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

Vladimir A. Krasnopolsky*

*Department of Physics, Catholic University of America, Washington, DC 20064, USA

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$_2$O 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$_2$O, and H$_2$CO are discussed in detail for both versions. The calculated model with the O$^+$ flux agrees with the observations of CO, CO$_2$, and H$_2$O, including recent H$_2$O 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$_2$O results in precipitation of CO on Triton and CO$_2$ on Pluto near perihelion.

© 2012 Elsevier Ltd. All rights reserved.

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.

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 $\theta$ = 60° 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.
neutral species observations near 1050 km (Magee et al., 2009). Eddy diffusion $K$ in Model 1 has three breakpoints at 100, 400, and 700 km with $K = 3 \times 10^7$, 105, 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 $3 \times 10^7$ 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 $(4 \pm 3) \times 10^7$ 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 $10^7$ cm$^2$ s$^{-1}$ was adopted in Model 3. Another change in Model 3 is an increase in the ammonia production by reactions

$$\text{NH}_2 + \text{H}_2 \rightarrow \text{HCN} + \text{NH}_3$$

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$_2$O 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 → AB + M are equal to $k_d[A][B][M]$ at low pressure and $k_{\cdot\cdot}\cdot[A][B]$ at high pressure.

<table>
<thead>
<tr>
<th>Model</th>
<th>h &lt; 500 km</th>
<th>INMS</th>
<th>INMS'</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lavvas et al. (2008)</td>
<td>4.30</td>
<td>4.49</td>
<td>16.1</td>
<td>5.63</td>
</tr>
<tr>
<td>Kr09</td>
<td>9.18</td>
<td>2.52</td>
<td>3.70</td>
<td>4.83</td>
</tr>
<tr>
<td>Kr09, Appendix</td>
<td>6.65</td>
<td>3.09</td>
<td>6.61</td>
<td>5.21</td>
</tr>
<tr>
<td>Kr10</td>
<td>9.28</td>
<td>3.01</td>
<td>4.65</td>
<td>5.45</td>
</tr>
<tr>
<td><strong>This model</strong></td>
<td><strong>3.91</strong></td>
<td><strong>2.35</strong></td>
<td><strong>3.21</strong></td>
<td><strong>3.16</strong></td>
</tr>
</tbody>
</table>

Kr09 and Kr10 are Krasnopolsky (2009, 2010), respectively. All my models in this table include influxes of H$_2$O 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.
Here $k_0$ (cm$^6$ s$^{-1}$) is the low pressure limit for the reaction rate coefficient, and $k_\infty$ (cm$^3$ s$^{-1}$) is the high pressure limit. We applied

$$k = \frac{k_0}{1+(k_0/k_\infty)[M]} = \frac{k_0}{1+(k_\infty/[M])} \quad \text{and} \quad M_\infty = \frac{k_\infty}{k_0}$$

in Kr09 and Kr10. Here $M_\infty$ has the dimension of number density, and the rate coefficient fits both low and high pressure limits in this formulation.

A more accurate approximation for the rate coefficient at intermediate pressures was obtained by Troe:

$$k = \frac{k_0}{1+(k_0/k_\infty)[M]} \times 0.6^{1+X^2} \quad \text{and} \quad X = \ln \left( \frac{k_0}{k_\infty} [M] \right)$$

We upgraded our model using the Troe approximation, though the effect from this improvement is insignificant.

Vuitton et al. (2012) suggested another approximation:

$$k = \frac{k_0[M]X+k_c}{1+(k_0[M]X/k_\infty)}$$

Here $k_c$ is the rate coefficient of radiative association and $X$ is a parameter that is determined by some complicated relationships. The approximation fits the high pressure limit but does not fit the low pressure limit, because e.g. $X \approx 50$ for very small [M] in the reaction $H$+$CH_3=H$+$CH_4$. The relationships for $X$ are given without any proof and explanation and overall do not conform the definition of the low pressure limit. Therefore we will not use the suggested approximation and the calculated low and high pressure limits for ten reactions in Vuitton et al. (2012). Radiative association reactions from that paper are discussed below.

### 4. Radiative association reactions

We checked effects of the radiative association reactions calculated by Vuitton et al. (2012) on the results of our model. Four of the ten reactions,

$$H+CH_2CN\rightarrow HCN+CH_3$$

affect the calculated abundances and have been included in the model. The most significant and unexpected effect is from reaction (2) that diminishes $CH_2CN$ above 900 km and enhances $C_2N_2$. This reaction initiates a cycle

$$H+CH_2\rightarrow CH_2+CH_3\rightarrow CH_3+CH_4$$

This cycle reduces densities of methyl $CH_3$ and therefore ethane $CH_4$. Another unexpected consequence of reactions (1–4) is the increase of the cyanogen abundance that is formed by

$$CN+CH_3\rightarrow CH_3CN$$

in our model. These species are controlled by $H$ via

$$CH_3CN+H=M\rightarrow CH_3CN+M$$

CHCN+$H\rightarrow C_2N+H_2$

A significant reduction of $H$ in the radiative associations results in an increase in $C_2N_2$. Both changes in $C_2H_6$ and $C_2N_2$ better agree with the INMS observations. Reaction (4) facilitates the production of benzene and also helps to fit the INMS observations (Table 1).

