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1 Optical constants of Pluto aerosol analogues from UV to near-IR

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15 Keywords

16 Pluto; Pluto, Aerosols, Haze; Pluto, Atmosphere; Pluto, Surface; Optical Constants

17

18 Abstract

Photochemical aerosols were detected as high as 350 km of altitude in Pluto's atmosphere during the *New Horizons* fly-by. These aerosols are thought to affect Pluto's climate, by acting as cooling agents, and the colours of Pluto's surface, in particular in the dark regions named Cthulhu and Krun and at the North Pole. Pluto atmospheric and surface models have so far used the optical constants of Titan aerosol analogues (tholins), whereas their chemical composition is known to differ from that of Pluto aerosol analogues.

In order to provide a new set of optical constants for Pluto tholins, we synthesized analogues

- 26 of Pluto's aerosols and determined with spectroscopic ellipsometry their optical constants from
- $270 to 2100 nm. Three types of samples were produced from N_2: CH_4: CO gas mixtures differing$

in their CH₄:N₂ mixing ratio, representative of different altitudes in Pluto's current atmosphere
or different seasons or epochs of Pluto.

Our analysis shows a strong absorption by Pluto tholins in the UV and visible spectral ranges, with k index of a few 10⁻¹ at 270 nm, in agreement with N- and O-bearing organic molecules. Pluto tholins are less absorbent in the near-IR than in the UV-Vis wavelength range, with k of a few 10⁻³ between 600 and 2100 nm. Our comparative study highlights the dependency of nand k indices to the CH₄:N₂ mixing ratio. Aerosols formed at different altitudes in Pluto's atmosphere or during different seasons or epochs of Pluto will therefore affect the budget of Pluto radiative transfer differently.

The optical constants presented in this study were tested with a Pluto surface model and with a model of light scattering. The surface modelling results highlight the suitability of these optical constants to reproduce Pluto compositional observations in the visible spectral range by MVIC and LEISA. The atmospheric modelling results conclude that Pluto tholins absorb 5 to 10 times less than Titan tholins at 500 nm, and this lower absorption is consistent with Alice observations of Pluto's haze.

43

44 I. Introduction

Pluto fly-by by the *New Horizons* spacecraft on July 14th, 2015 evidenced the presence of aerosols in Pluto's atmosphere by means of forward scattering observations and solar occultations. These aerosols, accounting for 0.05-0.1 ppmv of the atmosphere, enshroud Pluto and were detected at least as high as 350 km of altitude above the surface (Cheng et al. 2017; Gladstone et al. 2016; Stern et al. 2015; Young et al. 2018).

50 Two mechanisms are currently proposed for the formation of hazes in Pluto's atmosphere.

51 The first one concerns the formation of aerosols through photochemistry, similar to what occurs in Titan's upper atmosphere (e.g., Gladstone et al. 2015, 2016; Wong et al. 2017; Young et al. 52 2018). Pluto's aerosols are thought to be formed by a complex photochemistry taking place in 53 the upper atmosphere, below 300 km and up to 900 km of altitude (Stern et al. 2018; Young et 54 55 al. 2018). This photochemistry is initiated by extreme-ultraviolet (EUV) sunlight and solar Lyman-a photons. EUV radiation breaks the triple bonds of N2 and CO in the upper atmosphere, 56 57 while Lyman- α photons – arriving directly from the Sun or scattered by the interplanetary 58 medium – breaks the C–H bonds in CH₄ at lower altitudes (Gladstone et al. 2015, 2016; Grundy et al. 2018, and references therein), with a maximum CH₄ photolysis rate at 250 km of altitude above the surface (Bertrand & Forget 2017). Pluto's photochemistry involves neutral and ionic species created by the ionization and the dissociation of molecular nitrogen N₂, methane CH₄, and carbon monoxide CO that constitute Pluto's atmosphere (Gladstone et al. 2016; Lellouch et al. 2017; Young et al. 2018). This chemistry forms complex hydrocarbons, nitriles, and oxygenated molecules, including some that can further polymerize and generate solid aerosols (Krasnopolsky 2020; Wong et al. 2017).

The second mechanism, developed by Lavvas et al. (2020), would be different from that 66 proposed for Titan's hazes formation, due to the temperature difference between Pluto's and 67 Titan's upper atmospheres (~70 K versus ~150 K, respectively). This mechanism involves the 68 69 direct condensation of photochemical gases produced on Pluto, associated with a coating by 70 undersaturated light molecules (C_2 hydrocarbons) incorporated by heterogeneous processes (possibly chemisorption or physisorption). This coating represents ~30% of the aerosol material 71 (Lavvas et al. 2020). These coated aerosols are then subject to a photon flux causing their 72 73 ageing, as studied in Carrasco et al. (2018) for Titan's aerosols.

Note that the present study focuses on Pluto's aerosols formed by photochemistry.

Questions remain regarding the size distribution of Pluto's haze particles since no single 75 76 solution can satisfy measurements from all instruments onboard New Horizons. Cheng et al. 77 (2017) pointed out the contradiction between haze brightness I/F profiles inferred from Alice imaging spectrograph in the far-UV [52-187 nm] (Stern et al. 2008) and LORRI (LOng-Range 78 79 Reconnaissance Imager) panchromatic imaging instrument in the [350-850 nm] wavelength range (Cheng et al. 2008). A model of Mie scattering by 0.5 µm spheres reproduces fairly well 80 the phase function of Pluto's haze at peak I/F measured in the visible by LORRI. However, this 81 Mie model gives UV extinction lower by an order of magnitude than that retrieved from Alice 82 solar occultation. On the opposite, results from a model of scattering by aggregates with bulk 83 radius of 0.15 μ m composed of several thousands 0.01 μ m spherical monomers agree with the 84 measurements made by Alice. They also match with the visible phase function measured by 85 86 LORRI, but only at higher altitudes in Pluto's atmosphere (Cheng et al. 2017). At higher 87 altitudes, Pluto's haze is thus thought to be mostly composed of aggregates of 0.15 µm particles made up of 10 nm forward-scattering spheres. The haze particles present in the atmosphere 88 89 from the surface to ~15 km of altitude probably correspond to spherical particles that got larger by direct condensation of photochemical products onto nuclei (Cheng et al. 2017; Gao et al. 90 91 2017; Gladstone et al. 2016; Lavvas et al. 2020; Stern et al. 2015; Young et al. 2018).

The haze particles are suspected to scatter the UV sunlight and to be the dominant factor of extinction at wavelengths greater than ~150 nm, as the extinctions of hydrocarbons or nitriles become less important with increasing wavelength. The haze particles thus contribute to the spectrum of Pluto observed by the Alice instrument (Cheng et al. 2017; Steffl et al. 2020; Stern et al. 2008). Pluto's aerosols are also expected to significantly absorb in the UV-Visible and in the far-infrared spectral ranges and to be less absorbent in the near- and mid-IR (Grundy et al. 2018; Zhang et al. 2017; and references therein).

Recent numerical models have shown that these aerosols deeply affect Pluto's atmospheric 99 chemistry, for instance by depleting from the atmosphere small hydrocarbons that stick to the 100 101 negatively-charged aerosols, resulting in the formation of more complex ones (Krasnopolsky 102 2020; Luspay-Kuti et al. 2017; Wong et al. 2017). Pluto's climate is also affected by the aerosols, that can serve as condensation nuclei (Gao et al. 2017; Lavvas et al. 2016; Luspay-103 104 Kuti et al. 2017; Wong et al. 2017) or through direct radiative cooling of the atmosphere by the absorption of solar radiations (Zhang et al. 2017). Pluto's atmosphere temperature, at ~400 km 105 106 of altitude, is around 30-40 K colder than model predictions for an atmosphere in radiativeconductive equilibrium without haze (Gladstone et al. 2016; Zhang et al. 2017; Zhu et al. 2014). 107 Zhang et al. (2017) suggested this cooling to be due to the haze particles and their optical 108 properties. Due to a lack of both observational and experimental data on these optical properties, 109 the study by Zhang et al. (2017) was done using those of Titan aerosol analogues (Titan tholins) 110 111 produced on Earth. In addition, these photochemical aerosols have been suggested to account for all of Pluto's colours at large scales, from the dark red colour of Cthulhu and Krun Maculae 112 to the yellow hue on Pluto's North Pole (Lowell Regio) (Grundy et al. 2018; Protopapa et al. 113 2017, 2020). The modelling studies of Pluto New Horizons data across the full [0.4-2.5 µm] 114 115 wavelength range by Protopapa et al. (2020) used optical constants determined for Titan tholins by Khare et al. (1984) and Tran et al. (2003), given the lack of optical constants for Pluto tholins. 116 117 To explain the different colours on Pluto's surface, Grundy et al. (2018) used multiplescattering radiative transfer models with optical constants determined for Titan tholins by 118 119 several groups: Khare et al. (1984), Ramírez et al. (2002), Imanaka et al. (2004), Vuitton et al. (2009), and Sciamma-O'Brien et al. (2012). 120

Protopapa et al. (2020) pointed out the lack of optical constants for tholins in the Vis-near-IR wavelength range. Additionally, Zhang et al. (2017) highlighted that the optical constants determined for Titan aerosol analogues strongly vary with the mode of production and that the optical constants of Pluto's aerosols may be very different from those of Titan tholins. Note that the review by Brassé et al. (2015) discusses the different optical constants determined forTitan tholins.

Thus, to update and better constrain Pluto atmospheric models and to model Pluto's surface
spectra, the determination of the optical constants of Pluto aerosol analogues is strongly needed.
The aim of our work is to fill this gap, by providing optical constants of Pluto tholins from 270
to 2100 nm.

131 II. Experimental setup and protocol

132 **1. Production of Pluto aerosol analogues**

Following the protocol detailed in Jovanović et al. (2020), we used the experimental setup PAMPRE (Production d'Aérosols en Microgravité par Plasma REactif) (Alcouffe et al. 2010; Szopa, Cernogora et al. 2006), a cold plasma discharge to simulate the chemistry occurring in Pluto's atmosphere and produce analogues of Pluto's aerosols. The gas mixture flows through a cylindrical metallic grounded cage. Square silicon wafers of 1 cm² were placed at the bottom of the cage. When the plasma is switched on, tholins form as thin films onto the silicon wafers.

Note that the optical constants of tholins are highly dependent on the experimental conditions 139 of synthesis and measurements (Brassé et al. 2015; Zhang et al. 2017). For readers interested in 140 the effect of using a UV lamp rather than a plasma discharge to synthesize tholins, we 141 recommend reading the review by Cable et al. (2012). In summary, tholins formed by UV 142 photochemistry in the laboratory tend to be less rich in N-bearing compounds, since UV lamps 143 cannot mobilize nitrogen chemistry. Indeed, lamp windows cut off UV wavelengths below 144 ~115 nm, which prevents direct dissociation of N_2 , unlike what happens in natural atmospheres. 145 146 On the contrary, plasma setups such as PAMPRE tend to enhance nitrogen inclusion a bit too much. The electron energy distribution in PAMPRE mimics well at first order the one of solar 147 photons (Szopa, Cernogora et al. 2006). However, a small difference is due to the slightly more 148 energetic tail of the Maxwellian energy distribution of the electrons in the plasma compared to 149 the Planck energy distribution of solar photons. This slightly higher population of electrons 150 151 induces a small bias due to over-dissociation of N₂, that is well known and has been extensively studied regarding the tholins chemical composition. Since nitrogenous compounds tend to be 152 153 more absorbent, one could expect that tholins synthesized in laboratory by UV photochemistry would probably be less absorbent in the UV-Vis spectral range, due to a poorer content in N-154 155 bearing compounds. Where actual Pluto's aerosols would stand in that range is currently unknown (as for Titan's aerosols), which is why we strongly encourage any other experimental 156

teams with similar facilities to perform studies similar to ours to extend the range of possiblelaboratory data on this point.

