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► **To cite this version:**

P. Lavvas, E. Lellouch, D. Strobel, M. Gurwell, A. Cheng, et al.. A major ice component in Pluto's haze. *Nature Astronomy*, 2020, 5 (3), pp.289-297. 10.1038/s41550-020-01270-3 . hal-03418956

HAL Id: hal-03418956

<https://hal.science/hal-03418956v1>

Submitted on 8 Nov 2021

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A major ice component in Pluto's haze

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Pluto, Titan, and Triton, are all low-temperature environments with a N₂/CH₄/CO atmospheric composition on which solar radiation drives an intense organic photochemistry. Titan is rich in atmospheric hazes and *Cassini-Huygens* observations showed their formation initiates with the production of large molecules through ion-neutral reactions. *New Horizons* revealed that optical hazes are also ubiquitous in Pluto's atmosphere and it is thought that similar haze formation pathways are active in this atmosphere as well. However, we show here that Pluto's hazes may contain a major organic ice component (dominated by C₄H₂ ice) from the direct condensation of the primary photochemical products in this atmosphere. This contribution may imply that haze has a less important role in controlling Pluto's atmospheric thermal balance compared to Titan. Moreover, we expect that the haze composition of Triton is dominated by C₂H₄ ice.

Pluto's atmosphere is the equivalent of Titan's upper atmosphere above 400 km altitude, with comparable CH₄, CO, and N₂ density profiles and pressure scale heights¹. Photochemistry models for these environments demonstrate that the anticipated chemical products are similar^{2,3}, therefore Pluto's hazes are thought to be of a similar nature based on molecular growth⁴ (see [Methods for haze nomenclature](#)). The fraction of the mass flux generated from the photolysis of Titan's main atmospheric composition that ends in haze particles is ~30%^{5,6}. Such a yield for Pluto's haze would suggest a mass flux of ~6x10⁻¹⁵ gcm⁻²s⁻¹ (all reported mass fluxes are referred to Pluto's surface). However, the opacity of particles characterizing such a mass flux falls short of the available observations and a twice-higher haze formation efficiency is required to generate enough material to reproduce the UV extinction observations below 200 km⁷. As Pluto's upper atmosphere is much colder than Titan's (~70K compared to ~150K for Titan, see [Fig. 1](#)), an increased haze yield for Pluto is surprising. On the other hand, the photochemical gases produced on Pluto may condense at lower pressures than on Titan ([Fig. 1](#)). Therefore organic ices could be responsible for, or at least contribute to, the formation of the observed hazes in Pluto's atmosphere.

We explore the extent of this contribution using coupled models of atmospheric photochemistry and microphysics, and following the evolution of the organic ice haze particles from their formation in the upper atmosphere to their sedimentation on Pluto's surface. The models are adapted from previous studies of photochemistry and microphysics in Titan's atmosphere, taking into account high-resolution energy

49 deposition, complex chemical networks, atmospheric mixing and molecular diffusion,
50 particle sedimentation, and Brownian coagulation (see Methods).

51
52 We find that the first photochemical ice that condenses in Pluto's upper atmosphere is
53 HCN. However, although nucleation and subsequent condensation are energetically
54 possible, the kinetics of these processes are slow and translate into an insignificant loss
55 for gaseous HCN above ~ 500 km (**Fig. 2**). This result agrees with the *ALMA* observations
56 of the J=4-3 line that reveal a high degree of HCN super-saturation in Pluto's upper
57 atmosphere, near 700 km altitude⁸. We consider homogeneous nucleation, as well as
58 nucleation in the presence of ions, with the latter being significantly more efficient than
59 the former (see Methods). Our calculations show that at 70 K, for $S=10^8$ (the degree of
60 HCN super-saturation⁸ near 700 km) the homogeneous nucleation rate is $\sim 10^{-8}$ cm⁻³s⁻¹,
61 that is too small for any significant condensation. For an ion density of $\sim 10^3$ cm⁻³, which
62 is the peak density our calculations produce we calculate a corresponding ion nucleation
63 rate that is more than three orders of magnitude larger than the homogeneous
64 nucleation rate at the same conditions. Moreover, for smaller S values the ion nucleation
65 rate drops significantly slower than the neutral nucleation rate (**Extended Data Fig. 1**).
66 Heterogeneous nucleation^{9,10}, is also a possibility if nucleation sites are present in the
67 upper atmosphere. However, our simulated HCN profile provides a sufficiently good fit
68 to the observed HCN line-core without it, indicating that such heterogeneous loss is
69 relatively unimportant in Pluto's upper atmosphere.

70
71 As the HCN-ice particles settle, other gases condense and coat them. Thus, gas
72 abundances decrease and the condensate particle radius increases (**Extended Data Fig.**
73 **2**). We find that a significant mass flux of the photochemical products is directly
74 transferred to the condensed phase (7.5×10^{-15} g cm⁻² s⁻¹), forming organic-ice hazes (**Fig.**
75 **3a**). Major contributions to particle growth come from C₃H₄, C₄H₂, C₆H₆ with mass-
76 fractions varying with altitude, reflecting their individual photochemical abundances
77 and saturation limits (**Fig. 3b**). In contrast, the same species in Titan's atmosphere
78 participate in the formation of more complex gaseous compounds⁴, whose further
79 chemical growth leads to the formation of Titan-type hazes¹¹. We infer that this
80 difference in behavior is caused by the temperature difference between Titan and Pluto.
81 Note that condensates are also forming in Titan's atmosphere, but only in the lower
82 stratosphere/troposphere¹².

83
84 As the atmospheric density increases with decreasing altitude and particle settling
85 velocities drop, the organic-ice hazes accumulate in the lower atmosphere. We find that
86 below ~ 400 km collisions among particles become important, leading to a transition
87 from spherical growth, due to gas deposition, to aggregate growth, due to collisions
88 among the formed particles (**Fig. 4**). At the transition region, our simulated average
89 particle radius is ~ 9 nm, similar to the 10 nm radius derived from *New Horizons*
90 observations^{1,13} for the primary particles composing the haze aggregates near the
91 surface.

92
93 Pluto's most abundant gaseous photochemical products¹⁴, C₂H₆, C₂H₄, and C₂H₂,
94 condense only a few km above the surface¹⁵, and therefore should not partake in the
95 particle formation at higher altitudes. However, the observed profiles reveal a local
96 minimum in their abundances near 200 km altitude that is not reproduced by the
97 homogeneous chemistry simulations, and instead was attributed to heterogeneous

98 processes on the haze particles^{3,16}. We evaluate the contribution of this interaction to
99 the particle growth through an adsorption/desorption description for the C₂-
100 hydrocarbons (see Methods and Fig. 5). Our simulations suggest that heterogeneous
101 processes mainly affect the C₂H₂ and C₂H₆ profiles, while they have smaller impact on
102 the C₂H₄ profile. Desorption studies¹⁷ of these organic ices do demonstrate that C₂H₄
103 desorbs at lower temperature than C₂H₂ and C₂H₆ consistent with the qualitative picture
104 we find here from fitting the *New Horizons* observations. At its maximum contribution
105 between 100 and 200 km (Fig. 3), this heterogeneous coating contributes another
106 3.3×10^{-15} g cm⁻² s⁻¹ to the particle mass flux. Therefore, the *New Horizons* observations
107 reveal that -although not condensing- the C₂-hydrocarbons do partake in the growth of
108 the haze particles in Pluto's atmosphere. Such heterogeneous processes are also
109 anticipated for Titan's haze^{11,18}, but so far evidence of their role is equivocal (see
110 Methods).

