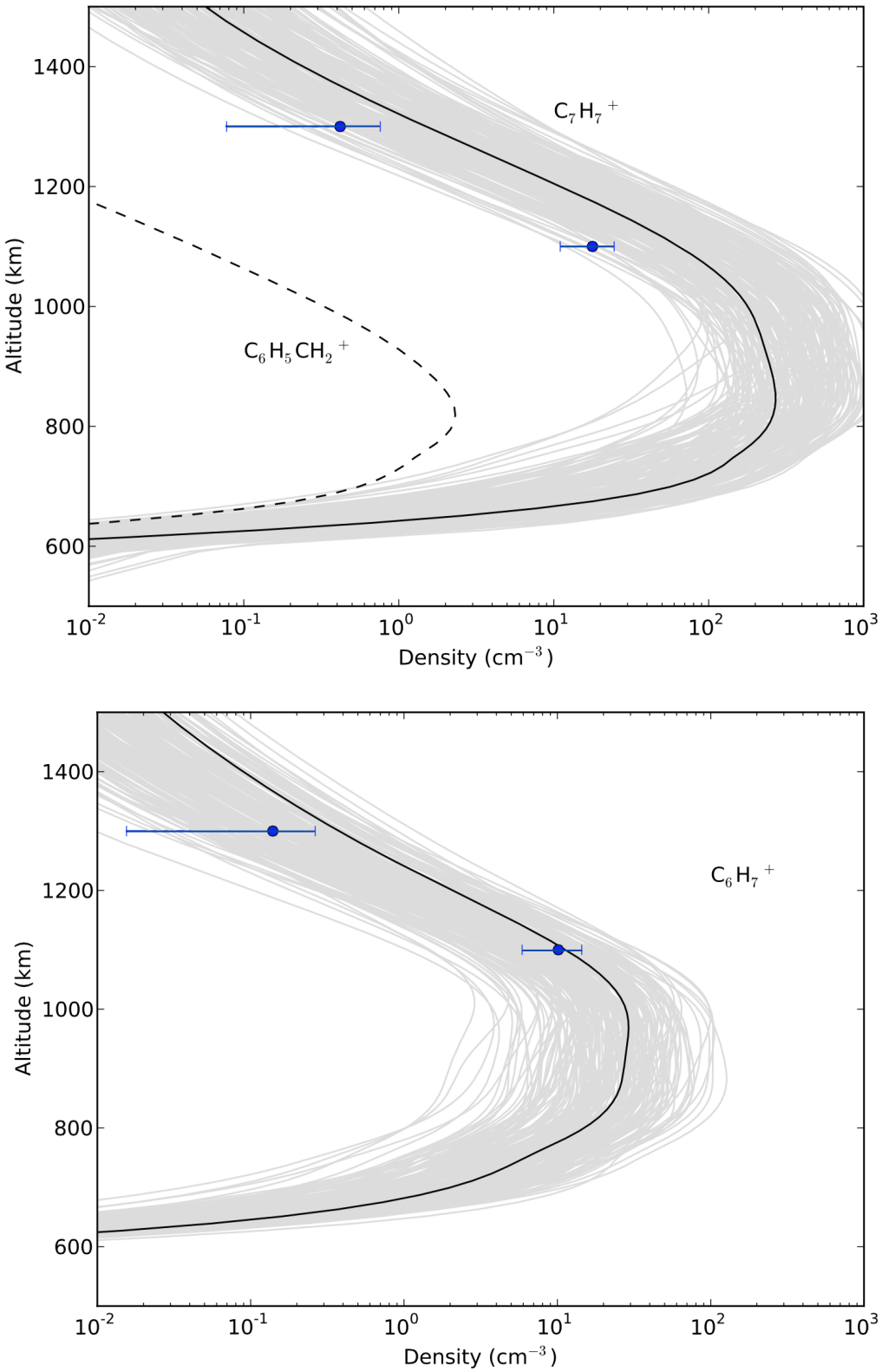

Fig. 9. Top: Nominal model densities in the ionosphere of $C_7H_7^+$ (plain line) and $C_6H_5CH_2^+$ (dashed line). Bottom: $C_6H_7^+$. Monte-Carlo density profiles are in grey (see section 3.6 for an explanation of these runs). INMS data are in blue (Mandt et al. (2012) corrected according to Teolis et al. (2015)). We assume that the mass $m/z = 79$ in INMS spectra is due to $C_6H_7^+$ with no contribution of other species.

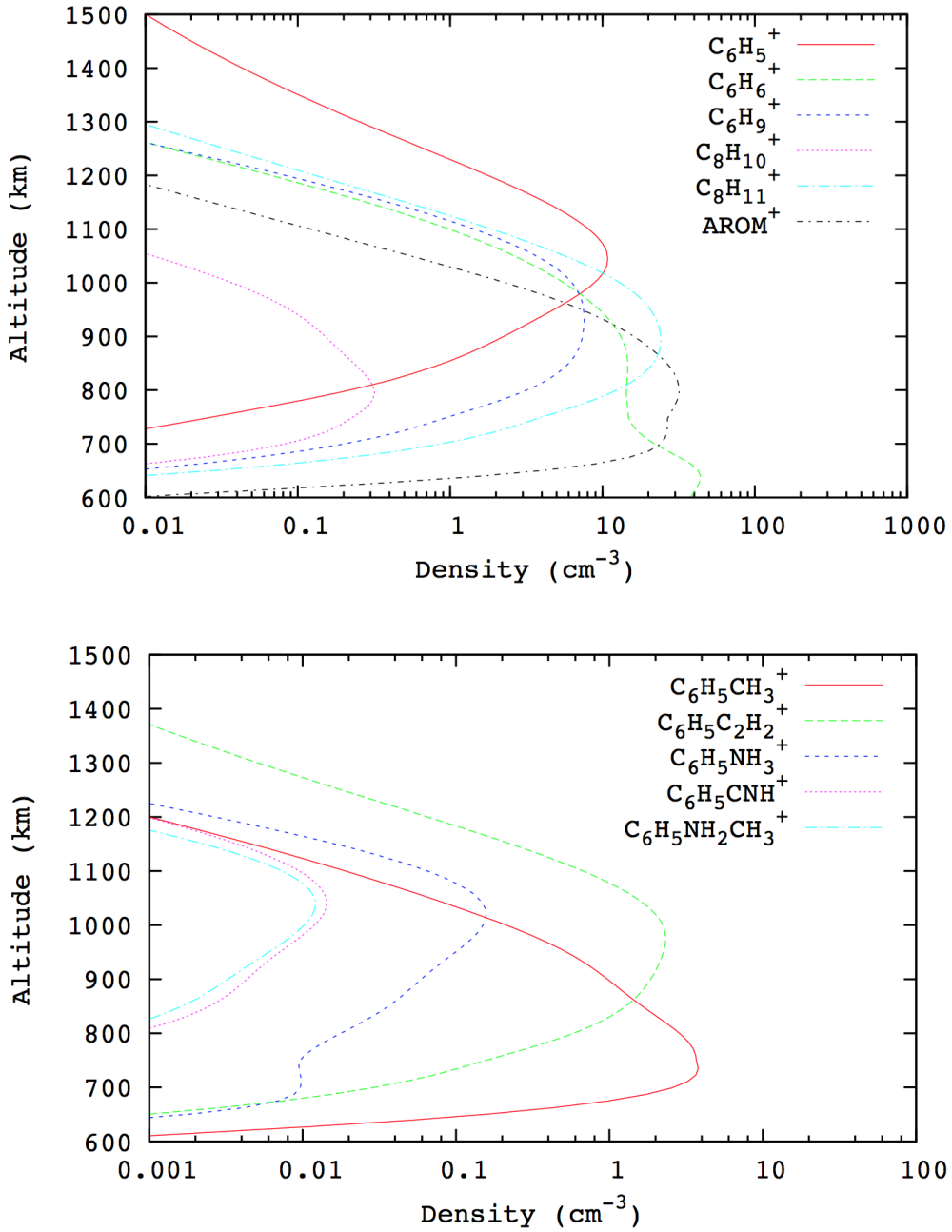

Fig. 10. Density profiles of aromatic related ions in the nominal model.

