

Simulating the 3.4-Micron Feature of Titan's Haze

Y. S. Kim, C. Ennis, and Sang Joon Kim^{†,*}

Department of Chemistry, University of Hawaii at Manoa, Honolulu, HI 96822, USA

*[†]School of Space Research, Kyung Hee University, Yongin 446-701, Korea. *E-mail: sjkim1@khu.ac.kr*

Received October 3, 2012, Accepted December 8, 2012

Four prominent features of Titan's haze are found within the '3.4- μm ' absorption to be uniform with recent vertically resolved Cassini/VIMS spectra.¹ These are absorptions at 2998 cm^{-1} (3.34 μm), 2968 cm^{-1} (3.37 μm), 2927 cm^{-1} (3.42 μm), and 2882 cm^{-1} (3.47 μm). A detailed fitting suggests that the 2998 cm^{-1} feature could originate from amorphous acetonitrile (CH_3CN) carrying about 25% of integrated optical depth; the remaining features, which account for 75% of the integrated optical depth, could arise from a distinct triplet (C-H stretching) structure of radiolyzed hydrocarbons. An additional feature was possibly evidenced at altitudes higher than 300 km and attributable to 'polymer-capped' methane (CH_4), significantly constraining the chemical composition of organic haze layers under Titan's active radiation field.

Key Words : Laboratory spectroscopy, Infrared, Astrochemistry, Cosmic rays, Solar system

Introduction

The elucidation of the chemical composition of Titan's haze has been an extensive topic of laboratory studies since the Voyager 1 spacecraft witnessed an optically thick haze, which completely obscured the surface of Titan.² In an attempt to simulate the formation of Titan's haze, thin films of carbon, hydrogen, and nitrogen-bearing reddish organic solids dubbed tholins were produced³ by discharging nitrogen and methane-based gas mixtures. The optical properties of tholins were then recorded in electromagnetic spectrum of 0.025-1,000 μm (10-40,000 cm^{-1}). Since this pioneering study, it has been a spectroscopic challenge to confirm the actual composition of tholins in the atmosphere of Titan. The spectral features of the organic haze could not be properly extractable from Titan's infrared spectra without discretion,^{4,5} which are complicated by strong mid-infrared thermal emissions and near-infrared absorptions of methane together with higher order hydrocarbons and nitriles.^{6,7} Such discretion could be also taken in the near-infrared windows (1.08-1.11, 1.24-1.29, 2.0-2.1 μm), where Titan's atmosphere is relatively transparent⁸ for unknown spectral influences of surface materials at the dawn of the Cassini mission. Embracing the challenge for analyzing Voyager 1 infrared spectra, it was suggested⁶ that condensates of various hydrocarbons, nitriles, water, and carbon dioxide are responsible for the unidentified continuum features in the 10-50 μm range of Titan's atmosphere. Following high resolution ground-based observations, the broad spectral feature (3.2-3.5 μm) of Titan was interpreted⁹ by carbon-hydrogen (C-H) stretching modes usually seen in the spectra of interstellar and cometary dust particles.¹⁰

During a Titan flyby on January 15th, 2006, the Visual Infrared Mapping Spectrometer (VIMS) onboard the Cassini spacecraft conducted a solar occultation experiment and recorded arrays of vertically resolved near infrared images

for altitudes of 100 to 800 km at the latitude of 71°S. The distribution and optical properties of the haze were subsequently retrieved.^{1,4,11} These data exposed that the overall shape of the 1 to 5 μm continuum of Titan's haze is significantly different from that of tholins,³ let alone a broad unidentified feature between 3.2 and 3.6 μm suggestive of C-H stretches of hydrocarbons,¹¹ but without disentangling the feature from an adjacent strong methane (CH_4) absorption. Subsequently, the detailed spectral features of Titan's haze were retrieved¹² from the very same VIMS data utilizing a radiative transfer program. This study demonstrated that these features are relatively uniform with altitude having slight deviations near 127 km and above 300 km. Reflecting the primary absorptions at 3.4 μm over a minor peak at 3 μm ,⁴ the chemical structure of the organic haze was proposed to bear multiple C-H bonds with scant N-H bonds.

