TITAN: THE ONLY KNOWN MOON WITH A PLANET-LIKE ATMOSPHERE

SAVERIO CAMBIONI

1 Graduate Assistant, Lunar and Planetary Laboratory, The University of Arizona, Tucson, AZ 85721, USA

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ABSTRACT

This project is about Titan, the largest moon of Saturn, and our understanding of its atmosphere. The focus will be also on how well we know this fascinating moon, as a consequence of the interpretation of both space-based observations and ground-based observations.

After a brief chronography of the main milestones in the discovery of Titan, the thermodynamics and radiative transfer of atmospheric gases is discussed; this concerns the pressure-temperature profile and its evolution with time. Then the project will report on the chemical composition of the atmosphere, together with information on its condensate phases (clouds) and haze. Regarding this, the key role of methane is emphasized, focusing on its contribution to the chemical interaction between the atmosphere and the surface of the satellite. The evolution of the atmosphere with respect to the geological timeline of the Solar System is also discussed. The final chapters are dedicated to the atmospheric dynamics of the satellite and open questions about Titan, such as the possibility of the presence of methanogenic life in liquid methane on the surface of Titan.

Keywords: Titan, remote sensing, atmospheres, thermodynamics, chemistry

Corresponding author: Saverio Cambioni
cambioni@lpl.arizona.edu, saverio.cambioni@gmail.com, saveriocambioni@email.arizona.edu
1. THE DISCOVERY OF TITAN

Titan was discovered by Christian Huygens on March 25, 1655, but only in the 1900s observers started to discuss the possibility that this moon could have an atmosphere. In 1943, Gerard P. Kuiper discovered the presence of methane in Titan atmosphere, capturing the attention of the scientific community on the Saturnian system; Titan was clearly a world worthy of further exploration, (1). Pioneer 11 was the first spacecraft to reach Saturn, but the first important data came from Voyager 1. This probes confirmed that the atmosphere is composed mainly by molecular nitrogen, with a few percent of methane. Moreover, presence of a complex organic chemistry was detected. These observations boosted the idea of sending a probe on Titan, in order to do in situ measurements of its hidden surface. The idea of the Huygens landing probe on board Cassini mission was born, (2).

2. TITAN’S ATMOSPHERE

PRESSURE-TEMPERATURE PROFILE

The atmosphere of Titan presents a well defined troposphere and middle atmosphere. The latter is composed by the stratosphere and mesosphere. These features are similar to those of Earth’s atmosphere, except that Earth is much warmer and the stratopause (the boundary between the stratosphere and mesosphere) occurs at higher pressure.

Figure 1. Vertical temperature profile at a latitude near 15°S, retrieved from a combination of nadir and limb-viewing spectra. Figure 1A from Flasar et al., (3).

Titan’s vertical temperature profile is reported in Figure 1 from Flasar et al., (3). The vertical axis are both pressure (in mbar) and altitude (km). The horizontal axis is the temperature (K). The temperature profile is recorded at a latitude near 15°S. The longitude is not specified since Titan’s atmosphere is characterized by zonal winds, which are winds along the local parallel of latitude. Due to the presence of wind, the atmosphere can be assumed as thermally isotropic in longitude; that is why specifying the longitude of the measurement is not needed. If the gravity is considered equal to the gravitational acceleration at the surface (g = 1.3334 m/s²) the scale height of Titan is around 33 km. More realistic models provides result in range for the scale height between 15 to 50 km.

The thermal profile is in figure 1. The solid black line portion results from the processing of early Cassini orbiter observations of Titan by the Composite Infrared Spectrometer (CIRS), which provides information about the middle atmosphere (mesosphere and stratosphere). The observations were made on July 2004 (flyby T0), shortly after Cassini was inserted into orbit around Saturn, and on December 2004 (flyby TB). CIRS uses Fourier-transform spectrometry by means of two interferometers. The far-infrared interferometer (wavenumber from 10 to 600 cm⁻¹) has a 4-mrad FOV (Field Of View) on the sky, while the mid-infrared interferometer (wavenumber from 600 to 1400 cm⁻¹) consists of two 1 x 10 arrays of 0.3-mrad pixel. The spectrometer is able to measure thermal emission from 10 to 1400 cm⁻¹ (wavelengths between 1 mm and 7 µm). CIRS captures infrared light and splits the light into its component wavelengths (or colors). Then the specific intensity of the light at each of those wavelengths is measured, (4). According to Plank’s law, the spectral radiance of a source, which describes the amount of energy it gives off as a radiation at different frequency, is a function of the absolute temperature of the source (under the assumption that the source is a black body). As a consequence, the thermal information can be retrieved from the incoming light intensity. In order to retrieve the thermal profile of the middle atmosphere, the portion of the CIRS spectra between 1210 and 1318 cm⁻¹ has been analyzed. This region contains the radiance peak in the ν4 fundamental band of CH₄. Since the abundance of CH₄ is known independently thanks to the Huygens data, it is possible to retrieve the temperatures in the upper stratosphere up to the 1-mbar level, (5).

