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Photochemistry on Pluto – I. Hydrocarbons and aerosols

Adrienn Luspay-Kuti^{1,*}, Kathleen Mandt^{1,2}, Kandis-Lea Jessup¹, Joshua Kammer¹, Vincent Hue¹, Mark Hamel^{1,2}, Rachael Filwett^{1,2}

¹Space Science and Engineering Division, Southwest Research Institute, 6220 Culebra Road, San Antonio, TX 78238, USA

²Department of Physics and Astronomy, University of Texas at San Antonio, One UTSA Blvd., San Antonio, TX 78249, USA

Abstract

In light of the recent *New Horizons* flyby measurements, we present a coupled ion–neutral-photochemistry model developed for simulating the atmosphere of Pluto. Our model results closely match the observed density profiles of CH₄, N₂ and the C₂ hydrocarbons in the altitude range where available *New Horizons* measurements are most accurate (above ~ 100–200 km). We found a high eddy coefficient of 10⁶ cm² s^{−1} from the surface to an altitude of 150 km, and 3 × 10⁶ cm² s^{−1} above 150 km for Pluto’s atmosphere. Our results demonstrate that C₂ hydrocarbons must stick to and be removed by aerosol particles in order to reproduce the C₂ profiles observed by *New Horizons*. Incorporation into aerosols in Pluto’s atmosphere is a significantly more effective process than condensation, and we found that condensation alone cannot account for the observed shape of the vertical profiles. We empirically determined the sticking efficiency of C₂ hydrocarbons to aerosol particles as a function of altitude, and found that the sticking efficiency of C₂ hydrocarbons is inversely related to the aerosol surface area. Aerosols must harden and become less sticky as they age in Pluto’s atmosphere. Such hardening with ageing is both necessary and sufficient to explain the vertical profiles of C₂ hydrocarbons in Pluto’s atmosphere. This result is in agreement with the fundamental idea of aerosols hardening as they age, as proposed for Titan’s aerosols.

Keywords

Kuiper belt objects; individual; Pluto-planets and satellites; atmospheres

1 INTRODUCTION

On 2015 July 14 the *New Horizons* spacecraft successfully flew through the Pluto system, providing critical details about Pluto’s atmosphere. Measurements made by the various instruments on-board *New Horizons* confirmed that the chemistry in Pluto’s atmosphere is

* aluspaykuti@swri.edu.

SUPPORTING INFORMATION

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strikingly similar to Titan's, including the growth of aerosols (Gladstone et al. 2016; Gao et al. 2017). Chemistry is initiated by ultraviolet photons dissociating and ionizing N_2 and CH_4 , whose photochemical products lead to the formation of complex hydrocarbons, nitriles and organic haze. Despite the similarities between Pluto's and Titan's chemistry, the differences in their size, thermal structure, atmospheric pressure, minor neutral composition and available photon flux are expected to result in important differences in their photochemical and transport processes, and hence the vertical atmospheric composition and structure. In the case of Pluto, these processes are also likely to have implications for the intimate relationship between the surface and the atmosphere, as Pluto's surface ices are maintained in vapour pressure equilibrium with the atmosphere (e.g. Hansen & Paige 1996).

Driven by the need to interpret data from the *Cassini-Huygens* mission over the past decade, Titan's photochemistry has been extensively studied (e.g. Yung, Allen & Pinto 1984; Wilson & Atreya 2004; Vuitton, Yelle & McEwan 2007; De La Haye et al. 2008; Lavvas, Coustenis & Vardavas 2008; Krasnopolsky 2009; Lavvas et al. 2011a), but photochemical models for Pluto have been sparse. Only a handful of Pluto photochemical models existed prior to the *New Horizons* flyby (Lara, Ip & Rodrigo 1997; Summers, Strobel & Gladstone 1997; Krasnopolsky & Cruikshank 1999), as there has historically been a lack of observational data to constrain models.

Measurements by the Alice UV instrument and the REX radio occultation experiment onboard *New Horizons* enabled the retrieval of the thermal structure, bulk density, and hydrocarbon composition and abundance in Pluto's atmosphere (Gladstone et al. 2016). In addition to determining the vertical profiles of the major constituents N_2 and CH_4 , abundances of C_2H_2 , C_2H_4 and C_2H_6 were also derived from Alice transmission data. These vertical profiles can now be used to model Pluto's atmosphere more accurately than in the pre-*New Horizons* era, and to better understand the physical and chemical processes at play.

Most recently, Wong et al. (2017) used their photochemical model to reproduce *New Horizons* observations of the detected hydrocarbon species and to constrain various related parameters. They proposed a low, constant-with-altitude eddy diffusivity based on their model fit to the observed CH_4 vertical profile, and found condensation to be key in fitting the C_2 hydrocarbon profiles. However, in order to be able to fit the C_2 hydrocarbon vertical profiles, they had to arbitrarily lower the saturation vapour pressure of C_2H_4 to that of C_2H_2 , which led them to conclude that C_2H_4 must have a much lower saturation vapour pressure than calculated via the extrapolation of laboratory measurements at somewhat higher temperatures.

Because of their comparable photochemistry, the haze in Pluto's atmosphere is likely similar to aerosols in Titan's atmosphere. Aerosol particles can act as condensation nuclei for the C_2 hydrocarbons, which play an important role in the production of more complex hydrocarbons, and ultimately, the hazes. The condensation and incorporation of hydrocarbons and nitriles onto Titan aerosols have recently been modelled providing good agreement with observations, suggesting that these processes are indeed important (Willacy, Allen & Yung 2016). The formation and distribution of aerosol particles in Pluto's

atmosphere were recently modelled based on *New Horizons* measurements by Gao et al. (2017).