In the present model, the main key reactions for C_6H_6 are the reactions of excited benzene (both $C_6H_6^{**}$ and $C_6H_6^{*}$): $C_6H_6^{**} \rightarrow C_6H_5 + H$, $C_6H_6^{**} + N_2 \rightarrow C_6H_6^{*} + N_2$ and the $C_6H_6^{*} + N_2 \rightarrow C_6H_6 + N_2$ reaction, a new reaction we added in the model. These reactions are not well characterized and control the loss of benzene as the photodissociation of $C_6H_6^{*}$ is the only process which can break open the aromatic ring. Uncertainties on these rate constants are responsible for the large distribution of profiles for C_6H_6.

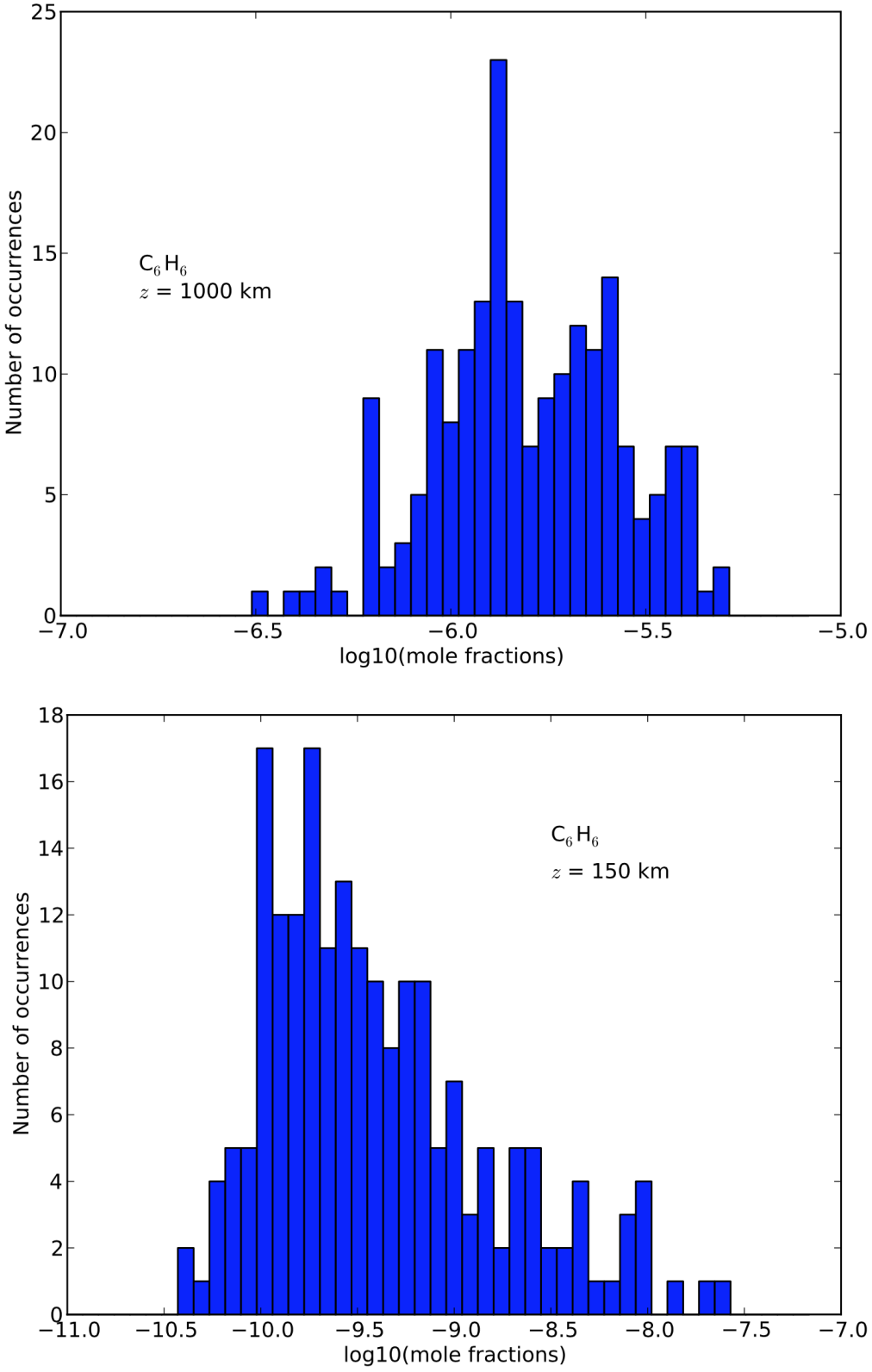

Fig. 11. Histograms of the logarithm of the mole fractions of C_6H_6 at two different altitudes extracted from Figure 6.

For toluene ($C_6H_5CH_3$), the distribution of mole fraction profiles is also quite large at all altitudes (see Figures 7 and 12). This is also the case for ethylbenzene (Figure 7). Our sensitivity analysis revealed many key reactions but the ones that contribute the most to the resulting uncertainties are the main reactions involved directly in its production: $H + C_6H_5CH_2 \rightarrow C_6H_5CH_3$ and $CH_3 + C_6H_5 \rightarrow C_6H_5CH_3$ (in addition to $C_2H_3 + C_4H_3 \rightarrow C_6H_5 + H$).

The complete lists of key reactions (reactions that have the strongest impact on the uncertainties of our model results) for three different altitudes are given in Appendix D.

4 Discussion

In our model, toluene could be as abundant as benzene or 10 times lower considering the uncertainties in the reaction rates. A signal at $m/z = 92$ has been detected by the Cassini/INMS instrument but Vuitton et al. (2008) found that, due to the time dependence of this signal, toluene is mostly formed in the INMS chamber through $CH_3 + C_6H_5$ recombination on the walls. Cui et al. (2009) obtained an upper limit for C_7H_8 as a function of altitude: at 1025 km for instance, the mixing ratio of C_7H_8 is lower than 8.73×10^{-8}. This value is lower than our nominal model toluene abundance. However, it is in agreement with some of the values we derived from our uncertainty propagation study. It should be noted that, in contrast to benzene, toluene is mainly produced by neutral reactions even at high altitude, namely through the $C_6H_5 + CH_3$ and $C_6H_5CH_2 + H$ reactions, the rate of these two reactions being only poorly known, particularly at low pressure. As a consequence, it is not clear whether our model might overestimate the production of toluene or INMS data should be re-analyzed considering the putative presence of toluene with a significant abundance.

In our nominal model, the integrated total production of aromatics above the condensation level is 2.6×10^9 $cm^{-2}s^{-1}$ (see Table 2). It is dominated by the production of benzene. Aromatics condense in the lower stratosphere. Their condensation level is around 70-90 km depending on the species. Considering the total production and loss rates of benzene, we infer a condensation rate equal to 18 $gcm^{-2}Gy^{-1}$, this would give a layer of ice of about 1 m accumulated over 4.5 Gy all over the planet.

