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Reflectance spectra and chemical structure of Titan's tholins: Application to the analysis of Cassini–Huygens observations

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Abstract

Titan's tholins are used as analogs of Titan's aerosols and N-rich organic solids present on many icy surfaces. However, it is not clear whether or not they are relevant analogs, and which kind of tholins should be used among a wide set available in literature. This paper presents reflectance spectral data of two tholins selected as end-members of a series of samples covering a very wide range of continuous chemical and optical properties. These samples were formed under experimental conditions fairly consistent with Titan's stratosphere. A general framework for using these laboratory data to the analysis of spectral observation of Titan's surface or other objects is suggested. Furthermore, the study reports the first in situ unambiguous identification of aromatics compounds and evidences variations in the sp^2 carbon structure, which controls the absorption properties in the visible/NIR. These results also point out it is very unlikely to derive quantitative chemical information (e.g., N content, sp^2/sp^3 ratio) from remote sensing reflectance data.

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Keywords: Titan; Organic chemistry; Satellites, surfaces

1. Introduction

The dense atmosphere of Titan is mostly composed of N_2 with a few percent of methane. It is the site of an intense chemistry where different kinds of aerosols form from radiolysis and/or photochemical reactions with solar photons and energetic particles incoming from Saturn's magnetosphere. These aerosols are expected to sediment onto the surface and to form a more or less thick layer, possibly transported through hydrocarbon-rich fluids (Tomasko et al., 2005). The formation mechanisms and chemical composition of these aerosols are unknown.

For more than twenty years, experiments carried out in several laboratories have attempted to simulate Titan's atmospheric

chemistry and to produce aerosol analogues that are now termed Titan's tholins (e.g., Sagan and Khare, 1979; reviews by Coll et al., 1997; Imanaka et al., 2004). The general framework of these experiments involves the irradiation of an initial gas mixture by energetic particles and/or photons, during experimental conditions that are assumed to be close to those prevailing in Titan's atmosphere. The resulting tholins are then recovered and studied using different techniques in order to determine their chemical composition and their spectral properties, that are required for interpreting the observational data (e.g., Khare et al., 1984; McDonald et al., 1994; Coll et al., 1999; Ramirez et al., 2002; Bernard et al., 2003). However, there is up to now no observational evidence that Titan's tholins are valid analogs of Titan's aerosols. The chemical pathways forming tholins, in any experimental set-up, are certainly very different than processes which do form the yellowish aerosols in Titan's atmosphere (photochemistry, diffusion through large scale in the atmosphere, etc.). One may consider that the more relevant tholins originate

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from experiments where the atmospheric composition of Titan is reproduced in terms of nature and abundance of molecules formed at the gaseous state (e.g., [Bernard et al., 2003](#)). Unfortunately, none of the experiments carried out up to now has been able to accurately mimic, qualitatively and quantitatively, the gaseous composition of Titan's atmosphere. Moreover, even for experimental conditions roughly similar to those expected in Titan, slight variations of experimental parameters (pressure, temperature, discharge intensity, etc.) induces large variations in the chemical composition and spectral properties of tholins ([Coll et al., 1997](#); [Khare and Sagan, 2002](#); [Bernard et al., 2002](#); [Imanaka et al., 2004](#)). Consequently, it is not possible to fix the precise set of experimental conditions and samples that are the most relevant to Titan's chemistry. This problem is of particular concern for anyone who wants to analyze observational spectral data, as the current state of literature is rather confusing. A wide set of optical constants and reflectance spectra are available, but they originate from various samples and experimental conditions, with many of them irrelevant to Titan's conditions (e.g., [Khare et al., 1984](#); [Cruikshank et al., 1991](#); [Imanaka et al., 2004](#)).

This short paper reports a first attempt in defining a new general framework for using tholins as analogs of Titan's aerosols for the analysis of spectral observations. Instead of tentatively providing the chimeric "ideal analog," a continuous set of tholins was produced from a DC-discharge experiment with physical conditions consistent with those of Titan's stratosphere ([Coll et al., 1999](#); [Bernard et al., 2002](#)). Two tholins were selected as the two end-members of this series exhibiting a continuous range of visible optical properties (i.e., with visual colors ranging from yellowish to brown/black). Their reflectance spectra have been measured in the range 0.4–4.5 μm , covering most of the solar range of interest for both the DISR and VIMS instruments, and they have been discussed in terms of analysis of spectral observations of Titan's surface. These new experimental data are the ones which were used for the preliminary analysis of the DISR data of the surface of Titan ([Tomasko et al., 2005](#)).