The growth of aerosols in Titan's atmosphere, though still relatively poorly understood, has been a focus of interest for some time. Aerosol growth has been simulated in the laboratory (e.g. Bar-Nun, Kleinfeld & Ganor 1988; Sekine et al. 2008; Sebree et al. 2016), modelled (e.g. Dimitrov & Bar-Nun 1999; Liang, Yung & Shermansky 2007a; Lavvas et al. 2011b) and observed with instruments on the *Cassini-Huygens* mission (e.g. Liang, Yung & Shermansky 2007a; Bellucci et al. 2009). The thermodynamic stabilization of aerosols has been evaluated in detail for Titan's atmosphere (see Bar-Nun, Dimitrov & Tomasko 2008 and references therein). Early laboratory studies (Bar-Nun et al. 1988) and modelling of aerosol growth (Dimitrov & Bar-Nun 1999) evaluated the energy and composition-dependent growth of aerosols through cohesion and consolidation. Dimitrov & Bar-Nun (1999) developed a model for aerosol growth in Titan's atmosphere based on laboratory studies in preparation for the planned *Cassini-Huygens* observations of Titan. This study found that the consolidation of two colliding particles depends on both their interaction energy and their chemical nature. As described in Dimitrov & Bar-Nun (1999), when primary particles collide and the collision is effective, they can physically stick together (coagulate) with weak intermolecular adhesion forces. These coagulated primary particles form aggregates while keeping their chemical individualities, and holding contact only in one point on their surfaces. Coagulated particles are not fused together. If there is a considerable energy excess following coagulation, the weak intermolecular forces (adhesion) that hold the coagulated particles together are replaced by stronger intermolecular bonds (cohesion), which leads to the particles becoming partly fused while still keeping their chemical individualities (coalescence). Coalescence leads to the formation of secondary aggregates. If the energy excess following coagulation exceeds the activation energy of a given bimolecular chemical reaction, then the subsequent evolution of the particles depends on their chemical activity. If the particles are chemically inactive, then the coalescence will become greater in intensity with the particles fusing to more and more depth, sometimes to the point of forming regular spheres. However, if the particles are chemically active, then intermolecular bonds are replaced by internal chemical bonds. This results in the complete sorption of the smaller particle by the larger one. In both the active and inactive cases, two initially chemically different particles end up forming a new chemical entity larger in size. In addition, Dimitrov & Bar-Nun (1999) found that the process of coagulation leading to coalescence depends on the total coagulated particle size and the ratio of the particles that merged, which meant that small particles colliding with large particles are more likely to coalesce (Dimitrov & Bar-Nun 1999). This suggests that hydrocarbons and nitriles colliding with aerosols could also be permanently lost through the process of coalescing – an idea that was explored for Titan by Willacy, Allen & Yung (2016).

The physics of aerosols in Titan's atmosphere were projected by Dimitrov & Bar-Nun (2002) to involve a process of growing, ageing and descending to the surface. They predicted that this would result in a mixture of unstable, locally formed particles and stable, earlier-formed particles. Laboratory studies have also shown that aerosols formed by polymerization of C_2H_2 with HCN harden as they age due to cross-linking and chain elongation of the polymer bonds through UV radiation and particle impact (Dimitrov & Bar-

Nun 2002, 2003; Bar-Nun et al. 2008). This ageing process makes aerosols less sticky so that they are less likely to coalesce and eventually unable to coagulate (Dimitrov & Bar-Nun 2002). Courtin, Kim & Bar-Nun (2015) evaluated the aerosol absorption features measured by the Cassini Visual Infrared Mapping Spectrometer (Bellucci et al. 2009) between 250 and 700 nm, which allowed them to separate aromatic (double C—C bonds or rings) from aliphatic (single C—C bonds) structural groups in Titan's haze. The steep decrease in the pseudo-ratio of aromatics to aliphatics was assumed to correspond to the transition between unannealed and hardened particles, providing support for the presence of this type of ageing process for aerosols in Titan's atmosphere. Because of the suspected similarity in composition of aerosols in Pluto's atmosphere, this ageing process is also likely to be relevant.

At Pluto, UV radiation is almost an order of magnitude less than at Titan, and the temperature of Pluto's atmosphere is much lower than that of Titan where photochemistry is most important (~ 70 and ~ 150 – 180 K, respectively). This implies a lower collision rate and less energy deposition in Pluto's atmosphere compared to Titan's. Therefore, the process of aerosol hardening will likely be slower at Pluto than at Titan, potentially increasing the rate of hydrocarbon and nitrile incorporation into Pluto's aerosols compared to at Titan. However, it must be noted that the annealing process depends heavily on the chemical composition of the aerosols (Dimitrov & Bar-Nun 2002). The complete chemical composition for aerosols in either atmosphere is poorly known, and may be different at Pluto compared to Titan, e.g. due to the higher abundance of CO in Pluto's atmosphere [515 ± 40 ppm at Pluto (Lellouch et al. 2017) versus ~ 10 – 60 ppm at Titan (Lutz, de Bergh & Owen 1983; Lellouch et al. 2003)].

On the other hand, Lavvas et al. (2011b) developed a complex model that simulated the production of aerosols in Titan's atmosphere through the aggregation and coagulation of aromatics, starting with benzene. They evaluated the interaction of radicals in Titan's atmosphere with the surface of the aerosols and find that these processes significantly impact the growth, shape, size and density of the aerosol particles. Processes of aerosol growth in Lavvas et al. (2011b) include the coagulation of spherical primary particles into asymmetric aggregated products and the conversion of aggregated particles into spherical primary particles through surface chemistry. The sticking efficiency of colliding particles was modelled based on an empirical formula derived from studies of soot particles (Appel, Bockhorn & Frenklach 2000; Raj et al. 2010) rather than laboratory studies conducted on Titan analogues (e.g. Bar-Nun et al. 1988).

The atmospheric C_2 hydrocarbon profiles in Pluto's atmosphere indicate that processes other than chemistry have a major impact on their altitude profiles (Wong et al. 2017). We evaluate here the photochemistry of C_2 hydrocarbons in Pluto's atmosphere, comparing the dominant production and loss processes with a special emphasis on the role of aerosol interaction.

