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This report consists of two parts and appendices. The two parts are drafts of papers that are being prepared for publication with co-author Roger Yelle. These papers are on the ionosphere of Titan and heating efficiencies in the Titan thermosphere. Appended to the report are copies of chapters published or in press that relate to the subject of this project, and the grant is acknowledged, where possible, in these manuscripts. They are “Ion chemistry in atmospheric and astrophysical plasmas” by A. Dalgarno and J. L. Fox, “Dissociative recombination in planetary ionospheres” by J. L. Fox, “Hydrocarbon ions in the ionospheres of Titan and Jupiter” by J. L. Fox, and “Aeronomy” (chapter for the Atomic and Molecular Physics Reference Book, AIP Press, 1996, edited by Gordon Drake) by J. L. Fox.

In addition, two talks based on work supported by this grant were given at annual meetings of the Division of Planetary Sciences of the American Astronomical Society: “Heating efficiencies in the Titan thermosphere” (J. L. Fox and R. V. Yelle) Palo Alto, November, 1991; “A new model of the ionosphere of Titan” (J. L. Fox and R. V. Yelle), Kona, October, 1995. Invited talks were also presented by J. L. Fox at the Second International Symposium on Dissociative Recombination (“Dissociative recombination in planetary ionospheres”) in St. Jacut, May, 1992, and at the Third International Symposium on Dissociative Recombination (“Hydrocarbon ions in the ionospheres of Jupiter and Titan”) in Ein Gedi, May, 1995. The subject matter of these talks included discussion of the Titan ionosphere based on work supported by this grant.
Abstract

We have constructed a coupled ion and neutral chemical model of the ionosphere and thermosphere of Titan. Along with density profiles of ions and minor neutrals, we have computed the heating rates and heating efficiencies for the neutrals and chemical heating rates and efficiencies for the ions. We find that the neutral heating efficiency in our standard model varies from about 30% near 800 km to 22% near 2000 km. The most important heating processes are neutral-neutral reactions and photodissociation. The ion chemical heating rates maximize at about 10 eV cm$^{-3}$s$^{-1}$, and the corresponding ion heating efficiencies peak near 1000 km at about 0.6%.
Introduction

The heating efficiency is the fraction of solar energy absorbed that is deposited locally as heat. The EUV (~100-1000 Å) and FUV (~1000–2000Å) regions of the solar spectrum are absorbed in the thermospheres of planets. Solar energy is transformed to heat in photodissociation and photoelectron impact dissociation of molecules, in exothermic reactions, including ion-molecule reactions, neutral-neutral reactions, and dissociative recombination of ions with electrons. Neutral heating efficiencies are important in determining the neutral temperature structure and thus the chemical structure of the thermosphere. Although the main source of ion heating in non-auroral planetary ionospheres during the daytime is Coulomb collisions with photoelectrons, ion-molecule reactions are a source of heat that can be important in the region of the ion peak (Rohrbaugh et al., 1979; Cravens et al., 1980).

We have modeled the thermosphere and ionosphere of Titan, with a view toward determining the ionospheric structure, altitude profiles of minor neutral species, and the EUV heating efficiencies. We have adopted the F79050N solar fluxes of Hinteregger [private communication; see also Torr et al., 1979], which is appropriate to a period of high solar activity, such as that which prevailed at the time of the Voyager 1 encounter with Saturn and Titan (1981). The solar zenith angle in our model is 60°. Photoionization and photodissociation are included for N₂, CH₄, C₂H₆, C₂H₄, C₂H₂, and H₂, as well as photoionization of H, N and C. In addition, photoionization of CH₃ by Lyman alpha and photodissociation of HCN are also included. Electron impact excitation and ionization are included for N₂, CH₄, H₂, H, C and N. The cross sections for photoionization and dissociative photoionization of N₂ from threshold to 116 Å were taken from Samson et al. (1987). The N₂ electron impact cross sections are the same as those adopted by Fox and Victor (1988) in their study of electron energy deposition in N₂ gas. The cross sections for photoionization of hydrocarbons, and electron impact on H₂, H and CH₄ are the same as those compiled by Kim and Fox (1990). The cross sections for photodissociation of HCN were taken from Nuth and Glicker (1982) and Lee (1980). The cross sections for photoionization of C and N were taken from LeDourneuf et al. (1976), Cantu et al. (1981), and Daltabuit and Cox (1972). The electron impact ionization cross sections for C and N were adopted from the measurements of Brook et al. (1978). The ionization potential of CH₃ is 9.84 eV, and photoionization by solar Lyman alpha is possible, but the cross section has not been computed or measured. We assume, as did Strobel (1975), that the cross section is equal to that of atomic carbon at threshold, 1.2 × 10⁻¹⁷ cm².
Sources of Heating

*Photodissociation.* In photodissociation, the amount of energy that goes into kinetic energy is the difference between the energy of the photon and the dissociation energy (which may include some internal excitation of the fragments). In the absence of information about the electronic states of the fragments, they are assumed to be produced in their ground states. When there are molecular products, some of the energy may be taken up as vibrational energy of the fragments. The energy that appears as vibrational excitation in photodissociation has been found to be small [cf. Fox, 1988 and references therein; this would be expected to be especially true when the fragments are H atoms. We assume here that 25% of the excess energy appears as vibrational energy of molecular products, and the remainder is converted to kinetic energy, as we have in previous calculations of heating efficiencies [e.g. Fox, 1988]. A half-collision model (Holdy et al., 1970) suggests, however, that when one of the fragments is very light, such as a hydrogen atom or molecule, the energy that appears as vibrational excitation of the other fragment may be very small.

It is possible that only 10-15% of the energy is taken up as vibrational excitation in photodissociation.

The N₂ dissociation threshold is large, about 9.76 eV, and because most of the dissociation occurs through discrete excitation into predissociating states in the singlet manifold, the effective dissociation threshold is larger. Consequently, N₂ does not absorb longward of about 985 Å. Although N₂ is the major species in the atmosphere, the peak heating rate due to photodissociation of N₂ is only 5.7 eV cm⁻³ s⁻¹ at about 1060 km near the ionospheric peak. By contrast, CH₄ is a strong absorber, and photodissociation of CH₄ is the most important heating process of this type. The peak heating rate is about 1.4 x 10⁹ eV cm⁻³ s⁻¹ at 770 km. Although at this altitude infrared heating may be more important than solar ultraviolet heating, the dominance of heating due to methane photodissociation extends to higher altitudes. At 1060 km, the heating rate due to methane photodissociation is 1.23 x 10⁹ eV cm⁻³ s⁻¹. Even HCN photodissociation is more important than that of N₂, with a heating rate of about 8 eV cm⁻³ s⁻¹ at 1060 km.

*Chemical reactions.* The energy released in exothermic reactions can appear as kinetic energy of the products, thus resulting in heating. The partitioning of kinetic energy between the products in any reaction is determined by conservation of momentum and energy. For the case in which there are only two products, the kinetic energies of species 1 and 2, ε₁ and ε₂, respectively, are given by

\[ ε₁ = m₂ / (m₁ - m₂) ε \]

and

\[ ε₂ = m₁ / (m₁ - m₂) ε \]

where \( m_j \) is the mass of species \( j \) and \( ε \) is the total kinetic energy released in the reaction.