Three types of tholins were synthesized in this work, from gas mixtures composed of various 159 N₂ (Air Liquide, ALPHAGAZ[™] 2) and CH₄ (Air Liquide, CRYSTAL mixture) percentages 160 and a fixed CO (Air Liquide, CRYSTAL mixture) amount of 500 ppm (see Table 1), at 161 0.9 ± 0.1 mbar and ambient temperature. For readers interested in the effect of synthesis 162 temperature on aerosol analogues optical constants, we recommend reading Mahjoub et al. 163 (2014) who studied this effect for Titan tholins. In the present work, experiments were 164 165 performed at ambient temperature to avoid heterogeneous chemistry effects as described in Mahjoub et al. (2014). 166

167 The CO atmospheric mole fraction of 515 ± 40 ppm (Lellouch et al. 2017; Young et al. 2018) is not expected to vary much over time and space. This is due to the volatility of CO being close 168 169 to that of N₂ and the absence of CO-rich ice deposits on Pluto's surface (Bertrand & Forget 2016). The first type of tholins was produced in a gas mixture composed of N₂:CH₄:CO at 170 99.5%:0.5%:500 ppm – we will thereafter call this material "P_H". Given that the CH₄ mixing 171 ratio was found to be ~0.3% below 350 km of altitude (Young et al. 2018), P_H is relevant to the 172 composition of Pluto's atmosphere as observed in 2015 below 350 km of altitude above the 173 surface. The second tholins sample was produced in a gas mixture containing N₂:CH₄:CO at 174 99%:1%:500ppm, mimicking Pluto's atmosphere at around 400 km of altitude above the 175 surface – thereafter called " P_{400} ". The third one was produced in a gas mixture made of 176 N₂:CH₄:CO at 95%:5%:500ppm, representative of Pluto's atmosphere between 600 and 177 700 km of altitude – thereafter called "P₆₅₀" (Lellouch et al., 2017, Young et al., 2018). 178

We note that the mean CH₄ atmospheric mixing ratio is predicted to vary from 0.01% to 5% over annual or astronomical timescales (Bertrand et al. 2019; Bertrand & Forget 2016). The tholins synthesized in the present work could therefore also serve as analogues for haze particles produced during past epochs or different seasons of Pluto, with implications to its past and future climates.

For the three types of tholins, the plasma ran for 90 minutes, forming films with thicknesses no more than 1 μ m (see Table 1) to ensure the validity of the spectroscopic ellipsometry technique for the measurements (Fujiwara 2007; Mahjoub et al. 2012; Sciamma-O'Brien et al. 2012).

Composition of the reactive mixture			Corresponding altitude above the	Acronym of the aerosol	Thickness of the
N ₂	CH ₄	СО	surface on Pluto	analogues	
99.5%	0.5%	500 ppm	< 350 km	P _H	$549.8\pm0.6~\text{nm}$
99%	1%	500 ppm	~ 400 km	P ₄₀₀	$540.9\pm0.2~\text{nm}$
95%	5%	500 ppm	600-700 km	P650	$651.0\pm0.7~\text{nm}$

188 Table 1: Table presenting the three types of Pluto aerosol analogues analysed in this study.

189

190 The thickness of the thin films was determined by spectroscopic ellipsometry with a modified 191 Tauc-Lorentz dispersion model, as detailed below. We note that for the same synthesis duration, 192 the thin-film thickness increases when the amount of CH₄ injected in the reactive gas mixture 193 increases significantly, as discussed by Mahjoub et al. (2012).

194 **2.** Spectroscopic ellipsometry

The tholins thin films were analysed by spectroscopic ellipsometry. Using this analysis technique, it is possible to determine the thickness of the tholins thin films, as well as their optical constants n and k, the real and imaginary parts respectively of the complex refractive index.

Spectroscopic ellipsometry measures the change in the polarization state between incident and reflected light on the sample (the reader is referred to *e.g.*, Azzam & Bashara (1977), Tompkins & Irene (2005) and Fujiwara (2007) for complete information on spectroscopic ellipsometry technique). Incident light is linearly polarized, while reflected light is elliptically polarized.

The measured values are the ellipsometric parameters Ψ and Δ , related to the ratio of the Fresnel amplitude reflection coefficients of the sample by fundamental equation:

205 206

$$r_{\rm p}/r_{\rm s} = \tan \psi \, {\rm e}^{i\Delta} \quad (1)$$

207

for p- and s-polarized light¹ with the electric field in the plane of incidence and perpendicular
to the plane of incidence, respectively.

¹ r_p is the reflection coefficient of the sample for a polarization parallel to the plane of incidence ("p" for parallel) and r_s is the reflection coefficient of the sample for a polarization perpendicular to the plane of incidence ("s" for perpendicular, "senkrecht" in German).

Variable Angle Spectroscopic Ellipsometry (VASE) measurements were carried out using a 210 phase-modulated spectroscopic ellipsometer (UVISEL, Horiba Jobin Yvon), equipped with a 211 150 W Xenon light source. Corresponding ellipsometric parameters were obtained through 212 $(I_s(\lambda), I_c(\lambda))$ in the spectral range [270-2100 nm] with 5 nm steps according an integration time 213 of 1000 ms, where $I_s = \sin(2\Psi) \sin(\Delta)$ and $I_c = \sin(2\Psi) \cos(\Delta)$, respectively. All 214 measurements were performed for incidence angles between 60 and 75 degrees with 5° steps. 215 By way of comparison, the ellipsometric analyses performed on Titan tholins thin films by 216 Mahjoub et al. (2012, 2014) and Sciamma-O'Brien et al. (2012) were conducted for a single 217 incidence angle of 70°. 218

The parameters of the optical model were adjusted by minimizing the Mean Square Error (MSE) defined as:

221

222
$$MSE = \frac{1}{N-1} \sum_{i=1}^{N} \left[\left(I_{s,i}^{calc}(\lambda) - I_{s,i}^{exp}(\lambda) \right)^2 + \left(I_{c,i}^{calc}(\lambda) - I_{c,i}^{exp}(\lambda) \right)^2 \right]$$
(2)

223

where *calc* stands for the calculated and *exp* for the experimental values of (I_s , I_c) and *N* the number of experimental data ($I_s(\lambda)$, $I_c(\lambda)$).

226 DeltaPsi2[®] software² was used to fit ellipsometric data.

227 The inversion of ellipsometric data was performed using a model of the sample [Si substrate /

- 228 Tholins layer / Roughness layer / Air] as schematized in Figure 1.
- 229



230 231

Figure 1: Scheme of the model of the samples analysed by spectroscopic ellipsometry.

In this model, the thickness of the roughness layer, the thickness of the tholins layer, and the dielectric function of the tholins layer were unknown, while the roughness layer was modelled by a mixture of 50% air and 50% tholins, according to Bruggeman Effective Medium Approximation (BEMA) (Bruggeman 1935).

² DeltaPsi2[®] software: <u>https://www.horiba.com/en_en/products/detail/action/show/Product/deltapsi2-software-1648/</u>

Determination of the optical constants of Pluto tholins with two different inversion methods: modified Tauc-Lorentz and "wavelength-by-wavelength" (λ-by-λ)

239 Spectroscopic ellipsometry is an indirect technique for determination of the sample physical properties (*i.e.* thickness and optical constants). Using a model to describe the ellipsometric 240 241 response of the sample by adjusting specific fit parameters is thus necessary. Basically, the model calculates the reflection coefficients r_p and r_s to retrieve the measured ellipsometric 242 parameters Ψ and Δ . An equation system for each wavelength λ is generated: $\Psi = f(n, k, t)$ and 243 $\Delta = g$ (n, k, t), with $n(\lambda)$ and $k(\lambda)$ the real and imaginary parts respectively of the complex 244 refractive index, and t the thickness of the tholins thin film. The thickness t of the thin film and 245 the *n* index are initially determined in a transparent region of the thin film. Then, the fixed *t*-246 value is used as an input parameter to determine *n* and *k* indices in an absorbing region of the 247 thin film. The inversion method, based on the natures of the analysed material and the 248 underlying substrate, is used to calculate *n* and *k* indices of the material for each wavelength. 249

In this work, we used sequentially two types of inversion method: modified Tauc-Lorentz dispersion model to find the proper estimates of the initialization parameters, and "wavelengthby-wavelength" (λ -by- λ) numerical inversion to determine precisely the optical constants *n* and *k* of the tholins material.

a. Determination of the thickness and the optical constants of Pluto tholins by a modified Tauc-Lorentz dispersion model

The first model we used is a Tauc-Lorentz dispersion model, based on the Tauc joint density of states and the Lorentz oscillator, which was developed by Jellison and Modine (1996). This dispersion model was developed to better describe the optical properties of semiconductor and amorphous materials. This fitting model is thus adapted for tholins produced with the PAMPRE experimental setup, as Hadamcik et al. (2009) observed these samples with Scanning Electron Microscopy and showed that they present an amorphous structure.

In this model, the imaginary part $\varepsilon_{i,TL}$ of the complex relative dielectric constant is given by the product of the imaginary part of Tauc's dielectric constant $\varepsilon_{i,T}$ (Tauc et al. 1966) with a Lorentzian oscillator $\varepsilon_{i,L}$:

265
$$\epsilon_{i,TL}(E) = \epsilon_{i,T} \times \epsilon_{i,L} = \begin{cases} \frac{1}{E} \frac{AE_0 C(E-E_g)^2}{(E^2 - E_0^2)^2 + C^2 E^2} & \text{for } E > E_g \\ 0 & \text{for } E \le E_g \end{cases}$$
(3)

where E (in eV) is the photon energy; E_g (in eV) is the optical bandgap energy specifying at which energy the material becomes absorbent; E_0 (in eV) is the energy of the major absorption peak in the UV (the Lorentz peak) ($E_g < E_0$); A is the oscillator amplitude; and C is the broadening term.

270 The real part $\varepsilon_{r,TL}$ of the complex relative dielectric constant is derived from the expression of 271 $\varepsilon_{i,TL}$ (Equation (3)) using the Kramers-Kronig integration (Kramers 1927; Kronig 1926):

272
$$\varepsilon_{r,TL}(E) = \varepsilon_{\infty} + \frac{2}{\pi} \cdot P \cdot \int_{E_g}^{\infty} \frac{\xi \cdot \varepsilon_{i,TL}(\xi)}{\xi^2 - E^2} d\xi$$
(4)

where ε_{∞} is the high-frequency real dielectric constant; and P is the Cauchy principal value.

The optical constants n and k are then deduced from the real and imaginary parts of the complex

relative dielectric constant (Equations (3) and (4)) by the relation:

276
$$\varepsilon_{r,\text{TL}} + i \times \varepsilon_{i,\text{TL}} = (n + i \times k)^2 \quad (5)$$

In the standard Tauc-Lorentz model, the imaginary part k of the complex refractive index becomes null for energies below the bandgap energy. This is due to the resolution of Kramers-Kronig equations, but not to the intrinsic material properties. However, this k index is necessary for numerical models (*e.g.*, radiative transfer, albedo, surface composition, haze vertical profile).

