

Negative ions at Titan and Enceladus: recent results

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Received 30th March 2010, Accepted 14th April 2010

DOI: 10.1039/c004700g

The detection of heavy negative ions (up to 13 800 amu) in Titan's ionosphere is one of the tantalizing new results from the Cassini mission. These heavy ions indicate for the first time the existence of heavy hydrocarbon and nitrile molecules in this primitive Earth-like atmosphere. These ions were suggested to be precursors of aerosols in Titan's atmosphere and may precipitate to the surface as tholins. We present the evidence for and the analysis of these heavy negative ions at Titan. In addition we examine the variation of the maximum mass of the Titan negative ions with altitude and latitude for the relevant encounters so far, and we discuss the implications for the negative ion formation process. We present data from a recent set of encounters where the latitude was varied between encounters, with other parameters fixed. Models are beginning to explain the low mass negative ions, but the formation process for the higher mass ions is still not understood. It is possible that the structures may be chains, rings or even fullerenes. Negative ions, mainly water clusters in this case, were seen during Cassini's recent close flybys of Enceladus. We present mass spectra from the Enceladus plume, showing water clusters and additional species. As at Titan, the negative ions indicate chemical complexities which were unknown before the Cassini encounters, and are indicative of a complex balance between neutrals and positively and negatively charged ions.

1. Introduction

The detection of heavy negative ions (up to 13 800 amu q^{-1}) in Titan's ionosphere is one of the tantalizing new results from the Cassini mission.^{1–3} These heavy ions indicate for the first time the existence of heavy hydrocarbon and nitrile molecules in this primitive Earth-like atmosphere. These ions were suggested^{1,2,4} to be precursors of aerosols in Titan's atmosphere and may precipitate to the surface as tholins.⁵ We present the evidence for and the analysis of these heavy negative ions at Titan. In addition we examine the variation of the maximum mass⁶ of the Titan negative ions with altitude and latitude for the relevant encounters so far, and we discuss

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the implications for the negative ion formation process. We present data from a recent set of encounters where the latitude was varied between encounters, with other parameters fixed. Models are beginning to explain the low mass negative ions,⁷ but the formation process for the higher mass ions is still not understood. It is possible that the structures may be chains, rings or even fullerenes.⁸

Negative ions, mainly water clusters in this case, were seen during Cassini's recent close flybys of Enceladus.⁹ We present mass spectra from the Enceladus plume, showing water clusters and additional species. As at Titan, the negative ions indicate chemical complexities which were unknown before the Cassini encounters, and are indicative of a complex balance between neutrals and positively and negatively charged ions.

The Cassini mission to Saturn has already revealed a wealth of detailed information about Saturn and its moons.^{10,11} It has recently been announced (February 2010) that the mission will continue to explore Saturn's system until 2017, through Saturn's solstice, to allow the first studies of seasonal dependences in the system and gather more detailed data on this complex system.

Of the moons, Titan is unique in the solar system as it is the only moon with a dense, gravitationally bound atmosphere. Orbiting at 20 Saturn radii, it is usually located inside Saturn's magnetosphere though occasionally at or outside the magnetopause.¹² Following Voyager there has been considerable controversy over the role of Titan as a possible source of plasma for the inner magnetosphere. Cassini data have been used to resolve the issue: although important for many reasons in its own right, Titan turns out to be a very minor plasma source for the magnetosphere.

Due to their restriction to the visible wavelength range, the imagers on Voyager were unable to see below Titan's orange, smog-like haze in the atmosphere. The view from Cassini, in particular in the infrared and ultraviolet, has allowed much better remote sensing measurements of the surface through the haze. The haze itself clearly plays an important role in the atmospheric chemistry. *In situ* measurements, including those reported here, are revealing that plasma interactions with Titan's environment may provide the source of the haze.^{1,2,4}

In situ measurements by Cassini at Titan revealed a wealth of chemical complexity in the neutral¹³ and positively charged¹⁴ populations. In addition was the significant and unexpected discovery of heavy (up to 13 800 amu q^{-1}) negative ions in Titan's ionosphere.^{1,2} These ions were suggested^{1,2,4} to be precursors of the aerosols in the atmosphere which had hidden Titan's surface from the Voyager and Earth-based imagers.

