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John R. Brucato, Alessandra Migliorini, Maria Antonella Barucci, Jorge M. Carvano, Elisabetta Dotto, et al.. Reflectance spectra of Titan tholin between 7000 and 10 cm-1. Interpretation of Cassini/CIRS observation of Saturn's satellite Phoebe. *Astronomy and Astrophysics - A&A*, 2010, 516, pp.92. 10.1051/0004-6361/200912054 . hal-03786202

HAL Id: hal-03786202

<https://hal.science/hal-03786202v1>

Submitted on 1 Oct 2022

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Reflectance spectra of Titan tholin between 7000 and 10 cm^{-1}

Interpretation of Cassini/CIRS observation of Saturn's satellite Phoebe

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Received 12 March 2009 / Accepted 29 March 2010

ABSTRACT

Context. Laboratory experiments provide a great support to astronomical studies in that they are the most suited technique to reproduce, model and interpret the observational data.

Aims. We investigate the spectroscopic properties of particulate and flat slab of tholin samples in a wide MIR and FIR spectral range at cryogenic temperature to contribute to the interpretation of the observation of Saturn satellite Phoebe obtained with the Cassini CIRS instrument.

Methods. Reflectance spectra of Titan tholin were obtained in the 7000–10 cm^{-1} spectral region by a Fourier transform spectrometer operating in vacuum. Several optical setups were used to cover this wide spectral range. Specular and diffuse reflectance spectra were obtained. A cryostat was interfaced to the spectrometer for reflectance measurements at low temperatures. It was cooled by a continuum flux of cryogenic fluid from about 300 to 72 K.

Results. It is shown that powder and slab tholin have a different reflectance that depends on geometrical factors and wavelength ranges. The emissivity of Phoebe is reproduced by flat slab tholin covered by a thin layer of water ice.

Conclusions. A considerable amount of compact smooth millimeter-size carbonaceous compounds are present on the Phoebe satellite covered with water ice and tholin regolith. This confirms a surface highly processed by small object impacts and a peculiar nature of Phoebe with respect to other Saturn satellites. It could be a primitive Kuiper belt object captured by Saturn that contains an high amount of HCN-like polymers active in prebiotic chemistry.

Key words. methods: laboratory – techniques: spectroscopic – planets and satellites: general – planetary systems

1. Introduction

The Cassini-Huygens space mission, designed to deeply study the Saturnian system, is composed of 12 instruments on board the Cassini probe and six on the Huygens lander. The Composite InfraRed Spectrometer (CIRS) was designed to study the atmospheres of Saturn and its major satellite Titan and the emission properties of Saturn's icy satellites. Surface properties of Phoebe, Iapetus, Enceladus, Tethys and Hyperion were studied through CIRS observations (Spencer et al. 2006; Flasar et al. 2005) and the absence of spectral features were modeled by three different kinds of surface textures and materials: icy particles with large grains, mixtures of ices and dark materials or, finally, by small particles with large porosity (Carvano et al. 2007). A wide characterization of these satellites were also performed by the Visual and Infrared spectrometer (VIMS) on board Cassini and by ground observations, showing that all the surfaces are covered by water ice mixed with dark absorbing carbon-based materials like amorphous carbon, aromatic hydrocarbons, nitrogen-rich organic compounds and tholin (Clark et al. 2005; Cruikshank et al. 2005; Emery et al. 2005; Brown et al. 2006; Buratti et al. 2008). Observing that the emissivity spectra of all materials analyzed (water ice, tholin, amorphous carbon and montmorillonite) become featureless for high

porosity, it was concluded that the satellite surfaces are dominated by small particles and that the porosity of the surfaces is large (Carvano et al. 2007).

To interpret new CIRS data in a wider spectral range, new laboratory studies are required. Indeed, optical constants, necessary to model the spectroscopic properties of surfaces, are not available in the literature at the wavelengths of interest. Moreover, because Saturn's satellites' temperatures vary from 70 to 140 K, laboratory spectra at low temperatures are also needed. These cold surfaces are dominated by scattered sunlight in the visible near-infrared (Vis-NIR) spectral region up to 5 μm and by their thermal emission for larger wavelengths. In the mid-infrared (MIR) spectral range ices, carbonaceous materials and silicates show diagnostic features, which can be used to infer surface composition and roughness. Furthermore, spectra in the far-infrared (FIR) region depend on the surface temperature of the Solar System bodies and can be used to derive further information about the nature of the surfaces.

