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

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14

15 **Keywords**

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

17

18 **Abstract**

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

25 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  
27 270 to 2100 nm. Three types of samples were produced from N<sub>2</sub>:CH<sub>4</sub>:CO gas mixtures differing

28 in their CH<sub>4</sub>:N<sub>2</sub> mixing ratio, representative of different altitudes in Pluto's current atmosphere  
29 or different seasons or epochs of Pluto.

30 Our analysis shows a strong absorption by Pluto tholins in the UV and visible spectral ranges,  
31 with  $k$  index of a few  $10^{-1}$  at 270 nm, in agreement with N- and O-bearing organic molecules.  
32 Pluto tholins are less absorbent in the near-IR than in the UV-Vis wavelength range, with  $k$  of  
33 a few  $10^{-3}$  between 600 and 2100 nm. Our comparative study highlights the dependency of  $n$   
34 and  $k$  indices to the CH<sub>4</sub>:N<sub>2</sub> mixing ratio. Aerosols formed at different altitudes in Pluto's  
35 atmosphere or during different seasons or epochs of Pluto will therefore affect the budget of  
36 Pluto radiative transfer differently.

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

43

## 44 **I. Introduction**

45 Pluto fly-by by the *New Horizons* spacecraft on July 14<sup>th</sup>, 2015 evidenced the presence of  
46 aerosols in Pluto's atmosphere by means of forward scattering observations and solar  
47 occultations. These aerosols, accounting for 0.05-0.1 ppmv of the atmosphere, enshroud Pluto  
48 and were detected at least as high as 350 km of altitude above the surface (Cheng et al. 2017;  
49 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  
52 in Titan's upper atmosphere (*e.g.*, Gladstone et al. 2015, 2016; Wong et al. 2017; Young et al.  
53 2018). Pluto's aerosols are thought to be formed by a complex photochemistry taking place in  
54 the upper atmosphere, below 300 km and up to 900 km of altitude (Stern et al. 2018; Young et  
55 al. 2018). This photochemistry is initiated by extreme-ultraviolet (EUV) sunlight and solar  
56 Lyman- $\alpha$  photons. EUV radiation breaks the triple bonds of N<sub>2</sub> and CO in the upper atmosphere,  
57 while Lyman- $\alpha$  photons – arriving directly from the Sun or scattered by the interplanetary  
58 medium – breaks the C–H bonds in CH<sub>4</sub> at lower altitudes (Gladstone et al. 2015, 2016; Grundy

59 et al. 2018, and references therein), with a maximum CH<sub>4</sub> photolysis rate at 250 km of altitude  
60 above the surface (Bertrand & Forget 2017). Pluto's photochemistry involves neutral and ionic  
61 species created by the ionization and the dissociation of molecular nitrogen N<sub>2</sub>, methane CH<sub>4</sub>,  
62 and carbon monoxide CO that constitute Pluto's atmosphere (Gladstone et al. 2016; Lellouch  
63 et al. 2017; Young et al. 2018). This chemistry forms complex hydrocarbons, nitriles, and  
64 oxygenated molecules, including some that can further polymerize and generate solid aerosols  
65 (Krasnopolsky 2020; Wong et al. 2017).

66 The second mechanism, developed by Lavvas et al. (2020), would be different from that  
67 proposed for Titan's hazes formation, due to the temperature difference between Pluto's and  
68 Titan's upper atmospheres (~70 K versus ~150 K, respectively). This mechanism involves the  
69 direct condensation of photochemical gases produced on Pluto, associated with a coating by  
70 undersaturated light molecules (C<sub>2</sub> hydrocarbons) incorporated by heterogeneous processes  
71 (possibly chemisorption or physisorption). This coating represents ~30% of the aerosol material  
72 (Lavvas et al. 2020). These coated aerosols are then subject to a photon flux causing their  
73 ageing, as studied in Carrasco et al. (2018) for Titan's aerosols.

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

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

92 The haze particles are suspected to scatter the UV sunlight and to be the dominant factor of  
93 extinction at wavelengths greater than  $\sim 150$  nm, as the extinctions of hydrocarbons or nitriles  
94 become less important with increasing wavelength. The haze particles thus contribute to the  
95 spectrum of Pluto observed by the Alice instrument (Cheng et al. 2017; Steffl et al. 2020; Stern  
96 et al. 2008). Pluto's aerosols are also expected to significantly absorb in the UV-Visible and in  
97 the far-infrared spectral ranges and to be less absorbent in the near- and mid-IR (Grundy et al.  
98 2018; Zhang et al. 2017; and references therein).

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

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

125 that the review by Brassé et al. (2015) discusses the different optical constants determined for  
126 Titan tholins.

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

## 131 **II. Experimental setup and protocol**

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

133 Following the protocol detailed in Jovanović et al. (2020), we used the experimental setup  
134 PAMPRE (Production d'Aérosols en Microgravité par Plasma REactif) (Alcouffe et al. 2010;  
135 Szopa, Cernogora et al. 2006), a cold plasma discharge to simulate the chemistry occurring in  
136 Pluto's atmosphere and produce analogues of Pluto's aerosols. The gas mixture flows through  
137 a cylindrical metallic grounded cage. Square silicon wafers of 1 cm<sup>2</sup> were placed at the bottom  
138 of the cage. When the plasma is switched on, tholins form as thin films onto the silicon wafers.

139 Note that the optical constants of tholins are highly dependent on the experimental conditions  
140 of synthesis and measurements (Brassé et al. 2015; Zhang et al. 2017). For readers interested in  
141 the effect of using a UV lamp rather than a plasma discharge to synthesize tholins, we  
142 recommend reading the review by Cable et al. (2012). In summary, tholins formed by UV  
143 photochemistry in the laboratory tend to be less rich in N-bearing compounds, since UV lamps  
144 cannot mobilize nitrogen chemistry. Indeed, lamp windows cut off UV wavelengths below  
145 ~115 nm, which prevents direct dissociation of N<sub>2</sub>, unlike what happens in natural atmospheres.

146 On the contrary, plasma setups such as PAMPRE tend to enhance nitrogen inclusion a bit too  
147 much. The electron energy distribution in PAMPRE mimics well at first order the one of solar  
148 photons (Szopa, Cernogora et al. 2006). However, a small difference is due to the slightly more  
149 energetic tail of the Maxwellian energy distribution of the electrons in the plasma compared to  
150 the Planck energy distribution of solar photons. This slightly higher population of electrons  
151 induces a small bias due to over-dissociation of N<sub>2</sub>, that is well known and has been extensively  
152 studied regarding the tholins chemical composition. Since nitrogenous compounds tend to be  
153 more absorbent, one could expect that tholins synthesized in laboratory by UV photochemistry  
154 would probably be less absorbent in the UV-Vis spectral range, due to a poorer content in N-  
155 bearing compounds. Where actual Pluto's aerosols would stand in that range is currently  
156 unknown (as for Titan's aerosols), which is why we strongly encourage any other experimental

157 teams with similar facilities to perform studies similar to ours to extend the range of possible  
158 laboratory data on this point.

159 Three types of tholins were synthesized in this work, from gas mixtures composed of various  
160 N<sub>2</sub> (*Air Liquide*, ALPHAGAZ™ 2) and CH<sub>4</sub> (*Air Liquide*, CRYSTAL mixture) percentages  
161 and a fixed CO (*Air Liquide*, CRYSTAL mixture) amount of 500 ppm (see Table 1), at  
162  $0.9 \pm 0.1$  mbar and ambient temperature. For readers interested in the effect of synthesis  
163 temperature on aerosol analogues optical constants, we recommend reading Mahjoub et al.  
164 (2014) who studied this effect for Titan tholins. In the present work, experiments were  
165 performed at ambient temperature to avoid heterogeneous chemistry effects as described in  
166 Mahjoub et al. (2014).

167 The CO atmospheric mole fraction of  $515 \pm 40$  ppm (Lellouch et al. 2017; Young et al. 2018)  
168 is not expected to vary much over time and space. This is due to the volatility of CO being close  
169 to that of N<sub>2</sub> and the absence of CO-rich ice deposits on Pluto's surface (Bertrand & Forget  
170 2016). The first type of tholins was produced in a gas mixture composed of N<sub>2</sub>:CH<sub>4</sub>:CO at  
171 99.5%:0.5%:500ppm – we will thereafter call this material “P<sub>H</sub>”. Given that the CH<sub>4</sub> mixing  
172 ratio was found to be ~0.3% below 350 km of altitude (Young et al. 2018), P<sub>H</sub> is relevant to the  
173 composition of Pluto's atmosphere as observed in 2015 below 350 km of altitude above the  
174 surface. The second tholins sample was produced in a gas mixture containing N<sub>2</sub>:CH<sub>4</sub>:CO at  
175 99%:1%:500ppm, mimicking Pluto's atmosphere at around 400 km of altitude above the  
176 surface – thereafter called “P<sub>400</sub>”. The third one was produced in a gas mixture made of  
177 N<sub>2</sub>:CH<sub>4</sub>:CO at 95%:5%:500ppm, representative of Pluto's atmosphere between 600 and  
178 700 km of altitude – thereafter called “P<sub>650</sub>” (Lellouch et al., 2017, Young et al., 2018).

179 We note that the mean CH<sub>4</sub> atmospheric mixing ratio is predicted to vary from 0.01% to 5%  
180 over annual or astronomical timescales (Bertrand et al. 2019; Bertrand & Forget 2016). The  
181 tholins synthesized in the present work could therefore also serve as analogues for haze particles  
182 produced during past epochs or different seasons of Pluto, with implications to its past and  
183 future climates.

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

187

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

Composition of the reactive mixture			Corresponding altitude above the surface on Pluto	Acronym of the aerosol analogues	Thickness of the thin film
N <sub>2</sub>	CH <sub>4</sub>	CO			
99.5%	0.5%	500 ppm	< 350 km	P <sub>H</sub>	549.8 ± 0.6 nm
99%	1%	500 ppm	~ 400 km	P <sub>400</sub>	540.9 ± 0.2 nm
95%	5%	500 ppm	600-700 km	P <sub>650</sub>	651.0 ± 0.7 nm

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 CH<sub>4</sub> injected in the reactive gas mixture  
 193 increases significantly, as discussed by Mahjoub et al. (2012).

## 194 2. Spectroscopic ellipsometry

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

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

203 The measured values are the ellipsometric parameters  $\Psi$  and  $\Delta$ , related to the ratio of the Fresnel  
 204 amplitude reflection coefficients of the sample by fundamental equation:

205

$$206 \quad r_p/r_s = \tan \psi e^{i\Delta} \quad (1)$$

207

208 for p- and s-polarized light<sup>1</sup> with the electric field in the plane of incidence and perpendicular  
 209 to the plane of incidence, respectively.

---

<sup>1</sup>  $r_p$  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).



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

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

221

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

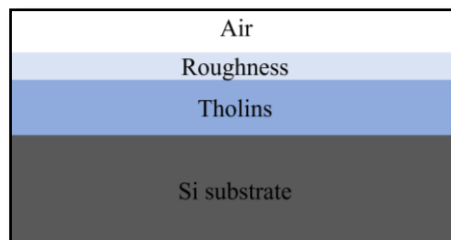
223

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

226 DeltaPsi2<sup>®</sup> software<sup>2</sup> 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.

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

236

<sup>2</sup> DeltaPsi2<sup>®</sup> software: [https://www.horiba.com/en\\_en/products/detail/action/show/Product/deltapsi2-software-1648/](https://www.horiba.com/en_en/products/detail/action/show/Product/deltapsi2-software-1648/)

237 **3. Determination of the optical constants of Pluto tholins with two different inversion**  
238 **methods: modified Tauc-Lorentz and “wavelength-by-wavelength” ( $\lambda$ -by- $\lambda$ )**

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

250 In this work, we used sequentially two types of inversion method: modified Tauc-Lorentz  
251 dispersion model to find the proper estimates of the initialization parameters, and “wavelength-  
252 by-wavelength” ( $\lambda$ -by- $\lambda$ ) numerical inversion to determine precisely the optical constants  $n$  and  
253  $k$  of the tholins material.