111
112 Near Pluto's temperature peak (~110 K) between 30 and 50 km, condensates are
113 expected to sublime and release their gases back to the atmosphere to an abundance
114 limited by their individual saturation limits. Were this true, however, the HCN
115 abundance would over-estimate the observed ALMA HCN J=4-3 satellite emissions⁸,
116 probing altitudes near 100 km (blue lines, Fig. 2). Instead, we find that the
117 heterogeneous coating is sufficiently thick to inhibit particle sublimation. Such an effect
118 has also been observed on the Earth's secondary organic aerosol¹⁹. Considering that the
119 effect of the coating depends on its thickness (see Methods) we derive an HCN
120 abundance in the lower atmosphere that fits well the observed satellite emissions (red
121 lines, Fig. 2). If the heterogeneous coating completely inhibited the sublimation of the
122 condensed ices, we would see an even lower HCN abundance, which however does not
123 provide a different emission spectrum (green lines, Fig. 2). Therefore, ALMA
124 observations cannot set further constraints on the magnitude of the heterogeneous
125 coating. However, further indications for the role of the heterogeneous component are
126 provided by the detection of CH₃C₂H from the analysis of Pluto's UV reflectance
127 spectrum²⁰. Under the nominal case of partial sublimation, we calculate a CH₃C₂H
128 column density of 2.2×10^{15} cm⁻², while for no sublimation we get 1.5×10^{14} cm⁻². The
129 former value is closer to the observed value of $\sim 5 \times 10^{15}$ cm⁻². We thus conclude that our
130 simple description of the heterogeneous coating provides a representative
131 characterization of its bulk properties.

132
133 The above processes control the variation of the average particle size and
134 corresponding number density with altitude in Pluto's atmosphere (Extended Data Fig.
135 2). Note that the particle mass density is not constant with altitude, but changes
136 reflecting the various organic ice contributions (see Extended Data Fig. 3 and
137 Methods). Below 400 km, organic ices provide the dominant contribution to the particle
138 bulk mass while the heterogeneous component has a maximum contribution of ~30%
139 (Fig. 3). The optical properties of this component are unknown, and we assume here
140 they are similar to those of the corresponding organic ices. At least for visible
141 wavelengths where the photon penetration depths are large this assumption will have a
142 negligible effect. The most abundant ice component is C₄H₂, thus we use it as a proxy for
143 the evaluation of the haze optical properties. The refractive index of condensed C₄H₂ is
144 measured in the visible²¹ and near IR²². In the UV, due to the lack of measurements, we
145 derived an estimate from the gas phase component and the Kramers-Kronig relationship
146 (see Methods and Extended Data Figs. 4 -7).

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Our simulated haze distribution is consistent with the *New Horizons* haze observations at UV⁸, visible¹³ and IR²³ wavelengths (**Fig. 6**). We note that the UV opacity attributed to hazes from the occultation measurements⁸ may contain contributions from unidentified gas components, and our calculations suggest that such contributions are significant above ~150 km. In addition, our simulated profiles reproduce the order of magnitude of the forward scattering and the UV extinction observations, but diverge from the observations in the back scattering near the surface, and at high altitudes (>100 km). These differences indicate the potential role of atmospheric circulation at high altitudes²⁴, the presence of horizontal haze variations¹³, the varying shape and optical properties of particles near the surface, as well as the limitations in the retrieval of I/F at low phase angle observations (see Methods). Notwithstanding these shortcomings, our results demonstrate that organic ices provide enough mass to reproduce observations and contribute significantly to Pluto's haze. We also present results for the case of Titan-type haze formation with a mass flux of $6 \times 10^{-15} \text{ g cm}^{-2} \text{ s}^{-1}$ assuming particles are produced in the upper atmosphere with a 10 nm radius and aggregate as they settle (blue lines in Fig. 6). Clearly this scenario falls short of the observations, demonstrating the need for a higher (~twice) haze production yield.

Nevertheless, contributions of Titan-type haze cannot be eliminated. Indeed, some of Pluto's surface features (e.g. Cthulhu region) demonstrate a spectral reddening^{23,25}, similar to the red slope of Titan's aerosol analogs^{26,27}. At Titan¹¹, 10% of the mass flux generated by ionizing EUV radiation in the ionosphere produces the mass flux of haze embryos observed by Cassini²⁸ ($\sim 3 \times 10^{-15} \text{ g cm}^{-2} \text{ s}^{-1}$ at 900 km). These embryos grow further through chemical processes before they reach the observed haze mass flux in the lower atmosphere ($3 \times 10^{-14} \text{ g cm}^{-2} \text{ s}^{-1}$)⁵, but the details of this chemical growth are unknown. In Pluto's ionosphere, we find that Titan-type hazes could be incepted with a mass flux of $7 \times 10^{-16} \text{ g cm}^{-2} \text{ s}^{-1}$ based on the incoming EUV radiation. However, it is unclear how fast these embryos can chemically grow in Pluto's much colder atmosphere and in the narrow altitude range between the ionization peak (~700 km) and the onset of condensation (below 600 km). Thus, although a Titan-type haze core could exist in Pluto's haze particles, its possible significance requires further investigation.

UV and cosmic ray radiation can further modify the optical properties of organic ices towards a more absorbing signature^{29,30}, which will make them consistent with Pluto's surface [properties](#). We find that photons with $\lambda > 150 \text{ nm}$ can penetrate Pluto's lower atmosphere and reach the surface providing an energy flux of $\sim 6 \times 10^{-2} \text{ W/m}^2$ (see Methods). Due to their high energy, cosmic rays are not significantly attenuated in the atmosphere, and deposit their energy on the surface. Our simulated haze particles have an atmospheric residence time (below 200 km) of about ~200 Pluto days. Given measured rates of ice modification by UV²⁹ we estimate that particles during their settling will be affected within a depth of only ~4 nm. Moreover, the ice processing by UV radiation competes with the variable coating of the particles by the heterogeneous chemistry, which is of similar depth. Therefore, further evolution of the settling organic ice particles is more likely to occur on Pluto's surface than in the atmosphere, making their signature consistent with the observed surface reddening.