The dashed portions of the curve represent the regions where temperatures are not well constrained by CIRS observations. These are more influenced by the Voyager radio-occultation profiles, and correspond to the troposphere and lower stratosphere. During its flight through the Saturnian system in November 1980, the Voyager 1 experienced a closest approach with Titan. After passing periapsis, the spacecraft was occulted by Titan for about 520 sec. During ingress, the radio tracking link was used to probe the evening atmosphere near 6.2N latitude. Measurements were also made during egress, which occurred on the morning side near 8.5S
latitude. Radio signals bend and slow down as they travel through an atmosphere. Both their spectra and amplitude are affected. The refractive index distribution of the atmosphere was derived from doppler frequency perturbations observed during the occultation, by supposing a perfectly stratified atmosphere with no horizontal changes in the regions probed. These observations have been used for the computation of number density (degree of concentration of particles) in the atmosphere. Each number density distribution may, in turn, be utilized to calculate the vertical pressure profile by employing the equation for hydrostatic equilibrium and integrating the density from the top of the detectable atmosphere and downward. Under the assumption of a N₂-atmosphere, the ideal gas law provides the temperature profile, once the density and pressure profiles are known, (6).

2.1. Dry thermodynamics of Titan’s atmosphere

The most basic indication of an atmosphere’s stability is the change in the atmospheric temperature, T, with altitude, z, that is, the lapse rate dT/dz. Titan’s lapse rate indicates three regimes of stability:

- Within the lowest ≈ 2 km of the atmosphere, a parcel which is nudged upward becomes buoyant and freely convect;
- Between 2 and 15 km, only saturated parcels convect;
- Above 15 km, no parcel freely convect.

In the first regime, the temperature varies according to Titan’s dry adiabatic lapse rate. This can be derived as follows. Let us consider the first principle of thermodynamics in its differential form:

\[ P \alpha dP + \alpha dP = NKdT \]

where \( P \) is the pressure, \( \alpha \) is the specific volume, \( N \) is the number of molecules, \( K \) is the Boltzmann constant. This can be also written as:

\[ P \alpha dP + \alpha dP = R/\alpha dT = (C_p - C_v)dT \]

where \( R \) is the universal gas constant, \( m \) is the mean molecular mass, \( C_p \) and \( C_v \) are the specific heat at constant pressure and volume respectively ([J/kgK]). The first principle of thermodynamics in its differential form is:

\[ C_v dT + p \alpha dq = 0, \]

where \( dq = 0 \) means that the process is adiabatic (\( q \) is the specific heat). By plugging in the equation of state, one yields:

\[ C_p dT = \alpha dP = 0 \]

Considering the equation of hydrostatic equilibrium expressed in terms of \( \alpha \):

\[ dP = -g \frac{dz}{\alpha} \]

one finally gets:

\[ \frac{dT}{dz} = -\frac{g}{C_p} \]

where \( g \) is the gravitational attraction at an altitude \( z \). Since this calculation concerns the first 2 km of atmosphere, the value of \( g \) can be approximated with the value at the surface: \( g = 1.3534 m/s^2 \). For Titan’s atmosphere, the specific heat at constant pressure is \( C_p = 1100 J/K kg \) considering a mixture of 98.4% of \( N_2 \) and 1.6% of Methane, (2). As a consequence, the dry adiabatic lapse rate for Titan results:

\[ \Gamma_d = \frac{g}{C_p} = 1.2273 K/km \]

This is the steepest lapse rate that is sustainable, because a steeper profile would cause overturning (because unstable), which would steer the profile to that of \( \Gamma_d \).

2.2. Wet Thermodynamics of Titan’s atmosphere

On Titan, the condensable (i.e. the chemical species that condensate in clouds) is methane, whose saturation mixing ratio is ≈ 0.114 at the surface. The dry lapse rate can be extended up to 5 km above the surface of Titan. Above that, methane drops has cooled sufficiently for becoming saturated. The gas experiences a phase transition as it lifts, since it is heated by the latent heat. As a result, above 5 km the parcels follow the wet lapse rate, which can be derived as follows, (7). Let us consider the first principle of thermodynamics in its general form:

\[ C_p dT - V dP = dq = -L d\alpha \]

where \( w_s \) is the mass of saturated methane (which is the condensable for Titan’s atmosphere) over the whole mass of gas and \( L \) the latent heat in J/kg. This can be rewritten as:

\[ C_p dT + g \frac{dz}{\alpha} = -L d\alpha \]

by inserting the equation for hydrostatic equilibrium. The liquid methane is assumed to fall out of the parcel and take no further part in its heat balance. If the amount of heat removed from the parcel by the liquid is small compared with that remaining in the parcel, the process can be considered quasi-adiabatic. Then it is valid that the mass of saturated air is:

\[ w_s = \frac{e_s}{P} \]

where \( e_s \) is the vapor pressure and \( P \) is the pressure of the whole gas. By differentiating:

\[ \frac{d\alpha}{w_s} = \frac{e_s}{P} \]