Tholin is a carbonaceous material, obtained as refractory residue after laboratory processing of gasses or ices containing hydrocarbons and nitrogen-based compounds (for details about tholin production see Bernard et al. 2003). This material has been largely investigated in the laboratory for its importance for planetary studies. It is widely accepted that tholin is a good

analog of Titan aerosols and of N-rich solids present on many Solar System icy bodies, because it adequately reproduces colors of surfaces and the spectral behavior of atmospheres. Differences in production methods are responsible for many types of tholins synthesized in the laboratory. Tholins poor in nitrile compounds are good analogs of material present on Triton (Khare et al. 1989) and, on the reverse, if a large amount of this compound is present, the so-called Titan tholin is synthesized (Bernard et al. 2003; Khare et al. 1986). Tholins have been detected as one of the major compounds on the surface of Titan (McKay et al. 2001; McCord et al. 2006), where a complex ion-neutral chemistry was discovered as the mechanism responsible for the synthesis of complex hydrocarbon molecules in its atmosphere (Waite et al. 2007). Recently, during the Cassini flyby encounter with Titan, the Ion Neutral Mass Spectrometer (INMS) instrument mapped the chemical composition of the Titan atmosphere between 950 and 1150 km altitude with unprecedented precision (Waite et al. 2007). The data showed that N_2 and CH_4 molecules, accompanied by a rich mixture of hydrocarbon-nitrile compounds, dominate the atmosphere. The molecular densities of N_2 and CH_4 were observed to vary from 0.975 and 0.0127 cm^{-3} at 1000 km to 0.965 and 0.0241 cm^{-3} at 950 km, respectively and, in particular, negative ions were discovered to play an important role in tholin formation. Complex chemical reactions thus occur at high altitude between methane and nitrogen molecules driven by the energy supply from UV photons and ion particles from Saturn magnetosphere that are responsible for the synthesis of tholin.

Tholins are also supposed to be abundant in the outer Solar System. Their presence has been hypothesized on the surface of Triton (Khare et al. 1989), asteroids (Fink et al. 1992), Jupiter Trojans (Dotto et al. 2008, and references therein), Centaurs and Trans-Neptunian Objects (Barucci et al. 2008, and references therein). Reflectance and transmittance spectra of tholins have been acquired in the laboratory from UV to NIR, and optical constants of Titan tholin were derived from soft X-ray to microwaves frequencies (Khare et al. 1984, 1993). However, spectroscopic data are poor in the FIR spectral range and especially reflectance spectra in the wavelengths covered by the CIRS instrument are missing. In the following sections specular and diffuse reflectances of Titan tholin from 7000 to 10 cm^{-1} ($1.4\text{ }\mu\text{m}$ – 1 mm) are derived and finally, a comparison between laboratory and CIRS data are studied.

2. Experimental

Titan tholins were produced from a $N_2:CH_4 = 98\%:2\%$ gaseous mixture exposed inside a reactor to an electric discharge in an open gas flow system and were provided to us by *Laboratoire Inter-Universitaire des Systemes Atmospheriques – Creteil, France*. The experimental set-up and procedures used to prepare tholin samples are described by Coll et al. (2001) and Bernard et al. (2003). Chemical and physical properties of tholins, synthesized varying the initial CH_4/N_2 gas pressure and mixtures, were investigated systematically in a laboratory by Imanaka et al. (2004). Concerning the spectroscopic properties, the ratio of aliphatic C-H to N-H bonds was observed by Imanaka et al. (2004) to increase only slightly with the increase of CH_4 ratio in the initial gas mixture and also the spectroscopic properties in the UV/Vis range do not change significantly. Thus the optical properties of tholin do not depend on the CH_4/N_2 initial mixing ratio deposition. Rather they depend on initial gas pressure (Cruikshank et al. 2005). This result allows us to easily combine the results of this work with those obtained by other authors by

using tholins that are produced under slightly different experimental conditions.