In addition to establishing that they are present at all suitable encounters,² further analysis⁸ showed that the largest ions ($\sim 13\,800$ amu q^{-1}) occur at the lowest observed altitudes (950 km). Some dependence on latitude and solar zenith angle is also observed; high masses are seen preferentially at high Titan latitudes and near the terminator. This structure provides some information on the production and destruction processes. The formation of heavy ions is apparently most efficient, or the dissociation processes are least efficient, when sunlight is attenuated or absent. However, it is not yet clear from these observations whether the heavy ions build up in size with decreasing altitude, or whether larger ions, or neutrals which then ionize, are brought upwards from below and then dissociate.

Recently, the first chemical model of Titan's upper ionosphere which included negative ions was provided.⁷ Several production processes were considered and corresponding rates estimated, with the conclusion that the main production process is dissociative electron attachment. The main loss processes were suggested to be associative detachment with some photodetachment. The conclusion was that the main low mass species were CN^- , C_3N^- and C_5N^- .

In order to investigate these processes further, we present data from recent scans in latitude taken during Titan encounters in 2009.

Cassini has also dramatically changed our view of the small icy moon Enceladus orbiting at 4 Saturn radii. It was discovered that strong plumes emanate from warm 'tiger stripe' features on the surface.^{15,16} These plumes of water vapour and ice grains

are thought to be the long-suspected source of particles making up Saturn's E-ring, and also the dominant source for plasma in Saturn's magnetosphere. *In situ* observations here revealed primarily water vapour and trace amounts of hydrocarbon-based neutral gas,¹⁷ as well as water-group -rich positive ions that slow, divert and even stagnate the magnetospheric flow.¹⁸ Directly over the plume sources, charged nanograin populations have been observed that are related to the tiger stripes but dispersed in their motion by Saturn's magnetic field.¹⁹ Negative water group ions, possibly with additional species consistent with hydrocarbons, are also seen.⁹

Here we further investigate the negative ion signatures at Enceladus, showing that multiple peaks are visible up to a multiple of ~ 100 times the mass of a water molecule.

2. Instrumentation

The CAPS electron spectrometer (ELS^{20,21}) is an electrostatic 'top-hat' analyser with a field of view $160^\circ \times 5^\circ$ (divided into 20° 'anode' segments) and an energy resolution ($\Delta E/E$) of 16.7%. It is mounted on top of the CAPS ion mass spectrometer (IMS) which has a similar field of view. Together with the ion beam spectrometer (IBS), the complement of three sensors is mounted on a rotatable actuator which partially compensates for the fact that Cassini is a 3-axis stabilized spacecraft. Operation of the actuator sweeps the fan-shaped fields of view around the spacecraft *z*-axis to increase the angular coverage at the expense of time resolution. During some of the intervals reported at Titan, and all of those at Enceladus, the actuator position was kept fixed near the spacecraft ram direction to improve time resolution and focus on cold particles.

Although designed to measure electrons, the ELS can act as a mass spectrometer for cold populations of negative ions with thermal speeds much less than the spacecraft ram velocity. Within the Titan ionosphere, the spacecraft potential is $V_{sc} \sim -0.5$ V,^{22,23} decelerating the negative ions entering the ELS. During Titan encounters, the relative speed of the spacecraft is ~ 6 km s^{-1} (see Table 1), thus the observed energy per charge E_{eV} ($eV q^{-1}$) can be converted to mass per charge m_{amu} ($amu q^{-1}$) using $m_{amu} = c (E_{eV} - V_{sc})$ with $c = 5.32$ $amu eV^{-1}$ and $V_{sc} = -0.5$ V. The charge q on the ions is assumed to be 1 elementary charge (1.6×10^{-19} C) in this paper, though the charge on the larger ions may be larger than 1 as discussed earlier² which would make the mass even higher. Note that for positive ion measurements the conversion is similar except that the negative spacecraft potential must be added to the observed energy reducing the energy from the observed value, as the positive ions are accelerated by the negative potential. For the Enceladus encounters E3 and E5 the speeds were higher and the values of c were 0.92 and 0.63 $amu eV^{-1}$ respectively, with $V_{sc} \sim -2$ V there.⁹

