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REVIEW

Composition and chemistry of Titan's thermosphere and ionosphere

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Titan has long been known to harbour the richest atmospheric chemistry in the Solar System. Until recently, it had been believed that complex hydrocarbons and nitriles were produced through neutral chemistry that would eventually lead to the formation of micrometre sized organic aerosols. However, recent measurements by the Cassini spacecraft are drastically changing our understanding of Titan's chemistry. The Ion and Neutral Mass Spectrometer (INMS) and the Cassini Plasma Spectrometer (CAPS) revealed an extraordinary complex ionospheric composition. INMS detected roughly 50 positive ions with $m/z<100$ and a density higher than $0.1\ \text{cm}^{-3}$. CAPS provided evidence for heavy (up to 350 amu) positively and negatively charged (up to 4000 amu) ions. These observations all indicate that Titan's ionospheric chemistry is incredibly complex and that molecular growth starts in the upper atmosphere rather than at lower altitude. Here, we review the recent progress made on ionospheric chemistry. The presence of heavy neutrals in the upper atmosphere has been inferred as a direct consequence of the presence of complex positive ions. Benzene (C_6H_6) is created by ion chemistry at high altitudes and its main photolysis product, the phenyl radical (C_6H_5), is at the origin of the formation of aromatic species at lower altitude.

Keywords: Titan; atmospheres; composition; ionospheres

1. Introduction

Titan has long been known to harbour the richest atmospheric chemistry in the Solar System that culminates in the generation of thick haze layers. Far ultraviolet solar radiation dissociates the major neutral species (nitrogen and methane) in the upper atmosphere and produces primary species such as HCN, C_2H_2 and C_2H_4 (Yung *et al.* 1984; Wilson & Atreya 2004). The first photochemical models investigating aerosol formation found a maximum production at approximately

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200 km through neutral chemistry involving complex hydrocarbons and nitriles (Lebonnois *et al.* 2002; Wilson & Atreya 2003). However, this result was in disagreement with microphysical models that required a production above 400 km in order to fit the geometric albedo (McKay *et al.* 2001).

It came as a surprise then, if not a shock, that Cassini instruments revealed some very complex molecules in Titan's upper thermosphere and ionosphere. The Ion and Neutral Mass Spectrometer (INMS) and the Cassini Plasma Spectrometer (CAPS) performed the first composition measurements of Titan's upper atmosphere. They revealed an extraordinarily complex ionospheric composition. INMS detected roughly 50 positive ions with $m/z<100$ and a density higher than 0.1 cm^{-3} (Cravens *et al.* 2006; Vuitton *et al.* 2006, 2007). CAPS provided evidence for heavy (up to 350 amu) positively and negatively charged (up to 4000 amu) ions (Coates *et al.* 2007; Waite *et al.* 2007). These species are probably the first intermediates in the formation of even larger molecules. As a consequence, they affect the composition of the bulk atmosphere, the composition and optical properties of the aerosols and the flux of condensable material to the surface.

Based on INMS results, we present here a brief review of the complex chemistry in Titan's thermosphere and ionosphere and further describe its larger role in chemical cycles. In §2, we show how modelling the ion composition constrains the density of minor neutral constituents. The species identified with this technique include a variety of aromatics, (cyano-) polyynes, nitriles, imines and ammonia. We compare the results to the predictions of the most recent photochemical models. We review formation mechanisms and highlight needs for new experimental and theoretical data.

In §3, we focus on benzene distribution and production. We show how the response of the INMS closed-source neutral (CSN) at $m/z=77$ and 78 can be understood as a combination of atmospheric C_6H_6 and a recombination of C_6H_5 radicals with H atoms on the walls of the instrument. We explain that the benzene and phenyl densities required to fit the data are consistent with the results of a state-of-the-art photochemical model. The model shows that benzene is efficiently produced by ion chemistry in the upper atmosphere. However, benzene is quickly photolysed and phenyl radicals (C_6H_5), the main photodissociation products, are approximately three times as abundant as benzene in the upper atmosphere. Loss of benzene occurs primarily through the reaction of phenyl with other radicals, producing more complex aromatic species. Section 4 presents some concluding thoughts.

