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Discovery of heavy negative ions in Titan's ionosphere

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[1] Titan's ionosphere contains a rich positive ion population including organic molecules. Here, using CAPS electron spectrometer data from sixteen Titan encounters, we reveal the existence of negative ions. These ions, with densities up to $\sim$100 cm^{-3}, are in mass groups of 10–30, 30–50, 50–80, 80–110, 110–200 and 200+ amu/charge. During one low encounter, negative ions with mass per charge as high as 10,000 amu/q are seen. Due to their unexpectedly high densities at $\sim$950 km altitude, these negative ions must play a key role in the ion chemistry and they may be important in the formation of organic-rich aerosols (tholins) eventually falling to the surface. **Citation:** Coates, A. J., F. J. Crary, G. R. Lewis, D. T. Young, J. H. Waite Jr., and E. C. Sittler Jr. (2007), Discovery of heavy negative ions in Titan's ionosphere, *Geophys. Res. Lett.*, *34*, L22103, doi:10.1029/2007GL030978.

[2] Titan has a thick atmosphere, principally nitrogen with a few percent by number density of methane [*Waite et al.*, 2005]. Observations by the Cassini spacecraft have shown that its ionosphere, extending from ($\sim$950–1200 km), contains a rich positive ion population of organic molecules at mass/charge ratios up to >100 amu [*Cravens et al.*, 2006]. Here, we show that heavy ion chemistry takes place in Titan's upper atmosphere at altitudes much higher than had been predicted by models and that, because of their large abundance, negative ions must play an unexpectedly key role. A second consequence is that heavy negative ions may be important in formation of tholins, eventually falling through the atmosphere to the surface [*Waite et al.*, 2007].

[3] Negative ions are present in the ionosphere of Earth [e.g., *Hargreaves*, 1992], and can coexist with electrons at D-region altitudes as they are formed primarily by electron attachment to electronegative species such as O. Negative ions were measured in the inner coma of comet Halley, again coexisting with electrons [*Chaizy et al.*, 1991]. Before the Cassini-Huygens mission, negative ions were not expected in Titan's atmosphere [*Hunten et al.*, 1984]. Recently however, it was suggested that they may be present at low altitudes at night [*Borucki et al.*, 2006] and they may have a role in poly aromatic hydrocarbon (PAH) chemistry and aerosol production. If present, at low altitudes they may contribute to the electric field driving possible lightning discharges [*Desch et al.*, 2002].

[4] Here, we report on the discovery of negative ions in Titan's ionosphere by the Electron Spectrometer (ELS) [*Linder et al.*, 1998], one of three sensors making up the Cassini Plasma Spectrometer (CAPS) [*Young et al.*, 2004]. ELS is a 'top-hat' electrostatic analyser with energy per charge (E/q) range for negatively charged particles of 0.6–28,000 eV/q, energy resolution 16.7% and angular range 160° × 20° × 5° divided into 8 × 20° pixels. ELS could detect other negative species in addition to electrons. However, it is not a mass spectrometer. What makes the negative ion observations reported here possible is that Cassini rams through Titan's cold ionosphere ($\sim$130–160 K) at supersonic velocities (5.9–6.3 km/s; see Table 1), causing the ion population to appear as a very sharply defined beam in the ELS frame of reference. During the encounters discussed here the 5° width of the ELS field-of-view was swept across the spacecraft ram direction multiple times by the CAPS actuator, resulting in numerous negative ion spectra during each encounter.

[5] Negative ions were first seen in Titan encounter TA in 2004 and have subsequently been confirmed on 15 further encounters up to October 2007 (see Table 1 for encounter nomenclature and parameters). Of these, most were in sunlit conditions, though some (e.g. T16) were on the night side in highly attenuated (by Titan's atmosphere) sunlight conditions. T25–T28 included a 'night-time' interval of Titan eclipse. We conclude from this that negative ions were present whenever the CAPS pointing conditions were favourable and they may be a permanent, though variable, feature of Titan's ionosphere.