By the use of the Clasius-Clapeyron equation:

\[ \frac{d\alpha}{dT} = \frac{Le_s}{R_e T^2} \]
where \( R_v = R/m_{w,v} \) is the specific gas constant for the vapor, and \( T \) is the temperature, one gets:

\[
\frac{1}{c_s} \frac{de_s}{dT} \cdot \frac{L}{R_v T^2}
\]

Moreover, from the equation for hydrostatic equilibrium we have: \( \frac{dP}{dz} = \frac{-g}{(R_v T)} \). This yields:

\[
\frac{dw_s}{w_s} = \frac{L dT}{R_v T^2} - \frac{gdz}{RT}
\]

and substituting in the first principle equation, one gets:

\[
\left( c_p + \frac{L^2 w_s}{R_v T^2} \right) dT + \left( 1 + \frac{L w_s}{RT} \right) dz = 0
\]

Finally, for \( dz \rightarrow 0 \) one yields:

\[
\frac{dT}{dz} = \Gamma_d \frac{1 + \frac{L w_s}{RT}}{1 + \frac{L^2 w_s}{c_p R_v T^2}} = 0.4120K/km
\]

by considering a surface pressure of 1500 hPa, a temperature of 94 K, a molecular weight for methane \( m_w = 14g/mol \) and a mixture ratio of 0.114, Table 6.1 in (2). The specific heat at constant pressure is assumed to be the same of the dry air. The wet lapse rate is less steep than the dry lapse rate, as expected.

2.3. A more realistic Titan’s atmosphere

Titan’s atmosphere shows a well defined troposphere and middle atmosphere. The middle atmosphere has been extensively sounded by remote sensing in the thermal infrared, compared to a limited available radiative occultation based retrievals of Titan’s troposphere. Even though we know more about Titan’s troposphere than about that of other bodies, many features need to be still characterized, such as the methane distribution on the surface. In the following, the thermal profile of these regions is described, focusing on the discrepancy with respect to the dry lapse rate.

Troposphere. Titan’s troposphere extends from the surface up to the tropopause, which is a very broad region which extends from an altitude of roughly 25 km to more than 50 km. In this part of the atmosphere, the temperature decreases with altitude. The lapse rate is close to dry adiabatic in the lowest 2 km of the atmosphere. As the altitude increases, the profile becomes more stable at mid- and high latitudes in both hemispheres. The profile at high northern latitude is nearly isothermal near the surface, Figure 2.

The dry lapse rate is due to the warming of the atmosphere by the surface. The temperature profile can deviate from this also because of the effect of seasonal variation in the incident solar flux. The lower part of the troposphere, however, does not respond markedly to this effect, because of its large radiative relaxation time, of about 80 years. \(^1\). This also explains why the decrease of temperature follows roughly the same lapse rate, which is more stable than the dry one, up to 25 km. At that level, the temperature rate starts to change since the broad tropopause is approached. The broadness of the tropopause is latitude dependent, reaching its maximum at low latitudes. The temperature variations between the winter and summer hemisphere at high latitudes is about 3.5 K and it can be explained by the large relaxation time of the atmosphere. The temperature variations between high and low latitude is still in the order of few degrees and requires the presence of dynamical heat transfer phenomena, such as axisymmetric meridional circulation. (2) Finally, it is important to mention that Titan has a significant greenhouse effect due to pressure-induced absorption from the pairs \( N_2 - N_2 \), \( CH_4 - N_2 \) and \( H_2 - N_2 \) in different spectral regions. The greenhouse effect results when atmospheric gases are transparent at solar wavelengths, allowing sunlight to reach the surface, but opaque in the thermal infrared, trapping the outgoing thermal radiation and raising the surface temperature above the planetary effective temperature. Because of this phenomenon, the temperature in Titan’s troposphere is up to 20 K warmer than the result expected from a radiative model.

Middle atmosphere. The stratosphere and mesosphere comprise the middle atmosphere. The strato-

\(^1\) The radiative relaxation time is a measure of the relaxation of an atmospheric perturbation to a steady equilibrium.
sphere is characterized by a positive temperature gradient; this is due to the anti-greenhouse effect which strongly affects Titan’s middle atmosphere. The anti-greenhouse effect is the opposite of the greenhouse effect; aerosol hazes are able to absorb 40% of the incoming sunlight. This phenomenon affect both the incident flux on the surface of Titan (which is roughly 10% of the overall flux at the top of the atmosphere) and allows for the increase of temperature in the troposphere. As a consequence of this, the approximation of a temperature profile dominated by the dry lapse rate is no longer acceptable in this region. The temperature inversion in the tropopause is similar to that on Earth’s, even if the latter is faster due to the smaller scale height. The increase of temperature in Earth’s stratosphere, however, is due to the presence of ozone, which absorb incoming UV light. This phenomenon plays a crucial role in the radiative shielding of Earth’s surface.

