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Titan aerosol analog absorption features produced from aromatics in the far infrared

Joshua A. Sebree [a,b,*], Melissa G. Trainer [b], Mark J. Loeffler [b], Carrie M. Anderson [b]

[a] *University of Northern Iowa, Department of Chemistry and Biochemistry, Cedar Falls, IA 50614, USA*
[b] *NASA Goddard Space Flight Center, Solar System Exploration Division, Greenbelt, MD 20771, USA*

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A B S T R A C T

We present results on the formation of Titan aerosol analogs produced via far-UV irradiation of five aromatic precursors: benzene, naphthalene, pyridine, quinoline and isoquinoline. This is the first reported evidence of far-IR emission features observed below 200 cm^{-1} in laboratory-created Titan aerosols. These laboratory studies were motivated by recent analyses of Cassini Composite Infrared Spectrometer (CIRS) spectra that show a broad aerosol emission feature in the far-IR spectral region centered near 140 cm^{-1}, which is unique to Titan's photochemically-produced aerosol (Anderson, C.M., Samuelson, R.E. [2011]. Icarus 212, 762–778). We find that all three of the aerosol analogs formed from nitrogen-containing aromatics have similar broad emission features near that of the observed CIRS far-IR aerosol spectral feature. In addition, the inclusion of 1.5% methane to that of trace amounts of benzene also gives rise to an aerosol with a weak far-IR emission feature located below 200 cm^{-1}.

1. Introduction

Since Saturn orbit insertion in 2004, numerous instruments onboard the Cassini spacecraft continue to provide detailed information relating to the chemistry occurring in Titan's atmosphere. Early observations in the far-IR spectral region between 10 and 600 cm^{-1} recorded by the Cassini Composite Infrared Spectrometer (CIRS), a successor to the Voyager InfraRed Interferometer Spectrometer (IRIS), revealed a broad emission feature of unknown particulate composition centered at 140 cm^{-1} (de Kok et al., 2007). This emission feature was initially attributed by de Kok et al. (2007) to a haze with a different chemical composition than that of Titan's main photochemical aerosol present throughout the stratosphere. More recent analyses of CIRS far-IR spectra by Anderson and Samuelson (2011) interpret instead that the far-IR emission feature at 140 cm^{-1} cannot be distinguished from Titan's main photochemical aerosol and that the previously assigned separate hazes (de Kok et al.) probably have the same chemical makeup; the spectrum is shown by the black curve in Fig. 1. Anderson and Samuelson (2011) speculated that this broad aerosol emission feature may arise from low-energy vibrations of two-dimensional lattice structures, such as polycyclic aromatic hydrocarbons (PAHs) or nitrogenated aromatics. Recently, using spectra from the NASA Ames PAH IR Spectroscopic Database (Bauschlicher et al., 2010), a previously unassigned feature observed in Titan's upper atmosphere by the Cassini Visible and Infrared Mapping Spectrometer (VIMS), was identified as a composite of several PAH spectral features (López-Puertas et al., 2013). Many of the PAHs identified in the VIMS-based study also have spectral features in the far-IR below 200 cm^{-1}, suggesting an important link between the near- and far-IR observations.

Most Titan aerosol-analog laboratory studies have focused on the mid-IR spectral region above 400 cm^{-1} (Imanaka et al., 2004, 2012; Quirico et al., 2008) since the mid-IR provides valuable information regarding the aromatic and aliphatic nature of species. However, as the CIRS's instrument has a spectral range that extends into the far-IR region, where low-energy vibrations from the aerosol composite are probed, more laboratory work focused in the far-IR may prove useful in understanding the physical and chemical nature in Titan's aerosol. In fact, recently radiative transfer analysis of CIRS far-IR limb spectra revealed that existing laboratory spectra of photochemically produced aerosols (Khare et al., 1984) do not match Titan's observed aerosol opacity below 200 cm^{-1} (blue curve in Fig. 1). Similarly, a more recent far-IR study examined Titan aerosol analogs produced in a plasma discharge from mixtures of 1–10% CH_4 in N_2 (Gautier et al., 2012, Fig. 1, red curve) and found that these plasma analogs also do not show spectral features below 200 cm^{-1}. Thus, the lack of a feature in this region in previous laboratory studies indicates that one

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* Corresponding author at: University of Northern Iowa, Department of Chemistry and Biochemistry, Cedar Falls, IA 50614, USA.
E-mail address: joshua.sebree@uni.edu (J.A. Sebree).

