SESSION 9

https://doi.org/10.1017/S174392132000054X Published online by Cambridge University Press

Laboratory Astrophysics: from Observations to Interpretation
Proceedings IAU Symposium No. 350, 2019
F. Salama & H. Linnartz, eds.
doi:10.1017/S174392132000054X

C_6H_6 condensation on Titan's stratospheric aerosols: An integrated laboratory, modeling and experimental approach

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Abstract. Saturn's moon Titan was explored by the Cassini mission for nearly 13 years. Important discoveries made during the Cassini mission include the observations of stratospheric clouds in Titan's cold polar regions in which spectral features or organic molecules were detected in the infrared (<100 μm). In particular, benzene (C_6H_6) ice spectral signatures were recently detected at unexpectedly high altitudes over the South Pole. The combined experimental, modeling and observational effort presented here has been devised and executed in order to interpret these high altitude benzene observations. Our multi-disciplinary approach aims to understand and characterize the microphysics of benzene clouds in Titan's South Pole.

Keywords. satellites: Titan, atmospheric effects, methods: laboratory, methods: data analysis

1. Introduction

Aerosol particles in Titan's atmosphere impact its thermal structure and can serve as condensation nuclei for the formation of clouds. Following the northern spring equinox in August 2009, Titan's global atmospheric circulation reversed within the next two years. This event increased the mixing ratios of benzene (C_6H_6) and other molecules at the South Pole. Simultaneously, a strong cooling with temperatures dropping below 120 K favored the condensation of organic molecules at unusually high altitudes (>250 km). C_6H_6 ice has been detected by the Composite Infrared Spectrometer (CIRS) in the South polar cloud system (Vinatier *et al.* (2018)), but the existing laboratory data is insufficient to allow models to reproduce the formation of the observed cloud system. To address this issue, we are combining laboratory, modeling and observational studies to investigate the condensation of benzene on Titan's aerosol as a potentially important component of the South Polar cloud system that appeared during the autumn above 250 km altitude. Here, our main goals are (i) to measure the vapor pressure of benzene at Titan-relevant temperatures, (ii) to produce analogs of Titan's aerosols and investigate the conditions required for condensation of benzene on them, (iii) to use the experimental data and temperature/pressure profiles derived from CIRS data as input parameters in the Titan CARMA microphysical model which simulates nucleation, condensation, evaporation, sedimentation, and coagulation of cloud particles in order to determine expected cloud altitudes and particle sizes, and (iv) to compare our experimental data and modeling

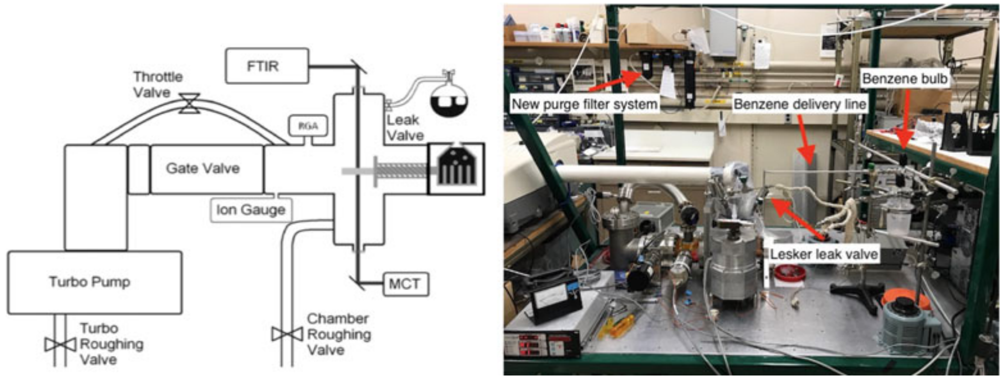

Figure 1. *Left*: Schematic of the ACL vacuum chamber. *Right:* Improved implementation of gas delivery systems for the ACL including a Lesker ultra-fine leak valve, a new filter system for the air purge generator, and new plumbing for benzene.

outputs to observations from CIRS in the 9–17 μm spectral region, therefore guiding the interpretation of the cloud system composition and vertical structure.

2. Combined observational, experimental and modeling methodology

Observations: the Cassini-CIRS dataset

The end goal of the project is to analyze CIRS spectra acquired at the South Pole during the 2012–2016 period, in order to determine the vertical temperature profiles and study the vertical distribution of the C_6H_6 cloud as well as the spectral emissions features. 17 CIRS observations of the South Pole will be analyzed. As the observed thermal emission strongly depends on temperature, when analyzing CIRS data, we first derive the temperature vertical profile by fitting the ν_4 CH_4 band at 1305 cm^{-1}, assuming a CH_4 volume mixing ratio constant with altitude and latitude and equal to 1.48%. The retrieved temperature profile is then used as a fixed parameter to reproduce the thermal emission of gas ro-vibrational bands observed in the CIRS spectra. An inversion algorithm is used to retrieve volume mixing ratios from the fits of molecular emission bands (Vinatier *et al.* (2018)).

Here, we analyzed CIRS spectra acquired with focal planes FP3 (600–1100 cm^{-1}) and FP4 (1100–1500 cm^{-1}) during Flyby T110, on March 16, 2015, and retrieved the C_6H_6 mixing ratio as well as temperature profile at 87 S latitude. Both the temperature profile and benzene mixing ratio were incorporated in the CARMA model as input parameters.