To overcome this problem, we modified the standard Tauc-Lorentz model by adding oscillators characterized by ε_{osc} :

284
$$\varepsilon_{\rm osc} = \frac{f_j w_{0j}^2}{w_{0j}^2 - w^2 + i\gamma_j w} \qquad (6)$$

where ε_{osc} is the dielectric function; *w* is the light pulsation; f_j is the oscillator strength of the jth resonator; *w*_{0j} is the natural pulsation of the jth resonator; and γ_j is the damping rate of the jth resonator (friction coefficient).

Oscillators were added one by one to the model at different wavelengths, until the addition of an additional oscillator had no longer significant improvement in the MSE (Equation (2)). In this work, although the modified Tauc-Lorentz model was adapted for the determination of the thin-films thickness, the addition of oscillators was not sufficient to retrieve k indices below the bandgap energy (see Figure 3).

b. Determination of the optical constants of Pluto tholins by a "λ-by-λ" numerical inversion method

Once the thickness of the thin films and the initial couples $[n_{270nm}, k_{270nm}]$ characterized by the modified Tauc-Lorentz dispersion model (values used as input parameters), we used the " λ -by- λ " numerical inversion method to determine the optical constants of Pluto tholins.

In the " λ -by- λ " inversion method (also known as "direct data inversion" or "exact numerical 299 inversion"), n and k indices are calculated for each wavelength by applying mathematical 300 301 inversion of the Equation (1) (Fujiwara 2007). Theoretical ellipsometric parameters are calculated (Ψ_{calc} and Δ_{calc}) and the values are compared to the experimentally measured 302 ellipsometric parameters (Ψ_{exp} and Δ_{exp}). A linear regression algorithm introduces for the initial 303 couple $[n_{270nm}, k_{270nm}]$ the corrections needed to match ($\Psi_{calc}, \Delta_{calc}$) and (Ψ_{exp}, Δ_{exp}). Then, the 304 process is applied iteratively over the whole spectral range (from 270 to 2100 nm): the values 305 for the couple $[n_{\lambda}, k_{\lambda}]$ are calculated from the values of the couple $[n_{\lambda-\delta\lambda}, k_{\lambda-\delta\lambda}]$ with $\delta\lambda$ the 306 307 wavelength step between two measurements (here, 5 nm) (Fujiwara 2007; Keita et al. 2010; Likhachev et al. 2015). 308

The " λ -by- λ " numerical inversion method gives a mathematical solution for $[n_{\lambda}, k_{\lambda}]$ couples from measured ellipsometric parameters Ψ and Δ , disregarding the *n* and *k* dependency on each other at different wavelengths. For this procedure, other parameters, such as the thickness of the thin film, and the optical properties of the underlying silicon substrate and the overlying roughness layer, need to be accurately known, otherwise it can lead to multiple solutions, unphysical dispersion or discontinuities in the optical constants, generally present at lower energies in the inversion spectrum (Fujiwara 2007; Keita et al. 2010; Likhachev et al. 2015).

316

c. Procedure to determine the optical constants *n* and *k* of Pluto tholins

In summary, modified Tauc-Lorentz dispersion model is used to extract both thickness and 317 optical constants n and k by fitting the thickness values and the Tauc-Lorentz parameters. " λ -318 by- λ " numerical inversion enables an exact modelling of the optical constants *n* and *k* in spectral 319 ranges where the fit is difficult with dispersion formulas and to check the optical constants 320 results obtained by dispersion formulas (modified Tauc-Lorentz in this work). A " λ -by- λ " fit 321 322 of the experimental data is performed on the only unknown optical constants n and k of the thin film without fitting any parameter. To use this numerical inversion method, all parameters of 323 324 the optical model, such as thicknesses, must be known, which is not the case for tholins material and thus induces much larger uncertainties. This method requires a (even rough) knowledge of 325

the order of magnitude of n and k indices for initialization. We thus used a two-pronged 326 approach, where the modified Tauc-Lorentz dispersion model is used to determine the 327 initialization parameters of the " λ -by- λ " numerical inversion method, which in return gives us 328 the optical properties with much higher confidence. Therefore, our procedure, based on two 329 sequential modified Tauc-Lorentz and " λ -by- λ " methods, is a good way to determine correctly 330 the optical constants n and k of the original sample system when the optical responses are not 331 available in the literature. The reader is referred to Keita et al. (2010) for more details about 332 333 these two methods.

334 III. Results: Optical constants of Pluto aerosol analogues

Figures 2 and 3 respectively display the real and imaginary parts n and k of the complex 335 refractive index determined for P_H sample with a modified Tauc-Lorentz dispersion model (in 336 turquoise blue) and with a " λ -by- λ " numerical inversion method (in dark blue). The 2σ error 337 bars determined for the " λ -by- λ " inversion method (see Table SI.4 in Supplementary 338 Information) were calculated based on the uncertainties of I_s^{exp} and I_c^{exp} at different 339 wavelengths. The uncertainties were then linearly interpolated between two error bars in order 340 to obtain an envelope of uncertainty (in light blue). Note that these error bars do not include all 341 the uncertainties on n- and k-values. Indeed, the uncertainties on the raw 342 ellipsometric measurements before modelling are known and are modest, given the quality of the setting of 343 the analytical instrument; these uncertainties are therefore not included in the error bars 344 presented. The major source of uncertainties corresponds to the inversion model used, including 345 *e.g.*, the number of fitting parameters and of oscillators used, the problem of presence of local 346 minima during the fit, and in particular the absence of initial values for the inversion. We can 347 348 nevertheless expect that the actual uncertainties on the optical constants of Pluto tholins would be slightly higher than those presented here. 349



350

Figure 2: Real part *n* of the complex refractive index of Pluto aerosol analogues P_H determined by spectroscopic ellipsometry with a modified Tauc-Lorentz dispersion model (in turquoise blue) and with a " λ -by- λ " numerical inversion method (in dark blue). The 2σ error bars were experimentally determined for the " λ -by- λ " inversion method at different wavelengths. The uncertainties were then linearly interpolated between two error bars in order to obtain the envelope of 2σ uncertainty (in light blue).

356



359 Figure 3: Imaginary part k of the complex refractive index of Pluto aerosol analogues P_H determined by spectroscopic ellipsometry with a modified Tauc-Lorentz dispersion model (in turquoise blue) and with 360 a " λ -by- λ " numerical inversion method (in dark blue). The 2σ error bars were experimentally determined 361 for the " λ -by- λ " inversion method at different wavelengths. The uncertainties were then linearly 362 363 interpolated between two error bars in order to obtain the envelope of 2σ uncertainty (in light blue). The envelope determined by dashed lines corresponds to 1σ uncertainty. Note that the y-axis was cropped at 364 10^{-6} , while the 2σ uncertainties of k-values reach 0 in the [800-850], [1450-1650] and [1820-2100] nm 365 regions. 366

In Figure 2, the dark-blue and turquoise-blue curves present the same profile, with a maximal 367 *n*-value of about 1.77 at 325-330 nm and decreasing values of *n* index between 330 and 368 2100 nm. In Figure 3, k-values determined with the two models are very similar in the [270-369 490] and [1150-2100] nm regions. The dark-blue and turquoise-blue curves share the same 370 slope, indicating similar values for the bandgap energy (also called "absorption edge", *i.e.* the 371 wavelength at which there is a sharp increase of the k index). The bandgap energy determined 372 with the modified Tauc-Lorentz dispersion model (turquoise-blue curve) is around 575 nm, 373 while it is around 595 nm with the " λ -by- λ " numerical inversion method (dark-blue curve). 374 Beyond the bandgap energy, the behaviour of the *k* indices is the same, reaching an asymptotic 375 value of $\sim 2 \times 10^{-3}$ between 600 and 2100 nm. 376

From Figures 2 and 3, we can conclude that the choice of the fitting model – modified Tauc-377 Lorentz or " λ -by- λ " – has no significant impact on the *n* and *k* indices determined for P_H sample 378 in the [270-600] and [1150-2100] nm regions. Each method has advantages and drawbacks 379 (specified in Sections II.3.a, II.3.b, and II.3.c). In this work, while the modified Tauc-Lorentz 380 dispersion model was adapted for the determination of the thin-films thickness, it could not 381 manage to determine non-null values for k indices between 740 and 1105 nm. This is due to the 382 software used, which cannot compute k-values below 10⁻⁴. Therefore, we list in Tables SI.1, 383 SI.2 and SI.3 (found in Supplementary Information) the optical constants of Pluto aerosol 384 analogues P_H, P₄₀₀ and P₆₅₀ obtained by spectroscopic ellipsometry and determined with the "\lambda-385 by- λ " fitting method from 270 to 2100 nm with a 5 nm increment. Note that *n* and *k* indices 386 387 presented in all the figures of the manuscript and listed in Tables SI.1-3 were smoothed by a moving mean with a step of 15 data points. All the subsequent figures display the smoothed 388 389 optical constants determined with the " λ -by- λ " numerical inversion method.

IV. Impact of the altitude (or epoch) of aerosol formation on the optical constants and implications for radiative transfer

392 P_H, P₄₀₀ and P₆₅₀ samples were produced with different N₂:CH₄:CO ratios. As CH₄ mixing ratio 393 strongly varies throughout the atmospheric column (Young et al. 2018), the purpose of 394 comparing these three samples is to determine if the altitude of formation of the aerosols in 395 Pluto's atmosphere has an impact on their optical constants.

1. Effect on real part *n* of the complex refractive index

Figures 4 shows the real part *n* of the complex refractive index of P_H , P_{400} and P_{650} samples as a function of wavelength. In this figure, the blue curve corresponds to P_H sample, the red curve to P_{400} sample and the green curve to P_{650} sample. The 2σ error bars (see Table SI.4 in Supplementary Information) were calculated based on the uncertainties of I_s^{exp} and I_c^{exp} for different wavelengths. The uncertainties were then linearly interpolated between two error bars in order to obtain the envelopes of uncertainty (in light blue, light red and light green).



404 Figure 4: Real part *n* of the complex refractive index of Pluto tholins determined by spectroscopic 405 ellipsometry with a "λ-by-λ" numerical inversion method. The blue, red and green curves respectively 406 correspond to the samples P_{H} , P_{400} and P_{650} . The 2σ error bars were experimentally determined for 407 different wavelengths and were then linearly interpolated in-between in order to obtain the envelopes of 408 2σ uncertainty (in light blue, light red and light green). Note that the small variations observed in the *n*-409 curves at wavelengths above 600 nm should be considered with caution.

In Figure 4, we observe that the values of n indices of $P_{\rm H}$ and P_{400} samples are relatively similar, 410 but substantially different from those of P₆₅₀ sample. For P_H and P₄₀₀ samples, *n*-values increase 411 from 1.71-1.73 to ~1.77 between 270 and 330 nm. Then, *n*-values decrease with a steep slope 412 from ~1.77 to around 1.67 between 330 and 650 nm. The slope attenuates between 650 and 413 1100 nm. Finally, the *n* indices of P_H and P₄₀₀ reach an asymptotic value of 1.62-1.63 between 414 415 1100 and 2100 nm. For P₆₅₀ sample, n index increases from 1.72 to around 1.74 between 270 and 305 nm, followed by a steep decrease from around 1.74 to 1.64 between 305 and 600 nm. 416 The decreasing slope then attenuates between 600 and 1200 nm, before n index reaches an 417 asymptotic value of 1.60-1.61 between 1200 and 2100 nm. In summary, the increase of the 418 CH₄:N₂ mixing ratio in the reactive gas mixture producing Pluto tholins leads to a decrease of 419 *n* index over the entire spectral range considered. As well, the maximum of *n*-value is shifted 420 421 towards shorter wavelengths.