The CAPS ion beam spectrometer (IBS²⁰) is a crossed fan electrostatic analyser measuring positive ions with an energy resolution ($\Delta E/E$) of 1.7% and a field of view for each fan of $150^\circ \times 1.4^\circ$. It is not designed as a mass spectrometer, but as with ELS cold ion energy spectra such as those in Titan's ionosphere may be converted to mass spectra using $m_{amu} = 5.32 \cdot (E_{eV} + V_{sc})$ in this case. The energy range used during the Titan encounters shown here is 3–207 eV, and we use data from one of the fans. At Enceladus, the ion populations are more fully covered by IMS.¹⁸

CAPS includes a third sensor, the Ion Mass Spectrometer (IMS). This sensitive mass spectrometer was not designed for the intense cold ionospheric plasma at Titan; it therefore saturates near closest approach to Titan and data are not shown in this paper. Enceladus data from IMS are shown elsewhere.¹⁸

3. Titan

At Titan, negative ions are always seen in CAPS electron spectrometer data during flybys below ~ 1400 km whenever CAPS ELS is orientated in the ram direction.^{2,6}

Table 1 Encounter parameters for the flybys shown in this paper

	Date DOY	UT	Minimum altitude/km	Local time		Latitude ($^{\circ}$ N)	Relative velocity/km s $^{-1}$	Solar zenith angle SZA ($^{\circ}$)	Cassini in Titan shadow (night)
				Saturn (hh : mm)	Titan (hh : mm)				
T16	22/7/06 203	00 : 25 : 26	949.9	17 : 06	02 : 27	85.38	5.97	105.32	no
T55	21/5/09 141	21 : 26 : 41	965.7	21 : 53	21 : 57	-21.87	5.99	141.52	yes
T56	06/6/09 157	20 : 00 : 00	967.7	21 : 50	21 : 55	-31.93	5.99	135.06	yes
T57	22/6/09 173	18 : 32 : 35	955.0	21 : 46	21 : 52	-42.00	5.99	127.83	no
T58	08/7/09 189	17 : 04 : 03	965.8	21 : 42	21 : 50	-52.06	5.99	120.16	no
T59	24/7/09 205	15 : 34 : 03	956.2	21 : 36	21 : 47	-62.11	5.99	112.16	no

