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Photochemistry on Pluto: part II HCN and nitrogen isotope fractionation

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Abstract

We have converted our Titan one-dimensional photochemical model to simulate the photochemistry of Pluto's atmosphere and include condensation and aerosol trapping in the model. We find that condensation and aerosol trapping are important processes in producing the HCN altitude profile observed by the Atacama Large Millimeter Array (ALMA). The nitrogen isotope chemistry in Pluto's atmosphere does not appear to significantly fractionate the isotope ratio between N₂ and HCN as occurs at Titan. However, our simulations only cover a brief period of time in a Pluto year, and thus only a brief portion of the solar forcing conditions that Pluto's atmosphere experiences. More work is needed to evaluate photochemical fractionation over a Pluto year. Condensation and aerosol trapping appear to have a major impact on the altitude profile of the isotope ratio in HCN. Since ALMA did not detect HC¹⁵N in Pluto's atmosphere, we conclude that condensation and aerosol trapping must be much more efficient for HC¹⁵N compared to HC¹⁴N. The large uncertainty in photochemical fractionation makes it difficult to use any potential current measurement of ¹⁴N/¹⁵N in N₂ to determine the origin of Pluto's nitrogen. More work is needed to understand photochemical fractionation and to evaluate how condensation, sublimation and aerosol trapping will fractionate N₂ and HCN.

Keywords

Kuiper belt objects; individual; Pluto – planets and satellites; atmospheres – planets and satellites; composition – planets and satellites; individual; Titan

1 INTRODUCTION

Molecular nitrogen is the most abundant molecule in the atmospheres of Pluto and Saturn's moon Titan. The presence of methane in each atmosphere allows complex photochemistry

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initiated by the photodissociation of nitrogen and methane that leads to the production of complex organic aerosols. These aerosols form layers of haze in each atmosphere that eventually precipitate on the surface. The composition of this haze is of great interest to the astrobiology community because the presence of nitrogen in the organic molecules could lead to the production of prebiotic molecules (e.g. Neish et al. 2009; Imanaka & Smith 2010). However, the process of incorporating nitrogen into aerosols is poorly understood.

Laboratory studies simulating the production of aerosols in Titan-like conditions have shown that hydrogen cyanide, or HCN, plays an essential role in the incorporation of nitrogen into aerosols (Imanaka & Smith 2010). HCN also acts as an important coolant in any atmosphere (Yelle 1991) and can have a major impact on the energy balance.

The *New Horizons* fly-by of Pluto demonstrated that the energy balance of outer solar system atmospheres is far more complex than expected (Stern et al. 2015). The upper atmosphere of Pluto was predicted to have temperatures that were high enough to cause thermal escape of nitrogen (Strobel 2008; Tucker et al. 2012). However, the Alice Ultraviolet Spectrometer (Alice-UVS; Stern et al. 2008) on *New Horizons* found that the upper atmosphere of Pluto was much cooler than expected and that nitrogen was escaping from the atmosphere at rates that are three orders of magnitude lower than expected (Gladstone et al. 2016). Observations of the HCN abundance made by the Atacama Large Millimeter Array (ALMA) show that HCN cooling is not likely to be sufficient to explain these low temperatures and that the energy balance in Pluto's atmosphere is more complex than current understanding can explain (Lellouch et al. 2017). Because HCN plays such an important role in the atmospheres of Pluto and Titan, it is critical to understand the processes that determine the abundance of this molecule in these atmospheres.

The exact abundance of HCN in the atmospheres of Pluto and Titan is at the present time poorly understood. Many attempts have been made to measure HCN in Titan's atmosphere, but observed abundances can vary by as much as two orders of magnitude in a single altitude range (see fig. 1 of Luspay-Kuti et al. 2015). A detailed analysis of Cassini Ion Neutral Mass Spectrometer (INMS; Waite et al. 2004) data from 49 Titan fly-bys shows abundance variability of up to a factor of 3 in HCN abundance in the upper atmosphere and a clear diurnal variation (Cui et al. 2016). This suggests both that measuring HCN is challenging and that the production and loss of HCN in Titan's atmosphere is highly variable. The recent observations of HCN in Pluto's atmosphere by ALMA are even more unexpected and show that HCN is supersaturated in the upper atmosphere of Pluto with abundances that are up to eight orders of magnitude greater than the saturation vapour pressure (Lellouch et al. 2017). In order to improve our understanding of these most recent observations of Pluto's atmosphere, we apply our experience with nitrogen chemistry in Titan's atmosphere to evaluate the processes that will influence the abundances of HC^{14}N and HC^{15}N in Pluto's atmosphere.

