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The photochemical fractionation of nitrogen isotopologues in Titan's atmosphere

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Nitrogen isotopologues could give in principle valuable constraints on the formation and evolution of Titan's atmosphere and its interior over geological time. For this purpose, we developed the first photochemical model dedicated to the study of the fractionation of several nitrogen isotopologues. Emphasis has been placed on several nitriles: HCN, CH_3CN, HC_3N, C_2H_3CN, C_2H_5CN. We show that the $HCN/HC^{15}N$ and $HC_3N/HC_3{}^{15}N$ ratios are very sensitive to the production of magnetospheric electrons. So, these compounds can serve as probes to study the putative evolution with time of the production of magnetospheric electrons throughout the atmosphere. We also show that the $CH_3CN/CH_3C^{15}N$ and $C_2H_5CN/C_2H_5C^{15}N$ ratios are highly sensitive to cosmic rays. So, they can serve as probes to estimate their effect in the lower atmosphere of Titan (100–300 km). Detection of new isotopologues (particularly $CH_3C^{15}N$) could give strong constraints to photochemical models and could improve our understanding of the main physical and chemical processes at work in Titan's atmosphere.

1. Introduction

Molecular nitrogen (N_2) is the major atmospheric constituent of Titan's atmosphere but its origin is still a matter of debate. Mandt et al. (2009) developed a model to study the evolution with time of the stable isotopes in Titan's major constituents (N_2, CH_4 and H_2). Mandt et al. (2014) improved this model revisiting the mass-dependent fractionation during atmospheric escape. They concluded that N_2 in Titan's atmosphere must have originated as ammonia ice formed in the protosolar nebula under conditions similar to that of cometary formation. Theses studies show the importance to evaluate the $^{14}N/^{15}N$ ratio in Titan's atmosphere, in N_2 in particular, but also in various nitrogen species, in order to give more constraints on the formation and evolution of its atmosphere and its interior over geological time. Unfortunately, only few observations give the isotopic $^{14}N/^{15}N$ ratio in the atmosphere.

From the Gas Chromatograph Mass Spectrometer (GCMS) instrument on the Huygens probe, Niemann et al. (2005) reported direct atmospheric measurements of the isotopic $^{14}N/^{15}N$ ratio in N_2 in the atmosphere of Titan. They found a ratio of 183 ± 5 between 36 km and 41 km of altitude. Reanalysis made by Niemann et al. (2010) gave a more precise value of 167.7 ± 0.6. Using the Ion and Neutral Mass Spectrometer (INMS) instrument, Waite et al. (2005) obtained from the first flyby of Titan a $^{14}N/^{15}N$ ratio in N_2 at high altitude (above 1175 km) equal to 180 ± 22. More recently, Mandt et al. (2012) determined the $^{14}N/^{15}N$ ratio in N_2 from INMS data for T40 and T48 flybys as a function of altitude showing high variations at the higher altitude. The $^{14}N/^{15}N$ ratio observed in HCN by ground-based telescopes (Marten et al., 2002; Gurwell et al., 2011), Cassini CIRS (Vinatier et al., 2007) and Herschel SPIRE instruments (Courtin et al. (2011)) is quite different from the ratio in N_2. The more recent detection from ALMA gave a ratio of 72.2 ± 2.2 (see Molter et al. (2016) and references therein for previous measurements). Liang et al. (2007) explained this difference by the photolytic fractionation of $^{14}N^{15}N$ and $^{14}N^{14}N$ using high resolution photodissociation cross sections of these two species. This result has been confirmed by Mandt et al. (2012), Luspay-Kuti et al. (2015) and Krasnopolsky (2016).

In the present paper, we investigate the photochemical fractionation of several nitrogen isotopologues in Titan's atmosphere using a new chemical scheme. The first objective is to confirm the model results given in previous studies to explain the different measurements obtained in N_2 and HCN. The main objective is to determine whether other nitrogen species could be photochemically

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Table 1
List of the 59 nitrogen species included in the model.

Neutral species	Ions
HNC HCN H_2CN CH_2NH C_2N HCCN N_2 H_2C_3N C_2H_3CN HC_3N CH_3CN CH_2CN $N(^4S)$ NH $N(^2D)$ CN C_3N C_2H_4CN C_2H_5CN	CH_3CNH^+ $HCNH^+$ $C_2H_3CNH^+$ $C_2H_5CNH^+$ HC_3NH^+ N^+ HCN^+ N_2^+ N_2H^+ $CH_2NH_2^+$
$H^{15}NC$ $HC^{15}N$ $H_2C^{15}N$ $CH_2{}^{15}NH$ $C_2{}^{15}N$ $HCC^{15}N$ $H_2C_3{}^{15}N$ $C_2H_3C^{15}N$ $HC_3{}^{15}N$ $CH_3C^{15}N$ $CH_2C^{15}N$ $^{15}N(^4S)$ ^{15}NH $N^{15}N$ $^{15}N(^2D)$ $C^{15}N$ $C_3{}^{15}N$ $C_2H_4C^{15}N$ $C_2H_5C^{15}N$	$CH_3C^{15}NH^+$ $HC^{15}NH^+$ $C_2H_3C^{15}NH^+$ $HC_3{}^{15}NH^+$ $^{15}N^+$ $HC^{15}N^+$ $N^{15}N^+$ $N^{15}NH^+$ $^{15}NNH^+$ $CH_2{}^{15}NH_2^+$ $C_2H_5C^{15}NH^+$

fractionated, giving additional constraints on the formation and evolution of Titan's atmosphere.