Herein, we simulate the 3.0-3.8 μm haze opacity of Titan's atmosphere by fitting these features based on laboratory spectra of (radiolyzed) hydrocarbons and nitriles in the condensed phase.^{13,14} The prominent 3.4- μm feature was particularly targeted in a pool of pristine and radiolyzed hydrocarbons that may carry such triplet structures of distinct C-H stretching modes. Previously, we irradiated potential aerosol components of Titan's atmosphere, condensed ethane (C_2H_6) and propane (C_3H_8), with energetic electrons,^{12,13} aiming to better simulate those ionizing interactions of incoming particles from Saturn's magnetosphere and of galactic cosmic rays upon penetrating the upper atmosphere^{15,16} and down to the lower atmosphere of Titan.^{17,18} The radiolysis-induced production of heavy hydrocarbons such as butane (C_4H_{10}) and butene (C_4H_8) were particularly monitored and constrained in electron-irradiated ethane (C_2H_6) varying in solid morphology (crystalline versus amorphous) and in temperatures¹⁹ under ultrahigh vacuum conditions. Possibly formed in this radiolysis, lighter hydrocarbons such as methane (CH_4) could replenish into Titan's stratosphere at

temperatures of 120-150 K. Lastly in the astrophysical context, we discuss the likelihood of detailing the chemical structures of Titan's haze layers in the upper and lower atmosphere under the active radiation field of energetic ions and photons.

Experimental

Titan's haze opacity (τ) from 3.0 to 3.8 μm was retrieved from the VIMS spectra obtained on January 15th, 2006.¹² Shortly, a simple haze model was utilized to extract a uniform haze feature from the vertically resolved VIMS spectra. The resultant haze opacities are shown in Figure 1 for altitudes (z) > 300 km, $127 < z < 300$ km, and near 127 km. Small altitudinal deviations were observable at lower wavelengths and attributable to unknown aerosol features and gaseous/condensed absorptions.^{4,12} The 3.0-3.8 μm haze spectra were then converted to a wavenumber scale of 2 cm^{-1} data spacing in order to compare with condensed phase spectra of (radiolyzed) hydrocarbons and nitriles recorded at 4 cm^{-1} spectral resolution or better. Resolved by this conversion were, for example, the peak positions of 3.4 μm haze features at 2968 cm^{-1} (3.37 μm), 2927 cm^{-1} (3.42 μm), and 2882 cm^{-1} (3.47 μm) (Table 1); these values were further found comparable to those of haze analogs formed either from gaseous nitrogen (N_2)/methane (CH_4) mixtures²⁰ under electrostatic levitation or from the ionizing interaction of energetic electrons with crystalline solid ethane (C_2H_6).¹³

The laboratory simulation of Titan's 3.4- μm feature began with recording condensed phase spectra of linear and branched hydrocarbons. Some of literature spectra were also referenced²¹ for targeting as heavy and versatile species as *n*-butane (C_4H_{10}), isobutane (C_4H_{10}), *n*-hexane (C_6H_{14}), 2-methyl pentane (C_6H_{14}), and 2,3-dimethyl butane (C_6H_{14}). Those gas/liquid samples were then vapor-deposited onto a substrate held at 10 K in a contamination-free and ultrahigh vacuum (UHV) chamber. As the experimental methodology detailed in a paper,²² the deposited samples in this way ensured free of crystalline feature at 3.4 μm region with the

