Negative ions at Titan: tholins for Titan’s haze?

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With thanks to Frank Crary, Dave Young, Hunter Waite, SwRI, Gethyn Lewis MSSL
Plasma environment:

<table>
<thead>
<tr>
<th></th>
<th>Density (cm⁻³)</th>
<th>Temperature (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetosphere</td>
<td>0.1-1</td>
<td>100-1000</td>
</tr>
<tr>
<td>Solar wind (few %)</td>
<td>&lt;0.1</td>
<td>few</td>
</tr>
</tbody>
</table>

Titan:

Radius 2575 km

Atmosphere: mostly $N_2$, some $CH_4$ (~5% near surface),...

Unmagnetized object with an ionosphere

Haze in atmosphere, dunes, evidence for lakes and for recent surface modification
Solar radiation
**CAPS instrument**

- Three sensors + DPU, actuator

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Measures</th>
<th>Energy range (eV/q)</th>
<th>Energy resolution ($\Delta E/E$, %)</th>
<th>Angle range ($^\circ$)</th>
<th>Angle bin ($^\circ$)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ion mass spectrometer (IMS)</strong></td>
<td>Ion mass, energy and direction</td>
<td>1-50,000</td>
<td>17</td>
<td>160x8</td>
<td>20x8</td>
</tr>
<tr>
<td><strong>Ion beam spectrometer (IBS)</strong></td>
<td>Narrow ion beams; energy and direction</td>
<td>1-50,000</td>
<td>1.4</td>
<td>150x1.4</td>
<td>1.5x1.4</td>
</tr>
<tr>
<td><strong>Electron spectrometer (ELS)</strong></td>
<td>Electron energy and direction</td>
<td>0.6-28,000</td>
<td>17</td>
<td>160x5</td>
<td>20x5</td>
</tr>
</tbody>
</table>
Negative ions in ionospheres

- Negative ions present in Earth’s ionosphere (electronegative species e.g. O⁻)
- Have also been seen in inner coma of comet Halley, mass 7-19, 22-65 and 85-110 amu (Chaizy et al, Nature 349, 393-396, 1991)
- At the comet, charge exchange processes produce positive and negative ions
- Suspected at Europa
- Negative ions were not expected high in Titan’s ionosphere – electronegative species not anticipated – but were expected lower
Titan interaction

Adapted from Blanc et al, 2002
Electric field always away from Saturn

Titan always has same face to Saturn
CAPS ELS overview near Ta
Rev 00A Titan (TA)  Inbound
2004–300T15:30:23

Altitude 1200 km
△ Closest approach
○ Inbound Leg
5 minute ticks
Sun direction
Saturn direction
Woke

E  Saturn

Sun
Corotating
flow
CAPS ELS high resolution data 

E Dad 

Saturn 

Negative ions (ram direction) 

Ionospheric photoelectrons 

Cold plasma
CAPS IBS ions

CAPS ELS electrons

Negative ions
Conversion of energy to negative ion mass

\[ \frac{1}{2} m_{amu} m_p v^2 = qE_{eV} \]

or

\[ m_{amu} = \frac{2qE_{eV}}{m_p v^2} \]

For Cassini Titan encounters,

\[ m_{amu} \approx 5.32E_{eV} \]
Ta spectrum at 15:28:42
Ta spectrum at 15:28:42
Evidence that these are negative ions

- In ram direction
- Narrow distributions in energy and angle
- Cannot be electrons – would have to be highly non-gyrotropic and seen several times
- Instrumental effects (e.g. discharge, scattering, etc) ruled out

Observed as mass groups 10-30, 30-50, 50-80, 80-110, 110-200, (200-500, 500+)
Confirmed in more recent low altitude encounters

Titan negative ions
- Unexpected!
- Ram direction
- Near closest approach

Originally seen on TA in 2004...
T16
953 km
Charge on these large ions

- ELS measures energy/q – what is q?
- 10,000 amu ions are the size of aerosols (~10 - 30 nm).
- Assuming $T_e \sim 1000 K$ and $n_e \sim 1 \times 10^3 \text{cm}^{-3}$, $\lambda_D \sim 0.07 \text{m}$
- ~30nm grains would assume a potential (Goetz, 1989) of $\varphi \sim -2.5 kT_e/e \sim -0.25 \text{ V}$
- Charge given by $Q = 4\pi \varepsilon_0 a \varphi e x p(-a/\lambda_D)$
- Corresponds to ~5 electrons
- Actual mass could then be ~50,000 amu!
Using ram assumption to calculate density
Total density \( \sim 200 \text{ cm}^{-3} \) (T16)
## Possible negative ions