As pointed out by Vuitton et al. (2008), the production of benzene in the ionosphere is greatly enhanced by the coupled ion-neutral chemistry compared to the neutral chemistry alone. This is particularly noticeable in the ionosphere, whereas a neutral model can reproduce the observational IR data in the lower stratosphere (see Figure 13). As shown in Table 2, this is also the case for

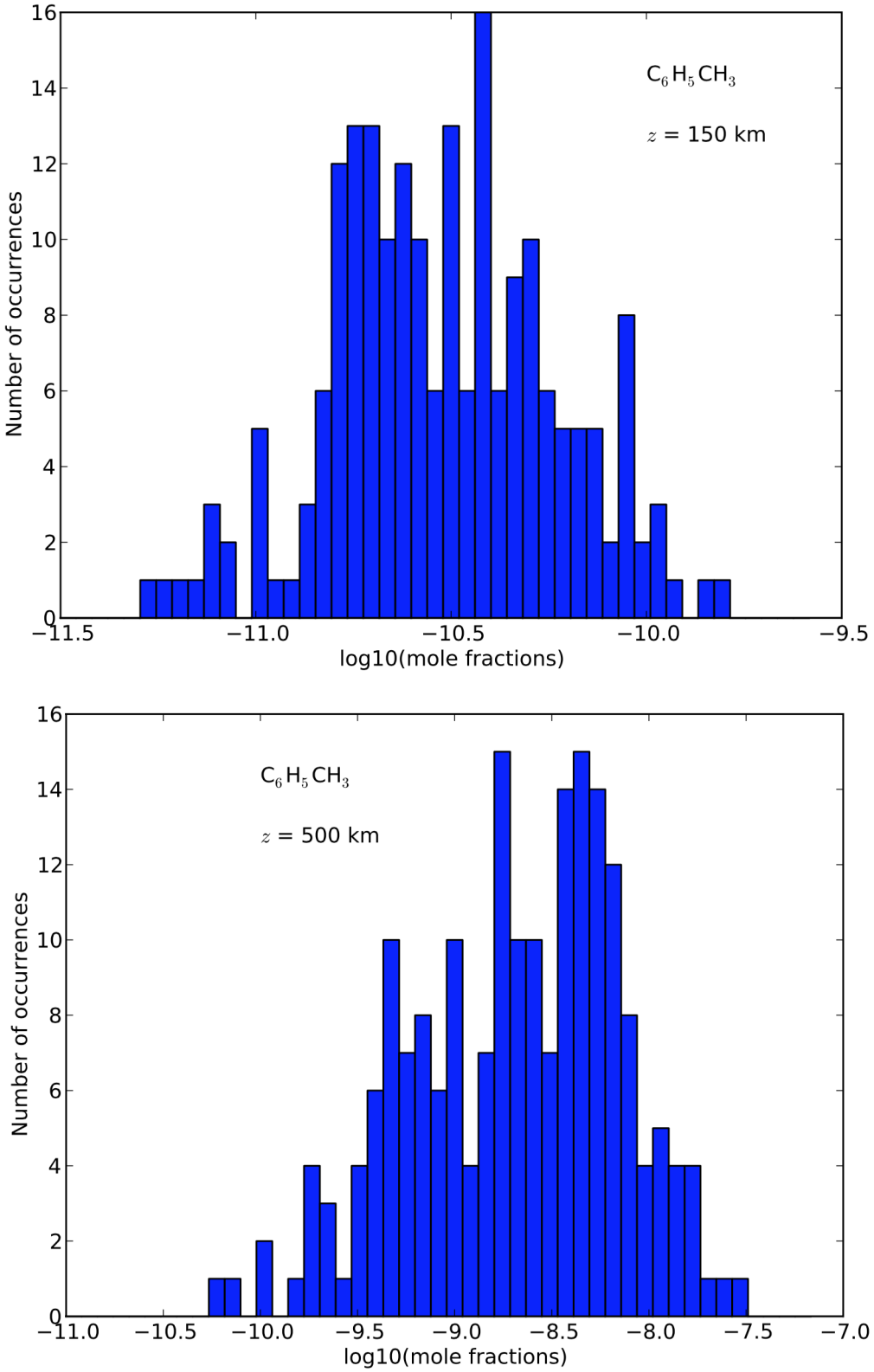

Fig. 12. Histograms of the logarithm of the mole fractions of $C_6H_5CH_3$ at two different altitudes extracted from Figure 7.

Table 2
P: Integrated total production rate ($cm^{-2}s^{-1}$) - Value referred to the surface. w = column density (cm^{-2}). The total production considered that C_6H_6, $C_6H_5CH_3$ and AROM are the main aromatics in Titan's atmosphere. Results correspond to the nominal model.

	Neutral model				Coupled ions-neutral model			
	Above tropopause		Ionosphere		Above tropopause		Ionosphere	
			($z > 500$ km)				($z > 500$ km)	
	w	P	w	P	w	P	w	P
C_6H_6	7.3×10^{14}	2.9×10^{8}	8.1×10^{11}	4.9×10^{6}	1.0×10^{15}	1.8×10^{9}	8.7×10^{13}	5.5×10^{8}
$C_6H_5CH_3$	6.2×10^{13}	2.2×10^{8}	3.0×10^{10}	3.8×10^{5}	1.2×10^{14}	7.4×10^{8}	6.0×10^{13}	8.0×10^{7}
AROM	1.1×10^{15}	3.0×10^{7}	1.4×10^{10}	3.3×10^{3}	1.2×10^{15}	5.8×10^{7}	5.4×10^{12}	2.3×10^{7}
total		5.4×10^{8}		5.3×10^{6}		2.6×10^{9}		6.8×10^{8}

toluene (and the other aromatics).

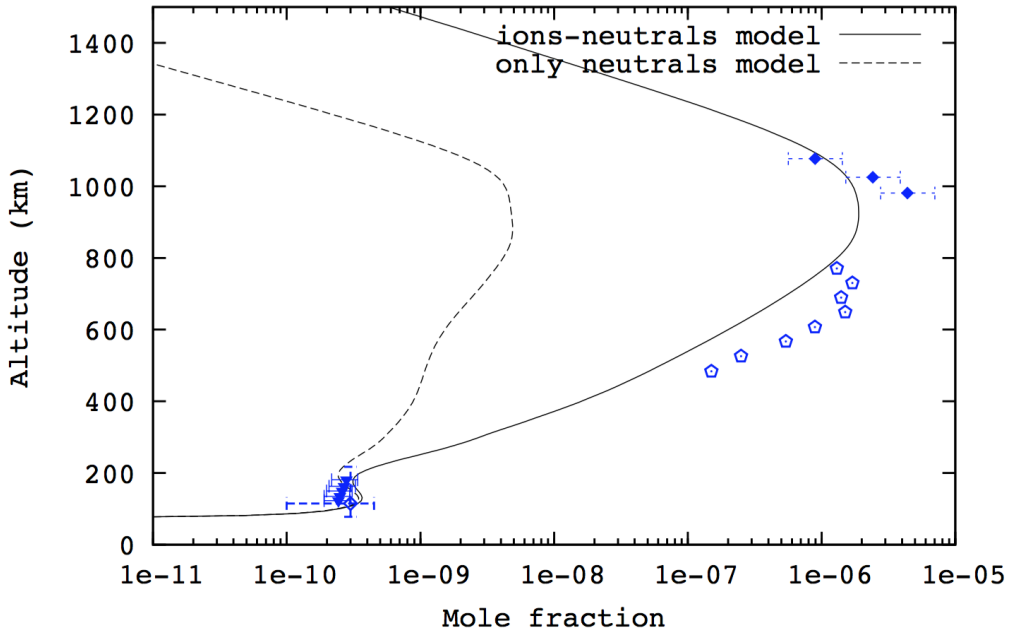

Fig. 13. Mole fraction profiles of benzene for two model results: (1) The coupled chemistry of ions and neutrals has been turned on, and (2) the chemistry of ions has been turned off. Comparison with various data (see Figure 6 for caption).