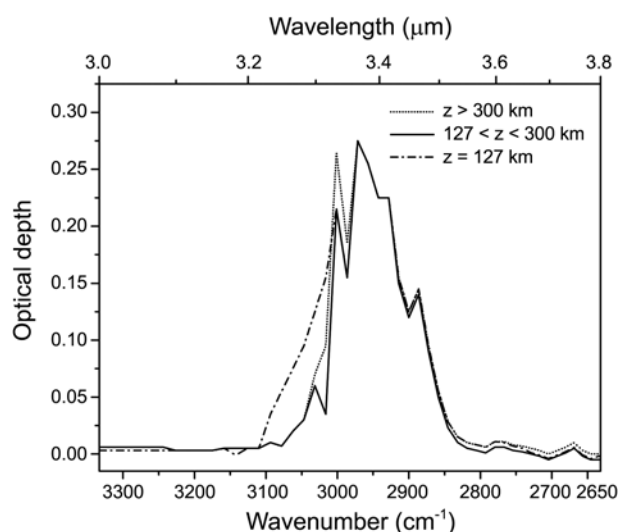


Figure 1. Titan's haze opacity from 3.0 to 3.8 μm . A haze model is utilized to extract the uniform haze feature from vertically resolved VIMS spectra. Small altitudinal deviations at lower wavelengths could be due to unknown aerosol features and gaseous/condensed absorptions.

exception of a methane (CH_4) sample. Accordingly, mid-infrared spectra were recorded from 6,000 to 500 cm^{-1} with 4 and 2 cm^{-1} spectral resolution utilizing a Nicolet 6700 FT-IR unit. Among those pristine solid spectra recorded, *n*-hexane (C_6H_{14}) and its 2,3-dimethyl butane isomer (C_6H_{14}) made a strong case having multiple carbon-hydrogen bonds. Lacking $-\text{CH}_2-$ group, the branched isomer possesses a doublet feature of 2959 cm^{-1} and 2872 cm^{-1} , the peak to peak interval matching the VIMS data (86 cm^{-1} ; Table 1). On the other hand, the linear chain isomer shows a characteristic C-H triplet of 2959, 2924, and 2872 cm^{-1} , the middle frequency assigned to $-\text{CH}_2-$ asymmetric stretch. Nonetheless, both C_6H_{14} isomers could not be the carriers of Titan's haze, because they do not have optical depths of 3.4 μm matched in Titan's haze (Figure 1). Meanwhile, the absorption spectra of nitriles were also constructed from available optical parameters of solid nitriles at 3.4 μm ¹⁴ varying in

Table 1. Peak positions of Titan's 3.4- μm haze opacity (τ) and of potential carriers

VIMS ^a		Tholins ^b (2008)		Irradiated C_2H_6 ^c		CH_4 in sublimation ^d		Amorphous CH_3CN ^e	
(cm^{-1})	(μm)	(cm^{-1})	(μm)	(cm^{-1})	(μm)	(cm^{-1})	(μm)	(cm^{-1})	(μm)
3028 ^f	3.30	3027	3.30
3013 ^f	3.32	3011	3.32
2998	3.34	3001	3.33
2968 ^g	3.37	2959	3.38	2961	3.38
2945	3.40	2941	3.40
2927 ^g	3.42	2924	3.42	2931	3.41
(2923) ^h	3.42
(2892) ^h	3.46
2882 ^g	3.47	2874	3.48	2873	3.48

^aIn 2 cm^{-1} data spacing. ^bFrom a reference.²⁰ ^cRoom temperature residues formed after 3 h electron irradiation (5 keV, 500 nA) of crystalline C_2H_6 held at 50 K; Broad underlying features are not shown for clarity; Part of this work from a reference.¹³ ^d1 μm -thick solid deposited and heated with a gradient 0.5 K/min up to the sublimation point. ^eExtinction coefficient (k) determined at 50 K and available from <http://science.gsfc.nasa.gov/691/cosmicice>. ^fOnly at $z > 300$ km. ^gTitan's C-H triplet feature. ^hBroad underlying features of the C-H triplet from the $127 < z < 300$ km spectrum.

morphology and temperatures.

Next, Titan's 3.4- μm features were sought in radiolyzed solid hydrocarbons such as ethane.^{13,19} For this purpose, the electron beams (5 keV electrons) were generated with an electron gun (Specs EQ 22-35) and scanned over the target area of $3.2 \pm 0.3 \text{ cm}^{-2}$. The radiolysis-induced chemical processing was then monitored by online and in situ FT-IR spectroscopy. Fluence was controlled to maximize the production of 3.4- μm features such as in crystalline ethane (0.1 μm thick) held at 50 K under UHV conditions.¹³ The radiolyzed solids were heated with a 0.5 K min^{-1} gradient up to 300 K, leaving behind organic residues (haze analogs) on the substrate.