If Pluto's haze composition is dominated by organic ices, its impact on the atmospheric thermal structure will be different than [that based on](#) the currently assumed Titan-type

196 composition³¹. Organic ices have weak absorptivity at visible and near-IR wavelengths³²
197 that will reduce the haze heating effect, while their thermal IR opacity is limited to
198 narrow absorption bands (compared to the continuous absorption of Titan-analogs)
199 that will limit their cooling effect. Clearly, an updated thermal structure evaluation is
200 required, but this task is complicated by the lack of optical properties for the organic ice
201 mixture. A preliminary evaluation of the cooling rate based only on the narrow
202 absorption bands of C₄H₂ ice near 40 μm suggests a value of 10⁻¹⁰ Wm⁻³ at 200 km that is
203 ~20 times lower than the previous estimate based on Titan's analogs³¹. Clearly, a
204 different equilibrium will be established and it remains to be evaluated if it will be able
205 to explain Pluto's cold upper atmosphere. Another suggested coolant is water vapor
206 resulting from the ablation of meteoroid material³³. Including a source of H₂O in our
207 calculations we find that although above ~400 km condensation is negligible, at lower
208 altitudes the mixing ratio rapidly decreases reaching to 10⁻¹² near 200 km. This
209 abundance is 10,000 times smaller than the abundance required to explain the observed
210 temperature profile¹⁰. As other molecular candidates, (e.g. nitriles), have smaller
211 abundances than the main species (CH₄, HCN, C₂H₂, CO)³³ considered for the
212 atmospheric cooling, it is potentially more promising for future studies to seek a
213 solution not for an increased cooling contribution but rather for a reduced gas heating,
214 i.e. a smaller atmospheric heating efficiency than the currently assumed.

215
216 Compared to Pluto, in Triton's colder atmosphere condensation could be even more
217 important for the formed hazes³⁴. Applying our model to Triton, we find particle
218 formation also starts from the nucleation of HCN (**Fig. 7**). However, as Triton's methane
219 is photochemically depleted at high altitudes, production of heavier hydrocarbons is
220 prominent only at altitudes below 200 km, where also the low temperature allows for
221 their condensation (**Fig. 7a**). Thus, particle growth is efficient in the lower atmosphere
222 with C₂H₄ providing the major contribution to the particle mass (**Fig. 7b**). Collisions
223 among the formed particles become efficient below 50 km in Triton's atmosphere, and
224 particles form aggregates with a primary particle radius of ~20 nm (**Fig. 7c**).
225 Heterogeneous reactions for the C₂-species are less important in Triton's atmosphere
226 because in the altitude region where they can contribute, these species also condense
227 out; thus, we did not include them in our simulations. The resulting particle size
228 distribution has an average bulk radius of 0.25 μm near the surface with a
229 corresponding particle density of 4 cm⁻³ (see **Extended Data Fig. 2**), while the total mass
230 flux reaches ~6x10⁻¹⁵ gcm⁻²s⁻¹. Our simulated particle distribution for Triton's **organic**
231 **ice** haze is consistent with the Voyager 2 haze observations^{35,36,37} at multiple
232 wavelengths/phase angles (**Fig. 8**), thus providing further support to our description of
233 condensate haze formation for both Pluto and Triton.

234
235 Our work reveals two end-member processes of haze formation, i.e. molecular growth
236 (Titan) and condensation (Triton). Pluto at the time of New Horizons observations is in
237 between these two limits. Future observations with JWST focusing at IR wavelengths
238 could potentially identify the spectral signatures of the main organic ices in Pluto's haze
239 and help constrain the relative contribution of the Titan-type component. The ν₄ (3293
240 cm⁻¹) and ν₈ (664 cm⁻¹) absorption bands of solid C₄H₂ would be good starting points³⁸,
241 although co-condensates could demonstrate shifts relative to the anticipated mono-
242 condensate spectra³⁹. However, given that Pluto's eccentric orbit will modify its
243 atmospheric temperature, this variation could have an impact on the haze load, as well
244 as on the nature of the hazes formed across the orbit. Orbiting further away from the

245 Sun will decrease the atmospheric temperature. The main atmospheric composition is
246 likely to change with decreasing temperature, with the CH₄/CO ratio decreasing with
247 increasing heliocentric distance in which case haze formation pathways based on CO
248 may become more important although with a smaller yield⁴⁰⁻⁴⁴. On the other hand the
249 reduced insolation will decrease the abundance of photochemical products. Saturation
250 vapor pressures will decrease, but the kinetics of condensation will be even slower; this
251 may reduce condensation rates, as we find here for HCN in Pluto's upper atmosphere,
252 implying that supersaturation ratios may change with distance. A self-consistent
253 evaluation of the thermal structure and composition is necessary for evaluating how the
254 haze abundance/composition varies along Pluto's orbit.
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359 **Acknowledgements** P.L. acknowledges support from the Programme National de
360 Planétologie (PNP-INSU, projects: AMG & TISSAGE).

361 **Author Contributions** P.L. designed and performed the research, and wrote the
362 manuscript. E.L. and M.A.G. provided comparison of model results with the *ALMA*
363 observations. D.F.S., A.C., L.A.Y., and R.G. provided insight on the treatment of the *New*
364 *Horizons* observations. All authors discussed the manuscript.

365 **Materials requests & Correspondence** should be addressed to the corresponding
366 author.

367 **Competing interests** The authors declare no competing interests.

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392 Main Figure Legends

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394 **Fig. 1 Thermal structures of Pluto and Titan** The two black curves for Pluto present
395 the temperature profiles derived from *New Horizons*¹⁴ (dashed line) and *ALMA*⁸ (solid
396 line) observations, while the black line for Titan is the *in situ* profile measured by
397 Huygens⁴⁵. Altitudes for each profile are presented by the bars with associated numbers
398 in km. Colored lines present the saturation temperatures for different photochemical
399 products with abundances calculated with our photochemical model. The interception
400 point of each curve with the temperature profile (approaching from lower
401 temperatures) indicates the approximate altitude where the condensation of each gas
402 may start. In Pluto for example, C₂H₆ condensation is possible only near the surface,
403 while C₆H₆ condensation starts in the upper atmosphere. In Titan all photochemical
404 products condense in the lower ~100 km.

405

406 **Fig. 2 HCN in Pluto's atmosphere** Simulated HCN mixing ratio (red line) in Pluto's
407 atmosphere relative to the anticipated saturation limit (black dashed line). The large
408 degree of super-saturation above ~250 km is due to condensation inefficiency owing to
409 slow kinetics. This is consistent with the *ALMA* observations (central peak in inset plot,
410 black for observed and red for the simulated emission; the gray area presents the
411 uncertainty in the observations)⁸. Near ~500 km, HCN loss to condensation becomes
412 important thus the gaseous abundance decreases. In the lower atmosphere, a saturated
413 HCN profile is inconsistent with *ALMA* observations (blue line). According to our model
414 (red line), HCN remains sub-saturated near the temperature maximum (at an altitude of
415 50-70 km), as the coating of the particles from heterogeneous nucleation inhibits
416 sublimation. A complete suppression of sublimation (green line) also fits the data well.

417

418 **Fig. 3 Organic ice haze in Pluto's atmosphere** Simulated haze mass flux in Pluto's
419 atmosphere (panel a, black line) showing contributions of HCN nucleation (dash triple
420 dotted), condensation of gases (dotted), and heterogeneous chemistry (dashed). The red
421 line shows Titan's haze mass flux⁵ and the purple line our simulated mass flux of
422 Triton's haze. Major contributions from the condensation of individual gases in Pluto's
423 atmosphere, in terms of their percent contribution to the total particle mass flux, are
424 shown on panel b with different colors and linestyles, while the short dashed black line
425 shows the contribution of the heterogeneous component. The dash-dotted black line
426 presents the cumulative contribution of all organic ices.