We have performed a local sensitivity analysis to study the effect of Galactic Cosmic Rays (GCR) on the production of benzene (and other aromatics). The results for benzene and AROM are presented in Figure 14. The effect for benzene is quite low (lower than the uncertainties on the abundances derived from observations). In contrast, the GCR induced chemistry has a noticeable effect on the generic species AROM, suggesting that some aromatics might be sensitive to GCR chemistry.

Finally, we also tested the importance of the photolysis of the generic species AROM. Considering that AROM photodissociation does not lead to any of the aromatic compounds present in our network (C_6H_4, C_6H_6, toluene,...), which

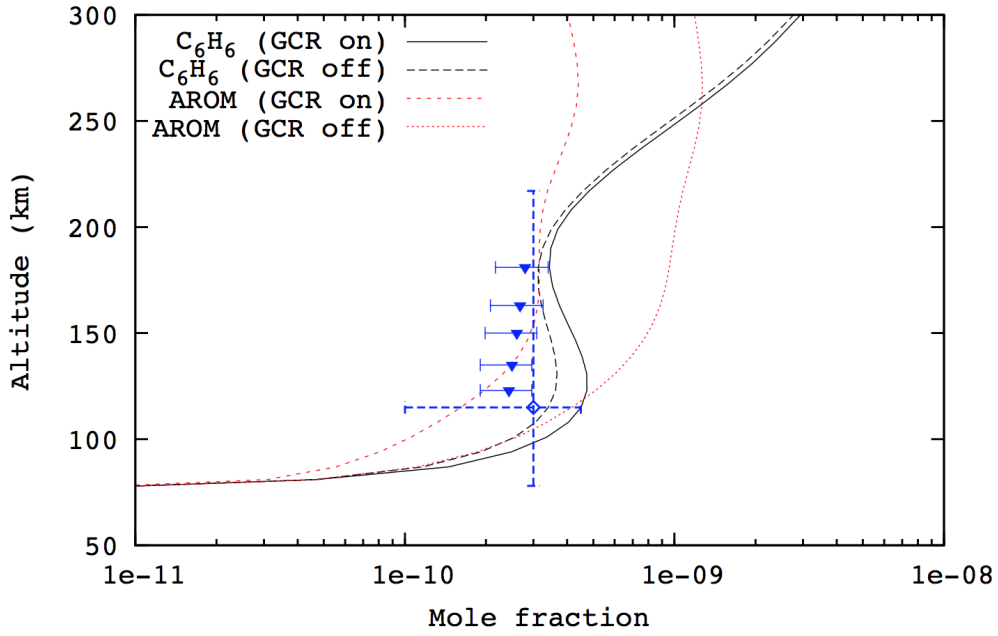

Fig. 14. Mole fraction profiles of C_6H_6 and AROM) and comparison with various data Comparison of model results when the chemistry induced by Galactic Cosmic Rays has been turned on/off is shown.

seems very unlikely, the mole fraction of benzene in the lower atmosphere is too low by a factor of about 4. However, due to large uncertainties in the model results, our model is in agreement with observations. Adding a small production of benzene through AROM photodissociation (even with a branching ratio as low as 1%), leads to good agreement between the model results and the C_6H_6 abundance derived from IR observations (see Figure 15).

Heterogeneous chemistry is neglected in this study, but might play a role for benzene production in the lower atmosphere as proposed by Plane et al. (2018). In their model, the bulk of cosmic dust particles of 10 μm do not ablate in Titan's atmosphere and might provide a significant surface for such heterogeneous chemistry. A precise quantification of such processes is very delicate and requires further studies.

5 Conclusion

We have updated the chemical scheme used in Titan's atmospheric models to study the production of aromatic molecules. Due to the large number of potential aromatics, only 24 aromatic species (neutrals and ions) have been considered, which should be the most abundant aromatics in the atmosphere.

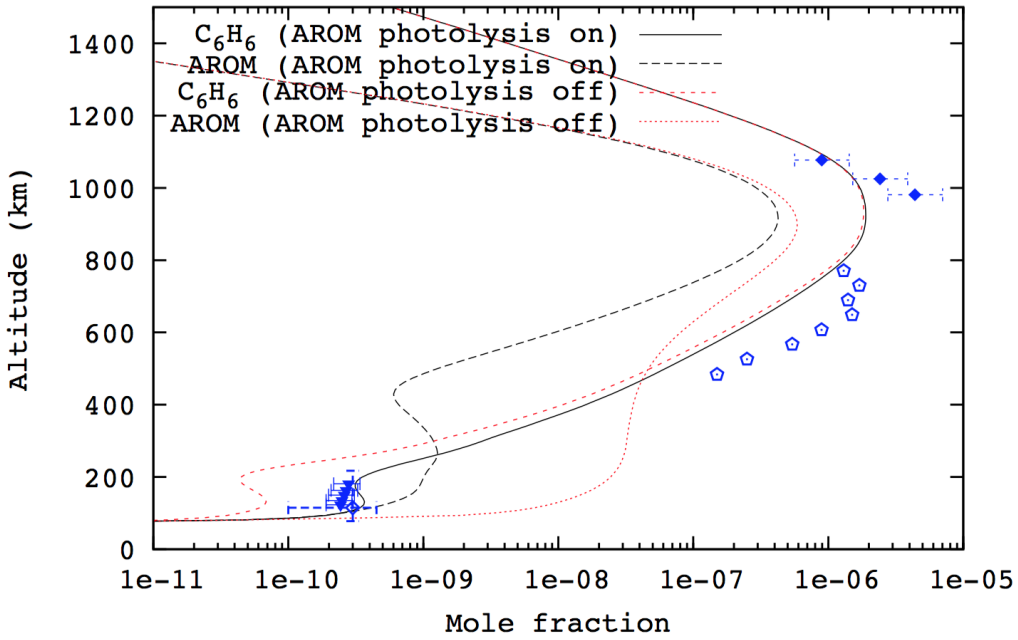

Fig. 15. Mole fraction profiles of C_6H_6 and AROM, and comparison with various C_6H_6 observations (in the ionosphere: INMS data from Cui et al. (2009); In the lower stratosphere: CIRS data from Vinatier et al. (2015) and Coustenis et al. (2007); in the middle atmosphere: UVIS data from Koskinen et al. (2011)). Comparison of model results when the photolysis of AROM has been turned on (in black) or off (in blue) is shown.

In the ionosphere, the most abundant aromatic molecules in our model are benzene, toluene and ethylbenzene. In the stratosphere (around 200 km for instance), only benzene and toluene are relatively abundant. Considering its abundance, toluene might be detectable in the future. In contrast, other nitriles like ethynylbenzene and benzonitrile are not abundant enough and are unlikely to be detectable either through IR or microwave spectroscopy with current instruments.

Our model results confirm previous studies: C_6H_6 is mainly produced in the thermosphere by ion chemistry while neutral chemistry dominates in the lower stratosphere, both being of a comparable importance. The large abundance of C_6H_6 in the thermosphere is not due to efficient formation pathways, but instead due to the fact that once produced, the aromatic ring is preserved from photodissociation and from DR of protonated benzene. Then, C_6H_6 accumulates in the upper atmosphere reaching a relative abundance as high as 10^{-6}. The GCR related chemistry in the lower atmosphere has a moderate impact on benzene production.

The model results currently have large uncertainties and a wide range of experimental and theoretical studies are required to reduce the rate constant

uncertainties for those reactions leading to aromatic production (and loss) and to determine the main reaction products and their branching ratios.

Ionic chemistry is an important way to produce benzene and consequently leads to relatively high abundances for some aromatic ions, particularly $C_6H_6^+$, $C_6H_7^+$ and $C_7H_7^+$ (tropylium). A key point for polyaromatic formation is the reactivity of aromatic ions with unsaturated hydrocarbons as noted by Anicich et al. (2006); Westlake et al. (2014). These reactions, particularly the association reactions, are not well characterized and may be an efficient way to increase molecular complexity in Titan's atmosphere. Further theoretical and experimental studies are clearly needed.

