Composition of Titan's ionosphere

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[1] We present Cassini Ion and Neutral Mass Spectrometer (INMS) measurements of ion densities on the nightside of Titan from April 16, 2005, and show that a substantial ionosphere exists on the nightside and that complex ion chemistry is operating there. The total ionospheric densities measured both by the INMS and the Cassini Radio and Plasma Wave (RPWS) experiments on Cassini suggest that precipitation from the magnetosphere into the atmosphere of electrons with energies ranging from 25 eV up to about 2 keV is taking place. The absence of ionospheric composition measurements has been a major obstacle to understanding the ionosphere. Seven "families" of ion species, separated in mass-to-charge ratio by 12 Daltons (i.e., the mass of carbon), were observed and establish the importance of hydrocarbon and nitrile chains in the upper atmosphere. Several of the ion species measured by the INMS were predicted by models (e.g., $HCNH^+$ and $C_2H_5^+$). But the INMS also saw high densities at mass numbers not predicted by models, including mass 18, which we suggest will be ammonium ions (NH_4^+) produced by reaction of other ion species with neutral ammonia. **Citation:** Cravens, T. E., et al. (2006), Composition of Titan's ionosphere, *Geophys. Res. Lett.*, *33*, L07105, doi:10.1029/2005GL025575.

1. Introduction

[2] Titan is Saturn's largest satellite and it has a dense atmosphere composed of molecular nitrogen and methane, with minor amounts of many hydrocarbon and nitrile species [*Waite et al.*, 2005a]. Solar radiation and energetic plasma from Saturn's magnetosphere ionizes the neutral molecules, creating an ionosphere at altitudes above about 800 km [*Bird et al.*, 1997; *Wahlund et al.*, 2005; *Crary et al.*, 2006; *Keller et al.*, 1992; *Gan et al.*, 1992; *Cravens et al.*, 2005; *Galand et al.*, 1999; *Banaskiewicz et al.*, 2000; *Lilensten et al.*, 2005a]. The ionosphere provides a link between Saturn's magnetosphere and the neutral atmosphere of Titan [*Wahlund et al.*, 2005; *Crary et al.*, 2006; *Gan et al.*, 1992; *Ledvina and Cravens*, 1998; *Backes et al.*, 2005; *Ma et al.*, 2004] and plays a crucial role in the heat and chemical balance of the upper atmosphere [*Backes et al.*, 2005; *Ma et al.*, 2004; *Keller et al.*, 1998; *Fox and Yelle*, 1997; *Wilson and Atreya*, 2004; *Yelle*, 1991; *De La Haye*, 2005].

[3] An electron density profile at Titan was measured remotely in 1980 using the radio occultation technique [*Bird et al.*, 1997], and in situ measurements of the ionosphere were first made by the Cassini RPWS experiment during the October 26, 2004 (Ta), encounter [*Wahlund et al.*, 2005]. The Plasma Spectrometer (CAPS) instrument measured ion composition at low mass resolution, demonstrating the existence of several ion species [*Crary et al.*, 2006]. Here we describe the higher-mass resolution ionospheric measurements made during the T5 encounter by the INMS in its open source ion (OSI) mode. T5 INMS neutral measurements will be described in a later paper.

2. Instrument and T5 Encounter Geometry

[4] For the INMS OSI mode, ions enter the instrument aperture, are deflected by a quadropole switching lens, set to the necessary voltages, and are then guided to the radio-frequency quadropole mass analyzer, which selects ions according to the mass-to-charge ratio (M/Z) [*Waite et al.*, 2004, 2005a, 2005b; *Kasprzak et al.*, 1996]. The ions are detected with a secondary electron multiplier with pulse counting technology. The OSI field of view has a half-width of $\approx 3°$, and the instrument measures positive ions with energies, E, appropriate for a "compensation" speed equal to the spacecraft speed (6.02 km/s in this case). Note that doubly-charged positive ions will be observed at half the mass-to-charge value as a singly-charged ion with the same mass. The count rate C' (counts per second) measured by the instrument is given in terms of the incident ion flux, ϕ (units of molecules cm^{-2} s^{-1}), by the expression: $C' = \{1.34 \times 10^{-4} \times E(eV) + 0.988 \times 10^{-3}\}\phi$. Instrument calibration is accurate to 20% at low mass numbers and 50% at M/Z of 50 or higher. The integration period for each ion measurement is 31 ms, and the time interval between measurements for a given mass number was 10 s or less.

