The Ion Composition of Saturn’s Equatorial Ionosphere as Observed by Cassini


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Abstract The Cassini Orbiter made the first in situ measurements of the upper atmosphere and ionosphere of Saturn in 2017. The Ion and Neutral Mass Spectrometer (INMS) found molecular hydrogen and helium as well as minor species including water, methane, ammonia, and organics. INMS ion mode measurements of light ion species (H+, H2+, H3+, and He+) and Radio and Plasma Wave Science instrument measurements of electron densities are presented. A photochemical analysis of the INMS and Radio and Plasma Wave Science data indicates that the major ion species near the ionospheric peak must be heavy and molecular with a short chemical lifetime. A quantitative explanation of measured H+ and H3+ densities requires that they chemically react with one or more heavy neutral molecular species that have mixing ratios of about 100 ppm.

Plain Language Summary Solar ultraviolet radiation is absorbed by Saturn’s upper atmosphere and produces electrically charged molecules (or ions) and electrons in a region called the ionosphere. The Ion and Neutral Mass Spectrometer (INMS) instrument onboard the Cassini Orbiter made the first direct measurements of the composition of Saturn’s ionosphere when the Cassini spacecraft flew through the upper atmosphere in the equatorial region. This paper reports on INMS measurements of the abundances of ionospheric protons, charged molecular hydrogen and helium, and protonated molecular hydrogen as functions of altitude and latitude. The paper also describes a photochemical analysis of the data indicating the presence in the upper atmosphere of heavy molecular species such as water, methane, and ammonia, thought to come from the rings. The deduced mixing ratio of these species relative to hydrogen is about a part in 10,000, which is consistent with measurements made using the neutral mode of the INMS. The simple chemical analysis was also able to reproduce the densities of electrons measured by the Radio and Plasma Wave Science instrument onboard Cassini. This paper contributes to our growing appreciation of the strong effect that the rings have on Saturn’s atmosphere.

1. Introduction

Saturn’s ionosphere was observed by the Pioneer 11 and the Voyager spacecraft (e.g., Kliore et al., 1980) using the radio occultation technique. The measured electron densities were much less than theoretical models of that time predicted (Waite et al., 1979). Electrostatic wave detection by the Voyager planetary radio astronomy investigation confirmed that peak electron densities were \(10^8 \text{ cm}^{-3}\) or less (Kaiser et al., 1984) as did Cassini epoch radio occultation measurements made at the terminator (Kliore et al., 2009; Nagy et al., 2006).

The major neutral species in the atmosphere are molecular hydrogen and helium. Ionization of H2 produces H2+ ions \((\approx 90\%)\) or H+ ions \((\approx 10\%)\). H+ ions rapidly react with H2, producing H3+ ions, which can rapidly dissociatively recombine with electrons. However, electron recombination with H+ ions is radiative, which is a very slow process. Among the suggestions made for reducing the predicted electron density was the reaction of H+ with water coming from the rings, creating molecular ion species \(\text{H}_2\text{O}^+\) and then \(\text{H}_3\text{O}^+\) with short chemical lifetimes (Connerney & Waite, 1984; Moore et al., 2010). Infrared observations of ionospheric H3+ have shown latitudinal structure that appears to be related to ring structure, suggesting that ions could also be traveling from the rings to the ionosphere along magnetic field lines (O’Donoghue et al., 2013).
The first in situ measurements of Saturn’s upper atmosphere and ionosphere were made by the Cassini spacecraft in 2017 on the dayside (i.e., solar zenith angle about 20°), although information on the thermosphere from remote measurements was available earlier (e.g., Koskinen et al., 2015). The closed source neutral mode of the Ion and Neutral Mass Spectrometer (INMS) found that molecular hydrogen and helium were the major neutrals, but many minor species were also observed, including water, methane, carbon dioxide, ammonia, and organic compounds (Waite et al., 2018—herein called W18; Perry et al., 2018). The RPWS Langmuir probe measured the electron density \( N_e \) along the spacecraft track (Wahlund et al., 2017), and RPWS upper hybrid wave measurements gave independent determinations of \( N_e \) (Hadid et al., 2018; Persoon et al., 2019). Grains were detected in the upper atmosphere and exosphere extending to the D ring by the Magnetosphere Imaging Instrument Ion and Neutral Camera and Charge Energy Mass Spectrometer experiments (Mitchell et al., 2018). The present paper describes Cassini INMS composition measurements made with the open source ion mode. The paper also provides an empirical interpretation of the ion composition allowing heavy neutral species mixing ratios to be deduced. Related papers in this same special 2018 GRL issue include Hadid et al. (2018), Moore et al. (2018), Morooka et al. (2019), Perry et al. (2018), Persoon et al. (2019), and Yelle et al. (2018), particularly Moore et al. (2018).