[6] We note that during the lowest altitude Titan encounters the neutral particle density is highest. From INMS measurements [*Waite et al.*, 2007] the neutral particle isotropic pressure is very low, although at 950 km altitude ram pressures could be in the high 10^{-5} mbar range. ELS has operated in the laboratory at isotropic pressures this high without problem. In addition, any discharge within the instrument related to electrostatic analyzer voltage would appear at the highest energies, and if related to the microchannel plate bias there would be no special pattern in energy, whereas we observe a peaked pattern at low energies each time.

[7] Figure 1 is a high resolution (2s) energy spectrogram of the TA encounter. In addition to evidence for negative ions, several other electron populations are also present, which we will discuss briefly: Before $\sim$15:18 (times are given in UT) and after $\sim$15:40 we observe relatively hot magnetospheric electrons. These cool gradually on the inbound trajectory (i.e., on the side away from Saturn), while there is a sharper transition on the outbound side, consistent with ion gyroradius effects associated with pick-

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Table 1. Encounters on Which Negative Ions are Seen. Parameters are Given at Titan Closest Approach in Each Case

	Date	DOY, UT	Altitude (km)	Local time Saturn (hh:mm)	Local time Titan (hh:mm)	Latitude (°N)	Relative velocity (km s^{-1})	Solar zenith angle (sza^a) (°)	Cassini in Titan shadow (night)
Ta (in)	26/10/04	300, 15:30	1174	10:36	16:45	38.78	6.05	91.00	no
T16 (in)	22/7/06	203, 00:25	950	02:27	17:17	85.15	5.97	105.32	no
T17 (in)	7/9/06	250, 20:17	1000	02:20	10:28	22.82	5.96	44.54	no
T18 (in)	23/9/06	266, 18:59	960	02:17	14:24	70.92	5.96	89.81	no
T19 (in)	9/10/06	282, 17:30	980	02:14	14:20	60.75	5.96	80.96	no
T20 (in)	25/10/06	298, 15:58	1029	02:12	11:10	6.36	5.96	24.65	no
T21 (in)	12/12/06	346, 11:41	1000	02:03	20:20	43.12	5.96	125.18	no
T23 (in)	13/1/07	013, 08:39	1000	01:57	14:01	30.68	5.96	53.28	no
T25 (out)	22/2/07	053, 03:12	1000	13:51	00:34	30.35	6.23	161.24	yes
T26 (out)	10/3/07	069, 01:49	981	13:49	01:45	31.70	6.23	149.50	yes
T27 (out)	26/3/07	085, 00:23	1010	13:46	01:42	40.93	6.23	144.13	yes
T28 (out)	10/4/07	100, 22:58	991	13:43	01:39	50.17	6.23	137.37	yes
T29 (out)	26/4/07	116, 21:33	980	13:41	01:36	59.38	6.23	129.81	no
T30 (out)	12/5/07	132, 20:10	959	13:38	01:32	68.61	6.23	121.71	no
T32 (out)	13/6/07	164, 17:46	965	13:35	01:17	84.46	6.23	107.00	no
T36 (out)	2/10/07	275, 04:42	975	11:29	16:08	−59.90	6.31	67.40	no

[a] For SZA > 100°, sunlight will be highly attenuated by Titan's atmosphere.

up of Titan's atmosphere and ionosphere [e.g., *Blanc et al.*, 2002]. The electric field associated with corotation points away from Saturn, and pickup ions are initially accelerated along this direction in the first part of their cycloidal trajectory; there is related electron cooling here [e.g., *Hartle et al.*, 2006]. Attenuated remnants of this 100–1000 eV magnetospheric population are seen between 15:18 and 15:40; these play a role in heating the ionosphere and atmosphere [*Cravens et al.*, 2005; *Galand et al.*, 2006] and in ionisation. Prior to ~15:17 and after ~15:41 spacecraft photoelectrons indicate a small positive spacecraft potential.

[8] In between 15:18 and 15:40 is a region that we identify as Titan's ionosphere. Here the spacecraft potential is negative [*Wahlund et al.*, 2005], preventing ELS from measuring electrons below 1.2 eV. The coldest, densest part of the ionosphere is seen at ~15:25–15:33. Within this is a population of photoelectrons with a peak at ~20 eV characteristic of electron impact on N_2. These disappear once the spacecraft departs the sunlit ionosphere at ~15:30. Similar photoelectron populations have been observed in Saturn's ring ionosphere [*Coates et al.*, 2005], at Mars [*Frahm et al.*, 2006], at Venus [*Coates et al.*, 2007b], and at Earth [e.g., *Coates et al.*, 1985].

