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Chemical composition of Titan's atmosphere and ionosphere: Observations and the photochemical model

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ABSTRACT

Basic observational data on hydrocarbons, nitriles, and ions on Titan are compared with predictions of the photochemical model. Uncertainties of the observed abundances and differences between the data from different instruments and observing teams are comparable with the differences between the observations and the model results. Main reactions of production and loss for each species are quantitatively assessed and briefly discussed. Formation of haze by polymerization of hydrocarbons and nitriles and recombination of heavy ions is calculated along with condensation of various species near the tropopause. Overall deposition is a layer of 300 m thick for the age of the Solar System, and nitrogen constitutes 8% of the deposition. The model reproduces the basic observational data and adequately describes basic chemical processes in Titan's atmosphere and ionosphere. The presented model results and the observational data may be used as a reference to chemical composition of Titan's atmosphere and ionosphere.

1. Introduction

Photochemical modeling of Titan's atmosphere is a challenging task, and post-Voyager but pre-Cassini models were developed by Yung et al. (1984), Toublanc et al. (1995), Lara et al. (1996), Banaszkiewicz et al. (2000), and Wilson and Atreya (2004). (Here we do not mention partial models that consider a class of species in adopted background atmosphere.) The first three models did not involve the ion chemistry; Lara et al. (1996) and Banaszkiewicz et al. (2000) neglected effects of the nitrile chemistry on hydrocarbons and vertical transport on some species. However, all these models resulted in gradual progress in the problem. Wilson and Atreya (2004) created the first self-consistent (that is, without adopted background atmosphere) model for coupled neutral and ion chemistry on Titan.

Models by Lavvas et al. (2008) and Hebrard et al. (2007, 2013) were made after the beginning of the Cassini observations. These models do not include ion chemistry that significantly affects some neutral species observed near 1000 km by the ion and neutral mass spectrometer (INMS). Ion chemistry becomes also essential in the lower stratosphere near 100 km. The solar EUV and UV radiation does not reach this region, and the cosmic rays drive photochemistry here. Hebrard et al. (2007) is the most complete of ten papers published on their model. They studied in detail effects of uncertainties in reaction rate coefficients on the species abundances. The calculated uncertainties vary from a few percent to a factor of 40. However, there is no direct correlation between the model uncertainties and differences between the model and observed abundances.

Our self-consistent photochemical model for Titan's atmosphere and ionosphere (Krasnopolsky, 2009, 2010, 2012; henceforth Kr09, Kr10, Kr12) is used for various aspects of Titan's chemical composition. The hydrocarbon and nitrile chemistry of Titan may involve huge numbers of neutral and ion species and their reactions, and our model was aimed to reduce these species and reactions to those that are essential in Titan's chemistry. Finally we use 420 reactions of 83 neutrals and 33 ions, and the adopted reaction rate coefficients may be found in Kr09. Absorption of the solar UV and EUV photons was calculated interactively for the atmospheric gases and by radiative transfer using the aerosol observations from the Huygens probe. Other initial data of the model are the temperature and eddy diffusion profiles (Fig. 1a) and the N_2 and CH_4 densities at the surface. The model accounts for magnetospheric electrons, protons, and oxygen ions, meteorite influx of H_2O, and cosmic rays as well as vertical transport by eddy, molecular, and ambipolar diffusion.

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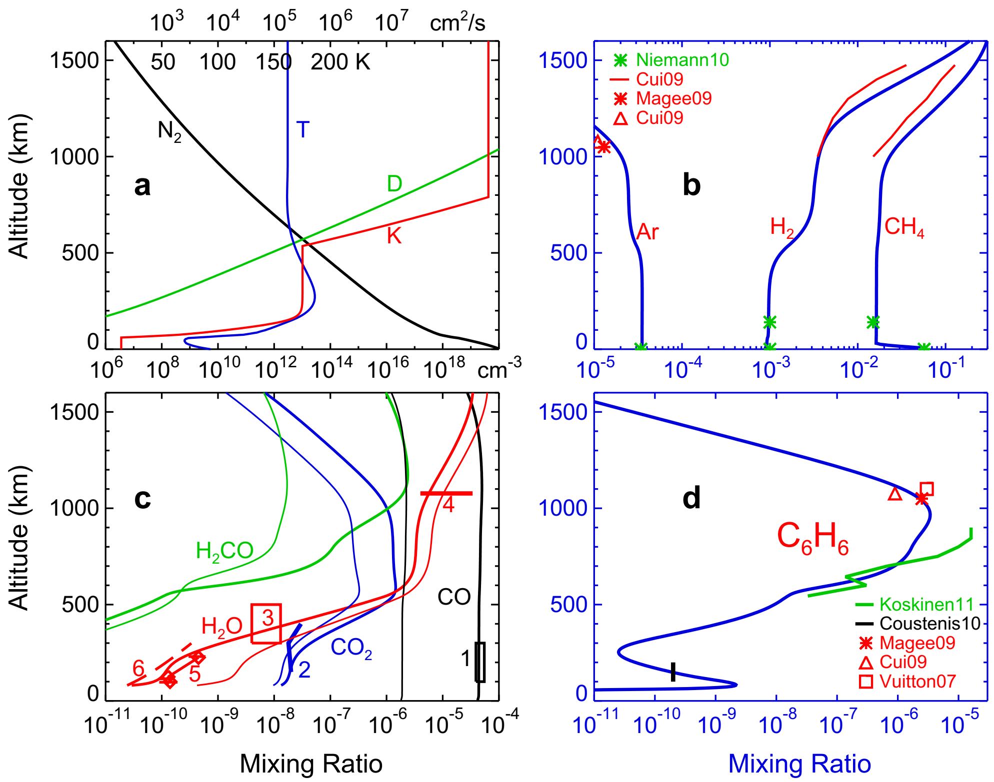