Kr09 and Kr10 adopted loss of species $i$ by condensation near and below the tropopause as $L_i=A\ln S_i$. Here $S_i=n_i/n_{i,0}$ is the supersaturation of $i$ species. Yung et al. (1984) applied $L_i = AS/(1+S) = A$ because typically $S_i \gg 1$. They adopted $A=10^{-9}$ s$^{-1}$ without any discussion, and we will use this $A$ in our model.

### 5. Eddy diffusion and improved photochemical model

We discussed in Section 2 that the steep increase in eddy diffusion $K=\eta/h^2$ in the stratosphere helps to fit the vertical profiles of species observed by CIRS on the limb (Tables 1 and 2). However, a more traditional profile of $K$ with a break near 700–800 km and a constant value above is favorable for the INMS observations. Here we will try to combine both profiles to get the best difference factors.

Similar to Kr09 and Kr10, eddy diffusion is given by three break points and therefore six parameters: the breakpoint altitudes $h_0$, $h_1$, and $h_2$ and values $K_0$, $K_1$, and $K_2$. Eddy diffusion is equal to

$$K = \frac{K_1}{1+(K_1/K_0)(\pi/7.5)^2}$$

between $h_0$ and $h_1$. It is constant below $h_0$, increases to $K_2$ at $h_2$ linearly in the log scale, and is constant above $h_2$. All values are chosen to minimize the difference factor. The best fit parameters are $61, 536$, and $790$ km and $2300, 3.2 \times 10^5$, and $6.5 \times 10^8$ cm$^2$ s$^{-1}$, respectively. The calculated profile of eddy diffusion is shown in Fig. 1a along with the temperature profile and the calculated $N_2$ densities. $K=190$ cm$^2$ s$^{-1}$ below 60 km, the profiles of $K$ and $D$ are rather close above 500 km, and the homopause $D=K$ is at 1000 km. The difference factor of the model is 3.16, better than 5.45 for the model in Kr10 (Table 2).

The calculated profiles of $CH_2$, $H_2$, $Ar$, and $C_2H_2$ hydrocarbons are shown in Fig. 1b; seven other abundant hydrocarbons and seven nitriles are exposed in Fig. 1c and d, respectively. The profiles in Fig. 1 may be compared with the observational data in Table 1.

Mean dayside ($z=60^\circ$) density profiles of the most abundant ions are given in Fig. 2a–c. The ionospheric peak with $e_{max}=3650$ cm$^{-3}$ is at 1070 km. Cassini radio occultations at $z=87^\circ$ resulted in $e_{max}=2000$ cm$^{-3}$ at 1200 km (Kliore et al., 2008). According to Cravens et al. (2005), the peak altitude moves up by $\sim 140$ km from $z=59^\circ$ to $90^\circ$ while the peak electron density reduces by a factor of 2. Therefore both the calculated peak density and its altitude in our model are in excellent agreement with the radio occultation observations. However, INMS measured a peak sum of all ions of 1800 cm$^{-3}$ at 1100 km during the dayside Cassini flyby T40 on January 5, 2008, at 12$^\circ$S and $z=38^\circ$ (Westlake et al., 2012). This peak electron density is even smaller than that observed at $z=87^\circ$ and disagrees with both radio occultations and our model. Two other instruments, Langmuir probe and CAPS-IBS, measured $e_{max}=2800$ cm$^{-3}$ at 1120 km in the T40 flyby (Westlake et al., 2012). This value is closer to the model prediction. The nighttime flyby T5 with a strong precipitation of magnetospheric electrons is therefore better for comparison of models with the INMS observations (Vuitton et al., 2007). Those measurements were modeled by Vuitton et al. (2007), Cravens et al. (2009), and Kr09.
Fig. 1. Initial data and calculated vertical profiles of neutral species in the model: (a) profiles of temperature, N$_2$ density, eddy and molecular (CH$_4$ in N$_2$) diffusion; (b) CH$_4$, H$_2$, Ar, and C$_2$H$_4$ hydrocarbon; (c) some other abundant hydrocarbons; (d) the most abundant nitriles.

Fig. 2. Ion composition in the daytime ionosphere above (a, b) and below (c) 600 km. The nighttime ionosphere (d) is calculated for the conditions of the T5 flyby with strong precipitation of magnetospheric electrons.
the difference factors are 1.74, 3.88, and 2.01, respectively (Table 7 in Kr09), and 2.15 for the current model (Fig. 2d). The abundances of 18 neutral species were fitting parameters in the model by Vuitton et al. (2007). Both neutral and ion compositions are calculated interactively in our models, and the difference factor obtained may be considered as very good.