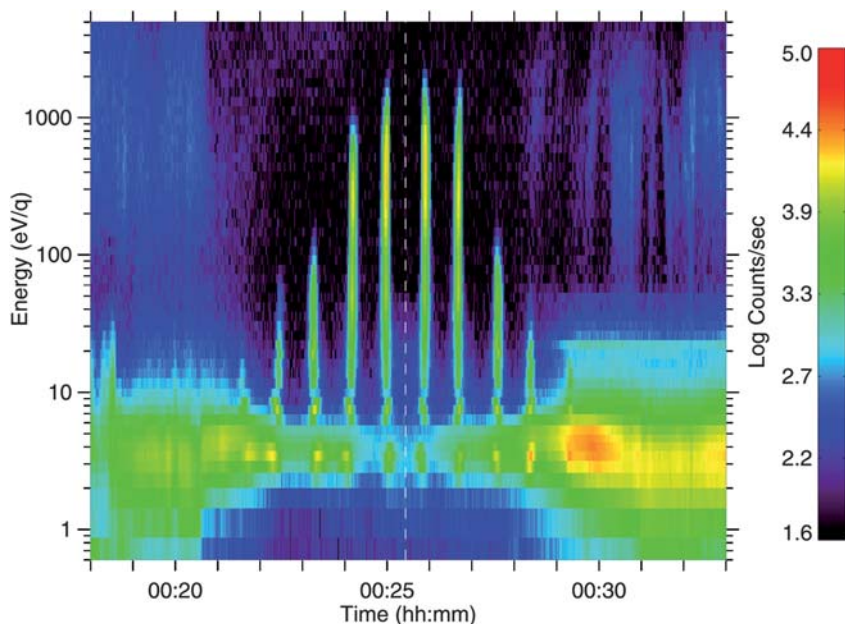


Fig. 1 CAPS ELS spectrogram for 25 min around closest approach during the T16 encounter. Count rate averaged over all anodes is colour scaled as a function of energy per charge (vertical axis) and time (horizontal axis). The vertical ‘spikes’ and associated peaks are identified as negative ions seen as the CAPS actuator sweeps the ELS field of view through the ram direction. Ionospheric electrons are seen below ~ 30 eV and magnetospheric electrons above this energy. During this encounter the highest mass ions so far (13) $800 \text{ amu } q^{-1}$, corresponding to $\sim 2500 \text{ eV } q^{-1}$ were seen. Closest approach is indicated by a white dashed line.

The altitude and latitude dependence of the high-mass negative ions was recently examined,⁶ and it was found that the maximum negative ion mass was higher at low altitude and at high latitudes. In addition, a weaker dependence of the maximum mass on solar zenith angle was found, though clearly illumination conditions were found to be important. The maximum ion mass ($13\,800 \text{ amu } q^{-1}$) was observed during Cassini’s T16 Titan encounter, the lowest closest approach altitude to date. The ELS results from this encounter are shown in Fig. 1. Count rate (proportional to differential energy flux) is colour-coded in this energy spectrogram. The plot covers 25 min centred on the 950 km closest approach, and the altitude at the beginning and end of the plot is ~ 1800 km inbound and outbound in this case. A succession of negative ion ‘spikes’ is seen as the CAPS actuator sweeps the field of view through the ram direction, sampling the cold negative ion population. Each spike contains a number of discrete peaks in energy, which we interpret as different mass groups of negative ions. The maximum energy, and thus the maximum observed mass, increases towards closest approach. Note that during this particular encounter, the measured energies in IBS were unfortunately too low to determine the maximum positive ion mass, though lower mass spectra were observed, thus the IBS data are not shown here.

Further encounters were analysed,⁶ and variations of the maximum negative ion mass with altitude, latitude and solar zenith angle were examined. It was suggested that the formation of the heaviest negative ions is most efficient, and/or the dissociation processes, including photodissociation and associative detachment, are less efficient, during times when sunlight is attenuated or even absent. However, as chemical growth is more usually associated with increased energy from sunlight,

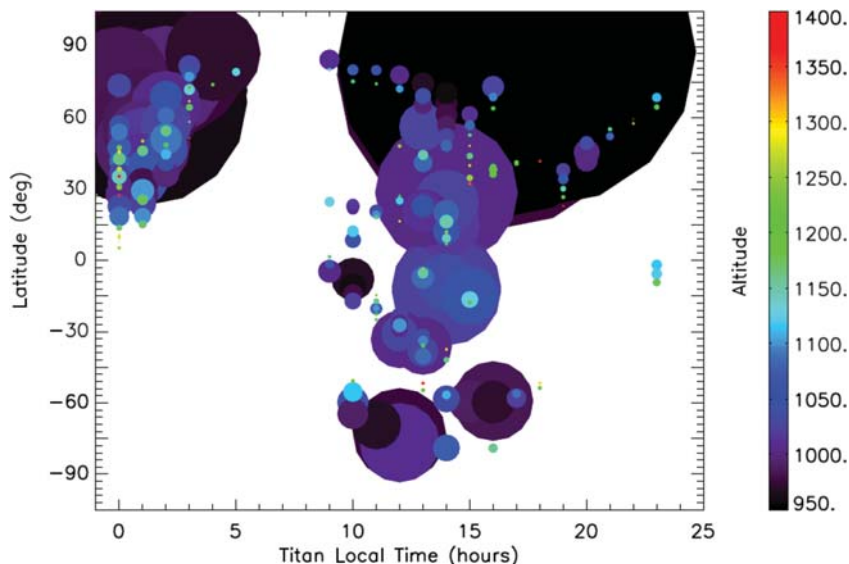


Fig. 2 Negative ion observations during 23 Titan encounters between TA and T48.⁶ The circles represent a negative ion observation (radius proportional to mass). The circles are colour coded with altitude and plotted with respect to Titan latitude and local time.

another possibility is growth of particles on the day side and transport to the night side. Also, the production process for the heavy negative ions is more efficient at low altitudes, where the ambient electron density and total ion and neutral densities are high (at least two out of these three conditions are required). This, and the trend in mass with decreasing altitude, suggests that even heavier ions may exist at even lower altitudes and that the ions we observe may be the precursors of the aerosols, perhaps tholins (organic aerosols), observed in the atmosphere during UV occultations.²⁴ The heavy negative ions may thus ultimately be the source of particles forming Titan's haze layers at several hundred km. A summary of the altitude and latitude data is shown in Fig. 2 (from⁶).