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

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

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

265 
$$\epsilon_{i,TL}(E) = \epsilon_{i,T} \times \epsilon_{i,L} = \begin{cases} \frac{1}{E} \frac{AE_0C(E-E_g)^2}{(E^2-E_0^2)^2+C^2E^2} & \text{for } E > E_g \\ 0 & \text{for } E \leq E_g \end{cases} \quad (3)$$

266 where  $E$  (in eV) is the photon energy;  $E_g$  (in eV) is the optical bandgap energy specifying at  
 267 which energy the material becomes absorbent;  $E_0$  (in eV) is the energy of the major absorption  
 268 peak in the UV (the Lorentz peak) ( $E_g < E_0$ );  $A$  is the oscillator amplitude; and  $C$  is the  
 269 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):

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

273 where  $\varepsilon_{\infty}$  is the high-frequency real dielectric constant; and  $P$  is the Cauchy principal value.

274 The optical constants  $n$  and  $k$  are then deduced from the real and imaginary parts of the complex  
 275 relative dielectric constant (Equations (3) and (4)) by the relation:

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

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

282 To overcome this problem, we modified the standard Tauc-Lorentz model by adding oscillators  
 283 characterized by  $\varepsilon_{osc}$ :

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

285 where  $\varepsilon_{osc}$  is the dielectric function;  $w$  is the light pulsation;  $f_j$  is the oscillator strength of the  
 286  $j^{\text{th}}$  resonator;  $w_{0j}$  is the natural pulsation of the  $j^{\text{th}}$  resonator; and  $\gamma_j$  is the damping rate of the  
 287  $j^{\text{th}}$  resonator (friction coefficient).

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

293

294 **b. Determination of the optical constants of Pluto tholins by a “ $\lambda$ -by- $\lambda$ ” numerical**  
295 **inversion method**

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

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

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

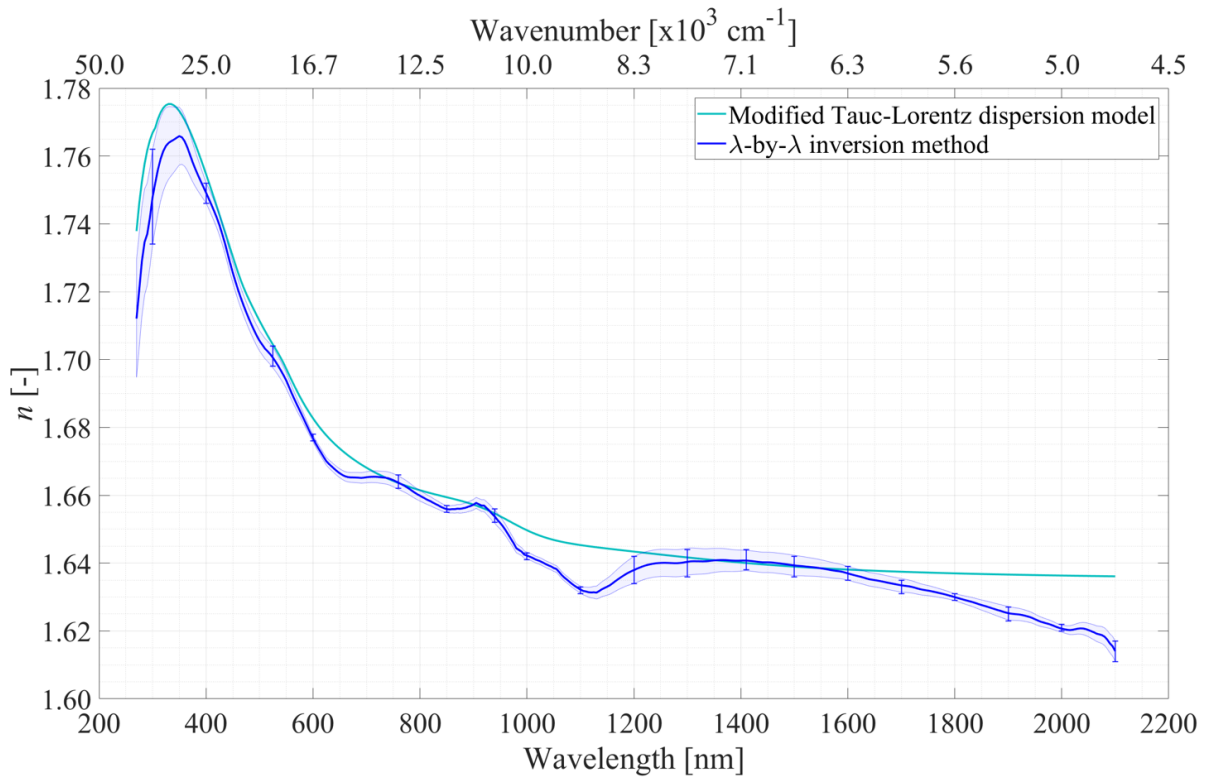
316 **c. Procedure to determine the optical constants  $n$  and  $k$  of Pluto tholins**

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

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

### 334 **III. Results: Optical constants of Pluto aerosol analogues**

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

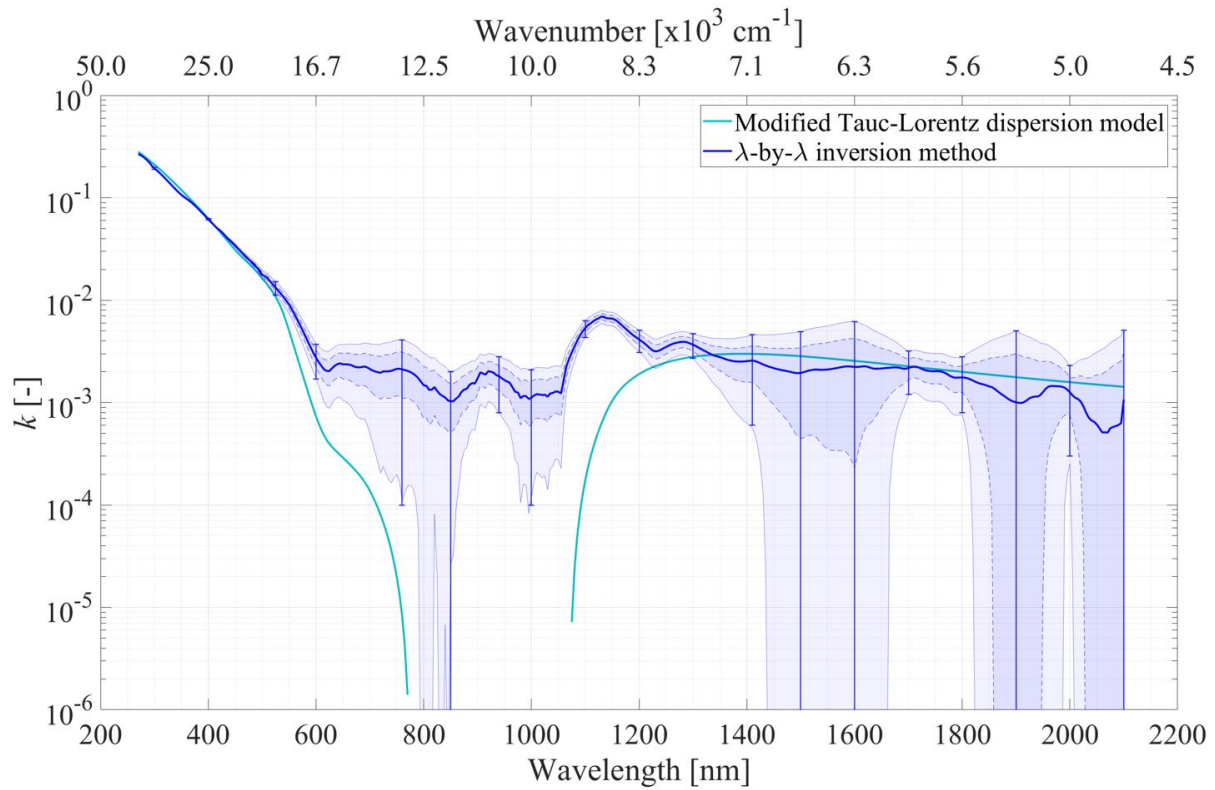


350

351 Figure 2: Real part  $n$  of the complex refractive index of Pluto aerosol analogues  $P_H$  determined by  
 352 spectroscopic ellipsometry with a modified Tauc-Lorentz dispersion model (in turquoise blue) and with  
 353 a “ $\lambda$ -by- $\lambda$ ” numerical inversion method (in dark blue). The  $2\sigma$  error bars were experimentally determined  
 354 for the “ $\lambda$ -by- $\lambda$ ” inversion method at different wavelengths. The uncertainties were then linearly  
 355 interpolated between two error bars in order to obtain the envelope of  $2\sigma$  uncertainty (in light blue).

356

357



358

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

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

377 From Figures 2 and 3, we can conclude that the choice of the fitting model – modified Tauc-  
378 Lorentz or “ $\lambda$ -by- $\lambda$ ” – has no significant impact on the  $n$  and  $k$  indices determined for  $P_H$  sample  
379 in the [270-600] and [1150-2100] nm regions. Each method has advantages and drawbacks  
380 (specified in Sections II.3.a, II.3.b, and II.3.c). In this work, while the modified Tauc-Lorentz  
381 dispersion model was adapted for the determination of the thin-films thickness, it could not  
382 manage to determine non-null values for  $k$  indices between 740 and 1105 nm. This is due to the  
383 software used, which cannot compute  $k$ -values below  $10^{-4}$ . Therefore, we list in Tables SI.1,  
384 SI.2 and SI.3 (found in Supplementary Information) the optical constants of Pluto aerosol  
385 analogues  $P_H$ ,  $P_{400}$  and  $P_{650}$  obtained by spectroscopic ellipsometry and determined with the “ $\lambda$ -  
386 by- $\lambda$ ” fitting method from 270 to 2100 nm with a 5 nm increment. Note that  $n$  and  $k$  indices  
387 presented in all the figures of the manuscript and listed in Tables SI.1-3 were smoothed by a  
388 moving mean with a step of 15 data points. All the subsequent figures display the smoothed  
389 optical constants determined with the “ $\lambda$ -by- $\lambda$ ” numerical inversion method.

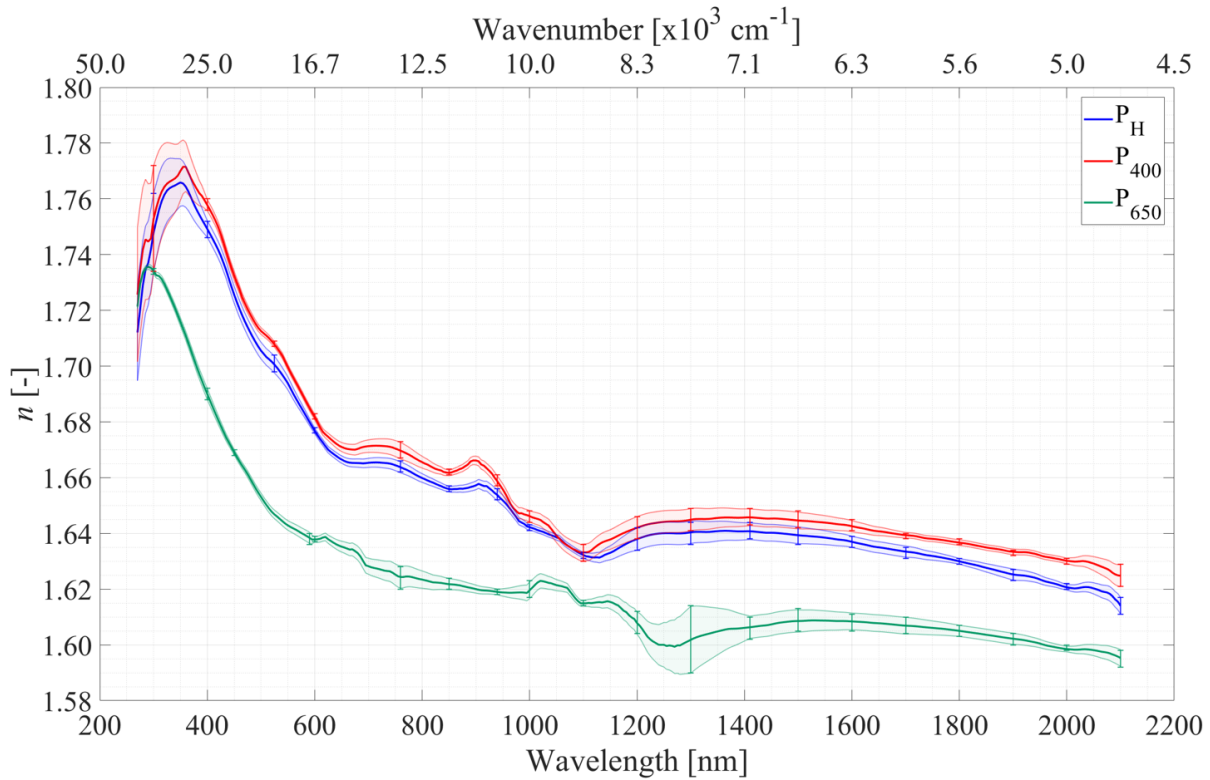
#### 390 **IV. Impact of the altitude (or epoch) of aerosol formation on the optical constants and** 391 **implications for radiative transfer**

392  $P_H$ ,  $P_{400}$  and  $P_{650}$  samples were produced with different  $N_2:CH_4:CO$  ratios. As  $CH_4$  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.