This paper also reports the first reliable Raman study of Titan's tholins, by resonant UV Raman spectroscopy. Aromatics compounds have been unambiguously detected in situ, and their abundance was found to correlate with sample color (e.g., visible gap). The amorphous structure of the samples is evidenced, as well as variation in the (C, N) skeleton between the two end-members. Thanks to these results, the chemical information which could be derived from reflectance spectral observations is discussed.

2. Experimental

The samples were produced from a $\text{N}_2:\text{CH}_4 = 98\%:2\%$ gaseous mixture ($P = 0.9$ mbar) exposed to an electric discharge (current 30 mA) in an open gas flow system. The experimental set-up located in LISA (Créteil, France) is described in detail elsewhere ([Bernard et al., 2003](#); [Coll et al., 1999](#)). The elemental composition of the samples was determined using a standard combustion/oxidation technique (ICSN-CNRS,

France). The structures and chemical compositions of samples were investigated by UV Raman microspectrometry (244 nm excitation), using a Labram HR800 Jobin-Yvon Raman spectrometer equipped with a microscope ($\times 40$ objective), and by mid-IR spectrometry on KBr pellets using an FTIR Nicolet 800 spectrometer (7000–400 cm^{-1} spectral range). The bidirectional reflectance spectra were measured using a homemade spectrogonio radiometer ([Brissaud et al., 2004](#)), in the spectral range 0.4–4.5 μm , using a collimated incident flux at normal incidence collected at an emergence angle of $30^\circ (\pm 2^\circ)$.

3. Results and discussion

3.1. Color, texture and elemental composition of samples

Two samples were extracted from the reactor walls surface: one close to the gas inlet point (BB), and the other at the middle of the tube (YO). These samples have different macroscopic colors and elemental compositions: the BB sample was black/brown, and had $\text{C/N} = 1.72$, $\text{C/H} = 0.95$, $[\text{C} + \text{N}]/[\text{H}] = 1.50$; YO was yellow/orange, $\text{C/N} = 2.56$, $\text{C/H} = 0.72$, $[\text{C} + \text{N}]/[\text{H}] = 1.00$ ([Fig. 1](#)). Both samples exhibited large textural, optical and chemical variations at the micrometric scale ([Fig. 1](#)). Black spheroidal nodules ($\sim 50 \mu\text{m}$) were present within YO samples, associated with the most abundant smaller micrograins that had wide variations in color ranging from white to black, through yellow, orange and red. In BB, most of the micrometer-sized components were brown or black, with textures that included needles, nodules, etc. For each sample, the macroscopic color reported represents an averaged contribution from the various micrometric constituents.

3.2. Transmission mid-IR spectra

The transmission infrared spectra ([Fig. 1](#)) are consistent with those of bulk tholins produced previously by other groups (e.g., [Imanaka et al., 2004](#)) and of hydrogenated CN_x thin films (e.g., [Mutsukura and Akita, 1999](#)). The main differences between the spectra of both samples observed here are: (1) the presence within YO samples of spectral features indicating CH_2 and CH_3 aliphatic groups (2850–2950 cm^{-1}), and (2) the structure of the band at $\sim 2200 \text{ cm}^{-1}$ assigned to nitrile ($-\text{CN}$) and/or isocyanide ($-\text{NC}$) functional groups. The absence of the aliphatic functional groups in BB is consistent with its high C/H ratio, and this might indicate an increase of the sp^2/sp^3 ratio with respect to YO ([Imanaka et al., 2004](#)). The spectral variations in the structure of the band at 2200 cm^{-1} provide evidence for different nitrogen speciation within the two samples. Previous investigations using various band decomposition models have provided inconsistent results, as different N-bearing compounds were tentatively identified, finally demonstrating that the interpretation is not univocal ([Imanaka et al., 2004](#); [Mutsukura and Akita, 1999](#), personal unpublished data).