Results and Astrophysical Implications

The potential carriers of Titan's 3.4- μm haze are presented in Figure 2. The uniform haze feature with altitude was best fit in two absorption spectra of acetonitrile (CH_3CN) and radiolyzed ethane (C_2H_6) in condensed phase (Figure 2(a)). An absorption feature of condensed methane (CH_4) was also included for the haze at altitudes (z) $> 300 \text{ km}$. There is also an additional feature at about 3030 cm^{-1} for the spectrum $127 < z < 300 \text{ km}$, which might be attributable to sp^2 C-H stretching modes of 1,3-butadiene (C_4H_6) and benzene (C_6H_6).²³ Based on these laboratory spectra (Figure 2(a)), a minimum set of Gaussians were utilized to simulate the VIMS slit function by virtue of deconvoluting the haze opacity in a wavenumber scale (Figure 2(b)). In this way we determined the peak positions of 3.4- μm haze feature at 2998 cm^{-1} (3.34 μm), 2968 cm^{-1} (3.37 μm), 2927 cm^{-1} (3.42 μm), and 2882 cm^{-1} (3.47 μm) (Table 1). Among these, the 2998 cm^{-1} band could be attributable to asymmetric $-\text{CH}_3$ stretch (ν_5) of acetonitrile (CH_3CN).^{14,24} The remaining three could be attributable to the C-H triplet of radiolyzed hydrocarbons.¹³ This deconvolution also brought in a much needed feature at 2945 cm^{-1} to fill in between the higher frequencies of the C-H triplet (Figure 2), which is assigned to symmetric $-\text{CH}_3$ stretch of CH_3CN (ν_1).

During the 3.4- μm feature simulation, it became clear that neither individual nor a combination of methane (CH_4), acetonitrile (CH_3CN), and ethane (C_2H_6) spectra were able to deliver an adequate fit of the VIMS data. Further, the condensed spectra of two C_6H_{14} isomers may have only the peak positions, but not their intensities, aligned to the Titan C-H triplet structure. Consequently, we shifted our attention to heavier hydrocarbons produced in radiolyzed solids such as ethane with energetic electrons as in Figure 2; ethane could condense in aerosols and droplets of Titan's lower atmosphere and likely exist in a crystalline form.²⁵ The best fit of Titan's C-H triplet could be obtained with organic residues formed after 3 hour irradiation of ethane at 50 K (Figure 2). We would like to stress that the following nitrile features were also considered but were ruled out because of their mismatch in peak positions and/or patterns: hydrogen cyanide (HCN), cyanogen (C_2N_2), and propionitrile ($\text{C}_2\text{H}_5\text{CN}$).¹⁴ Further, an additional absorber may exist at altitudes higher

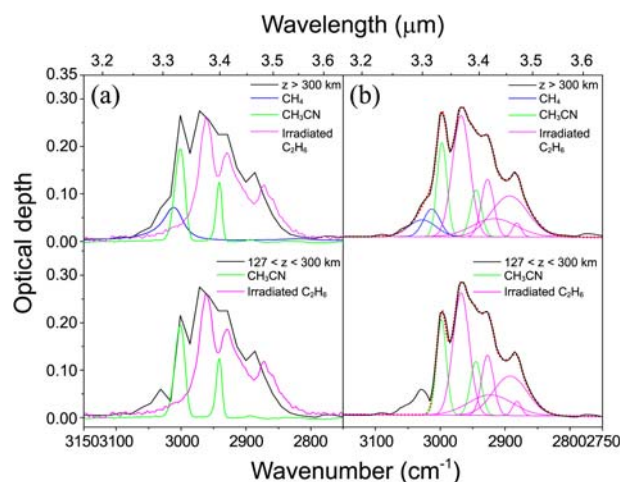


Figure 2. Carriers of Titan's 3.4- μm haze. In panel (a), irradiated ethane (C_2H_6) and acetonitrile (CH_3CN) of condensed phase are evidenced to carry the uniform haze feature with altitude. An absorption feature of condensed methane (CH_4) is also included for the haze at altitudes (z) higher than 300 km. In panel (b), a minimum set of Gaussians are utilized for deconvoluting the haze opacity in a wavenumber scale. The red-dotted lines are also shown for a resulting Gaussian fit. The peak positions and Gaussian contributions to the integrated optical depth (t) are compiled in Tables 1 and 2. A small feature near 3030 cm^{-1} ($127 < z < 300 \text{ km}$) may not be fit uniquely. Refer to the section, Results and Astrophysical Implications, for details.

