

Hydrocarbon ions in the ionosphere of Titan

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Abstract. We have constructed a new model of the ionosphere of Titan that includes 67 species and 626 reactions. Although N_2^+ is the major ion produced over most of the ionosphere, the ionization flows to ions whose parent neutrals have lower ionization potentials and to ions formed from species with large proton affinities. In contrast to other models, which have predicted that $HCNH^+$ should be the major ion, our calculations suggest that the major ions at and below the ion peak are hydrocarbon ions, and H, C, and N-containing ions. Our predicted peak electron density for a solar zenith angle of 60° is about $7.5 \times 10^3 \text{ cm}^{-3}$ at an altitude of 1040 km.

1. Introduction

In addition to N_2 and CH_4 , the thermosphere of Titan contains significant densities of H_2 , H, and non-methane hydrocarbons such as acetylene, ethane, and ethylene [e.g., *Hunten et al.*, 1984, *Strobel et al.*, 1992], and appears to be well-mixed to very high altitudes. The atmosphere may also contain as much as 14% Ar. The homopause in the model of *Strobel et al.* [1992] is near 1050 km, where the eddy diffusion coefficient is about $1 \times 10^9 \text{ cm}^2 \text{ s}^{-1}$. The exobase is at about 1500 km, and the density profiles of H and H_2 are altered appreciably by thermal escape at the top of the atmosphere.

Information about Titan's ionosphere is limited to the radio occultation measurements made by the Voyager 1 spacecraft. *Lindal et al.* [1983] reported only upper limits of $(3 - 5) \times 10^3 \text{ cm}^{-3}$ near the terminators as the spacecraft entered and exited the occultation region. Recently, *Bird et al.* [1995] reanalyzed the Voyager radio occultation data and reported a possible detection with a peak electron density of 2700 cm^{-3} at an altitude of 1190 km at the evening terminator.

The ionosphere of Titan has been predicted to arise from both solar photoionization and from the interaction of the neutral atmosphere with energetic electrons

from Saturn's magnetosphere, in which part of the orbit of Titan is embedded [e.g., *Strobel and Shemansky*, 1983; *Atreya*, 1986]. *Strobel et al.* [1991] found, however, that the N^+ 1085 Å and N_2 Lyman-Birge-Hopfield band intensities that were measured by the Voyager 1 spacecraft during its Titan flyby in 1980 could be reproduced with the solar source alone. Cravens and co-workers [*Keller et al.*, 1992; *Gan et al.*, 1992] constructed a model of the ionosphere of Titan that included the interaction of energetic magnetospheric electrons with the thermosphere and found it to be a minor source. We model here the ionosphere of Titan produced by photoionization and photoelectron-impact ionization alone. Although we ignore the interaction of the thermosphere with Saturn's magnetosphere, we do not mean to imply that magnetospheric electrons are unimportant all the time or for every process. In all probability, however, they are unimportant for ion production near and for a substantial distance above the dayside ion peak.

2. The Model

For the background atmosphere, the density profiles of N_2 and CH_4 are taken from *Strobel et al.* [1992], and mixing ratios of C_2H_2 , C_2H_4 , C_2H_6 , and C_4H_2 are taken from *Yung et al.* [1984]. The mixing ratio of methane has been estimated as 2–10% in the Titan atmosphere [*Hunten et al.*, 1984], but we have adopted a mixing ratio of 3%, consistent with the preferred model of *Strobel et al.* [1992]. The CO mixing ratio is adopted from the ground-based measurements of *Gurwell and Muhleman* [1995]. The density profiles of these species are shown in Figure 1. The densities of 32 neutral species and 35 ions are computed in the model, including H, H_2 , C, CH, CH_2 , 1CH_2 , CH_3 , C_2 , C_2H , C_2H_3 , C_2H_5 , C_4H_3 , N, $N(^2D)$, NH, NH_2 , NH_3 , CN, HCN, H_2CN , CNN, CHCN, C_2N_2 , HC_2N_2 , C_3N , HC_3N , H_2C_3N , CH_3CN , CH_3NH_2 , C_4N_2 , O, CO, H^+ , H_2^+ , H_3^+ , C^+ , CH^+ , CH_2^+ , CH_3^+ , CH_4^+ , CH_5^+ , C_2^+ , C_2H^+ , $C_2H_2^+$, $C_2H_3^+$, $C_2H_4^+$, $C_2H_5^+$, $C_2H_6^+$, $C_2H_7^+$, $C_4H_3^+$, $C_xH_y^+$, N^+ , NH^+ , NH_2^+ , NH_3^+ , NH_4^+ , HCN^+ , H_2CN^+ , CN^+ , C_2N^+ , $C_xH_yN_z^+$, N_2^+ , N_2H^+ , O^+ , CO^+ , HCO^+ , and NO^+ . The temperature profile is taken from *Strobel et al.* [1992], and is nearly isothermal at the exospheric temperature of approximately 175 K above about 1000 km. The electron temperatures have been computed by *Gan et al.*

