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Coupling of oxygen, nitrogen, and hydrocarbon species in the photochemistry of Titan's atmosphere

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ABSTRACT

Analysis of recent detections of water by Herschel/HIFI-PACS and Cassini/CIRS suggest for a steep gradient of the water profile in the lower stratosphere of Titan's atmosphere (Cottini, V., Nixon, C.A., Jennings, D.E., Anderson, C.M., Gorius, N., Bjoraker, G.L., Coustenis, A., Teanby, N.A., Achterberg, R.K., Béezard, B., de Kok, R., Lellouch, E., Irwin, P.G.J., Flasar, F.M., Bampasidis, G. [2012]. Icarus 220, 855–862; Moreno, R., Lellouch, E., Lara, L.M., Feuchtgruber, H., Rengel, M., Hartogh, P., Courtin, R. [2012]. Icarus 221, 753–767). This result provides a good opportunity to better understand the origin of oxygen compounds. However, the current photochemical models use an incomplete oxygen chemical scheme. In the present work, we improve the photochemistry of oxygen and introduce in particular a coupling between hydrocarbon, oxygen and nitrogen chemistries. Through the use of several different scenarios, we show that some oxygen compound abundances are sensitive to the nature of oxygen atoms (O^+, OH and H_2O) and the source of the flux (micrometeorites ablation or Enceladus' plume activity). Our model also predicts the presence of new and as yet undetected compounds such as NO (nitric oxide), HNO (nitrosyl hydride), HNCO (isocyanic acid) and N_2O (nitrous oxide). Their future putative detection will give valuable constraints to discriminate between the different hypotheses for the nature and the source of oxygen compounds in the atmosphere of Titan. Through the use of a Monte Carlo-based uncertainty propagation study and global sensitivity analysis, we identify the key reactions that should be studied in priority to improve coupled photochemical models of Titan's atmosphere.

1. Introduction

Two recent observations (Cottini et al., 2012; Moreno et al., 2012) give strong constraints on the vertical profile of water vapour in the lower atmosphere of Titan (above the tropopause up to about 300 km). These results provide a good opportunity to make an in depth investigation of the photochemistry of oxygen compounds in Titan's atmosphere. In particular, they should help us to better understand the origin of CO, the influx of oxygen into the upper atmosphere and the strength of vertical transport in the lower atmosphere. From large averages of Cassini/CIRS spectra in limb and nadir geometry, Cottini et al. (2012) demonstrated that the H_2O mole fraction increases with altitude from 125 to 225 km. Moreno et al. (2012) recently reported disc-averaged observations of water vapour in Titan's atmosphere acquired with the Herschel satellite. They obtained an accurate profile of water vapour, showing that the H_2O mole fraction strongly increases with altitude, a profile which also matches the original ISO observations of water. Unfortunately, the Cottini et al. (2012) results are significantly different from the results of Moreno et al. (2012). For instance, at an altitude of 115 km, the mole fraction derived by Cottini et al. (2012) is about $(1.3 \pm 0.4) \times 10^{-10}$ while the value derived by Moreno et al. (2012) is more than 4 times lower: $(3.0 \pm 1.0) \times 10^{-11}$. This current discrepancy might limit our ability to constrain the eddy diffusion coefficient in the lower atmosphere (above the saturation level of water) and to quantify the input of oxygen in the upper atmosphere. Another important issue concerning oxygen chemistry in the atmosphere of Titan is the origin of CO and CO_2. Using a surface (or primordial) source of CO in their photochemical model (with a mole fraction in agreement with observations) and an influx of OH/H_2O which reproduces the H_2O profile inferred from Herschel and ISO observations, Moreno et al. (2012) obtained a CO_2 mole fraction 10 times lower than the value derived from CIRS observations (de Kok et al., 2007). Based on atmospheric lifetimes, they suggested that the influx of OH/H_2O is time-dependent and could be currently much smaller than the average influx at earlier times. Hörst et al. (2008) proposed a very different scenario for

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the origin of CO, advocating an external source of Titan's oxygen. They showed that with an external flux of O^+ from Saturn's magnetosphere in agreement with the value inferred from the Cassini plasma spectrometer (Hartle et al., 2006) and an adequate influx of OH/H_2O, they could simultaneously explain the observations of H_2O, CO and CO_2. Krasnopolsky (2009) employing a similar chemical scheme reached the same conclusion as Hörst et al. (2008) favouring the photochemical formation of CO without the need for a primordial source.

A review of these photochemical models shows that they all use chemical schemes which are overly simplistic and these could be partially responsible for the controversial results obtained so far. Moreno et al. (2012), following the approach of Lara et al. (1996), used a simplified chemical scheme in which nitrogen chemistry is decoupled from the hydrocarbon–oxygen chemistry arguing that it has only a limited influence on the abundance on C-, H- and O-species. They used the oxygen chemistry of Hörst et al. (2008) and the hydrocarbon chemistry of Lara et al. (1996). Hörst et al. (2008) also used a simplified chemical scheme in which oxygen chemistry is decoupled from the hydrocarbon and nitrogen chemistries and considered a fixed background of N_2 and hydrocarbon species according to the abundances derived from the results of Vuitton et al. (2008). Their oxygen chemical scheme included 10 oxygen-bearing species participating in 32 reactions. Krasnopolsky (2009) strongly simplified the chemical scheme he used in his photochemical model for hydrocarbons and nitrogen species while his oxygen chemical scheme includes 31 reactions involving 12 oxygen species. More recently, Krasnopolsky (2012) updated his chemical scheme (specifically concerning termolecular and radiative association reactions) and noted that 10 species and 21 reactions involving oxygen atoms were similar to those in Hörst et al. (2008). In recent studies of HNC/HCN and hydrocarbon formation mechanisms (with a particular emphasis on chains containing 3 carbon atoms), Hébrard et al. (2012) and Hébrard et al. (2013) showed that it was important to complete chemical schemes by adding new pertinent compounds and reactions. They based their studies on an extensive and careful review of the kinetic literature as well as on calculations from simple theoretical considerations to estimate the reaction rates and their associated uncertainty factors. Following this methodology, Hébrard et al. (2012) found for instance new neutral production pathways to explain the presence of HNC in the upper atmosphere of Titan and Hébrard et al. (2013) showed that the update of the chemistry of C_3-hydrocarbons has a significant effect on the predicted abundances of several C_2-compounds.