New results from Titan are shown in Fig. 3. These data are from a recent sequence of encounters where many of the parameters of the encounters remained similar, but a range of Titan latitudes was covered (see Table 1). However the illumination conditions do vary during these encounters, with the solar zenith angle (SZA) varying between 142° and 112° at the different closest approaches; during each individual encounter the illumination conditions also vary substantially. In addition, the actuator angle was kept fixed in the ram direction to provide better altitude resolution.

For each latitude, Fig. 3 shows a pair of plots covering 20 min centred on closest approach while CAPS was measuring the ionosphere of Titan. In each case the minimum altitude is 955–975 km (see Table 1) and the plots start at 2150–2400 km altitude and end at 2350–2650 km. The upper panel shows the ELS energy spectra from 0.6–2,000 eV. The colour scale shows the count rate (proportional to differential energy flux) measured by ELS. In these plots, the population between ~20–1000 eV at the beginning and end of each plot corresponds to magnetospheric electrons. In each of the plots this population diminishes towards closest approach, corresponding to absorption of the magnetospheric electrons by the ionosphere of Titan. The population below ~10 eV corresponds to the ionospheric electrons. In each case, centred around closest approach, a succession of peaks is seen with energy, corresponding to the negative ion population. As mentioned above, the

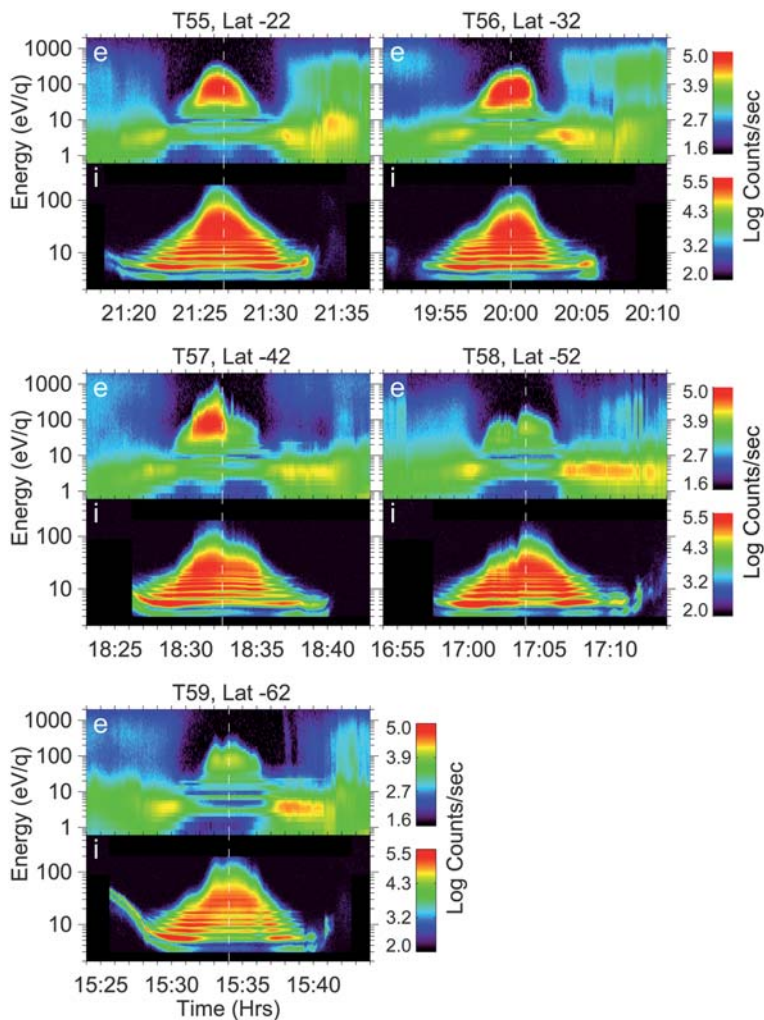


Fig. 3 CAPS ELS and IBS data for T55-59, representing a scan in Titan latitude (see text). Each panel shows ELS data averaged over all anodes (upper panel) and IBS data from fan 2 (lower panel) for 20 min around closest approach, which is indicated as a white dashed line in each case.