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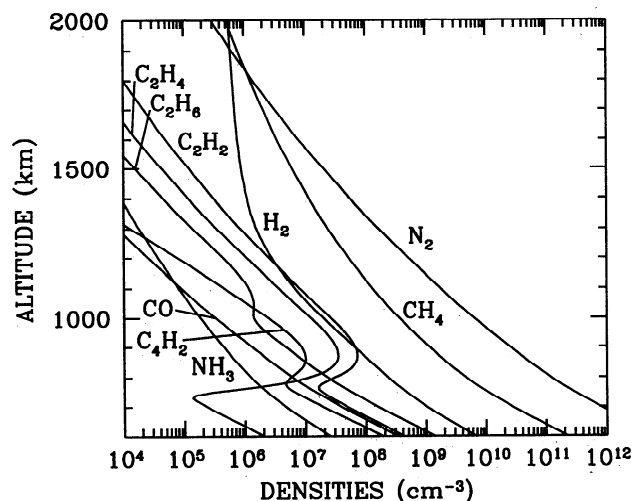


Figure 1. Neutral density profiles in the thermosphere of Titan that were adopted in these calculations.

[1992] and by *Roboz and Nagy* [1994]. We adopt here the profile of *Gan et al.* [1992].

The model includes photoabsorption and photoionization of N_2 , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , N , C , H and H_2 , photodissociation of HCN , and photoionization of CH_3 by Lyman alpha. The solar spectrum we have adopted is the high solar activity F79050N spectrum of *Hinteregger* [private communication, see also *Torr et al.*, 1979], and the solar zenith angle is 60° . Photoelectron-impact ionization is included for N_2 , CH_4 , H , H_2 , N and C . The most important ion production rate profiles are shown in Figure 2. The major ion produced is N_2^+ from 600 to 1800 km, and CH_4^+ above that altitude. Other important ions produced include N^+ , CH_3^+ , $C_2H_2^+$, and $C_2H_4^+$.

The ion density profiles were computed including 626 chemical reactions, most of which were taken from the compilations of *Anicich and Huntress* [1986] and *Ani-*

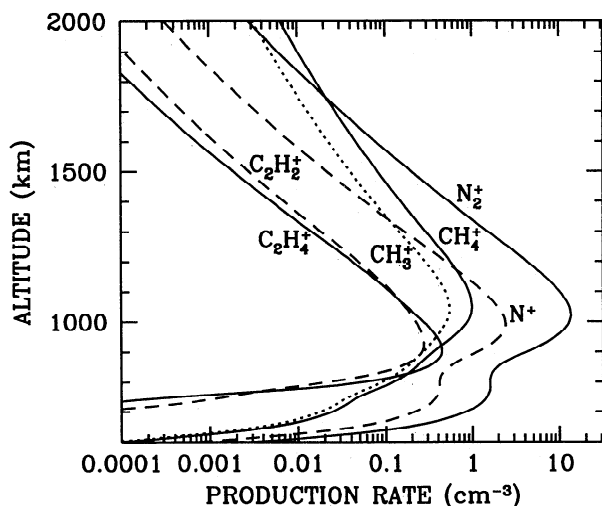
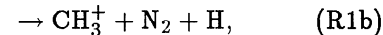
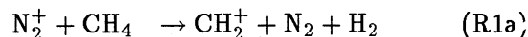


Figure 2. Computed production rate profiles for the most important ions produced in the Titan ionosphere.

cich [1993]. For neutral-neutral reactions, rate coefficients were taken from the model of *Yung et al.* [1984] and from models of the interstellar medium [e.g., *Millar et al.*, 1988]. For many of the most important dissociative recombination coefficients, the rates are unknown; where no measurements are available, values of $(3 - 3.5) \times 10^{-7} (300/T_e)^{0.5} \text{ cm}^3 \text{ s}^{-1}$ were assumed. Very recent measurements, which have not been incorporated into this model, have shown that dissociative recombination coefficients for protonated alkanes do not increase with the size of the ion, but remain in the range $(5 - 8) \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ at 300 K for C_1 - to C_8 - ions [Lefaoui et al., 1997]. We have also assumed that, in the absence of other information, the available channels in dissociative recombination reactions are populated with equal probability. Eddy and molecular diffusion for neutrals, and ambipolar diffusion of ions were included in our model, for which the lower and upper boundaries were at 600 km and 3000 km, respectively. A preliminary model based on the same chemistry was presented by *Fox and Yelle* [1995] and by *Fox* [1996a,b].