2. Complex hydrocarbons and nitrogen-bearing species in the ionosphere

(a) A variety of ions and their associated neutrals

Figure 1 shows the average ion spectrum in the 1027–1200 km region measured by INMS during the outbound of the T5 encounter (Vuitton *et al.* 2007). At the closest approach (C/A), the spacecraft was at latitude of 74° N, the solar zenith angle at this location was 127° and the encounter occurred in darkness. The mass spectrum of Titan's ionosphere is quite complex. There are 45 peaks between $m/z=1$ and 99, with a mass periodicity of 12 amu. The detection threshold is approximately 0.3 cm^{-3}.

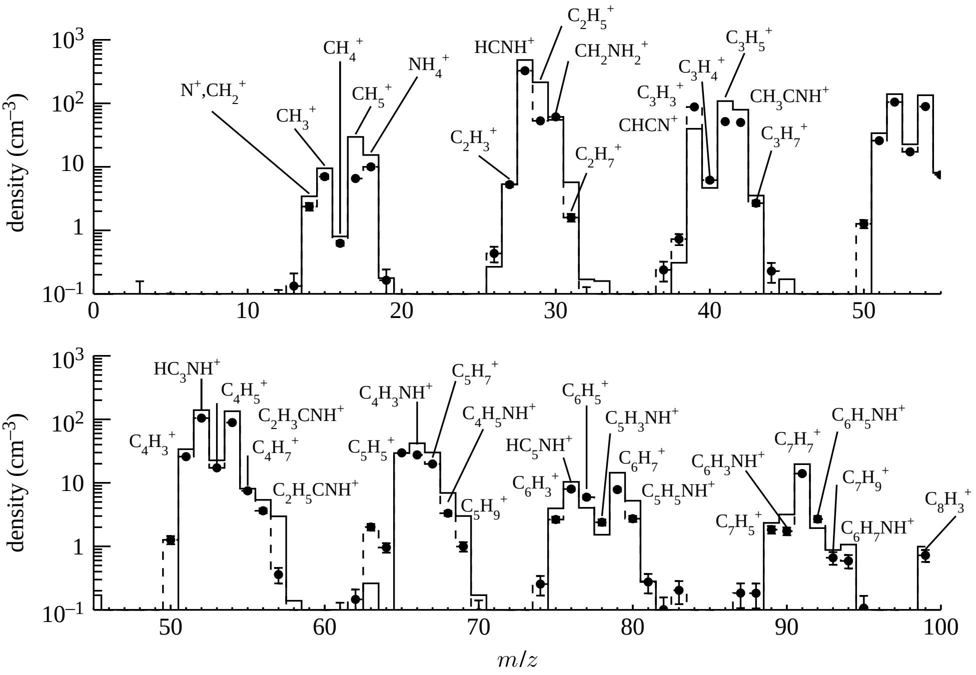

Figure 1. INMS measurements and the ion chemistry model output (from Vuitton *et al.* 2007). The data points show the INMS mass spectrum measured on 16 April 2005 (T5 flyby), averaged between the altitudes of 1027 and 1200 km. The dashed line connects the data points. Error bars are included with the points but are smaller than the symbol size for larger densities. They represent the uncertainty due to counting statistics. A systematic error of approximately 20% due to calibration uncertainties is not included. The solid line represents the modelled spectrum with densities of selected neutral species tuned to reproduce the observations.

Photochemical models (Ip 1990; Keller *et al.* 1992, 1998; Banaszkiewicz *et al.* 2000; Wilson & Atreya 2004) provide some insight into the chemistry and composition of Titan's ionosphere. Solar EUV photons, photoelectrons and Saturnian magnetospheric electrons ionize the major neutral species (nitrogen and methane) to produce N_2^+, N^+, CH_4^+, CH_3^+, CH_2^+ and CH^+ ions (Gan *et al.* 1992). Ion–neutral chemistry converts these ions to higher mass products. As in any reducing environment, ionization flows from species whose parent neutrals have smaller proton affinities (PA) to species whose parent neutrals have larger PA (Fox & Yelle 1997). Because proton exchange reactions drive the chemistry, the most abundant ions are essentially protonated neutrals (closed-shell ions). It follows that the ionospheric composition is a function of the neutral composition weighted by the PA of these neutrals.

With this approach, Vuitton *et al.* (2006, 2007) attributed many ions to nitrogen-bearing species that were not expected by pre-Cassini models. Moreover, by coupling a simple chemical model with the measured densities of ions, they determined the abundance of many minor neutrals, abundance that cannot be retrieved by any other technique. The mole fractions of 6 hydrocarbons and 10 nitrogen-bearing species are listed in table 1. These species include the most complex molecules identified so far on Titan.