2 THE COUPLED PLUTO ION–NEUTRAL-PHOTOCHEMISTRY MODEL

To study the photochemistry in Pluto's atmosphere, we developed a coupled ion–neutral-photochemistry model for Pluto (Pluto INP). Pluto INP is a 1D photochemical model based

on our coupled Titan ion–neutral thermal (INT) model, which has been previously validated for Titan’s atmosphere (De La Haye et al. 2008; Mandt et al. 2012; Luspay-Kuti et al. 2015, 2016). In this section, we discuss the specific details of the Pluto INP model. For a detailed description of the Titan INT model, the reader is referred to the aforementioned papers.

2.1 Photochemistry

Pluto INP couples the ion and neutral chemistry by solving the continuity equation at each 10 km altitude grid from the surface up to 1800 km. It includes a total of 46 neutral and 29 ion species (Tables 1 and 2). Pluto INP uses the thermal profile of Gladstone et al. (2016), which is consistent with the line-of-sight *New Horizons* Alice transmission results (Fig. 1, left). We set the surface temperature to 37 K, consistent with the entry value from radio occultation data by *New Horizons* REX (Gladstone et al. 2016; hereafter G16).

2.1.1. Eddy diffusivity and vertical transport—In order to calculate the vertical atmospheric flux of each species, we had to determine the eddy diffusivity in Pluto’s atmosphere. The thermal and molecular diffusion coefficients in the flux equation were calculated the same way as for Titan (De La Haye et al. 2008). We determined the eddy diffusion coefficient (K) by fitting the measured CH_4 densities from G16. After testing a number of calculations, we found that what best matched the *New Horizons* data is the method used by Bell et al. (2010):

$$K = K_0 \sqrt{\frac{n_0}{n}}, \quad (1a)$$

where K_0 is the eddy diffusion coefficient at the surface, and n_0 and n are the total neutral number density at the surface and the total neutral number density at altitude z , respectively. The eddy diffusion coefficient increases from the surface until it reaches a maximum value K_{max} , then remains constant above this altitude. Our best eddy diffusion profile and the fit to the measured CH_4 density profile (G16) are shown in Fig. 2. We found that $K_0 = 10^6 \text{ cm}^2 \text{ s}^{-1}$ and $K_{\text{max}} = 3 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$ at $z = 160 \text{ km}$ satisfies the *New Horizons* data best. We discuss our eddy diffusivity results compared to other recent model results in Section 4.

The Jeans escape flux is self-consistently calculated for all species in Pluto INP. The exobase altitude for H and H_2 is determined separately from the other species. We find an exobase altitude of 1680 km (1620 km for H and H_2), close to the value of $1610 \pm 50 \text{ km}$ found by G16.

The initial lower boundary total density is set to 10^{15} cm^{-3} based on the modelled N_2 density in G16, and is allowed to increase at the lower boundary due to photochemistry. We found that this approach results in a more physical representation of the lower boundary total density than keeping it fixed, and yields an atmospheric scaleheight consistent with temperature.

2.1.2 Photon absorption—The chemistry in Pluto’s atmosphere is driven by the UV photon absorption, which dissociates and ionizes its atmospheric gases. Pluto INP employs

temperature-dependent high-resolution $^{14}\text{N}_2$, $^{14}\text{N}^{15}\text{N}$ and CO cross-sections. As shown for Titan, high-resolution photoabsorption cross-sections are important to use, because the cross-sections of these species are highly structured in the absorbing wavelengths and affects the hydrocarbon and nitrile chemistry (Liang et al. 2007b; Lavvas et al. 2011a; Mandt et al. 2012; Luspay-Kuti et al. 2015; Dobrijevic et al. 2016). While CH_4 is a major constituent in Pluto's atmosphere, its relevant cross-sections change slowly with wavelength. We used the high-resolution $^{14}\text{N}_2$ and $^{14}\text{N}^{15}\text{N}$ cross-sections from the coupled-channel Schrödinger equation (CSE) for a temperature of 70 K, and binned them into 0.03 Å bins in the wavelength range of 845 and 1000 Å. The spectroscopy underlying the CSE model of the N_2 photoabsorption spectrum is discussed in detail in Lewis et al. (2008) and Haverd et al. (2005), and the validity of the method is provided in Heays et al. (2011) and related publications. At longer wavelengths where high-resolution cross-sections were not available, we used low-resolution cross-sections in 50 Å bins (Fennelly & Torr 1992). The CO high-resolution cross-sections incorporated into Pluto INP were also calculated using CSE based on data collected by Visser, Van Dishoeck & Black (2009) to generate cross-sections between 900 and 990.99 Å (Å. Heays, personal communication). At shorter wavelengths (840.45–900 Å) there is insufficient laboratory data to determine the temperature dependence; therefore, we used the available coarse (variable sampling) resolution room temperature CO cross-section data sampled to 0.03 Å.

Pluto INP calculates the high-resolution solar flux for any solar radio flux ($F^{107\text{ cm}}$) value with a bin size of 0.1 Å using the HUEVAC model (Richards, Woods & Peterson 2006). For this study, we used $F^{107\text{ cm}} = 110$ s.f.u., which corresponds to the *New Horizons* flyby. We then interpolated the solar flux into 0.03 Å bin sizes to ensure consistency with the high-resolution cross-sections. *New Horizons* Alice observations presented in Gladstone, Pryor & Stern (2015) indicate that scattered solar Lyman α is important at Pluto; thus, we scaled the Lyman α photon flux by 1.43 as also done by Wong et al. (2017). Furthermore, to ensure the best possible comparison with *New Horizons* observations, we used the distance of Pluto from the Sun at the time of the *New Horizons* flyby (33.12 au) in our solar flux calculation.

The photodissociation and photoionization reactions in Pluto INP are listed in Table A1.