ram velocity of the spacecraft, combined with the energy analysis provided by ELS, acts as a mass spectrometer, and the observed energy of the spectral features can be converted to mass per charge using $m_{\text{amu}} = 5.32 \cdot (E_{\text{eV}} - V_{\text{sc}})$. In each case the maximum mass of the negative ions increases towards closest approach, which corresponds to the deepest penetration into the ionosphere.

The lower panel in each case shows the positive ion data from the IBS from 20 eV to 500 eV (upper energy of the instrument is 207 eV as used here). A series of peaks is seen, with an increase in the maximum energy seen towards closest approach. The energy peaks are interpreted as positive ions, with $m_{\text{amu}} = 5.32 \cdot (E_{\text{eV}} + V_{\text{sc}})$ in this case. Thus the maximum mass of the positive ions also increases towards closest approach reaching beyond 350 $\text{amu } q^{-1}$ as previously observed^{1,23} reaching >1000 $\text{amu } q^{-1}$ in several of these cases.

Comparing the plots at different latitudes reveals several notable features:

1. The maximum negative ion mass appears during T57 at a latitude of -42° and where the solar zenith angle (SZA) is $\sim 128^\circ$.

2. The maximum positive ion mass was during T55; features are seen up to the highest energies observable by IBS ($207 \text{ eV } q^{-1}$, corresponding to $\sim 1100 \text{ amu } q^{-1}$), during this encounter. For T55, the latitude is -22° , the solar zenith angle is $\sim 142^\circ$ and the ionosphere is in shadow.

3. The positive and negative ion peak intensities are not always symmetrical about closest approach: during T56 and T58 for example, the maximum appears after closest approach, whereas during T57 the maximum intensity appeared before closest approach. T55 and T59 appear more symmetrical. This is probably due to the different illumination conditions before and after closest approach.

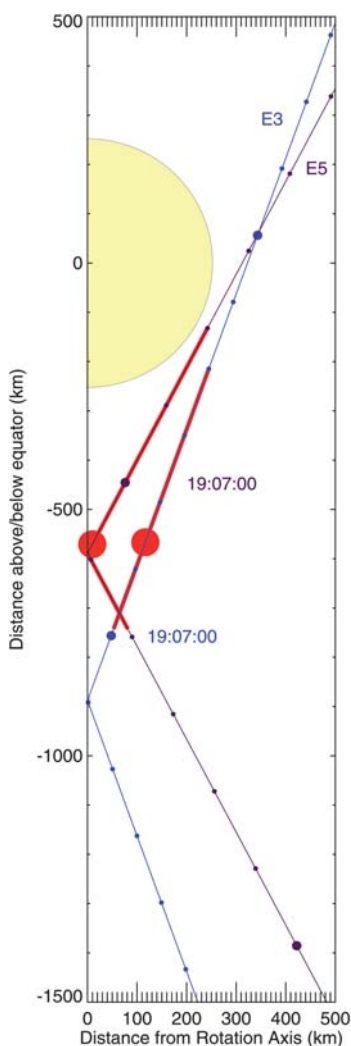


Fig. 4 Geometry of the spacecraft trajectory during the E3 and E5 Enceladus encounters. The overlaid red bars show the times during which negative ions were seen, and the red filled circles indicate the locations of the spectra in Fig. 5 and 6 respectively.