The bell-shaped appearance between 270 and 400 nm, although not observed in the studies of 422 optical constants of Titan aerosol analogues (Brassé et al. 2015), appears to be a consistent trend 423 in Pluto tholins, whatever inversion model – " λ -by- λ " or modified Tauc-Lorentz – is used. In 424 contrast, the small variations observed in the *n*-curves at wavelengths above 600 nm should be 425 considered with caution. Indeed, we cannot totally rule out the fact that these small variations 426 427 are introduced by the *n* index being a function of wavelength λ (Mistrik et al. 2017; Moise et al. 2015). Nevertheless, this dependence is especially observed on a large scale: when λ 428 429 increases, the n index increases or decreases monotonically. In addition, in the literature 430 concerning the optical constants of terrestrial aerosols or tholins materials (e.g., Cechalova et al. 2019; Khare et al. 1984; Liu et al. 2015; Mahjoub et al. 2012; Ramírez et al. 2002; Sciamma-431 432 O'Brien et al. 2012), the *n* indices are often represented as a smooth profile, suggesting that there may be no physical reason to observe fine-scale variations of *n* index. 433

The overall decreasing trend of *n* indices from UV to near-IR was also observed in the studies 434 of optical constants of Titan tholins, regardless of the production mode (type of energy source, 435 436 gas pressure, gas temperature, CH₄:N₂ mixing ratios...) or the type of measurement (spectroscopic ellipsometry, spectrophotometry...) (Brassé et al. 2015; Imanaka et al. 2004; 437 Khare et al. 1984; Mahjoub et al. 2012, 2014; Ramírez et al. 2002; Sciamma-O'Brien et al. 438 2012; Tran et al. 2003). In the considered wavelength range, n indices of Pluto aerosol 439 analogues vary from around 1.60 to 1.78. These values are similar to the *n*-values determined 440 for Titan aerosol analogues (Brassé et al. 2015). It thus seems that Pluto tholins, produced in 441 gas mixtures composed of N₂, CH₄ and CO, share first-order similar optical properties with 442 Titan tholins. This similarity also extends to the chemical composition. Indeed, Jovanović et al. 443 (2020) studied the chemical composition of Pluto aerosol analogues. They showed that the 444 445 molecules constituting the tholins are composed of a repetition of a (CH₂)_w(HCN)_z random pattern, such as molecules in Titan aerosol analogues (Gautier et al. 2017; Maillard et al. 2018; 446 447 Pernot et al. 2010), with, however, a significant incorporation of oxygen atoms. van Krevelen and te Nijenhuis (2009) reported that such *n*-values can also correspond to organic polymers 448 449 including polyamides -C(=O)-NH- and polyethers R-O-R'.

We also note in Figure 4 that the *n* indices are higher for P_H and P_{400} samples compared to the P₆₅₀ one, with a systematic difference of about 0.05 over the entire wavelength range. This difference between P_H/P_{400} and P_{650} is significant and beyond the uncertainties determined for the three samples at different wavelengths. Regarding the effect of CH₄:N₂ mixing ratio on *n*values, our results differ from those of Mahjoub et al. (2012). In this study concerning the influence of CH_4 concentration on the optical constants of Titan aerosol analogues, the higher the $CH_4:N_2$ mixing ratio, the higher the *n*-values. In the case of Pluto tholins, the relation is reversed, suggesting an increasing influence of CO at lower CH_4 concentration.

Aerosols formed in Pluto's lower atmosphere (≤ 400 km of altitude) are thus expected to scatter and polarize the light differently than the aerosols formed at higher altitudes (> 400 km of altitude), due to their different *n* indices (Boucher 2015; Kolokolova et al. 1997; Kolokolova & Jockers 1997; Nakayama et al. 2018, 2012), and therefore differently affect the photon flux reaching the lower layers of the atmosphere and the surface.

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2. Effect on imaginary part k of the complex refractive index

Figure 5 shows the imaginary part *k* of the complex refractive index computed for P_H (top panel, blue curve), P_{400} (middle panel, red curve) and P_{650} (bottom panel, green curve) samples as a function of wavelength. The 2σ error bars (see Table SI.4 in Supplementary Information) were calculated based on the uncertainties of I_s^{exp} and I_c^{exp} for different wavelengths. The uncertainties were then linearly interpolated in-between in order to obtain the envelopes of uncertainty (in light blue, light red and light green).





Figure 5: Imaginary part *k* of the complex refractive index of Pluto tholins determined by spectroscopic ellipsometry with a "λ-by-λ" numerical inversion method. The blue (top panel), red (middle panel) and green (bottom panel) curves respectively correspond to the samples P_H , P_{400} and P_{650} . The 2σ error bars were experimentally determined for different wavelengths and were then linearly interpolated in-

- 477 between in order to obtain the envelopes of 2σ uncertainty (in light blue, light red and light green). The
- 478 envelopes determined by dashed lines correspond to 1σ uncertainty. The y-axis was cropped at 10^{-4} . The
- 479 2σ uncertainties of k-values reach 0 in the [790-850], [1450-1650] and [1820-2100] nm regions for P_H
- 480 sample, in the [1870-1930] and [2020-2100] nm regions for P₄₀₀ sample and in the [980-1180], [1270-
- 481 1330] and [1880-2100] nm regions for P_{650} sample. Note that the large variations observed in the k-
- 482 curves at wavelengths above 600 nm should be considered with caution.
- In Figure 5, we observe that the k-values of P_H and P₄₀₀ are significantly higher for wavelengths 483 between 270 and 600 nm than those of P₆₅₀. From 600 to 2100 nm, the trend is less clear, 484 because of larger uncertainties on k-values. For P_H and P₄₀₀ samples, k-values plummet from 485 2.7×10^{-1} to around 4.5×10^{-3} between 270 and 590 nm. The bandgap energy is estimated to be 486 around 590 nm. For P₆₅₀ sample, the k index steeply decreases from 1.5×10^{-1} down to around 487 2×10^{-3} between 270 and 520 nm. The bandgap energy is estimated at around 520 nm. Due to 488 489 the large uncertainties on k-values determined for the three samples above 600 nm and because this kind of material is weakly absorbent in the near-IR (Brassé et al. 2015), the large variations 490 491 observed in the k-curves should be considered with caution. k indices for all samples probably reach an asymptotic value of a few 10^{-3} between 600 and 2100 nm. 492
- The 2-steps behaviour of *k*-values sharp decrease followed by a plateau was also observed
 for Titan aerosol analogues in the considered wavelength range (Brassé et al. 2015; Imanaka et
 al. 2004; Khare et al. 1984; Mahjoub et al. 2012, 2014; Ramírez et al. 2002; Sciamma-O'Brien
 et al. 2012; Tran et al. 2003).
- We do not have a definitive explanation for the variations observed beyond 600 nm in the k-497 498 curves of the 3 samples P_H, P₄₀₀ and P₆₅₀. Nevertheless, assuming that the variations observed are consistent absorption bands (see Table 2): (1) the absorption band around 725 nm observed 499 in P₆₅₀ sample could be ascribed to C–H stretching 4th overtone in –CH_x (x = 1, 2 and 3) and in 500 Aromatic-CH and to O-H stretching 3rd overtone in R-OH and in Aromatic-OH; (2) the 501 502 absorption band between 900 and 950 nm observed in all samples could be attributed to C-H stretching 3rd overtone and to O-H stretching 2nd overtone; (3) the absorption band between 503 1100 and 1150 nm observed in P_H and P₄₀₀ samples could correspond to C-H stretching 2nd 504 overtone and to -C=O stretching 4th overtone; (4) the absorption band between 1950 and 505 506 2000 nm observed in P_H and P₄₀₀ samples could be in agreement with -C=O stretching 2nd overtone in R-(C=O)-R', R-(C=O)-OR' and in R-(C=O)-NH₂ and to N-H combination in R-507 (C=O)–NH₂ and in aromatic amines (Stenberg et al. 2010; Workman & Weyer 2008; Xiaobo 508

et al. 2010). These overtones are conceivable, given the chemical composition determined for

- 510 Pluto tholins by Jovanović et al. (2020).
- 511 Table 2: Overtone and combination near-IR band assignment of potential absorption bands found in the
- 512 *k* profiles presented in Figure 5. The band assignments are based on Stenberg et al. (2010), Workman &
- 513 Weyer (2008) and Xiaobo et al. (2010).

Wavelength [nm]	length [nm] Overtone and combination near-IR band assignment	
725	• C-H stretching 4^{th} overtone in $-CH_x$ ($x = 1, 2$ and 3) and in Aromatic-CH	P ₆₅₀
	• O-H stretching 3 rd overtone in <i>R</i> -OH and in Aromatic-OH	
900-950	 C-H stretching 3rd overtone in -CH_x (x = 1, 2 and 3) and in Aromatic-CH O-H stretching 2nd overtone in <i>R</i>-OH and in Aromatic-OH 	P _H , P ₄₀₀ , P ₆₅₀
1100-1150	 C-H stretching 2nd overtone in -CH_x (x = 1, 2 and 3) and in AromaticCH -C=O stretching 4th overtone in R-(C=O)-R', R-(C=O)-OR' and in R-(C=O)-NH₂ 	
1950-2000	 -C=O stretching 2nd overtone in <i>R</i>-(C=O)-<i>R</i>', <i>R</i>-(C=O)-O<i>R</i>' and in <i>R</i>-(C=O)-NH₂ N-H combination in <i>R</i>-(C=O)-NH₂ and in aromatic amines 	

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515 From Figure 5, we can conclude that Pluto aerosol analogues significantly absorb UV and 516 visible radiations, while their absorption is more moderate above 600 nm. The strong absorption below 500-600 nm, in the blue-green spectral range, agrees with a brownish colour for Pluto 517 tholins. This absorption is likely due to the presence of N- and O-bearing organic molecules 518 with lone pair, such as -NH, -NH₂, -NHR, R-N-R', -NO₂, -OH, -COOH, -C=O, R-O-R' 519 functional groups (Desyaterik et al. 2013; Imanaka et al. 2004; Liu et al. 2015; Mahjoub et al. 520 2012; Moise et al. 2015; Rao 1975). Due to the delocalization of π electrons, fused aromatic 521 rings, N- and O-containing polycyclic aromatic compounds and unsaturated molecules with 522 extensive conjugated multiple bonds also participate to the strong absorption of UV and visible 523

wavelengths (D'Amico et al. 1980; Desyaterik et al. 2013; Imanaka et al. 2004; Lambe et al.
2013; Liu et al. 2015; Moise et al. 2015; Rao 1975; Tran et al. 2003; Zhong et al. 2012). Most
of these chemical functions were actually detected in Pluto aerosol analogues by Jovanović et
al. (2020), who showed the presence of unsaturated N- and O-bearing molecules in large
amount.

When CH₄ concentration increases, the bandgap energy shifts towards shorter wavelengths. *k* index thus depends on the CH₄:N₂ mixing ratio used to produce the tholins. Indeed, from 270 to around 600 nm, where the uncertainties are low, we can see that P_H and P₄₀₀ samples, produced with a lower CH₄ concentration, present higher *k*-values than P₆₅₀ sample, produced with a higher CH₄ concentration.

