National Aeronautics and Space Administration

Postdoc Research

Laboratory simulation of Pluto's and Triton's surface ice photochemistry

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Background

NASA's *New Horizons* and *Voyager 2* missions unveiled the first close-up images of Pluto and Triton, shedding light on their distinct surface color units [1-2]. Several hypotheses have been proposed as to the origin of these coloring agents, including the photolysis of the volatile surface ices N_2:CH_4:CO [1-2]. Laboratory experiments have provided significant insights into the characterization of the small and volatile molecules formed through the photolysis of these ices [3]. However, the complex refractory organic materials also produced in these experiments still lack comprehensive characterization of their optical properties. The optical constants *n* and *k* (*i.e.*, real and imaginary parts of the complex refractive index) are fundamental input parameters in models for interpreting data from NASA's space missions. Limitations in the variety of available optical constants of refractory organic materials remain a problem to date [4].

Objectives

Characterize the optical constants *n* and *k* of refractory organic materials formed by the photolysis of N_2:CH_4:CO ice mixtures. These optical constants can then be used in radiative transfer models to understand the origin and evolution of coloring agents at the surface of Pluto, Triton, and any other outer solar system objects or comets with similar surface composition.

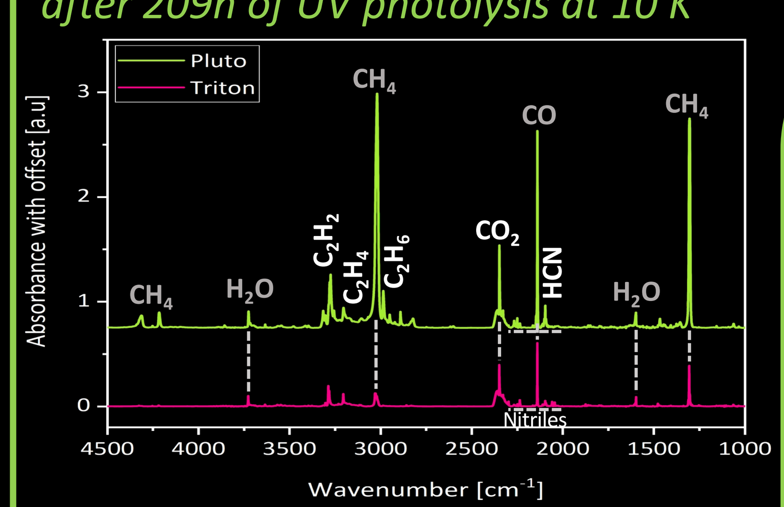
Fig. 1: Pictures of refractory organic residues analogous to Pluto's and Triton's surface organic material

Approach and Results

We reproduced in the laboratory Pluto's and Triton's surface ice photochemistry using a high-vacuum chamber equipped with a closed-cycle helium cryostat and a low-pressure microwave-discharge hydrogen UV lamp. We synthesized and analyzed refractory organic residues, also called '*ice tholins*' (see Fig. 1), analogous to the organic material detected on Pluto's and Triton's surfaces.

Preparation of gas mixtures N_2:CH_4:CO → Vapor-deposition and UV photolysis of ice analogs → Warming of photolyzed ice analogs → Collection of refractory organic residues → Microscopy Profilometry UV, Vis, NIR, MIR *n* and k

Fig. 2: Baseline-corrected IR spectra of Pluto and Triton ice analogs after 209h of UV photolysis at 10 K



