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# On the amount of heavy molecular ions in Titan's ionosphere

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## ABSTRACT

We present observational evidence that the ionosphere of Titan below an altitude of 1150 km is a significant source of heavy (>100 amu) molecular organic species. This study is based on measurements by five instruments (RPWS/LP, RPWS/E, INMS, CAPS/ELS, CAPS/IBS) onboard the Cassini spacecraft during three flybys (T17, T18, T32) of Titan. The ionospheric peaks encountered at altitudes of 950–1300 km had densities in the range 900–3000 cm<sup>-3</sup>. Below these peaks the number densities of heavy positively charged ions reached 100–2000 cm<sup>-3</sup> and approached 50–70% of the total ionospheric density with an increasing trend toward lowest measured altitudes. Simultaneously measured negatively charged ion densities were in the range 50–150 cm<sup>-3</sup>. These results imply that ~10<sup>5</sup>–10<sup>6</sup> heavy positively charged ions/m<sup>3</sup>/s are continuously recombining into heavy neutrals and supply the atmosphere of Titan. The ionosphere may in this way produce 0.1–1 Mt/yr of heavy organic compounds and is therefore a sizable source for aerosol formation. We also predict that Titan's ionosphere is dominated by heavy (> 100 amu) molecular ions below 950 km.

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## 1. Introduction

Titan has a dense atmosphere principally consisting of molecular nitrogen and 2–3% methane, with a rich mixture of hydrocarbon and nitrile trace compounds (e.g., Kunde et al., 1981; Waite et al., 2005; Yelle et al., 2006; Coustenis et al., 2007). The complex hydrocarbon–nitrile chemistry is the most likely source for the optically thick haze layers of 0.5–3  $\mu$ m aerosol particles (e.g., Rages et al., 1983; West et al., 1983; McKay et al., 2001). The haze analogues produced in laboratory experiments trying to resemble Titan haze conditions are often referred to as tholins (Sagan and Khare, 1979). However, the details of aerosol formation from simpler building blocks have so far not been monitored. Recent *in-situ* observations by instruments onboard the Cassini

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spacecraft indicate that complex ion-molecular reactions in the ionosphere can play an important role in aerosol formation (Waite et al., 2007).

Titan's atmosphere becomes partially ionised by the action of solar EUV and X-ray radiation, energetic plasma in Saturn's magnetosphere as well as cosmic radiation, which produces an ionosphere (e.g., Bird et al., 1997; Wahlund et al., 2005; Cravens et al., 2005, in press; Ågren et al., 2007; Kliore et al., 2008; López-Moreno et al., 2008). The dominant ionospheric peak occurs at altitudes between 950 and 1300 km and is associated with plasma number densities between 2500 and 3500 cm<sup>-3</sup> on the dayside and  $400-1000 \text{ cm}^{-3}$  on the nightside (Ågren et al., submitted for publication). Other prominent ionospheric peaks have been identified at 500-600 km altitude (Kliore et al., 2008; Cravens et al., 2008) and at 60-80 km altitude (López-Moreno et al., 2008), and mainly reflect the different ionisation sources acting on Titan's atmosphere at different altitudes. The ionisation levels remain high  $(100-1000 \,\mathrm{cm}^{-3})$  throughout the atmosphere where measurements have been made. The altitude region between 800 and 1500 km is the most electrical conductive region with perpendicular to the magnetic field conductivities (Hall and Pedersen) between  $10^{-3}$  and  $10^{-1}$  S/m (Rosenqvist et al., in press). In this region further energy deposition by Joule heating can take place.

Ion and electron spectrometer instruments on Cassini have carried out observations of heavy organic ions above an altitude of 950 km (e.g., Cravens et al., 2006; Coates et al., 2007; Vuitton et al., 2007; Waite et al., 2007; Crary et al., submitted for publication). The ionosphere was largely dominated by HCNH<sup>+</sup> and  $C_2H_5^+$  ions, while heavier ions like  $C_5H_5NH^+$  or  $C_6H_7^+$  become more abundant toward lower measured altitudes (e.g., Cravens et al., 2006; Vuitton et al., 2007). A most surprising discovery was the widespread appearance of heavy negative ions up to  $10,000 \operatorname{amu}/q$  below an altitude of  $1150 \operatorname{km}$  (Coates et al., 2007), which was interpreted in terms of negative ion derivates of polyaromatic hydrocarbons (PAH), polyenes and higher order nitriles like cyano-aromatics up to 40,000-50,000 amu. The negative ion number densities were estimated to range between 1 and  $200 \text{ cm}^{-3}$  in those observations. Vuitton et al. (submitted for publication) have shown that dissociative electron attachment to neutral molecules, associative detachment and proton transfer reactions dominate the production and loss of negative ions. A corresponding detection of widespread appearance of heavy positive ions up to at least 350 amu (Waite et al., 2007; Crary et al., submitted for publication) indicated the simultaneous occurrence of positive and negative ion chemistry.