6. Oxygen species

6.1. Observations

Oxygen species were first discovered on Titan by ground-based observations that revealed a significant abundance of CO (Lutz et al. 1983). Later CO was measured using ground-based infrared and microwave instruments and by the Voyager/IRIS and Cassini/CIRS. A summary of the observations may be found in De Kok (2007) and Hörst et al. (2008), and the mean CO (Fig. 3) is close to the CIRS value of 47 ± 8 ppm (De Kok, 2007). CO2 was detected by IRIS, ISO, and CIRS (see Hörst et al. (2008)), and the CIRS limb profiles at 5 km (Coustenis et al. 1998) using its rotational lines near 40 μm. H2O was detected by the Infrared Space Observatory (Coustenis et al. 1998) using its rotational lines near 40 μm. The measured mole fraction was equal to 8 ppm (De Kok, 2007), and the CIRS observations resulted in 4–34 ppm of H2O at a mean altitude of 1077 km (Cui et al., 2009), (5) CIRS (Cottini et al., 2012), and the CIRS limb profiles at 5 km (Coustenis et al. 1998) using its rotational lines near 40 μm. H2O was detected by the Infrared Space Observatory (Coustenis et al. 1998) using its rotational lines near 40 μm.

Recent water vapor was observed by the Herschel Space Observatory using its rotational lines in the far infrared and submillimeter ranges. The retrieved observed by the Herschel Space Observatory using its rotational lines in the far infrared and submillimeter ranges. The retrieved observed by the Herschel Space Observatory using its rotational lines in the far infrared and submillimeter ranges.

6.2. Previous models

Previous full photochemical models for Titan’s atmosphere that involved the oxygen chemistry (Yung et al., 1984; Touboul et al., 1995, Lara et al., 1996, Balaszkiewicz et al., 2000, Wilson and Atreya, 2004) adopted a meteorite influx of H2O and fixed the CO mixing ratio near the surface. The oxygen chemistry on Titan was studied in more detail by Wong et al. (2002) and Hörst et al. (2008).

Wong et al. (2002) applied the model by Yung et al. (1984) with updated kinetic data from Moses et al. (2000). Using the study by Pereira et al. (1997), they argued that a basic reaction of the CO production in the previous models, OH + CH3 → CO + 2H2, does not proceed, and H2O recycles after the photolysis via OH + CH3 → H2O + CH2. They adopted an H2O influx of 0.1 × 10^6 cm^-2 s^-1 and calculated a CO abundance of 1.8 ppm with no sources of CO at the surface or from space, much lower than the 47 ppm observed. A CO influx of 1.1 × 10^6 cm^-2 s^-1 was required to fit the observed CO.

Hartle (2006) analyzed the Voyager and Cassini/CAPS data and found a magnetochemical influx of O+ on Titan with a rate of ~10^6 cm^-2 s^-1. These ions of atomic oxygen may originate from Saturn’s ring and Enceladus. Hörst et al. (2008) calculated a model for the oxygen species on Titan using the influxes of OH and O and eddy diffusion as fitting parameters. Their best model is for \( \Phi_0 = 1.6 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1} \), \( \Phi_{OH} = 2.6 \times 10^6 \text{ cm}^{-2} \text{ s}^{-1} \), and eddy diffusion discussed in Section 2 for Model 2. Hörst et al. (2008) achieved an excellent agreement with the observations of CO, CO2, and H2O available at that time. However, the calculated H2O abundances were ~0.1, 2, and 2.3 ppm at 100, 200, and 300 km, respectively, that is, exceeding the recent measurements above 100 km.

6.3. Oxygen species in our models

Kr09 and Kr10 keep the basic ideas of the oxygen chemistry from Wong et al. (2002) and Hörst et al. (2008) with some changes. We assumed no influx of CO from the surface and space. Kr09 proved that the metastable oxygen states O(1D) and O(1S) may be neglected because of the low production and the strong quenching by N2. Five species (HOCO, CH3CHO, CH2CO, CH3OH, and HOCH2CH2) in Hörst et al. (2008) were assumed to ultimately produce either CO2 or CO. We concluded that two of those (HOCO, CH3CHO, and also CH3O) may be neglected as well and add photolyses of CH2CO and CH3OH to balance their production. The production of HOCH2CH2 is balanced by the reaction with H in our model. Overall, we reduced the numbers of oxygen species and reactions from 14 and 44 in Hörst et al. (2008) to 12 and 31, respectively (Table 3). 10 species and 21 reactions are similar to those in Hörst et al. (2008), and 1 species (CH3C0H) and 10 reactions were added and marked by asterisks in Table 3.