Supplementary material

A List of reactions and photodissociations

List of reactions (with rate constants) and references used in the present model.

B List of photodissociations

List of photodissociations and references used in the present model.

C Integrated column rates

For each reaction included in the model, the integrated column rate scaled to the surface (in $cm^{-2}s^{-1}$) and the mean altitude (in km) of the production are given.

D List of key reactions and photodissociations

In the three following files, we list the key reactions at 300 km, 500 km and 1000 km of altitude for all species in the present model.

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References

Alkemade, U., Homann, K. H., 1989. Formation of C_6H_6 Isomers by Recombination of Propynyl in the System Sodium Vapour/Propynylhalide. International journal of research in physical chemistry and chemical physics 161 (1-2), 19.

Anicich, V. G., 2003. An Index of the Literature for Bimolecular Gas Phase Cation-Molecule Reaction Kinetics. JPL Publication 2003, 03-19 NASA.

Anicich, V. G., Wilson, P. F., McEwan, M. J., 2006. An ICR Study of Ion-Molecules Reactions Relevant to Titan's Atmosphere: An Investigation of Binary Hydrocarbon Mixtures up to 1 Micron. J Am. Soc. Mass. Spectr. 17 (4), 544–561.

Atkinson, D. B., Hudgens, J. W., 1999. Rate Coefficients for the Propargyl Radical Self-Reaction and Oxygen Addition Reaction Measured Using Ultraviolet Cavity Ring-down Spectroscopy. Journal of Physical Chemistry A 103 (21), 4242–4252.

Ausloos, P., 1982. Structure and isomerization of $C_7H_7^+$ ions formed in the charge-transfer-induced fragmentation of ethylbenzene, toluene, and norbornadiene. Journal of the American Chemical Society 104 (20), 5259–5265. URL http://dx.doi.org/10.1021/ja00384a001

Ausloos, P., Jackson, J. A. A., Lias, S. G., 1980. Reactions of benzyl ions with alkanes, alkenes, and aromatic compounds. International Journal of Mass Spectrometry and Ion Physics 33 (3), 269–283.

Ausloos, P., Lias, S. G., Buckley, T. J., Rogers, E. E., 1989. Concerning the formation and the kinetics of phenylium ions. International Journal of Mass Spectrometry and Ion Processes 92 (0), 65–77.

Balucani, N., Pacifici, L., Skouteris, D., Caracciolo, A., Casavecchia, P., Rosi, M., 2018. A Theoretical Investigation of the Reaction $N(^2D)+C_6H_6$ and Implications for the Upper Atmosphere of Titan. In: Gervasi, O., Murgante, B., Misra, S., Stankova, E., Torre, C. M., Rocha, A. M. A. C., Taniar, D., Apduhan, B. O., Tarantino, E., Ryu, Y. (Eds.), Computational Science and Its Applications ICCSA 2018. Springer International Publishing, pp. 763–772.

Bergeat, A., Loison, J.-C., 2001. Reaction of carbon atoms, $C(2p^2, {}^3P)$ with C_2H_2, C_2H_4 and C_6H_6 : Overall rate constant and relative atomic hydrogen production. PCCP 3, 2038.

Berman, M., Fleming, J., Harvey, A., Lin, M., 1982. Temperature Dependence of the Reactions of CH Radicals with Unsaturated Hydrocarbons. Chem. Phys. 73, 27.

Berteloite, C., Le Picard, S. D., Balucani, N., Canosa, A., Sims, I. R., 2010. Low temperature rate coefficients for reactions of the butadiynyl radical, C_4H, with various hydrocarbons. Part II: reactions with alkenes (ethylene, propene, 1-butene), dienes (allene, 1,3-butadiene) and alkynes (acetylene, propyne and 1-butyne). Phys. Chem. Chem. Phys. 12 (15), 3677–3689. URL http://dx.doi.org/10.1039/B923867K

Capalbo, F. J., Bénilan, Y., Fray, N., Schwell, M., Champion, N., Es-sebbar, E.-t., Koskinen, T. T., Lehocki, I., Yelle, R. V., 2016. New benzene absorption cross sections in the VUV, relevance for Titan's upper atmosphere. Icarus 265, 95–109.

Carrasco, N., Alcaraz, C., Dutuit, O., Plessis, S., Thissen, R., Vuitton, V., Yelle, R., Pernot, P., Nov. 2008. Sensitivity of a Titan ionospheric model to the ion-molecule reaction parameters. Planetary and Space Science 56, 1644–1657.

Carrasco, N., Dutuit, O., Thissen, R., Banaszkiewicz, M., Pernot, P., Jan. 2007. Uncertainty analysis of bimolecular reactions in Titan ionosphere chemistry model. Planetary and Space Science 55, 141–157.

Cool, T. A., Wang, J., Nakajima, K., Taatjes, C. A., McLlroy, A., 2005. Photoionization cross sections for reaction intermediates in hydrocarbon combustion. International Journal of Mass Spectrometry 247 (1), 18–27.

Coustenis, A., Achterberg, R. K., Conrath, B. J., Jennings, D. E., Marten, A., Gautier, D., Nixon, C. A., Flasar, F. M., Teanby, N. A., Bézard, B., Samuelson, R. E., Carlson, R. C., Lellouch, E., Bjoraker, G. L., Romani, P. N., Taylor, F. W., Irwin, P. G. J., Fouchet, T., Hubert, A., Orton, G. S., Kunde, V. G., Vinatier, S., Mondellini, J., Abbas, M. M., Courtin, R., Jul. 2007. The composition of Titan's stratosphere from Cassini/CIRS mid-infrared spectra. Icarus 189, 35–62.

Coustenis, A., Salama, A., Schulz, B., Ott, S., Lellouch, E., Encrenaz, T. h., Gautier, D., Feuchtgruber, H., Feb. 2003. Titan's atmosphere from ISO mid-infrared spectroscopy. Icarus 161, 383–403.

Cremer, D., Kraka, E., Joo, H., Stearns, J. A., Zwier, T. S., 2006. Exploration of the potential energy surface of C_4H_4 for rearrangement and decomposition reactions of vinylacetylene: A computational study. Part I. Phys. Chem. Chem. Phys. 8 (45), 5304–5316.

Cui, J., Yelle, R. V., Vuitton, V., Waite, J. H., Kasprzak, W. T., Gell, D. A., Niemann, H. B., Müller-Wodarg, I. C. F., Borggren, N., Fletcher, G. G., Patrick, E. L., Raaen, E., Magee, B. A., Apr. 2009. Analysis of Titan's neutral upper atmosphere from Cassini Ion Neutral Mass Spectrometer measurements. Icarus 200, 581–615.

Delitsky, M. L., McKay, C. P., May 2010. The photochemical products of benzene in Titan's upper atmosphere. Icarus 207, 477–484.

Dheandhanoo, S., Forte, L., Fox, A., Bohme, D. K., 1986. Ion-molecule reactions with carbon chain molecules: reactions with diacetylene and the diacetylene cation. Canadian Journal of Chemistry 64 (4), 641–648.
URL `http://www.nrcresearchpress.com/doi/abs/10.1139/v86-104`

Dobrijevic, M., Carrasco, N., Hébrard, E., Pernot, P., Nov. 2008. Epistemic bimodality and kinetic hypersensitivity in photochemical models of Titan's atmosphere. Planetary and Space Science 56, 1630–1643.

Dobrijevic, M., Hébrard, E., Loison, J. C., Hickson, K. M., Jan. 2014. Coupling of oxygen, nitrogen, and hydrocarbon species in the photochemistry of Titan's atmosphere. Icarus 228, 324–346.

Dobrijevic, M., Loison, J. C., Hickson, K. M., 2016a. The eddy diffusion coefficient in the atmosphere of Titan: models comparison. Non-peer review paper.