<table>
<thead>
<tr>
<th>Mass group (amu/q)</th>
<th>Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-30</td>
<td>CN(^{-}), NH(_2)^{-}, O(^{-})</td>
</tr>
<tr>
<td>30-50</td>
<td>NCN(^{-}), HNCN(^{-}), C(_3)H(^{-})</td>
</tr>
<tr>
<td>50-80</td>
<td>C(_5)H(_5)^{-}, C(_6)H(^{-}), C(_6)H(_5)^{-}</td>
</tr>
<tr>
<td>80-110</td>
<td>Polyyynes, high order nitriles, PAHs, cyano-aromatics</td>
</tr>
<tr>
<td>110-200</td>
<td></td>
</tr>
<tr>
<td>200-500</td>
<td></td>
</tr>
<tr>
<td>500-10,000</td>
<td></td>
</tr>
</tbody>
</table>
Observed on 16 encounters between Ta & T36

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

<table>
<thead>
<tr>
<th>Date</th>
<th>DOY, UT</th>
<th>Altitude (km)</th>
<th>Local time Saturn (hh:mm)</th>
<th>Local time Titan (hh:mm)</th>
<th>Latitude (°N)</th>
<th>Relative velocity (km s⁻¹)</th>
<th>Solar zenith angle (sza°)</th>
<th>Cassini in Titan shadow (night)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta (in)</td>
<td>26/10/04</td>
<td>300, 15:30</td>
<td>1174</td>
<td>10:36</td>
<td>16:45</td>
<td>38.78</td>
<td>6.05</td>
<td>91.00</td>
</tr>
<tr>
<td>T16 (in)</td>
<td>22/7/06</td>
<td>203, 00:25</td>
<td>950</td>
<td>02:27</td>
<td>17:17</td>
<td>85.15</td>
<td>5.97</td>
<td>105.32</td>
</tr>
<tr>
<td>T17 (in)</td>
<td>7/9/06</td>
<td>250, 20:17</td>
<td>1000</td>
<td>02:20</td>
<td>10:28</td>
<td>22.82</td>
<td>5.96</td>
<td>44.54</td>
</tr>
<tr>
<td>T18 (in)</td>
<td>23/9/06</td>
<td>266, 18:59</td>
<td>960</td>
<td>02:17</td>
<td>14:24</td>
<td>70.92</td>
<td>5.96</td>
<td>89.81</td>
</tr>
<tr>
<td>T19 (in)</td>
<td>9/10/06</td>
<td>282, 17:30</td>
<td>980</td>
<td>02:14</td>
<td>14:20</td>
<td>60.75</td>
<td>5.96</td>
<td>80.96</td>
</tr>
<tr>
<td>T20 (in)</td>
<td>25/10/06</td>
<td>298, 15:58</td>
<td>1029</td>
<td>02:12</td>
<td>11:10</td>
<td>6.36</td>
<td>5.96</td>
<td>24.65</td>
</tr>
<tr>
<td>T21 (in)</td>
<td>12/12/06</td>
<td>346, 11:41</td>
<td>1000</td>
<td>02:03</td>
<td>20:20</td>
<td>43.12</td>
<td>5.96</td>
<td>125.18</td>
</tr>
<tr>
<td>T23 (in)</td>
<td>13/1/07</td>
<td>013, 08:39</td>
<td>1000</td>
<td>01:57</td>
<td>14:01</td>
<td>30.68</td>
<td>5.96</td>
<td>53.28</td>
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<tr>
<td>T25 (out)</td>
<td>22/2/07</td>
<td>053, 03:12</td>
<td>1000</td>
<td>13:51</td>
<td>00:34</td>
<td>30.35</td>
<td>6.23</td>
<td>161.24</td>
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<tr>
<td>T26 (out)</td>
<td>10/3/07</td>
<td>069, 01:49</td>
<td>981</td>
<td>13:49</td>
<td>01:45</td>
<td>31.70</td>
<td>6.23</td>
<td>149.50</td>
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<tr>
<td>T27 (out)</td>
<td>26/3/07</td>
<td>085, 00:23</td>
<td>1010</td>
<td>13:46</td>
<td>01:42</td>
<td>40.93</td>
<td>6.23</td>
<td>144.13</td>
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<tr>
<td>T28 (out)</td>
<td>10/4/07</td>
<td>100, 22:58</td>
<td>991</td>
<td>13:43</td>
<td>01:39</td>
<td>50.17</td>
<td>6.23</td>
<td>137.37</td>
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<tr>
<td>T29 (out)</td>
<td>26/4/07</td>
<td>116, 21:33</td>
<td>980</td>
<td>13:41</td>
<td>01:36</td>
<td>59.38</td>
<td>6.23</td>
<td>129.81</td>
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<tr>
<td>T30 (out)</td>
<td>12/5/07</td>
<td>132, 20:10</td>
<td>959</td>
<td>13:38</td>
<td>01:32</td>
<td>68.61</td>
<td>6.23</td>
<td>121.71</td>
</tr>
<tr>
<td>T32 (out)</td>
<td>13/6/07</td>
<td>164, 17:46</td>
<td>965</td>
<td>13:35</td>
<td>01:17</td>
<td>84.46</td>
<td>6.23</td>
<td>107.00</td>
</tr>
<tr>
<td>T36 (out)</td>
<td>2/10/07</td>
<td>275, 04:42</td>
<td>975</td>
<td>11:29</td>
<td>16:08</td>
<td>−59.90</td>
<td>6.31</td>
<td>67.40</td>
</tr>
</tbody>
</table>

°For SZA > 100°, sunlight will be highly attenuated by Titan’s atmosphere.