Table 1. Neutral mole fractions in Titan's upper atmosphere. (The mole fractions are determined from INMS ion measurements obtained on the Cassini T5 flyby at 74° N and 1100 km. The neutral mole fractions of selected compounds computed by the photochemical models of Wilson & Atreya (2004) and Lavvas *et al.* (2008*a*) are listed as well.)

	Vuitton *et al.* (2007)	Wilson & Atreya (2004)[a]	Lavvas *et al.* (2008*a*)
C_2H_4	1×10^{-3}	1×10^{-3}	5×10^{-4}
C_4H_2	1×10^{-5}	2×10^{-6}	1×10^{-6}
C_6H_2	8×10^{-7}	1×10^{-8}	3×10^{-9}
C_6H_6	3×10^{-6}	1×10^{-10}	6×10^{-10}
C_7H_8	2×10^{-7}	—	—
C_8H_2	2×10^{-7}	5×10^{-11}	—
HCN	2×10^{-4}	9×10^{-4}	9×10^{-4}
CH_3CN	3×10^{-6}	1×10^{-5}	1×10^{-5}
C_2H_3CN	1×10^{-5}	1×10^{-6}	4×10^{-6}
C_2H_5CN	5×10^{-7}	—	2×10^{-8}
HC_3N	4×10^{-5}	2×10^{-6}	4×10^{-6}
HC_5N	1×10^{-6}	—	2×10^{-8}
NH_3	7×10^{-6}	4×10^{-8}	2×10^{-7}
CH_2NH	1×10^{-5}	—	6×10^{-5}
C_2H_5N	3×10^{-7}	—	6×10^{-7}
CH_3NH_2	$<10^{-8}$	—	5×10^{-6}

[a]Values for solar minimum conditions.

(*b*) *Formation pathways of minor neutrals*

Photochemical models expected the presence in Titan's upper atmosphere of some of the species identified by INMS, as shown in table 1. These species include (cyano-) polyynes, HCN, CH_3CN (Yung *et al.* 1984; Toublanc *et al.* 1995; Banaszkiewicz *et al.* 2000) and in more recent models, C_6H_6, C_2H_3CN, NH_3, CH_2NH, CH_3NH_2 and C_2H_5N as well (Wilson & Atreya 2004; Lavvas *et al.* 2008*b*). The predictions of neutral mole fractions by photochemical models can be compared with the mole fractions inferred from INMS ion spectra in order to get some constraints on neutral formation pathways. However, spatial (latitude, longitude) as well as temporal (local time, season, solar cycle) variations can be large and observational as well as chemical uncertainties in both neutral (Hébrard *et al.* 2006, 2007) and ion (Carrasco *et al.* 2007) chemistry are important. As a consequence, it is unrealistic to aim for a 'perfect' agreement between models and observations. However, we consider that any discrepancy of more than one order of magnitude between both datasets has to be interpreted as a misrepresentation of the chemistry of the associated species. In the following, we focus on the recent results obtained for amine and imine species. The profiles resulting from the model of Lavvas *et al.* (2008*a*) are compared with the INMS densities in figure 2.

In the model of Wilson & Atreya (2004), the production of NH_3 in the thermosphere occurs via initial formation of NH_4^+ and its subsequent electron recombination to NH_3. However, this process is slow and the model underestimates

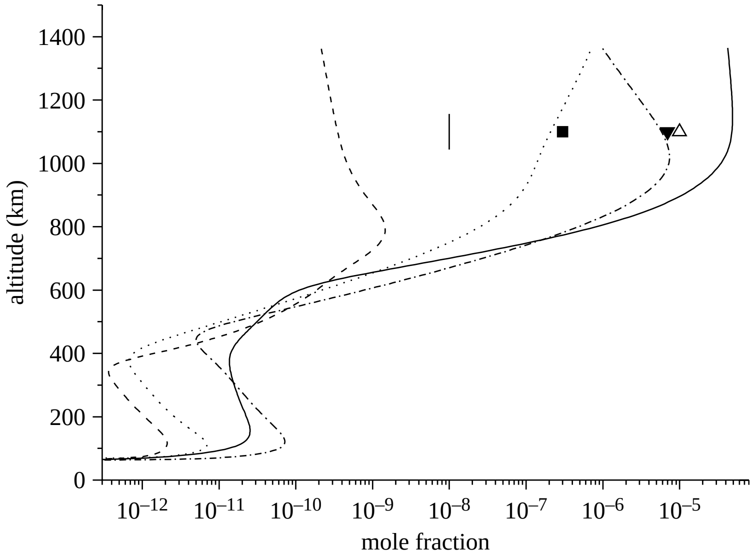

Figure 2. Comparison between retrieved abundances from the INMS T5 ion spectrum at 1100 km (Vuitton *et al.* 2007) and model calculated vertical profiles (Lavvas *et al.* 2008*b*) for CH_2NH (open triangle, solid curve), C_2H_5N (square, dash-dotted curve), CH_3NH_2 (vertical solid line, dashed curve) and NH_3 (filled triangle, dotted curve).

