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Optical constants of Titan aerosols and their tholins analogs: Experimental results and modeling/observational data

Coralie Brassé [a,*], Olga Muñoz [b], Patrice Coll [a], François Raulin [a]

[a] Laboratoire Interuniversitaire des Systèmes Atmosphériques, Universités Paris 12 – Paris 7, CNRS UMR 7583, 61 avenue du Général de Gaulle, 94010 Créteil Cedex, France
[b] Instituto de Astrofísica de Andalucía, CSIC, Glorieta de la Astronomía s/n, 18080 Granada, Spain

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ABSTRACT

Since Bishun Khare's pioneer works on Titan tholins, many studies have been performed to improve the experimental database of the optical constants of Titan tholins. The determination of the optical constants of Titan aerosols is indeed essential to quantify their capacity to absorb and scatter solar radiation, and thus to evaluate their role on Titan's radiative balance and climate. The study of the optical properties is also crucial to analyze and better interpret many of Titan's observational data, in particular those acquired during the Cassini–Huygens mission. This review paper critically summarizes these new results and presents constraints on Titan's aerosols optical constants. Finally, the information lacking in this field is highlighted as well as some possible investigations that could be carried out to fill these gaps.

1. Introduction

The particular dense atmosphere of Titan has inspired many observations since the early 1980s. Indeed, the largest satellite of Saturn is the only planetary body in the solar system that has a dense atmosphere comparable to that of the Earth by its surface pressure (1.5 bar) and main constituent (N_2). Furthermore it is the only object with Earth known to have permanent liquid reservoirs on its surface. Titan's atmosphere is mainly composed of molecular nitrogen (varying from 95% to 98.4% with altitude) and methane (varying from 5% to 1.48% with altitude) (see for instance Niemann et al. (2010)). Others species are present at trace levels, namely hydrocarbons (2-carbon hydrocarbons, propane, methylacetylene, diacetylene, benzene, propene), nitriles (cyanogen, cyanoacetylene, hydrogen cyanide etc.), molecular hydrogen, carbon monoxide, carbon dioxide, water vapor and argon in the stratosphere (Coustenis et al., 1998; Flasar et al., 2005; Jennings et al., 2009; Niemann et al., 2005, 2010; Nixon et al., 2013; Samuelson et al., 1983, 1997; Waite et al., 2005). Several other compounds, both neutrals and ions, have also been detected in the ionosphere (Waite et al., 2007).

Titan's atmospheric composition is driven by the coupled chemistry of N_2 and CH_4 (see e.g. Raulin et al., 2012). The dissociation of methane is induced by photons with wavelengths lower than 150 nm (providing radicals CH, CH_2 and CH_3). The dissociation of nitrogen is also generated by photons with wavelengths lower than 100 nm but mostly by energetic particles from Saturn's magnetosphere. The resulting products chemically evolve, coagulate and/or condense. This evolution yields more complex compounds up to the formation of macromolecular organic particles, forming Titan's haze. Thus the origin of Titan aerosols appears to be the growth of complex organic compounds in the upper atmosphere. These processes could involve large negative ions, as detected by the CAPS instrument on Cassini (Waite et al., 2007). The chemistry taking place in the upper atmosphere is so active that it is the source of different aerosol layers in the atmosphere conferring to Titan its characteristic orange–brown color in the visible spectral range. The haze hides the lower atmosphere and makes the atmosphere opaque in the UV–visible and Near-IR spectral range (see e.g. Rodriguez et al., 2003). Since the initial works on Titan's aerosol formation, models have assumed that they are aggregates of smaller coagulated particles, produced by the chemical (and photochemical) processes in the high atmosphere (e.g. West et al., 2014, and refs included).

Titan aerosols play an important role in the radiative transfer of Titan, absorbing both the solar radiation in the visible spectral range and the radiation from the troposphere and surface in the

* Corresponding author. Tel.: +33 145176549.
E-mail address: coralie.brasse@lisa.u-pec.fr (C. Brassé).

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thermal infrared wavelengths (McKay et al., 1989, 1991); they can thus strongly impact the atmospheric dynamics and the climate (Rannou et al., 2002). They are also involved in the composition and the properties of the atmosphere and the surface of Titan. Their contribution to the greenhouse effect and the anti greenhouse effect remains a key question remaining to be answered (Hasenkopf et al., 2010; McKay et al., 1991). The presence of aerosols (which strongly affects the intensity and wavelength distribution of radiations reaching the surface) also impacts the signal recovered by the Cassini orbiter instruments. For example, it turns out that the scattering of aerosols in Titan's atmosphere affects, among others, the data collected by the Cassini Visible and Infrared Mapping Spectrometer (VIMS). This instrument is used to observe the surface in the near infrared atmospheric window at 0.95 μm, 1.1 μm, 1.3 μm, 1.6 μm, 2.0 μm and 2.7 μm. It also permits the study of the chemical and dynamical processes that take place in the atmosphere (Bellucci, 2008). However, it was expected that light scattering from Titan aerosols would make Titan's atmosphere optically thick, so that diffuse radiation would have a considerable impact on the images and spectral measurements of the surface (Grieger et al., 2003). Indeed, the surface is hidden due to the absorption and scattering of the incident radiation by aerosols and gas. But it appears that aerosols are the dominant scattering source on Titan (Rannou et al., 2010).