than 300 km that contributes to the apparent gain of acetonitrile (CH_3CN) at about 3000 cm^{-1} (Figure 2). This feature could be reproducible with condensed methane (CH_4) such that it was best simulated in the laboratory by condensing 1 μm thick methane ice at 10 K and probing sublimation profile during warm-up phases thereafter. The blue trace in Figure 2(a) was indeed recorded during sublimation, feeding two Gaussians for the refined opacity at 3028 cm^{-1} (3.30 μm) and 3013 cm^{-1} (3.32 μm) in Figure 2(b).

The 3.4- μm opacity of Titan's haze was possibly simulated in the laboratory by two distinct carriers of amorphous acetonitrile (CH_3CN) and radiolyzed hydrocarbon (C_2H_6). Condensed methane (CH_4) was also featured in the haze spectrum of altitudes higher than 300 km. The current simulation merited on a radiative transfer of reducing vertically resolved VIMS data^{1,11} into a uniform model set (Figure 1) virtually free of gas phase contributions.¹² Four absorption features were identified to be uniform with altitude at 2998 cm^{-1} (3.34 μm), 2968 cm^{-1} (3.37 μm), 2927 cm^{-1} (3.42 μm), and 2882 cm^{-1} (3.47 μm) (Figures 1 and 2; Table 1). Among these, the 2998 cm^{-1} band could be attributable to asymmetric $-\text{CH}_3$ stretch (ν_5) of acetonitrile (CH_3CN), as matched in the laboratory spectrum (Figure 2).^{14,24} The other features were the C-H triplet of $-\text{CH}_3$ and $-\text{CH}_2-$ group vibrations as found in radiolyzed ethane (C_2H_6) (Figure 2).¹³ Condensed methane (CH_4) at $z > 300 \text{ km}$ was found to carry a broad low-lying feature at about 3010 cm^{-1} , possibly constraining the chemical composition of organic haze layers formed at these altitudes. In the laboratory analogy, polymer-like residues tend to form upon the radiolysis of simple organic

Table 2. Integrated optical depth (τ) and Gaussian contributions in Figure 2

VIMS	$\int \tau_{\nu} d\nu$, Total (cm^{-1})	Irradiated C_2H_6 , (cm^{-1})	CH_3CN^a (cm^{-1})	CH_4 (cm^{-1})
$z > 300$ km	31.5 ^b	21.7 (22.3)	3.9 (3.9)	3.8 (4.0)
$127 < z < 300$ km	27.0 ^b	20.7 (22.3)	3.9 (3.9)	...

Note. Values in parenthesis are integrated absorption of individual carriers, Figure 2(a). ^aArea of ν_5 (2998 cm^{-1}) only shown for clarity. ^bIncluding the buried ν_1 (2945 cm^{-1}) of CH_3CN .

precursors, which serve to retain volatile molecules such as methane (CH_4) and ethane (C_2H_6) in the solid state even after sample temperatures exceed the sublimation temperatures of the pristine samples. All in cases of proton, α -particle, and electron-irradiated samples we studied, the polymer layers are found to act like a ‘cap’ preventing the precursor molecules from subliming at their equilibrium temperatures.^{13,26}

In a quantitative sense, Gaussian contributions of individual carriers were summed up to the integrated optical depths (τ) and compared with absorptions relevant to ‘aliphatic groups’ of interstellar grains (Table 2).²⁷ The aliphatic hydrocarbons as identified via their C-H triplet could account for about 75% of the integrated optical depth and the acetonitrile (CH_3CN) features for the remaining 25%. Therefore, the current study can serve to constrain the chemical carriers of Titan’s 3.4- μm haze features as extracted from Cassini/VIMS data, whereby the majority of haze opacity are featured in radiolyzed ethane (C_2H_6).