[9] The evidence for negative ions is clearly seen in the form of vertical spikes in the ELS energy spectrogram between ~15:27 and 15:30.5 (Figure 1). Each spike consists of a collection of peaks in the energy spectra, which are seen as the actuator sweeps the field of view through the ram direction. Because the spacecraft velocity (6 km/s) is much greater than the ion thermal velocity (1.68 $M^{-1/2}$ km/s where M is ion mass in AMU), we can interpret the energy spectra as a proxy for mass spectra of negatively charged ions. Because the negatively charged ions were contemporaneous with positive ion spectra in the CAPS Ion Beam Spectrometer (IBS) we can use the energy of the most

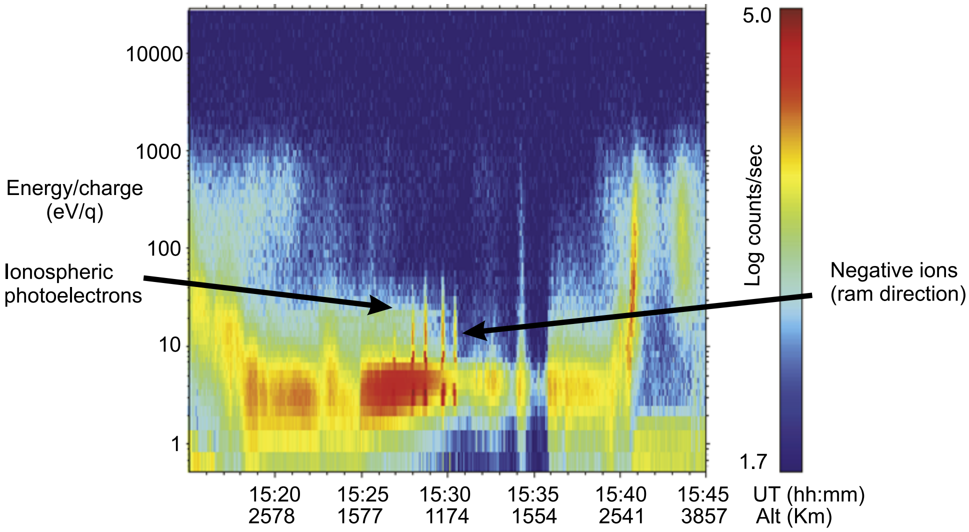

Figure 1. High time resolution (2s) energy-time spectrogram for a central ELS pixel for a 30 minute interval centred on the TA encounter. The colour scale on the right is proportional to the electron differential energy flux. Negative ions are seen as sharp vertical spikes between ~1525 and 1530 UT.