the NH_3 abundance inferred by INMS by two orders of magnitude. Lavvas *et al.* (2008*a*) obtain approximately 10 times as much NH_3 by including production of ethylenimine (C_2H_5N) through

$$N(^2D) + C_2H_6 \rightarrow C_2H_5N + H,$$

followed by its photolysis to NH_3. The corresponding mole fraction of C_2H_5N is 5×10^{-6}, about one order of magnitude larger than the INMS value, suggesting that the production of NH_3 from this pathway is overestimated. However, chemical loss pathways are not considered in the model and it is possible that including them would bring the C_2H_5N density into agreement with the observations. In any case, another source of NH_3 is required. Heterogeneous chemistry at the surface of aerosol particles might be the key.

In both models of Lavvas *et al.* (2008*a*) and Wilson & Atreya (2004), CH_3NH_2 is mainly produced by

$$NH_2 + CH_3 + M \rightarrow CH_3NH_2 + M.$$

The associated mole fraction at 1100 km is 3×10^{-10} and 3×10^{-11} in good agreement with the upper limit of 10^{-8} inferred from the INMS spectrum.

The evolution of CH_2NH has recently been followed in the photochemical model of Lavvas *et al.* (2008*a*) for the first time. In these calculations, CH_2NH is mainly produced by

$$N(^2D) + CH_4 \rightarrow CH_2NH + H$$

and

$$CH_3NH_2 + h\nu \rightarrow CH_2NH + 2H.$$

The calculated abundance is only slightly larger (by a factor of a few) than the one retrieved by the INMS measurements (Vuitton *et al.* 2007), suggesting that the production processes for CH_2NH are now fairly well understood. However,

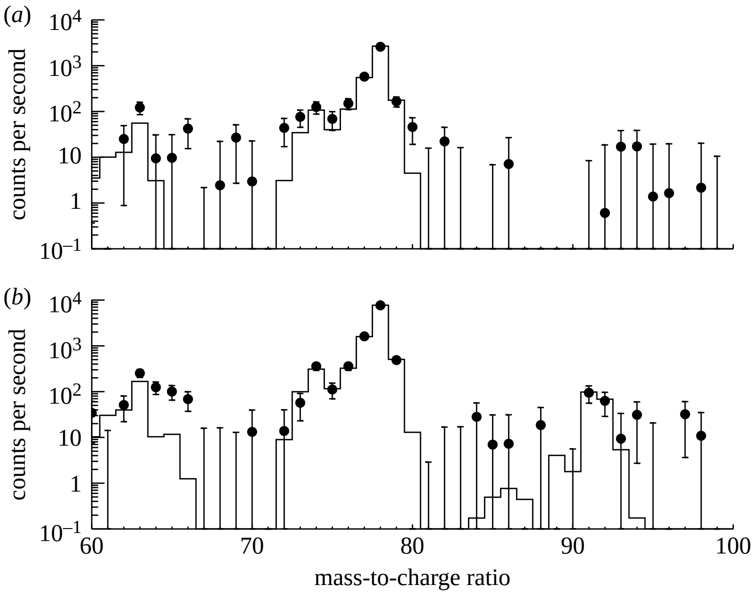

Figure 3. Data points represent a CSN spectrum in the m/z=60–99 region obtained during T16 and averaged over the 960–980 km range (from Vuitton *et al.* 2008). The solid line is a model for the benzene and toluene spectra based on the INMS calibration. (*a*) Inbound leg. (*b*) Outbound leg.

kinetic and spectroscopic data about the (photo-) chemical loss processes of CH_2NH are lacking and all reaction rates had to be estimated. In order to come to a clear conclusion, new laboratory measurements regarding the reactivity of CH_2NH are needed.