Dissociative recombination reactions in particular are often very exothermic and contribute significantly to neutral heating. On Mars and Venus, dissociative recombination of the major ion, O³⁺, is the most important chemical heat source for the neutrals [Fox and Dalgarno, 1979, 1981; Fox, 1988]. On the Earth, dissociative recombination of NO⁺ is the most important heat source among reactions of species in their ground states [Torr et al., 1980]. On Titan, we find that dissociative recombination is not as important as it
is on the terrestrial planets, partly because the ions are "processed" more, that is, they have undergone more transformations before they recombine. More important, however, is the presence of methane, which is a strong absorber, increasing both the heating rate due to photodissociation and the production rate of neutral fragments that can participate in neutral-neutral reactions compared to the terrestrial planets.

**Dissociative Recombination.** In dissociative recombination of polyatomic molecular ions, as in photodissociation, some uncertainty exists about how much of the exothermicity appears as vibrational excitation of the molecular products. And just as for photodissociation, a half-collision model suggests that little energy is expected to be deposited as vibrational excitation. We have assumed that 25% of the energy released appears as vibrational energy of molecular fragments; that value may be an overestimate where one of the products is an H atom. For example, an important dissociative recombination reaction for neutral heating is that of HCNH$.+$. There are four exothermic product channels for this reaction:

$$\text{HCNH}^+ + e \rightarrow \text{HCN} + \text{H}$$
$$\rightarrow \text{HNC} + \text{H}$$
$$\rightarrow \text{CH}_2 + \text{N}$$
$$\rightarrow \text{H}_2 + \text{CN}.$$  

The only information that is available about the product channels is the measurement of Adams et al. [1991], that indicated that 0.63 H atoms are produced per recombination. This implies that the sum of the branching ratios for the first two channels is 63% and the sum of the second two branching ratios is 37%. We somewhat arbitrarily assume that production of HCN, the more stable isomer, is the dominant channel of the first two. and that the third channel is more important than the fourth.

**Electron impact heating.** In electron impact dissociation some of the energy lost by the electron may appear as kinetic energy of the neutrals produced. In general, the fraction of energy that appears as kinetic energy is not fixed for a given process and it is therefore not possible to determine the heating due to electron impact dissociation exactly. An average value may be determined from time-of-flight studies, or derived from electron energy loss spectroscopy, but measurements are not available for all of the electron impact dissociations. Fortunately, Prokop and Zipf [1982] have measured the average kinetic energy of the N atoms that are released in electron impact dissociation and dissociative ionization of N$$_2$$, and report values of 0.45 eV and 3.0 eV, respectively. Since this is the most important species in the Titan atmosphere, it accounts for most of the photoelectron energy loss at the ion peak, near 1000 km. In computing the heating due to electron impact dissociation, we have adopted the measured values for N$$_2$$, and we have assumed a value of 1.0 eV per dissociation or dissociative ionization of H$$_2$$ and CH$$_4$$.

**Ion-molecule reactions.** In ion-molecule and neutral-neutral reactions, the exothermicity can appear as internal energy of the products, as well as kinetic energy. In general, little information is available about the partitioning of energy among the various modes. For our standard calculation, we have assumed that 60% of the energy appears as vibrational energy of the products. We also then compute lower and upper limits to the heating efficiency using the values 80 and 40%, respectively. As mentioned above, for ion-molecules reactions, the partitioning of kinetic energy between the the neutral and the ion product
is determined by momentum conservation. The most important ion-molecule reactions for thermospheric heating are

\[ \text{N}_2^- + \text{CH}_4 \rightarrow \text{CH}_3^+ + \text{N}_2 + \text{H} \]

and

\[ \text{CH}_3^- + \text{CH}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2. \]

The most important neutral-neutral reactions are:

\[ \text{CH}_2 + \text{CH}_2 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 \]

and

\[ \text{NH} + \text{N} \rightarrow \text{N}_2 + \text{H}. \]

Results

The neutral heating rates as a function of altitude are presented in Figure 1 and resulting heating efficiencies are shown in Figure 2. The standard values vary from about 0.30 at 800 km to 0.22 at 2000 km. The lower and upper limits are smaller and larger by about 0.05 near 800 km but converge to nearly the standard value at 2000 km. These heating efficiencies are very different from those appropriate to Earth, which are in excess of 0.50, and are more like those for Venus and Mars, which are about 0.20–0.24. It is apparent that in N2 atmospheres, it is the minor species that dominate the absorption and heating: O2 for the terrestrial case, and methane for Titan.

The ion chemical heating rates are shown in Figure 3 for the standard, upper and lower limit models and the corresponding heating efficiencies are shown in Figure 4. The chemical heating rates are much smaller than the neutral heating rates, and attain maximum values on the order of 10 eV cm^{-3}s^{-1} near the ion peak. The heating efficiencies maximize near the ion peak at values of 0.003, 0.006, and 0.009 for the lower limit, standard, and upper limit models. We can compare the ion chemical heating rates to those computed by Roboz and Nagy (1994). Their “solar-only” heating rates maximize near the ion peak with values that are much less than ours, about 0.3 eV cm^{-3}s^{-1}. The source of the difference is uncertain, but probably arises from our use of a more complete set of reactions.

References

Figure 1. Altitude profiles of the heating rates of the most important processes in the Titan thermosphere.

Figure 2. Altitude profiles for the heating efficiencies for solar radiation in the 14–2000 Å interval. The standard, upper limit and lower limit profiles are illustrated.

Figure 3. Altitude profiles of the ion chemical heating rates in the Titan thermosphere for the standard (solid curve), lower limit (short-dashed) and upper limit (long-dashed) models.

Figure 4. Altitude profiles for the ion heating efficiencies for solar radiation in the 14–2000 Å interval. The standard (solid curve), upper limit (short-dashed) and lower limit (long-dashed) models are illustrated.
PD=Photodissociation
NN=Neutral–Neutral Rxns
IM=Ion–Molecule Rxns
EI=Electron-Impact Dissociation
DR=Dissociative Recombination

Altitude (km)

Log Heating Rate (eV cm\(^{-3}\) s\(^{-1}\))

Fig 3.
DRAFT

A New Model of the Ionosphere of Titan

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Abstract
We have constructed a new model of the ionosphere of Titan that includes 69 species and 626 reactions. Although N_2^+ is the major ion produced in the ionosphere, the ionization flows to ions whose parent neutrals have lower ionization potentials and to species with large proton affinities. In contrast to other models, which have predicted that HCNH^- should be the major ion, we suggest that the major ions at and below the ion peak near 1050 km are hydrocarbon ions and H, C, and N-containing ions. Our predicted peak electron density for a solar zenith angle of 60° is 6.3 × 10^3 cm^{-3} at an altitude of 1050 km.

