Enceladus: A potential source of ammonia products and molecular nitrogen for Saturn’s magnetosphere

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1. Introduction

[1] The detection of nitrogen species in Saturn’s magnetosphere could, in principle, provide clues to the origin and evolution of its satellites and tenuous rings. Smith et al. (2005) first identified low-energy N+ using the Cassini Plasma Spectrometer (CAPS). N+ was predominantly seen in the Saturn’s inner magnetosphere (<~14 Rs), indicating an Enceladus nitrogen source rather than the expected Titan source. However, the parent molecular species was not confirmed. Subsequent modeling showed that a small N2 source at Enceladus consistent with ion neutral mass spectrometer observations could produce the observed spatial distribution of N+. Considering the significance of understanding the Enceladus plumes, identifying the molecular parent for the observed N+ (N2 or NH3) can provide clues to the subsurface composition of Enceladus and the processes generating this plume activity. In this paper, we expand on the work of Smith et al. (2007) to identify the source molecules for nitrogen ions detected in Saturn’s inner magnetosphere. We conduct an extensive study of all available CAPS data to determine if N2+ or ammonia is the parent molecule for these nitrogen ions. We present evidence for the detection of product ions (NH2+), likely from ammonia, and provide upper limits on the amount of N2 that may be present in the plasma in the inner magnetosphere.


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Modeling the N$^+$ density variation with distance from Saturn and the N$^-$ to water ion density ratio using data from a number of Cassini orbits, Smith et al. [2007] confirmed their earlier suggestion that Enceladus was the likely source of the observed nitrogen ions. These authors also attempted to model the parent molecule of these ions. During a close fly-by of Enceladus, the Cassini ion neutral mass spectrometer (INMS) detected neutral particles with an atomic mass of 28 in the plumes [Waite et al., 2005] at about a 4% relative amount. However, whether this was N$_2$ or CO could not be determined, although constraints based on Cassini Visual and Infrared Mapping Spectrometer (VIMS) and Ultraviolet Imaging Spectrograph (UVIS) observations suggested that N$_2$ was the most likely candidate [Waite et al., 2006]. Smith et al. positively detected N$^+$ but not N$_2^+$, while the INMS observations reported atomic mass 28 but not 14. Because the N$_2$ dissociation lifetime is shorter than its ionization lifetime, modeling showed that a small N$_2$ source at Enceladus could produce the observed spatial distribution of N$^+$ without an obvious N$_2^+$ detection because it is extremely difficult to detect such small amounts of N$_2^+$ using CAPS IMS.

The physical processes producing Enceladus plume activity are not well understood. Possible mechanisms range from tidal heating [Nimmo and Pappalardo, 2006] to the presence of subsurface ammonia (NH$_3$) which would lower the melting point of a hypothetical reservoir of water ice [Stevenson, 1982; Squyres et al., 1983; Matson et al., 2007]. Therefore establishing the presence or absence of NH$_3$ is critical for understanding the nature of the plume source. No confirmed ammonia detection at Enceladus has yet been reported. Lack of detection might not be surprising, however, because NH$_3$ should be present in only small amounts [Verbiscer et al., 2006] and direct observation by reflectance in the surface ice is hindered because it is a volatile species that can be depleted thermally or by sputtering [Lanzerotti et al., 1984]. Given the volatility of ammonia and the relatively large neutral densities required for direct Cassini INMS observation of NH$_3$ ($>10^4$/cm$^3$, Waite et al., 2004), CAPS IMS observations are critical because they are capable of detecting small amounts [as low as 10$^{-5}$/cm$^3$, Young et al., 2005] of ammonia product ions (NH$_3^+$ where x = 1–4).

Identifying the molecular parent for the observed N$^+$ (N$_2$ or NH$_3$) can therefore provide clues to the subsurface composition of Enceladus and the processes generating this plume activity. In this study, we present the results of a comprehensive examination of CAPS IMS data that indicates the presence of NH$_3^+$ as well as support for the presence of N$_2^+$, two species that are indicative of the parent molecules for the N$^+$ observed in Saturn’s inner magnetosphere.

2. Ammonia Products

Given the potential significance presented by the absence or presence of ammonia in Saturn’s inner magnetosphere detection of NH$_3^+$ is very important. The INMS placed upper limits on neutral ammonia detection in the Enceladus plume of 0.5% [Waite et al., 2006]. Considering these relatively small concentrations, detection of neutral ammonia molecules away from the plume itself is expected to be very difficult. However, products formed from the ionization/charge exchange of neutral ammonia might be detectable at relatively low densities by the CAPS.

