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# Stable Isotope Chemistry in Titan Haze Aerosol

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## Introduction and Motivation

### Why study Titan?

- Titan is the **largest satellite of Saturn** and has atmosphere composed of nitrogen and a few percent methane ($CH_4$).
- The **atmosphere is believed to be similar to that of early Earth.**
- **The haze layer of Titan is rich in organic chemistry** and can give new insights into **prebiotic chemistry and planetary habitability**.

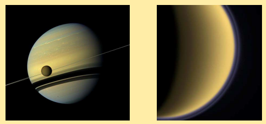


**Figure 1**. Images from the Cassini-Huygens mission. Titan is shown in orbit around Saturn (left) and the haze layer of Titan's atmosphere is observed as a hazy halo around the planet.
*Images courtesy of JPL-NASA*

### Why study isotopes on Titan?

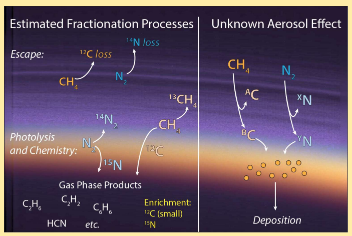
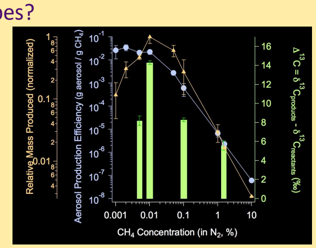



**Figure 2**. Known and unknown pathways to explain the isotopic fractionation occurring in Titan atmosphere.

- The measurements of stable isotope ratios give information on the **history and evolution of the atmosphere.**
- Measurements from Titan indicate that the $^{12}C/^{13}C$ ratio in $CH_4$ is similar to the protosolar ratio, which suggests that the **$CH_4$ is relatively young.**[1]
- The $^{14}N/^{15}N$ is **similar to the protosolar value** of $NH_3$ based on comet measurements.[2,5]

### Are aerosols a sink for stable isotopes?

- **Current models** of the observed isotope ratios on Titan **do not incorporate isotopic fractionation resulting from organic aerosol formation** and subsequent deposition onto the surface of Titan (Figure 2).
- Initial studies have shown that **fractionation** direction and magnitude are **dependent on the initial bulk composition of the gas mixture**[3] (Figure 3).




### Why study aromatic compounds?

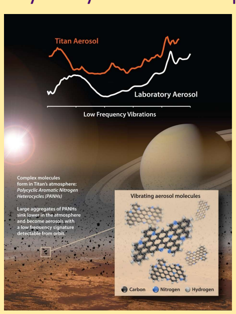



**Figure 4**. Far-infrared spectra from the Cassini spacecraft as compared to the spectra of laboratory aerosols produced from aromatic compounds.
*Image courtesy of JPL-NASA.*

- Cassini-borne instruments **have detected benzene in Titan's atmosphere.**
- Aromatics, such as benzene (below, left), has been shown to be an **important pathway in aerosol formation.**
- Far-IR spectral feature of Titan's haze layer is similar to that of aerosols produced from aromatic compounds.[3] (Figure 4)
- Though not observed in situ, pyridine (N-containing aromatic, below) is a likely product of Titan chemistry and produces laboratory aerosol with a strong Far-IR feature.

## Materials and Methods

### Aerosol Production

- **Titan aerosol analogs are produced in the laboratory to study their fractionation.**
- Gas mixtures used are trace gases ($CH_4$, benzene ($C_6H_6$), and pyridine ($C_5H_5N$) with nitrogen ($N_2$)) in mixing chamber as shown in Figure 6.
- **The gas mixture is irradiated with far-UV light** (115-400 nm) that leads to aerosol production. a quartz filter (Figure 7).
- Aerosol samples are collected in an inert, ex situ environment (Ar, $N_2$ or vacuum) and processed for Isotope Ratio Mass Spectrometry (IRMS) Analysis

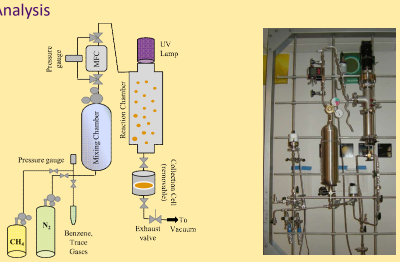



**Figure 6**. *Left:* Setup for generating Titan aerosol analogs. *Right:* Actual system for generating the aerosols. Note that the tanks of the reactant gases ($N_2$ and $CH_4$) are not shown in the picture.