The scattering by aerosols modifies the photon flux reaching the VIMS instrument (especially at short wavelengths) and it also makes the surface images hazy because it strongly reduces the contrast of the images (Keller et al., 2008). With the use of an algorithm to subtract Titan's haze contribution, it is possible to get a better look at the surface contrast, but it is not possible to completely exclude their presence, making it difficult to analyze the data (Vixie et al., 2010). Light scattering from Titan aerosols also prevents obtaining the measurements needed to determine the surface reflectivity and the identification of the surface constituents. This in particular concerns the search for condensed hydrocarbons on Titan's surface to explain abundance of methane in the atmosphere when its atmospheric photodissociation should make it disappear (Tomasko et al., 2005).

Consequently, the determination of the optical constants of Titan aerosols is essential to quantify their capacity to absorb and scatter solar radiation, and thus to evaluate their role in the radiative balance and the climate. The study of the optical properties is also necessary to analyze and better interpret many of Titan's observational data, in particular those acquired during the Cassini–Huygens mission. The optical parameter the most investigated is the refractive index. Indeed, the aerosol properties (as the aerosol size and single-scattering albedo with altitude) are usually deduced from observational data using theoretical models which need to consider the haze refractive index as an input parameter. Different and complementary approaches can be followed to determine this parameter, based on laboratory measurements, theoretical modeling and observational data. Several summary papers have already been published on this subject (i.e. Tomasko and West, 2009; Lorenz, et al., 2009), including a very recent review by West et al. (2014) based on the only available in situ measurements performed on Titan's haze which have been obtained, with the DISR experiment (Tomasko et al., 2005) on the Huygens probe of the Cassini–Huygens mission. Meanwhile, many experimental works have been carried out on laboratory analogs of Titan's aerosols, named Titan tholins. These tholins have frequently been used to characterize the optical properties of Titan's haze, in particular to estimate their complex refractive index. However, the properties of these tholins, including the optical ones, seem to be very dependent on the experimental conditions used for their synthesis (Cable et al., 2012) and it seemed necessary to perform a critical analysis of the many available data related to the refractive index of these laboratory analogs of Titan haze particles.

The first optical property measurements using Titan tholins were conducted by Khare et al. (1984) for a large range of wavelengths from the soft X-ray to the microwave spectral range (0.025–1000 μm). Khare's optical constants have been widely used by several research teams and been the reference for many sequences of interpretation and modeling works in the last decades. However, some new reports show that Khare's optical constant may not be fully representative of Titan aerosols' optical constant at different wavelengths. This will be detailed below in this review.

Only during the last years several studies have been performed to improve the experimental database of the optical constants of Titan tholins. This review paper summarizes the new results related to optical properties of Titan tholins and the constraints they place on those of Titan's aerosols.

2. Laboratory synthesis of Titan tholins

One way to constrain the optical constant of Titan aerosols is to determine the refractive indices of analogs of Titan haze particles, the complex organic material synthesized in the laboratory, usually named Titan tholins (Sagan and Khare, 1979). However the values of complex refractive indices depend on the chemical composition of the sample, and may also depend on the experimental conditions under which the measurements are performed and from which the optical constants will be derived. These conditions include, for instance, the surface state of the sample (if it is used as a film) or the size and the shape of the grains (if the sample is under the form of particles). Most of these three parameters are linked to the experimental conditions applied during the tholins synthesis, such as the energy source, gas mixing ratio, gas pressure, open or close reactor, flow rate and/or irradiation time, and also temperature. This variation will induce major uncertainties in the determination of the complex refractive indices.

One way to determine Titan aerosols optical constant is to measure the optical constants of the analogues of Titan complex organic material synthesized in the laboratory, usually named Titan tholins (Sagan and Khare, 1979). But the optical constants depend on the chemical composition and the size and the shape of particles. These three parameters will vary according to the experimental conditions such as the energy source, gas mixing ratio, gas pressure, flow rate and irradiation time.

Table 1 shows the different experimental synthesis conditions used for the production of Titan tholins specially designed to characterize their optical constant. Most experimental setups use cold plasma discharge as the energy source, except for Hasenkopf et al. (2010), Tran et al. (2003), and Vuitton et al. (2009) use UV irradiation. For cold plasma discharge, there exist three different kinds of discharges: (i) Direct Current (DC) plasma discharge used by Khare et al. (1984), Brucato et al. (2010), and Ramirez et al. (2002). But the applied current changes from one experiment to another. (ii) Inductively Coupled RF plasma (ICP) discharge at 13.5 MHz used by Imanaka et al. (2012). (iii) RF Capacitively Coupled plasma (CCP) discharge at 13.56 MHz used by Mahjoub et al. (2012) and Sciamma-O'Brien et al. (2012). Cold plasma discharges usually occur at low pressures, of the order of mbars. Concerning the UV-irradiation experiments, the light sources employed are a mercury lamp in the case of Tran et al. (2003) and Vuitton et al. (2009), and a deuterium lamp in the case of Hasenkopf et al. (2010). Mercury lamps emit mostly at 185 nm and 254 nm, whereas deuterium lamps emit a continuum from 115 nm to 400 nm, peaking at 160 nm. However, the direct dissociation of dinitrogen involves much shorter wavelengths ($\lambda < 100$ nm) (Cook and Metzger, 1964) which is why Tran et al. (2003) and Vuitton et al. (2009), who used the same experimental device, added to their initial gas mixture of $N_2/CH_4/H_2$ small quantities of cyanoacetylene (HC_3N), ethylene (C_2H_4) and acetylene (C_2H_2),