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 is near 1050 km, where the eddy diffusion coefficient is about 1 × 10^9 cm^{-1}s^{-1}. The exobase is near 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) × 10^3 cm^{-3} near the terminators as the spacecraft entered and exited the occultation region. Recently, Bird et al. (1995) have 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 near 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 the orbit of Titan is embedded during part of its orbit (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 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 here 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 ion peak.
The Model

The background model neutral thermosphere that we have adopted here is shown in Fig. 1. The density profiles of N$_2$ and CH$_4$ are taken from Strobel et al. (1992), and mixing ratios of C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, and C$_4$H$_2$ 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% at the lower boundary, 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 temperature profile is taken from Strobel et al. (1992), and is nearly isothermal at the exospheric temperature of approximately 175K above about 1000 km. The electron temperatures are taken from Gan et al. (1992).

In our model, the density profiles of six species were fixed, and we compute the densities of 34 neutral species and 35 ions, which are enumerated in Table 1. We have included photoabsorption and photoionization of N$_2$, CH$_4$, C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$, N, C, H and H$_2$, photodissociation of HCN, and photoionization of CH$_3$ by Lyman alpha. The solar spectrum used 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 was included for N$_2$, CH$_4$, H, H$_2$, N and C. The most important production rate profiles are shown in Fig. 2. The major ion produced is N$^-$ from 600 to 1800 km. and CH$_3^+$ above that altitude. Other important ions produced include N$^-$, CH$_3^-$, C$_2$H$_5^-$, and C$_2$H$_3^+$.

The ion density profiles were computed including 626 chemical reactions. The ion-molecule, neutral-neutral and dissociative recombination reactions in the model are listed in Table 2 along with their assumed rate coefficients. Most of the rate coefficients for the ion-molecule reactions were taken from the compilations of Anicich and Huntress (1986) and Anicich (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 $(3 - 3.5) \times 10^{-7}(300/T)^{0.5}$ cm$^3$ s$^{-1}$ were assumed. Even where dissociative recombination coefficients have been measured, in many cases there is little information about the product yields, for which in general there are many possibilities, especially for polyatomic ions. Because the ion and neutral chemistries are coupled, (and because the exothermicity and production of fast atoms depend on the channel by which the recombination proceeds), measurements of the product yields are important. Here we have assumed that the available channels 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.
The predicted densities of the major ions are shown in Fig. 3. The peak electron density is about $6.3 \times 10^3 \text{ cm}^{-3}$ near 1050 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. We would expect the densities to be substantially larger than ours, which are for the dayside at 60° solar zenith angle.

Although $N_2^+$ is the major ion produced up to about 1800 km, below about 1900 km it is lost by reaction with methane

$$N_2^- + CH_4 \rightarrow CH_2^+ + N_2 + H_2$$  \hspace{1cm} (1a)

$$\rightarrow CH_3 + N_2 + H,$$  \hspace{1cm} (1b)

and above that altitude by the reaction:

$$N_2^+ + H_2 \rightarrow N_2H^+ + H.$$  \hspace{1cm} (2)

Reaction with H and charge transfer to acetylene are minor loss processes in the lower ionosphere. Dissociative recombination becomes the second most important loss mechanism above about 2500 km. Altitude profiles for the loss processes are shown in Fig. 4.

The major ion at high altitudes is $N_2H^+$. The major production and loss mechanisms for $N_2H^+$ are shown in Fig. 5. $N_2H^+$ is produced mainly in the reaction of $N_2^+$ with $H_2$ (reaction 2) below 1300 km and above 1700 km. Over a limited altitude range, about 1300–1700 km, the most important source is

$$H_2^- + N_2 \rightarrow N_2H^+ + H$$  \hspace{1cm} (3)

Other minor sources include the reactions of $H_3^-$ with $N_2$ and $NH^-$ with $N_2$. The most important loss mechanism is dissociative recombination

$$N_2H^+ - e \rightarrow \text{products}$$  \hspace{1cm} (4)

above 2300 km and proton transfer to CH$_4$:

$$N_2H^- + CH_4 \rightarrow CH_5^+ + N_2$$  \hspace{1cm} (5)

below that altitude. Reaction with $C_2H_2$:

$$N_2H^- + C_2H_2 \rightarrow C_2H_5^+ + N_2$$  \hspace{1cm} (6)

is also significant near the ion peak.

In the altitude region from 1300–1800 km, the major ion is $C_2H_5^-$. At the peak near 1050 km the dominant ion is the pseudo-ion $C_2H_5^+$. The density of $C_4H_5^-$ exceeds that of
C$_x$H$_y^+$ near its peak at about 750 km. Most other models have predicted that HCNH$^+$ would be the major ion (Ip, 1990; Keller et al., 1992; Keller and Cravens, 1994). The major production and loss mechanisms for HCNH$^+$ in our model are shown in Fig. 6. Above about 1050 km, HCNH$^+$ is produced in the reaction:

$$N^+ + CH_4 \rightarrow HCNH^+ + H_2.$$  \hspace{1cm} (7)

Below the ion peak the most important source is proton transfer from C$_2$H$_3^-$ to HCN:

$$C_2H_5^+ + HCN \rightarrow HCNH^+ + C_2H_4.$$  \hspace{1cm} (8)

Minor sources include the reactions of HCN$^+$ with CH$_4$ at high altitudes and proton transfer of C$_2$H$_3^-$ to HCN at low altitudes. Below the ion peak, HCNH$^-$ is lost mainly by proton transfer to C$_4$H$_2$:

$$HCNH^- + C_4H_2 \rightarrow C_4H_3^+ + HCN.$$  \hspace{1cm} (10)

The proton transfer reactions with HC$_3$N, and with NH$_3$ are also significant below about 1000 km. Loss is by dissociative recombination above that altitude.

The major production reactions for C$_x$H$_y^-$ are reactions of C$_1$- and C$_2$- hydrocarbon ions with acetylene, C$_2$- hydrocarbon ions with methane and a few reactions of C$_1$- or C$_2$- hydrocarbon ions with ethylene and ethane. The most important production reactions are plotted in Fig. 7 and are listed below:

$$CH_5^- + C_2H_2 \rightarrow C_3H_3^- + H_2$$ \hspace{1cm} (10)

$$C_2H_4^- + C_2H_2 \rightarrow C_3H_3^- + CH_3$$ \hspace{1cm} (11)

$$C_2H_5^- + C_2H_2 \rightarrow C_4H_3^- + H$$ \hspace{1cm} (12)

$$C_2H_5^- + C_2H_2 \rightarrow C_3H_7^- + CH_4$$ \hspace{1cm} (13)

$$C_2H_5^- + C_2H_2 \rightarrow C_4H_3^- + H_2$$ \hspace{1cm} (14)

$$C_2H_5^- + CH_4 \rightarrow C_3H_7^- + H$$ \hspace{1cm} (15)

$$C_2H_3^- + CH_4 \rightarrow C_3H_7^- + H_2$$ \hspace{1cm} (16)

$$C_2H_4^- + C_2H_4 \rightarrow C_3H_7^- + CH_3$$ \hspace{1cm} (17)

$$C_2H_5^- + C_2H_4 \rightarrow C_3H_7^- + CH_4$$ \hspace{1cm} (18)

$$CH_5^- + C_2H_6 \rightarrow C_3H_7^- + H_2$$  \hspace{1cm} (19)

Although C$_x$H$_y^+$ clearly does not represent a single ion, and thus is not the major ion in that sense, the computed peak density of HCNH$^+$ is almost an order of magnitude less than the total electron density.
**Photoelectron fluxes**

A secondary but important source of ions near and below the ion peak is photoelectron impact ionization. The predicted primary and steady-state fluxes from of photoelectrons 0 to 200 eV at 0.5 eV resolution near 1000 km are shown in Fig. 8. The top spectrum is the initial spectrum and the bottom is the steady-state spectrum averaged over three intervals (1.5 eV). The spectrum displays a sharp drop-off above 70 eV, where photoelectrons produced by the the last of the strong solar lines appear. The spectrum appears similar to that of Gan et al. (1992) for their solar-only case, but the sharp bite-out from about 20 to 40 eV does not appear in our spectrum. The reason is unknown, but will be investigated.