3.3. Reflectance spectra

In order to model reflectance spectra of Titan, in particular DISR and VIMS data from the Cassini/Huygens mission, and

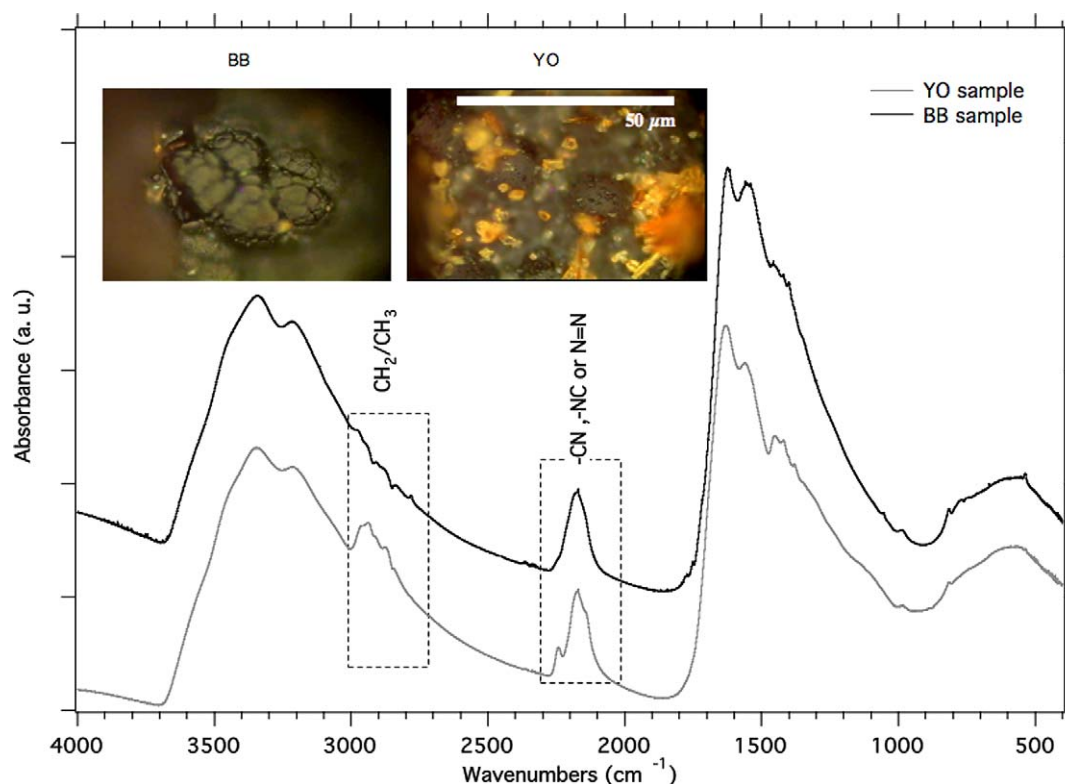


Fig. 1. The mid-IR spectra of the tholins BB and YO. The dotted rectangles point out the main differences between both spectra, including (left) the presence/absence of the stretching and anti-stretching vibration modes of the CH_2/CH_3 aliphatic organic functions and (right) the spectral structure of the band at $\sim 2200 \text{ cm}^{-1}$ due to CN, NC, and, maybe, NN vibrations. Optical micrographs of the samples are shown at the top of the figure: (left) sample BB, containing mostly black components with various textures (a spheroidal nodule is in the field of view); (right) sample YO, containing components with various colors ranging between black to yellow.

other reddish surfaces (e.g., Triton, Pluto, Hyperion, etc.), it is necessary to derive the optical constants of the organic material analogs and/or their reflectance spectra. Determining the optical constants in the UV–vis range is a very complicated task. A critical issue is the optical quality of the sample and, generally, a reliable quantitative determination of optical constants is mostly achieved for thin films directly condensed onto a window. As tholins produced in this study were powder, we did not attempt to determine their optical constants. Nevertheless, reflectance spectra might be more useful than optical constants. Thus, Titan's aerosols have submicrometric sizes, similar to the wavelength of visible photons. Assuming they form the dark organic layer at Titan's surface, reflectance modeling could not be performed as the optical geometric approximation (grain size \gg wavelength) of these models would be no longer valid.

Reflectance spectra of samples BB and YO are presented and compared in Fig. 2, for the visible–near-IR range ($0.4\text{--}4 \mu\text{m}$). Unlike the mid-IR transmission spectra (Fig. 1: $4000\text{--}450 \text{ cm}^{-1}$, $4.5\text{--}22 \mu\text{m}$), the vis–NIR reflectance spectra are very different between the samples. The overall bidirectional reflectance of BB is low, 0.27 at maximum around $2.5 \mu\text{m}$. A reddish slope dominates the spectrum from $0.5 \mu\text{m}$ (reflectance ~ 0.025) to about $2 \mu\text{m}$ (~ 0.25). In the visible range, the resulting color can be described as “reddish black.” No absorption band is visible within the spectral region of the DISR instrument. Above this wavelength, weak bands are present at 1.96 , 2.25 , and $2.52 \mu\text{m}$, as well as a strong and broad feature at

$\sim 3 \mu\text{m}$, that is partly due to the $-\text{NH}_2$ functional group (adsorbed water also contributes to this feature).