Dobrijevic, M., Loison, J. C., Hickson, K. M., 2018. The chemistry of CH_2 in the atmosphere of Titan in question. Non-peer review paper.

Dobrijevic, M., Loison, J. C., Hickson, K. M., Gronoff, G., 2016b. 1D-coupled photochemical model of neutrals, cations and anions in the atmosphere of Titan. Icarus 268, 313–339.

Douglas, K., Blitz, M. A., Feng, W., Heard, D. E., Plane, J. M. C., Slater, E., Willacy, K., Seakins, P. W., 2018. Low temperature studies of the removal reactions of $^1CH_2$ with particular relevance to the atmosphere of Titan. Icarus 303, 10–21.

Douguet, N., Fonseca dos Santos, S., Raoult, M., Dulieu, O., Orel, A. E., Kokoouline, V., 2015. Theoretical study of radiative electron attachment to CN, C_2H, and C_4H radicals. The Journal of Chemical Physics 142 (23), 234309.

Duran, R. P., Amorebieta, V. T., Colussi, A. J., 1988. Is the homogeneous thermal dimerization of acetylene a free-radical chain reaction? Kinetic and thermochemical analysis. The Journal of Physical Chemistry 92 (3), 636–640.
URL http://dx.doi.org/10.1021/j100314a014

Fahr, A., Nayak, A., 2000. Kinetics and products of propargyl (C_3H_3) radical self-reactions and propargyl-methyl cross-combination reactions. Int. J. Chem. Kinet. 32 (2), 118–124.

Fournier, J. A., Shuman, N. S., Melko, J. J., Ard, S. G., Viggiano, A. A., 2013. A novel technique for measurement of thermal rate constants and temperature dependences of dissociative recombination: CO_2^+, CF_3^+, N_2O^+, $C_7H_8^+$, $C_7H_7^+$, $C_6H_6^+$, $C_6H_5^+$, $C_5H_6^+$, $C_4H_4^+$, and $C_3H_3^+$. J. Chem. Phys. 138 (15), 154201–7.
URL http://dx.doi.org/10.1063/1.4801657

Frankland, V. L., James, A. D., Sánchez, J. D. C., Mangan, T. P., Willacy, K., Poppe, A. R., Plane, J. M. C., Nov. 2016. Uptake of acetylene on cosmic dust and production of benzene in Titan's atmosphere. Icarus 278, 88–99.

Fridgen, T. D., Troe, J., Viggiano, A. A., Midey, A. J., Williams, S., McMahon, T. B., 2004. Experimental and Theoretical Studies of the Benzylium+/Tropylium+ Ratios after Charge Transfer to Ethylbenzene. The Journal of Physical Chemistry A 108 (26), 5600–5609.
URL http://dx.doi.org/10.1021/jp031328s

Frochtenicht, R., 1995. The photodissociation of toluene studied by forward photofragment translational spectroscopy. The Journal of Chemical Physics 102 (12), 4850–4859.
URL http://scitation.aip.org/content/aip/journal/jcp/102/12/10.1063/1.469533

Gautier, T., Sebree, J. A., Li, X., Pinnick, V. T., Grubisic, A., Loeffler, M. J., Getty, S. A., Trainer, M. G., Brinckerhoff, W. B., Jun. 2017. Influence of trace aromatics on the chemical growth mechanisms of Titan aerosol ana-

logues. Planet. Space Sci. 140, 27–34.

Georgievskii, Y., Miller, J. A., Klippenstein, S. J., 2007. Association rate constants for reactions between resonance-stabilized radicals: C_3H_3 + C_3H_3, C_3H_3 + C_3H_5, and C_3H_5 + C_3H_5. Phys. Chem. Chem. Phys. 9 (31), 4259–4268.

Ghibaudi, E., Colussi, A. J., 1988. Kinetics and thermochemistry of the equilibrium 2 $C_2H_2 \leftrightarrow C_4H_4$: direct evidence against a chain mechanism. J. Phys. Chem. 92 (20), 5839–5842.

Goebbert, D., Liu, X., Wenthold, P., 2004. Reactions of diacetylene radical cation with ethylene. Journal of the American Society for Mass Spectrometry 15 (1), 114–120.
URL http://dx.doi.org/10.1016/j.jasms.2003.10.003

Hamberg, M., Vigren, E., Thomas, R., Zhaunerchyk, V., Zhang, M., Trippel, S., Kaminska, M., Kashperka, I., af Ugglas, M., Kellberg, A., Simonsson, A., Paal, A., Semaniak, J., Larsson, M., Geppert, W., 2011. Experimental studies of the dissociative recombination processes for the $C_6D_6^+$ and $C_6D_7^+$ ions. EAS Publications Series 46, 241–249.
URL http://dx.doi.org/10.1051/eas/1146026

Hébrard, E., Dobrijevic, M., Loison, J., Bergeat, A., Hickson, K., F., C., 2013. Photochemistry of C_3H_p hydrocarbons in Titan's stratosphere revisited. Astronomy and Astrophysics.

Hébrard, E., Dobrijevic, M., Loison, J. C., Bergeat, A., Hickson, K. M., May 2012. Neutral production of hydrogen isocyanide (HNC) and hydrogen cyanide (HCN) in Titan's upper atmosphere. Astronomy and Astrophysics 541, A21.

Hong, X.-P., Chen, W.-K., Cheng, P.-Y., 2001. Ultrafast photodissociation dynamics of cyanobenzene near the ionization threshold. Chemical Physics Letters 350 (5), 495–501.

Honjo, Y., Kinoshita, T., Yatsuhashi, T., Nakashima, N., 2005. Formation of 1,3-hexadiene-5-yne by two-photon chemistry of benzene via hot molecule. Journal of Photochemistry and Photobiology A: Chemistry 171 (3), 223–229.

Howe, P.-T., Fahr, A., 2003. Pressure and Temperature Effects on Product Channels of the Propargyl ($HC{:}CCH_2$) Combination Reaction and the Formation of the "First Ring". The Journal of Physical Chemistry A 107 (45), 9603–9610.
URL http://dx.doi.org/10.1021/jp0307497

Hsu, T. C., Shu, J., Chen, Y., Lin, J. J., Lee, Y. T., Yang, X., 2001. Dissociation rates of benzene at VUV excitation. The Journal of Chemical Physics 115 (21), 9623–9626.
URL http://dx.doi.org/10.1063/1.1423945

Huang, C.-L., Jiang, J.-C., Lin, S. H., Lee, Y. T., Ni, C.-K., 2002. Photodissociation of ethylbenzene at 248 nm. The Journal of Chemical Physics 116 (18), 7779–7782.
URL http://scitation.aip.org/content/aip/journal/jcp/116/18/10.1063/1.1475749

Jain, C., Morajkar, P., Schoemaecker, C., Fittschen, C., 2012. Formation of HO_2 Radicals from the 248 nm Two-Photon Excitation of Different Aromatic Hydrocarbons in the Presence of O_2. The Journal of Physical Chemistry A 116 (24), 6231–6239.
URL https://doi.org/10.1021/jp211520g

Kislov, V. V., Nguyen, T. L., Mebel, A. M., Lin, S. H., Smith, S. C., 2004. Photodissociation of benzene under collision-free conditions: An ab initio/RiceRamspergerKasselMarcus study. The Journal of Chemical Physics 120 (15), 7008–7017.
URL http://dx.doi.org/10.1063/1.1676275

Koizumi, H., 1991. Predominant decay channel for superexcited organic molecules. J. Chem. Phys. 95 (8), 5846–5852.
URL http://link.aip.org/link/?JCP/95/5846/1

Koskinen, T. T., Yelle, R. V., Snowden, D. S., Lavvas, P., Sandel, B. R., Capalbo, F. J., Bénilan, Y., West, R. A., Dec. 2011. The mesosphere and lower thermosphere of Titan revealed by Cassini/UVIS stellar occultations. Icarus 216, 507–534.