427

428 **Fig. 4 Transition from spheres to aggregates in Pluto's haze** Panel a presents the
429 ratio of mass growth by coagulation to total mass growth by coagulation and
430 condensation (the latter including heterogeneous chemistry) for different size particles
431 at different altitudes in Pluto's atmosphere. Particles collide below 400 km and form
432 aggregates. Based on these rates we derive the corresponding particle fractal dimension,
433 D_f ⁵, shown in panel b. The dashed line presents the D_f profile used in the simulations.
434 The inset shows that particles near the surface become more rounded due to the sharp
435 temperature drop that allows condensation of the C₂-hydrocarbons.

436

437 **Fig. 5 C₂-hydrocarbons in Pluto's atmosphere** Comparison of observed¹⁴ (symbols
438 with error bars) and simulated (solid lines) line of sight densities of the C₂-
439 hydrocarbons in Pluto's atmosphere. The simulated profiles include both homogeneous
440 and heterogeneous chemical process, with the latter considering both adsorption loss

441 and desorption gain of the gases on the surface of the haze particles. The inset
442 demonstrates how the simulated ethane profile would change if no heterogeneous loss
443 was included (dash dotted line) or if desorption was not considered (dashed line). The
444 observations demonstrate that both processes are active in Pluto's atmosphere.
445

446 **Fig. 6 Pluto's haze** Comparison of simulated (black) and observed (red) haze properties
447 for Pluto's atmosphere. Panels a-e present the scattered light observations (red lines) at
448 different phase angles towards Pluto's North Pole at visible wavelengths¹³. Red crosses
449 in panel d present the azimuthally averages I/F at this phase angle, demonstrating the
450 strong horizontal haze variations in Pluto's atmosphere. Panels f and g present the
451 wavelength-averaged near-IR scattered light profile at high phase angle and the
452 corresponding wavelength dependence of the average I/F in the lower 40 km of the
453 atmosphere, respectively²³. Panel h presents the UV line of sight opacity¹⁴. The dash-
454 dotted line presents the cumulative opacity from organic ice haze particles (solid) and
455 gas molecules (dashed). The blue lines present the case of Titan type haze formation
456 with a mass flux of $6 \times 10^{-15} \text{ g cm}^{-2} \text{ s}^{-1}$ and primary particle radius of 10 nm. **The gray**
457 **shaded area presents the uncertainty in the observed opacity.**
458

459 **Fig. 7 Organic ice haze in Triton's atmosphere** Haze mass flux (panel a) and
460 contributions of individual gas components (panel b) for Triton's haze composition.
461 **Panels c and d** present the transition from spherical to aggregate growth in Triton's
462 atmosphere. Here collisions dominate the particle growth below 50 km.
463

464 **Fig. 8 Triton's haze** Simulated I/F altitude profiles of Triton's atmosphere based on our
465 simulations of organic ice haze (lines) compared to the observed profiles (symbols)
466 from Voyager 2 images^{35,37}. **Each panel presents observation at different spectral filters**
467 **(Blue, Green, Orange, Violet at high phase angles, and Clear for low phase angle).**
468 **Symbols with associated numbers correspond to the observed phase angles. For the**
469 **high phase angle observations solid, dashed, and dash-dotted lines correspond to the**
470 **model results for 140°, 150°, and 160°. For the Clear filter observations the large circles**
471 **and solid line present the observed and simulated I/F profiles at 60° phase angle,**
472 **respectively. Similarly, the small circles and dotted line present the observed³⁶ and**
473 **simulated UV tangential opacity, respectively.**
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490 **Methods**

491

492 **Nomenclature** Through out the text the term haze is used to describe the presence of
493 an opacity source by small particles and does not presuppose anything about their
494 chemical composition. To make a distinction about the chemical composition of the haze
495 particles we add the characterizations of “organic ice” haze or “Titan-type” haze, which
496 describe hazes made through condensation of organic material or through molecular
497 growth processes, respectively. The term tholins has a wide range of applications but
498 here is used as a representative of the optical properties of Titan’s hazes derived from
499 laboratory experiments²⁷. [In this study we simulate exclusively the formation of organic
500 ices, but we discuss the implications of Titan-type contributions.](#)

501

502 **Models** The photochemical model is based on previous studies of Titan’s
503 photochemistry⁴⁶, updated with high-resolution energy deposition calculations⁶ and the
504 latest chemical reaction rates^{2,47,48}. The model solves the continuity equation taking into
505 account atmospheric mixing and molecular diffusion, the chemical production and loss
506 processes, and loss/gain due to condensation/evaporation, for each species considered.
507 We consider species of H/C/N/O composition that can be produced from the N₂/CH₄/CO
508 main atmospheric composition. The microphysical aspect of the simulation is based on
509 previous models for haze and cloud formation in Titan’s atmosphere^{5,49}. These consider
510 the Brownian (random collisions) growth of particles, as well as, their growth through
511 the deposition of gases on their surface. The model solves for the distribution of particle
512 sizes in a geometrically expanding grid ranging from 0.15 nm to 10 μm. The impact of
513 atmospheric mixing and particle sedimentation (according to size and shape) on the
514 particle distribution is included. At the top of the model (exobase) we assume escape at
515 the Jeans escape rate for gases and no escape for haze particles, and at the bottom all
516 simulated components (gases and hazes) are lost to the surface at the rate they arrive.

517 Pluto’s CH₄ mixing ratio at the surface is fixed at 0.4% and we assume a constant with
518 altitude eddy mixing profile of $K_{zz}=10^3 \text{ cm}^2\text{s}^{-1}$. We derived the K_{zz} value by matching our
519 simulated CH₄ and N₂ profiles in Pluto’s upper atmosphere with the profiles derived
520 from the New Horizons occultation measurements, using the temperature profile
521 derived from that analysis¹⁴. We note, that the characteristic time scales for
522 photochemistry/condensation or sedimentation of the main photochemical products or
523 haze particles, respectively, are significantly smaller than the corresponding
524 atmospheric mixing timescales. For example, C₂H₆, C₂H₄ and C₂H₂ have
525 photochemical/condensation time scales at all altitudes that are smaller by factors
526 greater than 10² from the corresponding eddy mixing time scales. For the haze particles
527 the sedimentation time scales are smaller from the eddy mixing time scales by factors of
528 5 at 10 km, 60 at 50 km, 130 at 100 km, and increasing to larger values at higher
529 altitudes. Thus, apart from altitudes near the surface, uncertainties by even a factor of
530 10 in the K_{zz} will not significantly affect our conclusions.

531 Pluto’s thermal structure exhibits a sharp temperature gradient close to the surface
532 that requires the use of a fine grid in our diffusion calculations (Fig. 1). Thus, we use a
533 pressure grid of 1,000 levels between the surface and Pluto’s exobase that results in
534 altitude layers of sub-km size close to the surface gradually increasing to ~10 km at the
535 highest altitudes of our simulation space. This altitude binning is a factor of ~10 smaller
536 than the corresponding atmospheric scale height at each altitude.