[5] The spacecraft was on the nightside of Titan during the outbound leg of the T5 pass (see Figure 1) with a solar zenith angle (SZA) at closest approach (CA) of 127° and

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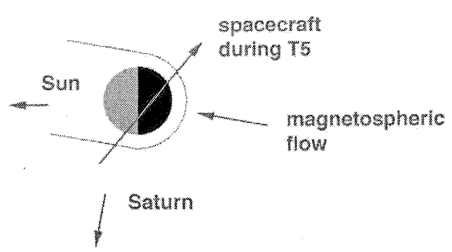

Figure 1. Schematic of Titan for the T5 Cassini encounter on April 15, 2005, with the spacecraft trajectory. The INMS ion measurements were made on the outbound part of the trajectory.

even larger at higher altitudes (Figure 2). Solar radiation cannot act as a local ionization source for this case. The CA location was also near the magnetospheric "ram" point, where Saturn's magnetospheric plasma impinges on the satellite, which suggests that magnetic field lines, which direct electron and electron transport, are in a "draped" configuration in the ionosphere [*Ledvina and Cravens*, 1998; *Backes et al.*, 2005; *Ma et al.*, 2004].

3. Measured Ion Densities

[6] Figure 2 displays ion density profiles measured by the INMS for a few ion species with M/Z = 17, 18, 28, 29, 41, 51, and 79 Daltons (i.e., for singly-charged ions M/Z is also just the mass number). The mass numbers 17, 28, 29, 41, and 51 very likely correspond to CH_5^+, $HCNH^+$, $C_2H_5^+$, $C_3H_5^+$, and $C_4H_3^+$, and mass 79 could be $C_5H_5N^+$ and/or $C_6H_7^+$. The total ion density (including all important ion species and *not* just the specific species shown in the figure) is $n_i \approx 1000$ cm^{-3} between altitudes, z, of 1027 km (CA) and 1400 km, but decreases at higher altitudes. Density profiles for individual species exhibit more structure than does the total density. The CH_5^+ and $C_2H_5^+$ density profiles

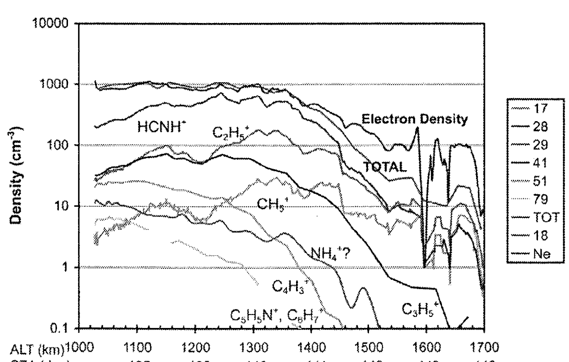

Figure 2. Density profiles of several important ion species. Densities measured by the INMS are shown versus altitude, time from CA, and solar zenith angle (SZA) for the outbound T5 encounter of Cassini with Titan. The latitude and local solar time at CA are 73.7°N and 0.7 hrs., respectively. Total INMS ion density and an electron density profile measured by the RPWS experiment are also shown.

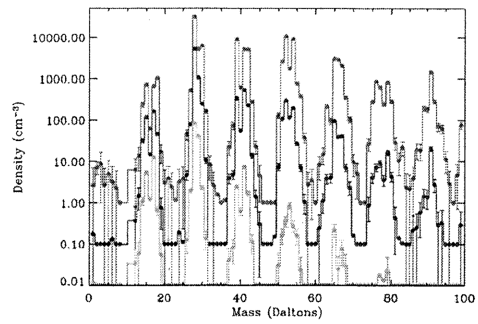

Figure 3. Measured mass spectra for three altitude intervals are shown – average density versus Mass (in Daltons). Red: 1027 km–1200 km, multiplied by a factor of 100. Blue: 1200 km–1400 km, multiplied by a factor of 10. Green: 1400 km–1600 km, multiplied by a factor of 1. 1σ statistical error bars are shown.

have several distinctive peaks, and $HCNH^+$ has a broad maximum with some small-scale peaks superimposed. On the other hand, the density profiles of the heavier species displayed ($C_3H_5^+$, $C_4H_3^+$, and $C_5H_5N^+$), but also the M/Z = 18 species, have less structure and fall off more rapidly with increasing altitude.