2.1.3 Chemistry—We model the chemical production and loss of molecules in Pluto's atmosphere via four types of chemical reactions: photodissociation and ionization, termolecular and bimolecular neutral reactions, ion–molecule reactions and electron recombination. Because of the similarities between the atmospheres of Pluto and Titan, the chemical schemes and reaction rate coefficients are based primarily on our Titan INT model (De La Haye et al. 2008; Mandt et al. 2012; Luspay-Kuti et al. 2015, 2016). However, CO is present in higher abundances in the atmosphere of Pluto than in the atmosphere of Titan (cf. Hörst, Vuitton & Yelle 2008; Lellouch et al. 2017), which necessitates the inclusion of CO reactions. We updated our chemical reaction list with the most important reactions affecting the production and loss of CO based on the total column production rates from the available literature (Krasnopolsky & Cruikshank 1999; Dobrijevic et al. 2016). A complete list of all Pluto INP reactions controlling the modelled chemistry of the 75 total neutral and ion species (Table 1) in Pluto's atmosphere is given in the Appendix (Tables A1–A5).

An inversion between ~200 and 400 km in the observed vertical profiles of the C₂ hydrocarbons (Fig. 4) suggests that processes other than chemistry may play an important role in Pluto's atmosphere (Wong et al. 2017). Hence, we incorporated condensation and aerosol sticking into Pluto INP, as described below.

2.2 Condensation

Condensation of particles depends on the availability of condensation nuclei, and requires that the partial pressure of an atmospheric constituent be greater than the saturation vapour pressure. Saturation pressures and densities for species known to be present in Pluto's atmosphere are shown in Fig. 3.

We incorporated into the model two different options to calculate the saturation vapour pressure of Pluto atmospheric constituents to evaluate the possible role of condensation with each method. The first method follows the expressions for saturated vapour pressure listed in table 2 of Willacy, Allen & Yung (2016) (hereafter W16), taken from Moses, Allen & Yung (1992) and Yaws (2007). The second method follows the analytical relation derived by Fray and Schmitt (2009) (hereafter F09), based on their extensive bibliographical review of experimental data. The coefficients of the polynomial expression of saturated vapour pressures are given in table 5 of F09.

Fig. 4 compares the saturated vapour densities calculated by the methods of W16 and F09 with observations of C₂ hydrocarbons made in Pluto's atmosphere. It is clear that the measured hydrocarbon densities are significantly lower than their saturation vapour pressures through most of the atmosphere in both the W16 and F09 scenarios, and that they will only condense near the surface. The only exception is C₂H₂ when calculating the saturation vapour pressure according to W16. In this scenario, C₂H₂ may condense between about 300 and 500 km.

The loss rate via condensation of a given molecule is then calculated based on the collision rate between the molecule and aerosol particles, and is given by W16 as

$$L_{\text{cond}} = \alpha \sigma v_{\text{th}} (n - n_{\text{sat}}), \quad (1b)$$

where α is the condensation coefficient describing the efficiency of condensation of the molecule onto a pre-existing aerosol particle, σ is the mean surface area of aerosols per volume (cm⁻¹), v_{th} (cm s⁻¹) is the thermal velocity of the molecule (cm s⁻¹), and n and n_{sat} (cm⁻³) are the molecule's density and saturation vapour density, respectively. We note that HCN, HC¹⁵N and HC₃N are also allowed to condense in the model. Because HCN is supersaturated in Pluto's atmosphere (Lellouch et al. 2017), condensation will play a role in shaping its vertical profile (Mandt et al. 2017). These nitrile species are important in the incorporation of nitrogen into haze particles, and are discussed in our companion paper by Mandt et al. (2017). We also calculate the saturation vapour pressure of CO, and note that based on our simulated density, CO will not condense in the model above the surface.

2.3 Incorporation into aerosols

Molecules colliding with aerosols could be permanently lost through incorporation into these particles. This process is different from condensation where aerosol particles act as condensation nuclei, and is independent of the saturation vapour pressure discussed in the previous section. Incorporation into aerosols happens when molecules collide with aerosol particles and physically stick to them, which results in their permanent loss (Willacy, Allen & Yung 2016). In this study, we evaluate the role that aerosols play in the altitude profiles of the C₂ hydrocarbons in Pluto's atmosphere. We use the aerosol properties inferred by Gao et al. (2017) from *New Horizons* observations (Gladstone et al. 2016), and also estimate the sticking of hydrocarbons to aerosols based on the methods outlined in Dimitrov & Bar-Nun (2002, 2003). However, we do not complete an independent simulation of the growth of aerosols as was done by Dimitrov & Bar-Nun (2002) or Lavvas et al. (2011b).

Laboratory studies have shown that aerosols are generally sticky when they first form, but as they grow larger over time they harden due to cross-linking and chain elongation of the polymer bonds through UV radiation and particle impact (Dimitrov & Bar-Nun 2002, 2003; Bar-Nun et al. 2008). This hardening by ageing makes aerosols less sticky. Dimitrov & Bar-Nun (2002) propose that the ageing process can be represented as an averaged index taking the form of a second-order chemical reaction, where the reaction rate, k is a function of the temperature, T , and the Van der Waals forces, E

$$k = D \exp(-E/RT) \quad (2)$$

where D is a constant. Although k is kinetically a rate coefficient, it effectively functions as a scaling of the coagulation and coalescence efficiency.

We calculate the loss rate of molecules by sticking to aerosols as

$$L_{\text{as}} = \beta v_{\text{th}} \sigma n = C A_{\text{scale}} v_{\text{th}} \sigma n, \quad (3)$$

where L_{as} (cm⁻³ s⁻¹) is the loss rate of C₂ hydrocarbons as a result of sticking to aerosols, β is the sticking efficiency, v_{th} (cm s⁻¹) is the thermal velocity of the molecule, σ (cm⁻¹) is the mean surface area of aerosols per volume and n is the atmospheric density of the molecule at a given altitude. We use the altitude-dependent σ values derived by Gao et al. (2017), which show an increase in the aerosol surface area with decreasing altitude (Fig. 5, left).