537 For the energy deposition from solar photons we use high-resolution N₂ cross
538 sections at wavelengths shorter than 100 nm, while we also consider the role of

539 photoelectrons⁶ in the dissociation/ionization of N₂ and CH₄. We use the observed solar
540 flux on July 14th, 2015 (New Horizons Pluto flyby) from the TIMED-SEE database
541 (<http://lasp.colorado.edu/home/see/>). At Pluto's orbit the solar insolation is small
542 enough for the contribution of resonantly scattered Ly- α photons from the
543 interplanetary hydrogen population (IPH) to be comparable to the direct solar
544 contribution (4.7×10^8 photons cm⁻² s⁻¹ at 32.91 au). Detailed modeling of this process
545 suggests⁵⁰ that the IPH Ly- α background at Pluto's location at the time of the *New*
546 *Horizons* flyby corresponds to a sky-averaged photon flux of 145 R. Thus, we consider a
547 total Ly- α flux of $\sim 1 \times 10^9$ photons cm⁻² s⁻¹. We find photons dominate the N₂ photolysis
548 near 750 km, while energetic electrons below 600 km. CH₄ photolysis peaks near 500
549 km and is dominated by Ly- α . Pluto's ionosphere is centered near 700 km with a peak
550 electron density of $\sim 10^3$ cm⁻³ consistent with observations⁵¹. The resulting abundance
551 profiles of the major photochemical products demonstrate that they can condense at
552 high altitudes in Pluto's atmosphere (Fig. 1).

553 For our investigation of Triton's haze we used input from the Voyager observations
554 regarding the thermal structure⁵² and energy input to the atmosphere from Neptune's
555 magnetosphere^{52,53}. Pluto's and Triton's atmospheres are not dense enough to attenuate
556 galactic cosmic rays (GCR), thus we do not consider this energy source for the
557 atmospheric chemistry. However, GCR could affect the surface optical properties (see
558 main text and section below).

559
560 **Nucleation/Condensation/Sublimation** For the investigation of the HCN profile we
561 consider neutral and ion homogeneous nucleation rates. The theory of these processes is
562 well documented and used for various solar system studies^{54,55,56}. For the evaluation of
563 these rates we use information for the saturation vapor pressure, surface tension, mass
564 density, and dielectric constant of condensed HCN^{55,57,58,59,60,61}. Vapor pressures
565 measurements at the low temperature conditions found in Pluto's and Triton's
566 atmospheres are rare and difficult to achieve experimentally. Thus, extrapolation from
567 higher temperature measurements is a common approach for such studies^{2,46,55,62,63}.

568 *New Horizons* observations¹⁴ up to 350 km altitude indicate that haze UV extinction
569 drops with a constant scale height of 77 km, i.e. the haze particle size and/or density
570 decreases with increasing altitude. Therefore, if haze particles are readily formed near
571 Pluto's ionosphere, where they could affect the HCN condensation, their size must be
572 small (sub-nm, based on the size of aerosols formed in Titan's ionosphere¹¹), and their
573 impact to nucleation comparable to that of the homogeneous mechanisms.

574 Nucleation provides the seeds on which condensation can proceed, but is only a
575 minor loss for the gaseous abundance of HCN. As the seeds gradually increase in size
576 through condensation, the condensation loss of gaseous HCN (as well as of other
577 condensing species) becomes progressively more important and eventually affects the
578 resulting gaseous abundance below 500 km. The Kelvin effect of the saturation vapor
579 pressure over curved surfaces is taken into account for each particle radius.

580 The smallest condensate particles populate the first bins of the bulk radius grid of our
581 simulations, depending on the size they are formed through the nucleation of HCN.
582 Subsequently, they grow to larger radii as HCN and other gases condense on their
583 surface. We consider contributions from C₂H₂, C₂H₄, C₂H₆, C₃H₄, C₃H₈, C₄H₂, C₄H₈, C₄H₁₀,
584 C₆H₂, C₆H₆, HCN, HNC, CH₃CN, HC₃N, C₂H₃CN, C₂H₅CN, C₂N₂, C₄N₂, and H₂CO. The relative
585 contributions from these species control the average particle mass density at each
586 altitude, which we evaluate by calculating the mass flux of each component and the
587 corresponding mass density of its condensate phase^{21,55}. We had to estimate the

588 densities for some of the organic ices from their liquid equivalents (species in italics
589 above) as measurements are lacking at the required low temperatures. **As demonstrated**
590 **in Supplementary Table 1, typically the solid density of organic ices is higher than the**
591 **corresponding liquid value with differences ranging from ~4% up to ~40% among the**
592 **species for which both evaluations are available.** For the heterogeneous component we
593 do not know its corresponding mass density and we assume a nominal value of 1 gcm^{-3} .
594 The simulations suggest that the particle mass density varies between 0.967 gcm^{-3} (the
595 mass density of HCN ice) in the upper atmosphere to an average value of $\sim 0.85 \text{ gcm}^{-3}$
596 in the lower atmosphere below 300 km (Extended Data Fig. 3). Assuming⁶⁵ a mass density
597 of 0.5 gcm^{-3} for the heterogeneous component, the average particle mass density in the
598 lower atmosphere drops to $\sim 0.75 \text{ gcm}^{-3}$.

599 The relative contributions of condensation and coagulation to the total mass growth
600 of particles (Fig. 4 for Pluto and Fig. 7 for Triton) define the transition from spherical to
601 aggregate growth that we describe through the aggregate fractal dimension, D_f , which
602 varies between 3 for spheres and 2 for aggregates¹⁸.

603 For particle sublimation we consider the impact of the heterogeneous chemistry
604 coating. Assuming a mass density for this component of 1 gcm^{-3} and a typical molecular
605 cross section of 10^{-15} cm^2 , the mean free path of evaporating molecules through the
606 coating would be $\lambda_{\text{coat}} \sim 0.5 \text{ nm}$. Thus, we consider that evaporation is inhibited by a
607 factor $\exp(-\delta r / \lambda_{\text{coat}})$, where δr is the difference in the particle size (evaluated as the
608 fractal radius⁵) due to the coating.