[7] The electron densities (n_e) measured by the RPWS experiment (also shown in Figure 2) agree very well with the INMS total densities below 1400 km. Indeed, quasi-neutrality demands that $n_e = n_i$. But the measured n_e and n_i start to deviate for z > 1450 km, although they have similar trends. The smaller INMS densities can be attributed to the deviation of the incident plasma flow out of the center of the instrument's field of view, which we estimate to occur when the ionospheric flow speeds exceed $\approx$0.5 km/s. Dynamical models of the ionosphere predict faster plasma flow at higher altitudes [*Ma et al.*, 2004]. If the flow velocity component orthogonal to the spacecraft velocity vector (and, hence, to the INMS aperture direction) exceeds $\approx$0.5 km/s, then the incident ions are shifted from the center of the field-of-view by more than the 3° half-width of the response function [*Waite et al.*, 2004].

[8] Complete mass spectra for three altitude ranges are shown in Figure 3. The most striking feature is the mass "periodicity" with a cadence of 12 Daltons (or amu). This mass spacing demonstrates that the chemistry is dominated

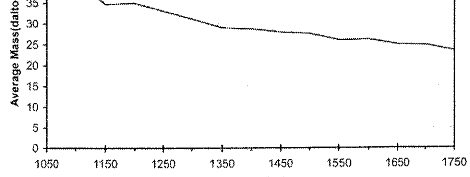

Figure 4. Average ion mass versus altitude. Average masses are from INMS densities.

by hydrocarbon ion species ($C_nH_m^+$, where n and m are integers) and by nitrile species ($C_nN_kH_m^+$). The highest mass species observed (m = 99) is probably $C_8H_3^+$. Higher mass families become less important at higher altitudes (green spectrum compared to the red), indicating that the ionosphere is chemically more complex at lower altitudes, which was not unexpected [*Keller et al.*, 1998; *Wilson and Atreya*, 2004; *Anicich et al.*, 2004]. This altitude "gradient" in chemical complexity is also evident in variation of the average ion mass with altitude (Figure 4). At z ≈ 1050 km, $\langle m \rangle \approx 42$, and at z ≈ 1600 km, $\langle m \rangle$ is only 25.

4. Discussion and Conclusion

[9] The data demonstrates that the most abundant species is the nitrile species $HCNH^+$ (mass number, m = 28), as predicted by most pre-Cassini models [*Keller et al.*, 1998; *Fox and Yelle*, 1997; *Wilson and Atreya*, 2004; *Anicich et al.*, 2004]. Other important predicted species evident in Figure 2 include $C_2H_5^+$, CH_5^+, and $C_3H_5^+$, as well as heavier ion species [*Keller et al.*, 1998] such as $C_7H_7^+$ and $C_3H_3N^+$. The "primary" ions must be produced from the major neutrals [*Waite et al.*, 2005a], N_2 and CH_4, by electron impact [*Cravens et al.*, 2005], but our measurements show that primary ion species (CH_4^+ from methane, and CH_3^+ from N_2^+ via a reaction with methane) have rather low densities. This emphasizes the importance of chemistry for this ionosphere. $C_2H_5^+$ is probably produced by the reaction of CH_3^+ with methane and ethane, and the important species $HCNH^+$ is thought to come from reaction of $C_2H_5^+$ with the important minor neutral species, HCN [*Keller et al.*, 1998; *Fox and Yelle*, 1997; *Wilson and Atreya*, 2004]. Only about a third of the total density consists of mass 28 near CA, thus indicating that a large number of ion species contribute to the total density and not just $HCNH^+$. Not all of these species are shown in Figure 2, but they are present in the Figure 3 mass spectra and include: $C_3H_3^+$, $C_3H_4^+$, $C_4H_5^+$, $C_5H_5^+$, $C_5H_7^+$, $C_6H_5^+$, and $C_3H_2N^+$. Mass numbers 18, 30, 54, and 66 also make important contributions to the total density and were not present in pre-Cassini models.

[10] A thorough interpretation of the complex mass spectra measured by the INMS is beyond the scope of this initial paper, but we now point out some features for which the model predictions were particularly deficient. Models [*Keller et al.*, 1998; *Fox and Yelle*, 1997; *Wilson and Atreya*, 2004] did predict the existence of several "families" of ion species separated by 12 amu, but the modeled families were much more "anemic" (i.e., many missing mass numbers) than the rich, full families evident in Figure 3. This chemically complex ionosphere introduces hydrocarbon species into the neutral atmosphere via electron-ion dissociative recombination reactions [*Wilson and Atreya*, 2004; *De La Haye*, 2005] and future models will need to include this hydrocarbon source.

