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► **To cite this version:**

Sang Kim, Régis Courtin. Spectral characteristics of the Titanian haze at 1–5 micron from Cassini /VIMS solar occultation data. *Astronomy and Astrophysics - A&A*, 2013, 557, pp.L6. 10.1051/0004-6361/201322173 . hal-02527711

HAL Id: hal-02527711

<https://hal.science/hal-02527711>

Submitted on 17 Nov 2022

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LETTER TO THE EDITOR

Spectral characteristics of the Titanian haze at 1–5 micron from *Cassini/VIMS* solar occultation data[★]

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Received 28 June 2013 / Accepted 12 August 2013

ABSTRACT

We retrieved optical-depth spectra of the Titanian haze in the range 1–5 μm from solar occultation data obtained by the *Cassini/Visual Infrared Mapping Spectrometer* (VIMS) at altitudes of 59–502 km. Only limited wavelength intervals within this spectral range have been analyzed before. The haze spectra we retrieved are mostly similar to those of alkane particles (or powders), with three major absorption peaks typical of alkane powders at 2.3, 3.4, and 4.3 μm . This result suggests that at least in the ~60–500 km altitude range, the Titanian haze is mostly composed of alkane particles, possibly with some trace impurities. The absence of the 3.0 and 4.6 μm features excludes the molecules containing NH and CN bonds that are typical of laboratory-made tholins reported in the literature. The alkane-like spectral characteristics of the haze we observed at ~60–500 km differ from previous results obtained at different or overlapping altitudes: a) the presence of aromatic compounds derived from solar-pumped emissions observed at high altitude (600–1250 km) by *Cassini/VIMS* near 3.3 μm ; and b) the detection of HCN and NH₃ in the cores of haze particles collected at low altitude (20–130 km) by the *Huygens/Aerosol Collector and Pyrolyser* (ACP). We suggest that these different characteristics arise from different structural layers formed by coagulation/coalescence during particle sedimentation.

Key words. planets and satellites: individual: Titan – planets and satellites: atmospheres – planets and satellites: composition – techniques: spectroscopic – radiative transfer – line: identification

1. Introduction

The *Cassini/Visual Infrared Mapping Spectrometer* (VIMS; Brown et al. 2004) generated 63 spectra with unprecedented vertical resolution from 49 to 987 km in the 1–5 μm range by observing the Sun through the atmosphere of Titan on January 15, 2006 (Bellucci et al. 2008; Bellucci et al. 2009). These data provide a unique opportunity of inferring the haze spectral properties because there is no contribution from the surface. These VIMS data were first analyzed (Bellucci et al. 2008; Bellucci et al. 2009) in limited spectral intervals by constructing model spectra including CH₄ and CO lines and assuming that any residual absorption was due to the haze. Analyzing the whole 1–5 μm range is difficult because it requires accurate information on the numerous ro-vibrational lines of the various molecules present in the Titan atmosphere, information that is far from complete, especially at shorter wavelengths.

More recently, the detailed spectral characteristics of the 3.0–3.8 μm haze absorption feature were extracted (Kim et al. 2011) from the same data by subtracting the influence of strong adjacent CH₄ lines and using a radiative transfer code including absorption and scattering by the haze particles as well as absorption and emission by the gas. Later on, the detailed characteristics of the 2–3 μm haze features were retrieved (Sim et al. 2013) with a similar radiative transfer code and a spectral model including the overtone bands ($\Delta\nu = 2$) pertaining to the same haze

constituents as those that give rise to the 3.4 μm feature in their fundamental state ($\Delta\nu = 1$). It was found that the 2–3 μm and 3–3.8 μm VIMS-derived haze features are similar to the absorption of a mixture of CH₄, C₂H₆, C₅H₁₂, CH₃CN, or C₆H₁₂ and C₆H₁₄ ices, which mainly belong to the alkane series. However, most of these molecules are hardly condensed in the stratosphere of Titan, and it was suggested that the observed features may be attributed to ices of heavier hydrocarbons (Kim et al. 2011; Sim et al. 2013).