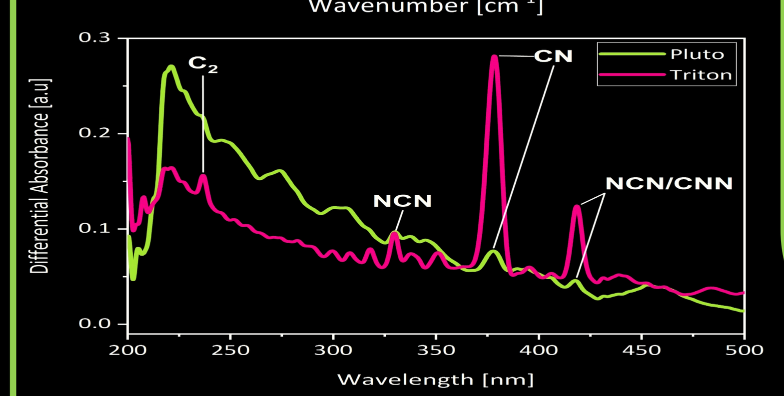
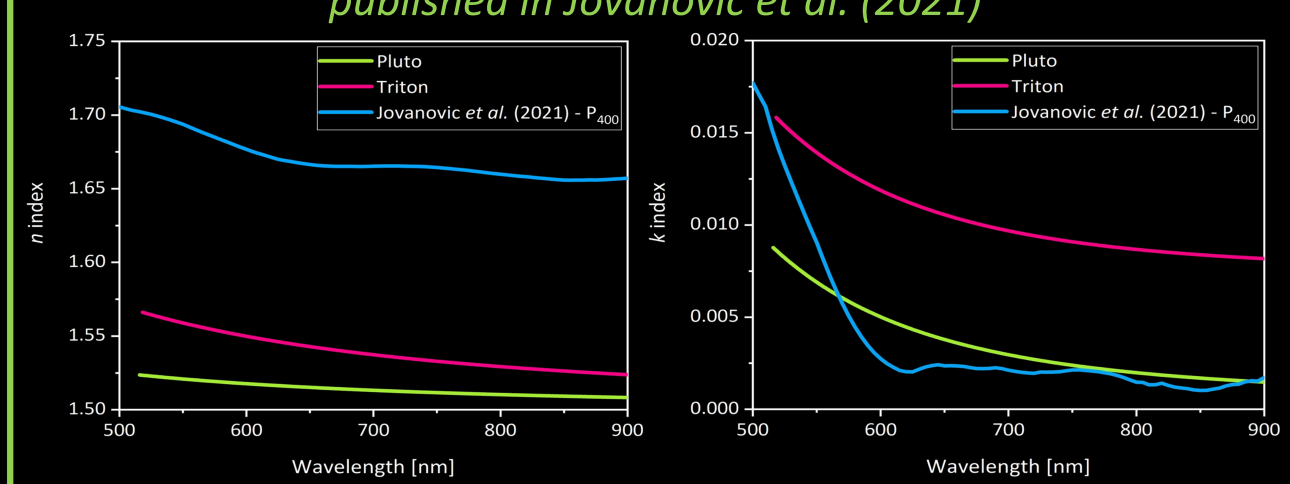


Fig. 3: UV-Vis spectra of photolyzed Pluto and Triton ice analogs after 40h of UV photolysis at 10 K

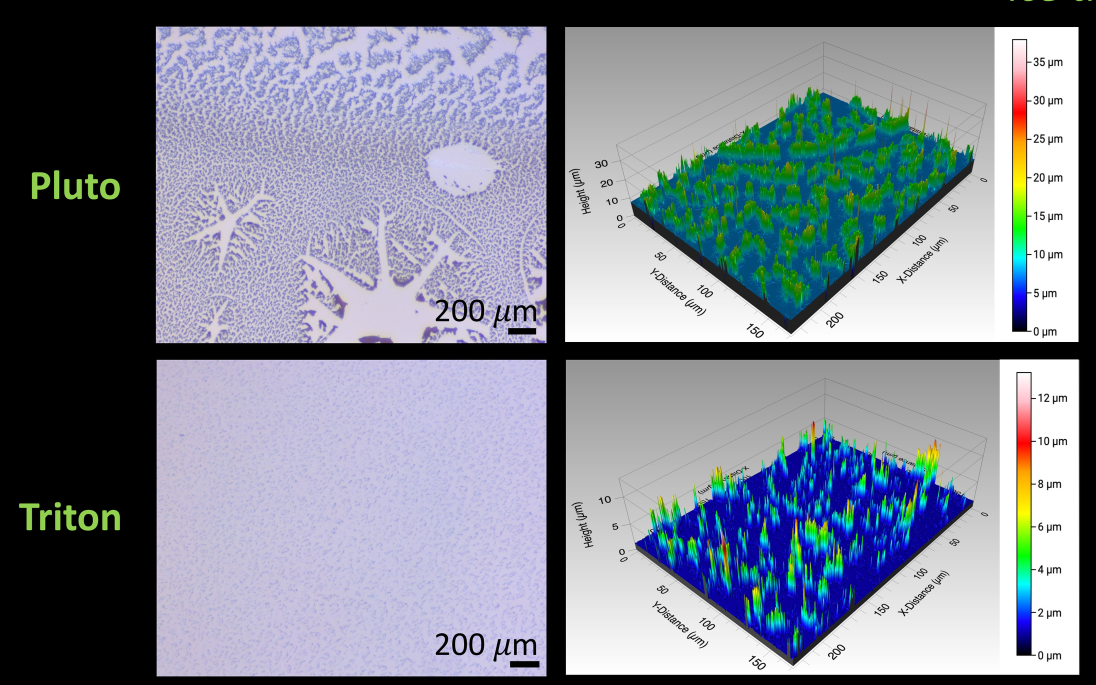
- Appearance of new volatile molecules: CO_2, C_2H_x, HCN
- Photoproducts more abundant in Pluto ice analogs, except radicals CNCN, C_2, NCN, CN, CNN
- Importance of radical chemistry in the formation of refractory organic residues

