Planetary and Space Science 73 (2012) 318–326

Contents lists available at SciVerse ScienceDirect

Planetary and Space Science

journal homepage: www.elsevier.com/locate/pss

Titan's photochemical model: Further update, oxygen species, and comparison with Triton and Pluto

Vladimir A. Krasnopolsky *

[a] Department of Physics, Catholic University of America, Washington, DC 20064, USA
[b] Moscow Institute of Physics and Technology, Dolgoprudnyy, Russia

ARTICLE INFO

Article history:
Received 4 May 2012
Received in revised form
7 August 2012
Accepted 10 August 2012
Available online 24 August 2012

Keywords:
Titan
Triton
Pluto
Atmospheres, Composition
Photochemistry
Evolution

ABSTRACT

My photochemical model for Titan's atmosphere and ionosphere is improved using the Troe approximation for termolecular reactions and inclusion of four radiative association reactions from those calculated by Vuitton et al. (2012). Proper fitting of eddy diffusion results in a reduction of the mean difference between 63 observed mixing ratios and their calculated values from a factor of 5 in my previous models for Titan to a factor of 3 in the current model. Oxygen chemistry on Titan is initiated by influxes of H_2O from meteorites and O^+ from magnetospheric interactions with the Saturn rings and Enceladus. Two versions of the model were calculated, with and without the O^+ flux. Balances of CO, CO_2, H_2O, and H_2CO are discussed in detail for both versions. The calculated model with the O^+ flux agrees with the observations of CO, CO_2, and H_2O, including recent H_2O CIRS limb observations and measurements by the Herschel Space Observatory.

Major observational data and photochemical models for Triton and Pluto are briefly discussed. While the basic atmospheric species N_2, CH_4, and CO are similar on Triton and Pluto, properties of their atmospheres are very different with atomic species and ions dominating in Triton's upper atmosphere and ionosphere opposed to the molecular composition on Pluto. Calculations favor a transition between two types of photochemistry at the CH_4 mixing ratio of $\sim 5 \times 10^{-4}$. Therefore Triton's current photochemistry is still similar to that at the Voyager flyby despite the observed increase in N_2 and CH_4. The meteorite H_2O results in precipitation of CO on Triton and CO_2 on Pluto near perihelion.

1. Introduction

My self-consistent photochemical model for Titan's atmosphere and ionosphere (Krasnopolsky 2009, 2010; hereafter Kr09 and Kr10) is a convenient tool to study atmospheric chemical composition on Titan and to test various hypotheses related to the chemical composition. Using the N_2 and CH_4 densities near the surface, the model calculates vertical profiles of 83 neutral species and 33 ions up to 1600 km. The model computes radiative transfer based on the aerosol observations from the Huygens probe and gaseous absorptions calculated interactively. The self-consistent nature of the model is advantageous compared to partial models that are aimed at simulating just a few atmospheric species. Those models require a background atmosphere that is generally poorly known and neglect effects of the calculated species on the background atmosphere.

* Corrresponding author at: Catholic University of America, Department of Physics, 6100 Westchester Park Dr. #911, College Park, MD, Washington, DC 20064, USA. Tel.: +1 240 473 6831.
E-mail address: vlad.krasn@verizon.net

0032-0633/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.pss.2012.08.013

2. Versions of the model

My models of Titan's photochemistry are aimed to simulate the global mean conditions, that is, the solar zenith angle is $z = 60^\circ$ and the solar photon flux is for the medium solar activity and half that at Titan's heliocentric distance to account for the night side. The model results are therefore applicable to the low latitudes or to globally averaged data.

Both the Voyager 1 flyby and the Cassini/Huygens mission refer to the southern summer in the 30-years annual cycle of Titan. The CIRS observations demonstrate very strong latitudinal variations of the atmospheric species at 100–400 km. Eight years have passed since the beginning of the observations, and some seasonal trends have become available as well. However, the seasonal and latitudinal variations are not the subject of my modeling. Observational data that are used for comparison with my models are collected in Table 1.