The CAPS IMS measures ion TOF using two methods each with its own detector: the Straight-Through (ST) and the Linear Electric field (LEF). The ST is relatively more sensitive but has lower mass resolution (M/dM $\sim$8). Lower mass resolution is appropriate for many species, but not sufficient for this study because ammonia products are located in the same area of the TOF spectrum as the much more abundant water-group ions that dominate Saturn’s magnetosphere. This characteristic makes it very difficult to separate ammonia ions with any significant confidence level.

The LEF detector has much better mass resolution, however with a lower efficiency than the ST detector. In the LEF detector, the N$^+$ spectral peak is well resolved from products in the water group peak. Additionally, the signal from nitrogen ions derived from ammonia products form a shoulder on the atomic N$^+$ peak that can theoretically be resolved. Therefore, although detection is challenging, mass resolution is sufficient to identify the presence of ammonia products. Unfortunately, even with this better mass resolution, the signals are so low that it is difficult to conclusively identify ammonia when the relative abundance of ammonia to N$^+$ is less than $\sim$50%.

We have developed a method to analyze spectra accumulated over long periods of time in such a way that we can confidently identify the presence or absence of relatively small amounts of ammonia products. In particular, the LEF detector is constructed such that atomic species have narrow TOF peaks while molecular species have noticeably wider peaks. This is due to the angular and energy straggling that occurs when molecules break up into atomic fragments as they pass through the carbon foil that is the basis of the IMS TOF measurement [Young et al., 2004]. The N$^+$ spectra peak [Smith et al., 2005, 2007] is relatively narrow if it is produced only by atomic nitrogen ions. However, earlier, Smith et al. [2007] pointed out that in fact the N$^+$ peak is wider than predicted for a pure atomic N$^+$ source. If one assumes that contributions from molecular species widen the N$^+$ peak, then peak width analysis provides a method of detecting these molecular species.

In order to increase TOF signal statistics from the LEF, we summed data from 26 orbits (Cassini orbits 3–29). We then binned these data according to distance from Saturn in Saturn radii or Rs (1 Rs $\sim$ 60330 km). This data is an accumulation of 889 individual with the least amount of 43 spectra for the 5.5–6.0 radial bin. Additionally, we restricted the data to periods when Cassini was close to the equatorial plane ($\pm$0.25 Rs) to avoid compositional differences caused by scale height effects. Throughout this paper, we reference radial distance from Saturn, however because our data is in the inner magnetosphere and so close to the Saturn’s equatorial plane, these result can also roughly be considered as dipole L-shell values as well. Data were further selected for periods when the instrument viewing angle is generally pointing at the corotational plasma flow. The latter is essential because the flux of ions is appreciable only from that direction. Since the “flow” at these low energies is due to ExB drift there is no mass selection effect.
Figure 1. CAPS LEF spectra at 250 eV separated according to radial distance in Saturnian body radii (Rs). Black lines represent Cassini data, and red lines show the model fit to each spectrum. In the first panel, the spectral peaks associated with N$^+$ and W$^+$ (water group ions; O$^+$, OH$^+$, H$_2$O$^+$, and H$_3$O$^+$) are labeled. (The peak to the right of the W$^+$ peak currently eludes identification and may be an instrument effect.)
We divided the data into radial distance bins from Saturn because if Enceladus is producing ammonia, the relative abundance of molecular ions should decrease as a function of distance from the moon’s orbit as the molecular ions are dissociated. One would, therefore, expect the nitrogen peak in the TOF spectra to become increasingly narrow as a function of radial distance from Enceladus’ orbit.

Figure 1 shows the spectra for the energy level that has the highest signal strength for all spatial bins (235 eV) separated by radial distance from Saturn between ~4.5 Rs and ~14 Rs. Appendix A provides more detail on the accuracy and methodology of these model fits. Below ~4.5 Rs, high-energy electrons cause increasing amounts of background signal. Beyond ~14 Rs the signal strength is too low for statistically meaningful identifications. The rightmost peak in each panel is created by oxygen daughter products from the breakup of water group ions (“W” includes O+, OH+, H2O+ and H3O+) while the left peak is the previously identified N+ peak. In order to gain confidence in our analysis that N+ peak widening is caused by ammonia products; we first must eliminate all other species that could contribute to the N+ LEF peak. On the basis of results from calibration the species that could possibly widen the N+ peak are O2+, CO+, 15N+ and NHx+ (x = 1–4). We assume 15N/14N is not present in detectable quantities because 15N/14N is <0.5% in solar, terrestrial and Titan concentrations [Lammer et al., 2000; Waite et al., 2005]. To illustrate LEF spectral peak shapes and their TOF locations we show CAPS calibration data taken at 250 eV for O2+, CO+, CO2+, and N+ (Figure 2). Notice that an O+ fragment from an O2+ ion entering the instrument dissociating in the foil can widen the left shoulder of the N+ peak, while CO+ can similarly widen the right shoulder.