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

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





403

404 Figure 4: Real part  $n$  of the complex refractive index of Pluto tholins determined by spectroscopic  
 405 ellipsometry with a “ $\lambda$ -by- $\lambda$ ” numerical inversion method. The blue, red and green curves respectively  
 406 correspond to the samples  $P_H$ ,  $P_{400}$  and  $P_{650}$ . The  $2\sigma$  error bars were experimentally determined for  
 407 different wavelengths and were then linearly interpolated in-between in order to obtain the envelopes of  
 408  $2\sigma$  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.

410 In Figure 4, we observe that the values of  $n$  indices of  $P_H$  and  $P_{400}$  samples are relatively similar,  
 411 but substantially different from those of  $P_{650}$  sample. For  $P_H$  and  $P_{400}$  samples,  $n$ -values increase  
 412 from 1.71-1.73 to  $\sim$ 1.77 between 270 and 330 nm. Then,  $n$ -values decrease with a steep slope  
 413 from  $\sim$ 1.77 to around 1.67 between 330 and 650 nm. The slope attenuates between 650 and  
 414 1100 nm. Finally, the  $n$  indices of  $P_H$  and  $P_{400}$  reach an asymptotic value of 1.62-1.63 between  
 415 1100 and 2100 nm. For  $P_{650}$  sample,  $n$  index increases from 1.72 to around 1.74 between 270  
 416 and 305 nm, followed by a steep decrease from around 1.74 to 1.64 between 305 and 600 nm.  
 417 The decreasing slope then attenuates between 600 and 1200 nm, before  $n$  index reaches an  
 418 asymptotic value of 1.60-1.61 between 1200 and 2100 nm. In summary, the increase of the  
 419  $\text{CH}_4:\text{N}_2$  mixing ratio in the reactive gas mixture producing Pluto tholins leads to a decrease of  
 420  $n$  index over the entire spectral range considered. As well, the maximum of  $n$ -value is shifted  
 421 towards shorter wavelengths.

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

434 The overall decreasing trend of  $n$  indices from UV to near-IR was also observed in the studies  
435 of optical constants of Titan tholins, regardless of the production mode (type of energy source,  
436 gas pressure, gas temperature, CH<sub>4</sub>:N<sub>2</sub> mixing ratios...) or the type of measurement  
437 (spectroscopic ellipsometry, spectrophotometry...) (Brassé et al. 2015; Imanaka et al. 2004;  
438 Khare et al. 1984; Mahjoub et al. 2012, 2014; Ramírez et al. 2002; Sciamma-O’Brien et al.  
439 2012; Tran et al. 2003). In the considered wavelength range,  $n$  indices of Pluto aerosol  
440 analogues vary from around 1.60 to 1.78. These values are similar to the  $n$ -values determined  
441 for Titan aerosol analogues (Brassé et al. 2015). It thus seems that Pluto tholins, produced in  
442 gas mixtures composed of N<sub>2</sub>, CH<sub>4</sub> and CO, share first-order similar optical properties with  
443 Titan tholins. This similarity also extends to the chemical composition. Indeed, Jovanović et al.  
444 (2020) studied the chemical composition of Pluto aerosol analogues. They showed that the  
445 molecules constituting the tholins are composed of a repetition of a (CH<sub>2</sub>)<sub>w</sub>(HCN)<sub>z</sub> random  
446 pattern, such as molecules in Titan aerosol analogues (Gautier et al. 2017; Maillard et al. 2018;  
447 Pernot et al. 2010), with, however, a significant incorporation of oxygen atoms. van Krevelen  
448 and te Nijenhuis (2009) reported that such  $n$ -values can also correspond to organic polymers  
449 including polyamides –C(=O)–NH– and polyethers  $R$ –O– $R'$ .

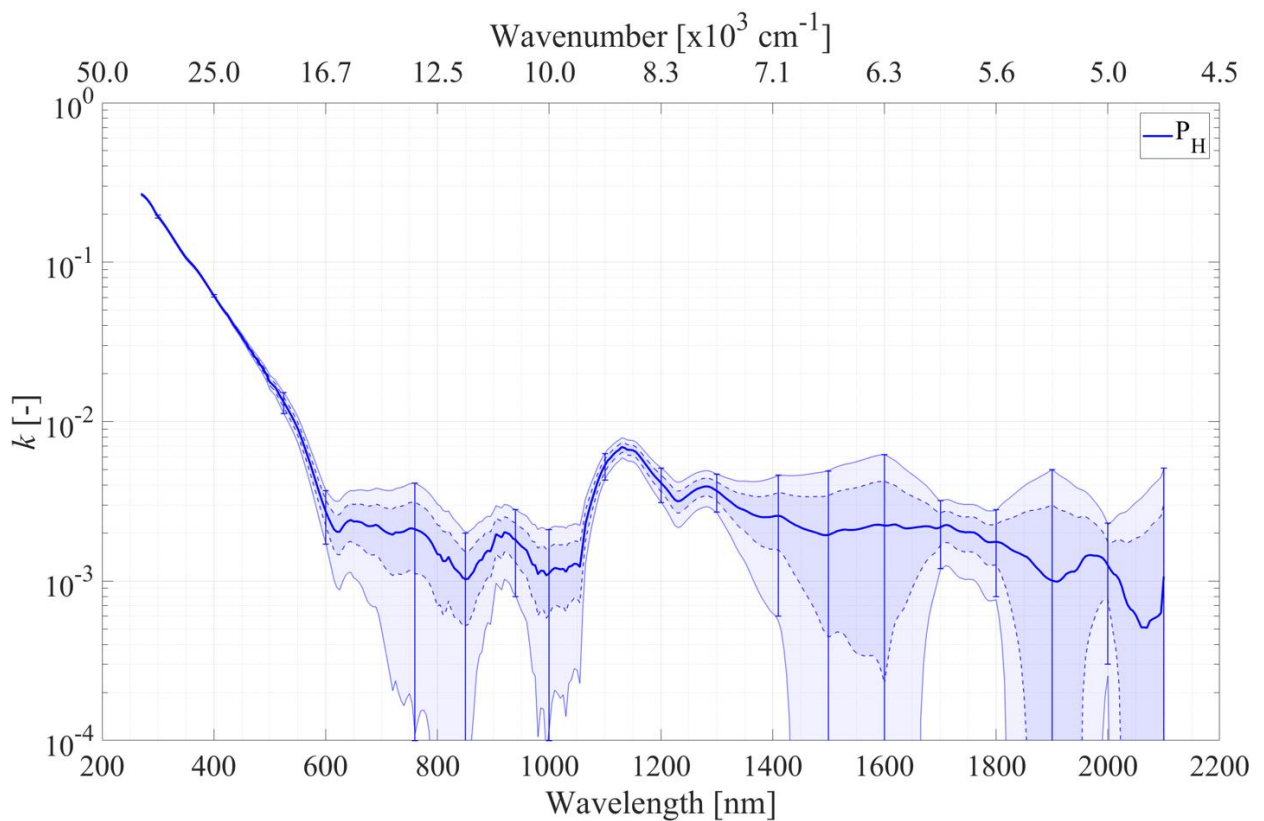
450 We also note in Figure 4 that the  $n$  indices are higher for P<sub>H</sub> and P<sub>400</sub> samples compared to the  
451 P<sub>650</sub> one, with a systematic difference of about 0.05 over the entire wavelength range. This  
452 difference between P<sub>H</sub>/P<sub>400</sub> and P<sub>650</sub> is significant and beyond the uncertainties determined for  
453 the three samples at different wavelengths. Regarding the effect of CH<sub>4</sub>:N<sub>2</sub> mixing ratio on  $n$ -  
454 values, our results differ from those of Mahjoub et al. (2012). In this study concerning the

455 influence of CH<sub>4</sub> concentration on the optical constants of Titan aerosol analogues, the higher  
 456 the CH<sub>4</sub>:N<sub>2</sub> mixing ratio, the higher the  $n$ -values. In the case of Pluto tholins, the relation is  
 457 reversed, suggesting an increasing influence of CO at lower CH<sub>4</sub> concentration.

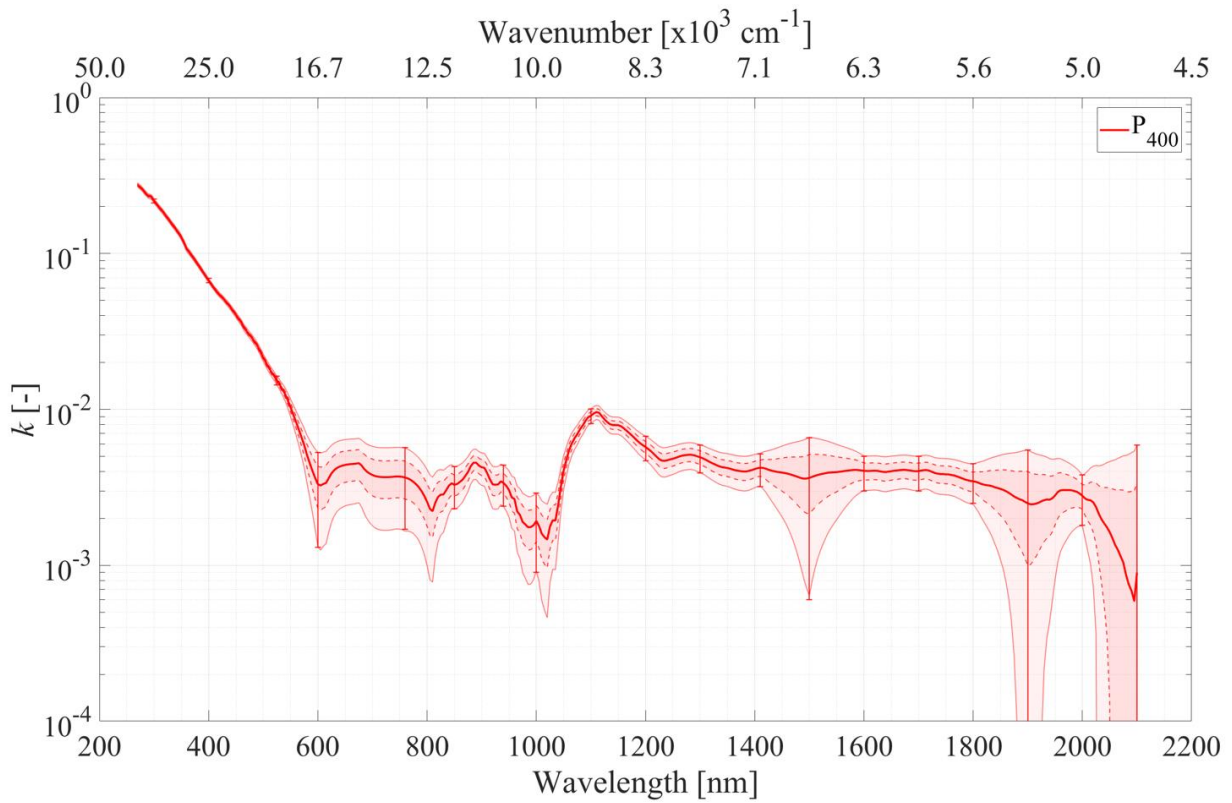
458 Aerosols formed in Pluto's lower atmosphere ( $\leq 400$  km of altitude) are thus expected to scatter  
 459 and polarize the light differently than the aerosols formed at higher altitudes ( $> 400$  km of  
 460 altitude), due to their different  $n$  indices (Boucher 2015; Kolokolova et al. 1997;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