**Discussion**

Solar ionizing photons are absorbed in the thermospheres of planets and satellites, and the peak ionization rate is usually found at a column density of about $10^{17}$ cm$^{-2}$. This altitude may be near or above the homopause, where the transition from transport by large scale mixing to that by molecular diffusion takes place. Although the density of CH$_4$ eventually exceeds that of N$_2$ at high altitudes on Titan, the ionization peak appears roughly at the homopause, which is near 1050 km in the Strobel (1992) model. There the major neutral species is N$_2$ and the mixing ratio of CH$_4$ is about 3%. Although hydrocarbon and related ions clearly comprise only a small fraction of the ions produced by photoionization and electron-impact ionization on Titan, our model shows that such ions may be abundant near and below the major ion peak.

The major ions produced in any ionosphere will be transformed by ion-neutral reactions if they are formed in the presence of sufficient densities of neutrals with which they can react. In reducing environments, such as the atmospheres of the outer planets and their satellites, ionization tends to flow from species whose parent neutrals have small proton affinities to species whose parent neutrals have large proton affinities. On the giant planets, the terminal ions will be large protonated hydrocarbons (e.g., Kim and Fox, 1991; 1994); on Titan, the major species will be hydrocarbon ions, protonated nitriles and other ion containing C, H and N. In most cases, the available information about ion chemistry is insufficient to identify the terminal ions in the bottomside ionospheres, but since larger molecules tend to have larger proton affinities, the average size of the ion probably increases with decreasing altitude. In order to improve our understanding of these ionospheres, rate coefficients and branching ratios for reactions of hydrocarbons and hydrocarbon ions, and neutral and ionic species containing C, H and N are needed, including those for dissociative recombination reactions. Some representative proton affinities are shown in Table 3.

Clearly, a major uncertainty in the ionosphere 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$_4$H$_2$ 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 chemical 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.

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References

Figure Captions

Fig. 1. Neutral density profiles in the thermosphere of Titan that were adopted in these calculations. The densities of N₂, CH₄, C₂H₂, C₂H₄, C₂H₆, and CO were assumed to be fixed. The density profiles of H₂ and H were computed self-consistently in the model.

Fig. 2. The computed production rate profiles for the most important ions produced in the Titan ionosphere.

Fig. 3. Computed steady-state densities of the most important ions produced. The solid curves are labeled by the ion produced dashed and the dashed curve is the electron density profile. C₂H⁺ is a pseudo-ion that represents all hydrocarbon other than those included explicitly.

Fig. 4. Altitude profiles of the major loss processes for N₂⁺ in the Titan ionosphere. The curves are labeled by the species with which the N₂⁺ ions react.

Fig. 5. Altitude profiles for the major sources (top) and sinks (bottom) of N₂H⁺ in the Titan ionosphere.

Fig. 6. Altitude profiles for the major sources (top) and sinks (bottom) of HCNH⁺ in the Titan ionosphere.

Fig. 7. Altitude profiles of the major sources of C₂H⁺ in the Titan ionosphere.

Fig. 8. Computed primary (top curve) and steady-state (bottom curve) photoelectron fluxes at 1050 km. The bin size for the primary fluxes is 0.5 eV. The steady-state fluxes have been averaged over three bins. The peak at 200 eV is an artifact that results from the treatment of photoelectrons with energies larger than 200 eV, which have been divided into one or more 200 eV electrons and an electron with the remainder of the energy.
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<td>$\text{O}$</td>
</tr>
<tr>
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<td>$\text{NH}_3$</td>
<td>$\text{NH}_3$</td>
<td>$\text{NH}_3$</td>
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<tr>
<td>$\text{CN}^+$</td>
<td>$\text{CN}$</td>
<td>$\text{CN}$</td>
<td>$\text{CN}$</td>
</tr>
<tr>
<td>$\text{HCN}^+$</td>
<td>$\text{HCN}$</td>
<td>$\text{HCN}$</td>
<td>$\text{HCN}$</td>
</tr>
<tr>
<td>$\text{CH}_3^+$</td>
<td>$\text{CH}_3$</td>
<td>$\text{CH}_3$</td>
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<tr>
<td>$\text{CH}_2^+$</td>
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<tr>
<td>$\text{CH}_1^+$</td>
<td>$\text{CH}_1$</td>
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<tr>
<td>$\text{H}^+$</td>
<td>$\text{H}$</td>
<td>$\text{H}$</td>
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</tr>
</tbody>
</table>

Table 2.