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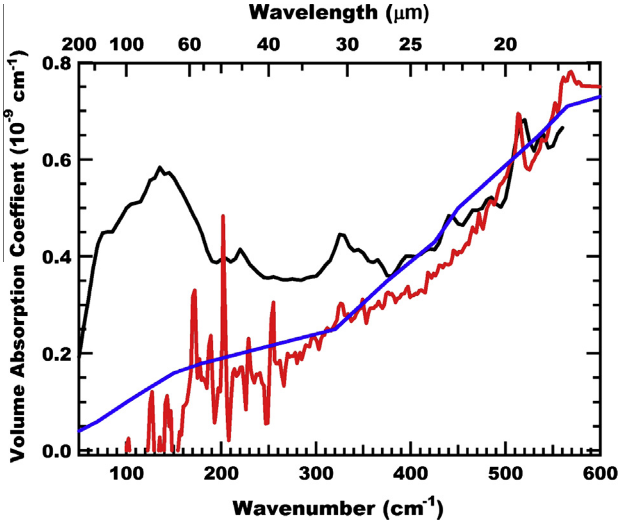

Fig. 1. The aerosol emission feature below 200 cm^{-1} (black curve) as determined by Anderson and Samuelson (2011) has not been reproduced by laboratory studies in pre-Cassini studies (Khare et al., 1984, blue curve). A more recent studies using plasma discharges with mixtures of 1–10% CH_4 in N_2 (Gautier et al., 2012, red curve) also do not show spectral features below 200 cm^{-1}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

or more of the formation conditions need to be re-examined in order to produce aerosols that contain the CIRS-derived aerosol spectral signature near 140 cm^{-1}.

Currently, analyses of data obtained by several instruments onboard Cassini have indicated that benzene and other aromatic species may play an important role in aerosol formation in Titan's atmosphere. For one, a low altitude flyby of Titan (~950 km) allowed for the direct detection of benzene at parts-per-million (ppm) concentration by the Cassini Ion Neutral Mass Spectrometer (Waite et al., 2007). This in situ measurement was accompanied by detections of other more complex species, tentatively reported as PAHs by the Cassini Plasma and Electron Spectrometer (CAPS/ELS; Coates et al., 2007, 2010; Crary et al., 2009). In this region of Titan's upper atmosphere, the formation of benzene and nitrogen-containing aromatics has been shown to be possible via ion-neutral chemistry (Vuitton et al., 2007). Benzene has also been identified in other regions of the atmosphere (500–900 km) by the Ultraviolet Imaging Spectrograph (UVIS; Koskinen et al., 2011) and in the stratosphere by CIRS (Vinatier et al., 2010). Moreover, recent reinterpretation of Cassini results by López-Puertas et al. (2013) demonstrate that PAHs and polycyclic aromatic nitrogen heterocycles (PANHs) may be prevalent in the both the atmosphere and the aerosol, as evidenced by the 3.28 μm band in the IR. Benzene is the first aromatic in a series of reactions leading to the formation of PAHs (Wilson and Atreya, 2009). Based upon the presence of benzene throughout the atmosphere, in a previous study, we showed that the inclusion of trace amounts of benzene (10 ppm) can have significant effects on the chemistry of the aerosol (Trainer et al., 2013). Here we continue to explore the effects that small aromatics have on bulk aerosol chemistry and optical properties. Our findings show that the inclusion of such compounds leads to far-IR spectral features previously unobserved in Titan aerosol analogs. In addition, the inclusion of heterocycles (aromatics that contain nitrogen) strengthens the observed far-IR emission feature intensities.