We approximated an H2O flux profile from English et al. (1996) by

\[
\frac{dF_{H_2O}}{dh} = \frac{0.185}{ch^{(1.5/100)}} = \frac{0.37}{\exp\left(\frac{h-750}{50}\right) + \exp\left(\frac{750-h}{50}\right)} \text{ cm}^{-3} \text{ s}^{-1}
\]

Here \( ch \) is hyperbolic cosine, and \( h \) is in km. The H2O flux is equal to 2.95 × 10^6 cm^-2 s^-1; scaled to the surface, it is 4.78 × 10^6 cm^-2 s^-1. This flux is within uncertainties of that observed on Saturn by Feuchgruber et al. (1997). The O+ flux was chosen at 1.70 × 10^6 cm^-2 s^-1 at 1100 km and 3.46 × 10^6 cm^-2 s^-1 scaled to the surface.

These fluxes and the oxygen chemistry (Table 3) remain unchanged in all our models including that in this paper. The model in Kr09 (Appendix) with eddy diffusion from Hörst et al. (2008) showed CO, CO2, and H2O rather similar to those in Hörst.
Table 3
Reactions of oxygen species in Titan's atmosphere.

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>Yield (γ)/Rate coefficient</th>
<th>Column rate</th>
<th>h (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO + hν → CO + O</td>
<td>predissociation, diss., ionization, electron impact dissociation</td>
<td>6.171 × 10^{-9}</td>
<td>1012</td>
</tr>
<tr>
<td>2</td>
<td>H2O + hν → OH + H</td>
<td>γ=0.78.10 (110–145–200 nm)</td>
<td>1.03 × 10^{-7}</td>
<td>569</td>
</tr>
<tr>
<td>3</td>
<td>O + H2</td>
<td>γ=0.22.0</td>
<td>9.62 × 10^{-4}</td>
<td>835</td>
</tr>
<tr>
<td>4</td>
<td>CO2 + hν → CO + O</td>
<td>–</td>
<td>2.56 × 10^{-6}</td>
<td>404</td>
</tr>
<tr>
<td>5</td>
<td>H2CO + hν → CO + H</td>
<td>6.4 × 10^{-7}</td>
<td>1.10 × 10^{-6}</td>
<td>763</td>
</tr>
<tr>
<td>6</td>
<td>CO + H2</td>
<td>2.1 × 10^{-7}</td>
<td>3.60 × 10^{-5}</td>
<td>763</td>
</tr>
<tr>
<td>7</td>
<td>HCO + H</td>
<td>3.6 × 10^{-7}</td>
<td>6.17 × 10^{-5}</td>
<td>763</td>
</tr>
<tr>
<td>8*</td>
<td>CH2O + hν → CH + CO + H</td>
<td>2 × 10^{-6}</td>
<td>7.60 × 10^{-4}</td>
<td>513</td>
</tr>
<tr>
<td>9*</td>
<td>CH3OH + hν → H + CO + H</td>
<td>–</td>
<td>3.11 × 10^{-4}</td>
<td>494</td>
</tr>
<tr>
<td>10</td>
<td>O + CH3 + H2CO + H</td>
<td>7 × 10^{-11}</td>
<td>2.03 × 10^{-6}</td>
<td>1034</td>
</tr>
<tr>
<td>11</td>
<td>CO + H2 + H</td>
<td>6 × 10^{-11}</td>
<td>1.74 × 10^{-6}</td>
<td>1034</td>
</tr>
<tr>
<td>12*</td>
<td>O + CH4 + CH2O + H</td>
<td>γ=0.3, 2.2 × 10^{-17} T^{-1.9} e^{-92/T}</td>
<td>1.83 × 10^{-4}</td>
<td>534</td>
</tr>
<tr>
<td>13*</td>
<td>CH3 + HCO</td>
<td>γ=0.6</td>
<td>3.66 × 10^{-4}</td>
<td>534</td>
</tr>
<tr>
<td>14*</td>
<td>H2O + CH3</td>
<td>γ=0.1</td>
<td>6.098 × 10^{-4}</td>
<td>534</td>
</tr>
<tr>
<td>15</td>
<td>OH + CH3 + CH2 + O</td>
<td>1.8 × 10^{-14} T^{-1.9} e^{-275/T}</td>
<td>4.41 × 10^{-6}</td>
<td>653</td>
</tr>
<tr>
<td>16</td>
<td>H2CO + H</td>
<td>3.8 × 10^{-14} T^{-0.12} e^{200/T}</td>
<td>93.4 × 10^{-6}</td>
<td>653</td>
</tr>
<tr>
<td>17</td>
<td>OH + CH3 + M → CH2OH + M</td>
<td>1.1 × 10^{-10} T^{-0.21} e^{-677/T}, 4 × 10^{-15}</td>
<td>3.11 × 10^{-4}</td>
<td>521</td>
</tr>
<tr>
<td>18</td>
<td>OH + CH2 + CH2 + H</td>
<td>2.5 × 10^{-12} e^{-177/T}</td>
<td>1.14 × 10^{-12}</td>
<td>504</td>
</tr>
<tr>
<td>19</td>
<td>OH + CO2 → CO2 + H</td>
<td>2.8 × 10^{-15} e^{-170/T}</td>
<td>4.35 × 10^{-6}</td>
<td>503</td>
</tr>
<tr>
<td>20</td>
<td>OH + CH3 + H2O + H</td>
<td>9 × 10^{-13} e^{-150/T}</td>
<td>1.67 × 10^{-5}</td>
<td>526</td>
</tr>
<tr>
<td>21</td>
<td>OH + CH2 + CH2 + CH2O + M</td>
<td>5.5 × 10^{-30}</td>
<td>5.5 × 10^{-16}</td>
<td>467</td>
</tr>
<tr>
<td>22</td>
<td>OH + CH2 + H + HOCO + CH2 + M3</td>
<td>1.4 × 10^{-17} T^{-4.5}, 10^{-16}</td>
<td>2.14 × 10^{-5}</td>
<td>553</td>
</tr>
<tr>
<td>23</td>
<td>HCO + H → CO + H2</td>
<td>1.8 × 10^{-10}</td>
<td>6.67 × 10^{-5}</td>
<td>713</td>
</tr>
<tr>
<td>24</td>
<td>HCO + CH2 + CH2 + CO</td>
<td>9 × 10^{-11}</td>
<td>1.10 × 10^{-5}</td>
<td>715</td>
</tr>
<tr>
<td>25*</td>
<td>CH3CO + H + CO2 + CH2</td>
<td>3.6 × 10^{-11}</td>
<td>1.24 × 10^{-5}</td>
<td>529</td>
</tr>
<tr>
<td>26*</td>
<td>CH2O + H2</td>
<td>1.9 × 10^{-11}</td>
<td>6.56 × 10^{-6}</td>
<td>529</td>
</tr>
<tr>
<td>27</td>
<td>CH3CO + H + CH2O + CH2</td>
<td>10^{-11}</td>
<td>1.08 × 10^{-4}</td>
<td>436</td>
</tr>
<tr>
<td>28</td>
<td>CO + CH3</td>
<td>4.8 × 10^{-11}</td>
<td>5.17 × 10^{-4}</td>
<td>436</td>
</tr>
<tr>
<td>29*</td>
<td>CH2O + H + CO2 + CH2</td>
<td>1.3 × 10^{-10} T=1400/T</td>
<td>403</td>
<td>320</td>
</tr>
<tr>
<td>30*</td>
<td>CH3CO + H + CH2 + H2</td>
<td>7 × 10^{-15} T=1210/T</td>
<td>2.14 × 10^{-5}</td>
<td>508</td>
</tr>
<tr>
<td>31*</td>
<td>HOCO + CH2 + H + CH2O + H2</td>
<td>3.3 × 10^{-11}</td>
<td>2.14 × 10^{-5}</td>
<td>553</td>
</tr>
<tr>
<td>32</td>
<td>H2O meteorite flux</td>
<td>4.78 × 10^{-6}</td>
<td>704</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>O+ influx</td>
<td>3.46 × 10^{-6}</td>
<td>1103</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>H2O condensation</td>
<td>6.13 × 10^{-4}</td>
<td>&lt;84</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>CO2 condensation</td>
<td>4.08 × 10^{-6}</td>
<td>&lt;60</td>
<td></td>
</tr>
</tbody>
</table>

