The photochemical model of Titan's atmosphere and ionosphere: A version without hydrodynamic escape

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ABSTRACT

There are observational and theoretical evidences both in favor of and against hydrodynamic escape (HDE) on Titan, and the problem remains unsolved. A test presented here for a static thermosphere does not support HDE on Titan and Triton but favors HDE on Pluto. Cooling of the atmosphere by the HCN rotational lines is limited by rotational relaxation above 1100 km and self-absorption below 900 km on Titan. HDE can affect the structure and composition of the atmosphere and its evolution. Hydrocarbon, nitrile, and ion chemistries are strongly coupled on Titan, and attempts to calculate them separately may result in significant errors. Here we apply our photochemical model of Titan's atmosphere and ionosphere to the case of no hydrodynamic escape. Our model is still the only after-Cassini self-consistent model of coupled neutral and ion chemistry. The lack of HDE is a distinct possibility, and comparing models with and without HDE is of practical interest. The mean difference between the models and the neutral and ion compositions observed by INMS are somewhat better for the model with HDE. A reaction of NH_2 with H_2CN suggested by Yelle et al. (2009) reduces but does not remove a significant difference between the ammonia abundances in the models and INMS observations. Losses of methane and nitrogen and production and deposition to the surface of hydrocarbons and nitriles are evaluated in the model, along with lifetimes and evolutionary aspects.

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1. Introduction

Self-consistent photochemical models are a powerful tool to study atmospheric chemical composition. These models fix the densities of parent species (N_2 and CH_4 for Titan) at the surface as boundary conditions in order to calculate vertical profiles of numerous photochemical products throughout the atmosphere. Currently, the only published post-Cassini self-consistent models for Titan's atmosphere are those by Lavvas et al. (2008a,b) and Krasnopolsky (2009), hereafter LCV and Paper I, respectively.

A partial photochemical model uses a chosen background atmosphere to calculate densities of some species but neglects effects of the calculated species on the background atmosphere. The choice of the background atmosphere in the partial models gives some degrees of freedom that facilitate fitting the calculated species to observations.

Ionospheric models are examples of a partial photochemical model. Ion–neutral reactions are usually much faster than reactions between neutral species in the upper atmosphere of Titan and can strongly affect the densities of some neutral species. Therefore, neglect of the reactions in models of Titan's

atmosphere may be a source of error. Of course each model is an approximation of reality, and some errors are inevitable. However, models with coupled neutral and ion chemistry have some advantages. There are currently two models of this type for Titan's atmosphere: the pre-Cassini model by Wilson and Atreya (2004, hereafter WA) and Paper I. A model by Banaszkiewicz et al. (2000) does include the ionosphere; however, hydrocarbons, nitriles, and ions were calculated separately in that model.

The model of Titan's atmosphere and ionosphere in Paper I is a convenient tool to study various hypotheses related to the atmospheric chemical composition. Here I investigate (1) the effect of a new reaction of NH_3 formation proposed by Yelle et al. (2009), (2) consider two tests for hydrodynamic escape on Titan, Triton, and Pluto, and (3) compare versions of the model with and without hydrodynamic escape against INMS data (Cui et al., 2009; Magee et al., 2009; Waite et al., 2009).

2. Ammonia in Titan's thermosphere

The INMS ion spectrum averaged over the Cassini flyby T5 is of special interest because it was observed during a strong precipitation of magnetospheric electrons. The solar zenith angle was 127° at the closest approach at altitude 1027 km, that is, the conditions were nighttime. The averaged ion spectrum

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(Vuitton et al., 2007) refers to a mean altitude of 1100 km. The spectrum was fitted by a local (i.e., without transport) ion chemistry model with densities of neutral species as fitting parameters. The densities of 19 species were retrieved (Vuitton et al., 2007) using this approach. Although the obtained densities are model-dependent to some extent, they originate in the measured ion spectrum.
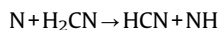
Peaks at $m/e = 18$ in the ion spectra observed by INMS are due to NH_4^+. This ion forms in reactions of NH_3 with other ions, and the derived ammonia mixing ratio is 6.7 ppm at 1100 km in Vuitton et al. (2007). Analysis of the INMS neutral spectra results in an even higher NH_3 abundance of 30 ppm at 1077 km (Cui et al., 2009). This may be compared with an upper limit of 6 ppb for ammonia in the stratosphere from Voyager/IRIS spectra (Bernard et al., 2003). Clearly, ammonia forms in the upper atmosphere; however, the models predict much lower NH_3 abundances near 1100 km than the INMS values: 0.4 ppm in Paper I, 0.2 ppm in LCV, and 0.04 ppm in WA.