2. INMS Instrument and Proximal Orbit Geometry

The INMS instrument is a radio-frequency quadrupole mass spectrometer that measures both ion and neutral composition in its open source ion and closed source neutral modes, respectively (Waite et al., 2004). The spacecraft (s/c) velocity with respect to Saturn during the proximal orbits was 31 km/s, which corresponds to 25 times higher kinetic energy per nucleon for incident molecules than during the Titan encounters. Heavier neutral species, or even grains, break up in the closed source antechamber at these speeds (Teolis et al., 2010). INMS ion measurements at these speeds limit observable ion species to those with mass numbers less than 8 Da (i.e., only lighter ions).

The derivation of densities, \( n_j \), where \( j \) is mass number, from instrumental counts, \( C_j \), per integration period, \( \Delta t = 0.031 \) s, has been described elsewhere (see Waite et al., 2004) but can be expressed as
\[
C_j = (10^{-5} n_0)/(S_j u_{sc} \Delta t),
\]
where \( S_j \) is a sensitivity factor that depends on mass number and \( u_{sc} = 32 \) km/s (for the Cassini proximal orbits) is the s/c speed in km/s. Values of \( S_j \) for Titan-like speeds were found during instrument calibration in the lab but Saturn conditions are different, leaving about a factor of 2 uncertainty. However, comparison of \( m = 1 \) (H\(^+\)) and \( m = 3 \) (H\(_3^+\)) densities measured by INMS and electron densities measured by RPWS (e.g., Persoon et al., 2019; Wahlund et al., 2017) strongly constrain \( S_1 \) and \( S_3 \) to much better than this factor (\( S_1 = 0.006 \) and \( S_3 = 0.0011 \)). From very simple and known H\(_2^+\) chemistry (discussed later), we find that \( S_2 = 0.0010 \). We arbitrarily adopt \( S_4 = S_2 \). Note that extensive laboratory calibration (cf. Waite et al., 2004) confirms the overall reasonableness of these values.

The s/c entered the atmosphere in the Northern Hemisphere and crossed the ring plane (equatorial plane) at a radial distance of \( r = 62,170 \) km for Cassini proximal orbit P288 (see W18). Closest approach (CA) was reached in the southern hemisphere at a distance below the equatorial plane of \(-7,421 \) km, or a latitude of \( \lambda \approx -7 \), or a planetocentric radial distance of \( r = 61,908 \) km, or a height above the 1-bar atmospheric level of \( \approx 1,710 \) km (see Mueller-Wodarg et al., 2006, for information on atmospheric structure). The maximum neutral density was found at \( \lambda \approx -4.5^\circ \).

3. Overview of Ionospheric Data

Figure 1 shows INMS densities versus time from CA for ion mass numbers 1, 2, 3, and 4, with probable identifications of H\(^+\), H\(_2^+\), H\(_3^+\), and He\(^+\), respectively, although deuterated species D\(^+\), HD\(^+\), and H\(_2\)D\(^+\) might make minor contributions to these mass signals.

The neutral density decreases with altitude exponentially as one would expect (see W18 for a presentation of INMS H\(_2\) density data). The measured H\(_2\) density at CA for P288 was \( 7 \times 10^9 \) cm\(^{-3}\) and at the equatorial plane \( (\lambda = 0 \) or latitude \( \lambda = 0^\circ) \) was \( 1.5 \times 10^9 \) cm\(^{-3}\). The H\(^+\) and electron densities are almost equal at higher altitudes, but H\(_3^+\) is an important species at lower altitudes. At the lowest altitudes near CA, and spanning the equatorial region, the total ion density measured by INMS (i.e., light ions) falls well short of the measured electron density. This density “gap” points to the existence of heavier ion species with mass numbers exceeding...
the INMS limit of 8 Da. The He\(^{+}\) density profile \((m = 4)\) follows from the measured neutral He density and the expected ion chemistry for this species (see Moore et al., 2018). The H\(_2^{+}\) density is quite low \((n_{H_2^+} \approx 0.6 \text{ cm}^{-3}\) and is associated with the major ionization process, as discussed in the next section.

