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1D-coupled photochemical model of neutrals, cations and anions in the atmosphere of Titan

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ABSTRACT

Many models with different characteristics have been published so far to study the chemical processes at work in Titan's atmosphere. Some models focus on neutral species in the stratosphere or ionic species in the ionosphere, but few of them couple all the species throughout the whole atmosphere. Very few of these emphasize the importance of uncertainties in the chemical scheme and study their propagation in the model.

We have developed a new 1D-photochemical model of Titan's atmosphere coupling neutral species with positive and negative ions from the lower atmosphere up to the ionosphere and have compared our results with observations to have a comprehensive view of the chemical processes driving the composition of the stratosphere and ionosphere of Titan. We have updated the neutral, positive ion and negative ion chemistry and have improved the description of N_2 photodissociation by introducing high resolution N_2 absorption cross sections. We performed for the first time an uncertainty propagation study in a fully coupled ion-neutral model.

We determine how uncertainties on rate constants on both neutral and ionic reactions influence the model results and pinpoint the key reactions responsible for this behavior. We find very good agreement between our model results and observations in both the stratosphere and in the ionosphere for most neutral compounds. Our results are also in good agreement with an average INMS mass spectrum and specific flybys in the dayside suggesting that our chemical model (for both neutral and ions) provides a good approximation of Titan's atmospheric chemistry as a whole. Our uncertainty propagation study highlights the difficulty to interpret the INMS mass spectra for masses 14, 31, 41 and we identified the key reactions responsible for these ambiguities.

Despite an overall improvement in the chemical model, disagreement for some specific compounds (HC_3N, C_2H_5CN, C_2H_4) highlights the role that certain physical processes could play (meridional dynamics or sticking on aerosols). We find that some critical key reactions are important for many compounds including both neutrals and ions and should be studied in priority to lower the remaining model uncertainties. Extensive studies for some specific processes (including photolyses) are required.

1. Introduction

Numerous models have been published that simulate the chemical processes at work in Titan's stratosphere and ionosphere. Keller et al. (1998) first included a rather detailed ionospheric chemistry. Banaszkiewicz et al. (2000) and Wilson and Atreya (2004) proposed the first coupled models of neutral species and ions. The study of Titan's ionosphere expanded rapidly with the Cassini mission. INMS ion data was first reported by Cravens et al. (2006) followed by numerous studies (see for instance De La Haye et al. (2008), Vuitton et al. (2009), Lavvas et al. (2011), Krasnopolsky (2014)). A detailed review on Titan's ionosphere is given in Galand et al. (2014). Mandt et al. (2012) listed the main photochemical models of Titan's ionosphere that had been published at that time, presenting what they considered as the main strengths and limitations of these models. Following Mandt et al.

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(2012), some of the most relevant features which are important for modeling Titan's ionosphere are the following:

- Detailed ion and neutral chemistry. A thorough evaluation of ion chemistry is required to improve models.
- A careful sensitivity study of uncertainty propagation in ion chemistry models. Such investigations are required to evaluate the level of predictivity of these models and to pinpoint important chemical processes.
- The way neutral densities are determined. Many models use partially or completely uncoupled neutral abundances leading to an absence of chemical feedback between ions and neutrals. Such fixed-neutral profile models allow the richness of heavy ion chemistry to be explored due to a lower computational time that makes it possible to include many more ions compared to ion-neutral coupled 1D models.
- The use of suitable cross-sections and quantum yields for photo-absorptions. In particular, several studies (Lavvas et al., 2011; Mandt et al., 2012; Luspay-Kuti et al., 2015) highlighted the need to use high resolution cross-sections for N_2.
- A study of vertical and horizontal transport including diurnal and seasonal variations. 2D–3D photochemical models are computationally time consuming and require a reduced chemical scheme.

We (and others) have developed during the last few years a methodology to improve chemical schemes for Titan's atmosphere based on two complementary tasks (see Hébrard et al. (2009) and Loison et al. (2015) for details on the methodology): (1) the determination of key reactions through uncertainty propagation studies and global sensitivity analyses and (2) the completeness of the chemical scheme. Since the papers of Hébrard et al. (2006, 2007) for neutral species and Carrasco et al. (2007a) for ions, we see that this methodology improves the agreement between model results and observations by comparison with Loison et al. (2015) and the present paper. Also, uncertainties on model results, at least for C_2H_x and some nitrogen species like HCN, have significantly decreased. We think that an improvement on the knowledge of the chemistry of Titan's atmosphere is a prerequisite for constraining many physical parameters. The aim of the present study is to develop a new photochemical model of Titan's atmosphere following this methodology, combining the strengths of several previous models. In particular:

- We propose a detailed chemical scheme that improves previous works. Following the recent papers of Hébrard et al. (2012, 2013), Dobrijevic et al. (2014), Hickson et al. (2014) and Loison et al. (2015), we continue in the present paper to improve the chemistry of Titan's atmosphere with thorough evaluations and updates, especially for neutral chemistry, the dissociative recombination of positive ions and negative ion chemistry.
- We develop a 1D photochemical model with vertical transport coupling neutral species with positive and negative ions. Since the production of ions is likely to be strongly related to the density of neutrals, our model computes abundance profiles from the surface up to 1500 km to be as consistent as possible with the various neutral species that have been observed in the lower and middle stratosphere and in the ionosphere.
- Most of the chemical rate constants have relatively large uncertainties. It is therefore important to study how these uncertainties propagate into the model and to determine the most influential chemical processes affecting the results. A global sensitivity analysis is performed to pinpoint the key reactions and to determine the importance of feedback between neutral and ion species.

In Section 2, we present our model, highlighting the main chemical processes that have been taken into account for the ion chemistry and the major modifications compared to the model of Loison et al. (2015) for neutral species. Our results, comparisons with Cassini/INMS data and the propagation of uncertainties are presented in Section 3, with a particular emphasis on ion species. Specific points are discussed in Section 4 before concluding in Section 5.

2. Model

2.1. Neutral species

Details of the model (eddy diffusion coefficient, boundary conditions, UV absorption by haze, condensation, etc.) are given in Loison et al. (2015). Only major modifications are outlined in the following. The chemical scheme of neutral species is similar to the one presented in Loison et al. (2015) with some minor changes. To reduce the computational time of our full 1D-coupled model, we have limited the chemistry of hydrocarbons to C_4-species and therefore do not consider C_6H_x species. We have excluded some nitriles with high molecular mass (HC_5N, C_3H_5CN, C_3H_7CN, etc.) because our previous model (Loison et al., 2015) shows that these compounds have very low abundances. We include CH_3C_3N because the same model predicts it to have a relatively high abundance. We consider isomers only for C_3H (linear and cyclic), C_3H_4 (methylacetylene and allene) and CH_3CN (considering also CH_2-NCH) as they have notably different reactivities. In the case of C_3H_2 we check that the use of only one isomer (the cyclic one) is enough to describe the chemistry in the present model as the main reactions of the two less stable C_3H_2 isomers (the carbene: H_2CCC and the linear one: HCCCH) should be with hydrogen atoms leading to the most stable cyclic isomer (Hébrard et al., 2013). Also, we do not consider reactions with very small fluxes (such as the CH + CH reaction for instance). Consequently, we obtained a much smaller number of chemical reactions (137 neutral bimolecular reactions instead of 801, and 73 neutral termolecular reaction instead of 168). The complete list of reactions considered in the present study is given in appendix A (available in the Supplementary material). We carefully checked that the omission of these chemical reactions has very little, if any, effect on the species considered in the model. The chemical scheme has been slightly updated, particularly for C_4H_x species. Sulfur chemistry (Hickson et al., 2014) is not included in the present model since no sulfur-bearing species have been detected so far. The chemical scheme includes 74 neutral species, which are listed in Table 1. Our model includes vertical transport (eddy and vertical diffusion) for neutral species from the surface up to 1500 km. We use the high resolution ($\Delta\lambda = 0.004$ nm) solar spectrum of Curdt et al. (2001, 2004) between 67 nm and 160 nm. This spectrum is scaled to the solar spectrum (at the solar minimum) of Thuillier et al. (2004) using the continuum at 150 nm. For the Monte-Carlo procedure, we use global-mean photolysis rates which are calculated using a Solar Zenith Angle (SZA) of about 60° and a diurnally averaged solar flux half of that at Saturn's distance from the Sun.

The high resolution absorption cross sections for N_2 at 150 K (Heays, A.N, personal communication) between 84 nm and 100 nm are included in the present model. The high resolution (HR) cross sections of N_2 ($\Delta\lambda = 0.004$ nm) are presented in Fig. 1 and are compared to the low resolution (LR) cross sections ($\Delta\lambda = 1$ nm) of N_2, CH_4 and H_2. The use of HR could have a noticeable effect on the calculation of the photodissociation rate of N_2, CH_4 and H_2 due to the existence of many lines in the HR cross sections of N_2 (for the wavelength range considered here).