Rate coefficients of photolyses (in cm s^{-1}) are halves of the daytime values at λ > 200 nm, those for two-body reactions are in cm^3 s^{-1}, and termolecular rate coefficients are low-pressure limits (in cm^3 s^{-1} H) and limiting densities (ratios of high/low pressure limits at 170 K). References to the photolysis cross sections and reaction rate coefficients are given in Tables 3 and 4 in Kr109. Column rates are in cm^3 s^{-1} and scaled to the surface (see Kr09); h is the reaction weighted-mean altitude for the model with the flux of O^{-}. Reaction marked by asterisks are lacking in Hörst et al. (2008). 4.16 × 6 = 4.16 × 10^9.

et al. (2008). Results of our current model with and without the O^{-} flux are shown in Fig. 3, and the column reaction rates are in Table 3. We will consider the following the O^{-} flux.

The H2O photolysis branch that forms O (R3) is very weak because of the strong CH4 absorption at λ < 140 nm. There are three basic pathways for OH after photolysis of H2O: (1) to restore H2O in reactions with CH3, CH4 and H2 (R15, 18, 20); (2) to form CO in reactions with CH3, CH2H2, and CH4 (R16, 17, 21, 22) because the products in these reactions decompose further to CO; (3) to remove CO and form CO2 in R19. Photolysis cross sections of CO2 at 170–200 nm are smaller than those of H2O in this range by a factor of ~300; therefore photolysis of CO2 is weak, and CO2 mostly irreversibly condenses in our model. Photodestruction of CO is very slow (R1), and the CO abundance without the O^{-} flux is determined by a balance between pathways (2) and (3) and equal to 1.9 ppm, similar to that in Wong et al. (2002). Its lifetime is very long, and CO2 is constant throughout the atmosphere.