To begin with, the isotopic composition observed in N_2 and HCN in Titan's atmosphere provides an important constraint on processes affecting the abundance of HCN (Liang et al. 2007; Mandt et al. 2009, 2014). In Titan's atmosphere, the isotope ratio, $^{14}\text{N}/^{15}\text{N}$, of N_2 and HCN are 167.7 ± 0.6 and 68.6 ± 15.7 , respectively (see Table 1 for references). These ratios

differ by more than a factor of 2 because HCN is significantly enriched in ^{15}N relative to N_2 as a result of the process of photochemical self-shielding. This process occurs because the photodissociation cross-section of $^{14}\text{N}^{15}\text{N}$ is offset in wavelength from the cross-section of $^{14}\text{N}_2$. This allows photons that dissociate $^{14}\text{N}^{15}\text{N}$ to penetrate to lower altitudes in the atmosphere, while the photons that dissociate $^{14}\text{N}_2$ are absorbed at higher altitudes. This will free up more ^{15}N to participate in neutral chemistry that is dominant at lower altitudes, allowing it to be preferentially incorporated into HCN (Liang et al. 2007). Although the same process is expected to be effective at Pluto (Mandt et al. 2016), ALMA did not detect the isotopologue HC^{15}N , which sets a limit for the nitrogen isotope ratio, $^{14}\text{N}/^{15}\text{N}$, in Pluto's HCN of > 125 (Lellouch et al. 2017). The non-detection of HC^{15}N could be caused by one of the following: (1) $^{14}\text{N}/^{15}\text{N}$ in N_2 is too high to produce a $^{14}\text{N}/^{15}\text{N}$ in HCN that is lower than 125; (2) photochemical fractionation is less effective at Pluto; or (3) other processes are at work countering any effect of photochemical fractionation. We attempt to evaluate these possibilities through photochemical simulations of the nitrogen chemistry in Pluto's atmosphere.

Thanks to the successful fly-by of Pluto by *New Horizons* (Stern et al. 2015), altitude profiles of N_2 , CH_4 and the C_2 hydrocarbons are now available (Gladstone et al. 2016) to provide constraints for photochemical models seeking to simulate nitrogen isotope fractionation in Pluto's atmosphere. One of the major outcomes of these observations has been the discovery that condensation and aerosol sticking play a significant role in the altitude profiles of the C_2 hydrocarbons (Gladstone et al. 2016; Luspay-Kuti et al. 2017; Wong et al. 2017) as well as the HCN altitude profile (Lellouch et al. 2017; Wong et al. 2017). However, the exact influence of condensation and aerosol sticking on the HCN isotope ratio is not known.

We have adapted our Titan Ion-Neutral-Thermal model (Titan-INT; De la Haye et al. 2008; Mandt et al. 2012a; Luspay-Kuti et al. 2015, 2016) to Pluto's atmosphere in order to investigate the role of chemistry, condensation and aerosol sticking on the isotope ratio of HCN in Pluto's atmosphere. The details of the Pluto Ion-Neutral-Photochemical (Pluto-INP) model are provided in companion paper Luspay-Kuti et al. (2017).

2 MODELLING ALTITUDE PROFILES OF HCN

The altitude profiles of a species in an atmosphere vary based on vertical and horizontal transport processes as well as altitude-dependent production and loss rates. When simulating the chemistry in an atmosphere in one dimension (1D), we use the following equation to determine the altitude profile of a species, s

$$\partial n_s / \partial t + \frac{1}{r^2} \frac{\partial (r^2 n_s \omega_s)}{\partial r} = P_s - L_s, \quad (1)$$

where n_s is the density of the species, t is the time, r is the distance from the centre of the body, P_s and L_s are the production and loss rates and ω_s is the vertical velocity of the species.