Experimental: C_6H_6 vapor pressure measurements with the ACL

In this project, we exploit two experimental setups developed at NASA Ames. The first one is the Atmospheric Chemistry Laboratory (ACL), with which we are investigating the condensation of pure benzene to determine for the first time in the laboratory the equilibrium vapor pressure of solid benzene at Titan-relevant temperatures, between 140 K and 170 K. This setup will also be used in the future to study the nucleation of benzene ice onto analogs of Titan's aerosols produced in the NASA Ames COSmIC/THS experimental setup (see below), in order to evaluate their potential influence on the formation of benzene clouds.

The ACL experimental setup (cf. Figure 1) is composed of a stainless-steel vacuum chamber (volume $\sim$10 L evacuated with a turbomolecular pump) in the center of which a silicon wafer is suspended. KBr windows above and below the substrate allow passage of an infrared (IR) beam. A vacuum-jacketed liquid nitrogen cryostat is used to cool the silicon substrate from 300 K to 77 K (Iraci *et al.* (2010) and Figure 1). The temperature

https://doi.org/10.1017/S174392132000054X Published online by Cambridge University Press

of the substrate is regulated through a Kapton heater. Using an ultra-fine Lesker leak valve (model # VZLVM940R), gas phase molecular species can be introduced into the vacuum chamber for controlled deposition onto the substrate. Temperature is monitored with K-type thermocouples while the vapor partial pressure is measured with an ion gauge (Terranova model 934) calibrated to a Baratron capacitance manometer (0.1 Torr full scale). In order to obtain benzene vapor, liquid benzene contained in a glass bulb is first freeze-pumped over an ethanol/dry ice slush. Then, a stable flow of benzene is introduced into the chamber using the leak valve, and the substrate is cooled in steps while continuously acquiring absorption spectra and monitoring a specific benzene band near 14.5 μm, as well as the C-H stretch, C-H bend and C-C stretch bands near 3.3 μm, 5.4 μm, and 6.7 μm, respectively. Ice nucleation is monitored with a Nicolet Nexus 670 Fourier Transform Infrared (FT-IR) spectrometer. The pressure of benzene gas observed when the ice is stable is, by definition, the equilibrium vapor pressure at the experimental temperature.

Comparing our preliminary vapor pressure values obtained between 140 K and 165 K to the values provided by Fray & Schmitt (2009) from extrapolation from higher temperature, we observe that our experimental measurements give lower vapor pressure values than the extrapolated values of Fray & Schmitt (2009) above 155 K, and higher values below 155 K. Our experimental values will be used in the CARMA model as input parameters.

Experimental: Investigating C_6H_6 nucleation on aerosols with COSmIC

The second NASA Ames experimental setup that will be utilized for this project is the Titan Haze Simulation experiment (THS, Sciamma-O'Brien *et al.* (2016, 2017)) developed on the COsmic SImulation Chamber (COSmIC, Salama *et al.* (2018)). Using the COSmIC/THS, Titan aerosol analogs (or tholins) will be produced in a jet-cooled N_2-CH_4-based plasma expansion and then transferred to the ACL chamber in order to investigate their role as benzene cloud condensation nuclei in the C_6H_6 ACL condensation experiments as well as characterize their IR absorption spectra with and without the presence of benzene ice.

The COSmIC/THS experimental setup was designed to study Titan's gas and solid phase atmospheric chemistry at low temperature. COSmIC/THS uses a pulsed, supersonic expansion to cool down a N_2-CH_4-based gas mixture to Titan-like temperatures (150 K) before inducing the chemistry by plasma discharge (Biennier *et al.* (2006); Sciamma-O'Brien *et al.* (2014, 2017)). The THS tholins are in the shape of nm- to μm-sized grains and aggregates. They form in the gas expansion and are jet-deposited onto various substrates downstream of the expansion for further ex situ analyses.

For this project, THS tholins will be produced in different N_2-CH_4-based gas mixtures to produce analogs of Titan's aerosols with varying compositions, in order to investigate the influence of the aerosol composition on the nucleation onset of benzene ice, and on the IR spectra in the wavelength range of interest for this study, 9-17 μm. The IR spectra will be directly compared to CIRS data to help with their interpretation.

Modeling the microphysics of C_6H_6 cloud formation with CARMA

In addition to the observational and experimental aspect of our project, we will investigate the size and number of C_6H_6 cloud particles as a function of altitude using microphysical model simulations conducted with the CARMA model. The Community Aerosol and Radiation Model for Atmospheres (CARMA) simulates the microphysical evolution of aerosol particles in an atmospheric column (Barth (2017)). The particles are modeled using discrete size bins. Cloud particles are created through heterogeneous

https://doi.org/10.1017/S174392132000054X Published online by Cambridge University Press

nucleation using the haze particles as cloud condensation nuclei. All particles are transported vertically through sedimentation as well as eddy diffusion; though due to their sizes, the smaller involatile particles generally move through diffusion, and cloud particles generally fall. All particles in our simulations are also subject to coagulation. Cloud particle formation and growth is controlled by the vapor pressure of C_6H_6.

For this project, we will simulate the southern polar atmosphere in CARMA by initializing the model with temperature/pressure profile from CIRS data and using our new laboratory measurements of C_6H_6 vapor pressures at Titan-relevant temperatures as input to enhance the simulation of C_6H_6 cloud particle formation and growth.

Acknowledgment

This research is supported by the CDAP Program of NASA SMD. The authors acknowledge outstanding technical support of E. Quigley.

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