The mean altitude of CO2 formation is 500 km (R19). Eddy diffusion is high above this altitude, and the CO2 mole fraction is constant up to the homopause near 1000 km in this model with a further decrease (Fig. 3) because of diffusive separation with the large CO2 molecular mass. CO2 is decreasing below 400 km to the tropopause where it condenses. This decrease is partly compensated by eddy diffusion K ≈ An^{-2} to fit the CO2 and some other CIRS limb observations (Vinatier, 2010). This increase in eddy diffusion is by a factor of 140 and from 60 to 200 km in our model, while it is by a factor of 70,000 from 100 to 300 km in Hörst et al. (2008). The production of H2O by meteorites (R32) and pathway (1) is balanced by the photolysis (R2-3) with a minor contribution from condensation (R34). The H2O profile differs from that of CO2 above the homopause due to diffusive separation with the low H2O molecular mass. The H2O decrease is steeper than CO2 below 400 km because of the higher photolysis rate.

In the case of the O^{-} flux (R33, 3.46 × 10^6 cm^{-2} s^{-1}), it is completely spent to form CO in reactions (10–11) with CH3H2. Each CO2 photolysis event adds two CO2 molecules as well, because O is converted into CO. The reactions of pathway (2) give 2.75 × 10^6 cm^{-2} s^{-1}, and the total CO production is 4.36 × 10^6 cm^{-2} s^{-1}. It is balanced by the reaction with OH giving a CO mole fraction of 44 ppm, in accord with the observations and larger than that without the O^{-} flux by a factor of 23. The CO mole fraction is constant up to ~1200 km and decreases above this altitude because of diffusive enrichment in CH4 and H2.

The CO2 production of 4.36 × 10^6 cm^{-2} s^{-1} in R19 CO + OH is balanced by its condensation (R35) and photolysis (R4). The calculated CO2 mole fraction agrees with the observed profile below ~300 km (Fig. 3).

The production of H2O by OH in R15 and R18 with CH3 and CH4 becomes smaller because of the competing reaction with CO and equals 5.55 × 10^6 cm^{-2} s^{-1}. Adding the meteorite production results in 1.03 × 10^7 cm^{-2} s^{-1} that is perfectly balanced by the
photolysis and condensation. The H₂O abundance is smaller than that without the O⁺ flux due to the greater loss of OH in the reaction with CO.

The calculated H₂O profile (Fig. 3) is between the Herschel (Moreno et al., 2012) and CIRS (Cottini et al., 2012) observations. It intersects the square of the ISO observations (Coustenis et al., 1998) near the middle. The ISO value of 8±6 =4–14 ppb near 400 km was obtained by scaling of the H₂O profile from Lara et al. (1996). Our H₂O profile equals to 8 and 14 ppb at 370 and 390 km, respectively, well within the ISO contribution function with a broad peak at 400 km. Furthermore, the ISO observation corresponds to an H₂O column of (2.6±1.0) × 10¹⁴= (1.0–4.5) × 10¹⁴ cm⁻² above 100 km, and the model gives 4.7 × 10¹⁴ cm⁻², near the uncertainty of the observation. The H₂O model values are also within the scatter of the INMS measurements (Cui, 2009). We emphasize that the combination of the Herschel, CIRS, and ISO data with the INMS measurements requires a steep decrease in the H₂O fraction below 600 km, and this decrease is simulated by the model because of the significant effect of the H₂O photolysis.

Atomic oxygen reacts with methyl in the upper atmosphere and forms formaldehyde H₂CO. Therefore formaldehyde in the upper atmosphere is much more abundant in the case of the O⁺ flux (Fig. 3). This source becomes small below 500 km where the calculated H₂CO profile is almost insensitive to the O⁺ flux.

The CO lifetime is a ratio of its column abundance and its column loss rate in the reaction with OH and equals 75 Myr. This may be compared with chemical lifetimes of N₂ and CH₄ on Titan, 25 Byr and 21 Myr, respectively (Kr09). Lifetimes of the other photochemical products are very much shorter (Table 6 in Kr09).

Although CO is abundant on Titan, it forms photochemically and does not require a source on the surface. It cannot condense and deposit to the surface. Precipitation of H₂O ice is negligible as well, and that of CO₂ is 9 g cm⁻² Byr⁻¹, that is, ~10⁻³ of the total precipitation (Kr10).

7. Comparison with Triton and Pluto

There are three bodies with the nitrogen-methane atmospheres in the Solar System: Titan, Triton, and Pluto. Triton is at ~10 AU from the Sun, and its N₂ is completely in the atmosphere that is very dense. Triton and Pluto are at ~30 AU from the Sun and have tenuous atmospheres that are in equilibrium with ices of N₂, CH₄, and CO. In addition to these ices, ices of CO₂, H₂O, and HCN have been detected on Triton (Burgdorf et al., 2010) and deposit to the surface. Precipitation of H₂O ice is negligible as it does not require a source on the surface. It cannot condense and does not require a source on the surface. It cannot condense and deposit to the surface. Precipitation of H₂O ice is negligible as well, and that of CO₂ is 9 g cm⁻² Byr⁻¹, that is, ~10⁻³ of the total precipitation (Kr10).