In this work reflectance spectra were obtained in the widest spectral region possible (7000 – 10 cm^{-1} ; 1.43 – $1000\text{ }\mu\text{m}$) by a Fourier transform spectrometer (Bruker IFS 66v) operating at a pressure of 1 mbar to reduce air absorption. Several optical setups of the spectrophotometer were used to cover the whole spectral range. A mercury lamp, four mylar beamsplitters with thicknesses ranging from $6\text{ }\mu\text{m}$ to $125\text{ }\mu\text{m}$, a deuterated triglycine sulfate thermal element with a polyethylene window, and a Si bolometer were used for the FIR-mm spectral region. The bolometer, equipped with a cold low-pass filter (cut-off = $200\text{ }\mu\text{m}$), was operated at 1.4 K by pumping a liquid helium bath in a Dewar mounted on an external port of the spectrometer with a polyethylene window. In each spectral range the spectra were derived by the standard fast Fourier transform technique from interferograms obtained by co-adding several scans. Specular and diffuse reflectance spectra were obtained using two different optical geometries. The A-510 Bruker accessory was used for specular bidirectional reflectance measurements with an aperture angle between incident and reflected beam of 11° . Diffuse reflectance measurements were obtained by equipping the spectrometer with a Graseby Specac Mod. Selector accessory. The optical configuration used was biconical, i.e. the infrared beam was focused onto the sample by means of an ellipsoidal mirror and collected by another ellipsoidal mirror, at 90° from the incident beam inside a light cone of 30° wide. This configuration has the advantage of a very high collection efficiency and it is appropriate for accurate determination of the reflectance profile by measuring diffuse reflectance at 90° with respect to the principal plane. This experimental set-up prevents possible distortion of the Christiansen feature, due to preferential forward scattering, which can occur when biconical reflectance is measured in the principal plane.

The tholin powder has a granular structure with irregular shapes showing sizes that range from a few micrometers up to about one millimeter. Powder tholin was used for the diffuse reflectance measurements. Tholin pressed at 10 tons in vacuum was used to produce compact slab samples for specular reflectance measurements. Reference spectra for biconical reflectance were acquired of cesium iodide and polyethylene powder in MIR and FIR ranges, respectively, while a slab of optically polished gold was used as reference for bidirectional reflectance spectra. A cryostat was interfaced to the spectrometer through the A-510 accessory for reflectance measurements at low temperatures. It was cooled by a continuum flux of cryogenic fluid. For the purpose of this study, liquid nitrogen was used as the coolant obtaining temperatures ranging from about 300 to 72 K. The specular reflectances at low temperatures were acquired in the spectral range 400 – 7000 cm^{-1} . Spectral resolution was chosen to vary from 0.5 cm^{-1} in the FIR, up to 1 cm^{-1} in the MIR range. The overlap between the spectral ranges resulting from each optical configuration allowed the corresponding spectra to be reliably knitted together into a single spectrum. Finally, a thin layer of water ice was accreted onto the flat tholin sample in thermal contact with a cold finger. Water vapor was prepared in a pre-chamber and admitted by a gas inlet through a needle valve into the cold finger chamber. Vacuum pressure inside the chamber was 10^{-6} mbar and the temperature of the sample was maintained at $72 \pm 0.1\text{ K}$. This pressure is sufficiently low to avoid any spurious deposit on the cold sample of environmental water or gaseous contaminant during the experimental time. The specular bidirectional reflectance at 11° was then acquired in the range 10 – 600 cm^{-1} with the A-510 Bruker accessory.

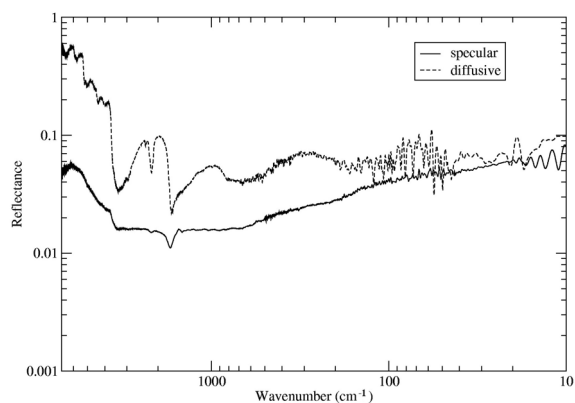


Fig. 1. Diffuse (dashed line) and specular (continuum line) biconical reflectance spectra of tholin.