To illustrate spectral peak widening caused by an increased fraction of molecular components, Figure 3 shows the full width at half maximum (FWHM, computed from the measured spectra) for the LEF water group ions shown in Figure 1 and other energies. The peak becomes narrower with increasing distance from Saturn, consistent with an increase in the amount of atomic ion components relative to molecular ions. This is because the primary source of heavy ions that compete with N+ is H2O from Enceladus. Over time and distance from the source, these molecules are scattered outward [Johnson et al., 2006] and become dissociated, forming OH+ and O2+ [e.g., Jurac and Richardson, 2005]. This causes the water group ion peak to become increasingly dominated by atomic species with increasing distance from the source thus resulting in a narrower TOF peak. We similarly examine the observed spatial trend in the N+ peak width to determine if the same trend toward an atomic concentration is also present in the nitrogen peak.

Before we consider the effect of NH+ ions on the nominal N+ peak, we applied a computational de-convolution algorithm to the spectra shown in Figure 1 and to similar data collected at 58, 83, 118, 167, 236 and 333 eV to account for other possible contributions in the spectra. Our program fits the spectra for CO2+, CO+, O2+, N+, N2+, C+, H2O+, OH+, O+, and H2O+ by incrementally testing possible relative concentrations of each species and evaluating the quality of the total fit using the least squares method. The iteration with the lowest value is then deemed to have the best fit. While this de-convolution provides a good estimate of major species’ abundances, it is more difficult to determine minor species (e.g., CO2+, CO+, N2+ and C+). Because O2+ abundances are known [Martens et al., 2008], we have a high confidence in the amount of O2+ counts that must be removed (as indicated by our spectral deconvolution above and explained in Appendix A) from the N+ peak to produce a “residual” N+ peak. Figure 4 shows the full width half maximum (FWHM) of the residual N+ peaks (same format as Figure 3) as a function of radial distance from Saturn for energies from 58 to 333 eV. Although at the smallest and largest radial distances there is large scatter, this plot shows a clear trend similar in the water-group ion FWHM presented above (Figure 3) where the peak becomes, on average, narrower as a function of radial distance from Saturn.

![Figure 2. CAPS LEF calibration spectra taken at 250 eV. Spectra shown for N+ (black line), O2+ (blue line), CO+ (red line), and CO2+ (green line) as a function of normalized peak height and instrument time-of-flight channel.](image)

![Figure 3. Spectral peak full width at half maximum (FWHM measured as the number of time-of-flight channel) for water group ions in CAPS LEF at various energies. Data are shown as a function of radial distance from Saturn (4.5 to >10 Rs).](image)
We now examine possible reasons for this observed behavior. A peak could widen because of a spread in ion energies contributing to the peak. We remove this effect by separating the data into specific energy bins so there is no energy dependence in the data. Peak narrowing occurs consistently in each energy band which provides confidence that widening does not occur as a result of changes in energy as a function of radial distance. Therefore, unless there is an unidentified instrument problem, peak widening should be caused by the presence of unidentified molecular ion species contributing to the \( \text{N}^+ \) peak. Additionally, the abundance of molecular species appears to decrease as a function of radial distance from Saturn, as indicated by the narrowing of the peak widths, which is consistent with observations of the water group peak. This indicates decreasing molecular contributions as Cassini moves further from Enceladus’ orbit.

To examine which molecules could contribute to the broadening, we simulate peak widening by adding molecular species other than \( \text{NH}_x^+ \) using model fits based on instrument calibration. Although we have already removed the best fit amounts of \( \text{O}_2^+ \) from the \( \text{N}^+ \) spectral peak, we now examine if it is possible to produce the observed peak widening by adding additional \( \text{O}_2^+ \) even though the fit would not be optimized. Therefore we examine whether there could be any additional contribution from \( \text{O}_2^+ \) (\( \text{O}^+ \) fragments from this species have approximately the same spectral TOF location as ammonia) that was not included in the initial correction discussed above. The amount of \( \text{O}_2^+ \) needed to produce the total change in peak width between the radial extremes (4.5 Rs and 14 Rs) requires an \( \text{O}_2^+/\text{N}^+ \) of \( 2.4 \) at the maximum abundance location. Note that the approximate \( \text{N}^+ \) composition is \( \text{N}^+/\text{W}^+ \sim 0.1 \). For the change in \( \text{N}^+ \) peak width to be caused by additional \( \text{O}_2^+ \), the relative abundance of water-group ions would require an \( \text{O}_2^+/\text{W}^+ \) of \( \sim 0.24 \) (24%). However Martens et al. [2008] show that the total \( \text{O}_2^+ \) percentage always remains approx-
from Saturn. Therefore the data in Figure 6 show the increasing amount of ammonia products required to fit the data as Cassini moves closer to Enceladus’ orbit.