The reflectance spectrum of YO is quite different. Its overall reflectance is much higher than that of BB, reaching a value of 0.8 at $1.3 \mu\text{m}$. The reflectance increases strongly from 0.4 to $1.1 \mu\text{m}$, resulting in a much larger reddish slope. Above $1.3 \mu\text{m}$, the reflectance decreases but with an overall value much higher than that of BB. These photometric and spectral variations are consistent with the bright yellow–orange macroscopic color observed of the sample. In the near-IR region, several absorption bands are observed (~ 1.05 , 1.19 , 1.52 , 1.74 , 1.94 , 1.99 , 2.29 , $2.51 \mu\text{m}$). These bands are due to various overtones and combinations of the fundamental N–H, C–H, C–N, C–C, etc. modes observed in the mid-IR. Due to the high transparency of this material in the near-IR region, photons penetrate deeper into the granular medium of YO than the BB sample, resulting in more intense absorption bands. A firm assignment of these bands is not yet established and will be the subject of future studies. Note that the stretching and anti-stretching modes of the CH_2 and CH_3 functional groups ($\sim 3.4\text{--}3.5 \mu\text{m}$) are clearly observable in YO, but only marginally in BB.

3.4. UV Raman spectra

All components in BB and YO, independent of their size, color, and shape (i.e., nodules, micrograins, needles, etc.), exhibited a strong fluorescence signal under 514 nm laser irradiation. The shape of the fluorescence spectrum was correlated

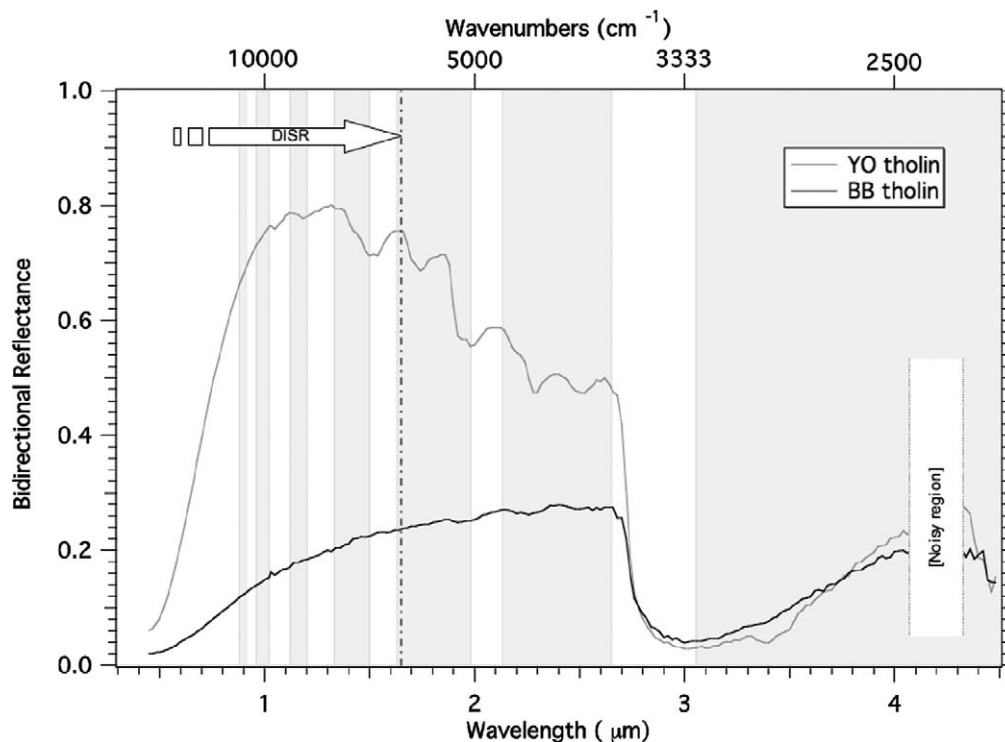


Fig. 2. The visible and NIR reflectance spectra of tholins BB and YO. The mixed vertical lines and the arrow show the spectral range of the DISR UV photometer and vis-NIR spectrometers. The dotted grey area show the wavelength ranges out of Titan's atmospheric windows, allowing surface observations from the VIMS spectrometer and ground-based telescopes. Note that adsorbed atmospheric water contributes to the broad feature at $\sim 3 \mu\text{m}$.