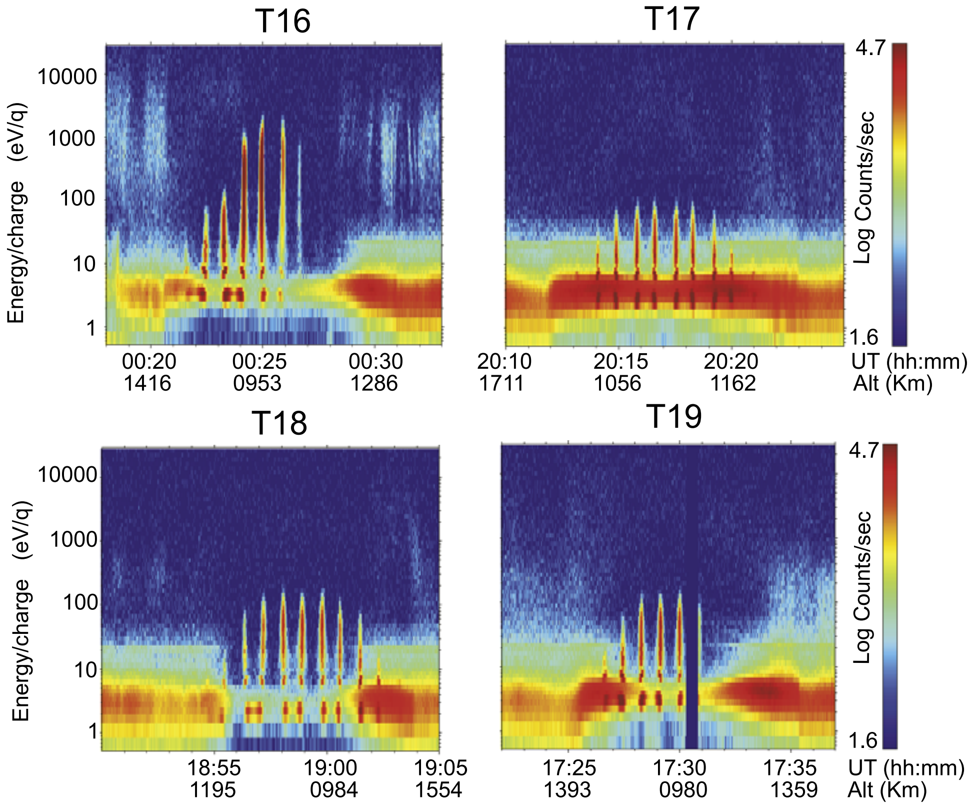

Figure 2. Energy-time spectrograms for 15 minute intervals centred on the T16-19 encounters. Negative ions can be seen in each case.

abundant positive ion species (M = 28, corresponding [*Cravens et al.*, 2006] to HCNH$^+$) to calculate a correction potential of -0.6 V. (A spacecraft potential of -1 V is inferred from the Langmuir probe [*Wahlund et al.*, 2005] located on a different part of the spacecraft.) The ELS spectra were then corrected by -0.6 V to estimate negative ion mass and density.

[10] We suggest that these peaks are due to cold negative ions for the following reasons. The particles must be negative due to the voltages on the electrostatic analyzer. The sharpness of the peaks is consistent with the spacecraft ramming through a cold ionospheric population, so that as seen by ELS the ions are supersonic and therefore narrow. The sharp peaks, in energy and in (ram) angle, indicate negative ions rather than electrons, because although the ionospheric electrons are "cold" they are highly subsonic (higher thermal speed than the ram velocity) and therefore much more isotropic, as observed during all encounters [e.g., *Coates et al.*, 2007a]. Also, if the populations were electrons they would have to be highly non-gyrotropic at each energy level and time where they are seen. This is not possible because the magnetic field would need to be in the ram direction at all times during each of the negative ion observations, which is not observed (M. K. Dougherty et al., personal communication, 2007).

[11] Figure 2 shows ELS energy-time spectrograms from the T16–T19 encounters. We see similar mass peaks each time the ELS field-of-view passes through the ram direction. We can convert the observed ram energy of the peaks into mass using the kinetic energy associated with the relative speed for each encounter (e.g., $m_{amu} = 5.32E_{eV}$ for a flyby speed of 6 km s^{-1}). This conversion assumes singly charged negative ions; if there are multiple charges, as expected for relatively large cluster molecules, or for aerosols [*Horanyi et al.*, 2004], in a plasma, then the converted mass would be even higher since ELS measures E/q.

[12] Using this conversion the ELS energy range makes it in principle sensitive to negative ion masses between 3 and roughly 150,000 amu/q, compared with positive ion and neutral atom limits of 100 amu for INMS [*Waite et al.*, 2005] and ~370 amu/q for the IBS [*Young et al.*, 2004] as operated during the encounters discussed here. However, we have not yet observed ions with masses >10,000.

[13] Figure 3a shows a typical spectrum from the T16 encounter at an altitude of 953 km plotted against both energy and mass, assuming singly charged negative ions. Peaks are seen at several masses, including extremely heavy ions up to 10,000 amu/q. As mentioned above, this high M/q value may be a lower limit for the ion mass. We estimate that these ions are the size of aerosols (~10–30 nm). Using representative numbers in Titan's ionosphere [*Wahlund et al.*, 2005] $T_e \sim 1000$ K and $n_e \sim 1 \times 10^3 \mathrm{cm}^{-3}$, gives $\lambda_D \sim 0.07$ m. Then ~30 nm aerosols would develop a potential [*Goetz*, 1989] of $\varphi \sim -2.5\, kT_e/e \sim -0.25$ V and may have a charge given by $Q = 4\pi\varepsilon_0 a\varphi\exp(-a/\lambda_D)$, corresponding to ~5 electrons [see also *Waite et al.*, 2007]. The actual mass could then be ~50,000 amu. Figure 3b shows the density as a function of energy, converted assuming the particles are a rammed population of ions observed with an assumed 5% efficiency, with mass/charge given in amu/q.