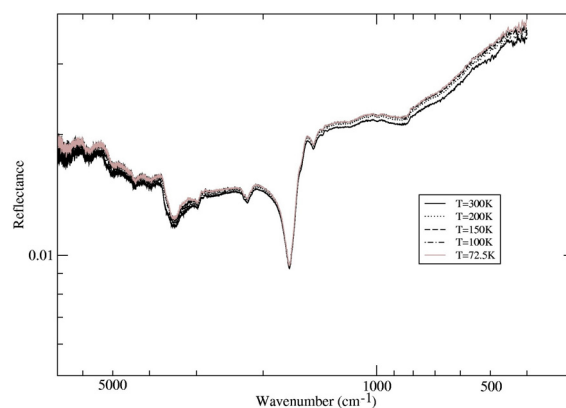


Fig. 2. Bidirectional reflectance spectra of tholin pellet sample at temperatures of 300, 200, 150, 100 and 72.5 K.

3. Results

The diffuse and specular reflectance spectra of tholin are reported in Fig. 1. From the figure it is evident that at wavenumbers larger than 4000 cm⁻¹ the diffuse reflectance is about 10 times higher than the specular reflectance. This is a common phenomenon due to differences between multiple scattering of light occurring inside the volume of a particulate sample and the reflection of light taking place on a flat surface (Hapke 1981; Salisbury & Estes 1985). At wavelength ranges between and adjacent to the strong molecular absorption bands (≤ 4000 , 2500–1860, 1200–800, 450–160 cm⁻¹), the absorption coefficient of light decreases. Thus the light is no longer strongly absorbed and it may cross a larger number of grains. If the grain size is comparable to or larger than the wavelength, the light will be scattered. As a consequence, the reflectance intensity measured between and adjacent to the molecular bands enhances and the bands become deeper. On the other hand, at lower wavenumbers (or larger wavelengths) the intensity of diffuse reflectance decreases. At these wavenumbers the multiple scattering actually diminishes because the number of particles with a size comparable to or larger than the wavelength of light are less abundant (for a better discussion see Moersch & Christensen 1995). The differences between powder and bulk samples are thus less pronounced than observed in Fig. 1 at wavenumbers lower than about 150 cm⁻¹.

The reduced band contrast that is observed in specular reflectance spectrum at wavenumbers larger than 1000 cm⁻¹ is mainly due to the absence of multiple scattering of light that usually occurs within the powder. The single reflection of IR radiation on the flat surface is responsible for reduced absorption feature intensities of 1685 (–NH bending), 2170 (–NCO stretching), 2950 (–CH stretching), and 3400 cm⁻¹ (–OH and/or NH stretching) functional groups and the difference in intensity between diffuse and specular reflectance decreases at lower wavenumbers until it becomes negligible for wavenumbers lower than 150 cm⁻¹.

The diffuse reflectance spectrum shows a series of weaker features observed at 3982, 4377, 5030, 5210, 5750 and 6590 cm⁻¹ that are due to combination and overtone bands. At lower wavenumbers the spectrum is going to be more noisy due to the very low signal detected for the powder sample. However, the two spectra follow different spectral slopes at wavenumbers ≤ 600 cm⁻¹ that approach the same albedo of 0.08 at about 10 cm⁻¹. At these wavenumbers no diagnostic spectral band is observed. The extremely low imaginary part of the reflective

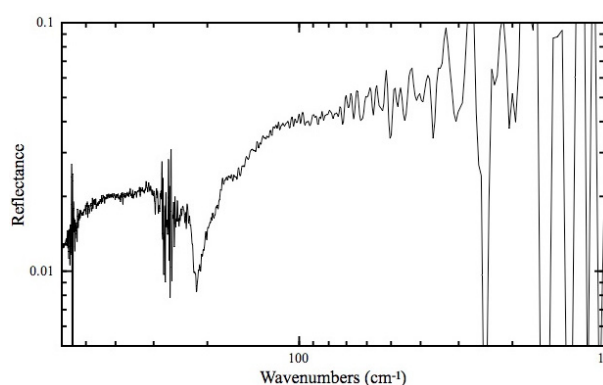


Fig. 3. Bidirectional reflectance spectra of the tholin pellet with a thin coating of water ice at temperatures of 72 K.

index and the sample thickness of 1.3 mm are responsible for the interference observed in the specular reflectance at wavenumbers ≤ 10 cm⁻¹. However, the reflectance measured for powder sample in the near-infrared is similar to that obtained at NASA-AMES in terms of intensity of reflected light and features observed (Roush & Dalton 2004). This might be related to a similar sample nature and optical configuration used.