3. Distribution and formation of benzene

(*a*) *Benzene distribution*

Figure 3*a*,*b* shows low altitudes INMS CSN spectra from the inbound and outbound legs of T16 (Vuitton *et al.* 2008). The spectra show a clear signal in the m/z=62–63 and m/z=73–79 regions that is interpreted as evidence for benzene based on the INMS calibration (Cui *et al.* submitted). This attribution is supported by a simple diffusive equilibrium model for a species of mass 78 amu, which provides an excellent fit to the m/z=78 inbound data from 1350 to 950 km. This model assumes a constant temperature determined from analysis of the N_2 density distribution (Müller-Wodarg *et al.* 2008). In addition to the benzene features, the outbound T16 spectrum, shown in figure 3*b*, has sizeable peaks at m/z=91–92. The molecular weight suggests the chemical formula is C_7H_8 and the feature is well fit by an INMS calibration spectrum for toluene.

The benzene and toluene signals peak approximately 20 s after C/A rather than at C/A (Vuitton *et al.* 2008). This time dependence is quite peculiar. The densities for all species in Titan's upper atmosphere decrease exponentially with altitude and the temporal response of the INMS is extremely fast (tens of microseconds), implying that the measured signal should increase with time up

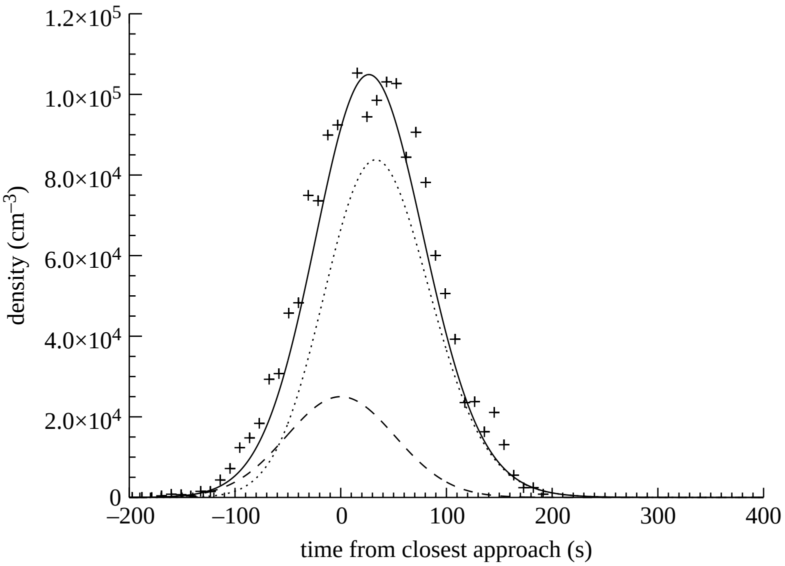

Figure 4. Time-dependence model fit for benzene (m/z=78) (from Vuitton *et al.* 2008). Data points represent the density in the closed source obtained during T16 from −200 to 400 s around the closest approach. The dotted line corresponds to the recombination of radicals on the walls of the closed source. The dashed line represents the direct gaseous source. The solid line is the sum of the dotted and dashed lines and represents the best fit of the data based on the surface chemistry model.

to C/A and decrease thereafter. For example, measurements of ethane (C_2H_6) at m/z=30 during T16 have a maximum at C/A and are fairly symmetric about this time.

The anomalous time behaviour of the signals is attributed to an internal process in the instrument rather than a property of the atmosphere. It is unlikely that the asymmetry around C/A is caused by large horizontal variations in the atmosphere. First, there is no evidence that the time shift varies from pass to pass, as would be expected if it were due to horizontal variations. Second, horizontal variations would have to be extremely large to cause the observed asymmetry, inconsistent with the observed density variations between passes.

The CSN operational mode uses an enhancement chamber in front of the mass spectrometer that concentrates atmospheric molecules resulting in higher sensitivity (Waite *et al.* 2005). Radical recombination on chamber walls is a common phenomenon in spaceflight mass spectrometers (Hedin *et al.* 1973; Kasprzak *et al.* 1980). Photochemical calculations show that H, CH_3 and C_6H_5 radicals have a large abundance in Titan's upper atmosphere and it follows that benzene and toluene are produced partly by radical recombination on the walls of the INMS closed source. This hypothesis explains the presence of both C_6H_6 and C_7H_8 because these are the products produced by reaction of the main radicals in the upper atmosphere. It explains the time delay observed for these species because the surface chemistry should require a significant amount of time.

