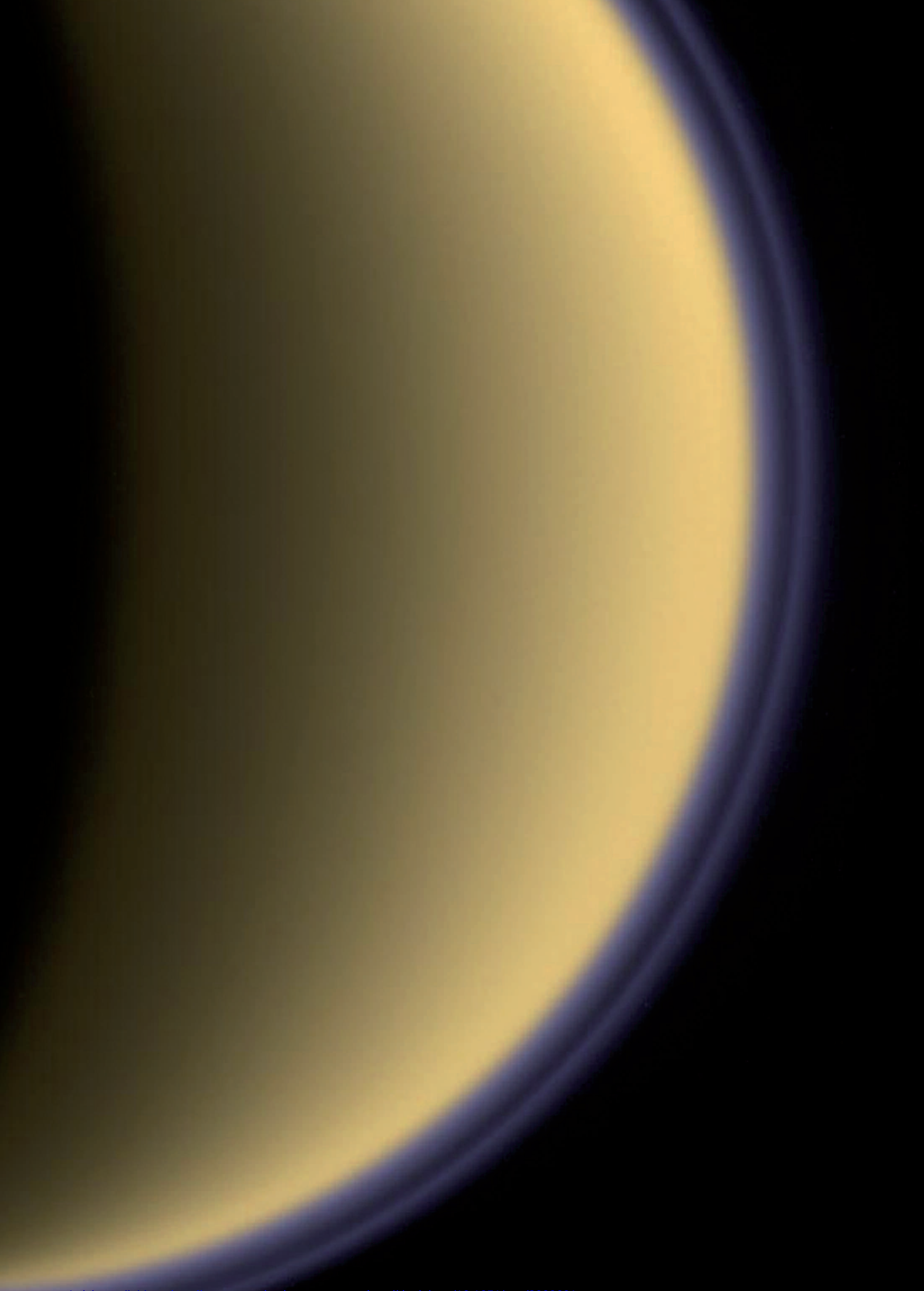

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METHANE IN TITAN'S ATMOSPHERE:

FROM FUNDAMENTAL SPECTROSCOPY TO PLANETOLOGY[1]