The hardening/aging process of aerosols is taken into account via the sticking efficiency (β), which is a combination of (i) the probability of a given hydrocarbon sticking to an aerosol, represented in our loss rate by the variable C , and (ii) the general stickiness of the receiving aerosol particles represented in our loss rate by an altitude-dependent scaling factor A_{scale} . We determine the sticking parameters (C and A_{scale}) by empirical fits to the *New Horizons* hydrocarbon observations. We first empirically constrained the scaling factor A_{scale} (Fig. 5) to get the best fit for the altitude dependence of the general dropout in the C₂ hydrocarbon profiles observed above 200 km. This step involved the testing of multiple different

equations for A_{scale} through numerous simulations until the equation that best reproduced the general dropout associated with the inversion in all C_2 profiles was found. Once the general trend of the inversion was reproduced, we then varied the sticking efficiency (C) until we obtained the best fit to each of the observed individual hydrocarbon profiles, and determined $C(C_2H_2) = 5.15 \times 10^{-4}$; $C(C_2H_4) = 1.13 \times 10^{-3}$; $C(C_2H_6) = 3.20 \times 10^{-4}$. This means that in our model the aerosol aging/hardening process is represented as a function of altitude rather than by temperature as is indicated by equation (2) of Dimitrov & Bar-Nun (2002). The sticking efficiency of the aerosols as a function of altitude, A_{scale} , is shown in Fig. 5, while the total sticking efficiency, β , for each of the C_2 hydrocarbons is shown in Fig. 6.

On Titan, aerosols are thought to form from the conversion of unsaturated molecules via the Diels–Alder synthesis (Dimitrov & Bar-Nun 2002, 2003). In this process, triple and double bonds of the unsaturated compounds open either spontaneously, or under an external effect (e.g. UV photolysis, particle impact), and form radicals. These radicals initiate chain reactions in which the unsaturated compounds are added to the chain, producing various polymers and telomers. As intra- and intermolecular unsaturated double and triple bonds close in the aerosols (annealing or ageing), the aerosols harden due to cross-linking and chain elongation of the polymer bonds. It is important to note though that the microphysics of Pluto's aerosols after the C_2 hydrocarbon sticking is beyond the scope of this paper. For the purpose of this work, we are only concerned about the C_2 hydrocarbons being permanently removed from the atmosphere by the process of aerosol trapping in order to try to match the *New Horizons* profiles. Once these hydrocarbons stick to the aerosol particles, we are not concerned about their successive evolution; i.e. what fraction of them remains adsorbed and/or gets fully incorporated into the aerosol particles via chemical bonds.

3 HYDROCARBONS ON PLUTO

To evaluate the dominant production and loss processes of C_2 hydrocarbons in Pluto's atmosphere, with special emphasis on the role of aerosol interaction in their altitude profiles, we ran the full photochemical model in four configurations: (a) chemistry only, (b) chemistry and condensation with saturation pressures from W16, (c) chemistry, condensation with saturation pressures from W16, and incorporation into aerosols and (d) chemistry, condensation with saturation pressures from F09, and incorporation into aerosols (Table 3). The lower boundary C_2 densities were set to an initial value that produced the appropriate altitude profiles above 500 km and then were allowed to float based on production and loss processes calculated in the model. We only fit the model in the altitude range where the *New Horizons* data well constrains the hydrocarbon profiles. Atmospheric absorption during the solar occultation resulted in distinct altitude regions within which each species was well-constrained. At higher altitudes, the line-of-sight (LOS) abundances of each absorber (and thus its contribution to UV absorption) may be too low to detect relative to the background, and only upper limits may be obtained. At lower altitudes, the wavelength-dependent transmission of sunlight approaches zero, resulting in an ability to place only lower limits on each species depending on which wavelengths they absorb most strongly at. For these reasons, we are not concerned about the model fit at the very low and very high altitudes as defined above in this work. Based on the solar UV emission spectrum

as well as each species' absorption cross-section and relative abundance in Pluto's atmosphere, the approximate altitude regions for which each species is well-constrained (including lower limits) are N_2 , 900–1100 km; CH_4 , 80–1200 km; C_2H_2 , 0–600 km; C_2H_4 , 0–650 km; C_2H_6 , 40–550 km; haze, 0–300 km (J. Kammer, personal communication).

Fig. 7 compares the results with each model configuration to the local densities of C_2 hydrocarbons derived from *New Horizons*. The inversion in the profiles indicates a significant non-chemical loss process between ~100 and 400 km. With the inclusion of condensation and aerosol trapping we are able to reproduce the observed vertical profiles in the altitudes range where the data of the studied species are well-constrained, as described above. It is apparent from Fig. 7 that (i) condensation only (configuration 'b') cannot reproduce the observed inversion in any of the C_2 hydrocarbon profiles and (ii) there is no difference between the results of configurations 'c' and 'd'. This suggests that the difference in the method of saturation vapour pressure calculation does not affect the model output, most likely because condensation has minimal effect on the C_2 hydrocarbon altitude profiles. As shown in Fig. 4, the only altitude region where condensation might occur is between 300 and 500 km, and only for C_2H_2 if saturation is modelled following W16. Yet, there is no perceivable (or even statistically significant) difference in the profile plots presented in panels 'a' and 'b', and between 'c' and 'd' in the 300–500 km range. In fact, we tested a number of condensation coefficients (α) for C_2H_2 spanning an order of magnitude from $\alpha_{\text{C}_2\text{H}_2} = 10^{-5}$ to 10^{-4} for configuration 'b' to investigate its potential effect on the C_2H_2 profile. Surprisingly, we found no effect of α on the C_2H_2 profile in the altitude range where the inversion occurs, even for a value as high as 10^{-4} (shown in Fig. 7). The high condensation coefficient only has an effect in the lowest altitudes though, where condensation becomes more important. This strongly implies that the dominant loss process that defines the altitude profiles below 500 km is sticking to aerosols rather than condensation.

While Pluto INP calculates the local density of each species as a function of altitude, it is important to note that the local densities shown in G16 and Wong et al. (2017) were derived from the LOS abundances measured by *New Horizons* Alice. The fundamental quantity measured during the Alice UV solar occultation was not local density, but rather each species' LOS column abundance. It is therefore most straightforward (and statistically robust) to compare our model results in those terms as well. We converted our model local densities (cm^{-3}) to LOS column abundances (cm^{-2}) using the Abel transform. For simplicity, we assumed during calculation of the Abel transform that the atmosphere was locally spherically symmetric. Although the model has an upper boundary of 1800 km altitude, we assume an exponential decrease in density of each species above this region in order to perform the Abel transform calculation. The results are shown in Fig. 8.