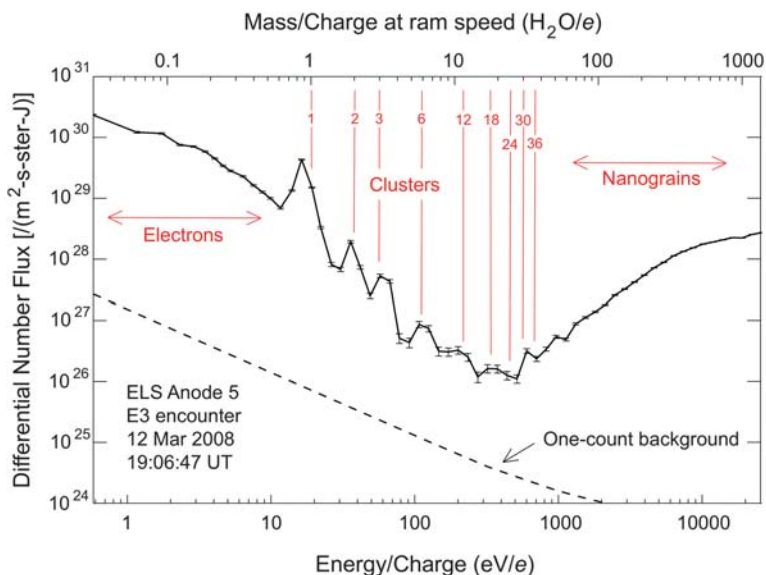


Fig. 5 CAPS ELS spectrum at 19 : 06 : 47 UT during the E3 encounter, plotted as differential number flux. The negative ion peaks are superimposed on electron and charged nanograin populations. The mass is also shown (details of conversion in the text) and multiples of $18 \text{ amu } q^{-1}$ are indicated.

4. During some of the encounters, *e.g.*, T57 (outbound) and T58 (inbound), there are significant time variations in the negative ion intensity, usually correlated with positive ion intensity.

5. At the beginning of the T55 and T59 IBS plots, and at the end of all of the IBS plots, the low mass peaks appear to increase in energy, perhaps due to an increase in the negative spacecraft potential at these times.

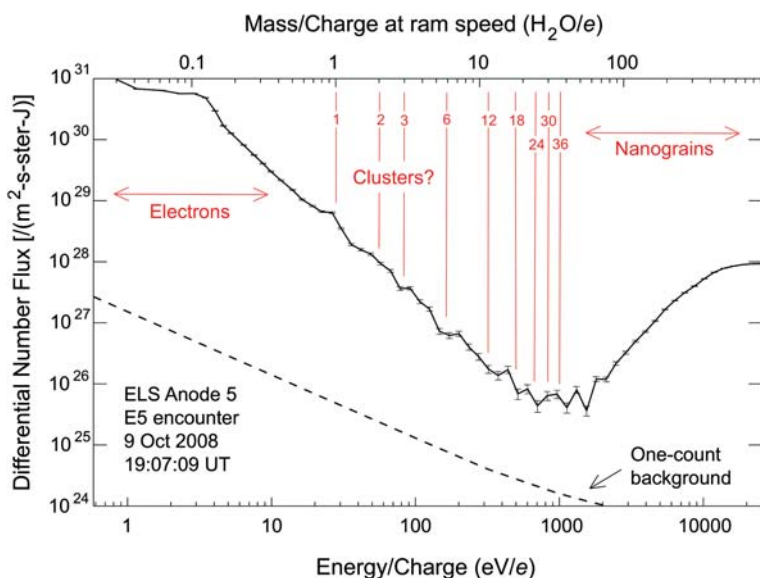


Fig. 6 As Fig. 5 but for the E5 encounter at 19 : 07 : 09 UT.

While it is difficult from these plots alone to reveal additional systematic trends beyond those observed already,⁵ it is clear that there are significant differences between the different encounters. Moreover, the role of illumination, altitude and latitude are seen to be critical to the observation of high mass negative ions, confirming the earlier results.⁶ Individual analyses of the encounters are however beyond the scope of the current paper.

4. Enceladus

Analysis of negative ion spectra during the E3 encounter⁹ showed negative ion peaks in the spectra that plausibly correspond to water cluster ions. Here, we examine individual spectra from the E3 and E5 encounters, when the ELS was oriented in the ram direction, at the times of the maximum intensity of the negative ion peaks.