The GCMS abundances of CH_4 and Ar are applied as the lower boundary conditions, while the H_2 fraction may be computed with the models. Vertical profiles of nine species at 150–300 or 150–400 km are taken from the CIRS limb observations at 5°N (Vinatier, 2010), and values at the boundaries are compared with

Table 1
Summary of the observational data on Titan's chemical composition (mixing ratios).

h (km)	0[a]	150[b]	300[b]	400[b]	1050[c]	1400[d]	1100[e]
CH_4	0.057	0.015[a]	–	–	0.022	0.11	–
Ar	3.4–5[f]	–	–	–	1.3–5	–	–
H_2	1.0–3	–	–	–	3.4–3	0.02	–
C_2H_2	–	3–6	3–6	2–6	3.4–4	–	–
C_2H_4	–	1.5–7	3–8	–	3.9–4	–	1–3
C_2H_6	–	1–5	1.4–5	1.7–5	4.6–5	–	–
C_3H_4	–	1–8	1–8	–	9.2-6	–	–
C_3H_6	–	–	–	–	2.3–6	–	–
C_3H_8	–	1.3–6	1–6	5–7	2.9–6	–	–
C_4H_2	–	2–9	6–9	8–9	5.6–6	–	1–5
C_6H_2	–	–	–	–	–	–	8–7
C_6H_6	–	2–10[g]	–	–	2.5–6	–	3–6
C_7H_4	–	–	–	–	–	–	3–7
C_7H_8	–	–	–	–	2.5–8	–	2–7
NH_3	–	–	–	–	–	–	7-6
CH_2NH	–	–	–	–	–	–	1–5
HCN	–	2.5–7	5–7	3–7	2.5–4	–	2–4
CH_3CN	–	6–9[h]	1.4–8[h]	3–8[h]	–	–	3–6
C_2H_3CN	–	–	–	–	3.5–7	–	1–5
C_2H_5CN	–	–	–	–	1.5–7	–	5–7
HC_3N	–	1–11	1–9	–	1.5–6	–	4–5
C_4H_3N	–	–	–	–	–	–	4–6
HC_5N	–	–	–	–	–	–	1–6
C_5H_5N	–	–	–	–	–	–	4–7
C_6H_3N[i]	–	–	–	–	–	–	3–7
C_6H_7N[i]	–	–	–	–	–	–	1–7
C_2N_2	–	2–10[j]	–	–	2.1–6	–	–
H_2O[k]	–	7–11[l]	3–10[m]	–	1.2–5	–	–
CO	–	4.7–5	–	–	–	–	–
CO_2	–	2–8	1.8–8	3–8	–	–	–

[a] GCMS (Niemann et al., 2010).
[b] CIRS limb (Vinatier, 2010) at 5 °N.
[c] INMS (Magee et al., 2009).
[d] INMS (Cui et al., 2009).
[e] Derived from INMS ion spectra (Vuitton et al., 2007).
[f] $3.4–5 = 3.4 \times 10^{-5}$.
[g] CIRS nadir (Coustenis, 2010), low latitudes.
[h] IRAM results at 170, 300, and 400 km (Marten et al., 2002).
[i] Our model does not involve this species.
[j] At ~100 km and 5–30°N (from Fig. 9 in Teanby et al. (2009)).
[k] Mean of CIRS (Cottini et al., 2012) and Herschel (Moreno et al., 2012) observations.
[l] At 100 km.
[m] At 250 km.

the models. Mixing ratios of C_6H_6 and C_2N_2 from the CIRS nadir observations near the equator, the CH_3CN profile from the IRAM data, mean H_2O abundances from the CIRS and Herschel observations, and the CO value from De Kok (2007) are included in Table 1 (27 values at $h < 500$ km to evaluate the model results).

The next set of data (20 values) is the summary of the INMS neutral species observations near 1050 km (Magee et al., 2009) and 1400 km (Cui et al., 2009). Finally, Vuitton et al. (2007) fitted the INMS T5 ion spectrum at 1100 km by a model with numerous abundances of neutrals as free parameters. The best fit fractions are given in Table 1 as well (18 values, and C_6H_3N and C_6H_7N are not involved in our models). Overall, 63 observed mixing ratios from Table 1 will be used for comparison with our models.