Fig. 1. Panel a: temperature, eddy and molecular (CH_4 in N_2) diffusion profiles (initial data of the model) and the calculated N_2. Panel b: basic species. Panel c: oxygen species (from Kr12). Observations: (1) De Kok et al. (2007), (2) Vinatier et al. (2010), (3) Coustenis et al. (1998), (4) Cui et al. (2009), (5) Cottini et al., 2012), (6) Moreno et al. (2012). The model without flux of O^+ is shown by thin lines. Panel d: observed and calculated benzene.

There are two versions of the model with hydrodynamic escape of light (less than 20 atomic mass units) species in Kr09 and two versions without hydrodynamic escape (Kr10 and Kr12); thermal escape and escape of ions by the rotating magnetosphere of Saturn remain in these versions. Eddy diffusion was adjusted to provide the best fit to the observational data in the latest version Kr12. Its profile given by six parameters was the only means to improve agreement with the observations. Detailed comparison with the observations was not made in Kr12, while this comparison is important for our understanding of Titan's chemistry. This is a goal of this paper.

The Cassini operations cover currently almost a decade and make it possible to study seasonal variations in the 30-years annual cycle of Titan (Bampasidis et al., 2012; Coustenis et al., 2013). However, our model is aimed at reproduction of the global-mean conditions that are applicable to low and middle latitudes. (All photolysis rates are calculated for the solar zenith angle of 60°, and the sunlight is reduced by a factor of 2 to account for the night side.) Therefore our model is not the best tool to study variations in Titan's atmosphere.

2. Observations

Here we will consider observational data that can be directly compared with our model. The ion and neutral mass spectrometer (INMS) provides in situ measurements of the neutral and ion composition above 900 km. However, sampling of the atmosphere and interactions between the sampled species and between those and the instrument are complicated and require modeling in the laboratory. This work was done by two independent teams, and summaries of their results are presented by Magee et al. (2009) and Cui et al. (2009).

Detailed study of the nighttime ion composition at 1100 km during a strong precipitation event T5 was made by Vuitton et al. (2007). The observed ion composition was simulated by a model for this altitude that involved 1250 reactions of 150 ions. Numerous densities of neutral species were parameters of the model, and their best-fit values may be considered as indirect data on the chemical composition at 1100 km.

The ion composition in the T5 encounter was also calculated by Cravens et al. (2009) and in our models. Ionospheric INMS observations from the dayside encounters (Westlake et al., 2012; Mandt et al., 2012) show sums of positive ions that are smaller than electron densities observed simultaneously by the Langmuir probe at RPWS (radio and plasma wave science) and properly extrapolated from the radio occultation observations (Kliore et al., 2008, 2011).

A region of 450–1000 km is covered by stellar occultations (Koskinen et al., 2011) using the ultraviolet imaging spectrometer (UVIS). However, Titan's mesospheric composition is very complicated and includes species whose UV absorption spectra are unknown, while spectra of some other species have not been measured at low temperatures and pressures. This incompleteness of the laboratory data restricts the quality of the UVIS retrievals.

The altitudes below 500 km are probed by limb observations using the composite infrared spectrometer (CIRS). These observations were analyzed by Vinatier et al. (2010) and Nixon et al. (2013), Kutepov et al. (2013) argued that non-LTE effects may affect the retrievals. CIRS nadir observations (Coustenis et al., 2010) refer to altitudes of 100–200 km. There are a few publications on analysis of the CIRS observations; we will use the latest results for low latitudes.

Some data from the IRAM telescope for the millimeter range (Bezard et al., 1993; Marten et al., 2002), the Infrared Space Observatory (ISO, Coustenis et al., 1998), and the Herschel Submillimeter