As shown in Fig. 8, we also get a great agreement with the LOS abundance data using both model configurations with condensation and sticking to aerosols. It is interesting though that the goodness of the fit for the individual hydrocarbon species is slightly different. Most notable is C_2H_4 , for which we get an excellent match with the calculated LOS abundance, but the model underestimates its local density at about 120 km. This likely points to a reduced ability to constrain the lower limit of local density minima using LOS profiles, as

altitudes of relatively higher density above the local minimum effectively mask information about the depleted layer.

Figs 9–11 show the contribution of the various loss processes to the total loss of the three C_2 hydrocarbons. These figures clearly demonstrate that for each of the C_2 hydrocarbons, aerosol trapping dominates the loss process between ~50 and 500 km. Above 500 km the total surface area of the aerosols is close to zero (Gao et al. 2017), and no sticking is assumed to remove the C_2 hydrocarbons. At altitudes lower than ~50 km, the relative importance of condensation increases, and it becomes the most important loss process near the surface. Even though production from neutral chemistry is high near the surface, the increased loss rates from condensation surpass the total production by about four orders of magnitude (Figs 13–15). Between 500 and 950 km, bimolecular neutral reactions are the primary contributors to both C_2 hydrocarbon production and loss. In this altitude range, loss occurs at a significantly lower rate than production (Figs 13–15). Starting at altitudes higher than 500 km, loss through ion–molecule reactions increases, and is expected to dominate loss above 1100 km. The total ion density is shown in Fig. 12, and is below the estimated upper limit of $\sim 1500 \text{ cm}^{-3}$ (McComas et al. 2016). In fact, above 500 km, photochemical loss rates increase while production rates decrease. Nevertheless, the ratios presented in Figs 13–15 show that above 500 km the total production rate is higher than the total loss rate. The loss rates by aerosol sticking (in s^{-1} , independent of the atmospheric density profiles) are shown in Fig. 16.

In summary, our results show that sticking to aerosol particles is the dominant process shaping the vertical profiles in the altitude range where the *New Horizons* local densities as shown in G16 and Wong et al. (2017) are most accurate.

4 DISCUSSION

4.1 Atmospheric dynamics

Fitting the hydrocarbon profiles, in particular, the CH_4 profile, provides information about atmospheric dynamics, such as the eddy diffusivity. The eddy diffusion coefficient we found that works best with the *New Horizons* data is quite different from the eddy diffusion coefficient proposed by Wong et al. (2017) (Fig. 2). When we run Pluto INP with the low eddy diffusion coefficient of $K = 1000 \text{ cm}^2 \text{ s}^{-1}$ derived by Wong et al. (2017), we cannot reproduce the *New Horizons* measurements, as illustrated in Fig. 2. However, our best-fitting eddy diffusion coefficients are in very good agreement with those in G16 (7.5×10^5 and $3 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$ for K_0 and K_{max} , respectively), with our surface value being only a factor of 1.3 higher. Our results are also close to the value of $10^6 \text{ cm}^2 \text{ s}^{-1}$ used by Lellouch et al. (2017) above 200 km. The only way we are able to achieve a good fit to the CH_4 data by using the constant formulation of Wong et al. (2017) is if we increase the eddy diffusion coefficient by a factor of 500 from 1000 to $5 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$ (Fig. 2). However, due to the limited details provided about the model in Wong et al. (2016), it is not clear at this point how the same set of observations can be fit by models using the same diffusion equation yet applying eddy diffusion coefficients that are a factor of 500 different.

4.2 C₂ hydrocarbon loss processes

The lack of difference between the simulations with the two different saturation density methods (Pluto INP simulations ‘c’ and ‘d’) suggests that condensation is not an important process in the altitude range where the C₂ density inversion occurs. In fact, our results show that the process of aerosol trapping is the most efficient sink to C₂ hydrocarbons between ~30 and 500 km, and shapes the altitude profiles of C₂ hydrocarbons in the altitude range where the available *New Horizons* observations are most accurate. Contrary to the results stated in Wong et al. (2017), our results show that condensation is not responsible for the inversion between 200 and 400 km, and cannot explain the shape of the C₂ vertical profiles. This is because in all cases but one (C₂H₂) the saturation vapour densities of C₂ hydrocarbons are significantly higher than their atmospheric densities (Fig. 4); thus, they will not condense in the atmosphere, or onto the surface of aerosol particles between 200 and 400 km. Instead, in all these cases the C₂ hydrocarbons must be permanently removed from the atmosphere by sticking to aerosol particles. This sticking is so efficient that it absolutely dominates loss in this altitude range. Even in our configuration ‘c’ where C₂H₂ does become saturated between 200 and 400 km, loss via aerosol trapping dominates loss by condensation (Fig. 9). When taken in isolation, we find that condensation alone is not sufficient enough to lead to the observed density inversion of C₂H₂, or the other C₂ hydrocarbons. The insignificance of condensation for the C₂ density inversion is further demonstrated by the lack of difference between the chemistry only (configuration ‘a’) and chemistry and condensation (configuration ‘b’) runs shown in Fig. 7. Not even a condensation coefficient ($\alpha_{\text{C}_2\text{H}_2} = 10^{-4}$) significantly higher than the value of 2×10^{-5} reported to work by Wong et al. (2017) for the only condensable species, C₂H₂, makes a difference in the C₂H₂ profile in the altitude range where the inversion occurs.