Bidirectional reflectance spectra of a tholin pellet sample at temperatures of 300, 200, 150, 100 and 72.5 K are reported in Fig. 2. It is evident from the figure how the reflectance increases at lower temperatures with an overall variation of about 5% in the whole range 300–72.5 K. At 72.5 K the features at about 3400 cm⁻¹ become narrower and those at 2950 and 5030 cm⁻¹ increase in intensity by about 3%. The absorption features become slightly intense and sharpen with decreasing temperature.

The spectrum of flat tholin overlaid with a thin coating of water ice acquired from 10 to 600 cm⁻¹ is shown in Fig. 3. The wide absorption band between 300 and 600 cm⁻¹ and centered at 220 cm⁻¹ is due to the water ice layer. The observed spectrum is the result of the combination of two fraction of IR radiation: the one that is reflected at the ice/vacuum interface and that which is unreflected and crosses the ice, is attenuated by the ice absorption, is reflected at the second interface ice/tholin, again crosses the ice, once more is attenuated and again emerges. Thus the spectrum in Fig. 3 can be seen as the IR reflectance of the tholin slab diminished by the multiple absorption by the overlaid water ice layer.

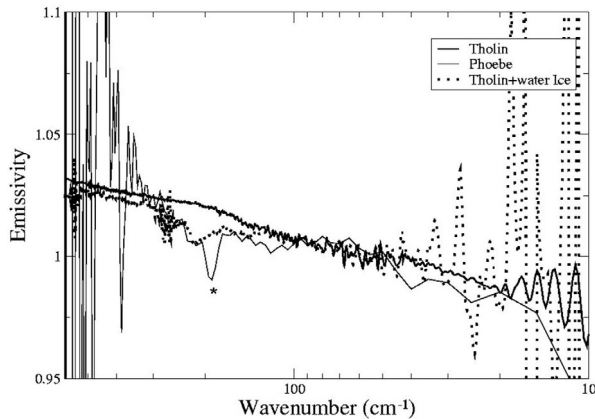


Fig. 4. Comparison of emissivity spectra of Phoebe obtained by CIRS (Carvano et al. 2007) and that of a flat tholin sample covered by thin layer of water ice. The spectra are normalized at 100 cm^{-1} , the feature at about 220 cm^{-1} is due to absorption of water ice. The electronic spike at 190 cm^{-1} is marked with an asterisk.

4. Phoebe

The emissivity in the thermal infrared spectrum of the icy satellites of Saturn (Phoebe, Iapetus, Enceladus, Tethys, and Hyperion) observed by the Composite Infrared Spectrometer (CIRS) on board the Cassini spacecraft were previously analyzed (Carvano et al. 2007). Emissivity spectra were arbitrarily normalized at 100 cm^{-1} and they are characterized by a large noise at wavenumbers $\geq 300\text{ cm}^{-1}$ and by a sudden intensity decrease at 50 cm^{-1} for Iapetus, at 60 cm^{-1} for Enceladus and Tethys, and at 70 cm^{-1} for Hyperion. This occurrence could be due to a mismatching in the procedure of blackbody removal from the thermal emission spectra of the satellites. Phoebe is the only case in which this inconvenience does not occur, giving rise to an emissivity spectrum extending down to smaller wavenumbers.