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

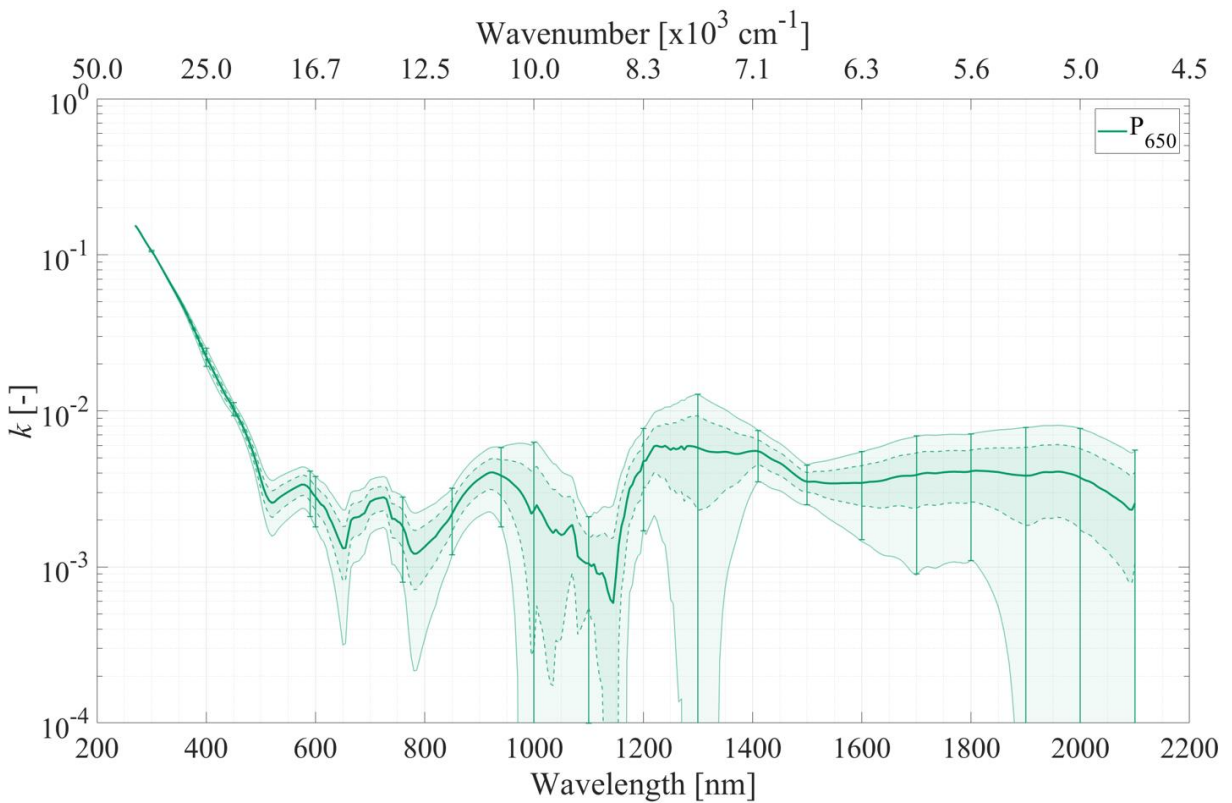
464 Figure 5 shows the imaginary part  $k$  of the complex refractive index computed for P<sub>H</sub> (top panel,  
 465 blue curve), P<sub>400</sub> (middle panel, red curve) and P<sub>650</sub> (bottom panel, green curve) samples as a  
 466 function of wavelength. The  $2\sigma$  error bars (see Table SI.4 in Supplementary Information) were  
 467 calculated based on the uncertainties of  $I_s^{exp}$  and  $I_c^{exp}$  for different wavelengths. The  
 468 uncertainties were then linearly interpolated in-between in order to obtain the envelopes of  
 469 uncertainty (in light blue, light red and light green).



470



471



472

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

477 between in order to obtain the envelopes of  $2\sigma$  uncertainty (in light blue, light red and light green). The  
478 envelopes determined by dashed lines correspond to  $1\sigma$  uncertainty. The y-axis was cropped at  $10^{-4}$ . The  
479  $2\sigma$  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  $P_{400}$  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.

483 In Figure 5, we observe that the  $k$ -values of  $P_H$  and  $P_{400}$  are significantly higher for wavelengths  
484 between 270 and 600 nm than those of  $P_{650}$ . From 600 to 2100 nm, the trend is less clear,  
485 because of larger uncertainties on  $k$ -values. For  $P_H$  and  $P_{400}$  samples,  $k$ -values plummet from  
486  $2.7 \times 10^{-1}$  to around  $4.5 \times 10^{-3}$  between 270 and 590 nm. The bandgap energy is estimated to be  
487 around 590 nm. For  $P_{650}$  sample, the  $k$  index steeply decreases from  $1.5 \times 10^{-1}$  down to around  
488  $2 \times 10^{-3}$  between 270 and 520 nm. The bandgap energy is estimated at around 520 nm. Due to  
489 the large uncertainties on  $k$ -values determined for the three samples above 600 nm and because  
490 this kind of material is weakly absorbent in the near-IR (Brassé et al. 2015), the large variations  
491 observed in the  $k$ -curves should be considered with caution.  $k$  indices for all samples probably  
492 reach an asymptotic value of a few  $10^{-3}$  between 600 and 2100 nm.

493 The 2-steps behaviour of  $k$ -values – sharp decrease followed by a plateau – was also observed  
494 for Titan aerosol analogues in the considered wavelength range (Brassé et al. 2015; Imanaka et  
495 al. 2004; Khare et al. 1984; Mahjoub et al. 2012, 2014; Ramírez et al. 2002; Sciamma-O'Brien  
496 et al. 2012; Tran et al. 2003).

497 We do not have a definitive explanation for the variations observed beyond 600 nm in the  $k$ -  
498 curves of the 3 samples  $P_H$ ,  $P_{400}$  and  $P_{650}$ . Nevertheless, assuming that the variations observed  
499 are consistent absorption bands (see Table 2): (1) the absorption band around 725 nm observed  
500 in  $P_{650}$  sample could be ascribed to C–H stretching 4<sup>th</sup> overtone in  $-\text{CH}_x$  ( $x = 1, 2$  and 3) and in  
501 Aromatic–CH and to O–H stretching 3<sup>rd</sup> overtone in  $R\text{--OH}$  and in Aromatic–OH; (2) the  
502 absorption band between 900 and 950 nm observed in all samples could be attributed to C–H  
503 stretching 3<sup>rd</sup> overtone and to O–H stretching 2<sup>nd</sup> overtone; (3) the absorption band between  
504 1100 and 1150 nm observed in  $P_H$  and  $P_{400}$  samples could correspond to C–H stretching 2<sup>nd</sup>  
505 overtone and to  $-\text{C}=\text{O}$  stretching 4<sup>th</sup> overtone; (4) the absorption band between 1950 and  
506 2000 nm observed in  $P_H$  and  $P_{400}$  samples could be in agreement with  $-\text{C}=\text{O}$  stretching 2<sup>nd</sup>  
507 overtone in  $R\text{--}(\text{C}=\text{O})\text{--}R'$ ,  $R\text{--}(\text{C}=\text{O})\text{--OR}'$  and in  $R\text{--}(\text{C}=\text{O})\text{--NH}_2$  and to N–H combination in  $R\text{--}$   
508  $(\text{C}=\text{O})\text{--NH}_2$  and in aromatic amines (Stenberg et al. 2010; Workman & Weyer 2008; Xiaobo

509 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]	Overtone and combination near-IR band assignment	Present in sample $P_x$
725	<ul style="list-style-type: none"> <li>• C–H stretching 4<sup>th</sup> overtone in <math>-\text{CH}_x</math> (<math>x = 1, 2</math> and <math>3</math>) and in Aromatic–CH</li> <li>• O–H stretching 3<sup>rd</sup> overtone in <math>R\text{--OH}</math> and in Aromatic–OH</li> </ul>	$P_{650}$
900-950	<ul style="list-style-type: none"> <li>• C–H stretching 3<sup>rd</sup> overtone in <math>-\text{CH}_x</math> (<math>x = 1, 2</math> and <math>3</math>) and in Aromatic–CH</li> <li>• O–H stretching 2<sup>nd</sup> overtone in <math>R\text{--OH}</math> and in Aromatic–OH</li> </ul>	$P_H, P_{400}, P_{650}$
1100-1150	<ul style="list-style-type: none"> <li>• C–H stretching 2<sup>nd</sup> overtone in <math>-\text{CH}_x</math> (<math>x = 1, 2</math> and <math>3</math>) and in Aromatic–CH</li> <li>• <math>-\text{C}=\text{O}</math> stretching 4<sup>th</sup> overtone in <math>R\text{--}(\text{C}=\text{O})\text{--}R'</math>, <math>R\text{--}(\text{C}=\text{O})\text{--OR}'</math> and in <math>R\text{--}(\text{C}=\text{O})\text{--NH}_2</math></li> </ul>	$P_H, P_{400}$
1950-2000	<ul style="list-style-type: none"> <li>• <math>-\text{C}=\text{O}</math> stretching 2<sup>nd</sup> overtone in <math>R\text{--}(\text{C}=\text{O})\text{--}R'</math>, <math>R\text{--}(\text{C}=\text{O})\text{--OR}'</math> and in <math>R\text{--}(\text{C}=\text{O})\text{--NH}_2</math></li> <li>• N–H combination in <math>R\text{--}(\text{C}=\text{O})\text{--NH}_2</math> and in aromatic amines</li> </ul>	$P_H, P_{400}$

514

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  
 517 below 500-600 nm, in the blue-green spectral range, agrees with a brownish colour for Pluto  
 518 tholins. This absorption is likely due to the presence of N- and O-bearing organic molecules  
 519 with lone pair, such as  $-\text{NH}$ ,  $-\text{NH}_2$ ,  $-\text{NHR}$ ,  $R\text{--N--}R'$ ,  $-\text{NO}_2$ ,  $-\text{OH}$ ,  $-\text{COOH}$ ,  $-\text{C}=\text{O}$ ,  $R\text{--O--}R'$   
 520 functional groups (Desyaterik et al. 2013; Imanaka et al. 2004; Liu et al. 2015; Mahjoub et al.  
 521 2012; Moise et al. 2015; Rao 1975). Due to the delocalization of  $\pi$  electrons, fused aromatic  
 522 rings, N- and O-containing polycyclic aromatic compounds and unsaturated molecules with  
 523 extensive conjugated multiple bonds also participate to the strong absorption of UV and visible

524 wavelengths (D'Amico et al. 1980; Desyaterik et al. 2013; Imanaka et al. 2004; Lambe et al.  
525 2013; Liu et al. 2015; Moise et al. 2015; Rao 1975; Tran et al. 2003; Zhong et al. 2012). Most  
526 of these chemical functions were actually detected in Pluto aerosol analogues by Jovanović et  
527 al. (2020), who showed the presence of unsaturated N- and O-bearing molecules in large  
528 amount.

529 When CH<sub>4</sub> concentration increases, the bandgap energy shifts towards shorter wavelengths.  
530 *k* index thus depends on the CH<sub>4</sub>:N<sub>2</sub> mixing ratio used to produce the tholins. Indeed, from 270  
531 to around 600 nm, where the uncertainties are low, we can see that P<sub>H</sub> and P<sub>400</sub> samples,  
532 produced with a lower CH<sub>4</sub> concentration, present higher *k*-values than P<sub>650</sub> sample, produced  
533 with a higher CH<sub>4</sub> concentration.