Since there is no consensus on the mole fraction of H_2O in the lower atmosphere of Titan (due to the aforementioned discrepancy between CIRS and Herschel observations) and the lack of a consensus regarding the source of oxygen compounds in the upper atmosphere and the origin of CO, we propose, as a first step to settle this situation, an improvement of the previous models by updating Titan's oxygen chemistry and in particular by reducing the incompleteness of the oxygen chemical scheme. In this paper we present a chemical scheme containing new oxygen compounds involved in new reactions which allow the chemistry of oxygen to be coupled with the chemistry of hydrocarbons and nitrogen compounds. We first test this chemical scheme through comparison with observations of the 3 main oxygen compounds H_2O, CO and CO_2 and we investigate different scenarios for the origin of oxygen. In particular, we try to constrain the nature and the flux of oxygen species at the top and the bottom of the atmosphere. This work serves as a basis for the second part of our study which is to determine the abundance profiles of some of the new oxygen compounds that we have introduced as a consequence of the coupling of C, N and O species. We also study how the uncertainties in reaction rates propagate in the model, affecting the model output (mole fractions of each compound as a function of altitude) and we propose a list of key reactions that should be investigated in depth at low temperature to improve our knowledge of oxygen chemistry in the atmosphere of Titan.

2. Photochemical model

The photochemical model used in the present work as well as the chemical scheme for hydrocarbons and nitrogen species comes from Hébrard et al. (2012, 2013). The chemistry of oxygen species has been completely updated since these two papers. It is presented below. The vertical temperature and density profiles come from Moreno et al. (2012). The set of continuity equations is solved for all compounds from the surface up to 1300 km. Different boundary conditions are used depending on the scenarios for the source of CO. We first explore the possibility that CO has a photochemical origin driven by an input of $O(^3P)$ and OH (or H_2O) into the upper atmosphere. For that scenario, we follow the work of Hörst et al. (2008) assuming that all O^+ ions precipitate from Saturn's magnetosphere in the form of $O(^3P)$ atoms at the top of the atmosphere. In this case, CO has zero velocity at the lower boundary. In the scenarios where an internal source of CO is assumed, we use a fixed value for the mole fraction of CO at the lower boundary in agreement with observations: $y_{CO} = 5.1 \times 10^{-5}$ (see Gurwell (2004), de Kok et al. (2007), Teanby et al. (2010) and Courtin et al. (2011)). We have also tested two possible origins for the external flux of OH/H_2O: (i) a micrometeoritic ablation source, in this case we use a Chapman production function with a peak at 750 km for the external OH/H_2O input, (ii) a local source (Enceladus' plume activity), in this case the flux of OH/H_2O is set at the upper boundary of our atmospheric model. The photolysis rates are calculated to account for the global mean conditions according to Hörst et al. (2008), Krasnopolsky (2009, 2012) and Moreno et al. (2012). The actinic flux is computed several times for each scenario from the initial condition up to the end of the calculations. The different scenarios are listed in Tables 2 and 3. The eddy diffusion coefficient used in the present model is presented Fig. 1. This profile allows us to obtain H_2O and CO_2 mole fraction profiles in agreement with observations, in particular considering the slope of the H_2O profile between 100 and 400 km compared to the profiles of Moreno et al. (2012) and Cottini et al. (2012) (see Figs. 3 and 5).

3. Chemical scheme

In contrast to current assumptions, the oxygen and nitrogen chemical cycles of Titan's atmosphere are linked through various

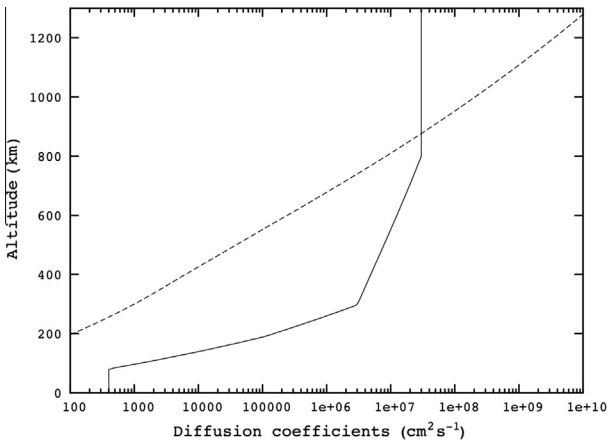

Fig. 1. Methane diffusion coefficient (dashed line) and eddy diffusion coefficient (solid line) used in the present study. The eddy diffusion profile has been inferred to obtain a H_2O mole fraction profile in agreement with observations in the lower atmosphere (see Figs. 3 and 5).