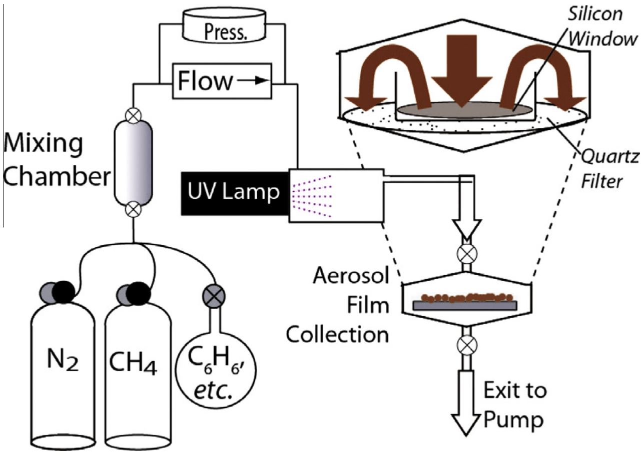

Fig. 2. The photochemical flow-through reaction cell is used for the generation and collection of the Titan aerosol analogs under study.

2. Experimental

2.1. Aerosol generation

The Titan aerosol analogs used in this study were generated using the photochemical reaction system shown in Fig. 2. This system has been designed to allow for the incorporation of various starting gas mixtures. A similar system has been used previously to explore the properties of aerosols created from CH_4 and N_2 (Trainer et al., 2006). High-pressure (~800 psi) gas mixtures were made in a 2 L stainless steel mixing chamber that allowed for organic concentrations ranging from 10 ppm to 10%. After homogenization, the prepared mixtures were flowed at 100 standard cm^3 min^{-1} (sccm) through a ~300 cm^3 glass photochemical reaction cell and then into a collection chamber. A pressure of 600 torr was maintained in order to provide consistency with previous compositional experiments (Trainer et al., 2006, 2012, 2013).

Photochemistry was initiated by a deuterium lamp (Hamamatsu, L1835) with MgF_2 windows inserted directly in to the reaction cell. The lamp is a continuum source with a range of 115–400 nm, and all the reactant species used here have photochemical activity in this wavelength region. Photodissociation of CH_4 primarily occurs at the Lyman-α line (121.6 nm) with a cut off ~145 nm (Trainer et al., 2013). The aromatics are photochemically active at longer wavelengths.

Once produced, the aerosols were collected as a thin film on a silicon wafer within the collection chamber. Aerosols that did not stick to the surface of the wafer were collected via a quartz fiber filter upon exiting the chamber, thus ensuring a near 100% collection efficiency of aerosols larger than 10 nm in diameter. This collection efficiency was confirmed using a nanoparticle condensation particle counter (TSI, Model 3007) downstream from our filter housing, which reported 0% transmission for aerosol particles ⩾10 nm. Sample collection times were on the order of 175–200 h with production rates of approximately 0.1 mg/h. The sample mass was not determined for each of far-IR collections, but the production rate was measured during a run in which the sample was only collected on a filter, and weighed before and after aerosol formation. Upon completion, the collection chamber was decoupled from the system and transferred to a glove box. Samples were prepped and stored under an inert (N_2 or argon) atmosphere until they were analyzed with infrared spectroscopy.

Gas mixtures of 100 ppm aromatic reactant in N_2 were individually prepared from benzene (Sigma Aldrich, ⩾99.9%), pyridine (Sigma Aldrich, ⩾99.0%), naphthalene (Sigma Aldrich, ⩾99%), quinoline (Aldrich, ⩾98%) and isoquinoline (Aldrich, ⩾97%). The concentration of 100 ppm was selected to allow for the collection