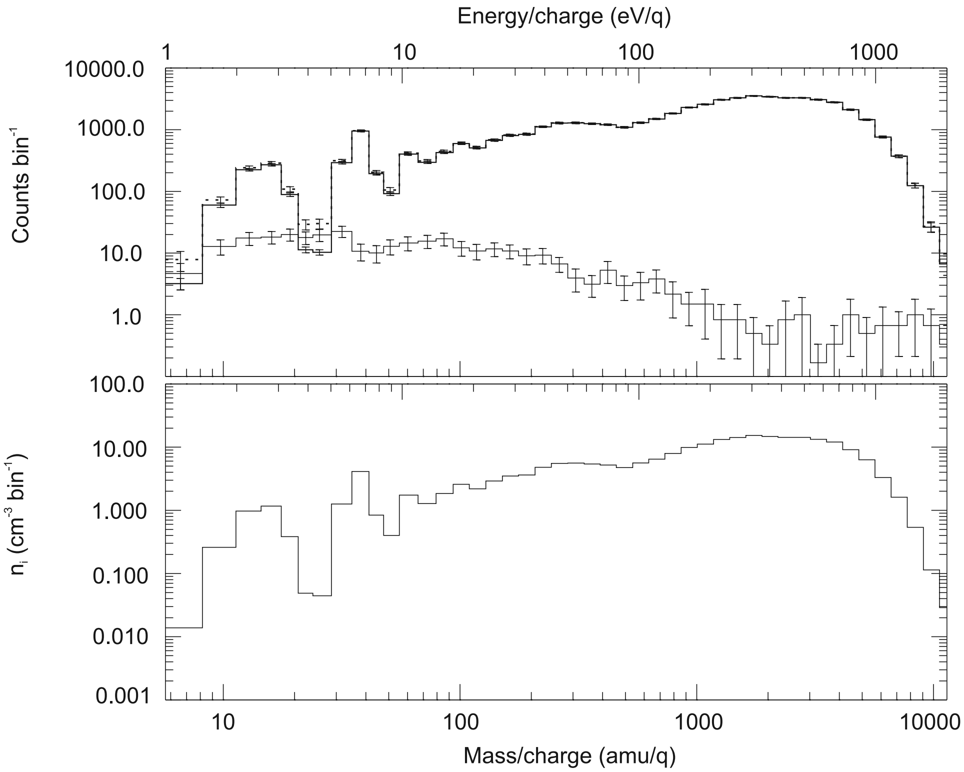

Figure 3. Energy (and mass, converted assuming singly charged ions) spectra at an altitude of 953 km during the T16 encounter. (top) Dotted trace shows total counts, dashed trace shows signal due to ionospheric electrons, and solid trace shows counts due to negative ions only. (bottom) Negative ion density measured in each ELS energy bin. In each case error bars are associated with statistical uncertainties on the counts.