Acknowledgments. S.J.K acknowledges a support by WCU program through the National Research Foundation of Korea funded by the Ministry of Education, Science, and Technology (R31-10016).

References

- Bellucci, A. **2008**, Ph.D. thesis. Université Pierre et Marie Curie.
- Stone, E. C.; Miner, E. D. *Science* **1981**, *212*, 159.
- Khare, B. N.; Sagan, C.; Arakawa, E. T.; Suits, F.; Callcott, T. A.; Williams, M. W. *Icarus* **1984**, *60*, 127.
- Rannou, P.; Cours, T.; Le Mouélic, S.; Rodriguez, S.; Sotin, C.; Drossart, P.; Brown, R. *Icarus* **2010**, *208*, 850.
- Vinatier, S.; Rannou, P.; Anderson, C. M.; Bézard, B.; Kok, R. de.; Samuelson, R. E. *Icarus* **2012**, *219*, 5.
- Coustenis, A.; Schmitt, B.; Khanna, R. K.; Trotta, F. *Planet. Space Sci.* **1999**, *47*, 1305.
- Coustenis, A. *et al. Icarus* **2006**, *180*, 176.
- Griffith, C. A. *Nature* **1993**, *364*, 511.
- Kim, S. J.; Geballe, T. R.; Noll, K. S.; Courtin, R. *Icarus* **2005**, *173*, 522.
- Kwok, S.; Zhang, Y. *Nature* **2011**, *479*, 80.
- Bellucci, A.; Sicardy, B.; Drossart, P.; Rannou, P.; Nicholson, P. D.; Hedman, M.; Baines, K. H.; Burrati, B. *Icarus* **2009**, *201*, 198.
- Kim, S. J.; Jung, A.; Sim, C. K.; Courtin, R.; Bellucci, A.; Sicardy, B.; Song, I. O.; Minh, Y. C. *Planet. Space Sci.* **2011**, *59*, 699.
- Kaiser, R. I. *et al. Faraday Discuss.* **2010**, *147*, 429.
- Moore, M. H.; Ferrante, R. F.; Moore, W. J.; Hudson, R. *Astrophys. J. Supp.* **2010**, *191*, 96.
- Coates, A. J. *Phil. Trans. R. Soc. A* **2009**, *367*, 773.
- Krasnopolsky, V. A. *Icarus* **2009**, *201*, 226.
- Molina-Cuberos, G. J.; López-Moreno, J. J.; Rodrigo, R.; Lara, L. M.; O’Brian, K. *Planet. Space Sci.* **1999**, *47*, 1347.
- Whitten, R. C.; Borucki, W. J.; Tripathi, S. J. *Geophys. Res.* **2007**, *112*, E04001.
- Kim, Y. S.; Bennett, C. J.; Chen, L.-H.; O’Brian, K.; Kaiser, R. I. *Astrophys. J.* **2010**, *711*, 744.
- Quirico, E. *et al. Icarus* **2008**, *198*, 218.
- Bohn, R. B.; Sandford, S. A.; Allamandola, L. J.; Cruikshank, D. P. *Icarus* **1994**, *111*, 151.
- Bennett, C. J.; Jamieson, C.; Mebel, A. M.; Kaiser, R. I. *Phys. Chem. Chem. Phys.* **2004**, *6*, 735.
- Zhou, L.; Zheng, W.; Kaiser, R. I.; Landera, A.; Mebel, A. M.; Liang, M.-C.; Yung, Y. L. *Astrophys. J.* **2010**, *718*, 1243.
- Russo, N. D.; Khanna, R. K. *Icarus* **1996**, *123*, 366.
- Bauerecker, S.; Dartois, E. *Icarus* **2009**, *199*, 564.
- Kaiser, R. I.; Roessler, K. *Astrophys. J.* **1998**, *503*, 959.
- d’Hendecourt, L. B.; Allamandola, L. J. *Astron. Astrophys. Supp.* **1986**, *64*, 453.