The loss of NH_3 through reactions with $HCNH^+$ and $C_2H_5^+$ in our model is perfectly balanced by the production of NH_3 through recombination of NH_4^+, and we may thus neglect ion reactions in the NH_3 balance. According to Paper I, NH_3 forms in the upper atmosphere in reactions of N with C_2H_5 and C_3H_6, and photolysis provides the only loss of NH_3 (Fig. 1). This figure shows a significant difference between the production and loss of NH_3 above $\sim$500 km that reflects transport by eddy and molecular diffusion.
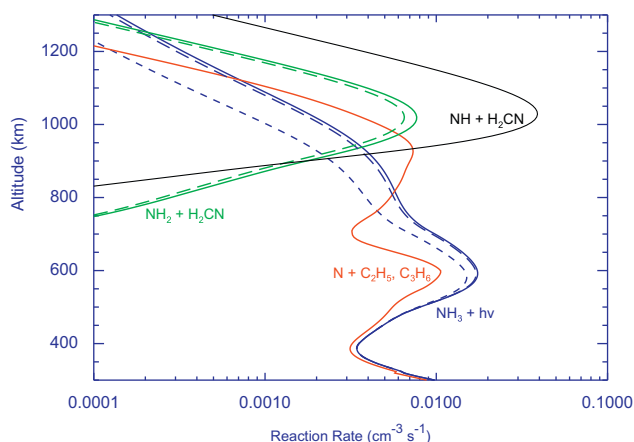
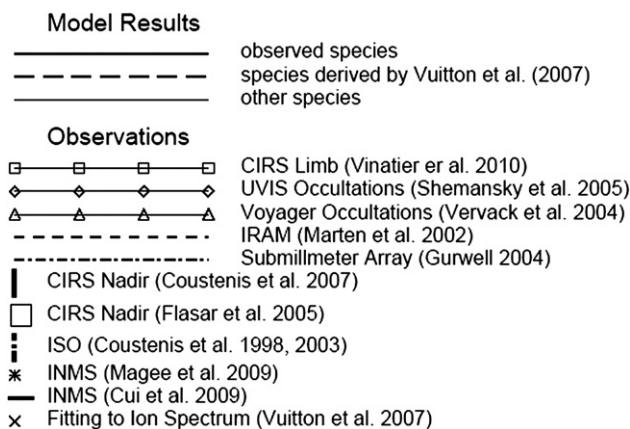To increase the production of ammonia, Yelle et al. (2009) suggested the reaction

$$NH_2 + H_2CN \rightarrow HCN + NH_3.$$
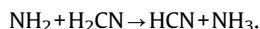
This reaction has not been studied in the laboratory, and its rate coefficient is unknown. This reaction may be compared to

$$N + H_2CN \rightarrow HCN + NH$$

with a rate coefficient of $k = 10^{-10}e^{-200/T}$ cm^3 s^{-1} (Nesbitt et al., 1990). Since the bond energies of H in NH, NH_2, and NH_3 are rather similar (3.54, 4.10, and 4.40 eV, respectively), and

the masses of N, NH, and NH_2 are close; we adopt the above rate coefficient for the reaction of $NH_2 + H_2CN$.

Ammonia production at 1100 km increases by a factor of 4 with this reaction (Fig. 1), while its density increases by a factor of 2.3. Photolysis of NH_3 is mostly due to the near UV solar flux, Titan's atmosphere is transparent above the haze in this range, and the NH_3 photolysis rates in Fig. 1 show variations of the ammonia density. The increase in density is smaller than the increase in production due to molecular and eddy diffusion.

NH is mostly formed in the upper atmosphere by the reactions of N(^{2}D) with some hydrocarbons and is more abundant than NH_2 above 900 km (Paper I). The reaction

$$NH + H_2CN \rightarrow HCN + NH_2$$
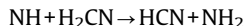
may add to the production of NH_2 and therefore NH_3. This reaction has not been studied in the laboratory either, and we likewise adopt $k = 10^{-10}e^{-200/T}$ cm^3 s^{-1} for its rate coefficient. Its rate exceeds that of $NH_2 + H_2CN$ by a factor of 5 (Fig. 1); however, the increase in NH_3 abundance from this reaction is just 10%.

As mentioned above, these reactions enhance the abundance of NH_3 at 1100 km by a factor of 2.5 to a value of 1.0 ppm. This is still significantly below the values retrieved from the INMS ion and neutral spectra (Vuitton et al., 2007; Cui et al., 2009). Thus, inclusion of these reactions reduces but does not remove the difference in ammonia abundances observed by INMS and calculated in the photochemical models. Yelle et al. (2009) discuss possible effects of heterogeneous chemistry on NH_3; however, investigating such effects is currently beyond our model. The significant difference between ammonia abundances retrieved from the INMS spectra in the neutral and ion modes, 30 and 6.7 ppm, may also indicate some problems in the NH_3 measurements.

3. Controversy of hydrodynamic escape

The CH_4/N_2 ratio observed in Titan's upper atmosphere by INMS was unexpectedly low (Yelle et al., 2006), and this can be explained by either very strong eddy diffusion or strong escape of methane. Yelle et al. (2008) compared the INMS detection of ^{40}Ar at a mixing ratio of 12 ppm near 1050 km with the ^{40}Ar mixing ratio of 43 ppm measured in the lower atmosphere by the GCMS on the Huygens probe (Niemann et al., 2005); this results in an eddy diffusion coefficient $K = 3 \times 10^7$ cm^2 s^{-1} in the upper atmosphere, and the upward flux of methane required to fit


Fig. 2. Designations for comparison of the model results with the observations (Coustenis et al., 1998,2003,2007; Flasar et al., 2005; Gurwell, 2004; Marten et al., 2002; Shemansky et al., 2005; Vervack et al., 2004; Vinatier et al., 2010).

Fig. 1. Main reactions of NH_3 formation and loss. Ion reactions $NH_3 + HCNH^+$, $C_2H_5^+$ are perfectly balanced by recombination of NH_4^+ and not shown. NH_3 photolysis is shown for three versions of the model: without $NH_2 + H_2CN$ (short dashes), inclusion of $NH_2 + H_2CN$ (long dashes), and inclusion of both NH_2 and $NH + H_2CN$ (solid line). This photolysis reflects an increase in NH_3 at 1100 km by factors of 2.3 and 2.5, respectively. The $NH_2 + H_2CN$ reaction is shown without and with $NH + H_2CN$ (dashed and solid lines, respectively).