[11] Consider just one of the unidentified species mentioned above (m = 30). The *Keller et al.* [1998] model predicted ethane ions ($C_2H_6^+$) at m = 30 but with a rather low density. Neutral formaldehyde (m = 30) and other oxygen-bearing species such as CO were predicted for the upper atmosphere [*Wilson and Atreya*, 2004]. However, reaction of major ion species with H_2CO tends to produce protonated formaldehyde ions (H_2COH^+) (M/Z = 31) rather than M/Z = 30 ions. This could help to explain the M/Z = 31 measurements, but still leaves the M/Z = 30 problem. *Wilson and Atreya* [2004] considered the source of oxygen-bearing species and suggested that carbon monoxide might diffuse up from the lower atmosphere. Energetic oxygen ions have been observed in the magnetosphere near Titan by the CAPS instrument, and the CAPS investigators have postulated an external oxygen source for Titan [*Crary et al.*, 2006]. Perhaps the incident O^+ ions, once thermalized, can react with N_2 or perhaps neutral O can react with N_2^+, producing NO^+ ions (M/Z = 30); however, these are likely to be minor contributors. Neutral nitric oxide in the atmosphere would also give rise to NO^+ ions if a sufficient source of neutral NO exists. V. Vuitton et al. (manuscript in preparation, 2006) argue against NO^+ and suggest that mass 30 is CH_3NH^+.

[12] Another species with a measured abundance much higher than expected is mass 18. The *Keller et al.* [1998] model predicted H_2O^+ but with low density and accompanied by H_3O^+ (mass 19) ions produced by reaction of $HCNH^+$ with H_2O. Mass 19 is virtually absent in the measured spectra (Figure 3). NH_4^+ (the ammonium ion) is a likely suspect for mass 18 because it can be produced by reaction of almost any of the major ion species observed at Titan with neutral ammonia. This ion should be lost mainly by dissociative recombination ($\alpha = 4.1 \times 10^{-5}/T_e^{0.6}$ cm^3 s^{-1}) [*Allen et al.*, 1987]. Simple chemistry yields this expression for the NH_3 density: $[NH_3] \approx (k/\alpha)[NH_4^+]$. Using the measured mass 18 density and rate coefficient $k = 2.3 \times 10^{-9}$ cm^3 s^{-1} for the reaction of $HCNH^+$ with ammonia [*Anicich and McEwan*, 1997], we find an ammonia abundance at z ≈ 1050 km of ≈ 1 ppmv. *Wilson and Atreya* [2004] predicted a relative ammonia abundance of only ≈.03 ppmv at this altitude, and suggested that NH_3 could be produced by ionization by galactic cosmic rays at low altitudes followed by some chemistry including three-body reactions of NH_2.

[13] *Lilensten et al.* [2005b] suggested that doubly-charged ions (e.g., N_2^{++}) are present in the dayside Titan ionosphere, which would be consistent with Auger electron production [*Cravens et al.*, 2004]. Unfortunately, this species would appear at mass 14 where it has strong competition from N^+ and CH_2^+ ions, but perhaps the 1.5 cm^{-3} density peak measured by the INMS for m = 7 near CA (Figure 3) could be N^{++} ions.

[14] Experience with the ionospheres of Venus and Mars [*Nagy and Cravens*, 2002] suggests that both transport of ionospheric plasma from the dayside and impact ionization of neutrals by energetic electrons could be operating; however, the transport source is probably not effective at Titan, at least near 1000 km, due to the short chemical lifetimes of the molecular ion species that were observed, and also because the magnetospheric ram point is on the nightside and magnetic forces would tend to drive plasma toward rather than away from the dayside [*Backes et al.*, 2005; *Ma et al.*, 2004]. This leaves electron precipitation as the most likely ionization source for T5 conditions. Measured nightside (this paper) and dayside [*Wahlund et al.*, 2005] electron densities can be used to crudely estimate that the energy influx to the ionosphere from the magnetosphere is roughly 10% of the influx from solar ionizing radiation

globally, although more extensive measurements and modeling will be needed to confirm this.

[15] Ion production rates associated with 100 eV Maxwellian magnetospheric electrons precipitating along draped magnetic field lines were calculated for Ta conditions [*Cravens et al.*, 2005], with peak ion production occurring near z $\approx$ 1200 km. But for T5, electrons with energies sufficient to reach the CA altitude of 1027 km are needed, and preliminary energetic electron transport calculations show that to explain the very broad, low-altitude, ionospheric density region seen at T5, one needs incident electrons with energies ranging from $\approx$25 eV up to $\approx$2 keV. Data from the Cassini INMS, and other experiments, show that Saturn's magnetosphere plays an important role in controlling the upper atmosphere and ionosphere of Titan.

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