The results of the empirical surface chemistry model for the production of C_6H_6 described in Vuitton *et al.* (2008) are shown in figure 4. The model gives a correlation of the gas density in the chamber, i.e. the density measured by the INMS detection system, with the ambient atmospheric density of benzene. The benzene density in the closed-source chamber is determined by the instantaneous balance between outflow from the entrance aperture to the chamber and the combination of the flow of benzene into the chamber from Titan's atmosphere and desorption of benzene from the chamber walls. The desorption rate of benzene is assumed to be proportional to the triple product of phenyl surface density, atomic hydrogen surface density and the inverse of an empirical time constant. The C_6H_5 and C_6H_6 densities are adjusted to fit the data, but the H and CH_3 are held fixed at the values predicted by a photochemical model for the atmosphere described in §3*b*. The time constant corresponds to the rate of diffusion over the surface of the chamber and the intrinsic reaction rate for the adsorbed C_6H_5 and H. However, knowledge of surface chemistry for these radicals is too uncertain to permit determination of the chemical time constants from first principles, so they are treated as empirical parameters determined through fits of the model to the T16 data.

A chemical time constant of 15 s for $H+C_6H_5$ provides the best fit to the data. The required direct gaseous source of C_6H_6, shown as the dashed line in figure 4, corresponds to a density of $2.5\times10^4\ \mathrm{cm}^{-3}$ or a mole fraction of 1.3×10^{-6} at an altitude of 950 km. The signal-to-noise ratio of the toluene signal is too low to meaningfully constrain its density. However, the time constant that we determined for $H+C_6H_5$ is adequate to fit the signal at $m/z=92$, suggesting that toluene is mostly produced by surface chemistry as well.

The INMS is really measuring the sum of benzene and phenyl and the density of phenyl in Titan's atmosphere is roughly trice as much as that of benzene. The wall reaction hypothesis helps to reconcile the photochemical models with the measured C_6H_6 signal because, as discussed in §3*b*, the phenyl abundance in the upper atmosphere is predicted to be larger than the benzene abundance. The required production rate of benzene is significantly reduced compared with what is required if it were to be assumed that the signal were due to benzene alone.

(*b*) *Benzene formation*

Photochemical models (Wilson *et al.* 2003; Wilson & Atreya 2004; Lebonnois 2005; Lavvas *et al.* 2008*a*) find that the primary benzene production channel is the following three-body reaction:

$$C_3H_3 + C_3H_3 + M \rightarrow C_6H_6 + M.$$

This reaction can account for the observed benzene density of a few ppm in the lower stratosphere (Coustenis *et al.* 2007), but is extremely inefficient at the low densities in Titan's thermosphere. As a consequence, the models of Wilson & Atreya (2004) and Lavvas *et al.* (2008*a*) fail to predict the large benzene mole fractions observed in the thermosphere. In the model of Lebonnois (2005), benzene reaches a thermospheric abundance similar to that measured by INMS. However, this is an artefact caused by the lack of efficient chemical loss for C_6H_5, the main photodissociation product of benzene. As a consequence, the most probable fate of C_6H_5 is to re-form benzene by reaction with H atoms and benzene accumulates in the atmosphere. Clearly, the fact that the abundance of benzene in the thermosphere is larger than in the stratosphere indicates that an efficient chemical pathway to synthesize benzene at high altitude is required.

Laboratory simulations of Titan's chemistry can provide clues on benzene formation pathways. Imanaka & Smith (2007) investigated the formation of complex species from a N_2/CH_4 gas mixture as a function of irradiation wavelengths from 50 to 150 nm. The formation of benzene is observed at wavelengths less than 80 nm, which corresponds to the photoionization threshold of N_2. This indicates that the benzene in this system is probably synthesized by ion chemistry. Benzene has also been observed on Jupiter (Kim *et al.* 1985). Under high-latitude conditions where precipitation of energetic electrons is important, benzene is produced through successive ion–neutral reactions followed by electron recombination of $C_6H_7^+$ (Wong *et al.* 2003). In their study dedicated to the mechanisms for the formation of benzene in the atmosphere of Titan, Wilson *et al.* (2003) also considered ion–neutral reactions and found that electron recombination of $C_6H_7^+$ controls the benzene production in the upper atmosphere. However, the production rate is too low to account for the observed benzene abundance in the thermosphere (Wilson & Atreya 2004).