Here we present observations from three flybys (T17, T18, T32) of Titan by the Cassini spacecraft in an effort to determine simultaneously the number densities of electrons, light and heavy positively charged ions, as well as negatively charged ions and their variations with altitude. This requires the comparison of five instruments dataset; the Radio and Plasma Wave Science Langmuir Probe (RPWS/LP) and electric field sensors (RPWS/E), the Ion and Neutral Mass Spectrometer (INMS), and the Cassini Plasma Spectrometer's Ion Beam Sensor (CAPS/IBS) and its Electron Spectrometer (CAPS/ELS). The particular three flybys were selected because detailed calibrated data from all the instruments above happened to be available simultaneously.

Section 2 describes the instrument methods used and derived physical parameters. Section 3.1 presents the flyby characteristics and overview data set along with a discussion of possible error sources. Section 3.2 presents the altitude profiles of the number densities of different compound groups. A discussion is presented in Section 4 before concluding in Section 5.

# 2. Measurement principles and data reduction

#### 2.1. Electron number density from upper hybrid emissions

A full description of the RPWS instruments can be found in Gurnett et al. (2004). The RPWS investigation employs several different methods to estimate the electron number density ( $n_e$ ). One method makes use of the upper hybrid emission line which peaks in electric spectra at the frequency  $f_{UH} = \sqrt{f_{ge}^2 + f_{pe}^2}$ , where  $f_{ge}$  is the electron gyro-frequency and  $f_{pe}$  is the electron plasma frequency. Knowing the magnetic field strength gives  $n_e$ . For most of the measurements in Titan's ionosphere  $f_{ge}^2 \ll f_{pe}^2$ . Another method makes use of Langmuir probe voltage sweeps as described below.

# 2.2. Langmuir probe (RPWS/LP)

The spherical 5 cm diameter Langmuir probe (LP) sensor is situated 1.5 m from the Cassini spacecraft main body. It samples

the total electrical current from the plasma by making 512 or 1024 points voltage sweeps ( $\pm 4$  or  $\pm 32$  V) usually every 24 s during Titan flybys. This method determines several thermal plasma parameters of importance for characterizing the properties of Titan's plasma environment, of which the electron and ion number densities ( $n_e$  and  $n_i$ ) are relevant for this study. The voltage sweep also determines the spacecraft potential ( $U_{SC}$ ), which is calculated from the spacecraft potential measured at the probe ( $U_1$  or floating potential) according to ( $U_{SC}-U_1$ ) =  $c \exp(-d_{LP}/\lambda_D)$ , where  $d_{LP} = 1.5$  m is the distance of the probe to the spacecraft main body surface,  $\lambda_D$  the Debye length of the surrounding plasma and  $c \approx 5/6$  is a constant.

The electron parameter results are based on a theoretical fit to the LP voltage sweeps taking into account up to three electron populations (e.g., Mott-Smith and Langmuir, 1926; Medicus, 1962; Whipple Jr., 1965; Hoegy and Brace, 1999). One electron component corresponds to the spacecraft photoelectrons (of no interest here), while the others give the values of the core magnetospheric and ionospheric electron populations. It is therefore most often possible to correct for the photoelectron contamination from the spacecraft. The electron current to the probe in orbit motion limited (OML) approximation for one electron population, for positive voltages, can be written

$$I_e = I_{e0}(1 - \chi_e)$$

where

$$I_{e0} = A_{LP} n_e q_e \sqrt{\frac{k_B T_e}{2\pi m_e}}$$

is the random current,  $A_{LP}$  is the probe area, and

$$\chi_e = \frac{q_e(U_{bias} + U_1)}{k_B T_e}$$

where  $U_{bias}$  is the applied bias voltage and  $U_1$  is the floating potential (in case of spacecraft photoelectrons), or the characteristic potential of the electron population in the plasma (in case of ambient plasma electrons). For negative voltages,  $(U_{bias}+U_1)<0$  the electron temperature is estimated from the exponential part as

