

# Investigating the condensation of benzene (C<sub>6</sub>H<sub>6</sub>) in Titan's South polar cloud system

**David Dubois** (1,2), Ella Sciamma-O'Brien (1), Laura T. Iraci (1), Erika L. Barth (3), Farid Salama (1) and Sandrine Vinatier (4)

(1) NASA Ames Research Center, Moffett Field, CA, USA (2) Bay Area Environmental Research Institute, Moffett Field, CA, USA (3) Southwest Research Institute, Boulder, CO, USA (4) LESIA, Observatoire de Paris, Université PSL, CNRS, Sorbonne Université, Université de Paris, 5 place Jules Janssen, 92195 Meudon, France (david.f.dubois@nasa.gov)

## Abstract

Major discoveries made during the Cassini mission include observations of organics-rich stratospheric clouds in Titan's cold polar regions in IR spectral regions <100  $\mu\text{m}$ . In particular, the detection of benzene (C<sub>6</sub>H<sub>6</sub>) clouds at unexpected high altitudes in the South polar region has reinforced the need for combined experimental, modeling and observational effort in order to understand their microphysical formation at high altitude. Our project proposes to address this very issue. Here, we present our first results, focused on the formation of benzene clouds at 87°S latitude in the South polar region in the autumn.

## 1. Introduction

Titan goes through a 29-year seasonal cycle as it orbits around Saturn. Over the course of the Cassini mission, Titan underwent a global circulation reversal within the two years following the Northern Spring Equinox in August 2009. Simultaneously, cold air subsidence due to the global atmospheric circulation resulted in an enrichment of many organic volatiles at high southern latitudes. This event ultimately affected the thermal profile of Titan's atmosphere with a strong cooling ( $T < 120$  K) and thus enabled the condensation of volatile species in the South polar region at much higher altitude (>250 km) than observed elsewhere. Recent observations made by the Cassini Composite Infrared Spectrometer (CIRS), detected for the first time a spectral signature consistent with the presence of benzene (C<sub>6</sub>H<sub>6</sub>) ice in the South polar region at these high altitudes [4]. Current laboratory data is insufficient to allow models to reproduce the formation of this high-altitude cloud.

Here, we present concerted experimental, modeling and observational work addressing the

chemical and microphysical processes leading to the formation of this cloud system. Our synergistic approach relies on understanding and characterizing the fundamental nucleation mechanism of C<sub>6</sub>H<sub>6</sub> at Titan-like temperatures (140–170 K) for which no laboratory data is available. Accurate equilibrium benzene vapor pressure and critical saturation values at Titan-like temperatures are an important input parameter for microphysical models in order to reduce some of the modeling uncertainty and reproduce the formation of this polar cloud. Our pluridisciplinary project draws laboratory expertise from both Planetary and Earth Sciences to measure the vapor pressure and IR absorbance of benzene condensed on Titan aerosol analogs at Titan-relevant temperatures. Our analysis of CIRS data also provides temperature profiles and benzene mixing ratios and allows to investigate the evolution in time and at various latitudes and altitudes of the benzene cloud. These experimental and observational parameters are then used to constrain nucleation and condensation in the coupled aerosol microphysics and radiative transfer CARMA model, in order to determine expected cloud altitudes and particle sizes.

## 2. Experimental C<sub>6</sub>H<sub>6</sub> vapor pressure

In the first phase of the project, temperature-dependent equilibrium benzene vapor pressure measurements were performed at the NASA Ames Atmospheric Laboratory (ACL) on a temperature-controlled silicon wafer. ACL is composed of a stainless-steel chamber in the center of which a silicon wafer is suspended, with KBr windows above and below to allow passage of an infrared beam. A liquid nitrogen cryostat allows the cooling of the silicon wafer from 300 K to 77 K [3] (cf. Figure 1). The temperature of the substrate can be regulated through a Kapton heater. C<sub>6</sub>H<sub>6</sub> vapor deposition is controlled using an ultra-fine leak valve. Temperature is

monitored with K-type thermocouples while the vapor partial pressure is measured with an ion gauge.