Our configuration ‘c’ employs expressions for the C₂ hydrocarbon saturation vapour pressures from W16, extrapolated down to Pluto temperatures. All these expressions but one (for C₂H₆ at temperatures higher than 90 K) are the same as the expressions in Moses, Allen & Yung (1992), which is also what was used by Wong et al. (2017). While we do use a different expression for calculating the saturation vapour pressure of C₂H₆ above 90 K [Yaws (2007) following W16] in our configuration ‘c’, this only results in a slight discrepancy (a factor of ~1.2 at 50 km) in the C₂H₆ saturation vapour pressures between our work and Wong et al. (2017). This slight discrepancy cannot account for the reported condensation of C₂H₆ in Wong et al. (2017). In addition, since Wong et al. (2017) employs the same expressions for the calculation of the C₂H₂ and C₂H₄ saturation vapour density as we do in our configuration ‘c’, it is unclear how these species are able to condense in their model. They proposed that in order to reproduce the inversion of C₂H₄, its saturation vapour pressure must be lower than what would result from extrapolation under the low temperature conditions of Pluto’s atmosphere. The authors suggest that the saturation vapour pressure of C₂H₄ is the same as that of C₂H₂ in order to be able to reproduce the C₂ hydrocarbon profiles. However, the detailed work of F09, which is the most comprehensive study to date based on their thorough review of all published laboratory data, and empirical and thermodynamic relations, shows no indication for such behaviour of the C₂H₄ vapour pressure.

Our results do not require the assumption of Wong et al. (2017) to reproduce the density inversion. Instead, we are able to reproduce the inversion with simulating the sticking of molecules to aerosol particles – a clear indication of the high importance of this physical process in the atmosphere of Pluto.

The transition between the chemistry-dominated and aerosol-sticking-dominated regimes occurs very abruptly, as seen in Figs 9–11. This happens because the *New Horizons* aerosol profile employed in our model shows that the aerosol density is negligible above ~500 km. However, our results clearly show that sticking to aerosols is a very effective loss process, which suggests that even a small amount of aerosols (perhaps below the *New Horizons* detection limit) present may make a difference in the C₂ hydrocarbon profiles. If there were significant sticking to aerosols occurring above 500 km, then the altitude where the inversion on the C₂ profiles occurs would be shifted to higher altitudes. None the less, the altitude where the inversion occurs coincides with the altitude where aerosols ‘appear’ based on the *New Horizons* data. Therefore, the *New Horizons* data imply that no significant sticking is occurring above 500 km.

4.3 Observed ageing of aerosols

By reproducing the observed C₂ hydrocarbon profiles, we were able to empirically determine the stickiness of aerosol particles as a function of altitude (Fig. 5). Our results show that in order to be able to fit the C₂ densities determined from *New Horizons* observations, the stickiness of aerosols must decrease with decreasing altitude, with a profile shown in Fig. 5. This is an important result, as it indicates that aerosols do indeed harden, i.e. become less sticky as they age in Pluto’s atmosphere, as predicted by the aging kinetics model of Dimitrov & Bar-Nun (2002) for Titan’s aerosols.

Based on how well our model simulations agree with observations above ~50 km, we predict an abrupt change in loss at ~500 km, above which the aerosol density is negligible. Thus, the atmosphere of Pluto can be divided into three regimes based on the importance of a given physical/chemical process: (i) a photochemistry-dominated upper layer (>500 km), (ii) a mid-layer dominated by aerosol trapping (30–500 km) and (iii) a lower layer dominated by condensation (<30 km). Given the limitations of available observations near the surface and the lack of published uncertainties on the data, it is difficult to tell if the sudden change in the dominant processes affects the vertical profiles in the lower atmospheric layers. We also note that the obvious worse agreement between model and shown data is partially due to the coarse resolution of our model at the lowest altitudes. Model results in this lower altitude range will be re-evaluated as updated *New Horizons* profiles and a full analysis of the profile uncertainty become available in the literature.

What is most important to note is that while the total aerosol surface area per volume increases with decreasing altitude down to near the surface (Gao et al. 2017), the stickiness of the aerosol particles themselves, and the sticking efficiency of C₂ hydrocarbons decrease with decreasing altitude (Figs 5 and 6). Therefore, the sticking efficiency of C₂ hydrocarbons is inversely related to the aerosol surface area. This result is consistent with the fundamental conclusion of the simulations of Dimitrov & Bar-Nun (2002) regarding the life cycle of hydrocarbon aerosols in Titan’s atmosphere, wherein stickiness decreases as the

coalescence becomes more dominant. Coalescence becomes dominant as the total coagulated particle size of the aerosol increases, while the size of aerosol is directly related to the number of previous collisions resulting in coagulation. Likewise, we find that in Pluto's atmosphere aerosols undergo a process of growing, ageing, and descending to the surface.

5 SUMMARY AND CONCLUSIONS

With our coupled ion–neutral-photochemistry model developed for the atmosphere of Pluto, we were able to closely match the observed density profiles of CH₄, N₂ and the C₂ hydrocarbons in the altitude range where observations for each species are most accurate. Our results imply that the eddy diffusion coefficient for Pluto's atmosphere must be high ($\sim 10^6 \text{ cm}^2 \text{ s}^{-1}$) and altitude dependent below 200 km (Fig. 2). Our altitude-dependent eddy diffusion coefficient is in quantitative agreement with G16, and qualitative agreement with Lellouch et al. (2017) matching their actual values within a factor of 3, but is a factor of 500 higher than that reported by Wong et al. (2017).

In order to reproduce the C₂ profiles observed by *New Horizons*, we have to consider that these hydrocarbons stick to the aerosols with a specific efficiency empirically determined by our model simulations. Condensation alone cannot account for the shape of the vertical profiles, as the number densities of all but one of the C₂ hydrocarbons are systematically lower than their corresponding saturation vapour densities. Furthermore, not even increasing the condensation coefficient by an order of magnitude for the only condensable species, C₂H₂, changed the results, indicating the relative unimportance of condensation. Instead, C₂ hydrocarbons are removed from the atmosphere primarily by incorporation into aerosols via sticking between 200 and 500 km, which is a significantly more effective process in the atmosphere of Pluto than condensation on particle surfaces.