7.1. Basic observational data

Triton was studied by the Voyager 2 flyby in 1989 (Broadfoot et al., 1989) that revealed vertical profiles of N₂, temperature, N (Krasnopolsky et al., 1993), and CH₄ (Herbert and Sandel, 1991), atmospheric pressure of 13.5 µbar and an electron density profile in the ionosphere (Tyler et al., 1989), a surface temperature of 38 ± 3 K (Conrath et al., 1989), and haze and clouds (Pollack et al., 1990, Krasnopolsky et al., 1992).

Stellar occultations in 1995 and 1997 (Olkin et al., 1997, Elliot et al., 2000) showed a significant increase in the atmospheric pressure since the Voyager flyby. Finally, gaseous CH₄ and CO were detected (Lellouch et al., 2010) by ground-based high-resolution spectroscopy using the CRIRES spectograph at the Very Large Telescope of the European South Observatory in Chile. The observed abundances are 0.08 ±0.03 cm-atm of CH₄ and 0.3 cm-atm of CO, the latter with an uncertainty within a factor of 3. The N₂ abundance during the observations was generally unknown, and Lellouch et al. (2010) adopted 4 µbar combining the Voyager data and the stellar occultations. This abundance is equal to 410 cm-atm using Triton’s gravity acceleration of 78 cm s⁻². The obtained mole fractions are given in Table 4 and compared with those in a photochemical model by Krasnopolsky and Cruikshank (1995) that was based on the Voyager results. The difference is well within the observation uncertainties. Methane varies with altitude on Triton and Pluto; henceforth its mixing ratio is a ratio of the column abundances of CH₄ and N₂.

Pluto’s atmosphere was studied by stellar occultations in 1988, 2002, and 2006 (Elliot and Young, 1992; Elliot et al., 2007, Young et al., 2008); recently the occultation curves from those events were fitted by radiative-conduction models to get basic atmospheric parameters (Zalucha et al., 2011). Search for gaseous species by ground-based high-resolution spectroscopy resulted in detections of CH₄ using CSHELL/IRTF (Young et al., 1997) and CH₄ and CO using CIRRES/VLT (Lellouch et al., 2009, 2011). Middle UV spectroscopy from the Hubble Space Telescope gave only upper limits to C₂H₆, C₂H₄, H₂CN, and C₂N₂ (Krasnopolsky, 2001). The upper limits are ~2 × 10¹⁶ cm⁻², that is, ~5 ppm scaled to an atmosphere of ~10 µbar. The observed CH₄ and CO abundances (Table 4) agree within their uncertainties with those adopted in a photochemical model for Pluto by Krasnopolsky and Cruikshank (1999).

7.2. Main features of photochemistry on Triton and Pluto

The CH₄ mole fraction was ~10⁻⁴ on Triton during the Voyager flyby. Photolysis by the Lyman-alpha photons from the Sun and the interplanetary background greatly depletes the profile of methane. Ion reactions further reduce CH₄ to ~1 ppm at 200 km (Krasnopolsky and Cruikshank, 1995). Therefore molecular species are scarce in the upper atmosphere, and this gives rise to atomic neutrals N, O, C, and H and atomic ions C⁺ and N⁺. The observed and calculated densities of N are equal to 5 × 10⁸ cm⁻³ at 200 km with a mole fraction of 0.2%. The slow radiative recombination of atomic ions results in an ionospheric peak density nₚₑₐₓ = 3 × 10⁷ cm⁻³, in accord with the Voyager radio occultations (Tyler et al., 1989). Low-energy electrons from the Neptunian magnetosphere significantly contribute to the formation of Triton’s ionosphere. The CH₄ photolysis peak is at 25 km where the N₂ density is high and facilitates production...
of HCN via
\[ \text{CH}_4 + \text{N}_2 + \text{N}_2 \rightarrow \text{HCN}_2 + \text{N}_2 \]
\[ \text{HCN}_2 + \text{H} \rightarrow \text{HCN} + \text{NH} \]

Net \( \text{CH}_4 + \text{H} + \text{N}_2 \rightarrow \text{HCN} + \text{NH} \).

These reaction rates are proportional to \([\text{N}_2]^2\) near the \(\text{CH}_4\) photoysis peak and greatly increase the production of HCN on Triton (Krasnopolsky and Cruikshank, 1995). The detection of HCN in Triton’s ice (Burgdorf et al, 2010) confirms this cycle.

Methane is more abundant on Pluto with a mole fraction of \(9 \times 10^{-3}\) at \(r = 1210\) km in model 2 by Krasnopolsky and Cruikshank (1999). The photoysis and ion reactions are insufficient to deplete this abundant methane and overcome its enrichment by diffusive separation. Hydrocarbon and nitrile chemistries are effective to deplete this abundant methane and overcome its enrichment by diffusive separation. Hydrocarbon and nitrile chemistries are effective, and production of these species is significant. Atomic nitrogen is diminished to a maximum of \(10^5\) cm\(^{-3}\) still keeps the Voyager-type chemistry.