In the study presented here, in order to obtain benzene vapor, liquid benzene contained in a glass bulb was first freeze-pumped over an ethanol/dry ice slush. Then, a stable flow of benzene was introduced into the chamber using the leak valve and the substrate was cooled in steps while continuously acquiring absorption spectra and monitoring a unique benzene band near  $14.5\ \mu\text{m}$ , as well as the C-H stretch, C-H bend and C-C stretch bands near  $3.3\ \mu\text{m}$ ,  $5.4\ \mu\text{m}$ , and  $6.7\ \mu\text{m}$ , respectively. The pressure of benzene gas observed when the ice was stable was, by definition, the equilibrium vapor pressure at the experimental temperature.

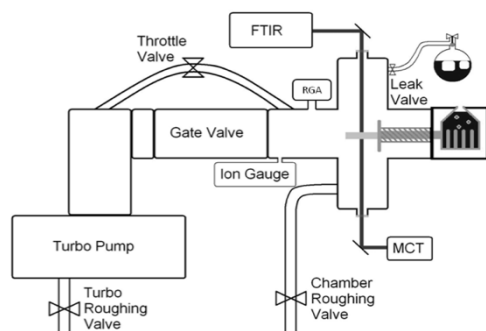


Figure 1: Schematics of the ice nucleation vacuum chamber.

Here, we present the first experimental values of benzene vapor pressure from 140 to 175 K and the associated critical saturation values and a comparison to the values provided by Fray and Schmitt (2009) from extrapolation from higher temperature values [2]. We observe that our experimental vapor pressure values are lower than the extrapolation from Fray and Schmitt above 155 K, and higher below 155 K. These values were used in the CARMA model as input parameters.

### 3. Microphysical modelling

CIRS spectra from Flyby T110 taken on March 16, 2015 at  $87^\circ\text{S}$  latitude were analyzed to retrieve  $\text{C}_6\text{H}_6$  gas mixing ratio and temperature profiles at this latitude [4].

These were incorporated in the CARMA model along with the experimental vapor pressure values to simulate the formation of benzene clouds at  $87^\circ\text{S}$  latitude in Titan's atmosphere.

The Community Aerosol and Radiation Model for Atmospheres (CARMA) simulates the microphysical evolution of aerosol particles in a column of atmosphere and has been applied to Titan [1]. CARMA simulates the effect of sedimentation, eddy diffusion, and vertical wind on the cloud and haze particles' transport as well as the effect of coagulation on the haze particle growth. Cloud particles are created through heterogeneous nucleation using the involatile particles as cloud condensation nuclei which then interact with the volatiles through condensational growth and evaporation. In this study, Titan CARMA simulations were conducted using the experimental vapor pressure as well as the temperature profiles and mixing ratios retrieved from CIRS observations at  $87^\circ\text{S}$  as input parameters.

Here we present the results of this simulation and discuss the impact of using the experimental values of benzene vapor pressure on the expected altitude of the benzene cloud formation. In the following phase of the project, we intend to repeat the same experiments with realistic (i.e., formed at Titan-relevant temperatures) Titan aerosol analogs and examine their impact on benzene condensation and presumably the expected altitude of the benzene cloud formation.

### Acknowledgements

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

### References

- [1] Barth, E. L.: Modeling survey of ices in Titan's stratosphere, *Planetary and Space Science*, Vol. 137, pp. 20-31, 2017.
- [2] Fray, N. and Schmitt, B.: Sublimation of ices of astrophysical interest: A bibliographic review, *Planetary and Space Science*, Vol. 57, pp. 2053-2080, 2009.
- [3] Iraci, L. T., Phebus, B.D., Stone, B. M., Colaprete, A., Water ice cloud formation on Mars is more difficult than presumed: Laboratory studies of ice nucleation on surrogate materials, *Icarus*, Vol. 210 (2), pp. 985-991, 2010.
- [4] Vinatier, S., Schmitt, B., Bézard, B., Rannou, P., Dauphin, C., de Kok, R., Jennings, D.E., Flasar, F.M., Study of Titan's fall southern stratospheric polar cloud composition with Cassini/CIRS: Detection of benzene ice, *Icarus*, Vol. 310, pp. 89-104, 2018.