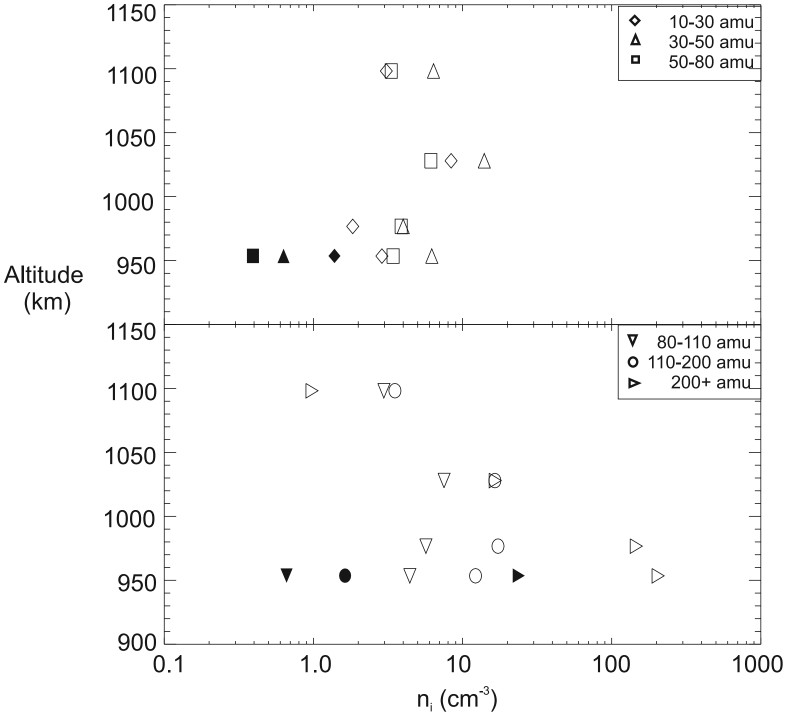

Figure 4. Density of negative ions versus altitude during the T16 encounter, plotted on a log-log scale. Key: 10–30 amu, diamond; 30–50 amu, upright triangle; 50–80 amu, square; 80–110 amu, inverse triangle; 110–200 amu, circle; and 200+, left handed triangle. Inbound symbols empty; outbound solid.

[14] In addition to the very massive ions, analysis of data from all suitable encounters shows that the mass spectra all have similar separate mass peaks in groups between $\sim$10–30, 30–50, 50–80, 80–110 and 110–200 amu/q. Particles of more than 200 amu/q are visible on many encounters, with T16 showing exceptionally high masses (see Figure 3).

[15] The density of each mass group varies with altitude as shown in Figure 4. This figure implies remarkably large scale heights for the negative ions, possibly indicating that they are supported by electric fields. It also shows a surprisingly high density of high mass particles, up to $\sim$100 cm^{-3}.

[16] It is important to note that the estimates of negative ion densities reported here are a surprisingly large fraction of the corresponding positive ion densities, but lower than the electron density. This may account for the discrepancy on some encounters, including T16, between RPWS electron and INMS ion density estimations (J.-E. Wahlund, personal communication, 2007).

[17] Candidate species for the first mass group are CN$^-$ (electron affinity (EA) = 3.862 eV) [*Bradforth et al.*, 1993], NH$_2^-$(EA = 0.77 eV) [*Wickham-Jones et al.*, 1989] and O$^-$ (EA = 1.48 eV) [*Branscomb*, 1958], although the presence of the latter would be surprising due to the dearth of oxygenated compounds so far observed in Titan's upper atmosphere. Candidates for the second mass group include NCN$^-$ (EA = 2.484 eV) [*Clifford et al.*, 1997], HNCN$^-$(EA = 2.622 eV), and C$_3$H$^-$(EA = 1.99 eV) [*Aoki et al.*, 1996]. The third group includes the resonantly-stabilised cyclopentadienyl anion, C$_5$H$_5^-$(EA = 1.786 eV) [*Engelking and Lineberger*, 1977] and the recently identified interstellar anion, C$_6$H$^-$(EA = 3.69 eV) [*Natterer et al.*, 1994] and C$_6$H$_5^-$ (EA = 1.2–1.6 eV) [*Bohme and Young*, 1971]. Mass groups with four, five, and higher numbers of carbon atoms most likely involve polyynes, higher order nitriles, PAHs (EA = −0.2 to 1.3 eV) [*Moustefaoui et al.*, 1998], and cyano-aromatics (EA = 3.5 to >5 eV) [*Zhang et al.*, 2006].

[18] The high densities of the highest mass negative ions ($\sim$200 cm^{-3}) will have a profound effect on the complex organic chemistry in the upper atmosphere [*Keller et al.*, 2006; *Waite et al.*, 2007]. By analogy with Earth's D-region, a possible mechanism for formation of negative ions is dissociative electron attachment. The detailed production and loss mechanisms for negative ions are beyond the scope of this paper. However, the extremely high masses seen on T16 are perhaps due to a combination of relative darkness (eliminating electron photodetachment processes) and higher densities during that encounter.