There are a number of processes expected to be playing a role in the altitude profile of HC^{14}N and HC^{15}N in Pluto's atmosphere. At Titan, production and loss of HCN are dominated by chemistry. However, observations of Pluto's atmosphere have shown that condensation (Wong et al. 2017) and sticking to aerosols (Luspay-Kuti et al. 2017) play an important role in the observed altitude profiles of the C_2 hydrocarbons. Lellouch et al. (2017) found that HCN is supersaturated in the upper atmosphere and follows a profile similar to that of the saturation vapour pressure in the lower atmosphere. Therefore, condensation of HC^{14}N is also important at Pluto. In the following sub-sections, we provide a detailed description of each process that may contribute to the altitude profile of HC^{14}N and HC^{15}N in Pluto's atmosphere and provide a comparison with what we know about these molecules in Titan's atmosphere.

2.1 Dynamics

Dynamics play an important role in the altitude profiles of atmospheric constituents and are accounted for by the vertical velocity, ω_s , in equation (1). The vertical velocity is calculated using diffusion coefficients and may be influenced by atmospheric escape if a species is light enough to easily escape the atmosphere.

The vertical velocity can be evaluated using the steady-state diffusion equations of minor constituents (Banks & Kockarts 1973). It is the sum of the velocity due to eddy diffusion, ω_s^K , and bimolecular diffusion, ω_s^D (De la Haye et al. 2008)

$$\omega_s = \omega_s^D + \omega_s^K = -D_s \left[\frac{1}{n_s} \frac{\partial n_s}{\partial r} + \frac{1}{H_s} + (1 + \alpha_T) \frac{1}{T} \frac{\partial T}{\partial r} \right] - K \left[\frac{1}{n_s} \frac{\partial n_s}{\partial r} + \frac{1}{H_a} + \frac{1}{T} \frac{\partial T}{\partial r} \right], \quad (2)$$

where D_s is the binary diffusion coefficient for the species, K is the eddy diffusion coefficient, H_a is the atmospheric scale height and H_s the scale height of species s , α_T is the thermal diffusion factor and T is the temperature. When the vertical velocity is nonzero, there is an upward or downward flux of the species. In some cases, this can lead to escape from the atmosphere. Escape of species from Pluto's atmosphere was found to be occurring due to Jeans escape (Gladstone et al. 2016), which is a slow evaporation due to thermal processes.

Binary diffusion represents non-turbulent flow of one species through another species of gas. This process depends on the major and minor species of gas as well as the temperature, the total neutral density and the density of the diffusing minor species. The eddy diffusion coefficient represents turbulent mixing processes in the atmosphere and is typically approximated to vary with altitude based on fits of equation (2) to observed altitude profiles of selected minor species that are not significantly influenced by photochemistry. For Pluto's atmosphere, the eddy diffusivity has been determined by fitting to the methane profile. As discussed in Luspay-Kuti et al. (2017), we found a high eddy coefficient of $10^6 \text{ cm}^2 \text{ s}^{-1}$ from the surface to an altitude of 150 km, and $3 \times 10^6 \text{ cm}^2 \text{ s}^{-1}$ above 150 km for Pluto's atmosphere, which is in very good agreement with that found by Gladstone et al. (2016).

2.2 Chemistry

In Titan's atmosphere, three reactions are the primary source of production of HCN:

Reaction (R1) has long been recognized to produce the most HCN in Titan's atmosphere (e.g. Lavvas, Coustenis & Vardavas 2008) and consistently produces the most HCN in our Titan-INT (Luspay-Kuti et al. 2015). Reactions (R2) and (R3) are also noted to be important in our simulations. We also find that up to 23 per cent of HCN production can be due to electron recombination of HCNH^+ depending on solar activity (see Table 2). As we evaluate the production rate of HCN in Pluto's atmosphere, we will determine if these reactions continue to dominate HCN production or if other reactions grow in importance in the different environment provided by Pluto.

The three reactions that dominate loss of HCN at Titan in order of importance are as follows:

In general, the net production of HCN is greater than the loss in our global average simulations for Titan's atmosphere. However, it is important to note that these are global

average simulations and do not properly capture diurnal variations in production and loss. De la Haye et al. (2008) explored diurnal variations in Titan's upper atmosphere and found that the HCN abundance above 1000 km could vary by as much as a factor of 5 over a Titan day. This is in good agreement with INMS observations reported by Cui et al. (2016).

We also note that Titan-INT only evaluates photochemistry above 600 km and does not include condensation or incorporation of molecules into aerosols as evaluated by Willacy, Allen & Yung (2016). In our Pluto-INP, we evaluate the photochemistry of the atmosphere from the surface to near the exobase and include the processes of condensation and sticking to aerosols described by Willacy, Allen & Yung (2016). The details of our methodology are provided in Luspay-Kuti et al. (2017), but we summarize our approach for these processes below.