534 This anti-correlation between *k*-values and CH<sub>4</sub>:N<sub>2</sub> mixing ratio was also detected by Mahjoub  
535 et al. (2012) in their study concerning Titan tholins. They attributed this anti-correlation to the  
536 proportion of N-bearing molecules: when CH<sub>4</sub> concentration decreases, N-containing  
537 molecules increase in proportion and contribute to a higher absorption of UV and visible  
538 radiations (Mahjoub et al. 2012, 2014). This conclusion was also proposed by Imanaka et al.  
539 (2004), when comparing their Titan tholins with Uranus/Neptune tholins from Khare et al.  
540 (1987) study, produced in CH<sub>4</sub>:H<sub>2</sub> gas mixtures. They hypothesized that N-incorporation in  
541 Titan tholins could increase *k*-values in the UV-Vis spectral range, in agreement with the  
542 laboratory experiments realized by Scattergood and Owen (1977). Indeed, nitrogen promotes  
543 unsaturation. When N<sub>2</sub> content is increased in the reactive gas mixture forming Pluto tholins  
544 (case of P<sub>H</sub> and P<sub>400</sub> samples), the formation of sp<sup>2</sup> bonds is favoured. In contrast, when the  
545 reactive gas mixture contains more CH<sub>4</sub> (case of P<sub>650</sub> sample), the presence of large amounts of  
546 hydrogen promotes the formation of sp<sup>3</sup> bonds, which have no effect on π-π\* electronic  
547 transitions in UV and visible wavelength ranges (Ferrari et al. 2003; Quirico et al. 2008).

548 Another explanation to both higher *n*- and *k*-values for P<sub>H</sub> and P<sub>400</sub> could be the higher oxidation  
549 of these samples. Indeed, Jovanović et al. (2020) showed that P<sub>400</sub> sample contains more oxygen  
550 in mass than P<sub>650</sub>. Studies realized on optical properties of terrestrial secondary organic aerosols  
551 (Cappa et al. 2011; Lambe et al. 2013; Moise et al. 2015; Nakayama et al. 2018, 2012) and of  
552 oxidized Early Earth- and Exoplanets-like aerosols (Gavilan et al. 2017) showed that *n* indices  
553 increase when the oxidation level of the aerosols increases. Moreover, the more the aerosols  
554 are oxidized, the more they absorb UV and visible radiations.



555 We can thus expect that aerosols formed at different altitudes in Pluto's atmosphere will  
556 differently absorb radiations reaching the atmosphere. In particular, Pluto's aerosols formed at  
557 or below 400 km of altitude above the surface, due to their higher N- and O-content, may absorb  
558 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  
560 analogues of aerosols produced during different seasons or epochs of Pluto (Bertrand et al.  
561 2019; Bertrand & Forget 2016; Stern et al. 2017a). In Bertrand and Forget (2016), their Pluto  
562 General Circulation Model (GCM) predicted a mean CH<sub>4</sub> atmospheric mixing ratio in ~2200  
563 (terrestrial year; northern winter/southern summer on Pluto) ~5 times higher than that observed  
564 in 2015. This is due to the condensation of N<sub>2</sub> onto the surface, which also leads to a decrease  
565 in surface pressure as low as 10<sup>-5</sup>-10<sup>-6</sup> mbar; the atmosphere being thinner, the methane is less  
566 diluted (Bertrand & Forget 2016; Stern et al. 2017a). However, considering that the pressure in  
567 the atmosphere would still be sufficient to allow the formation of haze particles (Johnson et al.  
568 2021), one would expect less absorbent aerosols, such as P<sub>650</sub> tholins, differently affecting the  
569 thermal profile of Pluto and the photon flux reaching the surface.

## 570 **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.

### 574 **1. Comparison of our optical constants with those of Titan tholins from the study by** 575 **Khare et al. (1984)**

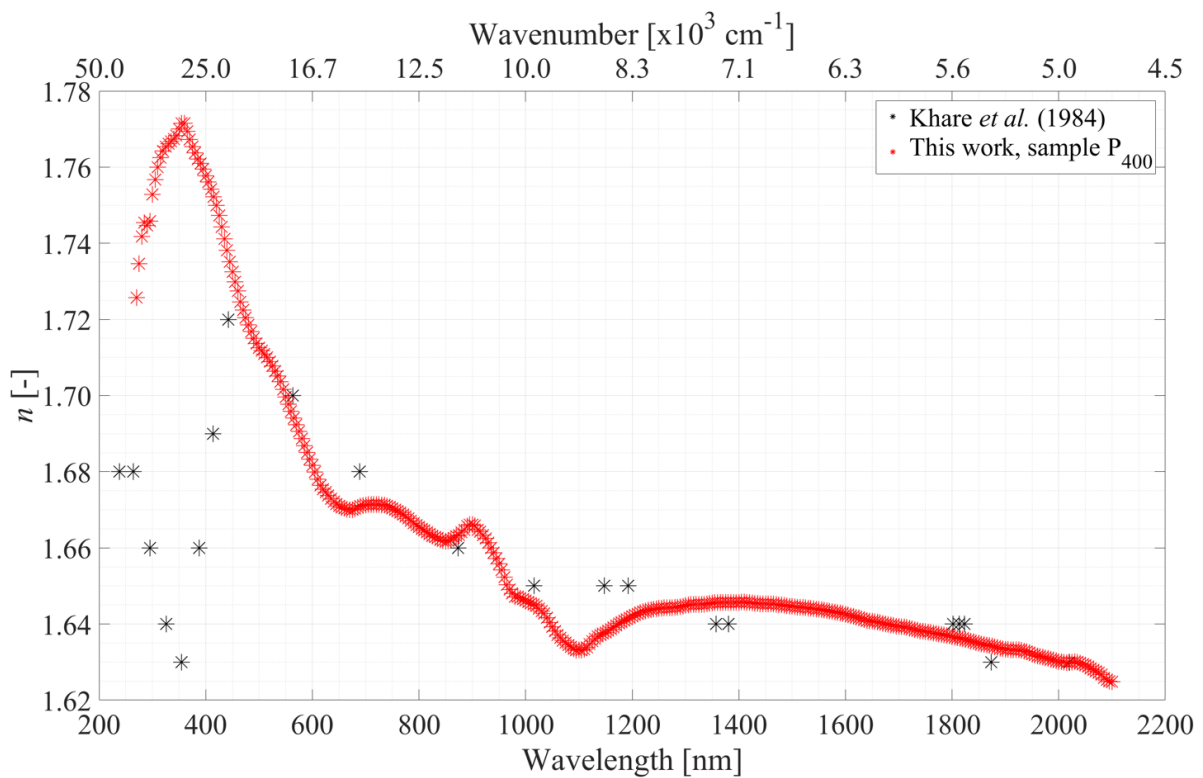
576 Khare et al. (1984) did a pioneer work to determine the optical constants  $n$  and  $k$  of Titan aerosol  
577 analogues from soft X-ray to microwave frequencies. For this purpose, they combined  
578 transmittance, specular reflectance, interferometric, Brewster angle and ellipsometric  
579 polarization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

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



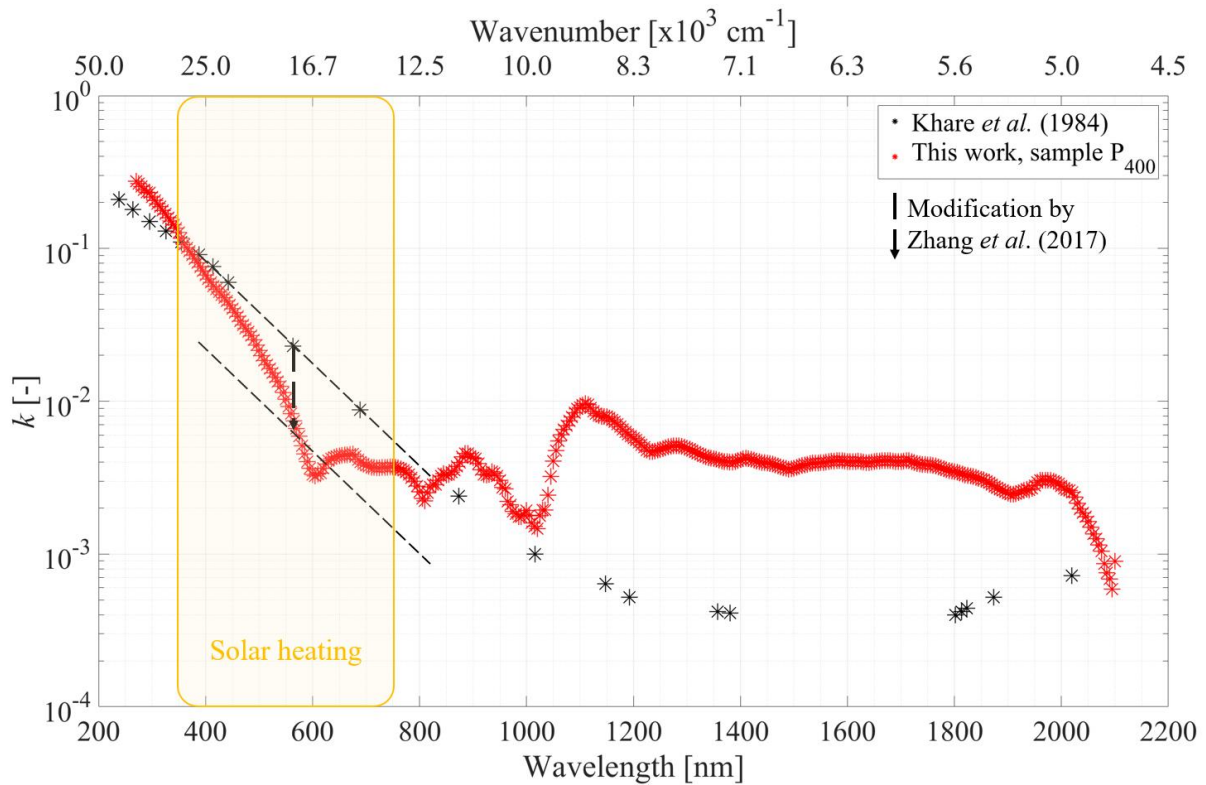
586 O'Brien et al. 2012; Tran et al. 2003; Vuitton et al. 2009), optical constants from Khare et al.  
 587 (1984) are still widely used by the modelling teams to explain atmospheric and surface  
 588 properties of Titan, often by introducing *ad hoc* modifications to them to fit the observations  
 589 better (Brossier et al. 2018; Fan et al. 2019; Griffith et al. 2012; Lavvas et al. 2009; Liang et al.  
 590 2007; Lopes et al. 2016; Seignovert et al. 2017), but also of Pluto (Cheng et al. 2017; Grundy  
 591 et al. 2018; Protopapa et al. 2017, 2020; Young et al. 2018; Zhang et al. 2017). This is partially  
 592 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<sub>400</sub> (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 N<sub>2</sub> and 10% of CH<sub>4</sub>.



599

600 Figure 6: Comparison between the real part  $n$  of the complex refractive index of our Pluto tholins P<sub>400</sub>  
 601 (red asterisks) and Titan tholins from Khare et al. (1984) study (black asterisks).



602

603 Figure 7: Comparison between the imaginary part  $k$  the complex refractive index of our Pluto tholins  
 604  $P_{400}$  (red asterisks) and Titan tholins from Khare et al. (1984) study (black asterisks). The black dashed  
 605 arrow indicates the modification implemented by Zhang et al. (2017) to the  $k$ -values from Khare et al.  
 606 (1984) in the region where solar heating dominates (represented by the yellow rectangle) in order to  
 607 adjust Pluto's thermal balance.

608 In Figure 6, we observe that the  $n$  index of Pluto tholins  $P_{400}$  is similar to that of Khare et al.  
 609 (1984) Titan tholins from 450 to 2100 nm. Below 450 nm, the behaviour is reversed. While  $n$ -  
 610 value reaches a maximum near 330 nm for  $P_{400}$ , Khare et al. (1984) data present a minimum  $n$ -  
 611 value near 350 nm. We do not have a definitive explanation for this behaviour of Khare et al.  
 612 (1984)  $n$  index, but it could be due to a low sampling combined with interpolation, a poor  
 613 definition of the optical properties of the substrates used for the synthesis of the tholins thin  
 614 films, or the light source used for the measurements being at the limit of its range.