This anti-correlation between k-values and CH₄:N₂ mixing ratio was also detected by Mahjoub 534 et al. (2012) in their study concerning Titan tholins. They attributed this anti-correlation to the 535 proportion of N-bearing molecules: when CH₄ concentration decreases, N-containing 536 molecules increase in proportion and contribute to a higher absorption of UV and visible 537 radiations (Mahjoub et al. 2012, 2014). This conclusion was also proposed by Imanaka et al. 538 539 (2004), when comparing their Titan tholins with Uranus/Neptune tholins from Khare et al. (1987) study, produced in CH₄:H₂ gas mixtures. They hypothesized that N-incorporation in 540 Titan tholins could increase k-values in the UV-Vis spectral range, in agreement with the 541 542 laboratory experiments realized by Scattergood and Owen (1977). Indeed, nitrogen promotes unsaturation. When N₂ content is increased in the reactive gas mixture forming Pluto tholins 543 (case of P_H and P_{400} samples), the formation of sp^2 bonds is favoured. In contrast, when the 544 545 reactive gas mixture contains more CH₄ (case of P₆₅₀ sample), the presence of large amounts of hydrogen promotes the formation of sp³ bonds, which have no effect on π - π * electronic 546 transitions in UV and visible wavelength ranges (Ferrari et al. 2003; Quirico et al. 2008). 547

Another explanation to both higher *n*- and *k*-values for P_H and P_{400} could be the higher oxidation of these samples. Indeed, Jovanović et al. (2020) showed that P_{400} sample contains more oxygen in mass than P_{650} . Studies realized on optical properties of terrestrial secondary organic aerosols (Cappa et al. 2011; Lambe et al. 2013; Moise et al. 2015; Nakayama et al. 2018, 2012) and of oxidized Early Earth- and Exoplanets-like aerosols (Gavilan et al. 2017) showed that *n* indices increase when the oxidation level of the aerosols increases. Moreover, the more the aerosols are oxidized, the more they absorb UV and visible radiations. We can thus expect that aerosols formed at different altitudes in Pluto's atmosphere will differently absorb radiations reaching the atmosphere. In particular, Pluto's aerosols formed at or below 400 km of altitude above the surface, due to their higher N- and O-content, may absorb more UV and visible wavelengths than aerosols formed above 400 km of altitude.

559 Besides, as mentioned in Section II.1, the samples studied here could also be considered as analogues of aerosols produced during different seasons or epochs of Pluto (Bertrand et al. 560 2019; Bertrand & Forget 2016; Stern et al. 2017a). In Bertrand and Forget (2016), their Pluto 561 General Circulation Model (GCM) predicted a mean CH₄ atmospheric mixing ratio in ~2200 562 (terrestrial year; northern winter/southern summer on Pluto) ~5 times higher than that observed 563 in 2015. This is due to the condensation of N₂ onto the surface, which also leads to a decrease 564 in surface pressure as low as 10^{-5} - 10^{-6} mbar; the atmosphere being thinner, the methane is less 565 diluted (Bertrand & Forget 2016; Stern et al. 2017a). However, considering that the pressure in 566 567 the atmosphere would still be sufficient to allow the formation of haze particles (Johnson et al. 2021), one would expect less absorbent aerosols, such as P₆₅₀ tholins, differently affecting the 568 569 thermal profile of Pluto and the photon flux reaching the surface.

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V. New input parameters for Pluto atmospheric and surface models

571 In this section, we first compare the optical constants determined in this study with those from 572 the study by Khare et al. (1984). Then, we discuss the application of our Pluto tholins optical 573 constants to the modelling of Pluto's surface and atmosphere.

Comparison of our optical constants with those of Titan tholins from the study by Khare et al. (1984)

Khare et al. (1984) did a pioneer work to determine the optical constants *n* and *k* of Titan aerosol 576 577 analogues from soft X-ray to microwave frequencies. For this purpose, they combined transmittance, specular reflectance, interferometric, Brewster angle and ellipsometric 578 polarization measurements on thin films synthesized on various substrates. Although the large 579 considered wavelength range is valuable, the employed method – combination of different thin 580 581 films and different measurement techniques, with interpolations – induces major uncertainties. Moreover, Brassé et al. (2015) reviewed why Khare et al. (1984) optical constants are not 582 representative of Titan's aerosols at different wavelengths. 583

Even though several other teams have since then determined optical properties of Titan aerosol
analogues (Imanaka et al. 2012; Mahjoub et al. 2012, 2014; Ramírez et al. 2002; Sciamma-

O'Brien et al. 2012; Tran et al. 2003; Vuitton et al. 2009), optical constants from Khare et al. (1984) are still widely used by the modelling teams to explain atmospheric and surface properties of Titan, often by introducing *ad hoc* modifications to them to fit the observations better (Brossier et al. 2018; Fan et al. 2019; Griffith et al. 2012; Lavvas et al. 2009; Liang et al. 2007; Lopes et al. 2016; Seignovert et al. 2017), but also of Pluto (Cheng et al. 2017; Grundy et al. 2018; Protopapa et al. 2017, 2020; Young et al. 2018; Zhang et al. 2017). This is partially due to the lack of optical constants of tholins-like materials covering a wide wavelength range.

593 Only the data by Khare et al. (1984) and Tran et al. (2003) for Titan tholins cover the same 594 wavelength range as the Pluto optical constants determined in this work, and therefore are used 595 for comparison purposes. In Figures 6 and 7, we respectively compare the *n* index and the *k* 596 index of Pluto aerosol analogues P_{400} (red asterisks) to Khare et al. (1984) data (black asterisks), 597 from 270 to 2100 nm. Note that Titan tholins from Khare et al. (1984) were produced in a 598 reactive gas mixture composed of 90% of N₂ and 10% of CH₄.



Figure 6: Comparison between the real part *n* of the complex refractive index of our Pluto tholins P_{400} (red asterisks) and Titan tholins from Khare et al. (1984) study (black asterisks).



Figure 7: Comparison between the imaginary part k the complex refractive index of our Pluto tholins P₄₀₀ (red asterisks) and Titan tholins from Khare et al. (1984) study (black asterisks). The black dashed arrow indicates the modification implemented by Zhang et al. (2017) to the k-values from Khare et al. (1984) in the region where solar heating dominates (represented by the yellow rectangle) in order to adjust Pluto's thermal balance.

In Figure 6, we observe that the *n* index of Pluto tholins P_{400} is similar to that of Khare et al. (1984) Titan tholins from 450 to 2100 nm. Below 450 nm, the behaviour is reversed. While *n*value reaches a maximum near 330 nm for P_{400} , Khare et al. (1984) data present a minimum *n*value near 350 nm. We do not have a definitive explanation for this behaviour of Khare et al. (1984) *n* index, but it could be due to a low sampling combined with interpolation, a poor definition of the optical properties of the substrates used for the synthesis of the tholins thin films, or the light source used for the measurements being at the limit of its range.

Concerning the *k* indices (Figure 7), the bandgap energy of Khare et al. (1984) tholins is shifted towards longer wavelengths (around 1200 nm) compared to P_{400} sample (around 590 nm). *k*values of P_{400} are higher than those of Khare et al. (1984) below 380 nm and in the near-IR (> 900 nm). These higher values can be explained by higher N- and O-content of Pluto aerosol analogues P_{400} (Cappa et al. 2011; Gavilan et al. 2017; Imanaka et al. 2004; Jovanović et al. 2020; Lambe et al. 2013; Mahjoub et al. 2012; Nakayama et al. 2018, 2012; Quirico et al. 2008).

From 380 to around 800 nm, k-values of P₄₀₀ are lower than those of Khare et al. (1984), due 621 to the shifted bandgap energy which is caused by higher k-values in the UV and a steeper slope 622 in the UV-Vis for our P₄₀₀ sample. 623

624 Even though k-values of P_{400} sample are one order of magnitude higher than those of Khare et 625 al. (1984) between 1000 and 2000 nm, they are constant and do not present the anomalous sharp increase beyond 1800 nm presented by the Khare et al. (1984) k-values. The fact that our k-626 values are one order of magnitude higher in the near-IR is consistent with published literature 627 on Titan's aerosols. For example, Lavvas et al. (2010) and Larson et al. (2015) reported that the 628 actual optical properties of Titan's aerosols should be about an order of magnitude larger in the 629 630 near-IR compared to the optical constants from Khare et al. (1984).

631

2. Application of our optical constants to Pluto's surface modelling

632 Recently, Protopapa et al. (2020) studied the colouring materials across Pluto's surface. To support the conclusion developed by Grundy et al. (2018), Pluto's photochemical aerosols were 633 634 considered as potential surface colouring agent. Thus, in their model, they implemented the k indices determined for Titan tholins by Khare et al. (1984) and Tran et al. (2003). 635 636 Nevertheless, in order to fit their models to spectra acquired in the regions of Cthulhu Macula and Lowell Regio by the imagers MVIC (Multispectral Visible Imaging Camera, a Vis-near-IR 637 638 [400-975 nm] imager) and LEISA (Linear Etalon Imaging Spectral Array, an IR [1.25-2.5 µm] 639 spectral imager) constituting the Ralph instrument (Reuter et al. 2008), some modifications of k indices by Khare et al. (1984) were necessary. Specifically, Protopapa et al. (2020): first 640 applied no change to the *n* index of Khare et al. (1984); secondly decreased the *k*-value of Khare 641 et al. (1984) at 690 nm by ~55% to match the observations of Pluto in the RED filter between 642 540 and 700 nm (note that Protopapa et al. (2020) preserved the original sampling of Khare et 643 al. (1984) explaining why the k-value was modified at 690 nm); and thirdly assumed k index to 644 be constant between 1800 and 2200 nm, given that the increase displayed by the k-values of 645 Khare et al. (1984) beyond 1.8 µm was not consistent with the observations. 646

647 Figure 8 was adapted from Protopapa et al. (2020). It displays the imaginary part k of the complex refractive index (right y-axis) of our P400 sample (red curve, with an envelope of 648 649 uncertainties represented in salmon pink), compared to those of the Titan tholins from the 650 studies by Khare et al. (1984) (orange triangles) and Tran et al. (2003) (blue dots). Additionally, 651 the set of k indices determined by Protopapa et al. (2020) (black squares) that best fits the MVIC 652 and LEISA New Horizons measurements acquired in the regions of Cthulhu Macula and Lowell Regio are shown, as well as the MVIC transmission filters (left *y*-axis). The reader is referred
to Protopapa et al. (2020) for details about the modelling of MVIC and LEISA spectra.



Figure 8: Figure adapted from Protopapa et al. (2020). Imaginary part *k* of the complex refractive index (right *y*-axis) is represented as a function of wavelength. The red curve with the salmon-pink envelope corresponds to the *k* index of our sample P_{400} . The orange triangles correspond to the *k* index determined by Khare et al. (1984), while the blue dots are from the study by Tran et al. (2003). The black squares are the *k*-values determined by Protopapa et al. (2020) that best fit the MVIC and LEISA data. The MVIC transmission filters (left *y*-axis) are shown for reference. The reader is referred to Protopapa et al. (2020) for details about the modelling.