Kovacs, T., Blitz, M. A., Seakins, P. W., Pilling, M. J., 2009. H atom formation from benzene and toluene photoexcitation at 248 nm. The Journal of Chemical Physics 131 (20), 204304–12.
URL http://link.aip.org/link/?JCP/131/204304/1

Krasnopolsky, V. A., May 2009. A photochemical model of Titan's atmosphere and ionosphere. Icarus 201, 226–256.

Krasnopolsky, V. A., Dec. 2012. Titan's photochemical model: Further update, oxygen species, and comparison with Triton and Pluto. Planetary and Space Science 73, 318–326.

Krasnopolsky, V. A., Jul. 2014. Chemical composition of Titan's atmosphere and ionosphere: Observations and the photochemical model. Icarus 236, 83–91.

Lebonnois, S., Bakes, E. L. O., McKay, C. P., Oct. 2002. Transition from Gaseous Compounds to Aerosols in Titan's Atmosphere. Icarus 159, 505–517.

Lee, Y.-R., Chen, C.-C., Lin, S.-M., 2003. Photoelimination of C_2H_2 and H_2 from styrene at 193 nm. The Journal of Chemical Physics 118 (20), 9073–9076.
URL http://dx.doi.org/10.1063/1.1576386

Li, C., Zhang, X., Kammer, J. A., Liang, M.-C., Shia, R.-L., Yung, Y. L., Dec. 2014. A non-monotonic eddy diffusivity profile of Titan's atmosphere revealed by Cassini observations. Planet. Space Sci. 104, 48–58.

Li, Y., Klippenstein, S. J., Zhou, C.-W., Curran, H. J., 2017. Theoretical Kinetics Analysis for $\dot{H}$ Atom Addition to 1,3-Butadiene and Related Reactions on the $\dot{C}_4H_7$ Potential Energy Surface. The Journal of Physical Chemistry A 121 (40), 7433–7445.
URL https://doi.org/10.1021/acs.jpca.7b05996

Lin, C.-K., Huang, C.-L., Jiang, J.-C., Chang, A. H. H., Lee, Y. T., Lin, S. H.,

Ni, C.-K., 2002. Photoisomerization and Photodissociation of Toluene in Molecular Beam. Journal of the American Chemical Society 124 (15), 4068–4075.
URL http://dx.doi.org/10.1021/ja0120678

Loison, J. C., Hébrard, E., Dobrijevic, M., Hickson, K. M., Caralp, F., Hue, V., Gronoff, G., Venot, O., Bénilan, Y., 2015. The neutral photochemistry of nitriles, amines and imines in the atmosphere of Titan. Icarus 247, 218–247.

Madden, L. K., Moskaleva, L. V., Kristyan, S., Lin, M. C., 1997. Ab initio MO study of the unimolecular decomposition of the phenyl radical. Journal of Physical Chemistry A 101 (36), 6790–6797.

Magee, B. A., Waite, J. H., Mandt, K. E., Westlake, J., Bell, J., Gell, D. A., Dec. 2009. INMS-derived composition of Titan's upper atmosphere: Analysis methods and model comparison. Planet. Space Sci. 57, 1895–1916.

Mahjoub, A., Schwell, M., Carrasco, N., Bénilan, Y., Cernogora, G., Szopa, C., Gazeau, M.-C., Oct. 2016. Characterization of aromaticity in analogues of titan's atmospheric aerosols with two-step laser desorption ionization mass spectrometry. Planetary and Space Sciences 131, 1–13.

Mandt, K. E., Gell, D. A., Perry, M., Hunter Waite, Jr., J., Crary, F. A., Young, D., Magee, B. A., Westlake, J. H., Cravens, T., Kasprzak, W., Miller, G., Wahlund, J.-E., Ågren, K., Edberg, N. J. T., Heays, A. N., Lewis, B. R., Gibson, S. T., de la Haye, V., Liang, M.-C., Oct. 2012. Ion densities and composition of Titan's upper atmosphere derived from the Cassini Ion Neutral Mass Spectrometer: Analysis methods and comparison of measured ion densities to photochemical model simulations. Journal of Geophysical Research (Planets) 117 (E16), 10006.

McGuire, B. A., Burkhardt, A. M., Kalenskii, S., Shingledecker, C. N., Remijan, A. J., Herbst, E., McCarthy, M. C., 2018. Detection of the aromatic molecule benzonitrile (c-C_6H_5CN) in the interstellar medium. Science 359, 202–205.

McKee, M. L., Reisenauer, H. P., Schreiner, P. R., 2014. Combined ab Initio Molecular Dynamics and Experimental Studies of Carbon Atom Addition to Benzene. The Journal of Physical Chemistry A 118 (15), 2801–2809.
URL http://dx.doi.org/10.1021/jp501107b

Mebel, A. M., Landera, A., Kaiser, R. I., 2017. Formation Mechanisms of Naphthalene and Indene: From the Interstellar Medium to Combustion Flames. The Journal of Physical Chemistry A 121 (5), 901–926.
URL https://doi.org/10.1021/acs.jpca.6b09735

Mebel, A. M., Lin, M. C., Chakraborty, D., Park, J., Lin, S. H., Lee, Y. T., 2001. Ab initio molecular orbital/RiceRamspergerKasselMarcus theory study of multichannel rate constants for the unimolecular decomposition of benzene and the H+C6H5 reaction over the ground electronic state. The Journal of Chemical Physics 114 (19), 8421–8435.
URL https://doi.org/10.1063/1.1360201

Mebel, A. M., Lin, M. C., Yu, T., Morokuma, K., 1997. Theoretical study of potential energy surface and thermal rate constants for the C_6H_5 + H_2 and

C_6H_6 + H reactions. Journal of Physical Chemistry A 101 (17), 3189–3196.
Miller, J. A., Klippenstein, S. J., 2001. The Recombination of Propargyl Radicals:? Solving the Master Equation. The Journal of Physical Chemistry A 105 (30), 7254–7266.
URL http://dx.doi.org/10.1021/jp0102973
Miller, J. A., Klippenstein, S. J., 2003. The Recombination of Propargyl Radicals and Other Reactions on a C_6H_6 Potential. J. Phys. Chem. A 107 (39), 7783–7799.
URL http://dx.doi.org/10.1021/jp030375h
Moreno, R., Lellouch, E., Lara, L. M., Feuchtgruber, H., Rengel, M., Hartogh, P., Courtin, R., Nov. 2012. The abundance, vertical distribution and origin of H_2O in Titan's atmosphere: Herschel observations and photochemical modelling. Icarus 221, 753–767.
Nakashima, N., Yoshihara, K., 1983. Laser flash photolysis of benzene. VIII. Formation of hot benzene from the S_2 state and its collisional deactivation. The Journal of Chemical Physics 79 (6), 2727–2735.
URL http://dx.doi.org/10.1063/1.446176
Negri, F., Zgierski, M. Z., 1995. Theoretical analysis of vibronic structure of absorption spectrum of fulvene. The Journal of Chemical Physics 102 (13), 5165–5173.
Ni, C.-K., Lee, Y. T., 2004. Photodissociation of simple aromatic molecules in a molecular beam. International Reviews in Physical Chemistry 23 (2), 187–218.
URL http://dx.doi.org/10.1080/01442350410001703799
Ni, C.-K., Tseng, C.-M., Lin, M.-F., Dyakov, Y. A., 2007. Photodissociation Dynamics of Small Aromatic Molecules Studied by Multimass Ion Imaging. The Journal of Physical Chemistry B 111 (44), 12631–12642.
URL http://dx.doi.org/10.1021/jp074904j
Ozturk, F., Moini, M., Brill, F. W., Eyler, J. R., Buckley, T. J., Lias, S. G., Ausloos, P. J., 1989. Reactions of $C_5H_3^+$ and $C_5H_5^+$ ions with acetylene and diacetylene. The Journal of Physical Chemistry 93 (10), 4038–4044.
URL http://dx.doi.org/10.1021/j100347a035
Park, J., Yu, C.-F., Bersohn, R., 1989. Photodissociation dynamics of the isomers phenyl cyanide and phenyl isocyanide. Chemical Physics 134 (2), 421–428.
Peverati, R., Partha, P. B., Timothy, J. L., Martin, H.-G., 2016. Insights into Hydrocarbon Chain and Aromatic Ring Formation in the Interstellar Medium: Computational Study of the Isomers of $C_4H_3^+$, $C_6H_3^+$ and $C_6H_5^+$ and Their Formation Pathways. The Astrophysical Journal 830 (2), 128.
Plane, J. M. C., Flynn, G. J., Määttänen, A., Moores, J. E., Poppe, A. R., Carrillo-Sanchez, J. D., Listowski, C., Feb. 2018. Impacts of Cosmic Dust on Planetary Atmospheres and Surfaces. Space Science Reviews 214, 23.
Plessis, S., Carrasco, N., Dobrijevic, M., Pernot, P., May 2012. Production of neutral species in Titan's ionosphere through dissociative recombination of ions. Icarus 219, 254–266.