615 Concerning the  $k$  indices (Figure 7), the bandgap energy of Khare et al. (1984) tholins is shifted  
 616 towards longer wavelengths (around 1200 nm) compared to  $P_{400}$  sample (around 590 nm).  $k$ -  
 617 values of  $P_{400}$  are higher than those of Khare et al. (1984) below 380 nm and in the near-IR  
 618 ( $> 900$  nm). These higher values can be explained by higher N- and O-content of Pluto aerosol  
 619 analogues  $P_{400}$  (Cappa et al. 2011; Gavilan et al. 2017; Imanaka et al. 2004; Jovanović et al.  
 620 2020; Lambe et al. 2013; Mahjoub et al. 2012; Nakayama et al. 2018, 2012; Quirico et al. 2008).

621 From 380 to around 800 nm,  $k$ -values of P<sub>400</sub> are lower than those of Khare et al. (1984), due  
622 to the shifted bandgap energy which is caused by higher  $k$ -values in the UV and a steeper slope  
623 in the UV-Vis for our P<sub>400</sub> sample.

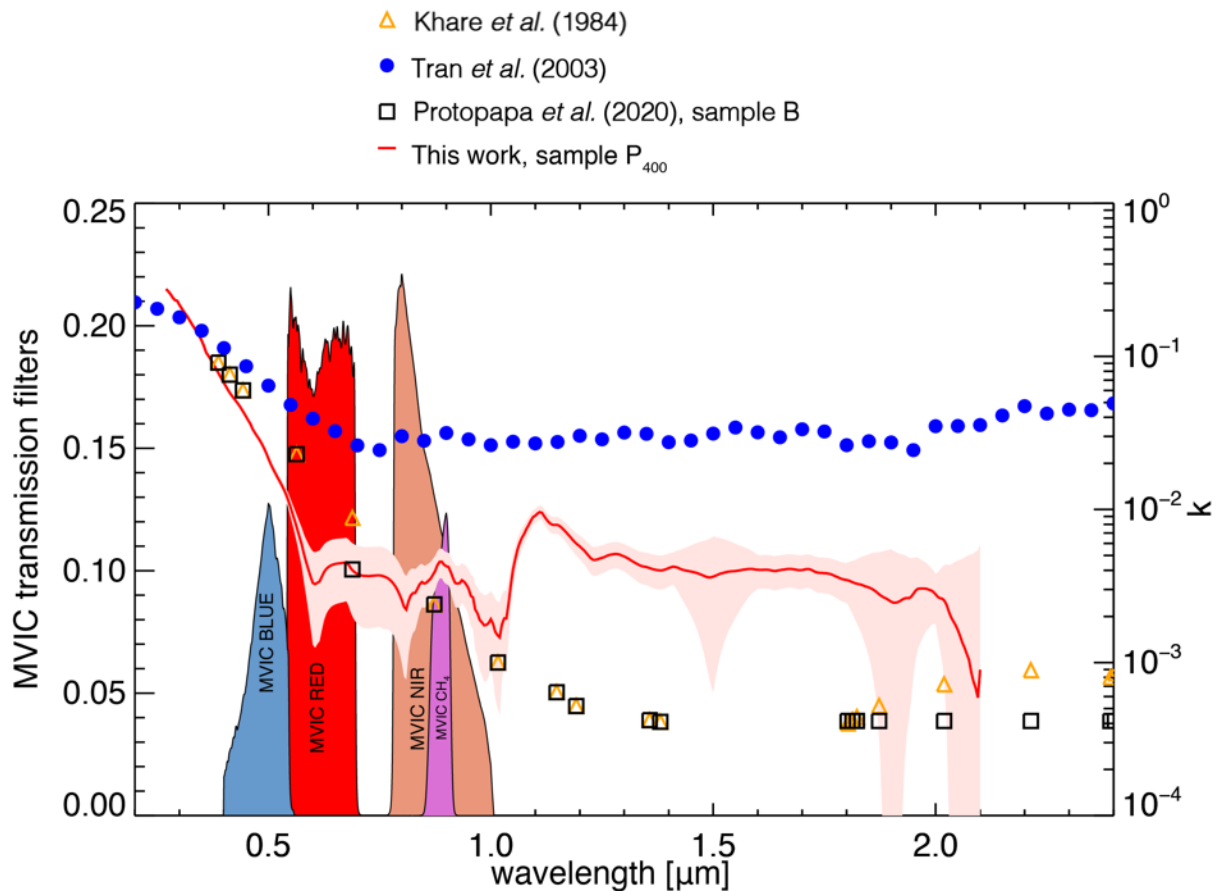
624 Even though  $k$ -values of P<sub>400</sub> sample are one order of magnitude higher than those of Khare et  
625 al. (1984) between 1000 and 2000 nm, they are constant and do not present the anomalous sharp  
626 increase beyond 1800 nm presented by the Khare et al. (1984)  $k$ -values. The fact that our  $k$ -  
627 values are one order of magnitude higher in the near-IR is consistent with published literature  
628 on Titan's aerosols. For example, Lavvas et al. (2010) and Larson et al. (2015) reported that the  
629 actual optical properties of Titan's aerosols should be about an order of magnitude larger in the  
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  
633 support the conclusion developed by Grundy et al. (2018), Pluto's photochemical aerosols were  
634 considered as potential surface colouring agent. Thus, in their model, they implemented the  
635  $k$  indices determined for Titan tholins by Khare et al. (1984) and Tran et al. (2003).  
636 Nevertheless, in order to fit their models to spectra acquired in the regions of Cthulhu Macula  
637 and Lowell Regio by the imagers MVIC (Multispectral Visible Imaging Camera, a Vis-near-IR  
638 [400-975 nm] imager) and LEISA (Linear Etalon Imaging Spectral Array, an IR [1.25-2.5  $\mu$ m]  
639 spectral imager) constituting the Ralph instrument (Reuter et al. 2008), some modifications of  
640  $k$  indices by Khare et al. (1984) were necessary. Specifically, Protopapa et al. (2020): first  
641 applied no change to the  $n$  index of Khare et al. (1984); secondly decreased the  $k$ -value of Khare  
642 et al. (1984) at 690 nm by  $\sim$ 55% to match the observations of Pluto in the *RED* filter between  
643 540 and 700 nm (note that Protopapa et al. (2020) preserved the original sampling of Khare et  
644 al. (1984) explaining why the  $k$ -value was modified at 690 nm); and thirdly assumed  $k$  index to  
645 be constant between 1800 and 2200 nm, given that the increase displayed by the  $k$ -values of  
646 Khare et al. (1984) beyond 1.8  $\mu$ m was not consistent with the observations.

647 Figure 8 was adapted from Protopapa et al. (2020). It displays the imaginary part  $k$  of the  
648 complex refractive index (right  $y$ -axis) of our P<sub>400</sub> sample (red curve, with an envelope of  
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

653 Regio are shown, as well as the MVIC transmission filters (left y-axis). The reader is referred  
 654 to Protopapa et al. (2020) for details about the modelling of MVIC and LEISA spectra.



655  
 656 Figure 8: Figure adapted from Protopapa et al. (2020). Imaginary part  $k$  of the complex refractive index  
 657 (right y-axis) is represented as a function of wavelength. The red curve with the salmon-pink envelope  
 658 corresponds to the  $k$  index of our sample  $P_{400}$ . The orange triangles correspond to the  $k$  index determined  
 659 by Khare et al. (1984), while the blue dots are from the study by Tran et al. (2003). The black squares  
 660 are the  $k$ -values determined by Protopapa et al. (2020) that best fit the MVIC and LEISA data. The  
 661 MVIC transmission filters (left y-axis) are shown for reference. The reader is referred to Protopapa et  
 662 al. (2020) for details about the modelling.

663 Protopapa et al. (2020) recognized that the  $k$ -values of Titan tholins by Khare et al. (1984)  
 664 present a sharp increase beyond  $1.8 \mu\text{m}$  (Figure 8, orange triangles), inconsistent with the Pluto  
 665 *New Horizons* data. Therefore, Protopapa et al. (2020) modified the  $k$ -values by Khare et al.  
 666 (1984) beyond  $1.8 \mu\text{m}$  assuming them to be constant with wavelengths up to  $2.4 \mu\text{m}$  and equal  
 667 to the mean value computed between  $1.35$  and  $1.45 \mu\text{m}$  (see Figure 8, sample B from Protopapa  
 668 et al. (2020)). This is consistent with our direct values for Pluto tholins  $P_{400}$ . Indeed, as noted  
 669 above, while the  $k$ -values of  $P_{400}$  sample are one order of magnitude higher than those of Khare

670 et al. (1984) between 1000 and 2000 nm, they are constant with wavelengths and do not display  
671 the sharp increase beyond 1.8  $\mu\text{m}$  presented by the Khare et al. (1984)  $k$ -values.

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

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

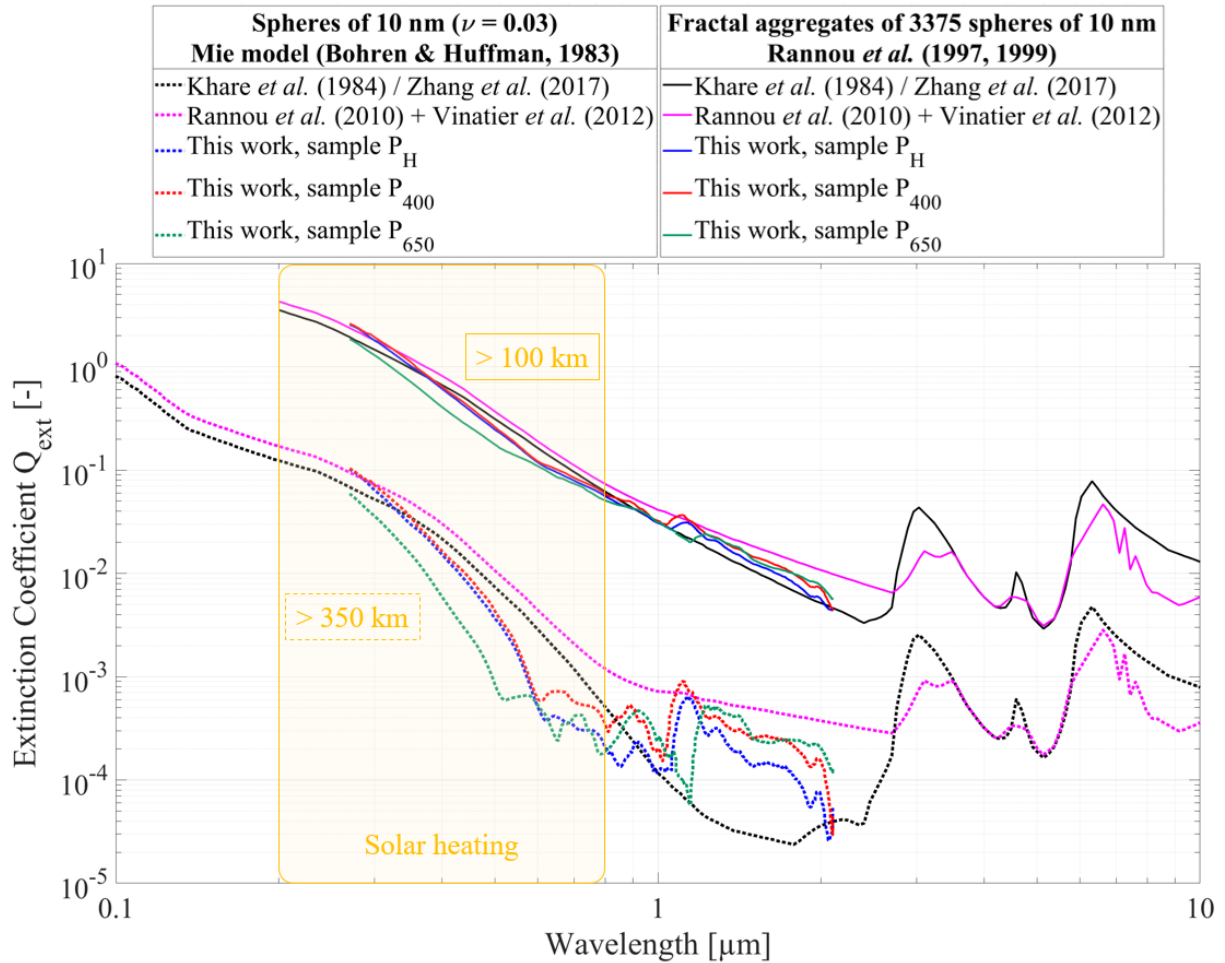
### 685 **3. Application of our optical constants to Pluto's atmosphere modelling**