Protopapa et al. (2020) recognized that the *k*-values of Titan tholins by Khare et al. (1984) present a sharp increase beyond $1.8 \,\mu\text{m}$ (Figure 8, orange triangles), inconsistent with the Pluto *New Horizons* data. Therefore, Protopapa et al. (2020) modified the *k*-values by Khare et al. (1984) beyond $1.8 \,\mu\text{m}$ assuming them to be constant with wavelengths up to $2.4 \,\mu\text{m}$ and equal to the mean value computed between $1.35 \,\text{and} 1.45 \,\mu\text{m}$ (see Figure 8, sample B from Protopapa et al. (2020)). This is consistent with our direct values for Pluto tholins P₄₀₀. Indeed, as noted above, while the *k*-values of P₄₀₀ sample are one order of magnitude higher than those of Khare et al. (1984) between 1000 and 2000 nm, they are constant with wavelengths and do not display
the sharp increase beyond 1.8 μm presented by the Khare et al. (1984) *k*-values.

In Figure 8, we observe that the change to the Khare et al. (1984) data implemented at 690 nm by Protopapa et al. (2020) (black squares) to match the Pluto *New Horizons* observations is consistent with the *k*-curve of our Pluto tholins P_{400} (red curve, with the salmon-pink envelope). Also, sample B from Protopapa et al. (2020) shares the same slope in the UV-Vis as our P_{400} sample and is in agreement, within the uncertainties, with our data between 0.8 and 1.0 μ m.

677 These considerations support the suitability of our optical constants to reproduce Pluto compositional observations at least in the UV and visible spectral ranges. Nevertheless, from 678 1.1 to 1.8 µm, our k-values are obviously larger by an order of magnitude with respect to the k-679 values adopted to reproduce Pluto New Horizons data by Protopapa et al. (2020). An in-depth 680 modelling analysis of the Pluto New Horizons observations using as inputs our Pluto tholins 681 optical constants throughout the full wavelength range, from 0.4 to 2.5 µm, is required to 682 confirm that Pluto's colouration and composition can be attributed to the photochemical 683 aerosols that we reproduced in our laboratory. 684

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3. Application of our optical constants to Pluto's atmosphere modelling

In order to evaluate the effect of our Pluto tholins optical constants on aerosol properties, and to compare with those of Titan, we display the extinction coefficient Q_{ext} (Figure 9), the singlescattering albedo ω (Figure 10), and the absorption coefficient Q_{abs} (Figure 11) for a spherical particle of 10 nm according to Mie theory (formalized in Bohren & Huffman (1983)) and for a fractal aggregate of spheres (Rannou et al. 1997, 1999).

These parameters are key in the atmospheric radiative transfer (Bohren & Huffman 1983). Qext 691 692 is the ratio of the extinction cross section (σ_{ext}) and the geometric projection of the particle (σ_{geo}) . It characterizes the extinction, *i.e.* the absorption and scattering of radiation by aerosols. 693 ω represents the fraction of scattered radiation, while $(1 - \omega)$ represents the fraction of absorbed 694 radiation. ω is equal to 0 for a perfect absorber and equal to 1 for a perfect scatterer. These two 695 coefficients control the amount of energy absorption by aerosols at solar wavelengths through 696 $Q_{abs} = (1 - \omega) \times Q_{ext}$ and the emission in thermal infrared $Q_{emi} = Q_{abs} = (1 - \omega) \times Q_{ext}$. 697 They participate to the thermal balance of Pluto's atmosphere, as demonstrated by Zhang et al. 698 699 (2017).

At first glance, the scattering of haze at Pluto's limb in the forward direction indicates particles 700 701 having radii in the range 0.1-0.5 µm (Gladstone et al. 2016; Stern et al. 2015). Further detailed analyses and arguments from microphysical models (Cheng et al. 2017; Gao et al. 2017; Zhang 702 703 et al. 2017) yielded a better result with fractal aggregates of small grains. In these studies, a fractal dimension $D_f = 2$ was assumed, the morphology of the haze particles is thus more like 704 705 that of snowflakes instead of solid spheres. The study by Cheng et al. (2017) showed that spherical monomers should have ~10 nm radius (R_m) and aggregates should have a "bulk 706 radius" (or "volume equivalent radius") of about $R_b = 0.15 \mu m$, corresponding to 707 $\mathcal{N} = (R_b/R_m)^3 \approx 3375$ monomers per aggregate. Such a fractal structure globally satisfies, 708 although not perfectly, the main requirements to explain Pluto New Horizons observations 709 710 (Cheng et al. 2017). This aerosol structure was also used by Zhang et al. (2017) to study Pluto's thermal balance. Note, however, that in the study by Gao et al. (2017), the particle size 711 distributions of their model are displayed as a function of the "effective radius" Rf. Since their 712 aerosols grow up to $R_f = 0.15 \mu m$, with a fractal dimension $D_f = 2$, the corresponding aggregates 713 appear much smaller ($\mathcal{N} = 225$) than those considered by Cheng et al. (2017), Zhang et al. 714 715 (2017) and Lavvas et al. (2020) ($\mathcal{N} = 3375$). The most probable reason for this difference stands in that Cheng et al. (2017) and Lavvas et al. (2020) matched data from New Horizons containing 716 717 information about the aerosol size, with observations made at different phase angles, while Gao et al. (2017) used data that are not sensitive to the aerosol size. Since aerosols are produced 718 from growth mechanisms, they are expected to start as small spherical particles at high altitudes 719 720 and continuously get larger by coagulation (direct gas-particle interactions) while sedimenting (Cheng et al. 2017; Gao et al. 2017; Zhang et al. 2017). Thus, both the properties of small 721 722 spherical monomers and fractal aggregates are interesting.

In Figures 9 and 10, we compare, for several sets of optical constants, the parameters Q_{ext} and ω computed for spherical monomers of 10 nm radius, distributed with a log-normal distribution and an effective variance v of 0.03 (dotted lines), and for fractal aggregates of 3375 monomers of 10 nm radius (plain lines). We used the optical constants determined in this work (P_H, P₄₀₀ and P₆₅₀, in blue, red and green respectively), optical constants determined for Titan tholins by Khare et al. (1984) (in black) and for Titan's aerosols from observations by Rannou et al. (2010) and Vinatier et al. (2012) (in pink).



730

731 Figure 9: Extinction coefficients Qext determined for spherical monomers of 10 nm radius (log-normal distribution, with effective variance v = 0.03) with a Mie model formalized in Bohren & Huffman (1983) 732 733 (dotted curves) and for fractal aggregates of 3375 monomers of 10 nm radius with the model developed 734 by Rannou et al. (1997, 1999) (plain curves). The black curves were generated with the optical constants determined by Khare et al. (1984) for Titan tholins. Note that these Khare et al. (1984) optical constants 735 were adopted in Zhang et al. (2017) study. The pink curves were generated with the optical constants 736 737 determined by Rannou et al. (2010) and Vinatier et al. (2012) for Titan's aerosols. The blue, red and green curves were generated with the optical constants determined respectively for our samples P_H, P₄₀₀ 738 and P_{650} . The yellow rectangle indicates the region where solar heating dominates. The dotted curves 739 740 (spherical monomers) give information on the radiative transfer in the upper layers of Pluto's atmosphere (> 350 km of altitude), while the plain curves (fractal aggregates) give information on the 741 742 radiative transfer in Pluto's lower atmosphere (between 100 and 300 km of altitude).



743

Figure 10: Same as Figure 9, but showing the single-scattering albedo ω .

In Figure 9, we remark that the extinction coefficients Q_{ext} for spherical particles or fractal aggregates computed with tholins relevant for Pluto have a steepest spectral slope at visible wavelengths (broadly from 0.2 to 0.8 µm, where most Pluto *New Horizons* photometrical data were taken, and where solar heating occurs) than those computed with optical constants relevant for Titan's aerosols.

In Figure 10, considering single spheres or fractal aggregates, we see that the single-scattering albedo ω is significantly higher in the UV and visible spectral ranges with the optical constants of Pluto tholins than with Titan optical constants. In the near-IR, ω of Pluto tholins are lower than that of Khare et al. (1984) Titan tholins. This suggests that Pluto's haze absorbs less in the UV-Vis wavelength range than Titan's haze.

However, to really assess the absorption efficiency of each type of particles, one has to compare the absorption coefficients $Q_{abs} = (1 - \omega) \times Q_{ext}$ (displayed in Figure 11).



757

758 Figure 11: Same as Figure 9, but showing the absorption coefficients Q_{abs}.

The absorption coefficients Q_{abs} (Figure 11) computed with Pluto tholins optical constants are about equal to those computed with Titan optical constants at 0.3 µm. Nevertheless, they drop much faster with wavelengths and are lower by a factor 3 to 10 at wavelengths larger than ~0.4-0.5 µm. This is true for small spherical particles and fractal aggregates.

Beyond 1 μ m, the marked structures of Pluto tholins set the extinction coefficients Q_{ext} (Figure 9) between those obtained with optical constants of Khare et al. (1984) and Rannou et al. (2010), but this has less consequence on data analysis or on the thermal balance. On the other hand, the scattering efficiency Q_{sca} = $\omega \times Q_{ext}$, the phase functions and the asymmetry parameters are not modified at all by optical constants (see Supplementary Information, Figures A and B).

This has an important consequence: using other optical constants than those already used to analyse scattering photometry at Pluto's limb (Cheng et al. 2017; Gao et al. 2017; Gladstone et

al. 2016; Stern et al. 2015) would not change the result about aerosol size and vertical profile.

771 Nevertheless, optical constants of Pluto tholins presented in this study deeply modify the link

between the scattering properties and the absorption properties, compared to Titan tholins. That is, for the same scattering efficiency, Pluto tholins absorb about 5 to 10 times less than Titan tholins at $0.5 \,\mu m$ (effective wavelength of solar input).

To adjust Pluto's thermal balance, Zhang et al. (2017) used the optical constants from Khare et al. (1984), and had to decrease significantly (up to a factor 4) the absorption efficiency of aerosols in the visible wavelength range (see Figure 7, black dashed arrow), to increase it in thermal IR and grossly keep the same extinction properties to match Alice UV spectrometer retrieval for the haze extinction (Stern et al. 2015). Here we see that low absorption is a natural outcome of Pluto tholins produced for this study with chemical conditions representative of Pluto's atmosphere.

782 VI. Conclusion and Perspectives

783 In this study, we determined the optical constants of Pluto aerosol analogues. Three types of 784 tholins were produced from gas mixtures with different N₂:CH₄:CO proportions, in order to 785 mimic aerosols formed at different altitudes in Pluto's current atmosphere. The sample P_H is expected to be representative of aerosols formed below 350 km of altitude above the surface. 786 787 The sample P_{400} is expected to mimic the aerosols formed at around 400 km of altitude. The sample P_{650} is expected to be analogous of aerosols formed between 600 and 700 km of altitude. 788 789 These three gas mixtures differing in their CH₄:N₂ mixing ratio can also be considered as 790 analogues of Pluto's atmosphere at different seasons or epochs.

791 Our results show:

- (1) A strong absorption of UV and visible radiations by Pluto tholins, attributed to their N bearing and O-bearing organic molecules.
- 794 (2) A moderate absorption in the near-IR spectral range by Pluto tholins with *k* indices of a 795 few 10^{-3} .
- (3) A dependency of *n* and *k* indices to the CH₄:N₂ mixing ratio, and thus to the altitude of
 aerosol formation in Pluto's atmosphere. The N- and O-content in Pluto low-altitude
 aerosols is enhanced, leading to an increase of both *n* and *k*-values. This dependency
 of the optical constants to the CH₄:N₂ mixing ratio has also implications for the seasonal
 and past epochal radiative transfer of Pluto.