We empirically determined the stickiness of aerosol particles as a function of altitude in order to reproduce the C₂ vertical profiles derived from *New Horizons* observations. We found that in Pluto's atmosphere the stickiness of aerosols is inversely related to the surface area of aerosols, which has been inferred from observation to increase as altitude decreases (Gao et al. 2017). Our results suggest that aerosols harden and become less sticky as they age in Pluto's atmosphere. This suggests that, similarly to Titan, the aerosols in Pluto's atmosphere undergo a process of growing, ageing and descending to the surface. Our calculations show that this process is both necessary and sufficient to explain the vertical profiles of C₂ hydrocarbons in Pluto's atmosphere.

The results of our work raise important questions about what happens to the C₂ hydrocarbons after they stick to the aerosol particles. Investigating the details of the physical nature of C₂ hydrocarbons and aerosol particles after the sticking is a natural next step to this work, and is to be explored in the future.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
Temperature profile used in the Pluto INP model (from G16).

Figure 2.

Left: Comparison of eddy diffusivity profiles in Pluto INP (black solid) with that in Wong et al. (2017) (MW16; dashed), Lellouch et al. (2017) (L16, grey) and Gladstone et al. (2016) (G16; dotted). Right: Comparison of various modelled altitude profiles to the observed *New Horizons* data (NH). We are able to closely match the observed CH_4 profile (circles) with the Pluto INP eddy diffusion coefficients. Also shown is the Pluto INP simulation using the constant eddy diffusivity profile from MW16, and the modelled profile when we increase the MW16 eddy diffusion coefficient by a factor of 500 to $5 \times 10^5 \text{cm}^2 \text{s}^{-1}$

Figure 3. Saturation vapour pressure (left-hand panel) and density (right-hand panel) for constituents known to be present in the atmosphere of Pluto. The solid and dashed lines are saturation vapour pressures calculated following Willacy, Allen & Yung (2016) and Fray and Schmitt (2009), respectively.

Figure 4.

Comparison of the saturation vapour densities of methane (top) and the C_2 hydrocarbons (bottom) present in Pluto's atmosphere with the *New Horizons* data.

Figure 5.

Left: Mean surface area of aerosols per volume from Gao et al. (2017). Right: Aerosol stickiness determined through empirical fits to the *New Horizons* data. The aerosol density is negligible above 500 km; thus, the stickiness is not shown.

Figure 6. Sticking efficiencies, β , of C_2 hydrocarbons determined through empirical fits to the *New Horizons* data. The sticking efficiency above 500 km is not shown, as the aerosol density is negligible at those altitudes.

Figure 7.

Comparison of model results (solid) to *New Horizons* (NH) observations (circles) for C₂ hydrocarbons for the four model configurations. Top left: chemistry only; top right: chemistry, condensation (W16); bottom left: chemistry, condensation (W16) and aerosol sticking; bottom right: chemistry, condensation (F09) and aerosol sticking. The filled circles indicate where the *New Horizons* data is well constraining for each hydrocarbon.

Figure 8.

Comparison of LOS model abundance (solid) to the LOS column abundance from *New Horizons* Alice for three model configurations. Left: chemistry only; middle: chemistry, condensation (W16) and aerosol sticking; right: chemistry, condensation (F09) and aerosol sticking.

Figure 9.

C_2H_2 loss rate from various types of chemistry/processes (left), and their fractional contribution to the total C_2H_2 loss (right) with configurations 'c' (top) and 'd' (bottom).

Figure 10.

C_2H_4 loss rate from various types of chemistry/processes (left), and their fractional contribution to the total C_2H_4 loss (right) with configurations 'c' (top) and 'd' (bottom).

Figure 11.

C_2H_6 loss rate from various types of chemistry/processes (left), and their fractional contribution to the total C_2H_6 loss (right) with configurations 'c' (top) and 'd' (bottom).

Figure 12.
Total ion density from Pluto INP as a function of altitude.

Figure 13.
Production to loss rate ratio of C_2H_2 from various types of chemistry for configuration 'c'.

Figure 14.
Production to loss rate ratio of C_2H_4 from various types of chemistry for configuration 'c'.

Figure 15.
Production to loss rate ratio of C_2H_6 from various types of chemistry for configuration 'c'.

Figure 16.
Loss rates of C_2 hydrocarbons by aerosol trapping for configuration 'c'.

Table 1.

List of the 46 neutral species in the Pluto INP model. Photon absorbing species in the model are marked in boldface.

H, H₂
C, CH, ¹ CH ₂ , ³ CH ₂ , CH₃ , CH₄
C ₂ , C ₂ H, C₂H₂ , C₂H₄ , C ₂ H ₅ , C ₂ H ₆
C ₃ H ₆ , C ₃ H ₇ , C₃H₈
C₄H₂
N(⁴ S), N(² D), N(² P), ¹⁵ N, ¹⁵ N(² D), N ₂ , ¹⁴ N ¹⁵ N
CN, C ¹⁵ N, C ₂ N ₂
NH, ¹⁵ NH, NH ₃
HCN , HC¹⁵N , H ₂ CN, H ₂ C ¹⁵ N, HC ₃ N, CH ₃ CN, CH ₃ C ₂ H, C ₃ H ₃ N, C ₃ H ₅ N, CH ₃ NH ₂
Ar
CO , HCO, H₂CO , O

Table 2.

List of the 29 ion species in the Pluto INP model.

H^+ , H_2^+ , H_3^+
CH^+ , CH_2^+ , CH_3^+ , CH_4^+ , CH_5^+
C_2H_2^+ , C_2H_3^+ , C_2H_4^+ , C_2H_5^+
cC_3H_3^+ , C_3H_5^+ , C_3H_7^+
C_5H_5^+
N^+ , $^{15}\text{N}^+$, N_2^+ , $^{14}\text{N}^{15}\text{N}^+$
NH^+ , $^{15}\text{NH}^+$, N_2H^+
HCN^+ , HC^{15}N^+ , HCNH^+ , $\text{HC}^{15}\text{NH}^+$
CO^+ , HCO^+

Table 3.

Pluto INP configurations for model simulations. P_{sat} is the saturation vapour pressure.

Model configuration	Condensation (P_{sat} method)	Aerosol trapping
a	No	No
b	W16	No
c	W16	Yes
d	F09	Yes