Species in the Titan model.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^+ + CH_4 \rightarrow CH_3^+ + H_2^+$</td>
<td>$3.690 \times 10^{-9}$</td>
</tr>
<tr>
<td>$H^+ + CH_4 \rightarrow CH_2^+ + H^+$</td>
<td>$8.100 \times 10^{-9}$</td>
</tr>
<tr>
<td>$H^+ + C_2H_6 \rightarrow C_2H_5^+ + H_2^+$</td>
<td>$1.300 \times 10^{-9}$</td>
</tr>
<tr>
<td>$H^+ + C_2H_6 \rightarrow C_2H_5^+ + H^+$</td>
<td>$1.300 \times 10^{-9}$</td>
</tr>
<tr>
<td>$H^+ + C_2H_6 \rightarrow C_2H_5^+ + H_2^+$</td>
<td>$1.300 \times 10^{-9}$</td>
</tr>
<tr>
<td>$H^+ + HCN \rightarrow HCN^+ + H^+$</td>
<td>$1.100 \times 10^{-8}$</td>
</tr>
<tr>
<td>$H^+ + NH_3 \rightarrow NH_2^+ + H^+$</td>
<td>$5.200 \times 10^{-9}$</td>
</tr>
<tr>
<td>$H^+ + NH \rightarrow NH^+ + H^+$</td>
<td>$2.100 \times 10^{-9}$</td>
</tr>
<tr>
<td>$H^+ + H_2 \rightarrow H_3^+$</td>
<td>$3.200 \times 10^{-9} (T_d/300)^{0.00} \exp(-0.00/T_d) [M]$</td>
</tr>
<tr>
<td>$H^+ + C_2H_2 \rightarrow C_2H^+ + H_2^+$</td>
<td>$4.300 \times 10^{-9}$</td>
</tr>
<tr>
<td>$H^+ + CH_4 \rightarrow CH_3^+ + H_2^+$</td>
<td>$2.280 \times 10^{-9}$</td>
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<tr>
<td>$H^+ + CH_4 \rightarrow CH_2^+ + H^+$</td>
<td>$1.410 \times 10^{-9}$</td>
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<td>$H^+ + C_2H_2 \rightarrow C_2H_2^+ + H$</td>
<td>$6.800 \times 10^{-9}$</td>
</tr>
<tr>
<td>$H^+ + C_2H_2 \rightarrow C_2H_2^+ + H_2$</td>
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</tr>
<tr>
<td>$H^+ + NH \rightarrow NH^+ + H_2^+$</td>
<td>$2.100 \times 10^{-9}$</td>
</tr>
<tr>
<td>$H_3^+ + CH_4 \rightarrow CH_3CH_3^+ + H_2$</td>
<td>$8.800 \times 10^{-10}$</td>
</tr>
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</tr>
<tr>
<td>$H_3^+ + C_2H_6 \rightarrow C_2H_5^+ + H_2$</td>
<td>$2.940 \times 10^{-9}$</td>
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<td>$2.940 \times 10^{-9}$</td>
</tr>
</tbody>
</table>
\[
\begin{align*}
CH_3^+ + CH_3NH_2 & \rightarrow C_2H_5N_2^+ + CH_2^- & 7.350 \times 10^{-10} \\
CH_3^+ + CH_3NH_2 & \rightarrow C_2H_5N_2^+ + CH_- & 1.160 \times 10^{-10} \\
CH_3^+ + CH_3NH_2 & \rightarrow C_2H_5N_2^+ + CH_- & 4.100 \times 10^{-10} \\
CH_3^+ + CH_3NH_2 & \rightarrow C_2H_5N_2^+ + CH_- & 1.000 \times 10^{-30} (T_n/300)^{6.00} \exp(-0.00 / T_n) [M] \\
CH_3^+ + CH_3NH_2 & \rightarrow C_2H_5N_2^+ + CH_- & 1.200 \times 10^{-9} \\
CH_3^+ + CH_3NH_2 & \rightarrow C_2H_5N_2^+ + CH_- & 1.100 \times 10^{-13} \\
CH_3^+ + CH_3NH_2 & \rightarrow C_2H_5N_2^+ + CH_- & 1.100 \times 10^{-28} (T_n/300)^{6.00} \exp(-0.00 / T_n) [M] \\
CH_3^+ + CH_3NH_2 & \rightarrow C_2H_5N_2^+ + CH_- & 1.200 \times 10^{-9} \\
CH_3^+ + CH_3NH_2 & \rightarrow C_2H_5N_2^+ + CH_- & 3.500 \times 10^{-10} \\
CH_3^+ + CH_3NH_2 & \rightarrow C_2H_5N_2^+ + CH_- & 4.600 \times 10^{-11} \\
CH_3^+ + CH_3NH_2 & \rightarrow C_2H_5N_2^+ + CH_- & 5.240 \times 10^{-10} \\
\end{align*}
\]
\[
\begin{align*}
\text{CH}_2^+ + \text{HC}_3\text{N} & \rightarrow \text{C}_2\text{H}_2\text{N}_2^- - \text{CH}_4^- & 4.50 \times 10^{-9} \\
\text{CH}_3^+ + \text{NH}_3 & \rightarrow \text{NH}_4^+ + \text{CH}_4^- & 2.30 \times 10^{-9} \\
\text{CH}_4^+ + \text{H} & \rightarrow \text{CH}_4^- + \text{H}_2^- & 1.50 \times 10^{-10} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow 2\text{C}_2^+ + \text{H} & 1.40 \times 10^{-9} \\
\text{C}_2^+ + \text{CH}_4 & \rightarrow \text{C}_2\text{H}_2^+ + \text{CH}_4^- & 2.38 \times 10^{-10} \\
\text{C}_2^+ + \text{CH}_4 & \rightarrow \text{C}_2\text{H}_2^+ + \text{CH}_2^- + \text{H} & 1.82 \times 10^{-10} \\
\text{C}_2^+ + \text{CH}_4 & \rightarrow \text{C}_2\text{H}_2^+ + \text{CH}_2^- + \text{H}_2 & 1.96 \times 10^{-10} \\
\text{C}_2^+ + \text{CH}_4 & \rightarrow 2\text{C}_2^+ + \text{H}_2^- + \text{H} & 5.74 \times 10^{-10} \\
\text{C}_2^+ + \text{CH}_4 & \rightarrow 2\text{C}_2^+ + \text{H}_2^- + \text{H}_2 & 2.10 \times 10^{-10} \\
\text{C}_2^+ + \text{CH}_4 & \rightarrow \text{C}_2\text{H}_2^+ + \text{H} & 1.20 \times 10^{-9} \\
\text{C}_2^+ + \text{C}_2\text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.90 \times 10^{-9} \\
\text{C}_2^+ + \text{HCN} & \rightarrow \text{C}_2\text{H}_4^+ + \text{CN} & 2.60 \times 10^{-10} \\
\text{C}_2^+ + \text{HCN} & \rightarrow \text{C}_2\text{H}_4^+ + \text{N} & 7.80 \times 10^{-10} \\
\text{C}_2^+ + \text{HCN} & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.56 \times 10^{-9} \\
\text{C}_2^+ + \text{C}_2\text{H}_4 & \rightarrow \text{C}_2\text{H}_4^+ + \text{C}_2 & 2.31 \times 10^{-10} \\
\text{C}_2^+ + \text{HC}_3\text{N} & \rightarrow \text{C}_2\text{H}_4^+ + \text{HCN} & 5.61 \times 10^{-10} \\
\text{C}_2^+ + \text{HC}_3\text{N} & \rightarrow \text{C}_2\text{H}_4^+ + \text{CN} & 1.29 \times 10^{-9} \\
\text{C}_2^+ + \text{HC}_3\text{N} & \rightarrow \text{C}_2\text{H}_4^+ + \text{C}_2 & 1.98 \times 10^{-10} \\
\text{C}_2^+ + \text{C}_2\text{H}_4 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.02 \times 10^{-9} \\
\text{C}_2^+ + \text{C}_2\text{H}_4 & \rightarrow \text{C}_2\text{H}_4^+ + \text{N} & 7.50 \times 10^{-10} \\
\text{C}_2^+ + \text{C}_2\text{H}_4 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 4.50 \times 10^{-10} \\
\text{C}_2^+ + \text{C}_2\text{H}_4 & \rightarrow \text{C}_2\text{H}_4^+ + \text{N}_2 & 3.00 \times 10^{-10} \\
\text{C}_2^+ + \text{NH} & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 3.30 \times 10^{-10} \\
\text{C}_2^+ + \text{CH}_4 & \rightarrow \text{C}_2\text{H}_4^+ + \text{CH}_4^- & 3.74 \times 10^{-10} \\
\text{C}_2^+ + \text{CH}_4 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 3.74 \times 10^{-10} \\
\text{C}_2^+ + \text{C}_2\text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.32 \times 10^{-10} \\