$$I_e = I_{e0} \exp(-\chi_e).$$

In order to achieve a better time resolution the RPWS/LP also samples continuous 20 samples/s density data in between the 24 s voltage sweeps, i.e., the electron current sampled at a constant bias voltage of +4V (or +10V). The sampled 20 Hz current is proportional to

$$n_e \sqrt{T_e} \left( 1 + \frac{1}{T_e} (U_{SC} + U_{bias}) \right)$$

and can therefore also be affected by the electron temperature and spacecraft potential. The 20 Hz "density" dc level has in this study been adjusted to the voltage sweep derived electron number density. Variations in this parameter in between the sweep derived electron number densities should therefore be interpreted as true electron density variations, since  $T_e$  and  $U_{SC}$ vary slowly in most cases.

The negative voltage branch of the sweeps gives information on ion drift speed (e.g., Fahleson et al., 1974), ion number density, average ion mass and integrated solar EUV intensity (photoelectrons emitted from the probe). The ion contribution to the current is given by

$$I_i = I_{i0}(1 - \chi_i)$$

where the random current

$$I_{i0}\approx -A_{LP}n_iq_i\frac{|v_i|}{4}$$

and

$$\chi_i \approx \frac{q_i(U_{bias} + U_1)}{m_i v_i^2/2e}$$

are assumed to be dominated by the ion ram flux to the probe. In the case of Titan's ionosphere, the ion number density is estimated from the ram flux assuming the spacecraft moves through the plasma at the spacecraft speed ( $\approx 6 \text{ km/s}$ ). The thermal component ( $k_B T_i$ ) is expected to be small in Titan's ionospheric plasma. A possible finite thermal component will have the effect of increasing the derived ion number density in the analysis, since it gives an additional current contribution. The photoelectron current emitted from the probe is a constant for negative voltages ( $I_{ph,0}$ ) and is, like the ion current, exponentially decreasing for positive voltages ( $U_{bias}+U_1$ )>0 as (Grard, 1973)

$$I_{ph} = I_{ph,0} \left( 1 + \frac{e(U_{bias} + U_1)}{k_B T_{ph}} \right) \exp\left(-\frac{e(U_{bias} + U_1)}{k_B T_{ph}}\right).$$

Error ranges depend on sweep signal strength and type of parameter estimated. The electron number density and spacecraft floating potential estimates have inherent errors below 10% in Titan's ionosphere. The ion flux, from which the ion number density is calculated, has similar inherent errors. The possible effects of current contributions from impacts of energetic radiation belt particles and associated secondary electrons (Eriksson and Wahlund, 2006) are not included in the analysis, as such anomalously enhanced probe currents have so far only been detected in the region  $6-15R_{\rm S}$  from Saturn.

#### 2.3. Ion neutral mass spectrometer (INMS)

The INMS measures ion mass spectra in its open source ion mode (OSI), where the positively charged ions enter the aperture and are deflected by an electrostatic switch lens to a radio frequency quadrupole mass-analyser that selects ions according to the mass-to-charge ratio and then detected by a secondary electron multiplier pulse counter [e.g., Waite et al., 2004]. A full mass spectrum is sampled each 10 s. The count rate is proportional to the incident ion flux, and the instrument covers mass-to-charge ratio values up to 100 amu/q with 20–50% accuracy. The OSI field-of-view of  $3^{\circ} \times 3^{\circ}$  is pointed toward the nominal ion ram flow direction caused by the spacecraft motion during a flyby. The OSI measures positively charged ions with energies appropriate for an assumed compensation speed equal to the spacecraft speed ( $\approx 6$  km/s around Titan).

The INMS instrument is sensitive to deviations of the incident plasma flow from the centre of the instrument's field-of-view. Orthogonal flow velocity vector deviations (due to ion drift motion in Titan's frame of reference) of more than 0.3 km/s will therefore shift the incident flow away for the instruments field-ofview and affect count rates accordingly. The count rate will likewise be affected by the incident energy change of the ions due to plasma convection and/or spacecraft charging near the INMS instrument. At altitudes above the main ionospheric peak (>1200 km altitude) care must therefore be taken and a compensation algorithm applied to the data. We have here only compensated for the spacecraft potential by using the RPWS/LP estimates of this parameter, while finite ion drift speed effects are not compensated for here. However, ion drift speed effects are small below the ionospheric peak (<1200 km altitude) due to slowdown by frequent collisions with neutral atmosphere particles (Cravens et al., in press) and therefore should not affect the conclusions presented in this study (c.f., Section 3.2).