After INMS revealed the richness of Titan's ion composition (Cravens *et al.* 2006; Vuitton *et al.* 2006), and in particular showed that protonated benzene, i.e. $C_6H_7^+$, is a significant ion (Vuitton *et al.* 2007), Vuitton *et al.* (2008) reinvestigated Titan's benzene chemistry. They first calculated the benzene production rate in the upper atmosphere with a dayside ionospheric model and used it as an input in a photochemical model for hydrocarbon chemistry. They extended considerably the chemical network considered in previous ion and neutral chemistry models and used density, temperature and eddy diffusion profiles recently constrained by the Cassini observations (Müller-Wodarg *et al.* 2008; Yelle *et al.* 2008).

On the dayside, N_2 and CH_4 are rapidly photoionized and $C_6H_7^+$ is efficiently produced by ion chemistry reactions (Waite *et al.* 2007; Vuitton *et al.* 2008). $C_6H_7^+$ is mostly produced by

$$C_6H_5^+ + C_2H_4 \rightarrow C_6H_7^+ + C_2H_2$$

and

$$C_6H_5^+ + H_2 \rightarrow C_6H_7^+ + h\nu.$$

$C_6H_5^+$ comes primarily from

$$C_4H_2^+ + C_2H_4 \rightarrow C_6H_5^+ + H.$$

$C_4H_2^+$ at $m/z = 50$ is a major ion in the INMS spectrum but none of the ion–molecule reactions present in the model efficiently produce $C_4H_2^+$. Fragmentation of heavier ions could possibly produce $C_4H_2^+$, but the lack of experimental constraints precludes from including such reactions in the model. As a consequence, the $C_4H_2^+$ production rate is scaled in order to get a forced agreement between observed and calculated $C_4H_2^+$ densities. Benzene is finally produced by electron recombination of $C_6H_7^+$:

$$C_6H_7^+ + e^- \rightarrow C_6H_6 + H.$$

The globally averaged column-integrated production rate of benzene from ion–neutral chemistry is approximately $10^7\ \mathrm{cm^{-2}\,s^{-1}}$, referred to the surface. This calculated ionospheric production rate is sufficient to produce large benzene densities in Titan's upper atmosphere, of the same order as those measured by the INMS.

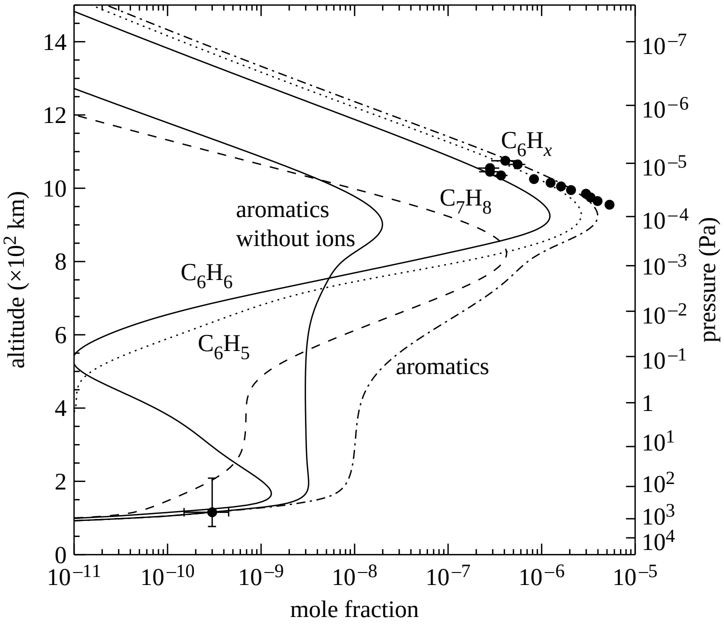

Figure 5. Modelled neutral vertical profiles and comparison with observations (from Vuitton *et al.* 2008). C_6H_x refers to a combination of the benzene and phenyl abundances, as explained in the text. The observed C_6H_6 mole fraction in the stratosphere was retrieved by CIRS at 15° S (Coustenis *et al.* 2007). Data points represent averages over 12 Titan passes of the C_6H_6 density measured by INMS. Error bars include statistic uncertainties but not calibration uncertainties. 'Aromatics' refers to heavy aromatic species that are not tracked in the model.