Vincent Boudon[1], **Jean-Paul Champion**[1], **Tony Gabard**[1], **Michel Loëte**[1], **Athéna Coustenis**[2], **Catherine De Bergh**[2], **Bruno Bézard**[2], **Emmanuel Lellouch**[2], **Pierre Drossart**[2], **Mathieu Hirtzig**[2], **Alberto Negrão**[3] and **Caitlin A. Griffith**[4],

[1] Institut Carnot de Bourgogne – UMR 5209 CNRS-Université de Bourgogne, Dijon, France

[2] Laboratoire d'Etudes Spatiales et d'Instrumentation en Astrophysique, Observatoire de Paris-Meudon, Meudon, France

[3] Istituto di Fisica dello Spazio Interplanetario, Via del Fosso del Cavaliere, I-00133 Roma, Italie et Faculdade de Engenharia da Universidade do Porto, Porto, Portugal

[2] Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721, USA

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The methane molecule (CH_4) is relatively abundant in the Universe and in particular in our Solar System. On Earth, it is the main compound of natural gas and is also the second greenhouse gas of anthropic origin. On Saturn's satellite Titan it plays a role similar to water on Earth and leads to a complex chemistry.

Methane is present in significant quantities in the atmosphere of various extraterrestrial objects: the giant planets of the Solar System (Jupiter, Saturn, Uranus and Neptune), but also Titan (satellite of Saturn), Triton (satellite of Neptune), Mars, Pluto and, further away, brown dwarves, some « cold» stars and giant exoplanets.

The principal method for the determination of the chemical composition and physical conditions of these planetary atmospheres is spectroscopy. This optical diagnostic technique allows chemical species to be identified from the light they absorb or emit at different wavelengths.

The understanding of a planetary atmospheric spectrum requires the ability to correctly model that of its different compounds. In many cases, strong methane absorption bands dominate the spectrum of such bodies. Thus, the detection of minor compounds (complex organic molecules, trace gases, etc…) or the determination of other parameters such as the surface properties, involves the subtraction of the CH_4 spectrum. This, in turn, requires an extremely reliable model valid over a wide spectral range (from microwaves to near infrared). Moreover, even at low or moderate resolution, the spectral absorption profile depends on the underlying fine structure. Its modeling thus requires the analysis of high-resolution laboratory spectra, which involves the study of a huge number of quantum states and the identification of a huge number of spectral lines.

◄ **This image of Titan was taken by the Cassini spacecraft during its first flyby of the largest moon of Saturn on July 2, 2004. It shows a thin, detached haze layer floating above the orange atmosphere. © NASA/JPL/Space Science Institute**

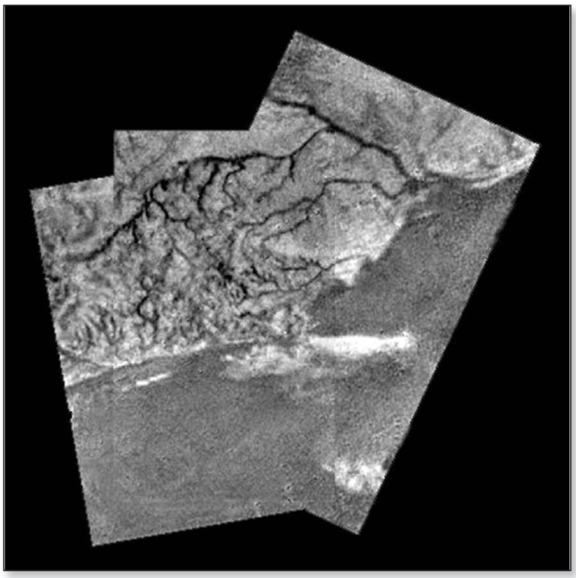
Methane on Titan

Titan, Saturn's main moon, has a 5150 km diameter and possesses a thick atmosphere mainly composed of nitrogen, N_2 (98 % in average), that does not absorb light, but also of an important quantity of methane (about 1.5% in the neutral atmosphere), a little oxygen, as well as various other organic molecules, the sign of a complex chemical activity.