with the color, evidencing chemical and structural variations within the samples. Using 244 nm excitation avoids excitation of the fluorescence signal and allows collection of a Raman spectrum of the mainly sp^2 -bonded solid (Ferrari and Robertson, 2001; Ferrari et al., 2003). The UV Raman spectra of BB and YO (Fig. 3), as measured on the more abundant black-brown and yellow components, respectively, provide several clues on the chemical structure. For both samples, the broad and asymmetric shape of the first-order carbon band with its maximum near $\sim 1600 \text{ cm}^{-1}$ points to an amorphous structure (Rodil et al., 2001; Ferrari et al., 2003). The carbon skeleton appears different between the two samples, as the spectral distribution of this feature points to different sp^2/sp^3 ratio and/or sp^2 clustering among BB and YO spectra (Ferrari et al., 2003). Note that the evolution trend of this spectral distribution as function of the N abundance is consistent with the measurements of Rodil et al. (2001). The narrow features observed at ~ 687 and $\sim 980 \text{ cm}^{-1}$ are assigned to breathing modes of small aromatic rings (fivefold or sixfold), likely N-substituted regarding the low C/N ratio, and inserted within the amorphous (C, N, H) network. Note that this identification ends the debate on the presence of aromatic compounds in tholins, which were not systematically detected in earlier experiments and/or might be subjected to artefact analysis of pyrolysis data (Khare et al., 1984; Sagan et al., 1993; Ehrefreund et al., 1995; Coll et al., 1999). The peak intensity (normalized to the maximum peak in the first-order carbon band at $\sim 1600 \text{ cm}^{-1}$) of the spectral features of these breathing modes points to a higher aromaticity of BB versus YO, which is consistent with the lack of CH_2 and CH_3 aliphatic functions and the higher C/H ratio.

These spectra also exhibit spectral features due to chemically bonded CN and/or NC near 2200 cm^{-1} . In BB, two features are observed at ~ 2185 and 2225 cm^{-1} , whereas mostly a single peak at $\sim 2225 \text{ cm}^{-1}$ is observed in YO. There is no clear connection with the CN/NC features observed in the infrared (Figs. 1, 3). These UV-Raman data might provide new information on the nature of the (C, N) skeleton; however, unambiguous identification of these bands must be completed first.

3.5. Chemical structure and absorption properties of Titan's tholins

The absorption properties of tholins in the UV-vis-near-IR spectral ranges are controlled by $\pi-\pi^*$ electronic transitions (Nassau, 1983). The qualitative and quantitative description of the sp^2 structure of these solids is thus a key step for understanding their optical properties. The very dark color of BB, compared to the brighter yellow-orange color of YO, is correlated with the absence of the aliphatic CH_2 and CH_3 stretching and anti-stretching vibration modes, with an increase of aromatics abundance and with a higher C/H ratio. This suggests the absorption in the UV-visible correlates with the carbon sp^2/sp^3 ratio. However, UV-visible absorption is also controlled by sp^2 clustering (ring versus conjugated chain, size of aromatic units, etc.) and by compositional factors (presence of heteroatoms, etc.). In sample BB, the larger sp^2/sp^3 ratio partly results from the increase of the abundance of small aromatic units. However, some changes in the amorphous carbon skeleton are also involved between both samples, likely contributing to the optical properties. It is worth noting that the trends observed in this