Fig. 4 illustrates the geometry with respect to Enceladus, indicating in particular the locations where negative ions were seen (red bars along the trajectories). The negative ions were observed well within the plume in both cases, and the times of the presented spectra are indicated by a filled red circle.

Fig. 5 shows an ELS spectrum from the E3 encounter. In each case, a negative ion spectrum is superimposed on the ambient electron population (at low energies, *cf.*^{9,18}) and a negatively charged dust population at high energies.¹⁹ The negative ion population indicates peaks at multiples of the mass of water, though due to the energy resolution ($\Delta E/E = 16.7\%$) of the ELS, the ions could also be OH⁻ and multiples thereof. What is particularly notable is that not all multiples are present, 1,2,3 and 6 at low masses, and then multiples of 6 up to 30 and perhaps higher up to ~ 100 .

In Fig. 6 we present a spectrum from the E5 encounter. This also shows evidence for narrow peaks, at multiples of the mass of a water molecule, similar to the E3 encounter. Some of the peaks seen on E3 are absent in the E5 data, and the low mass peaks in particular are not as prominent in this case. The peaks which were observed are, however, statistically significant beyond the electron and charged dust nanograin spectra.

In both Fig. 5 and 6, not all of the observed peaks correspond with water (or OH) multiples, indicating that other ions could be present.

5. Discussion

Chemical modeling⁷ successfully predicts the presence of low mass species of negative ions at Titan, consistent with our measurements. However the larger ions are at present unexplained and the following open questions for discussion emerge:

- What are the formation mechanisms for the large negative ions?
- What are the destruction mechanisms for the large negative ions?
- What is the lifetime of the ions?
- Sunlight clearly plays a key role in determining the maximum negative ion mass, but does it control production, or loss, or the balance between the two?
 - Do the ions formed in Titan's high ionosphere subsequently fall towards the surface, or are they formed at lower altitudes and somehow transported upwards?
- Are the large ions the precursors for material that ultimately reaches the surface and modifies the surface features?
 - Are the large ions chains, rings or even fullerenes?⁸
 - Are the formation and loss processes for the low mass ions sufficiently explained?⁷
- What is the role of the negative ion processes in the coupled scheme between neutrals and ions in Titan's upper atmosphere?
 - Are the negative ions picked up by the co-rotating plasma in a process analogous to that for positive ion pickup?
 - Are there negative ions in the magnetosphere?

The water cluster ion observations at Enceladus also led to some questions, including

- What is the dominant formation process?
- What is the dominant loss process?
- What is the lifetime of these ions in the plume?
- What is the source of the ions – ice grains and gas in the plume, or the surface or sub-surface of Enceladus, or both?
- Why are some multiples of negative water (or OH) ions absent?
- What is the relation between the observed negative ions and neutral and charged ice grains?
- Are there other ions present in addition to water? Can they be identified?
- What are the coupling processes between neutrals, positive ions and negative ions in the plume of Enceladus?

Some of the Enceladus topics are being addressed by current work in the CAPS team (*e.g.* the relationship between the negative ion and charged nanograin population, Hill *et al.*, in preparation), but additional discussion would also be welcomed.

6. Summary and conclusions

In summary, negative ions are always observed at Titan below 1400 km. The ions exhibit resolved low mass peaks and a broader mass group structure at higher masses. The variation of their maximum mass with altitude, latitude and solar zenith angle were studied.⁵ Currently, studies are underway to determine the dependence of density on similar parameters, though this is currently limited by the lack of knowledge of the detector efficiency for high mass ions, since the ELS was designed and calibrated for electrons.

In addition, negative ions are seen in the Enceladus plume during the E3 and E5 encounters. The ions are observed at multiples of the mass of water molecules (or hydroxyl radicals). Their location is well within the plume, indicating a short lifetime.

Negative ions at Titan and Enceladus represent two of the unexpected discoveries of the Cassini mission. While some work reported here has been done to characterize the populations and to explain them, there is a need for additional chemical modeling and process identification, particularly for the higher mass ions at both Titan and Enceladus.

Acknowledgements

We thank the CAPS and ELS operation teams, the STFC in the UK and NASA/JPL contract 1243218, for financial support of the CAPS investigation.

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