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

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

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

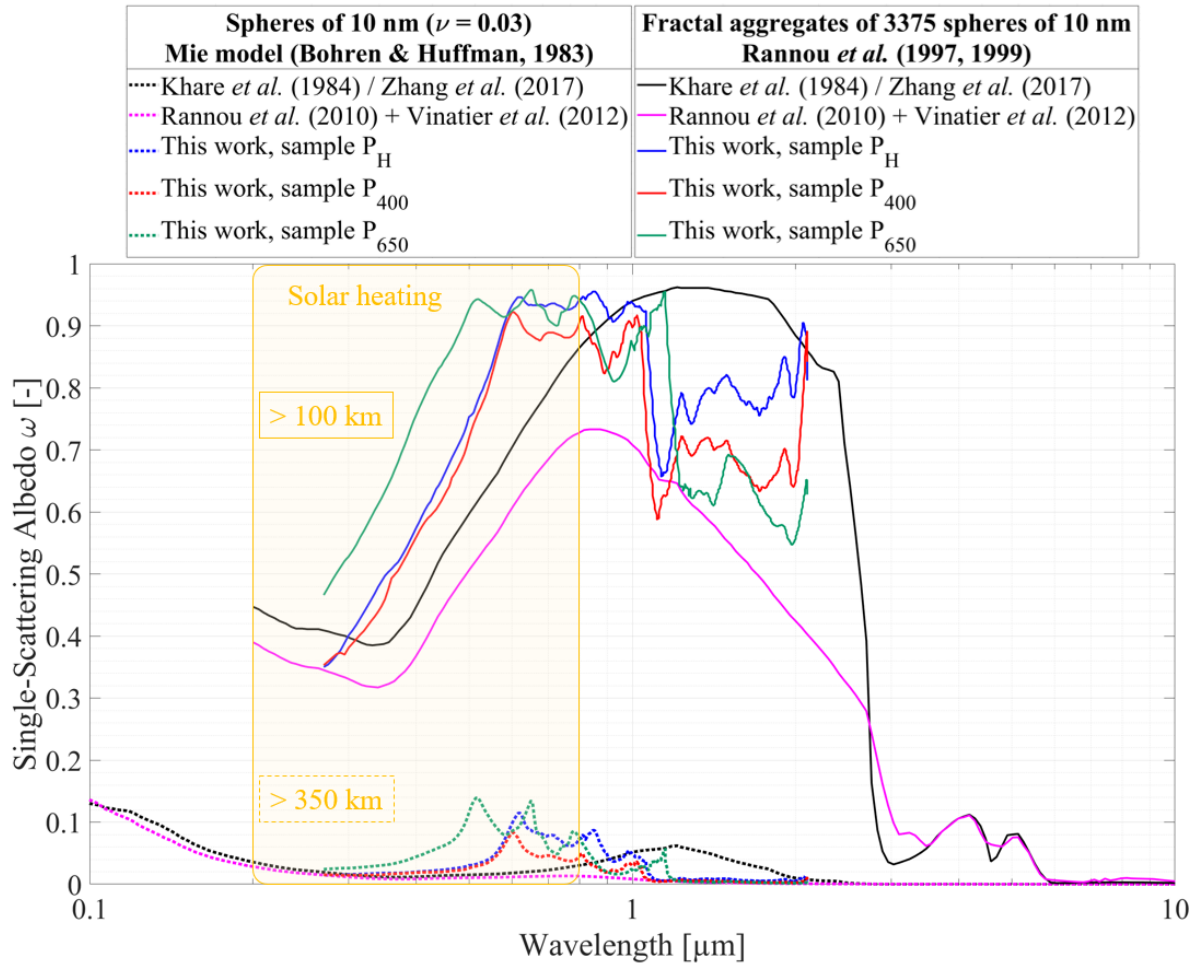
723 In Figures 9 and 10, we compare, for several sets of optical constants, the parameters  $Q_{\text{ext}}$  and  
724  $\omega$  computed for spherical monomers of 10 nm radius, distributed with a log-normal distribution  
725 and an effective variance  $v$  of 0.03 (dotted lines), and for fractal aggregates of 3375 monomers  
726 of 10 nm radius (plain lines). We used the optical constants determined in this work ( $P_H$ ,  $P_{400}$   
727 and  $P_{650}$ , in blue, red and green respectively), optical constants determined for Titan tholins by  
728 Khare et al. (1984) (in black) and for Titan’s aerosols from observations by Rannou et al. (2010)  
729 and Vinatier et al. (2012) (in pink).



730

731 Figure 9: Extinction coefficients  $Q_{\text{ext}}$  determined for spherical monomers of 10 nm radius (log-normal  
732 distribution, with effective variance  $\nu = 0.03$ ) with a Mie model formalized in Bohren & Huffman (1983)  
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  
735 determined by Khare *et al.* (1984) for Titan tholins. Note that these Khare *et al.* (1984) optical constants  
736 were adopted in Zhang *et al.* (2017) study. The pink curves were generated with the optical constants  
737 determined by Rannou *et al.* (2010) and Vinatier *et al.* (2012) for Titan's aerosols. The blue, red and  
738 green curves were generated with the optical constants determined respectively for our samples P<sub>H</sub>, P<sub>400</sub>  
739 and P<sub>650</sub>. The yellow rectangle indicates the region where solar heating dominates. The dotted curves  
740 (spherical monomers) give information on the radiative transfer in the upper layers of Pluto's  
741 atmosphere (> 350 km of altitude), while the plain curves (fractal aggregates) give information on the  
742 radiative transfer in Pluto's lower atmosphere (between 100 and 300 km of altitude).





743

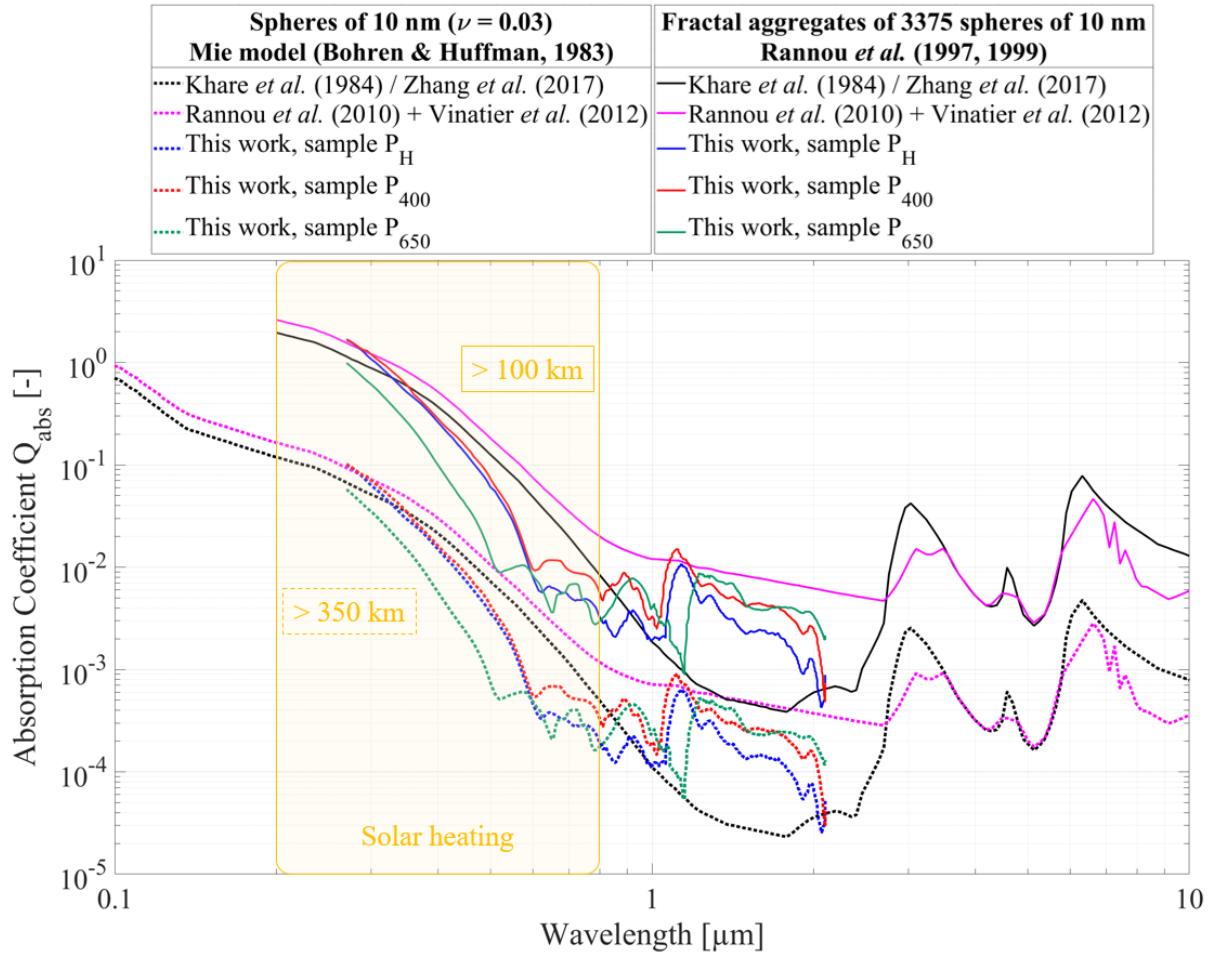
744 Figure 10: Same as Figure 9, but showing the single-scattering albedo  $\omega$ .

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

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

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





757

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

759 The absorption coefficients  $Q_{\text{abs}}$  (Figure 11) computed with Pluto tholins optical constants are  
 760 about equal to those computed with Titan optical constants at 0.3  $\mu\text{m}$ . Nevertheless, they drop  
 761 much faster with wavelengths and are lower by a factor 3 to 10 at wavelengths larger than ~0.4-  
 762 0.5  $\mu\text{m}$ . This is true for small spherical particles and fractal aggregates.

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

768 This has an important consequence: using other optical constants than those already used to  
 769 analyse scattering photometry at Pluto's limb (Cheng *et al.* 2017; Gao *et al.* 2017; Gladstone *et al.*  
 770 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

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

775 To adjust Pluto's thermal balance, Zhang et al. (2017) used the optical constants from Khare et  
776 al. (1984), and had to decrease significantly (up to a factor 4) the absorption efficiency of  
777 aerosols in the visible wavelength range (see Figure 7, black dashed arrow), to increase it in  
778 thermal IR and grossly keep the same extinction properties to match Alice UV spectrometer  
779 retrieval for the haze extinction (Stern et al. 2015). Here we see that low absorption is a natural  
780 outcome of Pluto tholins produced for this study with chemical conditions representative of  
781 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  $\text{N}_2:\text{CH}_4:\text{CO}$  proportions, in order to  
785 mimic aerosols formed at different altitudes in Pluto's current atmosphere. The sample  $\text{P}_\text{H}$  is  
786 expected to be representative of aerosols formed below 350 km of altitude above the surface.  
787 The sample  $\text{P}_{400}$  is expected to mimic the aerosols formed at around 400 km of altitude. The  
788 sample  $\text{P}_{650}$  is expected to be analogous of aerosols formed between 600 and 700 km of altitude.  
789 These three gas mixtures differing in their  $\text{CH}_4:\text{N}_2$  mixing ratio can also be considered as  
790 analogues of Pluto's atmosphere at different seasons or epochs.