\text{C}_2^+ + \text{CH}_4 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.00 \times 10^{-10}\left((T_n/300)^{1.0}\times \exp(-0.001T_n)\right)M^2 \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.20 \times 10^{-9} \\
\text{C}_2^+ + \text{C}_2\text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.70 \times 10^{-9} \\
\text{C}_2^+ + \text{N} & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.00 \times 10^{-11} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.35 \times 10^{-9} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.35 \times 10^{-9} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.35 \times 10^{-9} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.66 \times 10^{-10} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.10 \times 10^{-9} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.80 \times 10^{-9} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 3.68 \times 10^{-10} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.23 \times 10^{-10} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 5.16 \times 10^{-10} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 5.88 \times 10^{-10} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 3.75 \times 10^{-10} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 7.95 \times 10^{-10} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 3.30 \times 10^{-10} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 2.63 \times 10^{-10} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.31 \times 10^{-10} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 8.76 \times 10^{-11} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.46 \times 10^{-11} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 7.88 \times 10^{-10} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 7.30 \times 10^{-11} \\
\text{C}_2^+ + \text{H}_2 & \rightarrow \text{C}_2\text{H}_4^+ + \text{H} & 1.31 \times 10^{-10} 
\end{align*}
\]
\[
\begin{align*}
C_2H_2^+ + N &\rightarrow CH^+ + HCN + & 2.500 \times 10^{-11} \\
C_2H_2^+ + N &\rightarrow C_2N^+ + H_2 + & 7.500 \times 10^{-11} \\
C_2H_2^+ + N &\rightarrow C_2H_3N^+ + H - & 1.500 \times 10^{-10} \\
C_2H_2^+ + NH_3 &\rightarrow NH_3^+ + C_2H_2 + & 1.240 \times 10^{-9} \\
C_2H_2^+ + NH_3 &\rightarrow NH_3^+ - C_2H + & 1.860 \times 10^{-9} \\
C_2H_2^+ + HCN &\rightarrow C_2H_2N^+ + C_2H + & 6.720 \times 10^{-11} \\
C_2H_2^+ + HCN &\rightarrow C_2H_2N^+ - HCN - & 3.780 \times 10^{-11} \\
C_2H_2^+ + HCN &\rightarrow C_2H_2N_2^+ + C_2H - & 5.000 \times 10^{-28}(T_n/300)^{0.00} \exp(-0.00/T_n) [M] \\
C_2H_2^+ + HCN &\rightarrow C_2H_2N_2^+ - HCN - & 1.480 \times 10^{-9} \\
C_2H_2^+ + HCN &\rightarrow C_2H_2N_2^+ + C_2H - & 2.220 \times 10^{-9} \\
C_2H_2^+ + HCN &\rightarrow C_2H_2N_2^+ + C_2H - & 1.000 \times 10^{-11} \\
C_2H_2^+ + HCN &\rightarrow C_2H_2N_2^+ - C_2H - & 1.300 \times 10^{-9} \\
C_2H_2^+ + CH_3NH_2 &\rightarrow CH_3NH_2^+ + C_2H - & 7.560 \times 10^{-10} \\
C_2H_2^+ + CH_3NH_2 &\rightarrow CH_3NH_2^+ + C_2H - & 6.480 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ + C_2H - & 8.360 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ + C_2H - & 1.060 \times 10^{-9} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ + C_2H - & 1.060 \times 10^{-9} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 5.000 \times 10^{-28}(T_n/300)^{0.00} \exp(-0.00/T_n) [M] \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 1.200 \times 10^{-27}(T_n/300)^{0.00} \exp(-0.00/T_n) [M] \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 4.200 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 6.500 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 2.000 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 2.160 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 5.040 \times 10^{-11} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 9.300 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 2.910 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 2.480 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 8.060 \times 10^{-11} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 3.800 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 5.500 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 1.000 \times 10^{-28}(T_n/300)^{0.00} \exp(-0.00/T_n) [M] \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 1.600 \times 10^{-9} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 4.000 \times 10^{-11} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 1.000 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 2.200 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 6.730 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 2.370 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 7.190 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 7.110 \times 10^{-11} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 3.710 \times 10^{-13} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 4.930 \times 10^{-12} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 1.240 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 1.940 \times 10^{-9} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 1.000 \times 10^{-28}(T_n/300)^{0.00} \exp(-0.00/T_n) [M] \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 1.100 \times 10^{-9} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 3.000 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 1.000 \times 10^{-14} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 6.840 \times 10^{-11} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 1.220 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 3.550 \times 10^{-10} \\
C_2H_2^+ + CH_3CN &\rightarrow CH_3CN^+ - C_2H - & 3.270 \times 10^{-11} 
\end{align*}
\]
\[ \begin{align*}
C_2H_4^+ + C_2H_6 &\rightarrow C_2H_4^+ + CH_4^- \\
C_2H_4^+ + NH_3 &\rightarrow NH_2^+ + C_2H_4^- \\
C_2H_4^+ + CH_3NH_2 &\rightarrow C_2H_4^+ + C_2H_3N^- - H_2 \\