Titan's surface temperature is a low –179 °C and water can only exist there as ice. On Titan, CH_4 plays a role similar to water on Earth. It is present in the gaseous form in the atmosphere, forms clouds and there is evidence for methane rains leading to mixed methane and ethane rivers and lakes on the surface.

note

[1] An extended version of this paper was first published in French in May 2008 in *uB Sciences*, volume 3, the research journal of the *Université de Bourgogne*. A French shortened version similar to the present one was then published in *Reflets de la Physique*, volume 11, pp. 13–16 (2008), the journal of the *Société Française de Physique*.



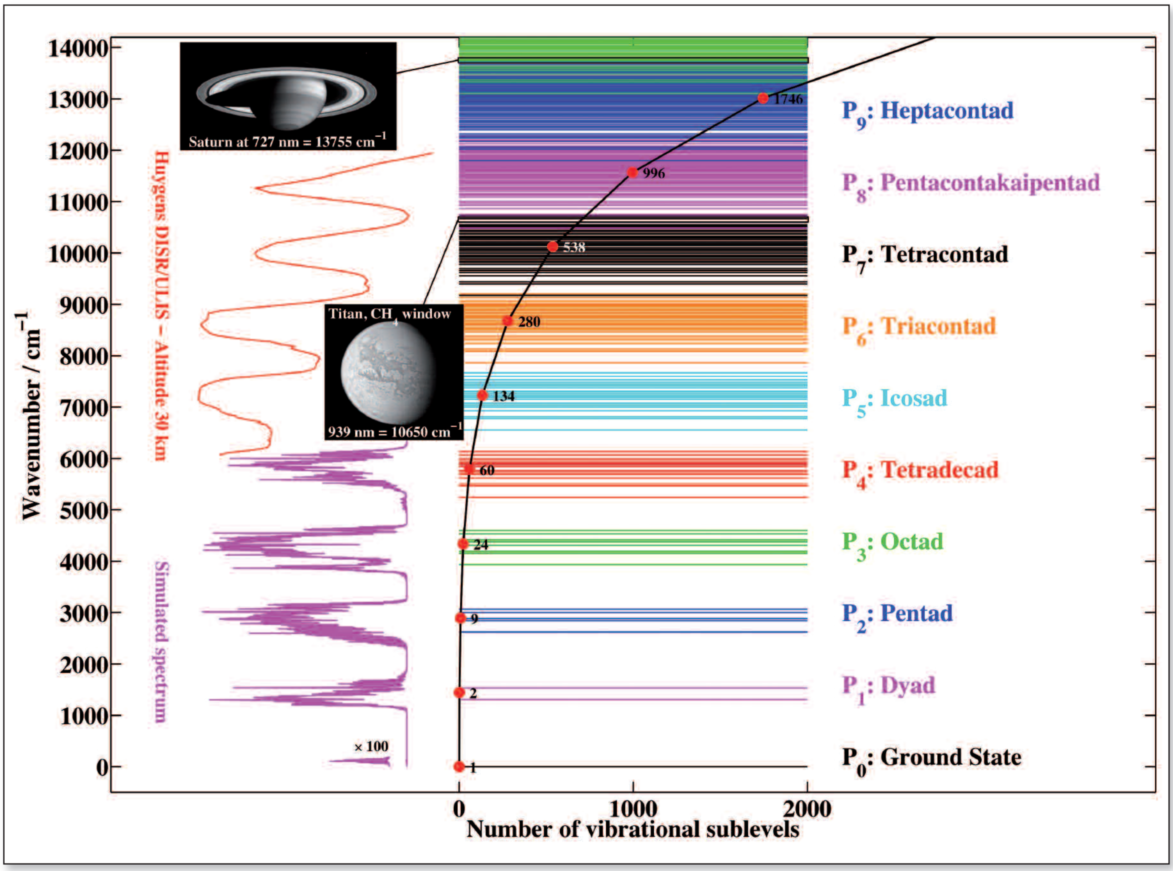
▶ **FIG. 1:** "Dried" methane rivers imaged by the Huygens probe during its descent on Titan. © NASA/JPL/ Space Science Institute.