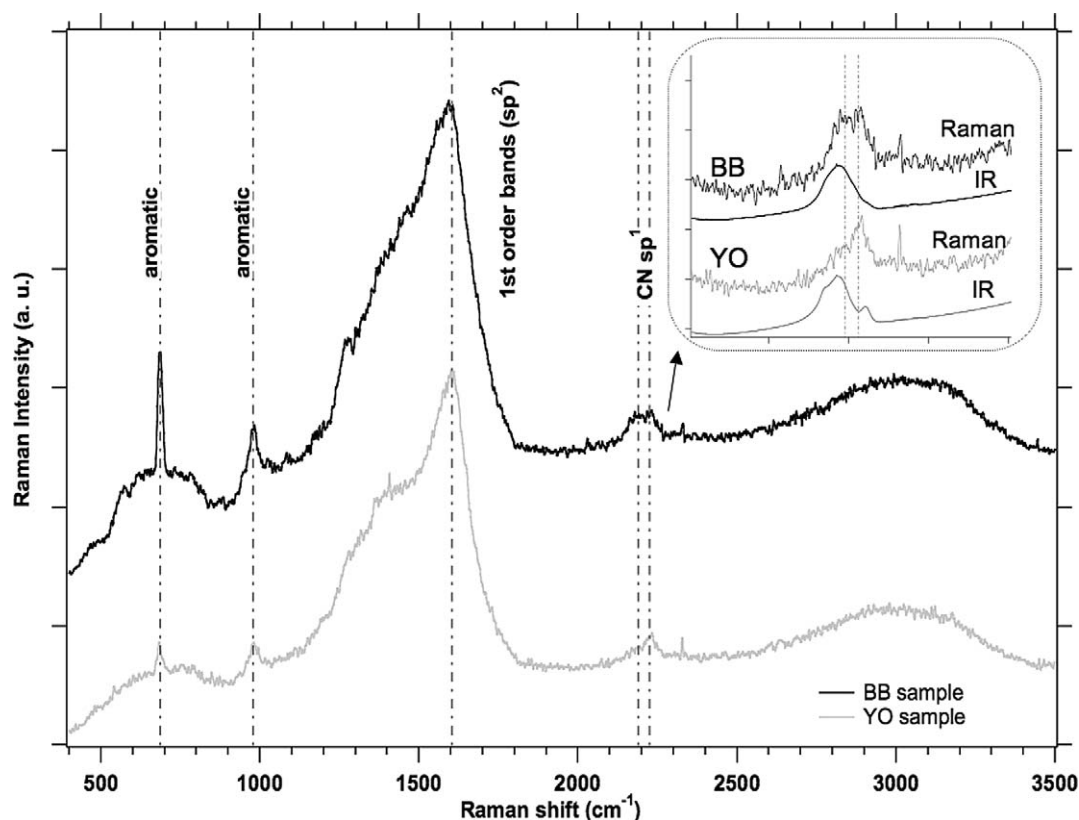


Fig. 3. UV Raman spectra of the tholins BB and YO recorded with 244 nm laser excitation. These spectra confirm the amorphous structure of these solids, and also the presence of small aromatic units inserted in the carbon skeleton, as well as differences in the carbon skeleton of both samples as pointed out by the spectral distribution of the first-order carbon bands and the sp^1 N speciation. The insert displays the comparison of Raman with mid-IR spectra in the 2200 cm^{-1} spectral region. From top to bottom: BB—Raman; BB—IR; YO—Raman; YO—IR.

experiment are similar to those observed in most carbon nitride synthesis: the higher is the hydrogen content, the weaker is the nitrogen content (e.g., Bouchet-Fabre et al., 2004). Moreover, the incorporation of nitrogen results in a higher sp^2 clustering, and consequently a decrease of the optical gap (i.e., sample darkening). In this study, the BB tholin was recovered very close to the gas inlet, where less hydrogen was available than at the middle of the reactor, where the YO tholin formed. The electric discharge being constant, the amount of hydrogen available in the plasma (from CH_4 dissociation) is controlled by the residence time of the gas and is thus function of the distance from the gas inlet. This interpretation is consistent with the absence of any deposits beyond the middle of the tube, where a too high amount of hydrogen made impossible the formation of any solid (Ferrari and Robertson, 2001). Only light hydrocarbons and nitriles are formed in this hydrogen-rich environment. This experiment thus allows to probe a very wide range of chemical compositions and optical properties of an homogeneous series of tholins, providing the most extreme situation which might expected in terms of absorption in the vis-NIR range. Finally, for this series of samples, the visible albedo appears mostly controlled by the sp^2/sp^3 ratio and the N content. However, as sp^2 clustering/ordering is an important cofactor influencing optical properties (Ferrari and Robertson, 2001), the validity of any quantitative determination of N content or sp^2/sp^3 ratio would require that Titan's tholins are perfect analogs.