Photolysis, the main loss for benzene, peaks at approximately 900 km (Vuitton *et al.* 2008). As shown in figure 5, the density of phenyl, the main photodissociation product, is roughly thrice as much as that of benzene, consistent with the INMS observations. Once formed, C_6H_5 diffuses downward and is involved in reactions with CH_3, C_2H_3 and C_2H_5 radicals that are responsible for the rapid decrease in benzene mole fraction below 900 km shown in figure 5. These radical reactions, which had never been considered before, are responsible for the conversion of benzene to heavier aromatics in the 350–800 km region, with a total production rate of approximately $10^7\,\mathrm{cm^{-2}\,s^{-1}}$. Benzene photolysis involves a transient benzene that, as the pressure increases, becomes efficiently deactivated by collisions with N_2 to form again benzene:

$$\begin{array}{ccc} C_6H_6 + h\nu \rightarrow & C_6H_6(S_0^*) & \rightarrow C_6H_5 + H. \\ & \downarrow N_2 & \\ & C_6H_6 & \end{array}$$

Its stabilization lifetime becomes comparable with its dissociation lifetime at a density of $10^{15}\,\mathrm{cm^{-3}}$ (approx. 350 km). Thus, in the lower atmosphere, stabilization of the transient state is a crucial process. Moreover, at 350 km, the recombination of H and C_6H_5 becomes equal to the photolysis rate and destruction of C_6H_6 by photolysis stops. Below 300 km, C_6H_6 is created by recombination of C_2H_3 and C_4H_3, and C_3H_3, producing a low-altitude peak in C_6H_6 density. These reactions contribute to most of the benzene formation via neutral chemistry, with a total integrated production rate of approximately $4\times10^6\,\mathrm{cm^{-2}\,s^{-1}}$. The mole fraction in the lower stratosphere is approximately 30 ppb, as shown in figure 5, which is consistent with that inferred from mid-IR spectroscopy (CIRS).

4. Conclusions

(i) The INMS provides for the first time some information about the chemical composition of Titan's upper atmosphere. The inversion of the ion spectra reveals the presence of the most complex neutrals ever detected on Titan: aromatics, (cyano-) polyynes, nitriles, ammonia and one imine. Modelling of the time dependence along the spacecraft trajectory of the CSN data allows the retrieval of the density of the phenyl radical (C_6H_5) and its parent molecule, benzene (C_6H_6).

(ii) Benzene is efficiently produced in the upper atmosphere via ion–neutral reactions followed by electron recombination of $C_6H_7^+$. The globally integrated production rate of benzene in the ionosphere is approximately $10^7\,\mathrm{cm^{-2}\,s^{-1}}$, of the same order of magnitude as the neutral production rate of approximately $4\times10^6\,\mathrm{cm^{-2}\,s^{-1}}$. This production rate is sufficient to reproduce the benzene mole fraction at 950 km of 1.3×10^{-6} measured by INMS.

(iii) Following benzene photolysis, the phenyl radical is quickly converted to heavier aromatics through reactions with other radicals. The total production rate of aromatics is approximately $10^7\,\mathrm{cm^{-2}\,s^{-1}}$ or $10^{-15}\,\mathrm{g\,cm^{-2}\,s^{-1}}$ and the total benzene condensation rate is approximately 10 per cent of this value. If such a deposition rate has been maintained over the age of the Solar System, an average layer of 3 m of solid aromatic material must be present on the surface of Titan, modifying its appearance and composition. However, according to the model of the history of Titan's interior from Tobie *et al.* (2006), CH_4 outgassing may have been episodic and, as a consequence, the total organic production rate may be lower.

(iv) By analysing the optical properties of the detached haze layer observed at 520 km in Titan's mesosphere, Lavvas *et al.* (submitted) retrieve a mass flux of haze particles (approx. $2\times10^{-14}\,\mathrm{g\,cm^{-2}\,s^{-1}}$) approximately equal to the mass flux required to explain the main haze layer. This is the first quantitative evidence that thermospheric chemistry is the main source of haze on Titan. This recent progress opened some questions that are not yet answered. As an example: can ionospheric chemistry be quantitatively linked to the production of the haze? How? Models need to implement these new data, and answer this.

We want to emphasize that there is a need for identification of the products of $C_6H_7^+ + e^-$ as well as rates and products for ion reactions involving more complex hydrocarbons and nitrogen-bearing species. Low pressure and temperature rates for reactions of H, CH_3, C_2H_3, C_3H_3 and C_6H_5 and discrimination of the different isomers in the C_3H_3 recombination reaction are required. Products branching ratios at shorter wavelength for benzene and other aromatics as well as studies of the reactivity of the transient state involved in benzene photodissociation would also be very useful. Finally, the production of $C_4H_2^+$, which is not at all understood, and forced in order to reproduce this ion abundance, is an essential open question, given the importance of this ion in the ionospheric production pathway of benzene.

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