2.3 Condensation

When condensation nuclei are available and the partial pressure of HCN is greater than the saturation vapour pressure, HCN may condense. Willacy, Allen & Yung (2016) found that condensation played a minor role in the altitude profile of HCN in Titan's atmosphere below 500 km, but that it significantly reduced the abundance of HCN below 100 km. Because HCN is supersaturated in Pluto's upper atmosphere and has an altitude profile similar to the saturation vapour pressure profile in the lower atmosphere (Lellouch et al. (2017)), its condensation appears to be even more important at Pluto than at Titan.

Saturation densities derived from the saturation vapour pressures for HCN and HC₃N are shown in Fig. 1. The shaded grey region in Fig. 1 represents the conditions at Pluto and illustrates that any HCN densities greater than 10⁸ will be subject to condensation, given sufficient availability of nuclei that are amenable to condensation.

In Fig. 1, we illustrate two different methods for calculating the saturation vapour pressure and densities based on information provided in the literature, which provide different vapour pressures for both HCN and HC₃N. The first method uses the parameters provided in table 2 of Willacy, Allen & Yung (2016), while the second method follows the analytical relation derived by Fray & Schmitt (2009) based on their review of experimental data and provided in their table 5. Pluto-INP is designed to simulate the chemistry in Pluto's atmosphere without any condensation and also to simulate condensation using the saturation vapour pressure through either of these methods. This allows us to study the sensitivity of the HCN altitude profiles based on each method. For this study, we apply the analytical relation from Fray & Schmitt (2009) because these results are based on an extensive bibliographical review of experimental data.

The loss rate due to condensation is calculated based on the collision rate between the molecules and the aerosol particles and is given in Willacy, Allen & Yung (2016) as

$$L_{\text{cond}} = \alpha \sigma v_{\text{th}} (n - n_{\text{sat}}), \quad (3)$$

where α is the condensation coefficient describing the efficiency of condensation of the molecule onto an aerosol particle, σ is the mean surface area of aerosols per volume (cm^{-1}), and n and n_{sat} (cm^{-3}) are the molecule's density and saturation vapour density, respectively. It is important to note that we do not evaluate the production or bulk composition of the aerosols observed in Pluto's atmosphere to determine the mean surface area of aerosols per volume, σ , but instead use the measurements provided by *New Horizons* as presented in Gao et al. (2017) as input to our model.

The thermal velocity of the molecule, v_{th} (cm s^{-1}), is calculated as

$$v_{\text{th}} = \sqrt{\frac{2kT}{m}}, \quad (4)$$

where k is Boltzmann's constant, T is the temperature and m is the mass of the particle. Therefore, the condensation loss rate is a function of the temperature, the density of the constituent compared to its saturation vapour density and the mass of the particle.

We explore a range of constant values for the condensation coefficient, α , for HCN and HC_3N to compare with the ALMA observations. We include HC_3N because although ALMA did not detect it we can compare our simulations with the upper limit provided by Lellouch et al. (2017).

2.4 Incorporation into aerosols

Several studies have suggested that molecules can collide with aerosols and be permanently lost through incorporation into these particles (e.g. Dimitrov & Bar-Nun 2002; Willacy, Allen & Yung 2016). This process is different from condensation, which depends on the saturation vapour pressure of the molecule. In the aerosol sticking process, molecules collide with aerosol particles, physically adhere or stick to them, and are then incorporated into them. Willacy, Allen & Yung (2016) found that HCN loss due to sticking to aerosols significantly impacts the altitude profile of HCN abundance below 600 km in Titan's atmosphere. Our evaluation of the altitude profiles for C_2 hydrocarbons in Pluto's atmosphere shows that this process is important at Pluto as well (Luspay-Kuti et al. 2017). Therefore, this process should also be important for understanding the loss of HCN in Pluto's atmosphere.

Laboratory studies have shown that aerosols are 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, Dimitrov & Tomasko 2008). This hardening by aging makes aerosols less sticky so that they are less likely to coalesce and eventually unable to coagulate (Dimitrov & Bar-Nun 2002, 2003). This also reduces the probability of molecules like HCN sticking to and eventually being incorporated into the aerosols.