In Titan’s stratosphere the radiative relaxation time is small enough that seasonal variation becomes significant, allowing significant seasonal variations. The retrieved Cassini radio occultation profiles at high northern latitudes in winter and at high and low latitudes in the southern hemisphere in summer proves that the temperature for the former are much colder than the temperatures of the latter. This observation agrees with expected seasonal variation of the temperature profile at high latitude in the stratosphere. The mesosphere starts with the stratopause, where the temperature profile experiences another inversion, Figure 1. The inversion is due to the decrease in the concentration of particles (the pressure decrease with altitude, and so the density). The lower concentration of particles reduces the solar flux absorbed by the atmosphere, which is not enough for heating it; the result is a negative temperature gradient.

2.4. Titan’s black body temperature

The blackbody temperature of Titan can be found by means of a simple radiative model. The Sun is the host star of the Saturnian system, and the solar luminosity $L_{\text{Sun}}$ is equal to $3.839 \times 10^{26} W$. The flux of sunlight at the surface of Titan at noon is:

$$I_{\text{Titan}} = \frac{L_{\text{Sun}}}{4\pi d_{\text{ST}}^2}(1 - A)(\pi R_T^2)$$

where $d_{\text{ST}}$ is the distance between Titan and the Sun (which can be approximated as the semimajor axis of Saturn’s orbit, equal to $1433.53 \times 10^6 km$), $A$ is the albedo ($A=0.2$) and $R_T = 2575 km$ is the mean radius of Titan. Since Titan is considered as a black body, the absorbed radiation in the UV/visible spectrum is re-emitted, according to the Stephan Boltzmann law:

$$I_{\text{emitted}} = \sigma T^4(4\pi R_T^2)$$

where $\sigma = 5.67 \times 10^{-8} W m^{-2} K^{-4}$. As a result:

$$I_{\text{absorbed}} = I_{\text{emitted}} \rightarrow T = \left(\frac{L_{\text{Sun}}(1 - A)}{16\pi d_{\text{ST}}^2\sigma}\right)^{\frac{1}{4}} = 85 K$$

In planetary atmospheres, this value is compatible with the temperature of the layers just below the tropopause; since the real value is around 80 K, the approximation is pretty good. Figure 3 is the Planck function associated with this model for Titan as a black body. By applying the Wien displacement law, the wavelength of the maxima is:

$$\lambda_{\text{max}} = \frac{2.89 \times 10^{-3} m K^{-1}}{T} = 34.04 \mu m$$

The Planck function of the Sun is identical in shape but the peak is at 0.51$\mu m$. Moreover, it is also by far more intense than the Titan’s one. As a consequence, the two spectra can be considered separately in order to retrieve the outgoing flux from the planet; they do not overlap. This allows to assume that there is not incident (infrared) solar radiation on the top of the atmosphere when a radiative model is built.

3. THE CHEMICAL COMPOSITION OF TITAN’S ATMOSPHERE

Titan’s atmosphere harbors a suite of hydrocarbons and nitrogen-bearing compounds formed from the dissociation of the two main species, nitrogen ($N_2$) and methane ($CH_4$). The presence of water and/or oxygen influences the presence of some oxygen compounds. The species play a fundamental role in the chemistry of Titan’s haze; atmosphere’s seasonal variability, radiative budget and general circulation are consequentially affected, (2).
Regarding the most five abundant species in Titan, many information have been retrieved by the use of Cassini - INMS (Ion and Neutron Mass Spectrometer) in the upper atmosphere and Huygens-GCMS (the gas chromatograph mass spectrometer instrument). Mass Spectrometry is an analytical technique able to measure the masses within a sample of different species by ionizing them and sorting the ions based on their mass-to-charge ratio. The intensity of the signal of a feature in the mass spectra is represented in terms of mass to charge ratios (m/z); as an example, the GCMS instrument has a mass to charge ratio threshold of (m/z)=22. From a signal point of view, this can be translated into a SNR (Signal to Noise ratio) limit; only signals above the SNR limit can be processed. Every time the atmosphere is sampled, a signal is associated with a certain molar abundance \( m_i \); after the experiment, the associated mean value is calculated, \( \bar{m} \). As a result, the standard deviation is given by:

\[
\sigma = \sqrt{\frac{(m_i - \bar{m})^2}{N}}
\]

where \( N \) is the number of samples.

1. Nitrogen, \( N_2 \). Titan’s is the only dense, nitrogen-rich atmosphere in the Solar System aside from Earth’s. The fly-by of Titan by the Voyager I spacecraft in November 1980 is a major milestone in the characterization of Titan’s atmosphere. Radio Science (RSS) occultation data established that the atmosphere was thick and provided the ratio between temperature and mean molecular mass \( (T/m) \), (6). The analysis of the IRIS (infrared) spectra indicated a surface temperature in the rage 94 to 97 K, which combined with the RSS results, yields to a mean molecular mass of \( m=28 \) amu, compatible with a \( N_2 \) rich atmosphere \( (m=28 \) is the mean molecular mass of \( N_2 \) molecules), (9). The final conclusion was drawn thanks to the detection of \( N_2 \) by the Voyager ultraviolet spectrometer (UVS), (10). The UVS instrument covers the wavelength range of 40 nm to 180 nm, looking for absorption by element and molecules in the UV domain, (2). By looking to the absence of certain colors in the UV pattern, the presence of a certain species is retrieved; this process is the identification of elements or compounds by atomic absorption; a sample spectrum is reported in figure 4. All this led to the conclusion that \( N_2 \) is the dominant constituent of the atmosphere and \( CH_4 \) only a minor compound. Quantitative results bring to an abundance of Nitrogen equal to roughly 95 ± 4%.