609
610 **Heterogeneous Processes** The heterogeneous loss of gases due to adsorption on
611 particles is evaluated as $L_{\text{Hetero}} = \sum_p [n_p \times S_p \times V_{T,\text{gas}} \times n_{\text{gas}} \times f_{\text{Stick}}(T)]$, where, the summation
612 is over the particle size distribution, n_p and S_p are the density and surface area of size- p
613 particles, $V_{T,\text{gas}}$ and n_{gas} are the thermal velocity and density of the hitting molecules, and
614 $f_{\text{Stick}}(T)$ is temperature-dependent sticking efficiency of each heterogeneously lost
615 molecule with the form $f_{\text{Stick}}(T) = A * (1 - \tanh(0.2 * (T - T_{\text{st}}))) / 2$ with A and T_{st} gas-
616 dependent parameters. This expression, based on measured sticking efficiencies of small
617 molecules on water ice⁶⁴, describes a sigmoidal increase of sticking efficiency below
618 temperature T_{st} , with a maximum sticking efficiency reaching to value A . Heterogeneous
619 gas production due to desorption is evaluated as $P_{\text{Hetero}} = \sum_p [n_p \times S_p \times V_{T,\text{atm}} \times n_{\text{atm}} \times e_{\text{gas}} \times$
620 $f_{\text{Disorpt}}(T)]$. In this expression e_{gas} is the contribution of each heterogeneously lost
621 molecule to the total mass of each particle (as in Fig. 2) and $f_{\text{Disorpt}} = B(1 - f_{\text{Stick}}/A)$. With
622 this temperature dependence desorption is active only when sticking is inefficient due
623 to the increased atmospheric temperature, i.e. temperature controls the interaction
624 between gases and particles. To match the observed C_2 -hydrocarbon profiles (Fig. 5)
625 with this scheme we use A values of 5×10^{-6} , 1×10^{-5} , 5×10^{-6} , with $T_{\text{st}} = 82\text{K}$, 90K , 82K and
626 $B = 1 \times 10^{-12}$, 1×10^{-12} , 3×10^{-12} for C_2H_6 , C_2H_4 and C_2H_2 , respectively. It is also interesting to
627 note that experiments on water ice suggest that CO , CH_4 , N_2 i.e. Pluto's main atmospheric
628 compounds, can stick on the ice surface at temperature similar to Pluto's⁶⁴. However, as
629 the nature of the substrate has a major role for the interaction with the impinging
630 molecules, we did not consider this effect in our study. It would be useful to explore this
631 option first through laboratory experiments on organic ices.

632 Various studies have suggested that there may be evidence for heterogeneous
633 reactions in Titan's atmosphere but the results seem to be contradictory with the
634 inclusion of heterogeneous processes improving the fits to some photochemical
635 products and worsening them for others². Unfortunately, the evaluation of
636 heterogeneous reactions in Titan's atmosphere is based on short-lived photochemical

637 products with most of them being significantly down the pathway of molecular growth
638 from the initial N₂/CH₄ mixture, where reaction pathways and rates are not as well
639 known as for the first steps. On the contrary, for Pluto's atmosphere the evidence of
640 heterogeneous processes is based on ethane and acetylene, which are long-lived
641 photochemical products with a relatively well understood photochemistry.

642
643 **Other processes** The differences between observed and simulated haze properties
644 indicate that additional processes could affect the particle properties. General
645 circulation models²⁴ demonstrate that for the calculated primary particle radius
646 circulation will result in longer residence times than those calculated with our 1D
647 simulations. This effect would increase the altitude slope in the I/F and UV extinction
648 profiles towards the observed. Moreover, observations demonstrate a strong increase in
649 haze scattering towards Pluto's North pole¹³. From high phase angle observations, the
650 local increase near the pole can be up to a factor of three from the azimuthally average
651 I/F (see Fig. 6). We also need to keep in mind that the UV opacity attributed to hazes in
652 the New Horizons occultation analysis could include contributions from gaseous
653 components not identifiable in the spectra. Near the surface, observations suggest that
654 the particle's shape becomes more spherical relative to the aggregate shape at 50 km.
655 Our calculations suggest that near the surface condensation of the C₂-hydrocarbons
656 provides enough mass to the particles to affect their shape (see inset in Fig. 4). However,
657 we did not include this effect in our current calculations. We note that changing the
658 particle shape towards a sphere will increase the sedimentation velocity, thus rapidly
659 decrease the local particle density. Also we did not consider the possible trapping of
660 other gases (e.g. N₂, CH₄, CO) in the condensates that would result in a smaller mass
661 density, while we had to make an assumption for the mass density of the heterogeneous
662 component (1 g cm⁻³). Changes in the particle mass density will directly affect the
663 sedimentation velocity of the haze particles and affect their vertical profiles. Sticking of
664 N₂, CH₄, and CO at the very low temperatures near the surface is also a possibility, given
665 the efficiency of such processes on water ice⁶⁴. This could further affect the particle
666 shape and refractive index, therefore the local scattered light properties. All the above
667 need to be evaluated in future investigations once a better understanding of the
668 heterogeneous interaction mechanisms is achieved. Finally, note that for the low phase
669 angle observations (20°, 67°) the derived scattered light profiles are based on the
670 removal of a surface scattering contribution, the latter being inferred from the surface of
671 Charon¹³. The uncertainties from this approach are not well constrained.

672
673 **Particle treatment by UV and cosmic rays** Due to the low atmospheric density and the
674 loss of photochemical products from condensation, as well as, the low opacity of the
675 haze, the atmosphere beyond ~150 nm is practically transparent and solar insolation
676 reaches the surface. Our calculations provide an energy flux of ~6x10⁻⁶ Wcm⁻² in the
677 wavelength range 200-350 nm. Laboratory experiments²⁹ studying the irradiation of
678 C₄N₂ ice at similar wavelengths show that 13% of ice thickness (200 nm) is polymerized
679 when irradiated by UV light for 84,000 s and a flux of 0.05 W cm⁻². Using this estimate
680 for Pluto's case and considering the particle residence time in the lower 200 km (~10⁸s)
681 we find that particles should be affected to a depth of 3.7 nm. However the production of
682 polymer material acts as a screen that absorbs the incoming high-energy photons and
683 eventually limits the growth of the polymer. Further input from laboratory studies is
684 required to investigate this effect on the organic ices identified here for the composition
685 of Pluto's haze. Cosmic rays provide a higher energy input (MeV-GeV) but with lower

686 flux. Each energetic particle can produce a cascade of high-energy photons/electrons
687 that amplifies the effect of each original impact. Cosmic rays have a higher penetration
688 depth compared to UV photons and can excite simultaneously multiple molecules in the
689 ice that are intermediates towards polymerization⁶⁵.

690

691 **Refractive indices** For C₄H₂ and C₂H₄ ices, which we find to be the major mass
692 contributors for Pluto's and Triton's hazes respectively, information for their (n,k) is
693 limited to IR wavelengths where their absorption bands are detected^{22,67}. Moreover, the
694 corresponding n values at visible wavelengths (n_{VIS}) are known⁶⁷, or can be estimated
695 from the liquid phase²¹. It is well established that organic ices have extremely low
696 absorptivity at visible wavelengths³², thus the lack of the exact knowledge of the k_{VIS}
697 values, will not affect our evaluation of the scattering properties of the particles at
698 visible wavelengths. However, for comparison with the UV observations we do need an
699 estimate for their (n,k)_{UV}. We generate such estimates based on the available refractive
700 indices at IR wavelengths and the Kramers-Kronig closure relationships⁶⁸. This is a well-
701 established technique used in laboratory studies to derive the refractive index at IR
702 based on absorptivity measurements and the known refractive index at visible,
703 n_{VIS}^{22,67,69}. Here we use this technique in a reverse approach, as the value of n_{VIS} is
704 dominated by the integrated contribution from shorter wavelengths. For the λ-
705 dependence of k_{UV} we can use the photoabsorption cross section (σ_{UV}) of the
706 corresponding gas phase to derive an estimate⁷⁰ for $k_{UV} = \rho_s \sigma_{UV} \lambda N_A / 4\pi M$, where M is the
707 molecular mass of the molecule and ρ_s the solid's mass density, and N_A Avogadro's
708 number. This approach has been used before for estimating the absorptivity of CH₄ ice⁷¹.
709 The accuracy of this approximation depends on the molecule considered. Studies of UV
710 absorptivities of molecules at gas and solid phases demonstrate that the phase
711 transition results in blue shifts of major electronic bands and the suppression of
712 vibrational features⁷². Moreover, such effects appear to be enhanced in polar relative to
713 non-polar molecules.