[21] To better characterize the contribution of the various ammonia fragment ions to the nitrogen peak, we first examine NH+. We find it is difficult to produce the observed peak widening with only NH+. However, if we assume, unrealistically, that the peak width broadening at the point closest to Enceladus’ orbit is only caused by NH+, it can almost be reproduced with >200% of NH+ relative to N+ (or >20% of the total heavy ion concentration). Given the high density of NH+ required, we should be able to detect NH+ using the ST detector but no detection is evident. Therefore we are confident that NH+ alone is not responsible for the observations. NH3 can cause the observed peak widening at the closest point with a 0.5 ratio of NH3 to N+ (equivalent to an upper limit of ~5% of the total heavy ion concentration—which again seems high because this much NH3 should be more obvious in the other detector). On the other hand, NH5 requires a ratio of only ~0.2 upper limit (or ~2% of the total density with a 10% concentration of N+) for data closest to Enceladus. The NH5 upper limit is also ~0.2 in this region. As a first examination of a multi-species composition, we attempt to fit the spectra with all of these species in equal proportions and derive an upper limit for ammonia products near Enceladus of NH5/N+ ~0.35 (~3.5% of the heavy ions). This is equivalent to ~0.09 for each species individually (~1% of total heavy ions).

3. Molecular Nitrogen

[22] Smith et al. [2005] detected N+ in Saturn’s inner magnetosphere but did not detect N2. However, considering the INMS mass 28 detection in the Encelalus plume [Waite et al., 2006], Smith et al. [2007] developed a neutral cloud model assuming N2 in the plume is the source of detected N+. Ignoring the peak width discussion above, they showed that the observed N+ could be produced by an N2 plume source, but they could not confirm that N2 was required to produce the observed N+. Therefore we now examine more closely the CAPS ability to detect low concentrations of N2.

[23] After normalizing N2 and N+ calibration data for incoming flux rate, an interesting picture emerges. Figure 7 shows the normalized TOF calibration spectra for N+ fragments from N+ and N2 at 64, 125, 250 and 375 eV. While both peaks represent the same number of ion detections, molecular fragments have a wider TOF dispersion than
atomic fragments. This dramatically spreads the travel time to the detector for the N$^+$ daughter fragment produced by N$_2^+$ incident on the carbon foil. As shown in Figure 7 the result is that the amplitude of N$_2^+$ is only 22% of the N$^+$ peak. Therefore, for the same amounts of N$_2^+$ and N$^+$, the peak associated with N$^+$ from molecular nitrogen has much lower amplitude and is much broader, making the signal/noise ratio smaller and therefore the peak more difficult to detect. This is especially a problem close to Enceladus orbit where both molecular ion component and the background would be expected to be largest. These results indicate that N$_2^+$ in the CAPS data of comparable amounts to N$^+$ at current signal strengths would be difficult to identify.

[24] To further investigate the presence of N$_2^+$, we return to the spatially ordered LEF spectra in Figure 1 where we were able to identify potentially small amounts of N$_2^+$. Figure 8 shows a spectrogram of the data presented in Figure 1 to illustrate that these data indicate the possible presence of N$_2^+$ closer to Saturn but no obvious indication of CO$^+$. This allows for the possibility of N$_2^+$ but does not confirm its presence. The situation is further complicated because C$^+$ would also appear at approximately the same location. To gain more insight into the composition we also examine data from the Straight-through (ST) detector which has lower mass resolution as the LEF but has higher detection efficiency. Although the ST is not well suited for separating CO$^+$ from N$_2^+$, it can help determine the presence of an aggregate of mass 28 species. Unfortunately detection of mass 28 is hindered because its location is very close to mass 32 (O$_2^+$) which has been detected [Young et al., 2005; Tokar et al., 2005; Johnson et al., 2006; Martens et al., 2008].