Detailed descriptions of the *Cassini/VIMS* observations and data reduction were previously given elsewhere (Bellucci 2008; Bellucci et al. 2009). In Fig. 1, we show the VIMS spectra recorded at altitudes between 59 and 502 km that we selected as representative of the vertical characteristics of the whole set.

In this work, we extend our previous analyses (Kim et al. 2011; Sim et al. 2013) to the 1–2 μm and 3.8–5 μm intervals, which enables us to present spectral characteristics of the Titanian haze for the whole 1–5 μm range. We then compare our results with a) the spectral characteristics of laboratory-made tholins reported in the literature (e.g., Khare et al. 1984; Quirico et al. 2008; Gautier et al. 2012); b) those derived from high-altitude (600–1250 km) emission observed by *Cassini/VIMS* (Dinelli et al. 2013; López-Puertas et al. 2013); and c) the low-altitude (20–130 km) results from the *Huygens/Aerosol Collector and Pyrolyser* (ACP; Israël et al. 2005).

2. Radiative transfer modeling

In the 1–2 μm interval, the CH₄ line-by-line parameters become increasingly complicated compared with those at longer

[★] Data contained in Figs. 1 and 2 are only available in electronic form at the CDS via anonymous ftp to cdsarc.u-strasbg.fr (130.79.128.5) or via <http://cdsarc.u-strasbg.fr/viz-bin/qcat?J/A+A/557/L6>

wavelengths, and are therefore poorly documented in the HITRAN (Rothman et al. 2009) and GEISA (Jacquinet-Husson et al. 2008) databases. Although linelists for the 1–2 μm bands of CH_4 have been included in HITRAN and have been used for the analysis of Titan spectra (Bellucci 2008; Bailey et al. 2011), significant discrepancies may remain between these linelists and laboratory data (Sromovsky et al. 2006; Karkoschka & Tomasko 2010). The lack of information on CH_4 weak lines in HITRAN severely limits the derivation of haze opacities from the VIMS spectra. To alleviate this problem, k-distributions derived from laboratory measurements have been traditionally used for radiative transfer calculations not only for the 1–2 μm range, but also shortward of 1 μm (Karkoschka & Tomasko 2010; Irwin et al. 2006; Irwin et al. 2012). In this work, we adopted such a k-distribution (Karkoschka & Tomasko 2010).

For the synthetic spectra in the 2–3.8 μm interval, we adopted results from our previous works (Kim et al. 2005; Seo et al. 2009; Kim et al. 2011; Sim et al. 2013). In addition to weak absorption from CH_4 and its isotopes, absorption from minor species, such as C_2H_2 , HCN, CO_2 , and CO is expected to occur between 3.8 and 5 μm (Baines et al. 2006). Among these molecules, the influence of C_2H_2 and HCN on the VIMS spectra is found to be negligible, at least within the error bars. We used the HITRAN2008 database for the CO_2 and CO linelists. An unidentified feature near 4.3 μm was previously reported (Bellucci et al. 2009). We found that most of that feature can be attributed to the $\nu_3+\nu_6$ band of C_2H_6 (Brown, 2012, priv. comm.), but unfortunately, this band has not been updated since 1949 (Brown, 2012, priv. comm.; Smith et al. 1949). The type and structure of this band are the same as those of the C_2H_6 band at 2.94 μm , which were previously established for an analysis of high-resolution ($R \sim 20\,000$) spectra of Titan (Seo et al. 2009). This 2.94 μm band was simply shifted to 4.3 μm and assigned the appropriate band intensity (Pierson et al. 1956); such a simple procedure may be justified for the analysis of low spectral resolution data such as the VIMS data.