The emissivity E of the laboratory samples was derived via Kirchhoff's law from the diffuse reflectance R as $E = 1 - R$. Phoebe's emission spectrum and that calculated for tholins were normalized at 100 cm^{-1} and compared. As is clear from Fig. 4, the emissivity of the Phoebe satellite measured by CIRS is well reproduced by that of flat tholin sample all over the spectral range. The emissivity of powder tholin does not match the Phoebe spectrum and hence is not reported in the figure. The spectroscopic behavior observed in this wavelengths range is compatible with a surface of Phoebe dominated by a smooth and compact terrain with composition similar to that of Titan tholin. Observations obtained at a shorter wavelength with the VIMS instrument on the other hand show that the surface spectra are best fitted by tholin grain sizes on the order of hundreds of micrometers (Buratti et al. 2008). In that case the authors found that Triton tholin is the most representative sample composition to match the Phoebe spectrum and that no good fit is found using Titan tholin. Two results seem in contradiction even if they have to be seen in strict relationship with the spectral regions of the investigation and with the spectroscopic properties of material at those wavelengths. What we are observing spectroscopically in the FIR-mm region is the dominance of flat tholin with respect to a particulate sample which is made, in our experimental conditions, by a large collection of grains with micrometer sizes. The physical conditions present on Phoebe could be seen as a surface made of compact bulk material covered by a fraction of tholin regolith and water ice. If the fraction of grains that is responsible for the bands observed in the NIR has sizes of hundreds

micrometers, the same fraction of grains will not be sufficient to be seen in the FIR, where the emission of smooth compact tholin dominates. These physical characteristics of Phoebe's surface are probably also responsible for the band profile observed in Fig. 4 around 220 cm^{-1} that we attribute water ice. The presence of noise in the Phoebe spectrum could, however, affect the profile of the water ice band. A qualitative estimate for water ice and tholin is here derived using experimental data.

As explained previously, the spectra of tholin and water ice obtained experimentally are a linear combination of the tholin reflectance and water ice absorption. In Phoebe's spectrum shown in Fig. 4 the band profile at 220 cm^{-1} resembles that of pure absorbance instead of emittance of water ice. Thus a pure inversion of the spectrum in Fig. 3 through Kirchhoff's law would produce a peak at 220 cm^{-1} instead of a valley and the observed Phoebe's spectrum would not be reproduced. Optically this could be related to the value of the complex refractive index of water ice (Hudgins et al. 1993). Using the Fresnel formulas we can calculate the reflection and transmission of light from a slab, thus it is possible to evaluate that transmission at 220 cm^{-1} from water ice is two orders of magnitude larger than reflection on the ice surface. Thus the absorption feature at 220 cm^{-1} could be attributed to water ice both embedded at the molecular level in a matrix of tholin grains settled on a smooth compact tholin surface or to water ice that covers the satellite surface as a thin layer. In Fig. 4 we compared the Phoebe spectrum with that obtained in laboratory. Specifically, the water ice spectrum in absorption was linearly added to the emission of flat tholin and the resulting spectrum scaled manually to match the 220 cm^{-1} band on Phoebe. As is clear from Fig. 4 the Phoebe spectrum is well reproduced by the laboratory one. This result is telling us that the infrared radiation emitted by Phoebe from a surface made by smooth tholin is absorbed by water ice present or in the small transparent grains or as a coating layer. The band observed at 190 cm^{-1} and marked in Fig. 4 with an asterisk is due to a spurious electronic spike (Carvano et al. 2007). Changes induced in laboratory spectra by temperature variations were observed to be negligible when compared to the uncertainties of CIRS data.

The slope of the emissivity spectrum of Phoebe is thus compatible with the emissivity spectrum of Titan tholin slabs, but not with spectrum of the particulate sample. Buratti et al. (2008), using data in the visible and NIR obtained with the VIMS instrument on board the Cassini spacecraft, found that the best-fit models for Phoebe included Triton tholins, and no good fits with Titan tholins could be found. However, Triton and Titan tholins are HCN-like polymers with slightly different nitrogen content that affects the band profiles in the NIR-MIR, but does not have any remarkable influence at larger wavelengths where the spectroscopic behavior is dependent only on the structure of materials. Therefore it is reasonable to expect that the overall slope trend seen in the emissivity spectrum would be also compatible with Triton tholins.

The emissivity of the icy saturnian moons was analyzed also by Carvano et al. (2007). The authors suggested that the absence of emissivity features in the CIRS spectra of icy moons – in particular of water ice features in ice-dominated moons – could be explained (and be compatible with the NIR spectra of those moons) if we assume a very high porosity for the ice in the surface of the moons. An other intriguing characteristic of the emissivity spectra of the icy moons was the drop in emissivity at wave numbers smaller than 50 cm^{-1} . Although the causes of this behavior are unclear, the fact that this drop is much less pronounced for Phoebe, whose NIR spectrum is dominated by

organic compounds, is interesting. It suggests that the drop in the emissivity of the other moons may be related to the predominance of water ice in their surfaces. On the other hand, the results presented here indicate that the emissivity spectrum of Phoebe could be explained by the predominance of tholins in large particles – which would be compatible with one of the models proposed by Buratti et al. (2008) – or even as smooth crust.