[25] Figure 9 shows example LEF (left) and ST (right) spectra for data integrated from 4.0–5.5 Rs. This figure shows the ST data fit is better using mass 28 (Chi-squared improvement of $\sim$1%) while the LEF data allows for a possible but not confirmed N$_2^+$ presence. We also de-convolved the ST and LEF data using the method described above and identified all of the possible locations in the data where mass 28 (ST) and N$_2^+$ (LEF) could contribute to the peaks seen in the ST and the LEF data at the same concentrations. Figure 10 shows the locations by energy where mass 28 can be fit into the ST data with an improved chi-squared fit of $\sim$1%. The red lines show the spatially dependent N$_2^+$ corotational energy or the approximate energy that newly generated N$_2^+$ should obtain if ionization occurred at that location. Additionally, Figure 11 shows the locations by energy where N$_2^+$ can be fit into the LEF data. These figures show that the potential N$_2^+$ detections occur in both CAPS IMS detectors at energies lower than pick-up energies.

[26] We also examined the ST data collected during Enceladus encounters and orbit crossing (day 195 & 67 2005) more closely and although the data supports the presence of small amounts of mass 28, the large amount of noise in this region makes a conclusive determination highly uncertain.

<table>
<thead>
<tr>
<th>Rs</th>
<th>ST Mass 28 Upper Limit (% of Heavy Ions)</th>
<th>LEF N$_2^+$ Upper Limits (% of Heavy Ions)</th>
<th>LEF Best Fit N$_2^+$/CO$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0–4.5</td>
<td>*</td>
<td>3.6</td>
<td>1.23</td>
</tr>
<tr>
<td>4.5–5.0</td>
<td>2.8</td>
<td>2.7</td>
<td>0.28</td>
</tr>
<tr>
<td>5.0–5.5</td>
<td>1.6</td>
<td>2.5</td>
<td>0.20</td>
</tr>
<tr>
<td>5.5–6.0</td>
<td>2.0</td>
<td>1.9</td>
<td>0.15</td>
</tr>
<tr>
<td>6.0–6.5</td>
<td>1.3</td>
<td>1.7</td>
<td>0.20</td>
</tr>
<tr>
<td>6.5–7.0</td>
<td>1.9</td>
<td>1.9</td>
<td>0.23</td>
</tr>
<tr>
<td>7.0–8.0</td>
<td>2.2</td>
<td>1.5</td>
<td>0.21</td>
</tr>
<tr>
<td>8.0–9.0</td>
<td>2.5</td>
<td>1.6</td>
<td>0.23</td>
</tr>
<tr>
<td>9.0–10.0</td>
<td>1.8</td>
<td>1.2</td>
<td>0.16</td>
</tr>
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<td>$&gt;10.0$</td>
<td>2.7</td>
<td>1.2</td>
<td>*</td>
</tr>
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</table>

*First column is for mass 28 based on CAPS ST data, and second column is for N$_2^+$ based on CAPS LEF data (as a percentage of the total heavy ion population). Third column is the CAPS LEF best fit for N$_2^+$ and CO$^+$ (ratio of the amount of N$_2^+$ to CO$^+$). Asterisk indicates data not available.
difficult. Our detections therefore represent an upper limit on the amount of \( \text{N}_2^+ \) possible in the data. We summarize the spatially dependent upper limits for Mass 28 based on CAPS ST data (as a percentage of the heavy ions) shown in Table 1. Note that the \( \text{N}_2^+ \) spectral peak location is very different from the \( \text{N}^+ \) peak discussed above. Likewise, Table 1 also shows the upper limit for \( \text{N}_2^+ \) in the CAPS LEF detector based on the spectral de-convolution process mentioned above. Additionally, based on the CAPS LEF detector we computed a best fit \( \text{N}_2^+/\text{CO}^+ \) ratio to the spectra as shown in Table 1. Also note that while Figure 8 shows that CAPS spectra do not contain enough \( \text{CO}^+ \) to explain the \( \text{N}^+ \) peak widening, the spectra do potentially allow for small amounts of \( \text{CO}^+ \) as indicated in Table 1. Finally, we then constrain the upper limits on \( \text{N}_2^+ \) as shown in Figure 12. Note, as mentioned above, penetrating background radiation causes larger uncertainty in our results for data obtained closer to Saturn.

4. Discussion

[27] Our goal was to determine the possible molecular parents of \( \text{N}^+ \) detected in Saturn’s inner magnetospheric plasma. The analysis of the \( \text{N}^+ \) spatial and energy distribution presented here suggests a source close to Enceladus’ orbit and is consistent with our earlier results [Smith et al., 2005, 2007]. The INMS detected mass 28 in the Enceladus plume [Waite et al., 2005], which they initially suggested was \( \text{N}_2 \) but could also be \( \text{CO} \). Therefore we first considered the existence of molecular nitrogen. We cannot directly confirm \( \text{N}_2^+ \) is present using the CAPS ion data but arguments presented here show that it could still be present and be indiscernible from the CAPS background because of a combination of low-incident fluxes of \( \text{N}_2 \) and detector efficiencies especially near Enceladus. Therefore we have used both ion mass detectors on the CAPS to place upper limits on the amount of this species. Although, as stated, these are not confirmed detections we show the observed spectra are fitted better by including small amounts of \( \text{N}_2^+ \) (<3.6% of total heavy ion population) and also possibly \( \text{CO}^+ \).