To synthesize the 1–5 μm absorption of the gaseous constituents, we used a modified version of the radiative transfer code and spherical-shell models that we previously applied to the analysis of the 2–3.8 μm VIMS data (Kim et al. 2011; Sim et al. 2013), along with the same temperature-pressure profile and vertical distributions. The radiative transfer code includes the radiative and collisional excitation and de-excitation of the above molecules, and the effects of anisotropic scattering (in the two-stream approximation) and absorption by haze particles. The haze optical depth (τ_h) is treated as the only adjustable parameter – with some constraints based on the DISR *Huygens* probe investigation (Tomasko et al. 2008) – to be determined by model comparison with the VIMS data, as previously described (Kim et al. 2011; Sim et al. 2013; Seo et al. 2009). We also took into account the refractive attenuation of light from dense atmospheric layers at the lowest altitudes, as discussed previously by Bellucci et al. (2009).

3. Results and discussion

In Fig. 1a, we compare the synthetic spectra computed in the 1–2 μm range with the VIMS spectra at the selected altitudes of 59, 115, 177, 217, 272, 315, 360, 390, and 502 km. In this comparison, we only focus on continuum fits because the k-distribution CH_4 models are known to be significantly more accurate than line-by-line models in the continuum (Sromovsky et al. 2006; Karkoschka & Tomasko 2010). However, k-distribution models for the $\Delta\nu = 3, 4,$ and 5 bands of

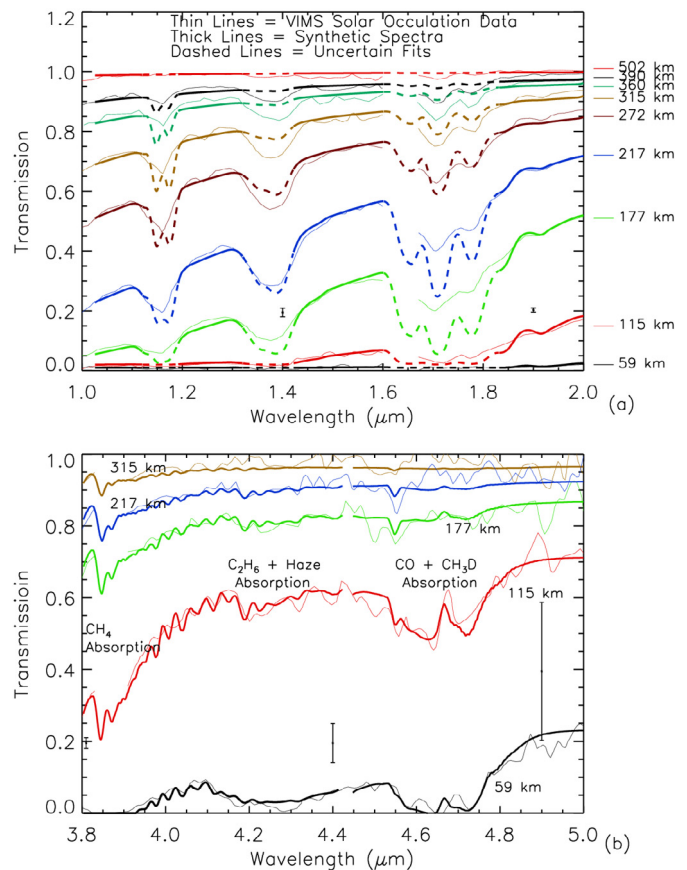


Fig. 1. Comparison between synthetic spectra and the VIMS spectra. **a)** In the 1–2 μm range for the selected altitudes of 59, 115, 177, 217, and 315 km. Wavelength intervals in which the model fits are not satisfactory are shown by dashed lines; they correspond to the centers of the $\Delta\nu = 3, 4,$ and 5 bands of CH_4 near 1.7, 1.4, and 1.2 μm . **b)** In the 3.8–5 μm range at the selected altitudes of 59, 115, 177, 217, and 315 km. The synthetic spectra include the influence of CH_4 , CH_3D , C_2H_6 , CO_2 , CO, and haze absorption and scattering. The $\pm 2\sigma$ error bars for the 1–1.6, 1.8–2, 3.8–4.8, and 4.8–5 μm intervals of the VIMS spectra are adopted from Bellucci et al. (2009).