Fig. 6: Real n (left) and imaginary k (right) refractive indices of Pluto and Triton ice tholins, compared to Pluto gas tholins P_{400} published in Jovanović et al. (2021)



- $n_{Pluto} < n_{Triton}$
- $k_{Pluto\ gas\ \&\ ice} << k_{Triton\ ice}$
- $n_{ice\ tholins} << n_{gas\ tholins}$
- Significant effect of N-incorporation on *n* and *k*

Fig. 4: Optical microscopy photographs (left) and profilometry measurements (right) of Pluto and Triton ice tholins



- Clusters of organic material surrounded by empty areas
- For the same UV fluence experienced, organic residues thicker for Pluto (avg. 8.5 µm) than for Triton (avg. 1.3 µm)
- Bands consistent with the literature: amine, (iso)nitrile, carbodiimide, C=C and C=N in (hetero)aromatic rings
- Different band ratios and shape of the (iso)nitrile band, suggesting different optical properties

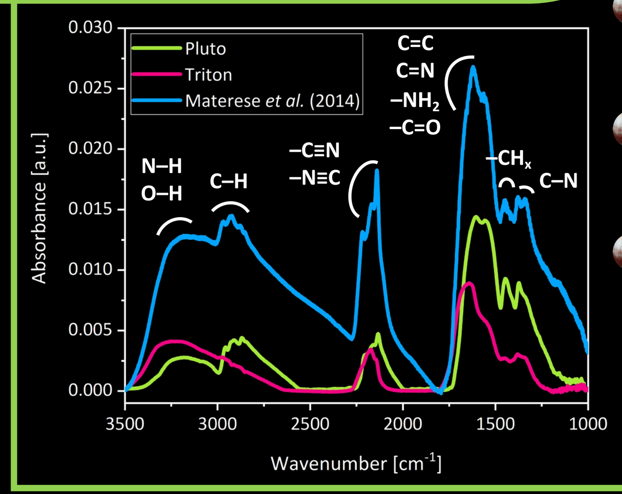


Fig. 5: Baseline-corrected IR spectra of Pluto and Triton ice tholins, compared to Pluto ice tholins published in Materese et al. (2014)

Significance of Results / Benefits to NASA/JPL

We are providing the scientific community for the first time with optical constants of refractory organic residues formed by UV photolysis of N_2:CH_4:CO ice mixtures of interest to outer solar system objects. This will enable us to assess the impact of this newly-characterized material on the synthetic spectra generated by radiative transfer models, and evaluate whether this type of material fits the Pluto and Triton observations better (and any other similar Kuiper belt objects or comets). This study is in line with scientific questions raised by the Planetary Science Decadal Survey of understanding ice giant systems and the role of external processes affecting the surfaces of solid bodies.

Future Work

So far, the optical constants have only been characterized in the visible range. The ongoing next step is to extend their characterization over a wider spectral range, from UV to mid-IR. In particular, the optical constants of ice tholins in the visible-near-IR can then be used in radiative transfer simulations of Pluto's surface and compared to *New Horizons* MVIC and LEISA spectra to provide new clues as to the origin of the organic matter on Pluto's surface. Once published, the optical constants will be added to the Optical Constants database (OCdb), to facilitate their access and use in analysis of observations from past, current and future NASA missions.

Publications

▻ Jovanović L. *et al.* (*in prep.*), Laboratory simulation of Pluto's and Triton's surface ice chemistry triggered by UV photolysis. Part I. Surface volatile ice chemistry ▻ Jovanović L. *et al.* (*in prep.*), Laboratory simulation of Pluto's and Triton's surface ice chemistry triggered by UV photolysis. Part II. Optical constants of refractory organic residues ▻ Jovanovic L. *et al.* (Oral presentation), Laboratory investigation of Pluto's surface organic matter: a surface photochemical origin?, *242nd AAS Meeting*, Albuquerque NM, June 4-8, 2023 ▻ Jovanovic L. *et al.* (Oral presentation), Laboratory investigation of Pluto's organic aerosols, *Blue Sky 2023 workshop*, Pasadena CA, August 2-4, 2023

References

[1] Stern *et al.* (2015), *Science* 350:6258. [2] Smith *et al.* (1989), *Science* 246:4936.
[3] Hudson *et al.* (2008), *The Solar System Beyond Neptune*, pp. 507-523.
[4] Barucci et al. (2021), *The Pluto System After New Horizons*, pp. 21-52.

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