The predicted densities of the major ions are shown in Figure 3. The peak electron density is about $7.5 \times 10^3 \text{ cm}^{-3}$ near 1030 km. This is larger than either the Voyager upper limits and the possible detection of *Bird et al.* [1995], but those measurements are for the terminator region, whereas our model is for the dayside at a solar zenith angle of 60° .

Although N_2^+ is the major ion produced over much of the ionosphere, it is destroyed by reaction with methane



and through reaction with H_2 :

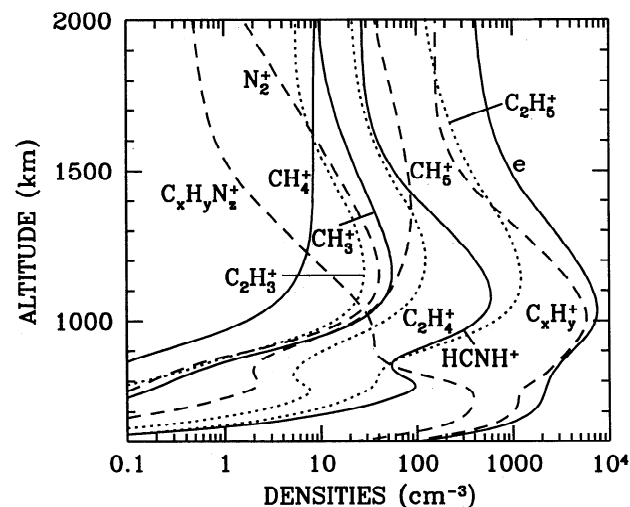
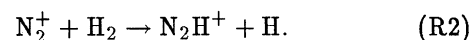
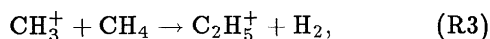


Figure 3. Computed steady-state densities of the most important ions in the Titan ionosphere. The curve labeled "e" is the electron density profile.

At altitudes below about 1900 km, reactions (R1a) and (R1b) dominate; above 1900, H₂ becomes the major constituent, and reaction (R2) is more important. The column integrated production rate of N₂⁺ is 7.3 × 10⁸ cm⁻² s⁻¹, and the column integrated rates for reactions (R1) and (R2) are 6.7 × 10⁸ cm⁻² s⁻¹, and 4.2 × 10⁷ cm⁻² s⁻¹, respectively.

The CH₃⁺ ion reacts with methane to produce C₂H₅⁺ via

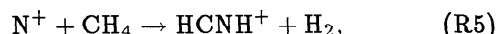


with a column integrated rate of 5.9 × 10⁸ cm⁻² s⁻¹. Once formed, C₂H₅⁺ reacts with HCN to produce HCNH⁺ through

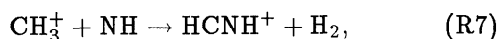


The column integrated rate for (R4) in our model is 1 × 10⁸ cm⁻² s⁻¹.

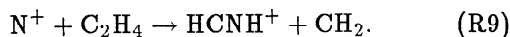
Production of N⁺ also leads to HCNH⁺ formation via the reaction:



which has a column integrated rate of 3.7 × 10⁷ cm⁻² s⁻¹. This reaction dominates HCNH⁺ production at altitudes above 1500 km, whereas the sequence (R1–R4) is more important below that altitude. Reactions (R4) and (R5) account for 63% and 25%, respectively, of HCNH⁺ production. Other reactions that contribute significantly to HCNH⁺ production include

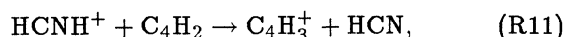
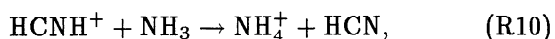


and



The total HCNH⁺ column production rate is 1.6 × 10⁸ cm⁻² s⁻¹.

The reaction sequences discussed above have been included in previous models of Titan's ionosphere [e.g., *Ip*, 1990; *Keller et al.*, 1992; *Keller and Cravens*, 1994]. These calculations predicted that HCNH⁺ should be the major ion at the ionospheric peak. Our model differs from earlier work in the sequence of reactions following HCNH⁺ production. Specifically, we include the reaction of HCNH⁺ with minor neutral species that have larger proton affinities than HCN or HNC. According to our model, HCNH⁺ is lost primarily through reactions with NH₃, C₄H₂, and HC₃N:



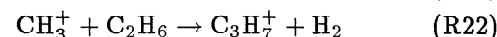
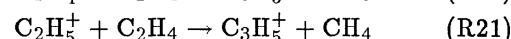
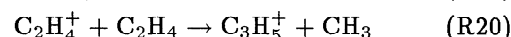
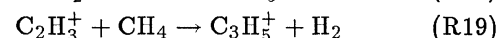
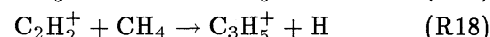
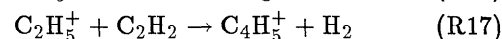
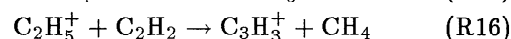
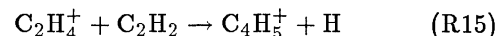
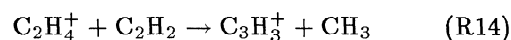
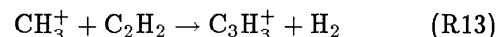
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which are characterized by rate coefficients of 2.4 × 10⁻⁹, 1.8 × 10⁻⁹, and 3.4 × 10⁻⁹ cm³ s⁻¹, respectively, and column integrated rates of 1.6 × 10⁷, 7.5 × 10⁷, and 0.7 × 10⁷ cm⁻² s⁻¹, respectively.

Although reactions (R10–R12) ensure that HCNH⁺ will not account for a large fraction of the total ion density, it is not clear what the dominant ion will be, or if there will be a single major ion. In fact, it is likely that a large number of ions may have comparable densities. Hydrocarbon ions, once formed, quickly react with hydrocarbon neutrals to produce larger hydrocarbon ions. When nitrogen is present, many of the ions also may incorporate one or more nitrogen atoms. The chemistry of such ions is largely incomplete, and tracking of only a few individual species is possible at this point. We therefore adopt two pseudo-ions: C_xH_y⁺, which represents a hydrocarbon ion with 3 or more carbon atoms; and C_xH_yN_z⁺, which represents a large ion containing C, H, and N. This allows us to track the essential character of the ionosphere, although detailed information is of necessity lost in this process. Similar pseudo-ions have been used in models of the ionosphere of Jupiter [e.g., *Kim and Fox*, 1994], and Titan [*Ip*, 1990; *Keller et al.*, 1992].

In our model, C_xH_y⁺ is the most important ion over most of the ionosphere. The major production reactions for C_xH_y⁺ are reactions of C₁- and C₂- hydrocarbon ions with acetylene, C₂- hydrocarbon ions with methane and a few reactions of C₁- or C₂- hydrocarbon ions with ethylene and ethane. Some of the more important reactions are listed below:



Although C_xH_y⁺ does not represent a single ion, the computed peak density of HCNH⁺ is almost an order of magnitude less than the total electron density. Thus HCNH⁺ is clearly less important than other models have found it to be.

3. Discussion and Conclusions

The ionization peak on Titan appears roughly at the homopause, which is near 1050 km in the *Strobel* [1992] model. There the major neutral species are N₂ and CH₄. Although hydrocarbon and related ions comprise only a small fraction of the ions produced by photoionization and photoelectron-impact ionization, our model

shows that such ions may be abundant none-the-less near and below the major ion peak, as well as in the topside ionosphere. The major ions produced in any ionosphere will be transformed by ion-molecule reactions if they are formed in the presence of sufficient densities of neutral species with which they can react. In reducing environments, ionization flows from species whose parent neutrals have smaller proton affinities to species whose parent neutrals have larger proton affinities.

A major uncertainty in the ionospheric model is the accuracy of the neutral model, including the density profiles computed by Yung *et al.* [1984]. We note here that the crucial C_4H_2 density was underestimated in the middle atmosphere in the Yung *et al.* model compared to measured values. It seems that, if anything, the actual values will be larger than those we have assumed. Moreover, the conclusion that $HCNH^+$ does not dominate the ion density profile depends only on the presence (with a large enough density) of some species that has a higher proton affinity than HNC or HCN, or of some other photochemical pathway to the protonated species. With a fairly large thermospheric mixing ratio of methane, and the presence of solar ultraviolet photons, that is all but certain.

Another interesting result of the calculations is that hydrocarbon ions dominate the ionosphere at high altitudes as well as at the ionospheric peak. The exobase of Titan is near 1500 km, where both $C_2H_5^+$ and $C_xH_y^+$ have densities that are on the order of several hundred cm^{-3} . Although the processes are not included in our model, ions above the exobase may escape into Saturn's magnetosphere. These processes have been investigated by Keller and Cravens [1994] using earlier chemical models that predicted $HCNH^+$ to be the major ion. The results presented here suggest that $C_2H_5^+$ and $C_xH_y^+$ may also be the dominant ions supplied to Saturn's magnetosphere.

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