3.6. Implication for surface observations analysis

The reflectance spectra presented in this study prove to be useful for interpreting observational data of organic-rich surfaces. The following criteria should be considered to select the most relevant tholins based on their vis-NIR spectra:

- the reflectance level in the visible;
- the slope and spectral shape of the reflectance curve in the visible and the very near-IR;
- the lack/presence of overtone and combination bands in the NIR, and the position of these bands, if present;
- the presence or lack of the $3.4\text{ }\mu\text{m}$ feature of the CH_2/CH_3 functional groups.

These criteria are mostly useful to state whether or not particular tholins may be considered as potential analogs, in the sense that their spectra (combined with those of other potential surface materials) are able to correctly fit the planetary observations. Rough information on the sp^2/sp^3 ratio and N content may also be derived.

Concerning applications to the study of the surface of Titan, different strategies should be considered regarding the nature of the observations: DISR spectrometers on the Huygens probe, VIMS spectro-imager on the Cassini orbiter, or ground-based observations. DISR reflectance spectra cover the spectral range

extending from the UV up to 1.65 μm (Fig. 2). The shape of the reflectance curve is firstly an excellent criteria for discriminating different tholins: YO has a rather constant reflectance level between 1 and 1.65 μm , while this latter continuously increases for BB. The presence/absence of the spectral feature at 1.52 μm is also a good marker of the type of tholins. The spectral slope in the visible and the visible–NIR absolute reflectance levels should also be considered, but only in connection with the other criteria because they also strongly depend on parameters such as the texture and abundance of organic materials at the surface.

For analyzing observations obtained through Titan's atmosphere (VIMS, ground based observations), the ratio between reflectances measured at the center of different atmospheric windows would be particularly useful. We suggest in particular to consider the series of windows with central wavelength ranging between 1.075 and 2.02 μm , which should provide information about the spectral shape and slope of the reflectance spectrum in this spectral region. However distinguishing tholins types through these near-IR ratios may prove to be tricky as other surface materials, such as widespread water ice (Lellouch et al., 2004), may strongly dominate part of the spectrum. The next atmospheric window centered at 2.75 μm should be considered here with care as adsorbed water from ambient atmosphere contributed to the experimental spectra. The last window around 4.95 μm (2020 cm^{-1}) is not useful to distinguish tholins types (Fig. 1) and unfortunately neither the CH_2/CH_3 fundamental bands (3.4–3.5 μm) nor the CN/NC bands (4.48–4.58 μm) are observable through Titan's atmosphere. The UV–visible spectral range and the very near-IR (especially up to about 1 μm) should also be used with great caution, regarding the large uncertainty currently affecting the derived surface albedo due to the yet ill-known scattering contribution by atmospheric aerosols to the reflected flux. However the situation should strongly improve with the new atmospheric and aerosol observations of Titan by the Huygens probe instruments, especially DISR. The much better modeling of aerosol scattering and CH_4 absorption that will ensue should allow us to extract from the windows a series of segments of the surface spectrum. This will open the possibility to probe the visible slope and some of the near-IR bands occurring in YO tholins type, especially the 1.05 and 1.52 μm bands as well as the wing of the 1.99 μm band (Fig. 2). The bands or spectral slopes extracted from each of these narrow windows will also help to differentiate between tholins-like and other types of surface materials (ices, minerals, etc.). The wide 2.75 μm window may also prove to be useful (Coustenis et al., 2006) but laboratory spectra of tholins in controlled dry atmosphere should be recorded before.

4. Conclusions

Titan's tholins are used as analogs of Titan's aerosols and N-rich organic solids present on many icy surfaces. However, it is not clear whether or not they are relevant analogs, and which kind of tholins should be used among a wide set available in literature. This paper presents reflectance spectral data of two

tholins selected as end-members of a series of samples covering a very wide range of continuous chemical and optical properties. These samples were formed under experimental conditions fairly consistent with Titan's stratosphere. A general framework for using these laboratory data to the analysis of spectral observation of Titan's surface or other objects is suggested. Note that these samples have been used for performing the preliminary analysis of the DISR spectra of Titan's surface (Tomasko et al., 2005).

Furthermore, the study reports the first reliable in situ unambiguous identification of aromatics compounds through Raman spectroscopy. Variations in the sp^2 carbon structure among both samples, which controls the absorption properties in the visible/NIR, are also evidenced. This is the first attempt in using UV Raman spectroscopy for investigating these samples. These results finally point out it is very unlikely to derive quantitative chemical information (e.g., N content, sp^2/sp^3 ratio) from remote sensing reflectance data.

Acknowledgments

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