5. Conclusions

The spectra of tholin have been obtained in a new wide spectral range from 7000 to 10 cm⁻¹. The tholin samples were studied in two different geometrical configurations, diffuse and specular biconical reflectance. Tholin features are observed on both spectra, with enhanced spectral contrast for the case of diffuse reflectance. In the mid-infrared the powder sample shows a reflectance ten times larger than the smooth surface, indicating that this spectral range is dominated by a scattering of small micron-size particles. At shorter wavenumbers this difference is diminishing and both reflectances approach the same albedo of about 0.08 at 10 cm⁻¹, indicating that this spectral range is dominated by a scattering of large millimeter-size grains. We also verified that the spectral behavior of tholin varies in the mid-infrared by only a small percentage with temperatures between 300 and 72.5 K.

The specular bidirectional reflectance spectrum of tholin coated with water ice layer was also obtained. The comparison between the CIRS spectrum and laboratory data shows an absorption feature at about 220 cm⁻¹ that is interpreted as water ice embedded at molecular level in the tholin or coating the surface as thin layer. The slope of the emissivity spectrum of Phoebe matches with that of the specular reflectance of flat tholin sample inverted to emissivity. This suggests that a considerable amount of smooth, compact millimeter-size or even larger carbonaceous compounds are present on Phoebe's surface. On the other hand, the data obtained with VIMS instrument at smaller wavelengths (Buratti et al. 2008) indicate that a fraction of tiny grains hundreds of micrometer in size overlays a smooth surface. Phoebe could thus be a primitive Kuiper belt object captured by Saturn, that contains a high amount of HCN-like polymers organized in a compact "crust" and small grains.

These results agree with the experimental data obtained by Strazzulla (1986) that showed on the basis of ion-irradiation experiments that the outer layers of Phoebe's surface would be carbonized by the cosmic protons, giving rise to a kind of organic crust. Moreover, meteorite impacts on Phoebe would lead to the ejection of material from deeper layers, like water ice, which could re-condense on the surface.

Tholins exhibit similarities with HCN polymers, which are suspected to be present also in cometary refractory dust (Quirico et al. 2008). Tholin composition produced at different pressures and compositions was intensively investigated by Imanaka et al. (2004). In our case, the Tholin sample used in this work shows similar chemical composition to that produced by Imanaka et al. (2004) at low pressure (0.13 hPa) and gas ratio N₂:CH₄ = 97.5:2.5. Disordered carbon and nitrogen branched chain networks bonded with hydrogen are found in matrix with clusters of nitrogen-containing polycyclic aromatic compounds (Imanaka et al. 2004) or unalkylated polycyclic aromatic hydrocarbons (PAHs) (Sagan et al. 1993). Tholin contains HCN polymeric forms, also named alzulmin, which are amorphous compounds that can be separated in water-soluble yellow-brown solids and water-insoluble black solids (Saladino et al. 2004). Hence, HCN-polymers contain the chemical information for the

synthesis of nucleic acid bases and have been used as macromolecular precursors of both purine and pyrimidine derivatives upon acidic or basic hydrolysis (Ferris et al. 1966). This material indicates that a polymerization process probably has occurred during Phoebe's history. Thus Phoebe could have experienced physical-chemical conditions able to process materials that are suitable for the synthesis of nucleic acid bases which were used in the form of analogues in laboratory as macromolecular precursors of both purine and pyrimidine derivatives upon acidic or basic hydrolysis (Ferris et al. 1972). These results show Phoebe to be a peculiar object with respect to other Saturn satellites and particularly interesting for the astrobiology.

Finally, the spectroscopic data obtained in this work at these large wavelengths would be useful for the interpretation of spectra that Herschel is going to obtain of solar system objects.

Acknowledgements. Part of this work was supported by *Italian Space Agency, ASI-ESS* project. We would like to thank the research group of *Laboratoire Inter-Universitaire des Systemes Atmospheriques – Creteil, France* who have provided the tholin sample. We also thank J. Emery who has critically improved the quality of the work.

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