#### 2.4. Ion beam spectrometer (CAPS/IBS)

The ion beam spectrometer measures the flux of positively charged ions versus their kinetic energy per charge in three wide  $(150^{\circ})$  and narrow  $(1.4^{\circ})$  angular sensors tilted  $30^{\circ}$  with respect to each other (Young et al., 2004). The sensors actuate forth and back every 52 s by 28° in order to cover a larger pitch-angle range, and this is therefore the time resolution of the presented IBS data. The energy range covers 3–207 eV in 255 steps, and is sampled every 2 s.

Maxwellian distributions for singly charged species are fitted to the data, which depend on the direction of ion ram flow and the measured flux of each species. The mass resolution  $(m_i | \Delta m_i)$  is a function of the ratio of the ram speed to the thermal ion speed. From the fits to the IBS spectrogram, both the total ion number density  $(n_{i,tot})$  and the ion number density for ions in the mass range 100–350 amu ( $n_{i,100}$ ) can be calculated. The CAPS/IBS measurements select energy sweeps and sensors with peak fluxes, and therefore ensure the sampling occurs when the instrument is looking into the ram flow direction. The CAPS/IBS data is still sensitive to deviations of incident ion speeds (energies) from the assumed spacecraft ram speed, as well as the local spacecraft potential where the CAPS/IBS instrument is situated. Comparing the mass spectrum with the INMS mass spectrum, and noting that these two instruments are situated close to each other on the spacecraft, one can compensate for the latter effect (Crary et al., submitted for publication). As will be evident in the data presentation below, the CAPS/IBS and the RPWS/LP ion data estimate the same total ion flux values to within only 20-30% below an altitude of 1300 km (c.f., Section 3.2).

## 2.5. Electron spectrometer (CAPS/ELS)

The CAPS/ELS instrument is a "top-hat" electrostatic analyser with energy per charge (E/q) range for negatively charged electrons and ions of 0.6-26,000 eV/q. The Cassini spacecraft moves through Titan's ionosphere with a supersonic speed  $(\approx 6 \text{ km/s})$ , and a negatively charged ion population will therefore appear as a narrow angle beam in the CAPS/ELS frame of reference. The CAPS/ELS field-of-view of 5° is swept periodically by an actuator across the spacecraft ram direction each 48 s. Enhanced periodic peaks in the CAPS/ELS count rates therefore identify the regions where negative ions appear.

The number densities of negatively charged ions for the specific events presented here have already been estimated to be in the range  $50-150 \text{ cm}^{-3}$  (Coates et al., 2007), and we here only display the CAPS/ELS count rates within three different selected energy ranges (0.58-9.89 eV, 11.64-91.76 eV and 0.1-26 keV). The nominal detector energy level does not give the ion energy. Rather, the higher the detected energy ranges correspond to ions like CN<sup>-</sup> and other cyano-derivates, while the highest energy range corresponds to higher order nitriles, PAHs and cyano-aromatics (see further Coates et al., 2007; Vuitton et al., submitted for publication).

## 3. Observations

## 3.1. Flyby characteristics

Figs. 1–3 give an observational overview of the three Titan flybys T17, T18 and T32 presented here. Flyby T17 occurred at low



**Fig. 1.** The plasma number densities (panel a), CAPS/ELS count rates (panel b) and the RPWS/LP spacecraft potential (panel c) during the Titan T17 flyby. Plasma number densities are the electron number density by RPWS/LP (blue) and RPWS/E (black), the total ion number density by two CAPS/IBS sensors (magenta stars) and INMS (green, < 100 amu) as well as RPWS/LP (magenta circles), the heavy (>100 amu) ion number densities by CAPS/IBS (red). The CAPS/IBS pair wise values correspond to the values from the two different sensors. The RPWS/LP data are both sweep data (blue stars) and the 20 samples/s constant bias data (adjusted to the sweep data, blue line). The CAPS/LS count rates are for the energy ranges 0.58–9.89 eV (blue), 11.64–91.76 eV (green) and 0.1–26 keV (red). Periodic peaks indicate presence of negative ions, and higher energy data correspond to larger negative ion mass. See text for further information.