CH_4 near 1.2, 1.4, and 1.7 μm show too much absorption in the band centers at low altitude (dashed lines in Fig. 1a). Similarly, we found that k-distribution models predict this over-absorption around 3.5 μm at low altitude, compared with calculations using the HITRAN2008 CH_4 linelist, in which most of the lines were rigorously checked against measurements (Brown et al. 2003). Therefore, we attributed the discrepancies in the 1–2 μm range to the inaccuracy of the present k-distribution models, and excluded the spectral intervals with poor fits from our results. We look forward to seeing improved CH_4 linelists for these bands in the future.

For the detailed model fits to the VIMS data in the 2–3.8 μm range, we refer to our previous works (Kim et al. 2011; Sim et al. 2013). In Fig. 1b, we compare the synthetic spectra computed in the 3.8–5 μm range with the VIMS spectra at the selected altitudes of 59, 115, 177, 217, and 315 km. The unidentified feature previously reported by Bellucci et al. (2009) near 4.3 μm is now mostly explained by the $\nu_3+\nu_6$ band absorption of C_2H_6 , although additional haze absorption is needed to fill in that feature at the altitudes of 59 and 115 km.

In Fig. 2a, we present the derived τ -spectra for the haze along with the spectra of tholins available from the literature (Khare et al. 1984; Quirico et al. 2008; Gautier et al. 2012). In

the 315–502 km range, the derived τ -spectra are largely similar, and the spectra derived in that range are omitted for clarity. The steep slope of the derived τ -spectra in the 1.0–1.6 μm range is consistent with the results on the haze optical depth from the Descent Imager/Spectral Radiometer instrument onboard the *Huygens* probe (Tomasko et al. 2008). The slope is not an intrinsic spectral property of the haze but rather a size-related effect, since the optical depth in the Mie regime should increase with decreasing wavelengths as long as the particle size remains small compared with the wavelength. From this comparison it is immediately clear that there are two significant discrepancies near 3.0 and 4.6 μm . The 3.0- μm feature in the tholins spectra is due to primary (–NH) and secondary amine (–NH₂) functional groups, whereas that at 4.6 μm can be attributed to nitrile (–CN) or isocyanide (–NC) functional groups (Gautier et al. 2012). Obviously, none of these features is apparent in the haze τ -spectra, suggesting the absence of these functional groups in the Titanian haze material.

In Fig. 2b, we compare the spectral properties of heavy alkanes in the ice phase (Clark et al. 2009), such as C₆H₁₄ (hexane), C₁₀H₂₂ (decane), and C₂₀₊H₄₂₊ (paraffin), with the τ -spectra at the selected altitudes of 59, 115, 217, and 315 km. The laboratory spectra of C₆H₁₄ ice were measured both in transmission and reflection, but that of C₁₀H₂₂ and C₂₀₊H₄₂₊ were only measured in reflection (Clark et al. 2009). Here, we derived a scaling factor from a comparison between the transmission and reflection spectra of the C₆H₁₄ ice, and applied this scaling to the C₁₀H₂₂ and C₂₀₊H₄₂₊ spectra. Thus, the absolute scale of the resulting optical depth spectra may not be very accurate. Nevertheless, Fig. 2b clearly shows that the three distinctive features of the haze τ -spectra at 2.3, 3.4, and 4.3 μm satisfactorily match the corresponding spectral peaks of the alkane powders. Furthermore, the gross structure of these features is roughly matched, but some of the less prominent features of alkane ices, for instance at 2.75, 3.1, and 3.4–3.9 μm , are not seen in the haze τ -spectra. In the 59 km τ -spectrum, an unidentified feature occurs at 2.65 μm (marked by ?), which does not match the alkane spectra, suggesting possible impurities in the haze particles at low altitude. Clearly, we need additional *absorption* spectra of heavy alkane powders for a more accurate comparison with the τ -spectra of the Titanian haze.