4. Simple Ionospheric Chemistry

The dominant ionization process at low latitudes is photoionization (Moore et al., 2006, 2010, 2018; Schunk & Nagy, 2009). This can be represented by

\[
\text{hv} + \text{H}_2 \rightarrow \text{H}_2^+ + e^- \quad \text{(90%)}
\]

\[
\text{H}^+ + \text{H}_2 + e^- \quad \text{(10%)}
\]

The H\(_2^{+}\) production rate, \(P_{H_2^+}\), can be obtained via standard aeronomical techniques (cf. Schunk & Nagy, 2009) using a solar radiation spectrum and photoionization cross sections versus wavelength. The solar flux at different altitudes must include optical depth effects that depend on wavelength and solar zenith angle. The peak ion production rate takes place where the optical depth equals unity level for a typical extreme ultraviolet photon \((\approx 50 \text{ nm})\). For solar zenith angles appropriate for the proximal orbits \((\gamma \approx 20^\circ)\) and for H\(_2\) gas, this level corresponds to a vertical column density of \(N_{H_2} \approx 10^{17} \text{ cm}^{-3}\) or density of \(n_{H_2} \approx N_{H_2}/A_{H_2} \approx 10^{10} \text{ cm}^{-3}\), which is found near CA. At high altitudes, the ionization frequency, or ion production rate per neutral molecule, depends only on the solar flux and cross sections and is equal to \(I_{H_2+} = 1.2 \times 10^{-9} \text{ s}^{-1}\) (Galand et al., 2009; Moore et al., 2010), including a \(\approx 10\%\) photoelectron contribution. Theoretical peak H\(_2^{+}\) production rates are \(\approx 10 \text{ cm}^{-3} / \text{s}\) at Saturn (cf. Moore et al., 2018). H\(^{+}\) ions are mainly produced by dissociative photoionization of H\(_2\) with ionization frequency \(I_{H+0} \approx 0.1 \ I_{H_2+0}\).

Ion-neutral chemistry changes the ion composition and ultimately produces a set of “terminal” ion species, which rapidly undergo electron-ion recombination. Figure 3 displays a simple chemical scheme. Species M and R are explained later. Empirical photochemical equilibrium (PCE) ion densities are calculated in this paper. The key PCE assumption is that local production equals local for each species, \(s\) (i.e., \(P_s = L_s\)). See Schunk and Nagy (2009).

The main chemical loss of H\(_2^{+}\) ions, and source of H\(_3^{+}\) ions, is reaction of H\(_2^{+}\) with H\(_2\):

\[
\text{H}_2^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{H} \quad k_2 = 2 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}.
\]

All individual rate coefficients used in this paper can be found in Anicich (2003). PCE requires that \(I_{H_2+}(r) n_{H_2} = k_2 n_{H_2^{+}}\). The H\(_3^{+}\) density can be written as \(n_{H_3^+} = P_{H_3^+}/(k_2 n_{H_2})\), and we also find that \(I_{H_3^+}(r) = I_{H_2+}(r) n_{H_2}/n_{H_2^{+}}\), where we have subsumed optical depth effects into \(I_{H_2+}(r)\). Radial distance is denoted by \(r\). See Figure 2. Note that at higher altitudes, \(I_{H_2+}(r) = I_{H_2+0} \approx 10^{-9} \text{ s}^{-1}\), independent of location. The decrease in \(I_{H_2+}(r)\) near CA is consistent with an EUV optical depth of \(\tau \approx 0.7\). The sharp falloff of ionization frequency near latitude \(\lambda \approx -15^\circ\) (also seen in the H\(_2^{+}\) density in Figure 1) is due to the shadow of the optically thick B ring (Hadid et al., 2018).
H$_3^+$ ions produced by reaction (2) can be chemically removed by dissociative recombination with rate coefficient of $\alpha_1 = 2 \times 10^{-7}$ cm$^3$/s (Larsson et al., 2008) at electron temperature $T_e \approx 1,000$ K (RPWS measurements—Wahlund et al., 2017).

$$H_3^+ + e -> H_2 + H \quad \alpha_2 = 2 \times 10^{-7} \text{cm}^3\text{s}^{-1}. \quad (3)$$

The H$_3^+$ density can be estimated by dividing the empirical H$_2^+$ production rate from equation (1) by the loss rate from reaction (3) to give $n_{H3^+} \approx 5,000$ cm$^{-3}$ near CA. This value is much greater than the measured density of $\approx 100$ cm$^{-3}$ (see Figure 1) indicating that an additional H$_3^+$ loss is needed. The next section introduces heavier neutral and ion molecular species as needed to explain measured H$^+$, H$_3^+$, and electron densities.