In the upper atmosphere, the abundance of \( N_2 \) has been retrieved by in situ Cassini-INMS measurements, during two flyby. The retrieved values are 98.4 ± 0.1 % at 981 km to 96.6 ± 0.1% at 1151 km.

![Figure 4. A sample spectra for atomic absorption in the UV-VIS region. The peak broadness and intensity give informations about the atomic abundance of the studied species.](http://voyager.jpl.nasa.gov/spacecraft/instruments_u_vs.html)

2. Methane, \( CH_4 \). The analysis of Voyager data about Methane mole fraction led to a very large range, from 0.5 to 4.5 %. The uncertainties were very high both in the stratosphere and troposphere. The methane vertical profile was precisely measured in the troposphere and lower stratosphere by the Huygens-GCMS during the probe descent. Figure 5 reports on the methane mole fraction as a function of altitude, together with the error bars. Up to approximately 7 km, the methane mole fraction is constant and equal to \( (5.65 \pm 0.18 \times 10^{-2})% \), corresponding to a relative humidity of \( \approx 50\% \). The stratospheric value is also constant between 75 and 140 km, where it is equal to \( (1.48 \pm 0.09 \times 10^{-2})\% \). The lower value of the mixing ratio in the stratosphere with respect to the value in the troposphere is due to condensation, (11).

An important point is the fact that the landing of Huygens provides precise information on the \( CH_4 \) profile at only a single location and time. Is this profile representative of Titan as a whole? Does the methane profile vary with location and time? This is a key question and a tentative answer will be also given in section 4. The summary is that high spatial and spectral resolution proves that currently there is no evidence for significant departures from the CGMS \( CH_4 \) profile on large scale on Titan.

In the mesosphere and thermosphere, \( CH_4 \) interacts with solar or stellar UV light. UV occultation by the Voyager mission, (6), provided a mixing ratio of 2.4% at 1125 km. Other measurements of the upper atmosphere has been done in situ by Cassini - INMS (Ion and Neutron Mass Spectrometer) between 950 and 1500 km of altitude, resulting in a mixing ratio of 1.31 ± 0.01 % at

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2 [http://voyager.jpl.nasa.gov/spacecraft/instruments_u_vs.html](http://voyager.jpl.nasa.gov/spacecraft/instruments_u_vs.html)
981 km to a 3.00 ± 0.01 % at 1151 km. The two altitudes are the two closest approach altitudes of Cassini to Titan.

3. Photochemical products: Hydrogen, $H_2$. Hydrogen is the third most abundant species. It is a by-product of methane photochemistry. Again using Huygens-GCMS data, $H_2$ has been proved to have a constant mixing ratio of $(1.01 \pm 0.16) \times 10^{-3} \%$ from the surface up to 144 km, (11). This value is representative of the mixing ratio at larger scales, as confirmed by Cassini - CIRS spectra $(0.96 \pm 0.24) \times 10^{-3} \%$, (12). In this last case, the mixing ratio retrieved by comparing model spectra based on different $H_2$ mole fraction and the CIRS data. A fitting scheme was applied to determine the mole fraction that provides the best match by minimizing the residuals, which have also been used for retrieving the standard deviation. In the upper atmosphere above 950 km, the Cassini-INMS give access to the $H_2$ mixing ratio, which is $(3.3 \pm 0.01) \times 10^{-3} \%$ at 981 km and $(3.90 \pm 0.01) \times 10^{-3} \%$ at 1151 km.

4. Photochemical products: CO. The retrieve of CO abundance has been done by analyzing the occultation spectra of Cassini-VIMS (Visible and Infrared Mapping Spectrometer), (13). The instrument Visible Channel (VIMS-V) wavelengths are from 0.35 to 1.07 m (96 channels), with a 32x32 mrad field of view; the Infrared Channel (VIMS-IR) wavelengths are from 0.85 to 5.1 m (256 channels), with a 32x32 mrad field of view. The challenge in determining the abundance of CO was related to the fact that the related signal belongs to the most noisy part of the spectrum, due to its weak signature. CO is supposed to be very stable and well-distributed in Titan’s atmosphere, because it has a lifetime much higher than the mixing timescale and it is not a condensable gas. The overall average CO value (on a set of 35 occultation) is $(0.46 \pm 0.16) \times 10^{-3} \%$.

5. Photochemical products: $C_2H_6$ vs $C_2H_2$. The coupled photochemistry of $N_2$ and $CH_4$ produces a host of hydrocarbons and haze particles. The following table reports on the abundance in percentage molar fraction of the two most abundant species at different altitude (lower stratosphere to upper mesosphere). The measurements are derived from different observations, which are summarized in (2), chapter 5. Not every uncertainty is available.

