EPSC Abstracts
Vol. 12, EPSC2018-195-1, 2018
European Planetary Science Congress 2018

UV irradiation of Titan organic haze

Nathalie Carrasco (1), Sarah Tigrine (1, 2), Lisseth Gavilan (1), Laurent Nahon (2) and Murthy Gudipati (3)
(1) LATMOS/IPSL, UVSQ, Université Paris-Saclay, UPMC Univ. Paris 06, CNRS, France, (2) SOLEIL synchrotron, France, (3) Jet Propulsion Laboratory, Science Division, California Institute of Technology, USA (nathalie.carrasco@uvsq.fr)

Abstract

The Cassini–Huygens space mission discovered that Titan's thick brownish haze is initiated high in the atmosphere at an altitude of about 1000km. So far, nothing is known on the possible photochemical evolution of the organic aerosols composing the haze. Here, we address this aging process, simulating in the laboratory how solar vacuum ultraviolet irradiation affects the aerosols. The chemical evolution is monitored by infrared spectroscopy.

1. Introduction

After their production in the ionosphere [1], Titan's aerosols are known to evolve through microphysics during their sedimentation down to Titan's surface [2]. As laboratory analogs of Titan's atmospheric aerosols (tholins) are strong UV absorbers [3], UV irradiation is suspected to induce a chemical evolution of Titan's aerosols during their descent in the atmosphere. The aim of this work is to simulate this irradiation process on Titan's aerosols and to address the impact on the chemical composition of the organic solids [4]. We have chosen two irradiation wavelengths to experimentally simulate the evolution of the aerosols high in the atmosphere: 95 nm representative of hard photons at about 1000 km and 121.6 nm (Lyman-α) a major VUV contribution in the solar spectrum penetrating down to 600 km.

2. Methodology

1.1 Sample synthesis

First tholins were produced in a 95-5% N_2-CH_4 radio-frequency plasma discharge as thin organic films of 440 ± 20 nm thicknesses deposited onto Silicon windows (with a surface of 11 mm² and a thickness of 0.5 mm). Film thickness was found by spectroscopic ellipsometry in the 370–1000 nm spectral range (M-2000V, Woollam Co).

1.2 VUV irradiation source

The 11-mm²-sample surface is entirely illuminated by the beam spot of the quasi-monochromatic DESIRS-synchrotron beamline [5]. Each sample is irradiated with a specific wavelength (95 or 121.6 nm) and a chosen irradiation-duration. With the chosen experimental configuration, the photon flux density is two orders of magnitude larger than the corresponding UV solar flux density. The dose is adjusted by choosing shorter irradiation times of typically a few hours in our experiments, in order to simulate approximately one-Titan day irradiation.

1.3 IR spectroscopy

The samples were characterized by ex-situ mid-IR absorption spectroscopy in the 1200-3500 cm^{-1} wavenumber range. All pre- and post-irradiation infrared measurements were performed by transmission analysis with the Thermo Scientific Nicolet iN10 MX spectrometer at the SMIS beamline of the synchrotron SOLEIL facility with a mercury cadmium telluride and a spectral resolution of 4 cm^{-1}.

3. Results

The effect of VUV irradiation is illustrated in Figure 1 with the comparison of the absorbance spectra of a single sample before and after 24 hours irradiation at 121.6 nm. We observe a decrease of the nitrile functions, C-H bonds and N-H bonds. The samples irradiated at 95 nm evolve similarly, with significant changes only observed at shorter irradiation durations for the nitrile functional group. As expected with the higher energy dose provided at 95 nm, absorption of the nitrile group decreases faster and more significant with 95 nm irradiation than with 121.6 nm. A loss of about 20% is obtained at 95 nm after 2 hours of irradiation, which is about twice compared to the one observed at 121.6 nm.

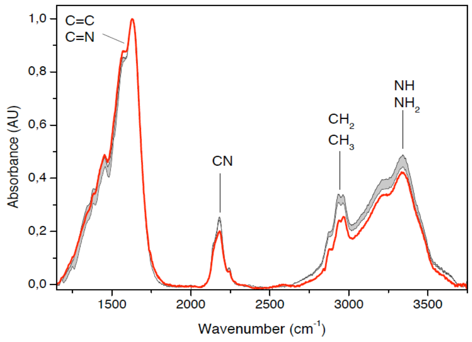

Figure 1: Infrared absorption spectra normalized to the highest absorption value at ~1550 cm^{-1}. The grey envelope shows the dispersion (2σ) of the non-irradiated sample in the 1200-3500 cm^{-1} range. The red spectrum is recorded after irradiation for 24h by VUV photons at 121.6 nm [4].

The penetration depth of the VUV radiation is about 20 nm in our organic sample (obtained from the imaginary part k of the VUV refractive index [6]). The effective layer thickness affected by the radiation is considered at four times the penetration depth with a residual radiation of 2%. The short penetration depth of VUV photons means that these photons are effective up to 100 nm of the 440 nm thick sample during VUV irradiation. The experimental 15-20% IR signature attenuation observed on Figure 1 is similar to the thickness contribution of the irradiated layer, showing that the irradiated layer possesses totally different IR properties from the non-irradiated layer.

4. Summary and Conclusions

This work provides evidence that VUV photochemistry with wavelengths below 150 nm could in particular deplete the sensible primary and secondary amine functions of aerosols in the upper atmosphere. This would be consistent with the VIMS measurements in the stratosphere [7], which show no evidence of these functions. The irradiation effect does preserve nitrogen-bearing functionalities that are more strongly bound in the aerosol skeleton, such as tertiary amines, imines and nitriles (except conjugated nitriles). This chemical transformation of the aerosol composition would thus allow the VIMS results to agree with the high nitrogen content reported by the Huygens-ACP instrument close to the surface [8].

Acknowledgements

N.C. and L.G. thank the European Research Council for funding via the ERC PrimChem project (grant agreement 636829). S.T. acknowledges the University of Paris-Saclay for thesis funding. The work of M.S.G. at the Jet Propulsion Laboratory, California Institute of Technology was performed under the NASA-SSW grant 'Photochemical Processes in Titan's Atmosphere'. L.N. acknowledges support from the Agence Nationale de la Recherche (ANR-07-BLAN-0293).

References

[1] Waite et al., Science, Vol. 316, p. 870-875, 2007.

[2] Lavvas et al., Astrophysical Journal, Vol. 728, p.80, 2011.

[3] Mahjoub et al., Icarus, Vol. 221, p. 670, 2012.

[4] Carrasco et al. Nature Astronomy, available online, 10.1038/s41550-018-0439-7, 2018.

[5] Nahon et al., J. Synchrotron Rad. Vol. 19, pp. 508-520, 2012.

[6] Khare, B. N. et al. Icarus, Vol. 60, pp.127-137, 1984.

[7] Kim, S. J. et al. Planetary and Space Science, Vol. 59, 699-704, 2011.

[8] Israel, G. et al. Nature, Vol. 438, pp. 796-799, 2005.