### 5. Heavy Molecular Ions and the Electron Density

InMS measured heavier neutral species including H$_2$O, CH$_4$, CO$_2$, and organic compounds in the upper atmosphere (denoted M and R in Figure 3; W18). In this section, we describe how such neutrals react with both H$^+$ and H$_3^+$ and produce heavier molecular ion species not detectable by INMS (M$^+$ and R$^+$ in Figure 3). The heavy ion species explain the gap evident in Figure 1 between the total light ion density and the electron density. We postulate a set of neutral molecular species, M, with generic total density $n_M$, or generic mixing ratio (by volume) of $f_M = n_M/n_{H2}$. Reaction of M with H$^+$ and/or H$_3^+$ produces a set of heavy ion species, denoted M$^+$. The resulting M$^+$ species could include H$_2$O$^+$, H$_3$O$^+$, CO$_2^+$, and CH$_3^+$. For example, the reaction for methane is H$^+$ + CH$_4$ $\rightarrow$ CH$_3^+$ + H + H (rate coefficient $k_{H^+CH4} = 4.5 \times 10^{-9}$ cm$^3$/s). We represent all this chemistry with the generic reaction:

$$H^+ + M \rightarrow M^+ + \text{neutrals}. \quad (4)$$

An effective (or species-averaged) rate coefficient for H$^+$ can be defined:

$$k_{Meff}f_M = \sum_j k_jf_j \quad \text{and} \quad f_M = \sum_j f_j. \quad (5)$$

The summations are over all neutral molecular species, $j$, that react with H$^+$ (each with mixing ratio, $f_j$). We adopt relative percentages of various species from the INMS neutral data (W18): CH$_4$ (35%), CO$_2$ (10%), H$_2$O (30%), NH$_3$ (20%), and also C$_2$H$_4$ (5%), excluding mass 28 species (as discussed below). The effective H$^+$ rate coefficient (i.e., the rate coefficient averaged over different heavy species) is $k_{Meff} = 5.0 \times 10^{-9}$ cm$^3$/s, differing only by 10% from a rate coefficient for pure methane. Generally, H$_3^+$ ions react with the same molecular species as H$^+$, but with somewhat different rate coefficients, $k_j$. For example, the reaction with methane is H$_3^+$ + CH$_4$ $\rightarrow$ CH$_3^+$ + H$_2$ (k$_{H3^+CH4}$ = $2.4 \times 10^{-9}$ cm$^3$/s). The effective rate coefficient for H$_3^+$ loss by species M is $k_{H3^+Meff}$ = $3.5 \times 10^{-9}$ cm$^3$/s.

H$_3^+$ densities are less than H$^+$ densities at low altitudes (or low latitude; see Figure 1), suggesting that that H$_3^+$ also reacts with additional neutral species that do not react with H$^+$. For example, N$_2$ and CO could fulfill this role—see Moore et al. (2018). We denote this new generic neutral species R (see Figure 3). We adopt rate coefficients for dissociative recombination of M$^+$ and R$^+$ species that are typical (i.e., the CH$_3^+$ rate coefficient): $\alpha_3 = 7 \times 10^{-7}$ (300/T$_e$)$^{0.61}$ cm$^3$/s $\approx 3.3 \times 10^{-7}$ cm$^3$/s (Richard et al., 2012). M$^+$ and R$^+$ are the heavier molecular ion species resulting from the chemistry (Figure 3).
The densities of the light ion species and the electron densities are taken from Cassini data (Figure 1), and we use a two-step photochemical analysis to deduce mixing ratios for species M and R, $f_M$ and $f_R$, respectively. The $H^+$ PCE expression is rearranged to give $f_M = 0.1 \frac{n_{H^+}}{|k_M n_{H^+}|}$. $I_{H^+}^+$ was already discussed and measurements are used for $n_{H^+}$. The dissociative ionization fraction is 0.1. The neutral species M mixing ratios obtained are shown in Figure 4. Note that $f_M = 0.5 \times 10^{-4}$ (or 50 ppmv) near the equator and/or at low altitudes, but $f_M$ is larger at higher altitudes, which implies that species M (e.g., CH$_4$) has an external source (such as the rings; see other special issue papers).