[28] Figure 9 shows that TOF spectra are best fit with mass 28 in the ST detector and, although the data are noisy, the LEF spectra can allow for a small amount of \( \text{N}_2^+ \). Using these results, we show the possible energy distribution of \( \text{N}_2^+ \) vs. distance from Saturn in Figures 10 and 11. The trend is similar to the pick-up ion energy, only shifted to lower energies.

[29] On the basis of this research we are able to place upper limits on the amount of mass 28 possible as a percentage of the heavy ion population (Figure 12). While this only represents an upper limit, the results are consistent with a potential Enceladus source. However we do experience more interference from background radiation at closer distances to Saturn. We tried to further constrain this detection by showing the spectral best fit ratio of \( \text{N}_2^+ \) to \( \text{CO}^+ \). The fit consistently shows that the spectra are best fit with at least some \( \text{N}_2^+ \) (<3.6%) in the spectra. The ratio also seems to favor a higher amount of \( \text{N}_2^+ \) closer to Enceladus’ orbit, however this is also the region where CAPS experiences the most interference from penetrating radiation (discussed above) so these upper limits do not necessarily confirm a higher amount of \( \text{N}_2^+ \) closer to Enceladus. By combining all of these results, we were able to produce \( \text{N}_2^+ \) upper limits as a function of distance from Saturn (Figures 10 and 11) showing that the upper limits increase closer to Enceladus which is consistent with the \( \text{N}_2 \) source model constructed by Smith et al. [2007]. As a cross instrument confirmation of these results, the \( \text{N}_2^+ \) upper limit closest to Enceladus is ~4% which is similar to the value of mass 28 percentage reported by Waite et al. [2005] in the Enceladus plume.

[30] We also showed the results of our \( \text{NH}_3^+ \) research. As mentioned earlier, the location and potential relative abundance of \( \text{NH}_3^+ \) prevents us from making a direct detection or de-convolution of these species in the CAPS spectra. However, our examination of the \( \text{N}^+ \) peak width produces results that indicate the presence of these species. The results in Figure 4 show the \( \text{N}^+ \) peak is noticeably wider as we move closer to Enceladus’ orbit. This is interesting because the atomic species generate noticeably narrower spectral peaks than molecular species in the CAPS LEF detector.

[31] We examined these data independently for each specific energy pass band to remove the possibility that differences in energy distribution could cause the peak to become wider with distance from Saturn. Because we observe the same peak width changes independently at each energy level, energy distribution changes cannot explain the trend. We also determined that no currently identified issue with the detector could produce such an effect. Therefore, assuming there is not some unknown detector issue, this change in \( \text{N}^+ \) spectra peak width should be caused by changes in the molecular vs. atomic species concentration.

[32] The possible molecular species that could contribute to this \( \text{N}^+ \) peak are \( \text{O}_2^+ \), \( \text{CO}^+ \) and \( \text{NH}_3^+ \) (\( x = 1–4 \)). \( \text{O}_2^+ \) has already been detected and shows a fairly conclusive fit in the spectra. Therefore we fit the spectra for \( \text{O}_2^+ \) and removed these counts from the \( \text{N}^+ \) spectra peak to produce a “residual” \( \text{N}^+ \) spectral peak. Even with the \( \text{O}_2^+ \) removed, the \( \text{N}^+ \) peak still shows a spatially dependent peak width.

Figure 12. Upper limit for \( \text{N}_2^+ \) and \( \text{NH}_3^+ \) based on CAPS LEF observations. Results shown as the upper limit \( \text{N}_2^+ \) (solid black lines) and \( \text{NH}_3^+ \) (dotted line) percentage of all heavy ions as a function of radial distance from Saturn in planetary radii (Rs). Error bars represent 1-sigma errors for peak widths. (Enceladus orbits at ~4 Rs, while Titan is ~20 Rs from Saturn.)
We then determined that there are insignificant amounts of CO\(^-\) or O\(_2\) fragments contributing to the peak width. We therefore propose that the narrowing peak width with increasing distance from Enceladus is due to the increase in the dissociation of ammonia with distance from Enceladus. Testing this assumption, we simulate the peak widening using NH\(^+\), NH\(_2\), NH\(_3\) or NH\(_4\) to place limits on the amount of these species that can be present. Assuming the NH\(^+\) spectra peak is composed almost entirely of atomic nitrogen (as suggested by the CAPS spectra models) beyond \(\sim 10 \text{ Rs}\), Figure 6 shows the relative amount of ammonia product ions that are present in the plasma close to Enceladus’ orbit. Additionally, assuming the residual peak width is only caused by equal amounts of ammonia-group ions, we show this abundance (as a percentage of the heavy ion population) relative to the N\(_2\) upper limits (as a function of distance from Saturn) in Figure 12.