latitudes and on the wake-side of Saturn's co-rotating plasma flow, while T18 and T32 occurred over the northern polar regions of Titan. The ionospheric peaks were on the dayside (SZA $\approx$ 41– 53°) during T17, while the other two presented flybys had the ionospheric peaks in the illumination terminator region (SZA $\approx$ 81–89°) except for the inbound of T32, which was on the nightside (SZA $\approx$ 127°, compare with Ågren et al., submitted for publication). The inbound of T32 was also special in the sense that it occurred most probably when Titan was situated in Saturn's magnetosheath (Bertucci et al., 2008) with a very large dynamic pressure applied on Titan's ionosphere (Garnier et al., submitted for publication). The ionospheric peak electron densities measured by RPWS/LP ranged from 900 cm<sup>-3</sup> (inbound T18) to 3000 cm<sup>-3</sup> (T17). The ionosphere conditions therefore varied considerably in many respects during the presented events.

The estimated ionospheric number densities by the various techniques used here is presented in panel a (Figs. 1–3). The total ion number densities measured by two of the three CAPS/IBS sensors (magenta stars), the RPWS/LP electron number densities (blue) and the RPWS upper hybrid derived electron number densities (black) agree within 10–20%, except near 20:20 UT on T17 and near 19:02 UT on T18 and near 17:50 UT during T32 where the CAPS/IBS total ion number densities are systematically up to a factor 2 above the RPWS electron number density values. These later times correspond to the region just above the ionospheric peaks, and will be discussed further in Section 3.2, as will the estimated total ion densities by the RPWS/LP (magenta circles).

The INMS ion number density (green) deviates at times from the other instrument estimates of the plasma density. However, this is due to known effects. The period before 20:12 UT during flyby T17, before 18:54:30 UT during flyby T18, and before 17:42:30 UT and after 17:50 UT during flyby T32, are all affected by plasma drift direction and magnitude deviations from the nominal spacecraft motion ram flow and possibly also sharp changes in the spacecraft potential (panel c, Figs. 1–3). These effects occur in altitude regions not used for the conclusions in this study.

More important is the systematic decrease of the INMS derived ion number density (for < 100 amu ions) within a few minutes of closest approach (C/A, 20:17 UT for T17, 18:59 UT for T18, and 17:46 UT for T32), as compared to RPWS/LP electron number density and CAPS/IBS total ion number density. The difference in number densities vary from  $200 \text{ cm}^{-3}$  (T32, Fig. 3) up to 2000 cm<sup>-3</sup> (T17, Fig. 1) near closest approach, and occurs simultaneous with a corresponding increase in the CAPS/IBS heavy (>100 amu) ion number density (Figs. 1–3, panel a, red) from  $100 \text{ cm}^{-3}$  (T17) to  $300 \text{ cm}^{-3}$  (T18). Note, the CAPS/IBS heavy ion density values are affected by sensitivity limitations for higher mass numbers above 350 amu. However, these CAPS/IBS measurements still support the conclusion made from the difference of the more accurate INMS ion and RPWS/LP electron number densities. The measured RPWS/LP spacecraft potential (Figs. 1–3, panel c) is relatively constant (-0.7 to -1.6 V), and we do not expect large ion drift speeds comparable to the spacecraft speed (6 km/s) below the ionospheric peak (c.f. Section 3.2). The INMS estimated ion number densities should therefore be valid, and the discrepancy with, e.g., the RPWS/LP electron number density can only be interpreted as due to the presence of heavy (>100 amu)



Fig. 2. The same as in Fig. 1, but for the T18 flyby. See text for further information.



Fig. 3. The same as in Fig. 1, but for the T32 flyby. See text for further information.

positively charged ions. We conclude that the number density of heavy (>100 amu) positive ions in Titan's ionosphere during the presented flybys near closest approach vary between 100 and 2000 cm<sup>-3</sup>.