The comparison of our data with the optical constants determined for Titan tholins by Khare et al. (1984) shows that Pluto tholins present globally similar *n*-values to those of Titan. However, differences are observed concerning the *k* indices. In particular, *k*-values of Pluto tholins are
one order of magnitude higher than those of Titan in the near-IR. In the UV spectral range, *k* indices of Pluto tholins are also higher, which is probably due to the reactivity of nitrogen and
carbon monoxide in the gas mixture producing Pluto's aerosols.

The optical properties of tholins depend on their chemical composition, and particularly on the N- and O-content. As Pluto tholins are compositionally different from Titan tholins, we propose the optical constants determined in this study as new input parameters from 270 to 2100 nm to model Pluto's atmosphere and surface properties.

Our Pluto optical constants were used as input parameters in a Pluto surface model developed by Protopapa et al. (2020). The modelling results concluded on the suitability of our optical constants to reproduce Pluto compositional observations by MVIC and LEISA, at least in the UV-Vis spectral ranges. Moreover, results from a model of light scattering developed by Rannou et al. (1997, 1999) concluded that Pluto tholins absorb 5 to 10 times less than Titan tholins at 500 nm. This lower absorption is consistent with Alice observations of Pluto's haze.

Our study focused on Pluto's aerosols formed by photochemistry. However, we remind that an 817 818 additional process for the formation of aerosols in Pluto's atmosphere was recently proposed by Lavvas et al. (2020) due to ice condensation on photochemical nuclei. In their hypothesis, 819 820 the first photochemical ice to condense in the upper atmosphere (near ~500 km of altitude) 821 would be HCN. Then, other photochemical gases, such as C₃H₄, C₆H₆ and predominantly C₄H₂, would condense and coat the HCN ice particles formerly formed. Note that, as Pluto's most 822 abundant gaseous photochemical products $-C_2H_2$, C_2H_4 , and C_2H_6 – condense only a few 823 kilometres above the surface (Stern et al. 2017b), they should not take part in the homogeneous 824 coating of HCN particles occurring at higher altitudes. Nevertheless, those C₂ hydrocarbons, as 825 well as CH₃C₂H, are suspected to be subject to heterogeneous adsorption/desorption processes 826 on the ice particles, between 100 and 200 km of altitude above the surface (Krasnopolsky 2020; 827 828 Luspay-Kuti et al. 2017; Wong et al. 2017), inhibiting the sublimation of the condensed ices.

Such condensation of gaseous molecules, resulting in coated photochemical aerosols (Krasnopolsky 2020; Luspay-Kuti et al. 2017; Wong et al. 2017), would occur on preexisting Pluto's aerosols formed by photochemistry, requiring to know their properties as well, as studied in the present work. The differences observed between our data and the *New Horizons* observations could be explained by this contribution of coated aerosols. By analogy with the C_4H_2 ice studied in Lavvas et al. (2020) presenting lower *n*- and *k*-values than those determined for our Pluto tholins in the common wavelength range [270-1000 nm], we can suppose that if gaseous molecules condense or adsorb on Pluto's photochemical aerosols, their optical constants n and k could be slightly lowered.

However, assessing the exact effect on the optical constants of [tholins/ices] mixture willrequire in depth modelling and experimental investigation, far beyond the scope of this study.

840

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855 **References**

- Alcouffe, G., Cavarroc, M., Cernogora, G., et al. 2010, Plasma Sources Sci Technol, 19,
- 857 15008, http://dx.doi.org/10.1088/0963-0252/19/1/015008
- Azzam, R. M. A., & Bashara, N. M. 1977, Ellipsometry and Polarized Light, Ellipsometry
- and Polarized Light (North-Holland Publishing Company)
- 860 Bertrand, T., & Forget, F. 2016, Nature, 540, 86, https://doi.org/10.1038/nature19337
- 861 Bertrand, T., & Forget, F. 2017, Icarus, 287, 72,
- http://www.sciencedirect.com/science/article/pii/S0019103517300477

- 863 Bertrand, T., Forget, F., Umurhan, O. M., et al. 2019, Icarus, 329, 148,
- 864 http://www.sciencedirect.com/science/article/pii/S0019103518305748
- Bohren, C. F., & Huffman, D. R. 1983, Absorption and Scattering of Light by Small Particles
 (John Wiley & Sons)
- 867 Boucher, O. 2015 (Springer Netherlands), https://doi.org/10.1007/978-94-017-9649-1_2
- 868 Brassé, C., Muñoz, O., Coll, P., & Raulin, F. 2015, Planet Space Sci, 109–110, 159,
- 869 http://www.sciencedirect.com/science/article/pii/S0032063315000471
- Brossier, J. F., Rodriguez, S., Cornet, T., et al. 2018, J Geophys Res Planets, 123, 1089,
- 871 https://doi.org/10.1029/2017JE005399
- 872 Bruggeman, D. A. G. 1935, Ann Phys, 416, 636, https://doi.org/10.1002/andp.19354160705
- 873 Cable, M. L., Hörst, S. M., Hodyss, R., et al. 2012, Chem Rev, 112, 1882,
- 874 https://doi.org/10.1021/cr200221x
- 875 Cappa, C. D., Che, D. L., Kessler, S. H., Kroll, J. H., & Wilson, K. R. 2011, J Geophys Res
- 876 Atmos, 116, https://doi.org/10.1029/2011JD015918
- 877 Carrasco, N., Tigrine, S., Gavilan, L., Nahon, L., & Gudipati, M. S. 2018, Nat Astron, 2, 489,
- 878 https://doi.org/10.1038/s41550-018-0439-7
- 879 Cechalova, B., Branecky, M., Klapetek, P., & Cech, V. 2019, Materials, Vol. 12
- 880 Cheng, A. F., Summers, M. E., Gladstone, G. R., et al. 2017, Icarus, 290, 112,
- 881 http://www.sciencedirect.com/science/article/pii/S0019103516303141
- 882 Cheng, A. F., Weaver, H. A., Conard, S. J., et al. 2008, Space Sci Rev, 140, 189,
- 883 https://doi.org/10.1007/s11214-007-9271-6
- 884 D'Amico, K. L., Manos, C., & Christensen, R. L. 1980, J Am Chem Soc, 102, 1777,
- 885 https://doi.org/10.1021/ja00526a003
- Desyaterik, Y., Sun, Y., Shen, X., et al. 2013, J Geophys Res Atmos, 118, 7389,
- 887 https://doi.org/10.1002/jgrd.50561
- 888 Fan, S., Shemansky, D. E., Li, C., et al. 2019, Earth Sp Sci, 6, 1057,
- 889 https://doi.org/10.1029/2018EA000477
- 890 Ferrari, A. C., Rodil, S. E., & Robertson, J. 2003, Phys Rev B Condens Matter Mater Phys,

- 67, 155306
- 892 Fujiwara, H. 2007, Spectroscopic Ellipsometry: Principles and Applications, Spectroscopic
- 893 Ellipsometry: Principles and Applications (John Wiley)
- Gao, P., Fan, S., Wong, M. L., et al. 2017, Icarus, 287, 116,
- http://www.sciencedirect.com/science/article/pii/S0019103516306170
- 896 Gautier, T., Sebree, J. A., Li, X., et al. 2017, Planet Space Sci, 140, 27,
- 897 http://www.sciencedirect.com/science/article/pii/S003206331630397X
- Gavilan, L., Broch, L., Carrasco, N., Fleury, B., & Vettier, L. 2017, Astrophys J, 848, L5,
- 899 http://dx.doi.org/10.3847/2041-8213/aa8cc4
- 900 Gladstone, G. R., Pryor, W. R., & Stern, S. A. 2015, Icarus, 246, 279,
- 901 http://www.sciencedirect.com/science/article/pii/S0019103514002085
- 902 Gladstone, G. R., Stern, S. A., Ennico, K. A., et al. 2016, Science (80-), 351,
- 903 http://science.sciencemag.org/content/351/6279/aad8866.abstract
- 904 Griffith, C. A., Doose, L., Tomasko, M. G., Penteado, P. F., & See, C. 2012, Icarus, 218, 975,
- 905 http://www.sciencedirect.com/science/article/pii/S0019103511004611
- 906 Grundy, W. M., Bertrand, T., Binzel, R. P., et al. 2018, Icarus, 314, 232,
- 907 http://www.sciencedirect.com/science/article/pii/S0019103517306012
- Hadamcik, E., Renard, J.-B., Alcouffe, G., et al. 2009, Planet Space Sci, 57, 1631,
- 909 http://www.sciencedirect.com/science/article/pii/S0032063309001834
- 910 Imanaka, H., Cruikshank, D. P., Khare, B. N., & McKay, C. P. 2012, Icarus, 218, 247,
- 911 http://www.sciencedirect.com/science/article/pii/S0019103511004453
- 912 Imanaka, H., Khare, B. N., Elsila, J. E., et al. 2004, Icarus, 168, 344,
- 913 http://www.sciencedirect.com/science/article/pii/S0019103504000041
- 914 Jellison, G. E. J., & Modine, F. A. 1996, Appl Phys Lett, 69, 371,
- 915 https://doi.org/10.1063/1.118064
- 916 Johnson, P. E., Young, L. A., Protopapa, S., et al. 2021, Icarus, 356, 114070,
- 917 http://www.sciencedirect.com/science/article/pii/S0019103520304188
- 918 Jovanović, L., Gautier, T., Vuitton, V., et al. 2020, Icarus, 346, 113774,

- 919 https://doi.org/10.1016/j.icarus.2020.113774
- 920 Keita, A.-S., En Naciri, A., Delachat, F., et al. 2010, J Appl Phys, 107, 93516,
- 921 https://doi.org/10.1063/1.3331551
- 922 Khare, B. N., Sagan, C., Arakawa, E. T., et al. 1984, Icarus, 60, 127,
- 923 http://www.sciencedirect.com/science/article/pii/0019103584901428
- 924 Khare, B. N., Sagan, C., Thompson, W. R., Arakawa, E. T., & Votaw, P. 1987, J Geophys
- 925 Res Sp Phys, 92, 15067, https://doi.org/10.1029/JA092iA13p15067
- 926 Kolokolova, L., & Jockers, K. 1997, Planet Space Sci, 45, 1543,
- 927 http://www.sciencedirect.com/science/article/pii/S0032063397000998
- 928 Kolokolova, L., Jockers, K., Chernova, G. P., & Kiselev, N. N. 1997, Icarus, 126, 351,
- 929 http://www.sciencedirect.com/science/article/pii/S0019103596956602
- 930 Kramers, H. A. 1927, in Atti. Cong. Intern. Fisica (Transactions of Volta Centenary
- 931 Congress) Como 2, 545
- 932 Krasnopolsky, V. A. 2020, Icarus, 335, 113374,
- 933 http://www.sciencedirect.com/science/article/pii/S0019103519302313
- van Krevelen, D. W., & te Nijenhuis, K. 2009, in Properties of Polymers Fourth edition,
- 935 287, http://www.sciencedirect.com/science/article/pii/B9780444828774500172
- 936 Kronig, R. de L. 1926, J Opt Soc Am, 12, 547,
- 937 http://www.osapublishing.org/abstract.cfm?URI=josa-12-6-547
- 238 Lambe, A. T., Cappa, C. D., Massoli, P., et al. 2013, Environ Sci Technol, 47, 6349,
- 939 https://doi.org/10.1021/es401043j
- 940 Larson, E. J. L., Toon, O. B., West, R. A., & Friedson, A. J. 2015, Icarus, 254, 122,
- 941 http://www.sciencedirect.com/science/article/pii/S0019103515001104
- 942 Lavvas, P., Lellouch, E., Strobel, D. F., et al. 2020, Nat Astron,
- 943 https://doi.org/10.1038/s41550-020-01270-3
- 944 Lavvas, P., Strobel, D. F., Lellouch, E., et al. 2016, in AAS/Division for Planetary Sciences
- 945 Meeting Abstracts #48, 224.06, https://ui.adsabs.harvard.edu/abs/2016DPS....4822406L
- 946 Lavvas, P., Yelle, R. V., & Griffith, C. A. 2010, Icarus, 210, 832,