This conception of Titan mainly comes form the observations and measurements made by spacecraft like Voyager 1 in 1980 and, essentially by the Cassini-Huygens mission (NASA/ESA/ASI) which, since July 2004, has revolutionized our knowledge of Saturn's system including Titan. One of its main features was the European Huygens probe descent in Titan's atmosphere and its landing on the surface on January 14, 2005 after a two and a half hour descent. The Cassini orbiter continues to regularly flyby Titan and the other kronian satellites with a host of different instruments (cameras, spectrometers, radar, …), supplementing observations made from Earth orbit (Hubble Space Telescope, ISO satellite) or from the ground, often at higher spectral resolution.

A series of large and regularly spaced absorption bands due to methane dominate the Titan spectra recorded by the DISR (Descent Imager/Spectral Radiometer) of the Huygens probe during its descent, and by VIMS (Visual and Infrared Mapping Spectrometer) on the orbiter.

Images taken during the Huygens descent combined with radar images from the Cassini orbiter provide valuable information. Fluvial networks cover around 1 % of the surface (see Figure 1). Large smooth areas, interpreted as methane and ethane lakes or seas, cover important parts of the polar regions.

Furthermore, methane decomposition in the upper atmosphere leads to a series of chemical reactions producing various organic compounds such as ethane (C_2H_6) and other more complex hydrocarbons. Nitrogen (N_2) dissociation and its recombination with methane leads to the formation of nitriles like hydrogen cyanide (HCN). Polymerization of some compounds produces a complex material, which constitutes the solid particles of the orange haze that fills the atmosphere. These particles become condensation cores for ethane and other gases and continuously fall on Titan's



▶ **FIG. 2:** Methane's spectrum complexity. Horizontal lines represent vibration energy levels. The black curve gives the number of vibrational sublevels for each polyad. The names correspond to the different absorption bands. Different spectral regions are illustrated by images and spectra: in pink, a simulated spectrum for lower polyads and, in red, an example of the spectra recorded on Titan by the Huygens probe. © NASA/JPL/ Space Science Institute).

surface. All this allows one to build up the scheme of a true "methane cycle" on Titan that mimics the water cycle on Earth.

The main question that arises about methane is that of its origin because this molecule is efficiently destroyed in the upper atmosphere by solar radiation and the processes we described in the previous paragraph. So it should have completely disappeared long ago. There must then exist methane sources capable of re-fueling the atmosphere. According to recent models, lakes alone (unless very deep), are not sufficient to explain the observed quantities (around 5 % of methane near the surface and 1.5 % in the stratosphere). Another possibility would be the presence of methane trapped in ice crystals or formed by other processes (such as serpentinization) in the interior of the satellite. It could then slowly find its way up to the surface where it would be released through cryovolcanic eruptions.

Methane spectrum

CH_4 has several remarkable spectroscopic properties. First, this molecule is highly symmetrical, the four hydrogen atoms placed at the vertices of a regular tetrahedron. A second essential characteristic of the methane spectrum is related to the ordering of its energy levels. The four characteristic vibrational frequencies of the atoms in the molecule display simple ratios between each other. The consequence is that the vibrational energy levels are grouped into sets called *polyads* that are regularly spaced. The more the energy increases, the bigger is the number of levels in each polyad (see Figure 2). This grouping is responsible for methane's large absorption bands.

In environments like a planetary atmosphere containing a few percent of methane and in which sunlight crosses several hundred kilometers, even highly excited polyads, although extremely weak when observed in the laboratory, can absorb almost all light at the corresponding wavelengths. Figure 2 shows a Saturn image taken by the Cassini spacecraft on which the dark zones correspond to the absorption of light in the region of a highly excited polyad. This absorption of light by methane is also responsible for the opacity of Titan's atmosphere. However, transparency windows between polyads exist. They allow observing other compounds in this atmosphere and, moreover, constitute the only means to glimpse at Titan's surface remotely. Again in Figure 2, another Titan image taken by the Cassini spacecraft through one of these spectral windows reveals the topography of the Saturnian moon.

Thus, the modeling of the absorption of light in such atmospheres necessitates considering a huge number of excited states. But the complexity goes further! The rotational structure of the spectrum superimposes onto the vibrational one. Because of the even higher number of rotational states (see Figure 3), it is mandatory to undertake high-resolution studies in order to finely reproduce the profile of the observed bands, since this depends on the underlying structure. Moreover, intensity calculations should be as precise as possible, in view of concentration measurements. Intensities also depend on the temperature. Reciprocally, the precision of the intensity model conditions that of the temperature measurement. Finally, a reliable model provides a much bigger flexibility than an interpolation from laboratory measurements, which is necessarily limited.