Further evidence that a truly complex chemistry takes place is that the identified periods of heavy positive ions occur simultaneously with the detection of heavy negative ions as measured by the periodic peaks in the CAPS/ELS counts rates (Figs. 1–3, panel b). The T17 flyby (Fig. 1) lacks a negative ion signature in the most energetic (0.1–26 keV, or 500–14000 amu/q) range (red), while a clear detection exists in all energy channels otherwise, and could be due to the dayside illumination conditions during the T17 flyby. However, future studies involving several more flybys are needed to detect a possible dependence with illumination (SZA) conditions. The number density of negative ions during the here presented events is in the range  $50-150 \,\mathrm{cm}^{-3}$  (Coates et al., 2007).

## 3.2. Altitude characteristics

The altitude variation of the discussed plasma particle number densities is displayed in Figs. 4–6, where we will also discuss the derived RPWS/LP ion number density (magenta circles) assuming the ions ram the Langmuir probe with the spacecraft speed (6 km/s). The inbound flybys are presented in panel a, and the outbound flybys are presented in panel b. A remarkable feature is that the RPWS/LP total ion number density and the CAPS/IBS total ion number densities (magenta stars) do not deviate from each other considering the larger uncertainty in the CAPS/IBS measurements. These different instruments therefore measure the same ion flux values, from which the ions density is estimated (assuming the spacecraft speed).

The same applies for the above noted regions where the CAPS/ IBS total ion density was found to be systematically above the RPWS electron number density values above 1100 km (T17, outbound, panel b; and T18, outbound, panel b; also T32, outbound, panel b). The errors in the RPWS electron number density values is not more than 10%, and an ion drift speed of 1-2 km/s may explain the difference between total ion and electron densities. This corresponds to 0.002-0.01 mV/m electric field induced ion drifts, which are reasonable fields for the magnetospheric electrodynamics near Titan (e.g., Rosenqvist et al., in press). No such discrepancies are observed below 1100 km, and plausible ion drift speeds must be less than 10% (measurement error limit) of the spacecraft speed (6 km/s) below this altitude during these flybys. We conclude that the total plasma density is very well determined by the combined RPWS and CAPS/IBS measurements for altitudes below 1300 km presented here.

The INMS ion number density is systematically lower than the total plasma number density below an altitude of 1050–1150 km (Figs. 4–6), and the difference increases toward lower altitudes. Since ion drift speeds are small at these altitudes, according to RPWS and CAPS/IBS combined measurements, the only factor that can affect the INMS ion number density measurements is the limitation in ion mass of 100 amu. The discrepancy with the RPWS and CAPS/IBS total plasma density can therefore be attributed to the presence of heavy (>100 amu) positively charged ions. The amount of such heavy positively charged ions reach 50–70% of the total ion density at the lowest measured altitudes (Figs. 4–6). We conclude that Titan's deep ionosphere is dominated by heavy molecular positively charged ions during the presented flybys near closest approach (or below 1150 km).



Fig. 4. Plasma number density estimates for inbound (panel a) and outbound (panel b) of the T17 flyby. Plasma number densities are the electron number density by RPWS/ LP (blue) and RPWS/E (black), the total ion number density by CAPS/IBS (magenta stars) and RPWS/LP (magenta circles) as well as INMS (green stars, <100 amu), the heavy (>100 amu) ion number densities by and CAPS/IBS (red stars).



Fig. 5. The same as in Fig. 4, but for the T18 flyby. See text for further information.



Fig. 6. The same as in Fig. 4, but for the T32 flyby. See text for further information.

#### 4. Discussion

The region below an altitude of 1150 km in Titan's ionosphere has been shown here to contain a large fraction of heavy (>100 amu) positively charged molecular ions reaching 50–70% of the total plasma number density in the lower measured altitude range 950–1000 km, which is much larger than previously predicted by theory. Simultaneously detected negatively charged ions may constitute up to 10% of the total plasma density according to CAPS/ELS measurements. Unfortunately no Cassini in-situ data have so far been sampled below 950 km altitude. However, we do know from radio occultation measurements (Kliore et al., 2008) that the main ionosphere, with number densities around  $1000 \,\mathrm{cm}^{-3}$ , indeed extends down to  $400 \,\mathrm{km}$ altitude. The selected events (T17, T18, 32) cover a wide range of solar and magnetospheric conditions, as well as different latitudes. A brief look at data from other flybys not presented here indicates that the large amount of heavy (>100 amu) molecular ions is a widespread phenomenon in Titan's ionosphere and not restricted to the presented flybys. A statistical study, including a large number of Titan flybys, is required to give an accurate account for the total amount of heavy organics produced in Titan's ionosphere. However, an order of magnitude estimate can be made from the data presented here.