[33] There is also a possibility that NH\(^+\) could be produced in the plasma by an ion molecule reaction of N\(_2\) or N\(_3\) with water products. However it is very difficult to reproduce the observed spectral peak widening with only NH\(^+\). Therefore it appears likely that other NH\(_x\) must be present.

5. Summary and Future Work

[34] In this paper, we expand on the work of Smith et al. [2007] to identify the source molecules for nitrogen ions detected in Saturn’s inner magnetosphere. We conducted an extensive study of all available CAPS data to determine if N\(_2\) or ammonia were the parent molecules for these nitrogen ions detected by Smith et al. in Saturn’s magnetosphere. We present evidence for the detection of product ions (NH\(_x\)) likely from ammonia We find that in order to explain our observations, if only one of these species is present, as a percentage of heavy ions, there needs to be \(\sim 3.4\%\) of NH\(_2\), \(\sim 2.0\%\) of either NH\(_3\) or NH\(_4\). Alternatively, if all four species are added in equal proportions, there only needs to be \(\sim 0.7\%\) of each to explain the spectral behavior we observed.

[35] Because the INMS detected neutral particles with an atomic mass of 28 but could not determine how much of this is from ionization of N\(_2\) or CO, we also looked for evidence for N\(_2\). Although we could not positively confirm the presence of N\(_2\) in Saturn magnetosphere through direct observation, we showed that a best fit to the CAPS data is obtained when including small amounts of N\(_2\). Also, we placed upper limits on the amount of mass 28 as well as the amount of N\(_2\). Interestingly, the upper limit we place on the amount of N\(_2\) close to Enceladus’ orbit is similar to the INMS mass 28 detection (\(\sim 4\%\)). Also of interest, the radial distribution of our N\(_2\) upper limits follows the trends modeled by Smith et al. for N\(_2\) in the Enceladus plumes.

[36] The indications of ammonia products and upper limits on N\(_2\) suggest that both ammonia and molecular nitrogen are emitted from Enceladus. This result now can be used to constrain the subsurface processes and composition of Enceladus. Further analysis of this data is underway and once Cassini returns to equatorial orbit in 2009, additional observations will be available. Considering the upcoming close encounters with Enceladus and well as occultations, Cassini observation should be able to build on the understanding of molecular sources of nitrogen considered here.

Appendix A: Time of Flight Spectra and Model Fitting Details

A1. CAPS Spectra TOF Channels

[37] The CAPS TOF spectra is measured in 2048 time-of-flight channels [Young et al., 2004] however only 512 channels of these data are sent back to Earth because of data band width constraints. The channels sent back to Earth are selected to focus on the mass region of the spectra most important to the specific Saturnian region being studied. The Young et al. [2004] instrument paper however divides the TOF channel numbers by four. For this paper, we plot data by radial distance form Saturn. The CAPS LEF spectra in this article coincides with TOF channels 650 to 1161 (i.e., original TOF channel 650 is channel 0 in this paper) and the CAPS ST spectra start with TOF channel 40 and then selects every second channel afterward. We have adjusted the calibration TOF channels to coincide with the operational data channels.

A2. Spectral Model Fitting Methodology

[38] Model fits to the CAPS spectra are created by comparing data obtained from NASA Goddard Space Flight Center, Los Alamos National Lab and Southwest Research Institute calibration experiments using a prototype version of the CAPS as well as the fight model onboard Cassini. These tests were conducted prior to launch for over 20 atomic and molecular ion species at multiple energy levels resulting in hundreds of calibration spectra.