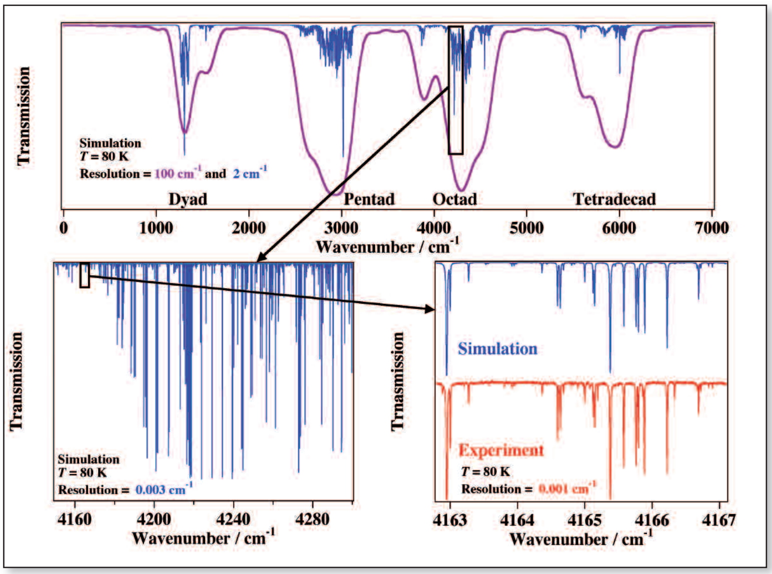
On **Titan, CH_4** plays a role **similar to water** on **Earth**

Recent results

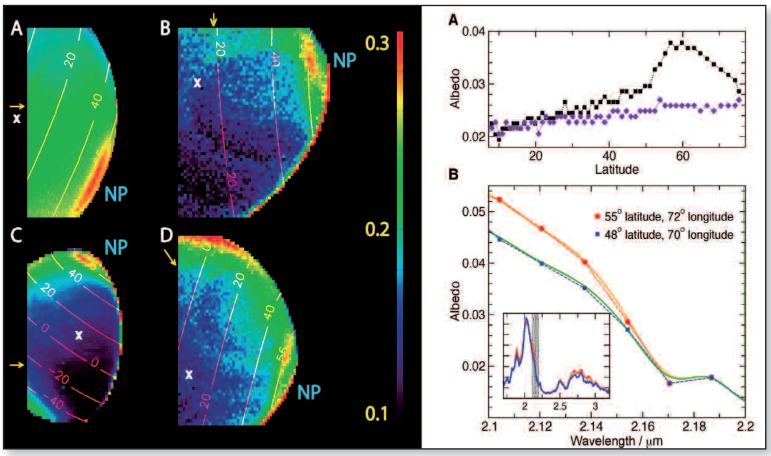
Calculated methane spectral line lists have recently allowed significant contributions to the analysis of some measurements concerning Titan.

For instance, using these lists, it was possible to interpret ISO satellite data from 1997 in the 2.4 – 4.9 μm spectral range [1]. The advantage of using a wide spectral range instead of a window-by-window study (as in previous works) is to allow for a better determination of the spectral behavior of Titan and hence a better constraint over the aerosol model for Titan, as well as a determination of the methane abundance in the lower atmosphere (below 3 %). Furthermore, albedo measurements of Titan's surface, obtained simultaneously through several infrared windows after the atmospheric subtraction, allowed scientists to constrain Titan's surface composition, shown to be compatible with the presence of water ice and organics.

▼ FIG. 3: Simulated methane spectrum at increasing spectral resolutions, showing the rotational structure **(in blue)**. In the upper panel, the magenta curve represents a low-resolution calculated spectrum. The lower right panel compares a very small part of the calculated spectrum with a laboratory measurement **(in red)**.