Recently, Dinelli et al. (2013) and López-Puertas et al. (2013) have attributed a daytime emission feature observed at 3.28 μm in *Cassini*/VIMS limb spectra to aromatic hydrocarbons contained in the haze at altitudes of 600–1250 km (with a maximum around 950 km). The predominant absorption by heavy alkane ices at ~60–500 km altitude in the 1–5 μm VIMS solar occultation spectra seems at odds with their results. Typical aromatic hydrocarbons have a strong band at 3.3 μm , whereas the C–H stretch bands of aliphatic hydrocarbons peak around 3.4 μm (e.g., d’Hendecourt & Allamandola 1986; Pendleton & Allamandola 2002). Analyzing the 3–4 μm range of the VIMS solar occultation spectra between 130–300 km altitudes, Kim et al. (2011) previously showed that a haze absorption band occurs at 3.33–3.37 μm , which lies approximately between the typical 3.3 μm aromatic or 3.4 μm aliphatic C–H stretch bands of hydrocarbons. These authors also stated that above 300 km the VIMS data start to show a more prominent feature near 3.3 μm that coincides with that of aromatic organic molecules. Above 500 km, however, the VIMS data are much less sensitive to haze absorption, and detailed spectral characteristics cannot be accurately retrieved. Because the two observations probe different altitude regions, they may still be reconciled by assuming that the alkane ices are the result of condensation processes on existing

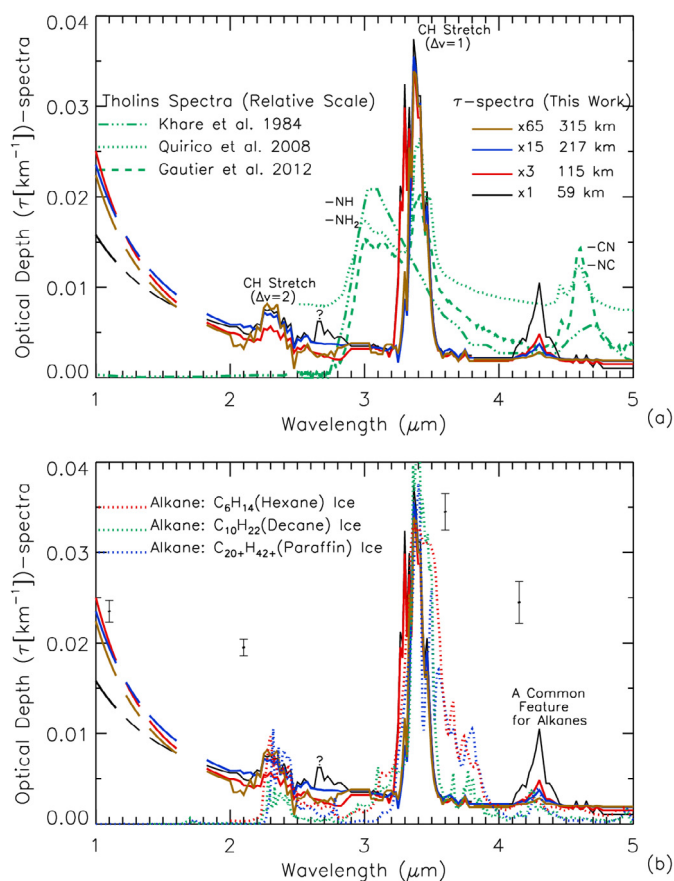


Fig. 2. Comparison between the derived haze τ -spectra (at the selected altitudes of 59, 115, 217, and 315 km) and the spectra of **a)** tholins and **b)** alkane ices. Between 1 and 2 μm , we discarded the wavelength intervals (shown as dashed lines in Fig. 1a) in which the τ -spectra are most uncertain. **a)** The tholin spectra are adopted from the literature (Khare et al. 1984; Quirico et al. 2008; Gautier et al. 2012). **b)** Spectra measured (Clark et al. 2009) for the alkane powders C₆H₁₄ (hexane), C₁₀H₂₂ (decane), and C₂₀₊H₄₂₊ (paraffin) provide a satisfactory fit to the three major peaks of the haze τ -spectra at 2.3, 3.4, and 4.3 μm . The $\pm 1\sigma$ error bars for the 1–1.6, 1.8–3, 3–3.9, and 3.9–4.8 μm intervals of the τ -spectra are shown.

nuclei made of aromatic hydrocarbons that sediment from the upper atmosphere.