<table>
<thead>
<tr>
<th>Species</th>
<th>150 km (at 54°S)</th>
<th>981 km</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2H_6$</td>
<td>$7.5 \times 10^{-4}$</td>
<td>$(5.33 \pm 0.16) \times 10^{-5}$</td>
</tr>
<tr>
<td>$C_2H_2$</td>
<td>$2.2 \times 10^{-4}$</td>
<td>$(1.16 \pm 0.01) \times 10^{-4}$</td>
</tr>
</tbody>
</table>

As it can be inferred from the table, $C_2H_6$ abundance and $C_2H_2$ abundance are comparable in the lower stratosphere. By contrast, in the upper mesosphere, the abundance of $C_2H_2$ is one order of magnitude higher that that of $C_2H_6$.

3.1. Evolution of the chemistry composition

The composition of the present-day atmosphere on Titan (which is nitrogen-dominated, with a few percent methane and lesser amount of other species) probably does not directly reflect the composition of the primordial building blocks and it is rather the result of complex evolutionary processes involving internal chemistry and outgassing, impact cratering, photochemistry and other processes. Measurement by the GCMS on Huygens probe suggests that nitrogen was brought to Titan not in the form of $N_2$ but rather in the form of NH$_3$. The instrument detected a low Ar/$N_2$ ratio, much lower than the solar composition of about 0.1, which would have been detected if the primary carrier of molecular nitrogen was $N_2$ itself. Since Ar and $N_2$ have similar volatility and affinity with water ice, their low ratio indicates that nitrogen has been brought in the form of easily condensable compounds, most likely ammonia, which then has been converted in situ by impact-driven chemistry or by photochemistry ((14)). Ammonia is one of the species that should have been present in the building blocks that formed Titan, accordingly to theoretical models of planetary formation (other gas compound are CO$_2$, CH$_4$ as well as sulfur compounds and traces of noble gases). Most of the gas compounds initially expected, however, have not been detected so far. Future missions could provide more information about the CO$_2$ fraction and noble gas fraction on Titan in order to provide key constraints on the conditions under which the building block formed.

Titan may not always have possessed a massive $N_2$-CH$_4$ atmosphere and the mass and composition may have varied along Titan’s evolution. Indeed, Titan likely

Figure 5. Molar mixing ratio of $CH_4$ in Titan atmosphere, as a function of latitude, at the landing site and time of Huygens. Figure 6 in (11).
acquired its atmosphere during its first hundreds millions of years, at the latest during the Late Heavy Bombardment (LHB). Following the post-accretional cooling phase, nitrogen probably rapidly became the dominant gas. Methane abundance has probably varied significantly through time, depending on the balance between replenishing and destruction. As a consequence of this, long periods without atmospheric methane may be envisioned (see also 4).

4. THE PARTICULATES IN TITAN’S ATMOSPHERE

The chemical species that plays the major role in defining the particulates in Titan’s atmosphere is methane. On Titan, methane experiences a cycle which is very similar to that which regulates the Earth’s environment and the evolution of life. There are methane clouds, rain and seas. The process that supply methane is still an ongoing research topic. The three most important theories suppose that methane can be produced by outgassing of deep reservoirs (15), from the interior chemistry of organic material (16) or by seepage of shallows subsurface methane reservoir ((17)). These can contribute all together in defining the abundance of methane in the atmosphere, but there could have been also dry periods in the history of the moon.

The chemistry of Titan is out of equilibrium. Indeed, a significant amount of CH$_4$ reaches the upper atmosphere where it undergoes UV photolysis. Methane gives birth to a very rich organic chemistry. Models predict that the atmospheric content should be exhausted in 30 million years. Methane photolysis is responsible for the huge Titan haze that characterizes the atmosphere from the surface up to an altitude of 1000 km. The haze is composed by the byproducts of the photolysis; the main haze species is Ethane (C$_2$H$_6$). Other important species are C$_2$H$_2$, HCN, C$_3$H$_8$. The byproducts of the photolysis from the upper atmosphere mixes with the lower atmosphere, where ethane controls the methane cycle. The vapor pressure equilibrium at the surface of lakes is between 5 and 15 km. In tropical atmosphere, the methane mixing ratio is close to saturation between 9 and 15 km and between 23 and 35 km. Below 9 km, the mixing ratio is constant and below the saturation level. Small vertical perturbations can cause condensation from the adiabatic cooling of the parcel. As far as cloud formation in the lower layer (9 to 15 km), the lifting of the parcel to the Level of Free Convection (LFC, at 9 km on Titan) can be caused by an extreme heating (more than 2 K) of the surface or mechanically from divergence or convergence of air to the Lifting Condensation Level (LCL, at 5 km on Titan).

Nearly 20 years ago, after Voyager mission, clouds were discovered on Titan by using ground-based observations by the NASA’s Infrared Telescope Facility (IRTF). At the wavelengths of investigation (λ ≈ 1.2 to 3.5 μm), the haze particles scatter less efficiently and atmospheric opacity can be inferred mainly by vibrational bands due to atmospheric methane gas. The altitude of clouds was inferred by the attenuation in the wings of methane signal; higher clouds have been found in spectral region of higher methane absorption. The optical depth of the clouds was inferred by exploiting its effect on the backscattering from the cloud (which is indicated by a flux increase).