Kr09 evaluated a mean difference between a model and observations by a difference factor

$$F = \exp\left(\frac{1}{n}\sum_{i=1}^{n}\left|\ln(f_i/f_{i0})\right|\right)$$

Here f_i and f_{i0} are the calculated and observed mixing ratios. F is equal to one if a model perfectly fits the observations; if F is, say, 3, then a mean difference between a model and observations is a factor of 3. Evidently the difference factor is not a perfect tool to estimate quality of a model: apart the calculated abundances, it is important how they have been calculated. However, it is convenient for comparison of our models with 63 observed mixing ratios in Table 1.

Kr09 and Kr10 suggest three versions of the model. Model 1 is a version with hydrodynamic escape of light species (molecular mass $\mu \le 18$) according to Strobel (2009). Eddy diffusion K in Model 1 has three breakpoints at 100, 400, and 700 km with $K = 3\times10^4$, 10^5, and 10^8 cm^2 s^{-1}, respectively. K is constant below 100 km and above 700 km and varies linearly between the breakpoints in the log scale. Difference factors for this model (Table 2) show a good agreement with both sets of the INMS data, while the calculated vertical profiles below 500 km are much steeper than those observed on the limb by CIRS.

To reduce vertical gradients in the calculated mixing ratios below 500 km, Hörst et al. (2008) proposed eddy diffusion increasing as n^{-2} (n is the atmospheric number density) from $K = 400$ cm^2 s^{-1} below 70 km to 3×10^7 cm^2 s^{-1} above ~300 km. (A similar but less steep profile of K was adopted in the model by Lavvas et al. (2008).) A model with this eddy diffusion was given in Appendix to Kr09. Improvements in the difference factors below 500 km (Table 2) are compensated by some deterioration in the upper atmosphere.

Model 3 was calculated in Kr10 assuming no hydrodynamic escape from Titan (Johnson et al. 2009). According to Yelle et al. (2008), the required eddy diffusion in the thermosphere is equal to $(4\pm3)\times10^9$ cm^2 s^{-1} to agree the CH_4 and Ar densities observed by INMS and GCMS (Niemann et al. 2010) in the upper and lower atmospheres, respectively, without hydrodynamic escape. The minimum value of 10^9 cm^2 s^{-1} was adopted in Model 3. Another change in Model 3 is an increase in the ammonia production by reactions

$$NH + H_2CN \rightarrow HCN + NH_2$$

$$NH_2 + HCN \rightarrow HCN + NH_3$$

the latter suggested by Yelle et al. (2009). These reactions reduce but cannot remove a significant difference between the INMS observations of ammonia and its model abundances. Difference factors for Model 3 (Table 2) are slightly worse than those for the models with hydrodynamic escape. However, this cannot be considered as a strong argument in favor of hydrodynamic escape on Titan.

Below we will make some improvements in the model, consider in more detail the chemistry of oxygen species on Titan, and compare the model results with recent observations of H_2O on Titan. Then we will discuss some effects of oxygen chemistry on Triton and Pluto.

3. Termolecular reactions

Rates of the termolecular reactions $A + B + M \rightarrow AB + M$ are equal to k_0[A][B][M] at low pressure and k_∞[A][B] at high pressure.

Table 2
Difference factors of the models relative to the observations in Table 1.

Model	$h < 500$ km	INMS	INMS*	Total
Lavvas et al. (2008)	4.30	4.49	16.1	5.63
Kr09	9.18	2.52	3.70	4.83
Kr09, Appendix	6.65	3.09	6.61	5.21
Kr10	9.28	3.01	4.65	5.45
This model	**3.91**	**2.35**	**3.21**	**3.16**

Kr09 and Kr10 are Krasnopolsky (2009, 2010), respectively. All my models in this table include influxes of H_2O and O^+. INMS is from columns 6 and 7 and INMS* from column 8 in Table 1. 46 mixing ratios from Lavvas et al. (2008) and 63 mixing ratios from each of my models are compared with the observations in Table 1.