714 As a demonstration of our approach we present the cases of CH₄ and H₂O ices for
715 which UV measurements are available^{73,74,75}. For CH₄ ice ([Extended Data Figure 4](#)), the
716 gas-phase estimate is consistent with the measured k_{UV} for which the laboratory
717 measurements show that the blue shift is small⁷³ (~3.8 nm at the peak of the lowest
718 absorption band, corresponding to energy shift of ~2,000 cm⁻¹). Moreover our estimate
719 is consistent with a previous estimate based on the same approach⁷¹. For the H₂O ice
720 ([Extended Data Figure 5](#)), the gas phase estimate does not provide an as good match to
721 the n_{VIS} as for the CH₄ case. For this polar molecule laboratory studies⁷⁶ show that the
722 blue shift is significantly larger (~23 nm). To evaluate this effect on our calculation we
723 fitted the k_{UV} from the gas phase with a set of gaussians which we subsequently blue
724 shifted by a constant energy. Applying a shift of ~10,000 cm⁻¹ brings the k_{UV} closer to the
725 observed spectrum while also improving the derived n_{VIS} value from 1.270 to 1.294 (note
726 that n_{VIS} values are measured to an accuracy of 1%⁷⁶, thus this difference could be
727 significant).

728 With this approach we derived the estimates for the k_{UV} of C₄H₂ and C₂H₄ ([Extended](#)
729 [Data Figures 6 & 7](#)). As these are also non-polar molecules we evaluated how the
730 refractive index would change assuming relatively small blueshifts (1,000-5,000 cm⁻¹
731 based on the above discussion). For the wavelength range sensitive to the haze retrieval
732 by New Horizons (175-188 nm) we estimate that the average C₄H₂ ice k_{UV} may vary
733 between 6x10⁻³ and 1.5x10⁻². The corresponding k_{UV} range for C₂H₄ ice for Voyager
734 observations (150-160 nm) is 0.65-0.72. We emphasize here that these are bulk

735 estimates used to derive an order of magnitude evaluation for the possible range of UV
736 extinction for our simulated haze distributions. Actual measurements are required for a
737 better evaluation, and we hope this work will motivate such laboratory studies.

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739

740 Methods References

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835

836 **Data availability** The data that support the plots within this paper and other findings of
837 this study are available from the corresponding author upon reasonable request.

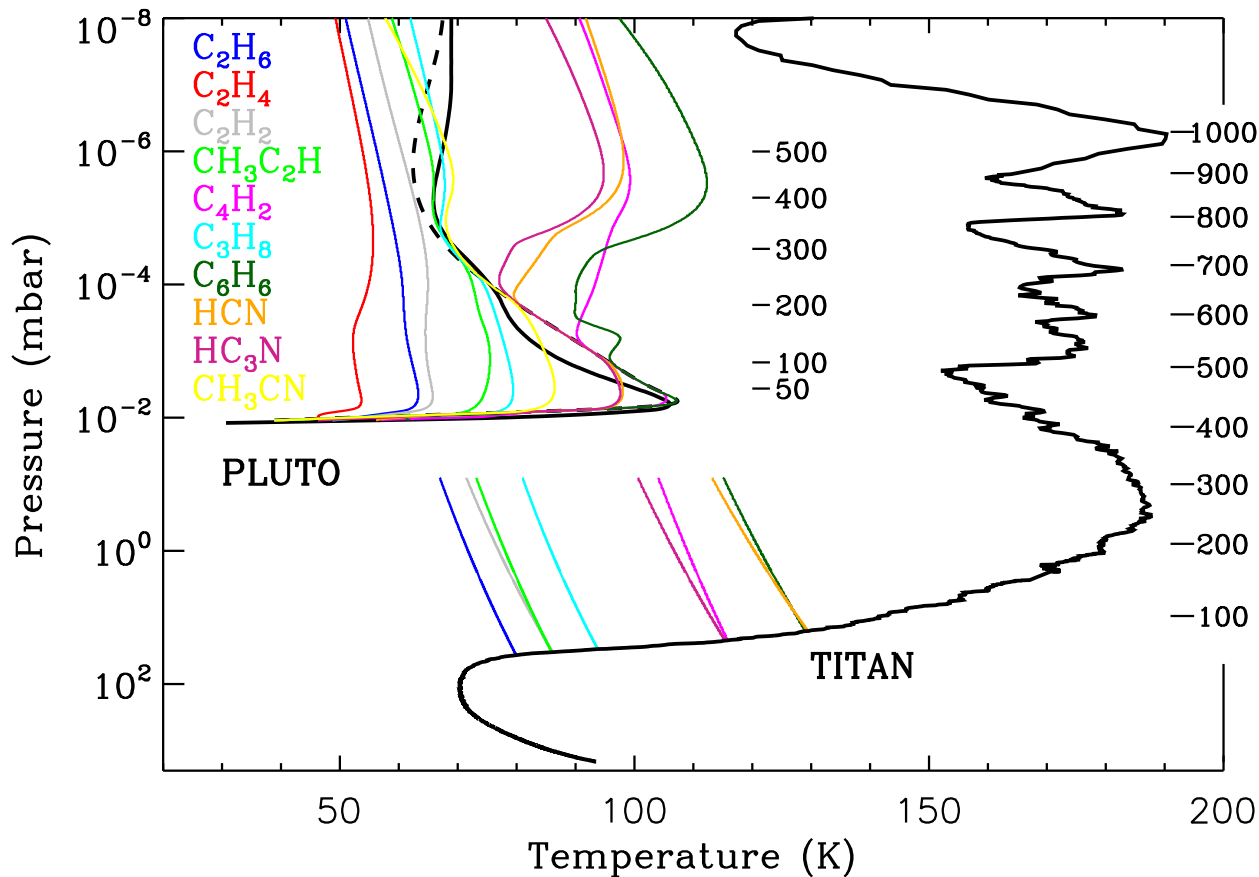
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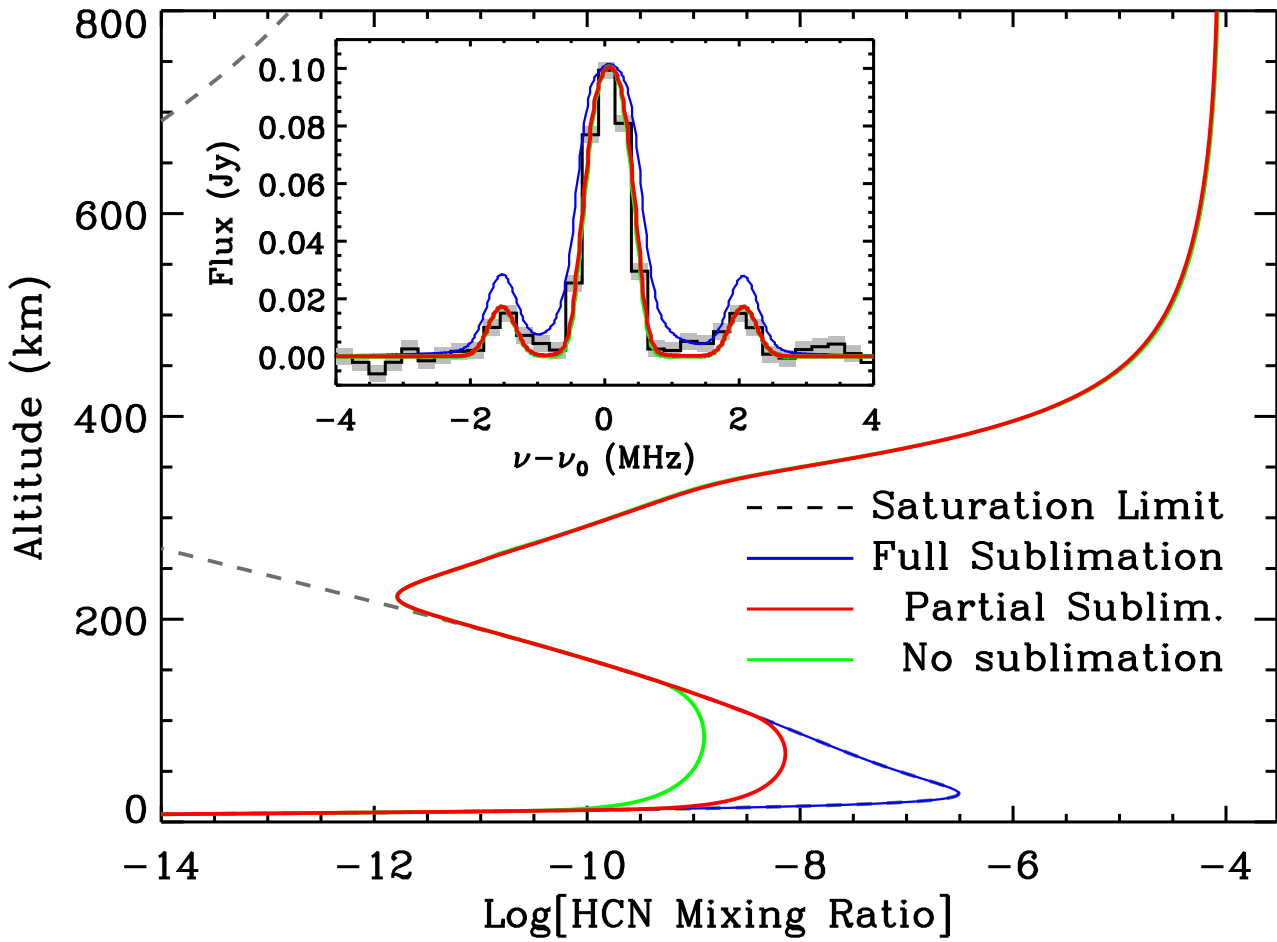
839 **Code availability** The codes used in this study are described in detail in previous
840 relevant publications (see references). They are not publicly available owing to their
841 undocumented intricacies.