See Coates et al, GRL Nov 07
...and on 6 more recent encounters

<table>
<thead>
<tr>
<th>Date z</th>
<th>UT z</th>
<th>Altitude z (km) z</th>
<th>Local z time z Saturn z (hh:mm) z</th>
<th>Local z time z Titan z (hh:mm) z</th>
<th>Latitude z (°N) z</th>
<th>Relative z velocity z (km s⁻¹) z</th>
<th>Solar z zenith angle z SZA z (°) z</th>
<th>Cassini in z Titan z shadow z (night) z</th>
</tr>
</thead>
<tbody>
<tr>
<td>T37 z</td>
<td>19/11/07 z</td>
<td>partial z</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T39 z</td>
<td>20/12/07 z</td>
<td>22:58 z</td>
<td>970 z</td>
<td>11:30 z</td>
<td>11:22 z</td>
<td>-70 z</td>
<td>6.33 z</td>
<td>61.4 z</td>
</tr>
<tr>
<td>T40 z</td>
<td>05/1/08 z</td>
<td>21:30 z</td>
<td>1010 z</td>
<td>14:32 z</td>
<td>11:20 z</td>
<td>-12 z</td>
<td>6.32 z</td>
<td>37.5 z</td>
</tr>
<tr>
<td>T41 z</td>
<td>22/2/08 z</td>
<td>17:32 z</td>
<td>1000 z</td>
<td>13:00 z</td>
<td>11:13 z</td>
<td>-35 z</td>
<td>6.34 z</td>
<td>30.2 z</td>
</tr>
<tr>
<td>T42 z</td>
<td>25/3/08 z</td>
<td>14:28 z</td>
<td>1000 z</td>
<td>12:36 z</td>
<td>11:07 z</td>
<td>-27 z</td>
<td>6.35 z</td>
<td>21.4 z</td>
</tr>
<tr>
<td>T43 z</td>
<td>12/5/08 z</td>
<td>10:02 z</td>
<td>1000 z</td>
<td>13:44 z</td>
<td>10:59 z</td>
<td>18 z</td>
<td>6.33 z</td>
<td>35.8 z</td>
</tr>
</tbody>
</table>
Encounters where negative ions are seen
Highest masses at low altitudes

...so may descend through atmosphere
Highest masses at high latitudes

...so may be larger if less sunlit
Highest masses near terminator

...so may be larger if less sunlit
Titan’s atmosphere: hydrocarbon-rich.

Effect on surface? E.g., dunes...

Heavy neutrals and positive ions: Waite et al., 2007.

Unexpected heavy negative ions: Coates et al., 2007.
Recent relevant work

- **Additional supporting evidence:** UVIS stellar occultation measurements supportive of heavy organics to >1000 km (Shemansky et al, 2006, Liang et al, 2007)

- **Additional supporting evidence:** discrepancy of $\sim 10^3$ cm$^{-3}$ between RPWS-LP ($n_e$) and INMS ($n_i$) density measurements on encounters where we see negative ions (Wahlund et al, personal communication) explained by our negative ion density observations

- **Theoretical approach:** heavy positive ions from lower altitudes ions may be levitated at higher altitudes by upward pointing, ambipolar electric fields in the homosphere (Gombosi et al). Heavy species can then acquire negative charge and are accelerated downwards
What are tholins?

• Term “tholin” coined by Sagan and Khare, 1979
• Products from energetic processing of mixtures of gases such as CH$_4$, N$_2$, and H$_2$O.
• Tholin from Greek for “muddy”
• Brownish, sticky residues formed by extensions of the Miller-Urey experiment (Miller and Urey, 1953) to simulate early Earth atmosphere.
• Can use electrical discharges or ultraviolet radiation
• Sagan and others tried to simulate the atmospheres of planets and moons, e.g. Titan, Triton (McDonald, et al., 1994) and Jupiter (Khare and Sagan, 1975).
Enceladus – actuator fixed

Negative ions also seen at Earth, comets, Titan; Europa?

Electrons

Positive ions

Negative ions $\sim 16$-500 amu

Ice grains
Conclusions

• Negative ions seen on 22 Titan encounters so far, when CAPS sees ram direction and altitude is low enough
• Lower mass groups similar at all encounters
• Extremely high masses (few thousand AMU) on T16
• Significant in upper atmosphere chemistry
• Higher mass negative ions are observed preferentially:
  • At low altitudes, with the highest mass ions (~10,000 amu) at 950 km (Cassini’s lowest altitude so far)
  • At high Titan latitudes
  • In the region of the terminator
• Early stage of tholins formation c.f. Sagan and colleagues?
• Links plasma interaction directly with the surface
• Waite et al, Science May 07, Coates et al, GRL Nov 07
• Also at Enceladus?