791 Our results show:

- 792 (1) A strong absorption of UV and visible radiations by Pluto tholins, attributed to their N-  
793 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  $10^{-3}$ .
- 796 (3) A dependency of  $n$  and  $k$  indices to the  $\text{CH}_4:\text{N}_2$  mixing ratio, and thus to the altitude of  
797 aerosol formation in Pluto's atmosphere. The N- and O-content in Pluto low-altitude  
798 aerosols is enhanced, leading to an increase of both  $n$ - and  $k$ -values. This dependency  
799 of the optical constants to the  $\text{CH}_4:\text{N}_2$  mixing ratio has also implications for the seasonal  
800 and past epochal radiative transfer of Pluto.

801 The comparison of our data with the optical constants determined for Titan tholins by Khare et  
802 al. (1984) shows that Pluto tholins present globally similar  $n$ -values to those of Titan. However,

803 differences are observed concerning the  $k$  indices. In particular,  $k$ -values of Pluto tholins are  
804 one order of magnitude higher than those of Titan in the near-IR. In the UV spectral range,  
805  $k$  indices of Pluto tholins are also higher, which is probably due to the reactivity of nitrogen and  
806 carbon monoxide in the gas mixture producing Pluto's aerosols.

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

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

817 Our study focused on Pluto's aerosols formed by photochemistry. However, we remind that an  
818 additional process for the formation of aerosols in Pluto's atmosphere was recently proposed  
819 by Lavvas et al. (2020) due to ice condensation on photochemical nuclei. In their hypothesis,  
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  $C_3H_4$ ,  $C_6H_6$  and predominantly  $C_4H_2$ ,  
822 would condense and coat the HCN ice particles formerly formed. Note that, as Pluto's most  
823 abundant gaseous photochemical products –  $C_2H_2$ ,  $C_2H_4$ , and  $C_2H_6$  – condense only a few  
824 kilometres above the surface (Stern et al. 2017b), they should not take part in the homogeneous  
825 coating of HCN particles occurring at higher altitudes. Nevertheless, those  $C_2$  hydrocarbons, as  
826 well as  $CH_3C_2H$ , are suspected to be subject to heterogeneous adsorption/desorption processes  
827 on the ice particles, between 100 and 200 km of altitude above the surface (Krasnopolsky 2020;  
828 Luspay-Kuti et al. 2017; Wong et al. 2017), inhibiting the sublimation of the condensed ices.

829 Such condensation of gaseous molecules, resulting in coated photochemical aerosols  
830 (Krasnopolsky 2020; Luspay-Kuti et al. 2017; Wong et al. 2017), would occur on preexisting  
831 Pluto's aerosols formed by photochemistry, requiring to know their properties as well, as  
832 studied in the present work. The differences observed between our data and the *New Horizons*  
833 observations could be explained by this contribution of coated aerosols. By analogy with the  
834  $C_4H_2$  ice studied in Lavvas et al. (2020) presenting lower  $n$ - and  $k$ -values than those determined

835 for our Pluto tholins in the common wavelength range [270-1000 nm], we can suppose that if  
836 gaseous molecules condense or adsorb on Pluto's photochemical aerosols, their optical  
837 constants  $n$  and  $k$  could be slightly lowered.

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

840

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854

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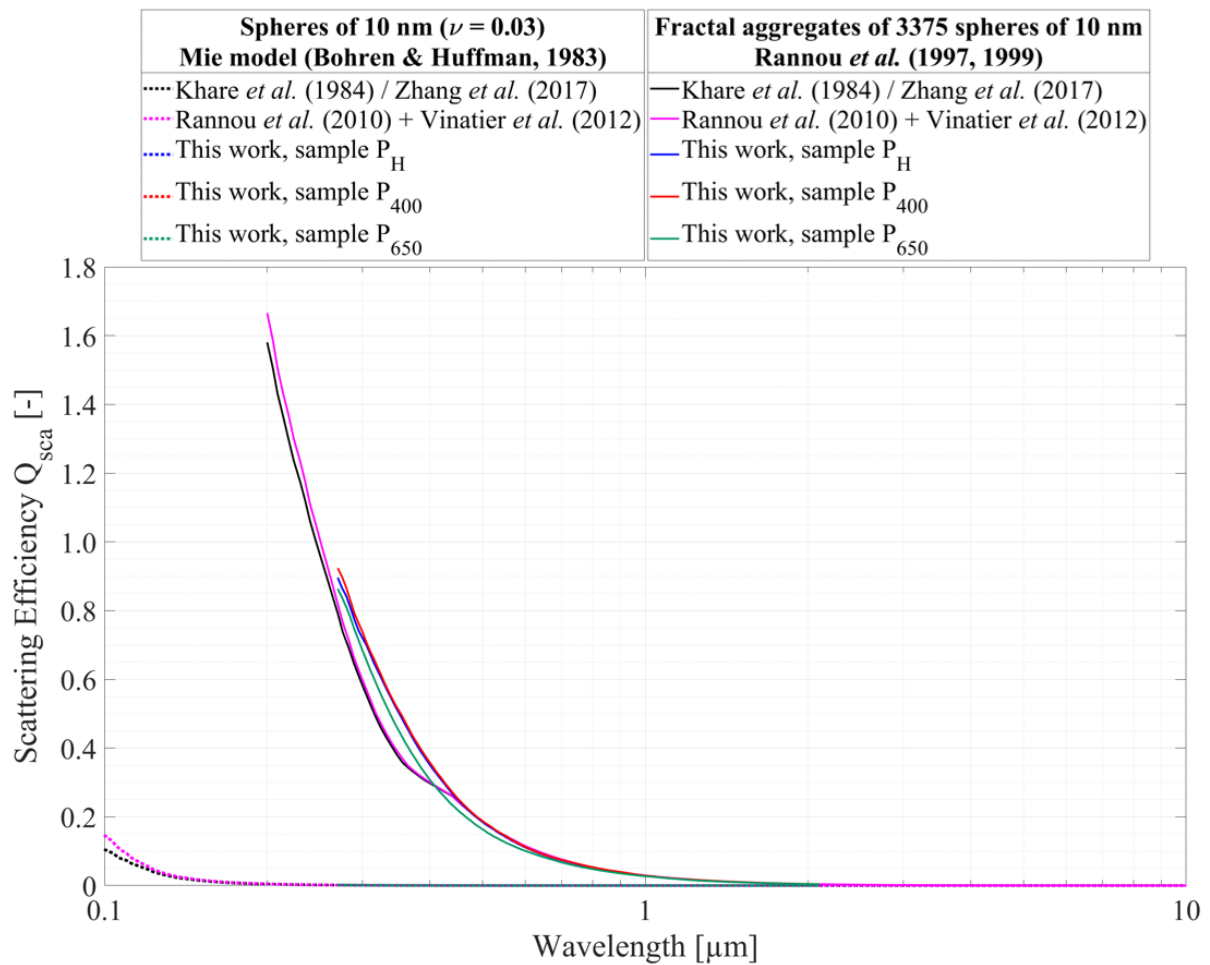
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1040 **Supplementary Information**

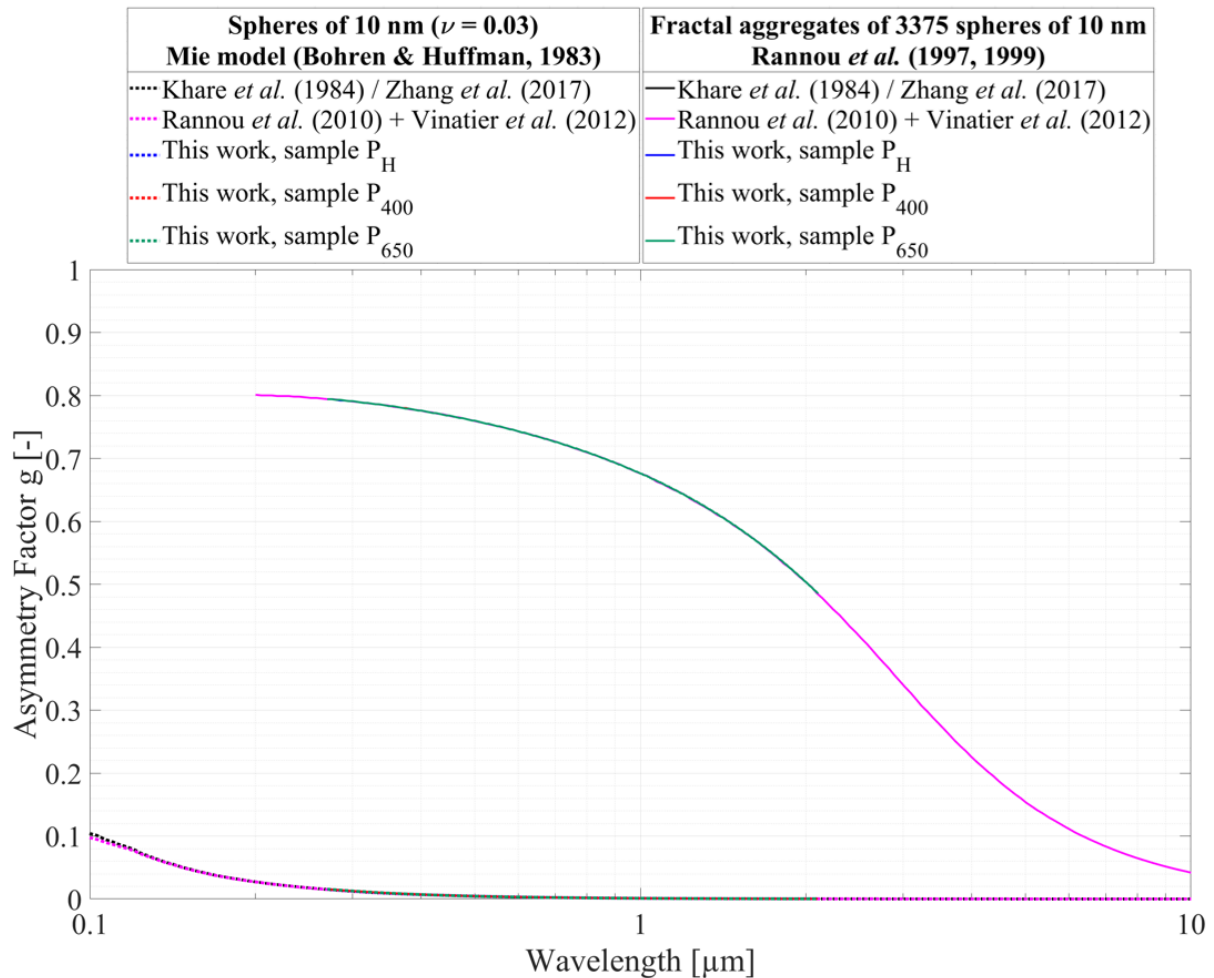
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1043 Figure A: Scattering efficiency  $Q_{sca}$  determined for spherical monomers of 10 nm radius (log-  
 1044 normal distribution, with effective variance  $\nu = 0.03$ ) with a Mie model formalized in Bohren

1045 & Huffman (1983) (dotted curves) and for fractal aggregates of 3375 monomers of 10 nm radius  
 1046 with the model developed by Rannou et al. (1997, 1999) (plain curves). The black curves were  
 1047 generated with the optical constants determined by Khare et al. (1984) for Titan tholins. Note  
 1048 that these Khare et al. (1984) optical constants were adopted in Zhang et al. (2017) study. The  
 1049 pink curves were generated with the optical constants determined by Rannou et al. (2010) and  
 1050 Vinatier et al. (2012) for Titan's aerosols. The blue, red and green curves were generated with  
 1051 the optical constants determined respectively for our samples P<sub>H</sub>, P<sub>400</sub> and P<sub>650</sub>.



1052  
 1053 Figure B: Asymmetry factor  $g$  determined for spherical monomers of 10 nm radius (log-normal  
 1054 distribution, with effective variance  $\nu = 0.03$ ) with a Mie model formalized in Bohren &  
 1055 Huffman (1983) (dotted curves) and for fractal aggregates of 3375 monomers of 10 nm radius  
 1056 with the model developed by Rannou et al. (1997, 1999) (plain curves). The black curves were  
 1057 generated with the optical constants determined by Khare et al. (1984) for Titan tholins. Note  
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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<sub>H</sub>, P<sub>400</sub> and P<sub>650</sub>.