Now, we use $H^+$ photochemistry to find the mixing ratio of neutral species R (i.e., the non-$H^+$ reacting neutral):

$$f_R + f_M \approx \left[ \frac{n_{H^+}}{|n_{H^+} - \alpha_3 (N_e/n_{H^+})|} \right]/k_R. \quad (6)$$

where $k_R \approx k_{H^+} + Meff$ is adopted. RPWS Langmuir Probe data are used for $N_e$ and INMS data used for $n_{H^+}$ and $n_{H^+}^+$, all shown in Figure 1. The resulting empirical mixing ratios, $f_M$, are shown in Figure 4. Estimated uncertainties in the derived mixing ratios are shown and become large far from CA. It is evident that $f_R$ decreases with latitude away from the equator and/or CA, unlike $f_M$, which increases. The different altitude/latitude variations of the mixing ratios for M and R suggest that they have different sources.

The major ion species appears to be a collection of heavier molecular ion species with density $n^+_{\text{heavy}} = n_{M^+} + n_{R^+}$. The total ion density (heavy plus light species) must equal the electron density, $N_e$, plus the densities of any negative ion species or grains (see Morooka et al., 2019) in order to enforce quasi-neutrality. The role of grains and negative ions needs to be further explored (e.g., Morooka et al., 2019), but for now we assume that $n^+_{\text{heavy}} \approx N_e$. Balancing source and sink of all ions (and electrons), we get $l_{H^+} + n_{H^+} = \alpha_M N_e / n_{H^+}^+$. Solving this balance equation (cf. Schunk & Nagy, 2009) gives this rough estimate:

$$N_e \approx \left( \frac{l_{H^+}}{\alpha_M N_e} / n_{H^+}^+ \right)^{1/2}. \quad (7)$$

Using $l_{H^+}$, from the present paper (Figure 2) and $n_{H^+}$ from INMS data, the derived electron densities are shown in Figure 5 and are compared with measured $N_e$. The model electron density has a maximum where the $H^+$ production rate has a maximum, roughly at CA, as does the measured $N_e$ (also see Moore et al., 2018).

6. Discussion

This paper demonstrated the existence of one or more heavy molecular ion species in the equatorial ionosphere that can explain the density gap in Figure 1. The analysis indicated that a neutral molecular (M) species exists that reacts with $H^+$ and $H^+_3$. The empirically deduced mixing ratio is $f_M = 10^{-4}$ and $f_M$ increases with altitude suggesting a high-altitude (i.e., ring) source. The high-mass species mixing ratios from INMS neutral data are similar (W18; Perry et al., 2018). Note that the methods are mostly independent. The surprisingly high mixing ratios are associated with high downward diffusive fluxes of $10^5$–$10^6$ cm$^{-2}$s$^{-1}$ of heavy neutrals such as CH$_4$ (Koskinen & Guerlet, 2018; Perry et al., 2018; Yelle et al., 2018). Note that the measurements, neutral and ion, were made well above the homopause and cannot be explained by upward diffusion (see Koskinen et al., 2015).

The other heavy neutral species, R, deduced from the ion chemistry has a mixing ratio that decreases with increasing altitude, suggesting a different source for R than for M and not entirely external. But given that altitude and latitude are at least partially confounded variables for the proximal orbits, one could also state that species R is more highly confined to the equatorial region than M. Perhaps the source of R is heavy neutrals generated by ablation of grains entering the atmosphere from the rings (Hamil et al., 2018; Mitchell et al., 2018; Moses & Bass, 2000; Moses & Poppe, 2017).
7. Summary
Cassini INMS ion composition measurements of Saturn’s equatorial ionosphere, plus measurements by other Cassini instruments, tell us the following about the ionosphere and its ring interaction:

1. The light ion species (H+, H2+, H3+, and He+) observed by INMS were those expected theoretically prior to the Cassini proximal orbits, but quantitatively the H+ and H2+ densities were lower than predicted.

2. Quantitatively, explaining the measured H+ and H2+ requires surprisingly high abundances of heavy neutral molecular species (e.g., water, methane, and organic compounds) in the ionosphere, with an overall mixing ratio of ≈100 ppmv. Cassini data suggest that these species are due to inputs from the rings, either as gas or as grains.

References

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