C_2H_4^+ + HCN &\rightarrow C_2H_4^+ + C_2H_4^- \\
C_2H_4^+ + CH_3CN &\rightarrow C_2H_4^+ + CH_4^- \\
C_2H_4^+ + C_2H_5^- &\rightarrow C_2H_4^+ + C_2H_5^- \\
C_2H_4^+ + H_2 &\rightarrow C_2H_4^+ + H_2 \\
C_2H_4^+ + CH_4 &\rightarrow C_2H_4^+ + CH_4 \\
C_2H_4^+ + CO &\rightarrow C_2H_4^+ + N_2 \\
N^+ + H_2 &\rightarrow NH^+ + H \\
N^+ + CH_4 &\rightarrow CH_3^+ + NH^- \\
N^+ + CH_4 &\rightarrow CH_3^+ + CH_3^- \\
N^+ + C_2H_4 &\rightarrow C_2H_4^+ + H_2 \\
N^+ + CH_3NH_2 &\rightarrow C_2H_4^+ + CH_3N^- \\
N^+ + CH_4 &\rightarrow C_2H_4^+ + CH_4 \\
N^+ + CO &\rightarrow CO^+ + N \\
N^+ + CO &\rightarrow NO^+ + C \\
N^+ + NH &\rightarrow NH^+ + N \\
N^+ + NH &\rightarrow N_2^+ + H \\
N^+ + HCN &\rightarrow HCN^+ + N \\
NH^+ + HCN &\rightarrow H_2CN^+ + N \\
\end{align*} \]
\[ HCN^+ + C_2H_2 \rightarrow C_2H_5N^+ + H_2^- \]
\[ 3.000 \times 10^{-10} \]
\[ HCN^+ + NH_3 \rightarrow NH_7^- - HCN^+ \]
\[ 1.680 \times 10^{-9} \]
\[ HCN^+ + NH_3 \rightarrow H_2CN^+ + NH_2^+ \]
\[ 8.400 \times 10^{-10} \]
\[ HCN^+ + NH_3 \rightarrow HCN^- + NH_7^- \]
\[ 1.400 \times 10^{-10} \]
\[ HCN^+ + HCN \rightarrow HCN^- + C_HN^+ \]
\[ 1.600 \times 10^{-9} \]
\[ HCN^+ + HCN \rightarrow C_HN^+ + C_HN^- + \]
\[ 2.000 \times 10^{-9} \]
\[ HCN^+ + C_2H_3N \rightarrow C_2H_5N^+ + HCN^- \]
\[ 2.390 \times 10^{-9} \]
\[ H_2CN^+ + NH_3 \rightarrow NH_7^- + HCN^+ \]
\[ 2.400 \times 10^{-9} \]
\[ H_2CN^+ + HC_6N \rightarrow C_2H_5N^+ + HCN^- \]
\[ 3.400 \times 10^{-9} \]
\[ H_2CN^+ + CH_3NH_2 \rightarrow C_2H_5N^+ + HCN^- \]
\[ 1.870 \times 10^{-9} \]
\[ H_2CN^+ + CH_3NH_2 \rightarrow C_2H_5N^+ + HCN^- \]
\[ 2.310 \times 10^{-10} \]
\[ H_2CN^+ + CH_3CN \rightarrow C_2H_5N^+ + HCN^- \]
\[ 3.800 \times 10^{-9} \]
\[ H_2CN^+ + C_3H_2 \rightarrow C_4H_5N^+ + HCN^- \]
\[ 1.400 \times 10^{-9} \]
\[ N_2^+ + CO \rightarrow CO^+ + N_2^- \]
\[ 7.400 \times 10^{-11} \]
\[ N_2^+ + CH_4 \rightarrow CH_5^+ + N_2^- \]
\[ 1.520 \times 10^{-9} \]
\[ N_2^+ + CH_4 \rightarrow CH_5^+ + N_2^+ \]
\[ 3.800 \times 10^{-10} \]
\[ N_2^+ + CH_4 \rightarrow CH_5^+ + N_2^- \]
\[ 4.300 \times 10^{-10} \]
\[ N_2^+ + H_2 \rightarrow N_2^+ + H^- \]
\[ 2.100 \times 10^{-9} \]
\[ N_2^+ + N \rightarrow N^+ + N_2^+ \]
\[ 5.000 \times 10^{-12} \]
\[ N_2^+ + NH_3 \rightarrow NH_7^- + N_2^- \]
\[ 2.000 \times 10^{-9} \]
\[ N_2^+ + HCN \rightarrow HCN^+ + N_2^+ \]
\[ 3.900 \times 10^{-10} \]
\[ N_2^+ + CH_3NH_2 \rightarrow C_2H_5N^+ + N_2^+ \]
\[ 7.200 \times 10^{-11} \]
\[ N_2^+ + CH_3NH_2 \rightarrow C_2H_5N^+ + N_2^- \]
\[ 8.760 \times 10^{-10} \]
\[ N_2^+ + CH_3NH_2 \rightarrow C_2H_5N^+ + N_2^- \]
\[ 2.520 \times 10^{-10} \]
\[ N_2^+ + C_2H_3N \rightarrow C_2H_5N^+ + N_2^- \]
\[ 2.900 \times 10^{-9} \]
\[ N_2^+ + C_2H_3N \rightarrow C_2H_5N^+ + N_2^- \]
\[ 8.600 \times 10^{-10} \]
\[ N_2^+ + C_2H_5CN \rightarrow C_2H_5N^+ + N_2^- \]
\[ 3.150 \times 10^{-10} \]
\[ N_2^+ + C_2H_5CN \rightarrow C_2H_5N^+ + N_2^- \]
\[ 1.370 \times 10^{-9} \]
\[ N_2^+ + C_2H_5CN \rightarrow C_2H_5N^+ + N_2^- \]
\[ 4.200 \times 10^{-10} \]
\[ N_2^+ + NH \rightarrow NH^+ + N_2^- \]
\[ 6.500 \times 10^{-10} \]
\[ N_2^+ + C \rightarrow C^+ + N_2^- \]
\[ 1.100 \times 10^{-10} \]
\[ N_2H^+ + CH_4 \rightarrow CH_5^- - N_2^- \]
\[ 8.900 \times 10^{-10} \]
\[ N_2H^+ + C_2H_2 \rightarrow C_2H_4^+ - N_2^- \]
\[ 1.140 \times 10^{-9} \]
\[ N_2H^+ + C_2H_5 \rightarrow C_2H_6^+ - N_2^- \]
\[ 1.300 \times 10^{-9} \]
\[ N_2H^+ + HCN \rightarrow H_2CN^+ + N_2^+ \]
\[ 3.200 \times 10^{-9} \]
\[ N_2H^+ + CH_3CN \rightarrow C_2H_5N^+ + N_2^- \]
\[ 4.100 \times 10^{-9} \]
\[ N_2H^+ + CH_3CN \rightarrow C_2H_5N^+ + N_2^- \]
\[ 4.300 \times 10^{-9} \]
\[ N_2H^+ + CH_3CN \rightarrow C_2H_5N^+ + N_2^- \]
\[ 4.300 \times 10^{-9} \]
\[ N_2H^+ + C_2N_2 \rightarrow C_2H_5N^+ + N_2^- \]
\[ 1.200 \times 10^{-9} \]
\[ N_2H^+ + CO \rightarrow HCO^- + N_2^- \]
\[ 8.800 \times 10^{-10} \]
\[ CN^+ + H_2 \rightarrow HCN^+ + H^- \]
\[ 5.500 \times 10^{-10} \]
\[ CN^+ + H_2 \rightarrow C_2H_4N^- + H^- \]
\[ 5.500 \times 10^{-10} \]
\[ CN^+ + CH_4 \rightarrow CH_5^- - HCN^+ \]
\[ 4.500 \times 10^{-10} \]
\[ CN^+ + CH_4 \rightarrow CH_5^- - CN^- \]
\[ 1.350 \times 10^{-10} \]
\[ CN^+ + CH_4 \rightarrow CH_5^- - CN^- \]
\[ 1.350 \times 10^{-10} \]
\[ CN^+ + CH_4 \rightarrow H_2CN^- - CH_3^+ \]
\[ 9.000 \times 10^{-11} \]
\[ CN^+ + CH_4 \rightarrow C_2H_4N^- - CH_2^+ \]
\[ 9.000 \times 10^{-11} \]
\[ CN^+ + C_2H_3 \rightarrow C_2H_4^+ - CN^- \]
\[ 1.350 \times 10^{-9} \]
\[ CN^+ + C_2H_3 \rightarrow C_2H_4N^- + H^- \]
\[ 1.500 \times 10^{-10} \]
\[ CN^+ + C_2H_4 \rightarrow C_2H_5^- - CN^- \]
\[ 7.000 \times 10^{-10} \]
\[ CN^+ + C_2H_4 \rightarrow HCN^+ + C_2H_2^+ \]
\[ 2.500 \times 10^{-10} \]
\[ CN^+ + C_2H_4 \rightarrow C_2H_5N^- + H_2^+ \]
\[ 5.000 \times 10^{-11} \]
\[ CN^+ + C_2H_2 \rightarrow C_2H_3N^- - HCN + H_2 \]
\[ 2.850 \times 10^{-10} \]
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<th>Reaction</th>
<th>Rate Constant (10^{-11} cm^3 molecule^{-1} s^{-1})</th>
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<td>CN^+ + C2H6 → C2H7^- + HCN - H</td>
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<td>CN^+ + C2H6 → C2H7^- + HCN -</td>
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<td>CN^+ + NH3 → NH2^- + HCN -</td>
<td>1.000 × 10^{-10}</td>
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<tr>
<td>CN^+ + NH3 → NH2^- + HCN -</td>
<td>1.200 × 10^{-9}</td>
</tr>
<tr>
<td>CN^+ + NH3 → HCN^- - NH -</td>
<td>4.000 × 10^{-10}</td>
</tr>
<tr>
<td>CN^+ + HCN → HCN^- - CN -</td>
<td>3.000 × 10^{-10}</td>
</tr>
<tr>
<td>CN^+ + HCN → CN^- - CN -</td>
<td>1.200 × 10^{-10}</td>
</tr>
<tr>
<td>CN^+ + NH3 → CN^- - CN -</td>
<td>6.300 × 10^{-10}</td>
</tr>
<tr>
<td>CN^+ + CO → CO^- + CN -</td>
<td>6.500 × 10^{-10}</td>
</tr>
<tr>
<td>C2N^+ + CH4 → C2H5^- + HCN -</td>