The predominance of alkanes at the ~60–500 km levels also seems inconsistent with the results from the *Huygens*/ACP in the 20–130 km range, where NH₃ and HCN were identified as the main pyrolysis products (Israel et al. 2005). Because NH₃ and HCN were not detected by the *Huygens*/Gas Chromatograph Mass Spectrometer (GCMS), Israel et al. (2005) concluded that both molecules indicate a solid organic refractory core in the Titanian haze. Kim et al. (2011) found that below 127 km level the haze spectra show an enhanced 3.3 μm feature, that also coincides with the absorption band of a nitrogen-containing ice, CH₃CN. However, as shown in Fig. 2b, the τ -spectra at 59 and 115 km do not show any obvious nitrogen signature near 3.0 and 4.6 μm , although there are some anomalous features in the 59 km spectrum, as mentioned above. The apparent contradiction between the VIMS and the ACP results may also be resolved if one assumes that they are relevant to different portions of the haze material. The VIMS occultation measurements are likely to probe the outer shell of the particles, whereas in the ACP experiment, which consisted of analyzing the pyrolysate obtained after heating the haze material first at 250°C and then at 600°C,

evaporation of any alkane-containing material would have occurred prior to the analysis (Israël et al. 2006).

4. Conclusion

We retrieved the 1–5 μm optical-depth spectra of the Titanian haze from *Cassini*/VIMS solar occultation data recorded at altitudes of ~ 60 –500 km, thus extending previous analyses that were restricted to smaller intervals in this spectral range (Kim et al. 2011; Sim et al. 2013). We found that the gross spectral characteristics of the haze are significantly different from that of tholin samples available in the literature (Khare et al. 1984; Quirico et al. 2008; Gautier et al. 2012). In particular, they lack the distinctive strong 3.0 and 4.6 μm absorptions corresponding to the $-\eta\text{NH}$ and $-\eta\text{CN}$ functional groups, respectively. The retrieved haze spectra roughly match laboratory spectra of alkane ices, in particular at the positions of three major absorption peaks typical of alkane ice at 2.3, 3.4, and 4.3 μm .

The predominance of alkane (aliphatic) absorption features in the haze spectra between ~ 60 –500 km is at odds with the analysis of high-altitude (600–1250 km) *Cassini*/VIMS observations (Dinelli et al. 2013; López-Puertas et al. 2013), which concluded that there are aromatic compounds in the ionospheric haze. At first glance, it seems also inconsistent with the detection of HCN and NH_3 in the cores of haze particles collected by *Huygens*/ACP at low altitude (20–130 km) (Israël et al. 2005), but it can be argued that the VIMS occultation measurements most likely probe only the outer shell of the particles.

Current haze formation scenarios on Titan (e.g., Waite et al. 2007) are based on the detection of very heavy ions in the ionosphere, which produce ~ 0.01 μm size monomers. These monomers subsequently undergo coagulation/coalescence, increasing in size during sedimentation. Active chemistry may also occur on the surface of the haze particles (Lavvas et al. 2011). In the future development of haze formation theories and/or laboratory simulations, the challenge will be to explain this contradictory evidence for aromatic hydrocarbons in the ionosphere (~ 950 km), for alkane particles in the 60–500 km altitude range, and for N- and C-bearing refractory cores in the 20–130 km range. We suggest that these characteristics belong to different structural layers that reflect the formation/evolution processes of the haze particles at different altitudes.

Acknowledgements. We thank P. G. J. Irwin for the discussion on the k-distribution parameters posted at <http://www.atm.ox.ac.uk/user/irwin/kdata.html>. S.J.K. acknowledges a useful discussion about alkane ices with M. Ádámkóvics. This research was supported by the World Class University (WCU) program through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology (R31-10016). We thank C. K. Sim and M. R. Sohn for their assistance in making the figures.

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