**Figure 7**. Image of laboratory produced aerosol before IRMS processing

### Isotope Ratio Mass Spectrometry (IRMS)

- **IRMS is used to measure the relative abundance of isotopes in a given sample.**
- The sample is combusted and is converted into $CO_2$ and $N_2$.
- Carbon and nitrogen stable isotope values are reported in standard δ notation in per mil (%) as defined by:

  $\delta(‰) = [(R_{sample} \div R_{standard})-1] \cdot 1000$

  where $R_{sample}$ is the ratio of the heavy to light isotope ($^{13}C/^{12}C$ or $^{15}N/^{14}N$) and $R_{standard}$ is the isotopic ratio of the standard.
- To determine the **isotope fractionation induced by the aerosol production**, the isotope ratios of the products and reactants are compared using the equation:

  $\Delta^{13}C = \delta^{13}C_{products} - \delta^{13}C_{reactants}$ or $\Delta^{15}N = \delta^{15}N_{products} - \delta^{15}N_{reactants}$

## Results

| Mixture | Pressure (Torr) | Collection Time (Hours) | $\Delta^{13}C$ | $\Delta^{15}N$ |
|---|---|---|---|---|
| 50 ppm Benzene | 100 | ~60 | -4.3 | 9.6 |
| 50 ppm Benzene; 0.1% $CH_4$ | 100 | ~120 | 13 | -9.1 |
| 50 ppm Pyridine | 100 | ~60 | 20 | 2.1 |
| 50 ppm Pyridine; 0.1% $CH_4$ | 100 | ~120 | 30 | 2.1 |

- **Significant differences in the isotopic ratios between the aerosols generated by the two different aromatic compounds** (benzene and pyridine).
- The addition of methane to the mixture significantly increases the aerosol production time
- The uncertainties of the data are still being assessed.

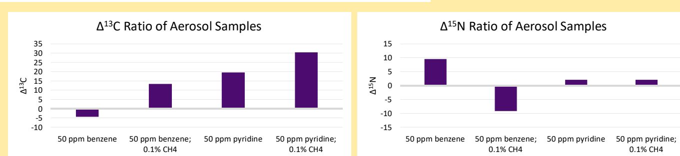



**Figure 8.** Comparison of the $\Delta^{13}C$ and $\Delta^{13}C$ values for the four different aerosol samples generated by aromatic gas mixtures in $N_2$

- The aerosols generated with **the pyridine/$N_2$** gas mixture are **enriched in the $^{13}C$ isotope,** while the aerosols generated by **benzene/$N_2$** gas mixture are **depleted in the $^{13}C$ isotope.**
- **Methane significantly increases the $\Delta^{13}C$ ratio for the aerosols generated by both aromatic compounds.** This consistent previous research where methane generated aerosols, which were enriched in the $^{13}C$ isotope.[4]
- The $\Delta^{15}N$ ratio for the benzene/$N_2$ generated aerosol seems to be significantly higher than the pyridine/$N_2$ generated aerosol but low amount of nitrogen in the sample could induce large uncertainties.
- **The addition of methane to the benzene/$N_2$ gas mixture caused an enrichment in the $^{14}N$ isotope over the $^{15}N$ isotope in the generated aerosols.**
- Methane addition to the pyridine/$N_2$ gas mixture did not significantly change the $\Delta^{15}N$ ratio for the generated aerosols. This could be because the primary contribution to the N in the aerosol is from pyridine

## Conclusions

- **The aerosols produced in the laboratory setting demonstrate a change in isotopic ratio for $^{13}C$ and $^{15}N$ from the starting products.**
- **The addition of methane to a gas mixture appears to partially inhibit aerosol formation and increase collection time.**
- **Further work will need to be done to asses the effects of temperature and pressure on aerosol formation and isotopic ratio for $^{13}C/^{12}C$, $^{15}N/^{14}N$ and D/H.**

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