The heavy positive ion number density in the altitude interval 950-1150 km varies between 100 and  $2000 \text{ cm}^{-3}$  during the presented events. We assume that this part of Titan's ionosphere is a spherical shell with a thickness of 200 km and consisting of heavy ions (>100 amu) with a steady state number density of 500 cm<sup>-3</sup>. The ions in this layer would recombine and form heavy neutral particles/molecules with an electron recombination rate ( $\alpha$ ) of approximately  $1-2 \times 10^{-6}$  cm<sup>3</sup>/s in this altitude range (Galand et al., in preparation). The production of heavy neutral particles per second  $(dn_n/dt)$  in the spherical shell would then be given by  $\alpha n_e^2 \sim 0.25$  particles/cm<sup>3</sup>/s. The mean mass of these particles must reflect the heavy parent molecular ions, and considering that the measured CAPS/IBS ion mass spectrum reached at least 350 amu for positive ions (Waite et al., 2007; Crary et al., submitted for publication), and for comparison CAPS/ ELS inferred 40,000-50,000 amu negatively charged ions (Coates et al., 2007), it is reasonable to assume these neutrals produced by electron recombination of positively charged ions are at least 200 amu on the average. This is supported by RPWS/LP mean ion mass estimates as well as CAPS/IBS mass spectra (not shown). The 200 km thick spherical shell around Titan would then continuously produce about 0.3 kg/s, or 95,000 t/yr. If the ionosphere down to 400 km altitude is taken into account (compare with Kliore et al., 2008), about 300,000 t/yr of heavy organic neutral particles is produced. Considering that the above calculation makes use of rather conservative estimates, we conclude that it is not unreasonable to expect 0.1-1 Mt/yr of heavy organic particles to be produced by ionospheric processing on Titan. Although, this result needs confirmation by further analysis of the Cassini data, it is indicative that the ionosphere of Titan is an important source of the complex chemistry leading to the formation of the aerosol haze and other heavy organic molecules found in Titan's atmosphere and on the surface of Titan.

Assuming spherical heavy neutral particles produced from the lower ionosphere (400–950 km), an aerosol density of  $0.5 \text{ g/cm}^3$ , and a mean mass of 200 amu implies a particle radius of about 5.5 Å. The corresponding sedimentation velocity

 $v_{sed} = 0.7 r_d g / (v_{gas} \rho_{gas})$ 

at 1000 km in Titan's atmosphere for such a particle would be near 200 cm/s. Here  $r_d$  is the particle radius, g is acceleration of gravity,

 $v_{gas}$  is the atmospheric thermal speed and  $\rho_{gas}$  is the atmospheric density. The empirical atmosphere model of Müller-Wodarg et al. (2008) for 56°N latitude and an altitude of 1000 km has been used for the latter two quantities. If an aerosol density of these particles is assumed to be near 1000 cm<sup>-3</sup>, the downward mass flux is around  $1.8 \times 10^{-15}$  g/cm<sup>2</sup>/s at 1000 km. At the surface, assuming a  $1/r^2$  dependence for the flux, gives a value of  $3.2 \times 10^{-15}$  g/cm<sup>2</sup>/s. This approach the flux inferred for the detached and main haze layers of  $0.5-5 \times 10^{-14}$  g/cm<sup>2</sup>/s (McKay et al., 2001; Wilson and Atreya, 2003; Lavvas et al., 2009), suggesting that a significant fraction of the aerosol formation occurs near or below 1000 km altitude on Titan and is initiated by electron recombination of heavy positively charged ions.

### 5. Conclusions

The combined measurements of RPWS, CAPS and INMS on board the Cassini spacecraft reveal that the ion population of the ionosphere of Titan below 1150km consists of 50–70% of heavy (>100 amu) positively charged organic ions. The corresponding ion number density is relatively large (100–2000 cm<sup>-3</sup>), and is expected to prevail down to at least 400 km altitude (compare with electron density profiles derived from the Radio Science experiment by Kliore et al., 2008). We have here shown that it may be a sizable source for the aerosol formation on Titan. Further observations are needed to quantify this contribution in detail and to reveal the associated complex physics and chemistry.

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