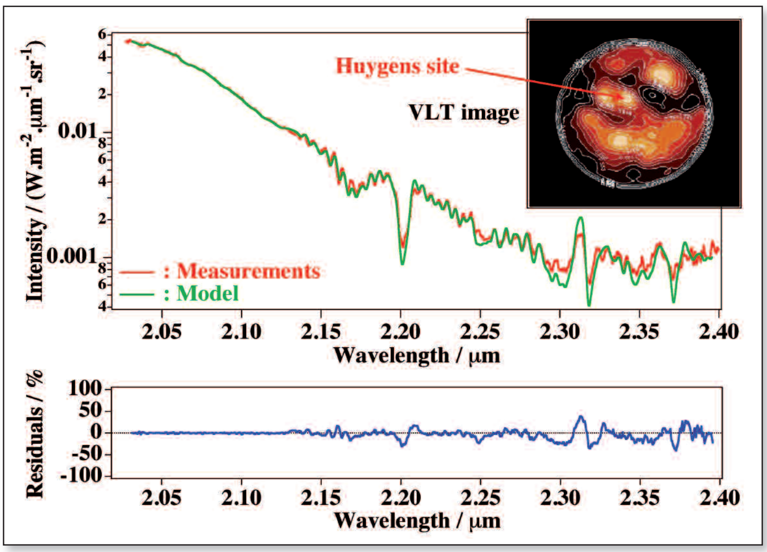


Another recent major contribution was the evidence of a vast polar ethane cloud at Titan's North pole [2]. This was made possible thanks to the simulation of the methane spectrum in the so-called octad region (see Figure 2) around 2.1 to 2.2 µm. As illustrated in Figure 4, it was shown that the difference between spectra inside and outside the cloud is due to diffusion by small particles in the 30 to 50 km altitude range, with characteristics indicating that this cloud is likely to be composed of ethane. Ethane (C_2H_6), the main product of methane photodissociation by solar radiation, should precipitate on the ground. The apparent absence of liquid ethane on the ground at mid latitudes of Titan was up to recently a mystery. These new observations suggest that in fact ethane seems to condensate in this type of polar clouds and is then likely to accumulate in the lakes that are present in these regions.



▲ **FIG. 4: Left:** Albedo (proportion of reflected solar light) maps of Titan at 2.8 µm obtained by the VIMS instrument of the Cassini spacecraft. Red areas have highest albedo. The red spot near the North Pole (NP) is an ethane cloud. **Upper right:** Albedo as a function of latitude at 2.11 µm (in black) and 2.17 µm (in magenta), revealing the diffusion by the cloud that is visible at 2.11 µm beyond 51°N. **Lower right:** measured (dots) and simulated (curves) spectra at two different latitudes. The difference between spectra at these two latitudes reflects the diffusion by the ethane cloud that is situated around 30 to 50 km altitude. Figure from Reference [2].

▼ **FIG. 5: Upper right:** VLT (Very Large Telescope) image. Bright zones correspond to high albedo regions. **Top:** Measured spectrum around the Huygens landing site with a resolving power of 700 **(in red)** and simulated spectrum **(in green)**. **Bottom:** relative difference between measurements and the best model **(in blue)**. Above 2.12 µm, the measurement error is ± 27 %. The vertical haze profile and the surface albedo at 2 µm were determined from these measurements.



Calculated methane absorption coefficients in the mid infrared allow for a correct modeling of Titan's atmospheric absorption as measured by the CFHT [3], from which surface albedo variations can be deduced.

Finally, spectra were recorded between 2.03 and 2.40 µm thanks to the VLT for different regions of Titan, including the Huygens probe landing site, as can be seen in Figure 5 [4]. Calculated absorption coefficients, using the methane abundance profile, as measured by the Huygens probe, allow again for a correct modeling of Titan's atmospheric absorption, from which the surface albedo can be deduced in a spectral domain that was not covered by Huygens' DISR instrument.

Perspectives

Advances in the theoretical model presented here (mainly with respect to higher polyads and spectral line shapes), associated with experimental work at Titan's atmospheric conditions, would allow us in the future to better constrain the methane opacity. This would lead to the resolution of remaining issues with the interpretation of Cassini-Huygens and Earth-based near-IR Titan data, concerning essentially the vertical haze profile and the composition of Titan's surface. ■

Acknowledgments

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