- 947 http://www.sciencedirect.com/science/article/pii/S0019103510003040
- 948 Lavvas, P., Yelle, R. V., & Vuitton, V. 2009, Icarus, 201, 626,
- 949 http://www.sciencedirect.com/science/article/pii/S0019103509000086
- 950 Lellouch, E., Gurwell, M. A., Butler, B. J., et al. 2017, Icarus, 286, 289,
- 951 http://www.sciencedirect.com/science/article/pii/S0019103516302755
- 952 Liang, M.-C., Yung, Y. L., & Shemansky, D. E. 2007, Astrophys J, 661, L199,
- 953 http://dx.doi.org/10.1086/518785
- Likhachev, D. V., Malkova, N., & Poslavsky, L. 2015, Thin Solid Films, 589, 844,
- 955 http://www.sciencedirect.com/science/article/pii/S0040609015007014
- 956 Liu, P. F., Abdelmalki, N., Hung, H.-M., et al. 2015, Atmos Chem Phys, 15, 1435,
- 957 https://ui.adsabs.harvard.edu/abs/2015ACP....15.1435L
- 958 Lopes, R. M. C., Malaska, M. J., Solomonidou, A., et al. 2016, Icarus, 270, 162,
- 959 http://www.sciencedirect.com/science/article/pii/S0019103515005576
- 960 Luspay-Kuti, A., Mandt, K. E., Jessup, K. L., et al. 2017, Mon Not R Astron Soc, 472, 104
- 961 Mahjoub, A., Carrasco, N., Dahoo, P.-R., et al. 2012, Icarus, 221, 670,
- 962 http://www.sciencedirect.com/science/article/pii/S001910351200334X
- Mahjoub, A., Carrasco, N., Dahoo, P.-R., et al. 2014, Plasma Process Polym, 11, 409,
- 964 https://doi.org/10.1002/ppap.201300150
- 965 Maillard, J., Carrasco, N., Schmitz-Afonso, I., Gautier, T., & Afonso, C. 2018, Earth Planet
- Sci Lett, 495, 185, http://www.sciencedirect.com/science/article/pii/S0012821X18302851
- 967 Mistrik, J., Kasap, S., Ruda, H. E., Koughia, C., & Singh, J. 2017 (Springer International
- 968 Publishing), https://doi.org/10.1007/978-3-319-48933-9_3
- 969 Moise, T., Flores, J. M., & Rudich, Y. 2015, Chem Rev, 115, 4400,
- 970 https://doi.org/10.1021/cr5005259
- 971 Nakayama, T., Sato, K., Imamura, T., & Matsumi, Y. 2018, Environ Sci Technol, 52, 2566,
- 972 https://doi.org/10.1021/acs.est.7b05852
- 973 Nakayama, T., Sato, K., Matsumi, Y., et al. 2012, SOLA, 8, 119
- Pernot, P., Carrasco, N., Thissen, R., & Schmitz-Afonso, I. 2010, Anal Chem, 82, 1371,

- 975 https://doi.org/10.1021/ac902458q
- 976 Protopapa, S., Grundy, W. M., Reuter, D. C., et al. 2017, Icarus, 287, 218,
- 977 http://www.sciencedirect.com/science/article/pii/S0019103516307692
- 978 Protopapa, S., Olkin, C. B., Grundy, W. M., et al. 2020, Astron J, 159, 74,
- 979 http://dx.doi.org/10.3847/1538-3881/ab5e82
- 980 Quirico, E., Montagnac, G., Lees, V., et al. 2008, Icarus, 198, 218,
- 981 http://www.sciencedirect.com/science/article/pii/S0019103508002819
- 982 Ramírez, S. I., Coll, P., da Silva, A., et al. 2002, Icarus, 156, 515,
- 983 http://www.sciencedirect.com/science/article/pii/S0019103501967831
- 984 Rannou, P., Cabane, M., Botet, R., & Chassefière, E. 1997, J Geophys Res Planets, 102,
- 985 10997, https://doi.org/10.1029/97JE00719
- 986 Rannou, P., Cours, T., Le Mouélic, S., et al. 2010, Icarus, 208, 850,
- 987 http://www.sciencedirect.com/science/article/pii/S0019103510001181
- 988 Rannou, P., McKay, C. P., Botet, R. S., & Cabane, M. 1999, Planet Space Sci, 47, 385,
- 989 http://www.sciencedirect.com/science/article/pii/S0032063399000070
- 990 Rao, C. N. R. 1975 (Butterworth)
- 991 Reuter, D. C., Stern, S. A., Scherrer, J., et al. 2008, Space Sci Rev, 140, 129,
- 992 https://doi.org/10.1007/s11214-008-9375-7
- 993 Scattergood, T., & Owen, T. 1977, Icarus, 30, 780,
- http://www.sciencedirect.com/science/article/pii/0019103577900951
- 995 Sciamma-O'Brien, E., Dahoo, P.-R., Hadamcik, E., et al. 2012, Icarus, 218, 356,
- 996 http://www.sciencedirect.com/science/article/pii/S0019103511004878
- 997 Seignovert, B., Rannou, P., Lavvas, P., Cours, T., & West, R. A. 2017, Icarus, 292, 13,
- 998 http://www.sciencedirect.com/science/article/pii/S0019103516306911
- 999 Steffl, A. J., Young, L. A., Strobel, D. F., et al. 2020, Astrophys J
- 1000 Stenberg, B., Viscarra Rossel, R. A., Mouazen, A. M., & Wetterlind, J. 2010, in Advances in
- 1001 Agronomy, ed. D. L. B. T.-A. in A. Sparks, Vol. 107 (Academic Press), 163,
- 1002 http://www.sciencedirect.com/science/article/pii/S0065211310070057

- 1003 Stern, S. A., Bagenal, F., Ennico, K. A., et al. 2015, Science (80-), 350,
- 1004 http://science.sciencemag.org/content/350/6258/aad1815.abstract
- 1005 Stern, S. A., Binzel, R. P., Earle, A. M., et al. 2017a, Icarus, 287, 47,
- 1006 http://www.sciencedirect.com/science/article/pii/S0019103516307588
- 1007 Stern, S. A., Grundy, W. M., McKinnon, W. B., Weaver, H. A., & Young, L. A. 2018, Annu
- 1008 Rev Astron Astrophys, 56, 357, https://doi.org/10.1146/annurev-astro-081817-051935
- 1009 Stern, S. A., Kammer, J. A., Barth, E. L., et al. 2017b, Astron J, 154, 43,
- 1010 http://dx.doi.org/10.3847/1538-3881/aa78ec
- 1011 Stern, S. A., Slater, D. C., Scherrer, J., et al. 2008, Space Sci Rev, 140, 155,
- 1012 https://doi.org/10.1007/s11214-008-9407-3
- 1013 Szopa, C., Cernogora, G., Boufendi, L., Correia, J.-J., & Coll, P. 2006, Planet Space Sci, 54,
- 1014 394, http://www.sciencedirect.com/science/article/pii/S003206330600002X
- 1015 Tauc, J., Grigorovici, R., & Vancu, A. 1966, Phys Status Solidi, 15, 627,
- 1016 https://doi.org/10.1002/pssb.19660150224
- 1017 Tompkins, H. G., & Irene, E. A. 2005, Handbook of Ellipsometry (William Andrew
- 1018 Publishing)
- 1019 Tran, B. N., Joseph, J. C., Ferris, J. P., Persans, P. D., & Chera, J. J. 2003, Icarus, 165, 379,
- 1020 http://www.sciencedirect.com/science/article/pii/S0019103503002094
- 1021 Vinatier, S., Rannou, P., Anderson, C. M., et al. 2012, Icarus, 219, 5,
- 1022 http://www.sciencedirect.com/science/article/pii/S0019103512000498
- 1023 Vuitton, V., Tran, B. N., Persans, P. D., & Ferris, J. P. 2009, Icarus, 203, 663,
- 1024 http://www.sciencedirect.com/science/article/pii/S0019103509001754
- 1025 Wong, M. L., Fan, S., Gao, P., et al. 2017, Icarus, 287, 110,
- 1026 http://www.sciencedirect.com/science/article/pii/S0019103516306145
- Workman, J., & Weyer, L. 2008, Practical Guide to Interpretive Near-Infrared Spectroscopy,
 Vol. 3
- 1029 Xiaobo, Z., Jiewen, Z., Povey, M. J. W., Holmes, M., & Hanpin, M. 2010, Anal Chim Acta,
- 1030 667, 14, http://www.sciencedirect.com/science/article/pii/S0003267010003582

- 1031 Young, L. A., Kammer, J. A., Steffl, A. J., et al. 2018, Icarus, 300, 174,
- 1032 http://www.sciencedirect.com/science/article/pii/S0019103517302609
- 1033 Zhang, X., Strobel, D. F., & Imanaka, H. 2017, Nature, 551, 352,
- 1034 https://doi.org/10.1038/nature24465
- 1035 Zhong, M., Jang, M., Oliferenko, A., Pillai, G. G., & Katritzky, A. R. 2012, Phys Chem Chem
- 1036 Phys, 14, 9058, http://dx.doi.org/10.1039/C2CP23906J
- 1037 Zhu, X., Strobel, D. F., & Erwin, J. T. 2014, Icarus, 228, 301,
- 1038 http://www.sciencedirect.com/science/article/pii/S0019103513004302
- 1039

1040 Supplementary Information





1043Figure A: Scattering efficiency Q_{sca} determined for spherical monomers of 10 nm radius (log-1044normal distribution, with effective variance v = 0.03) with a Mie model formalized in Bohren

& Huffman (1983) (dotted curves) and for fractal aggregates of 3375 monomers of 10 nm radius
with the model developed by Rannou et al. (1997, 1999) (plain curves). The black curves were
generated with the optical constants determined by Khare et al. (1984) for Titan tholins. Note
that these Khare et al. (1984) optical constants were adopted in Zhang et al. (2017) study. The
pink curves were generated with the optical constants determined by Rannou et al. (2010) and
Vinatier et al. (2012) for Titan's aerosols. The blue, red and green curves were generated with
the optical constants determined respectively for our samples P_H, P₄₀₀ and P₆₅₀.



Figure B: Asymmetry factor g determined for spherical monomers of 10 nm radius (log-normal distribution, with effective variance v = 0.03) with a Mie model formalized in Bohren & Huffman (1983) (dotted curves) and for fractal aggregates of 3375 monomers of 10 nm radius with the model developed by Rannou et al. (1997, 1999) (plain curves). The black curves were generated with the optical constants determined by Khare et al. (1984) for Titan tholins. Note that these Khare et al. (1984) optical constants were adopted in Zhang et al. (2017) study. The pink curves were generated with the optical constants determined by Rannou et al. (2010) and

- 1060 Vinatier et al. (2012) for Titan's aerosols. The blue, red and green curves were generated with
- 1061 the optical constants determined respectively for our samples P_{H} , P_{400} and P_{650} .