[19] A lower mass limit of $\sim$10,000 at $\sim$950 km is potentially very important for the initial stages of aerosol formation at high altitudes. The possibility exists that these heavy charged particles will polymerise further, creating high mass tholin aerosols that then fall through the atmosphere and rain down onto Titan's surface. Huygens data have been used to model the part of this process at altitudes <300 km [*Keller et al.*, 2006].

[20] Heavy ions at high altitudes are also sensitive to the prevailing corotation electric field that is directed on average away from Saturn (lighter ions have much smaller gyro radii and are simply stripped away). Thus the electric field tends to drive the heavy negative ions towards Titan on the anti-Saturnward side of the moon. Lower in the ionosphere this electric field would not penetrate; nevertheless, it is possible that over geological time this has had a preferential effect on the composition of the aerosol drizzle falling to the surface. In support of this, we note that in all the encounters on which we have observed negative ions so far, Cassini has sampled the anti-Saturnward side first, and there is a tendency to see the negative ions before closest approach in most cases.

[21] In summary, we have discovered significant quantities of heavy negative ions in Titan's ionosphere. Such ions have been observed on sixteen (up to T36) of Cassini's Titan encounters, whenever CAPS-ELS views in the ram direction and the altitude is $<\sim$1150 km. The ions are seen when the spacecraft is in direct or strongly attenuated sunlight, and at night. Lower mass groups ($\sim$10–30, 30–50, 50–80, 80–110 and 110–200 amu) have similar abundances and have been found at all encounters. Ions with extremely high masses (up to 10,000 amu) have been observed only on T16 so far. When present, the negative ion density can reach $\sim$10% of the negatively charged population at low altitudes. This result is significant for the chemistry of hydrocarbon atmospheres, the composition of Titan's aerosols, and may have long term effects on the composition of the moon's surface.

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References

Aoki, K., S. Ikuta, and A. Murakami (1996), Equilibrium geometries and stabilities of the C$_3$H radical: Ab initio MO study, *J. Mol. Struct. Theochem*, *365*, 103–110.

Blanc, M., et al. (2002), Magnetospheric and plasma science with Cassini-Huygens, *Space Sci. Rev.*, *104*, 253–346.

Bohme, D. K., and L. B. Young (1971), Electron affinities from thermal proton-transfer reactions: C$_6$H$_5$ and C$_6$H$_5$CH$_2$, *Can. J. Chem.*, *49*, 2918–2920.

Borucki, W. J., et al. (2006), Predictions of the electrical conductivity and charging of the aerosols in Titan's atmosphere, *Icarus*, *181*, 527–544.

Bradforth, S. E., et al. (1993), Photoelectron spectroscopy of CN$^-$, NCO$^-$, and NCS$^-$, *J. Chem. Phys.*, *98*, 800–810.

Branscomb, L. M. (1958), The electron affinity of atomic oxygen, *Nature*, *182*, 248–249.

Chaizy, P., et al. (1991), Negative ions in the coma of comet Halley, *Nature*, *349*, 393–396.

Clifford, E. P., et al. (1997), Photoelectron spectroscopy of the NCN- and HNCN- ions, *J. Phys. Chem. A*, *101*, 4338–4345.

Coates, A. J., et al. (1985), Ionospheric photoelectrons observed in the magnetosphere at distances of up to 7 Earth radii, *Planet. Space Sci.*, *33*, 1267–1275.

Coates, A. J., et al. (2005), Plasma electrons above Saturn's main rings: CAPS observations, *Geophys. Res. Lett.*, *32*, L14S09, doi:10.1029/2005GL022694.

Coates, A. J., F. J. Crary, D. T. Young, K. Szego, C. S. Arridge, Z. Bebesi, E. C. Sittler Jr., R. E. Hartle, and T. W. Hill (2007a), Ionospheric electrons in Titan's tail: Plasma structure during the Cassini T9 encounter, *Geophys. Res. Lett.*, *34*, L24S05, doi:10.1029/2007GL030919.

Coates, A. J., et al. (2007b), Ionospheric photoelectrons at Venus: Initial observations by ASPERA-4 ELS, *Planet. Space Sci. Lett.*, in press.