Following the approach used in Willacy, Allen & Yung (2016), we calculate the loss rate of molecules by sticking to aerosols as

$$L_{\text{as}} = \beta v_{\text{th}} \sigma n = C A_{\text{scale}} v_{\text{th}} \sigma n, \quad (5)$$

where L_{as} ($\text{cm}^{-3} \text{s}^{-1}$) is the loss rate of HC^{14}N , HC^{15}N and HC_3N 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 found with the C_2 hydrocarbons that the sticking efficiency, β , has two components: C , which defines the efficiency of the molecule for sticking to the aerosol, and A_{scale} , which is an altitude-dependent parameter that defines the varying stickiness of the aerosols as they grow larger at lower altitudes.

As with condensation, we use the altitude-dependent σ values derived by Gao et al. (2017) (see fig. 5 of Luspai-Kuti et al. 2017). We incorporate the ageing process for the aerosols by varying the sticking efficiency with altitude as discussed in Luspai-Kuti et al. (2017). In evaluating the HCN abundance in Pluto's atmosphere, we use the same A_{scale} profile derived for the C_2 hydrocarbons in Luspai-Kuti et al. (2017).

3 NITROGEN ISOTOPES AND FRACTIONATION

Our objective in studying nitrogen isotope processes in Pluto's atmosphere is to understand whether Pluto's nitrogen originated as N_2 or NH_3 in the protosolar nebula (PSN; see background in Mandt et al. 2016). We do this by evaluating how processes that change, or fractionate, the isotopes will influence the ratio in N_2 over geologic time-scales (first done for Titan in Mandt et al. 2009). These processes include escape, photochemistry, condensation, aerosol trapping and sublimation.

Fractionation of isotopes is characterized by a fractionation factor, f . No fractionation is occurring when $f=1$. When f is less than 1, the lighter isotope is lost at a rate greater than the heavier isotope. When f is greater than 1 the heavier isotope is preferentially lost compared to the lighter isotope. We describe here what is known about fractionation of the nitrogen isotopes at Titan and what needs to be done to constrain fractionation for Pluto. We then describe how we model the evolution of the ratio over time.

3.1 Dynamics

Fractionation due to dynamics occurs above the homopause due to binary diffusion differences related to the mass of each isotope. The isotope ratio, $^{14}\text{N}/^{15}\text{N}$ will increase with increasing altitude above the homopause and will be evident in the altitude profile of the two isotopes. This is a short-term effect that can be seen in altitude profiles produced by steady-state photochemical models as illustrated in Fig. 2 for Titan.

Additionally, isotopes will fractionate during escape if a constituent is escaping from the atmosphere. The atmosphere of Pluto was found to be escaping thermally due to Jeans escape. Thermal escape produces mass-dependent fractionation that varies as a function of the Jeans escape parameter, λ :

$$\lambda = \frac{GMm}{kTr_e}, \quad (6)$$

where G is the gravitational constant, M is the mass of Pluto and m is the mass of the escaping species. The parameter r_e is the distance from the centre of Pluto to the ‘escobase’, or the altitude at which escape is happening commonly assumed to be the exobase.

The Jeans escape rate in units of $\text{cm}^{-2}\text{s}^{-1}$ is given as

$$F_J = n_e \sqrt{\frac{kT}{2\pi m}} (1 + \lambda) e^{-\lambda} \quad (7)$$

where n_e is the density at the exobase. Fractionation due to Jeans escape is

$$f = \sqrt{\frac{m_1}{m_2}} \frac{(1 + m_2/m_1 \lambda) e^{-m_2/m_1 \lambda}}{(1 + \lambda) e^{-\lambda}}, \quad (8)$$

where the light species is represented by the subscript 1 and the heavy species is represented by the subscript 2. Fractionation due to escape will change the bulk isotopic composition of the atmosphere over million-year time-scales, but this fractionation will not be evident in steady-state photochemical simulations.

3.2 Photochemistry

As described earlier, the photochemistry within the atmospheres of both Titan and Pluto causes a net loss of molecular nitrogen by breaking up the molecules, where the freed nitrogen combines with hydrogen and carbon to form larger molecules and eventually aerosols. These aerosols are deposited onto the surface and the initial nitrogen is assumed to be permanently lost from the system.

HCN production is the first step in this process (Imanaka & Smith 2010). It has been demonstrated at Titan that photochemical fractionation in the loss of N_2 followed by the production of HCN is driven primarily by preferential dissociation of $^{14}\text{N}^{15}\text{N}$ at lower altitudes (Liang et al. 2007). It is possible that additional fractionation occurs in the process of forming HCN due to differences in reaction rates for isotopologues, but few measurements are available for isotopologue reaction rates. It is possible that the net effect of the self-shielding process at Titan is so significant that the impact of any differences in reaction rates is likely to be negligible.