[39] In order to translate these data into a form that can be used to deconvolve species in the operational spectra, we use a Logistic Power Peak Model, LPP, represented by:

\[
LPP(\chi) = \frac{a}{d} \left[ 1 + e^{\left(\frac{\chi + (b/c)}{-c}\right)}\right]^{\frac{-1}{d}} \left[ e^{\left(\frac{\chi + (b/c)}{-c}\right)}\right] \left[ (d + 1)^{\frac{1}{d}} \right]
\]

(A1)

Each ion species is defined by four parameters where “a” is the fragment probability, “b” is the peak center location, “c” is the peak width and “d” relates to peak asymmetry. These parameters are defined with parametric relationships based on calibration data using total molecule mass, fragment mass and particle energy. Using these equations, we produce spectra model fits for H\(_3\)O\(^+\), H\(_2\)O\(^+\), OH\(^+\), O\(^+\), N\(_2\), C\(^+\), CO\(^+\), CO\(_2\), O\(_2\), N\(_2\), NH\(^+\), NH\(_2\), NH\(_3\) and NH\(_4\). We then use a computational program that iteratively adjusts the relative amounts of each of these species and combines these model spectra into single simulated spectrum that is compared to the operational CAPS data. The quality of each model fit is determined using a “reduced chi-squared” \(\chi^2\) method. This method assesses the quality of a model fit using the equation:

\[
\chi^2 = \sum_{i=1}^{n} \frac{(\text{CAPS}_i - \text{LPP}_i)^2}{\text{LPP}_i} (n-1)
\]

(A2)

where there are n TOF channels and \(\text{CAPS}_i\) and \(\text{LPP}_i\) represent the number of counts at channel i in the
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operational and calibration spectra, respectively. The iteration with the lowest value of $\chi^2$ indicates the best fit to the spectra. The resulting abundances for each species constitute our spectral de-convolution. The $\chi^2$ results for Figure 1 are: 0.43 (4.5–5.0 Rs), 0.29 (5.0–5.5 Rs), 0.37 (5.5–6.0 Rs), 0.35 (6.0–6.5 Rs), 0.38 (6.5–7.0 Rs), 0.24 (7.0–8.0 Rs), 0.09 (8.0–9.0 Rs), 0.02 (9.0–10.0 Rs) and 0.01 (10.0–14.0 Rs).

While the chi-squared method provides the quality of a model fit, we also account for the statistical error in the operational data by computing the uncertainty of each peak using the “fractional 1σ” method, defined by:

\[
(1\sigma) = \sum_{i=1}^{n} \left( \frac{\sqrt{CAPS_{i}^2}}{CAPS_{i}} \right)^2
\]

This gives the probability that the actual numbers are within ±1 sigma (34.1%) of the observed count numbers. We use these values to set upper limits (and lower limits of zero) for the molecular nitrogen fitting results.

A3. FWHM Methodology

For the FWHM analysis, we determine the ion counts in each time-of-flight channel for $O_2^+$ (as determined by the model fitting above). Because this species contributes to the same spectra peak as $N^+$ and ammonia products, we remove these ion counts from the CAPS spectra (>10% of the total counts for all spectra). The remaining peak is a modified LEF $N_2^+$ spectral peak with the expected $O_2^+$ ion counts removed. Figure A1 shows a sample spectra with the $N^+$ and $O_2^+$ contributions identified.

Next we focus on analysis of this modified CAPS data only. Using an off the shelf peak fitting computational program, we fit a curve to the data (independent of the model constraints above) and calculate the full width and half maximum of each nitrogen spectral peak.

We calculate the FWHM uncertainty by generating a synthetic LEF spectrum with 1-sigma counts added to the spectrum. We then compute the FWHM of these increased spectra which represent the upper limit error bars for our FWHM results. Similarly, we remove the 1-sigma error counts from the spectra to determine the lower limit 1-sigma FWHM error.

A4. Modeling Fitting Issues

The CAPS model fits (above) must rely heavily on prototype instrument calibration data rather than flight instrument spectra because more data exists for the former instrument. It is known that spectra from these two instruments vary in terms of TOF channel locations for each species. Because water group ions are much more abundant than other heavy species, the “peak shift” between the two instruments is well understood and thus the water group peak fits are better in Figure 1 than the $N^+$ peak. However, the instrument team is becoming more confident in these model fits and we have examined in detail the offset in the $N^+$ peak and cannot find any ion species that can cause the excess counts on the right side of the nitrogen peak. Therefore it is likely model fits for this peak need to be slightly adjusted. However, this shift is not yet conclusively agreed on so we show the model fits in Figure 1 using the current models although we have confidence these counts are attributed to $N^+$.

In order to increase confidence in our results, we defined our FWHM technique of the $N^+$ peak so that this likely peak shift is not a factor in our analysis which is independent of the exact peak location. Additionally, the asymmetric tail of spectra begins at a height far below the 50% height and should not affect the analysis. Our $N_2$/mass 28 analysis uses spectra peaks that are located in TOF channels which allows use of both CAPS IMS detectors (LEF & ST). This cross analysis increases confidence in our model fits. Therefore out results should not be affected by further minor refinements of the CAPS spectra models.

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