Cravens, T. E., et al. (2005), Titan's ionosphere: Model comparisons with Cassini Ta data, *Geophys. Res. Lett.*, *32*, L12108, doi:10.1029/2005GL023249.

Cravens, T. E., et al. (2006), Composition of Titan's ionosphere, *Geophys. Res. Lett.*, *33*, L07105, doi:10.1029/2005GL025575.

Desch, S. J., et al. (2002), Progress in planetary lightning, *Rep. Prog. Phys.*, *65*, 955–997.

Engelking, P. C., and W. C. Lineberger (1977), Laser photoelectron spectrometry of C5H5$^-$: A determination of the electron affinity and Jahn-Teller coupling in cyclopentadienyl, *J. Chem. Phys.*, *67*, 1412–1417.

Frahm, R. A., et al. (2006), Carbon dioxide photoelectron peaks at Mars, *Icarus*, *182*, 371–382.

Galand, M., R. V. Yelle, A. J. Coates, H. Backes, and J.-E. Wahlund (2006), Electron temperature of Titan's sunlit ionosphere, *Geophys. Res. Lett.*, *33*, L21101, doi:10.1029/2006GL027488.

Goetz, C. K. (1989), Dusty plasmas in the solar system, *Rev. Geophys.*, *27*, 271–292.

Hargreaves, J. K. (1992), *The Solar-Terrestrial Environment*, *Cambridge Atmos. Space Sci. Ser.*, vol. 5, Cambridge Univ. Press, Cambridge, U. K.

Hartle, R. E., et al. (2006), Initial Interpretation of Titan plasma interaction as observed by the Cassini plasma spectrometer: Comparisons with Voyager 1, *Planet. Space Sci.*, *54*, 1211–1224.

Horanyi, M., T. W. Hartquist, O. Havnes, D. A. Mendis, and G. E. Morfill (2004), Dusty plasma effects in Saturn's magnetosphere, *Rev. Geophys.*, *42*, RG4002, doi:10.1029/2004RG000151.

Hunten, D. M., et al. (1984), Titan, in *Saturn*, edited by T. Gehrels and M. S. Matthews, Univ. of Arizona Press, Tucson.

Keller, H. U., et al. (2006), Microphysical transition of tholin aerosols in Titan atmosphere, *Eos Trans. AGU*, *87*(52), Fall Meet. Suppl., Abstract P21B-04.

Linder, D. R., et al. (1998), The Cassini CAPS electron spectrometer, in *Measurement Techniques in Space Plasmas: Particles*, *AGU Geophys. Monogr. Ser.*, vol. 102, edited by R. E. Pfaff, J. E. Borovsky, and D. T. Young, pp. 257–262, AGU, Washington, D. C.

Moustefaoui, T., et al. (1998), Low temperature electron attachment to polycyclic aromatic hydrocarbons, *Faraday Discuss.*, *109*, 71–82.

Natterer, J., et al. (1994), Combined experimental and theoretical study of the C-H bond strength and the gas phase acidity of triacetylene, C_6H_2, and the electron affinity of the C_6H^* radical, *Chem. Phys. Lett.*, *229*, 429–434.

Wahlund, J. E., et al. (2005), Cassini measurements of cold plasma in the ionosphere of Titan, *Science*, *308*, 986–989.

Waite, J. H., Jr., et al. (2005), Ion neutral mass spectrometer results from the first flyby of Titan, *Science*, *308*, 982–986, doi:10.1126/science.1110652.

Waite, J. H., et al. (2007), The process of tholin formation in Titan's upper atmosphere, *Science*, *316*, 870–875, doi:10.1126/science.1139727.

Wickham-Jones, C. T., et al. (1989), NH_2 electron affinity, *J. Chem. Phys.*, *91*, 2762–2763.

Young, D. T., et al. (2004), Cassini plasma spectrometer investigation, *Space Sci. Rev.*, *114*, 1–112.

Zhang, X., et al. (2006), Remarkable electron accepting properties of the simplest benzenoid cyanocarbons: Hexacyanobenzene, octacyanonaphthalene and decacyanoanthracene, *Chem. Commun.*, *2006*, 758–760, doi:10.1039/b515843e.

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