<td>4.200 × 10^{-10}</td>
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<tr>
<td>C2N^+ + CH4 → C2H5^- + HCN -</td>
<td>7.000 × 10^{-11}</td>
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<td>C2N^+ + C2H2 → C2H3N^- + C2H2+</td>
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<tr>
<td>C2N^+ + C2H2 → C2H3N^- + CN -</td>
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<td>C2N^+ + C2H2 → C2H3N^- + CN^-</td>
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</tr>
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<td>C2N^+ + C2H4 → C2H5^- + HCN - H</td>
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</tr>
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<td>C2N^+ + C2H4 → C2H5^- + HCN - H</td>
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<td>C2N^+ + NH3 → C2H5^- + C2H2+</td>
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<td>C2N^+ + NH3 → C2H5^- + C2H2+</td>
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<tr>
<td>C2N^+ + H2 → C2H5^- + C2H2-</td>
<td>8.100 × 10^{-11}</td>
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<tr>
<td>HCO^+ + C2H2 → C2H^- + CO -</td>
<td>1.300 × 10^{-9}</td>
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<tr>
<td>HCO^- + CH3H2O → C2H^- + CO -</td>
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<td>HCO^- + CH3H2O → C2H^- + CO -</td>
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<tr>
<td>HCO^- + CH3H2O → C2H^- + CO -</td>
<td>3.700 × 10^{-14}</td>
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<tr>
<td>O^+ + N2 → NO^- + N -</td>
<td>1.200 × 10^{-12}(T_n, 300K)^{-1440}exp(-0.00/T_n)</td>
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<tr>
<td>O^+ + CH3NH2 → C2H5^- + O -</td>
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<td>O^+ + CH3NH2 → C2H5^- + O -</td>
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<td>O^+ + CH3NH2 → C2H5^- + O -</td>
<td>1.100 × 10^{-10}</td>
</tr>
<tr>
<td>O^+ + C2H6 → C2H7^- -</td>
<td>1.330 × 10^{-9}</td>
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<tr>
<td>O^+ + C2H6 → C2H7^- -</td>
<td>5.700 × 10^{-10}</td>
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<tr>
<td>O^+ + H2 → OH^- + H -</td>
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<tr>
<td>CO^+ + H → H^+ + CO -</td>
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<tr>
<td>CO^+ + H2 → HCO^- + H +</td>
<td>1.300 × 10^{-9}</td>
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<tr>
<td>CO^+ + CH4 → CH5^- + CO -</td>
<td>9.790 × 10^{-10}</td>
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<td>CO^+ + CH4 → HCO^- + CH3-</td>
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<tr>
<td>CO^+ + CH4 → C2H7^- - H +</td>
<td>8.160 × 10^{-11}</td>
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<tr>
<td>CO^+ + C2H2 → C3H7^- - CO -</td>
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<tr>
<td>CO^+ + NH3 → NH7^- - CO +</td>
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<tr>
<td>CO^+ + O → O^- + CO -</td>
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<tr>
<td>CO^+ + HCN → HCN^- - CO -</td>
<td>3.400 × 10^{-9}</td>
</tr>
<tr>
<td>CO^+ + HCN → HCN^- - CO -</td>
<td>2.300 × 10^{-9}</td>
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<tr>
<td>Reaction</td>
<td>Rate Coefficient</td>
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<td>----------</td>
<td>------------------</td>
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<tr>
<td>( H_2^+ + E \rightarrow H + + )</td>
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<tr>
<td>( H_3^+ + E \rightarrow H + H + H )</td>
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<tr>
<td>( H_2^+ + E \rightarrow H_2 + H )</td>
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<tr>
<td>( H_2^+ + E \rightarrow H + H - H )</td>
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<tr>
<td>( C^+ + E \rightarrow C + + )</td>
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<tr>
<td>( CH^+_+ E \rightarrow CH + H )</td>
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<tr>
<td>( CH^+_+ E \rightarrow CH_2 + H )</td>
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<td>( C_2H^+_+ E \rightarrow CH_2 + CH - )</td>
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<td>( C_2H^+_+ E \rightarrow CH_3 + H - - )</td>
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<td>( C_2H^+_+ E \rightarrow C_2H_4 + H_2 + )</td>
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</table>
| \( C_2H^+_+ E \rightarrow C_2H_4 + H_2 + H \) | \( 9.030 \times 10^{-33} \) | \(-.390\)
\[ \begin{align*}
\text{H}_2 + \text{NH}_2 &\rightarrow \text{NH}_3 - \text{H} - & 6.320 \times 10^{-11} (T_n/300)^{0.176} \exp(-0.00/T_n) \\
\text{C} + \text{NH}_2 &\rightarrow + \text{H} - & 2.000 \times 10^{-11} (T_n/300)^{1.500} \exp(-0.00/T_n) \\
\text{O} + \text{NH}_2 &\rightarrow + \text{H} - & 3.200 \times 10^{-12} (T_n/300)^{0.000} \exp(-0.00/T_n) \\
\text{O} + \text{NH}_2 &\rightarrow \text{NH} - \text{OH} - & 3.500 \times 10^{-12} (T_n/300)^{0.500} \exp(-0.00/T_n)
\end{align*} \]
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<th>Neutral Species</th>
<th>Ion Produced</th>
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*a Computed from data taken from Lias et al. [1988]
Fig 1.
Fig 5
Figure 4

The graph shows the production (upper graph) and loss (lower graph) rates of various chemical species as a function of altitude. The production rates are given in units of cm$^{-3}$ s$^{-1}$. The species include HCN, CH$_4$, N$^+$ + CH$_4$, C$_2$H$_3^+$ + HCN, C$_2$H$_6^+$ + HCN, and HCNH$^+$. The loss processes include DR (discharge reaction) and the production of NH$_3$, HC$_3$N, C$_4$H$_2$, and other species. The altitude is measured in kilometers (km).
FLUX (cm$^{-2}$ s$^{-1}$ eV$^{-1}$ steradian$^{-1}$)