One approach for determining the photochemical fractionation factor, f_{p1} , is to divide the isotope ratio in the reactant by the isotope ratio of the product

$$f_{p1} = R_{\text{reactant}}/R_{\text{product}}. \quad (9)$$

This approach can be used to approximate the net fractionation assuming that all of the HCN observed originated as N₂. This may be a reasonable assumption for Titan because extensive atmospheric photochemistry provides sufficient production of HCN to explain the abundances measured in the atmosphere. Table 1 lists the observed ¹⁴N/¹⁵N in Titan's atmosphere. The observations made of ¹⁴N/¹⁵N in HCN provide a possible range of 40–107, although the two ratios presented by Gurwell (2004) are for the same observation with different assumed temperature profiles. It is unclear which value is more accurate, but the lower ratio is closer to the other two measurements made for Titan. The mean value of all five measurements is 68.6 with a standard deviation of 15.7. Using this mean value and the ¹⁴N/¹⁵N in N₂ measured by the Huygens Gas Chromatograph Mass Spectrometer (GCMS; Niemann et al. 2010), we find a fractionation factor of 2.44 ± 0.56 using equation (9).

It is important to note that all of these measurements were made under solar minimum conditions indicated by an F10.7 < 120. During solar maximum conditions, the F10.7 can be higher than 260, driving greater photochemical loss rates for N₂ and possibly increasing the fractionation between N₂ and HCN. The F10.7 during the *New Horizons* fly-by of Pluto was ~ 110.

A second method for determining fractionation is to calculate the column rates for all of the reactions involved in the production and loss of ¹⁴N₂ and ¹⁴N¹⁵N and determine the fractionation factor, f_{p2} , as

$$f_{p2} = F_2/F_1 \cdot n_1/n_2, \quad (10)$$

where F_i is the loss rate and n_i is the column density for the light and heavy isotope, designated with subscripts 1 and 2, respectively.

Table 3 lists the values used to calculate both fractionation factors for Titan based on our Titan-INT simulations for solar minimum, moderate and maximum conditions. The solar minimum simulation is constrained by Cassini observations made during solar minimum conditions. For solar moderate and maximum conditions the only parameter that was changed was the solar flux to isolate the influence of a changing photon flux on the chemistry (Luspay-Kuti et al. 2016).

For Pluto, the only option is to use equation (10) to determine photochemical fractionation given the lack of any isotope ratio measurements. As we evaluate Pluto photochemistry in an attempt to explain the ALMA observations, we will also explore whether production due to photochemistry is sufficient to explain the abundances observed in the atmosphere by ALMA (Lellouch et al. 2017).

3.3 Condensation

Fractionation of the isotopes of water during condensation has been studied extensively and is known to be temperature dependent (e.g. Dansgaard 1964). When evaluating the isotope ratio of the gas when condensation is occurring, the fractionation factor, f_c , is the ratio of the loss rate of the heavy component to the light component scaled by the isotope ratio in the atmosphere (similar to equation 10):

$$f_c = L_2/L_1^{1/R}, \quad (11)$$

where L is the loss rate from equation (3) and the subscripts 1 and 2 refer to the light and heavy isotopes, respectively, and R is the isotope ratio $^{14}\text{N}/^{15}\text{N}$. Several parameters in equation (3) could cause a difference in the loss rates for HC^{14}N and HC^{15}N . First, there is a difference in the thermal velocity due to the difference in mass of one atomic mass unit (amu) between HC^{14}N and HC^{15}N . This will cause the thermal velocity of HC^{14}N to be higher than the thermal velocity of HC^{15}N by a factor of $\sqrt{\frac{28}{27}}$ and the loss rate of HC^{14}N will be greater than the loss rate of HC^{15}N by the same factor. Furthermore, the difference between the saturation vapour density of HC^{14}N compared to HC^{15}N will be much greater because HC^{14}N is more abundant than HC^{15}N by a factor of R , or the ratio $^{14}\text{N}/^{15}\text{N}$. When HC^{14}N is supersaturated, but HC^{15}N is close to the saturation vapour density, this will significantly reduce the loss rate of HC^{15}N compared to that of HC^{14}N .