Rebrion-Rowe, C., Mostefaoui, T., Laubac, S., Mitchell, J. B. A., 2000. The dissociative recombination of hydrocarbon ions. III. Methyl-substituted benzene ring compounds. The Journal of Chemical Physics 113 (8), 3039–3045.
URL http://scitation.aip.org/content/aip/journal/jcp/113/8/10.1063/1.1286974

Shimada, T., Nakashima, N., Izawa, Y., Yamanaka, C., 1993. Laser photolysis of benzene at 158 nm. The Journal of Chemical Physics 98 (11), 9218–9219.
URL http://dx.doi.org/10.1063/1.464431

Shindo, K., Lipsky, S., 1966. Photochemistry of Benzene Vapor at 1849 A. The Journal of Chemical Physics 45 (6), 2292–2297.
URL http://dx.doi.org/10.1063/1.1727923

Sorkhabi, O., Qi, F., Rizvi, A. H., Suits, A. G., 2001. The Ultraviolet Photochemistry of Phenylacetylene and the Enthalpy of Formation of 1,3,5-Hexatriyne. Journal of the American Chemical Society 123 (4), 671–676.
URL http://dx.doi.org/10.1021/ja0017312

Stoecklin, T., Halvick, P., Yu, H.-G., Nyman, G., Ellinger, Y., 2018. On the gas-phase formation of the HCO radical: accurate quantum study of the H+CO radiative association. Monthly Notices of the Royal Astronomical Society 475 (2), 2545–2552.
URL http://dx.doi.org/10.1093/mnras/stx3348

Teolis, B. D., Niemann, H. B., Waite, J. H., Gell, D. A., Perryman, R. S., Kasprzak, W. T., Mandt, K. E., Yelle, R. V., Lee, A. Y., Pelletier, F. J., Miller, G. P., Young, D. T., Bell, J. M., Magee, B. A., Patrick, E. L., Grimes, J., Fletcher, G. G., Vuitton, V., 2015. A Revised Sensitivity Model for Cassini INMS: Results at Titan. Space Science Reviews.

Trevitt, A. J., Goulay, F., Taatjes, C. A., Osborn, D. L., Leone, S. R., 2009. Reactions of the CN Radical with Benzene and Toluene: Product Detection and Low-Temperature Kinetics. The Journal of Physical Chemistry A 114 (4), 1749–1755.
URL http://dx.doi.org/10.1021/jp909633a

Tsai, S.-T., Lin, C.-K., Lee, Y. T., Ni, C.-K., 2000. Dissociation rate of hot benzene. The Journal of Chemical Physics 113 (1), 67–70.
URL http://dx.doi.org/10.1063/1.481774

Tsai, S.-T., Lin, C.-K., Lee, Y. T., Ni, C.-K., 2001. Multimass ion imaging detection: Application to photodissociation. Review of Scientific Instruments 72 (4), 1963–1969.
URL http://dx.doi.org/10.1063/1.1359188

Žabka, J., Polášek, M., Ascenzi, D., Tosi, P., Roithová, J., Schröder, D., Oct. 2009. Reactivity of $C_2H_5^+$ with Benzene: Formation of Ethylbenzenium Ions and Implications for Titan's Ionospheric Chemistry. Journal of Physical Chemistry A 113, 11153–11160.

Vinatier, S., Bézard, B., Fouchet, T., Teanby, N. A., de Kok, R., Irwin, P. G. J., Conrath, B. J., Nixon, C. A., Romani, P. N., Flasar, F. M., Coustenis, A., May 2007. Vertical abundance profiles of hydrocarbons in Titan's atmosphere at 15°S and 80°N retrieved from Cassini/CIRS spectra. Icarus 188,

120–138.

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

Vuitton, V., Lavvas, P., Yelle, R. V., Galand, M., Wellbrock, A., Lewis, G. R., Coates, A. J., Wahlund, J.-E., Nov. 2009. Negative ion chemistry in Titan's upper atmosphere. Planet. Space Sci. 57, 1558–1572.

Vuitton, V., Yelle, R. V., Cui, J., 2008. Formation and distribution of benzene on Titan. J. Geophys. Res. 113 (E5), E05007.
URL http://dx.doi.org/10.1029/2007JE002997

Vuitton, V., Yelle, R. V., Lavvas, P., Klippenstein, S. J., 2012. Rapid Association Reactions at Low Pressure: Impact on the Formation of Hydrocarbons on Titan. ApJ 744 (1), 11.
URL http://stacks.iop.org/0004-637X/744/i=1/a=11

Waite, J. H., Bell, J., Lorenz, R., Achterberg, R., Flasar, F. M., Sep. 2013. A model of variability in Titan's atmospheric structure. Planet. Space Sci. 86, 45–56.

Waite, J. H., Young, D. T., Cravens, T. E., Coates, A. J., Crary, F. J., Magee, B., Westlake, J., May 2007. The Process of Tholin Formation in Titan' Upper Atmosphere. Science 316, 870.

West, N. A., Winner, J. D., Bowersox, R. D. W., North, S. W., 2016. Resolving the energy and temperature dependence of $C_6H_6^*$ collisional relaxation via time-dependent bath temperature measurements. The Journal of Chemical Physics 145 (1), 014308.
URL https://doi.org/10.1063/1.4954896

Westlake, J. H., Waite, J. H., Carrasco, N., Richard, M., Cravens, T., 2014. The role of ion-molecule reactions in the growth of heavy ions in Titan's ionosphere. Journal of Geophysical Research: Space Physics 119 (7), 2014JA020208.
URL http://dx.doi.org/10.1002/2014JA020208

Wilson, E., Atreya, S., 2003. Chemical sources of haze formation in Titan's atmosphere. Planet. Space Sci. 51 (14-15), 1017–1033.

Woon, D. E., 2006. Modeling chemical growth processes in Titan's atmosphere: 1. Theoretical rates for reactions between benzene and the ethynyl (C_2H) and cyano (CN) radicals at low temperature and pressure. Chem. Phys. 331 (1), 67–76.

Yokoyama, A., Zhao, X., Hintsa, E. J., Continetti, R. E., Lee, Y. T., 1990. Molecular beam studies of the photodissociation of benzene at 193 and 248 nm. The Journal of Chemical Physics 92 (7), 4222–4233.
URL http://dx.doi.org/10.1063/1.457780