To simulate the transition from the Voyager-type chemistry of Triton to that on Pluto, we calculated vertical profiles of methane on Triton for various \(\text{CH}_4\) mixing ratio near the surface. Loss of methane in chemical reactions was interpolated between the models for Triton and Pluto, while the major loss is by photoysis. The results are shown in Fig. 4. The transition between two types of the model occurs near \(f_{\text{CH}_4} \approx 5 \times 10^{-4}\). The \(\text{CH}_4\) mole fraction decreases up to 100 km by a factor of \(\sim 30\) for the smaller values near the surface and is nearly constant for the larger values. Therefore the current Triton with \(f_{\text{CH}_4} \approx 2 \times 10^{-4}\) still keeps the Voyager-type chemistry.

### 7.3. Results of meteorite supply of \(\text{H}_2\text{O}\) to Triton and Pluto

The meteorite injection of \(\text{H}_2\text{O}\) of \(\sim 2 \times 10^6\) cm\(^{-2}\) s\(^{-1}\) and the subsequent \(\text{H}_2\text{O}\) photoysis on Triton exceed the model production of OH by the reaction of \(\text{O} + \text{H} + \text{M}\) by an order of magnitude.

![Fig. 4. Calculated profiles of methane mixing ratio on Triton as functions of its ratio near the surface. Photoysis and chemical reactions tend to reduce methane while diffusive separation enhances it. Transition from the atmosphere with large \(N\) and \(n_e\) observed by Voyager to that with low \(N\), \(n_e\), and abundant hydrocarbons typical of Titan and the current Pluto is at the \(\text{CH}_4\) mole fraction of \(\sim 5 \times 10^{-4}\) near the surface.](image)

Loss of OH proceeds via
\[ \text{OH} + \text{N} \rightarrow \text{NO} + \text{H} \]
\[ \text{NO} + \text{N}_2 \rightarrow \text{O} + \text{N}_2 + \text{O} \]
\[ \text{Net OH} + 2\text{N} \rightarrow \text{O} + \text{H} + \text{N}_2 \]

Production of \(\text{N}\) is \(1.5 \times 10^6\) cm\(^{-2}\) s\(^{-1}\) on Triton, and the appearance of \(\text{H}_2\text{O}\) weakly affects the balance of \(\text{N}\). Therefore OH formed by photolysis of \(\text{H}_2\text{O}\) is immediately converted into \(\text{O}\) that forms CO in reactions with \(\text{CH}_4\), \(\text{CN}\), and \(\text{CNN}\). The production of CO from the meteorite water is larger than its loss by escape of \(\text{O}\) in the model by Krasnopolsky and Cruikshank (1995) by an order of magnitude, and the meteorite water results in precipitation of \(\sim 3\) g cm\(^{-2}\) yr\(^{-1}\) of CO on Triton. Photoysis of \(\text{CH}_4\) with escape of \(\text{H}\) and \(\text{H}_2\) produces some excess of carbon that is partly used to form CO.

For Pluto’s atmosphere near aphelion, OH radicals released by photolysis of the injected \(\text{H}_2\text{O}\) react mostly with the abundant \(\text{CO}\) and form \(\text{CO}_2\). Some \(\text{OH}\) radicals return water in the reaction with \(\text{CH}_3\). Photoysis of \(\text{H}_2\text{O}\) is much faster than that of \(\text{CO}_2\) (see section 5), and this facilitates the conversion of \(\text{H}_2\text{O}\) into \(\text{CO}_2\) that condenses on Pluto.

Pluto’s surface temperature is expected to be \(\sim 29\) K near aphelion at 50 AU, and the \(\text{N}_2\) saturated vapor pressure becomes smaller by a factor of \(\sim 1000\). This huge reduction should significantly affect properties of the atmosphere and its photochemistry.

### 8. Conclusions

My photochemical model for Titan’s atmosphere and ionosphere has been improved using the Troe approximation for termolecular reactions and inclusion of some radiative association reactions from Vuitton et al. (2012). The major improvement of the current model has been achieved by proper fitting of eddy diffusion. This 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 \(\text{H}_2\text{O}\) 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 \(\text{CO}, \text{CO}_2, \text{H}_2\text{O}\), and \(\text{H}_2\text{CO}\) are discussed in detail for both versions. The calculated model with the \(O^+\) flux agrees with the observations of \(\text{CO}, \text{CO}_2, \text{H}_2\text{O}\), including recent \(\text{H}_2\text{O}\) 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 \(\text{N}_2, \text{CH}_4, \text{and CO}\) 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 \(\text{CH}_4\) 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 \(\text{N}_2\) and \(\text{CH}_4\). Meteoritic \(\text{H}_2\text{O}\) results in precipitation of \(\text{CO}\) on Triton and \(\text{CO}_2\) on Pluto near perihelion.

### References