However, it has been shown that the saturation vapour pressure difference in water between isotopes causes the heavy isotope to condense faster than the lighter isotope during precipitation of water on Earth. The saturation vapour pressure is also likely to be different for HC^{15}N than it is for HC^{14}N , but we were not able to find any laboratory measurements of the HC^{15}N vapour pressure as a function of temperature. Studies of $^{15}\text{NH}_3$ compared to $^{14}\text{NH}_3$ find that the saturation vapour pressure of $^{15}\text{NH}_3$ is 72–85 per cent lower than the saturation vapour pressure of $^{14}\text{NH}_3$ (King et al. 1989) depending on the temperature. In our simulations, we will assume that a similar difference between the saturation vapour pressures of HC^{14}N and HC^{15}N exists, and evaluate whether this fractionation could effectively counter the enhanced loss rate of HC^{14}N compared to HC^{15}N due to thermal velocity and greater abundances in the atmosphere. Based on the potential fractionation due to the factors discussed above, the fractionation factor for condensation of HCN could be anywhere between 0.00 and 1.389, suggesting that condensation could either preferentially remove the heavy or the light isotope from the atmosphere.

Finally, there may be a difference between the condensation co-efficient, α , for HC^{14}N and HC^{15}N . Unfortunately, little is known about the condensation coefficient for either isotopologue, so this effect is difficult to constrain at this time. Comparing our simulation results with the ALMA observations will be a useful method for determining if a fractionation in the condensation coefficient is relevant in any way.

3.4 Incorporation into aerosols

The incorporation of HCN into aerosols will also fractionate due to the thermal velocity difference between HC^{14}N and HC^{15}N . Additionally, the sticking efficiency may differ between isotopologues but is difficult to define due to the lack of any studies. In our photochemical simulations, we assume only a fractionation factor for incorporation into aerosols of 0.982 based on the difference in the thermal velocities. As with condensation, comparing our simulation results with the ALMA observations will indicate whether a fractionation in the condensation coefficient is also relevant.

3.5 Modelling evolution

To model the evolution of the nitrogen isotopes, we evaluate how R/R_0 changes over time, where R is $^{14}\text{N}/^{15}\text{N}$ in N_2 and R_0 is the primordial ratio. We note that sublimation and condensation processes are known to be effective at Pluto, as evidenced by a large reservoir of N_2 ice in direct contact with the atmosphere (e.g. Grundy et al. 2016). Condensation onto the surface will store fractionated N_2 ice in the surface reservoir, thus removing fractionated N_2 from the atmosphere and reducing the time available for this N_2 to fractionate. Sublimation of N_2 from the surface reservoir will introduce unfractionated and previously fractionated N_2 into the atmosphere. Unfortunately, in order to effectively simulate the impact of this cycle of condensation and sublimation on the isotopes, we require an understanding of the condensation and sublimation rates that goes beyond what is available in the literature about Pluto at the present time. Furthermore, we need a better understanding of how condensation and sublimation could fractionate the isotopes. As we have seen for HCN, this is poorly understood. Based on our limited understanding of these processes, we expect that the main effect would be to reduce the fractionation predicted in this study by reducing the time during which the N_2 is exposed to atmospheric processes. Nitrogen could also be added to the atmosphere through outgassing from the interior. This nitrogen will have a ratio that is primordial and will dilute the effects of fractionation due to escape and photochemistry.

We track the evolution of the isotopes through equations that describe the net loss of $^{14}\text{N}_2$ and $^{14}\text{N}^{15}\text{N}$ as a function of time:

$$\frac{d^{14}\text{N}_2}{dt} = \phi_s - \phi_e - \phi_c \quad (12)$$

$$\frac{d^{14}\text{N}^{15}\text{N}}{dt} = f_s \mathfrak{R}_0 \phi_s - f_e \mathfrak{R}(t) \phi_e - f_c \mathfrak{R}(t) \phi_c, \quad (13)$$

where t is the time, $\mathfrak{R}$ is the ratio of $^{14}\text{N}^{15}\text{N}$ to $^{14}\text{N}_2$, f is the fractionation factor for each of the three types of loss or production processes, ϕ is the outgassing from an interior source (s), escape (e) and photochemical loss (c). Note that because $^{14}\text{N}_2$ has two ^{14}N atoms, $\mathfrak{R}$ can be approximated to be equal to $\frac{1}{2}$ the value of R because the value of $\mathfrak{R} \ll 1$. However,

also note that $\mathcal{R}/\mathcal{R}_0 = R/R_0$. No information is available about isotopic fractionation of nitrogen during outgassing from an interior source, so we assume that $f_s = 1.0$.