In Section 2, we present the photochemical model and the chemical scheme with the different nitrogen isotopologues and chemical and photolysis reactions that could lead to an isotopic fractionation. The main results are presented in Section 3. In Section 4, we discuss the sensitivity of our model to the chemistry and in particular to Galactic cosmic rays (GCR) and magnetospheric electrons (ME) induced chemistry. The conclusions of this work are presented in Section 5.

2. Model

The model used in the present study is similar to the recent model of Loison et al. (2017) for the oxygen isotopologues photochemistry with a more complete description of nitrile chemistry. It is derived from the model developed by Dobrijevic et al. (2016), which couples ions and neutral species throughout the whole atmosphere ($0-1500$ km). Only additions and major modifications compared to these two publications are outlined in the following.

2.1. Chemical model

The present model focuses on nitrogen species and their isotopologues. Since we have to duplicate all reactions with isotopologues, the computation time increases significantly when performing the uncertainty propagation model. So, we use a reduced chemical scheme for hydrocarbons and nitrogen species. It contains 89 species (57 neutrals and 32 ions) and 493 reactions (including photolysis processes). The list of nitrogen species and their isotopologues is given in Table 1. With this reduced scheme the density profiles of the major neutrals and ions are in a good agreement with our previous model and observations (see Dobrijevic et al. (2016) for comparison with various observations). Our reduced chemical scheme, the schematic diagrams highlighting the major production and loss pathways and the integrated column rate of the production for each reaction in the nominal model are given in Appendix A, Appendix B and Appendix C, respectively.

The most noteworthy changes compared to Dobrijevic et al. (2016) are that we do not consider C_3H_x compounds, as well as most of the C_4H_x compounds. We have removed the few neutral radiative association reactions used in our previous models. Since all the potential radiative association reactions were not considered, we think that the introduction of only a few of them might induce some bias in the results. A dedicated study of these reactions should be conducted, including an uncertainty propagation study, to determine their importance in photochemical models of Titan's atmosphere. Some large cations are considered as a reservoir in our chemical scheme (like C_3H_3+, C_3H_5+, etc.), i.e. it is an end product species that has no chemical loss process. In order to reproduce the electron density as a function of altitude, we consider the dissociative recombination (DR) of this reservoir cation, with a rate constant equal to $1.0 \times 10^{-6}(T/300)^{-0.7}$ similar to the DR of $C_3H_3^+$ and $C_3H_5^+$ for instance. We also introduced a H + "neutral reservoir" addition reaction to take into account H + C_3H_x and H + $C_4H_x (x = 5-9)$ reactions, which are not present in our reduced chemical scheme and play a role at low altitude as an important sink for H atoms. The rate constant for this addition reaction has been adjusted to reproduce the H atom profile abundance given by our more complete model (Loison et al., 2015).

Anions are not taken into account in the present model. Anion reactions involve very small fluxes in Titan's atmosphere (Dobrijevic et al., 2016; Vuitton et al., 2009). Dobrijevic et al. (2016) found that the contribution of anions in the production of nitriles is negligible (see HC_3N and CH_3CN for instance). Moreover, we didn't find any efficient ^{15}N fractionation reactions involving anions. So, we estimate that anions can't play an important role in ^{15}N fractionation although the main light anions are supposed to be nitrile ones (CN^- and C_3N^-). It should be noted that the relation between anions and the growth of complex organic molecules is not clear. Desai et al. (2017) proposed that anion chemistry plays a role in the formation of complex organics as the negative charge is increasingly carried by the larger species with decreasing altitudes in the ionosphere. However, a more efficient electron attachment by large molecules could also explain this apparent growth of anions. So, it is probable that anions might be only the signature of the production of large molecules through cationic or neutral pathways, rather an efficient component to the production of large molecules.

For all species in the present reduced model, the calculated abundances are very similar to the results obtained with our more complete model (i.e. well within the error bars of the model results). Considering the large abundance of N_2 in Titan's atmosphere and the fact that photodissociation of N_2 leads to 50% of the $N(^2D)$ production, the $^{15}N(^2D)$ + N_2 reaction can play an important role in the photochemical fractionation. The global quenching rate constant has been measured several times in the $198-372$ K range (Lin and Kaufman, 1971; Slanger and Black, 1976; Suzuki et al., 1993). There is a general agreement for the value at 300 K but not for the temperature dependence of the rate constants. Recently, rate constant for the electronic quenching $N(^2D)$ + N_2 → $N(^4S)$ + N_2 reaction and exchange rate constant $^{15}N(^2D)$ + N_2 → $^{14}N(^2D)$ + $N^{15}N$ have been estimated using a set of three global electronic potential energy surfaces for the N^3 system (Galvao et al., 2012; 2013; 2014). For the other mechanisms we use the methodology developed by Terzieva and Herbst (2000) and Roueff et al. (2015), leading to the fact that $N(^2D)$ + $N^{15}N$ has a slightly larger activation energy than $^{15}N(^2D)$ + N_2 and also that $N(^2D)$ + $N^{15}N$ rate constant is multiplied by a factor of 0.5 to take into account the symmetry number related to the number of equivalent entrance channels. The exchange reaction involving $N(^4S)$ and N_2 shows a very large barrier in the entrance valley and is neglected here. For the other chemical reactions, the zero point energy (ZPE) effect is always small. In the case of Titan's atmosphere, the temperature is around 170 K above 200 km, and the ZPE difference is always much below this value, typically around 20-30K for the most important reactions (see Roueff et al. (2015)). Then, the forward and backward reactions always involve similar fluxes leading to almost no fractionation (for example $N^{15}N^+$ + N_2 and $N^{15}N$ + N_2^+). However, these fractionation effects were considered in the network although they are small.