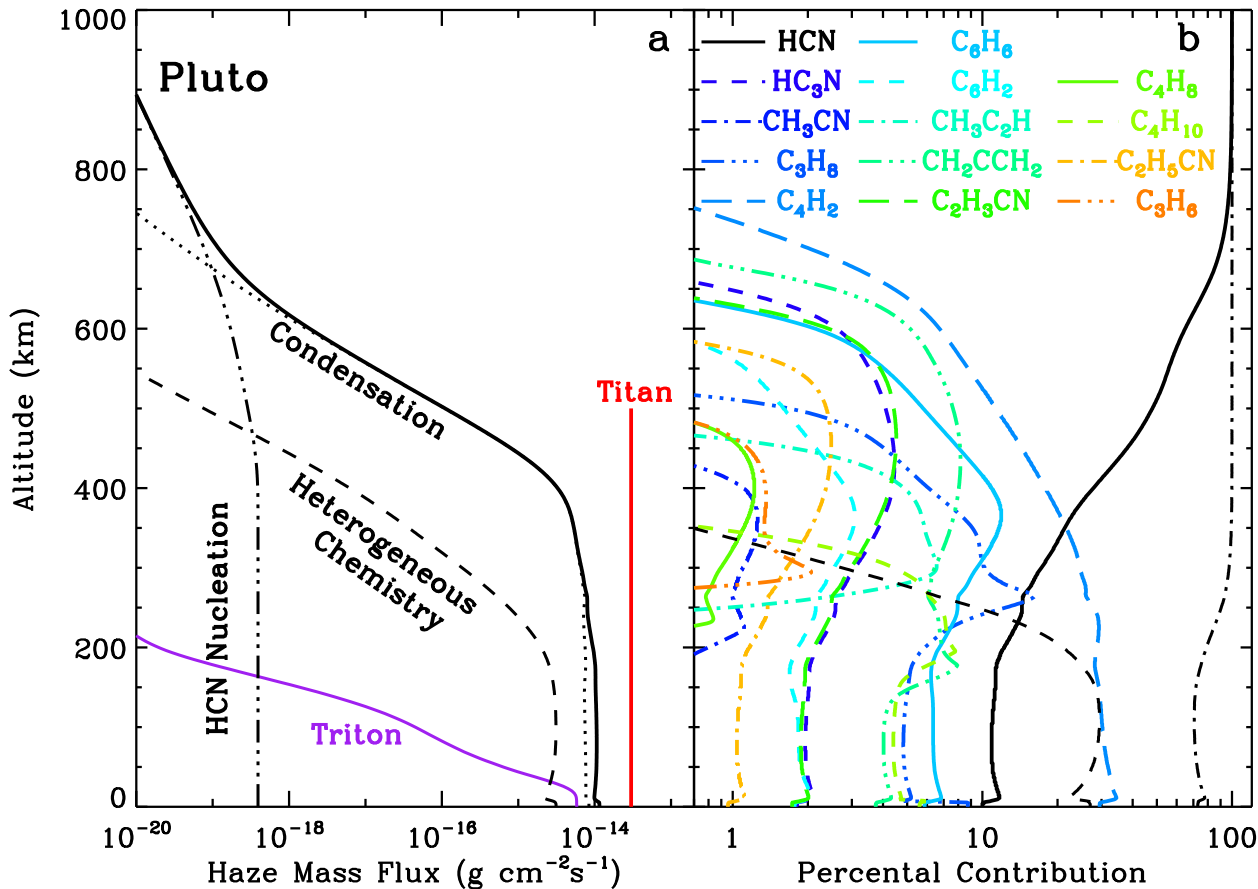
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$\text{Log}[dM(\text{Coag.})/(dM(\text{Cond.})+dM(\text{Coag.}))]$

-6 -5 -4 -3 -2 -1 0