More recently, Cassini VIMS measurement allowed to infer the thickness of clouds at the tropics, which is between 5 and 15 km. In tropical atmosphere, the methane mixing ratio is close to saturation between 9 and 15 km and between 23 and 35 km. Below 9 km, the mixing ratio is constant and below the saturation level. Small vertical perturbations can cause condensation from the adiabatic cooling of the parcel. As far as cloud formation in the lower layer (9 to 15 km), the lifting of the parcel to the Level of Free Convection (LFC, at 9 km on Titan) can be caused by an extreme heating (more than 2 K) of the surface or mechanically from divergence or convergence of air to the Lifting Condensation Level (LCL, at 5 km on Titan).

Figure 6 (A) reports on the comparison between Huygens temperature profile and that of a parcel that rises adiabatically from the surface, assuming a surface humidity of 45%; the LNB is the Level of Neutral Buoyancy, which is at 24 km on Titan. For a 45% humidity atmosphere, the Convective Available Potential Energy (CAPE), defined as:

\[ CAPE = \int_{LFC}^{LNB} g[(T_{\text{parcel}} - T_{\text{env}})/T_{\text{env}}]dz \]

is about 120 J/kg$^{-1}$, (19). For higher value of humidity, it can be even higher (860 120 J/kg$^{-1}$ for a humidity of 60%).

In the middle troposphere, the formation of clouds can be explained by the introduction of the potential temperature, which is defined as the temperature that
a parcel would have if it is moved adiabatically from its initial altitude (and pressure) to a reference pressure level, taken usually as the surface. Figure 6 (B) reports on the potential temperature as a function of altitude. Below 15 km, the atmosphere is conditionally unstable \((\partial \theta / \partial z < 0)\) meaning it is unstable if fully saturated. Since it gains momentum, the parcel can overshoot the LNB and this rising gives birth to cloud in that region. Finally, there is also evidence for low clouds at an altitude of 0.75 km, but the accuracy of the measurements at such altitudes is poor. Indeed, the radiative transfer retrieval cannot be more precise than the width of the contribution function associated to the region. Since this is about 2 km, the thickness and altitude of these clouds are not well constrained.

Longitudinally, Titan is also characterized by zonal winds which have a speed between 0 and 200 m/s ((20)); this has been inferred again using Cassini VIMS observations, spaced 20 minutes apart over a two hour period.

The maximum size of droplets for methane rain is about 9 mm, with seed nuclei dimension of \(\approx 10^{6} \text{ cm}^{-3}\). This influences also the optical depth of the clouds ((21)). Figure 7 reports on the mixing ratio of \(CH_4\) as a function of altitude for Huygens landing trajectory and landing site. A constant mixing ratio below 9 km indicates a constantly increasing humidity up to saturation.

The seasonal variability of clouds on Titan has been characterized from an extensive ground-based campaign. Methane clouds appear only at particular latitudes that depend on the season and the point of maximum insolation. General circulation models indicates 40°S as the latitude where clouds naturally form. Then, a seasonal migration from the south to the north polar region has been detected, occurring from the South Summer Solstice (SSS) in October 2002 to the North Summer Solstice (NSS) in May 2017. The seasonal changes are thought to be due to the updrafts that lift parcels such that they saturate; the updrafts are caused by the heating of the surface and therefore follow roughly the latitude of highest insolation. The updrafts, however, do not follow this precisely because the general circulation plays a role.

4.2. Titan’s Haze

Titan’s haze plays a key role in the moon’s radiative budget, since it strongly affects the radiative transfer in the thermal infrared by dominating the opacity at short wavelengths. The most important measurements come from the Discent Imager/Spectral radiometer (DISR) on the Huygens Probe. This instrument provided irregular timing measurement of the haze because of difficulties in reconstructing the attitude of the landing probe. The data products are the optical properties of the aerosol (optical depth ect.) reconstructed by photometric, polarimetric and spectral analysis. Secondly, the particle size and their chemical properties can be inferred. The spatial coverage of the measurement is from 150 km altitude to the surface, along the Huygens trajectory. Figure 8 reports on the distribution of the optical depth.
as a function of altitude. The best fit functions in the wavelength are also reported. The table at the end of the paragraph summarizes the main properties of the haze.

Figure 8. Haze optical depth as a function of wavelength for three altitude regions along with power-law fits to the data. Also shown (at bottom) are the spectral ranges associated with the DISR subsystems used to measure the optical depth. Figure from (23).

In the characterization of the haze, the main challenge is the description of the global (spatial, temporal) distribution of the haze by the use a limited amount of local information, such as the in situ measurement by Huygens and the upper atmosphere measurements by Cassini’s Plasma Spectrometer (CAPS) and Neutral Mass Spectrometer (INMS). The distribution in latitude/altitude in Figure 9 from (24) uses these measurement in a model which couple general circulation and microphysics. In the figure, it is evident also the thickness of the haze and the presence of the so-called "detached haze". Beyond the models, however, there is a lack in latitude and longitude observational coverage of the haze, which could be fixed by a future mission to Titan.

As far as the haze temporal (seasonal) variability is concerned, a reversal of the meridional circulation of haze has been detected to follow the change in seasonal insolation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Uncertainty</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Shape and size</strong></td>
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<td></td>
</tr>
<tr>
<td>Monomer radius (µm)</td>
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<td>0.02</td>
</tr>
<tr>
<td>Number of monomers in aggregated particle</td>
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<td>Factor of 2</td>
</tr>
<tr>
<td><strong>Vertical structure</strong></td>
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<td></td>
</tr>
<tr>
<td>Haze opacity</td>
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<td></td>
</tr>
<tr>
<td>(z &gt; 80\text{km})</td>
<td>65 km</td>
<td>20 km</td>
</tr>
<tr>
<td>(z 30 - 80 \text{ km})</td>
<td>Linear variation</td>
<td>up to 20%</td>
</tr>
<tr>
<td><strong>Wavelength variation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(z &gt; 80\text{km})</td>
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<td>10%</td>
</tr>
<tr>
<td>(z 30 - 80 \text{ km})</td>
<td>(2.029 \times 10^4 \lambda^{-1.049})</td>
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</tr>
<tr>
<td>(&lt; 30 \text{ km})</td>
<td>(6.270 \times 10^2 \lambda^{-0.971})</td>
<td>15%</td>
</tr>
</tbody>
</table>

5. GENERAL ATMOSPHERIC DYNAMICS ON TITAN

The atmosphere of Titan is characterized by superrotation, a feature in common with other solar system bodies such as Venus. Most of the middle and lower atmosphere rotates significantly faster than the underlying solid body; the zonal winds can reach about 200 m/s in the winter stratosphere. This peculiar atmospheric dynamic feature strongly interacts with the temperature profile, atmospheric chemical composition and haze and cloud formation. To understand Titan’s atmospheric dynamics three complementary approaches must be mixed: observations (Voyager 1, earth-based
and Cassini-Huygens observations), theory and climate modeling (GCM, General Circulation Models). Since a GCM discretizes the Navier-Stokes equations in order to fit the observation, a temporal record of spatially resolved observations is needed. For instance, the spatial and temporal distribution of methane mixing ratio on Titan as well as the atmospheric humidity can provide important indicators of atmospheric motions. Titan’s haze, however, remains the big tracer of atmospheric motions.

Due to the change in solar insulation, the stratosphere experiences a mean meridional circulation; this is dominated by a pole-to-pole Hadley-type cell, as predicted by theory. As already discussed in section 4, there are hints that this circulation experiences a seasonal variation, since after the equinox in August 2009 its reversal has been detected. The mean meridional circulation plays a crucial role in the angular momentum budget supporting the superrotation of the atmosphere, together with barotropic waves propagating in the winter stratosphere. Around the poles, Titan shows a winter polar vortex that is similar to that on Earth.

The intertropical convergence zone (ITCZ) experiences a seasonal evolution too, affecting cloud occurrence and surface temperature. Atmospheric vertical mixing close to the surface is indeed mostly controlled by the ITCZ, together with the diurnal cycle. The atmosphere is mostly in cyclostrophic balance (the horizontal pressure gradient and centrifugal forces push equally in opposite directions) while in the lower troposphere, where the winds are much less intense, the atmosphere is in the geostrophic regime (the winds theoretically result from an exact balance between the Coriolis Force and the pressure gradient force). Tropospheric circulation strongly interacts with the surface; resulting coupled features include the dune fields, the polar lakes or the impact on topography. The circulation reversal and the extents of the Hadley cell (up to high latitudes) are closely linked to the methane cycle in the troposphere and can be related to the observation of clouds and the seasonal evolution of their location and frequency.

6. POSSIBILITIES FOR METHANOGENIC LIFE IN LIQUID METHANE ON THE SURFACE OF TITAN

On Titan, photochemical products represent a disequilibrium state and a potential source of chemical energy. Photochemically produced acetylene, ethane and organic solids would release energy when consumed with atmospheric hydrogen, at levels of 334, 57, and 54 kJmol$^{-1}$, respectively. The presence of chemical energy in the form of organics in the atmosphere of Titan is of biological interest. On Earth, methanogenic bacteria can survive on this energy level. In order to show the effect of a biological activity, hydrogen may be the best molecule because it does not condense at the tropopause and has no sources or sinks in the troposphere. If the supposed biological consumption is greater than $10^8$cm$^{-2}$s$^{-1}$, it will have a measurable effect on the hydrogen mixing ratio in the troposphere. Although the energetics of methane-based life on Titan may be favorable, there are two important aspect to be taken into account:

- The low temperatures imply very low rates of reaction...but life could speed up any thermodynamically favorable reaction by catalysts;
- The low solubility of organic substances in liquid methane... but life could have develop strategies to overcome the low solubility of organics in liquid methane.

REFERENCES