The change of $\mathcal{R}$ as a function of time is based on equations (12) and (13):

$$\mathcal{R}(t) = 14N^{15}N(t)/14N_2(t) = \frac{\int(\mathcal{R}_0\phi_s - f_e\mathcal{R}(t)\phi_e - f_c\mathcal{R}(t)\phi_c)dt}{\int(\phi_s - \phi_e - \phi_c)dt}. \quad (14)$$

We solve equation (14) for a range of values for ϕ_s to evaluate the role of outgassing in the evolution of R/R_0 . The minimum case is an outgassing rate of zero, where all N_2 available to the atmosphere was outgassed at a single point in time early in Pluto's formation history. In the maximum outgassing case, unfractionated N_2 is added to the atmosphere at a rate equal sufficient to counter any fractionation leading to $R/R_0 = 1$.

4 RESULTS

The results of our Pluto-INP simulations compared to observations of methane and the C_2 hydrocarbons by *New Horizons* are outlined in companion paper Luspay-Kuti et al. (2017). The simulated nitrogen profile agrees well with the *New Horizons* line-of-sight transmission observations illustrated in Fig. 2 of Gladstone et al. (2016), demonstrating that the temperature profile used in our Pluto-INP simulations is a reasonable fit. The simulated methane altitude profile is best fit using an eddy diffusion profile that is in strong agreement with that used by Gladstone et al. (2016). We used model simulations of the C_2 hydrocarbon profiles including condensation and aerosol sticking parameters to derive the A_{scale} parameter that empirically characterizes the hardening of aerosols due to ageing. This parameter influences the efficiency with which HCN sticks to the aerosols and was used for the HCN study.

4.1 HCN altitude profiles

Our best-fitting profiles for $HC^{14}N$ and $HC^{15}N$ are illustrated in Fig. 3 and compared to the ALMA observation of $HC^{14}N$. Also shown are the temperature-dependent saturation vapour densities of $HC^{14}N$ and $HC^{15}N$ as a function of altitude, using the method outlined in Fray & Schmitt (2009) and assuming a difference in $HC^{15}N$ saturation vapour density similar to $^{15}NH_3$. As the profiles in Fig. 3 show, the ALMA altitude profile has an HCN abundance that is lower than the saturation vapour pressure between 30 and 175 km. We have seen through our simulations using chemistry only that photochemical loss rates are much lower than the condensation loss rates and are not sufficient to change the altitude profile of HCN (Luspay-Kuti et al. 2017). This means that the primary loss process in this altitude range is HCN sticking to aerosols that have not completely hardened. The first step, therefore, was to find the best-fitting sticking coefficient initially assuming a condensation coefficient of 3×10^{-3} . We selected 3×10^{-3} as a low value for the preliminary condensation coefficient because we wanted to avoid too much condensation above 175 km while we determined the best-fitting aerosol sticking coefficient. Once we found the best-fitting sticking coefficient based on the fit to the 30–175 km altitude range, we increased the condensation coefficient to simulate a column density that agrees best with the ALMA observation of $1.6 \pm 0.4 \times$

10^{14} cm^{-2} (Lellouch et al. 2017). Fig. 4 illustrates the influence of increasing the aerosol-sticking coefficient while using a constant condensation coefficient.

After running a large number of simulations trying to find the best-fitting altitude profile of HC^{14}N , we find that a sticking coefficient of 7×10^{-4} and a condensation coefficient of 4.5×10^{-3} are required to provide reasonable agreement with the ALMA altitude profile and to match the ALMA column density for HC^{14}N . Wong et al. (2017) conducted a similar investigation of a process that they identify as condensation, giving a condensation coefficient of 1×10^{-2} for HCN. However, their equation (3), which is stated to be for condensation does not include the saturation vapour pressure like our equation (3) and equation (9) of Willacy, Allen & Yung (2016). Instead, the equation given in Wong et al. (2017) is more like our equation (4) and equation (11) of Willacy, Allen & Yung (2016), which are used for aerosol sticking. Given the uncertainty in the type of loss process used in the Wong et al. (2017) model, it is unclear how we can directly compare our HCN condensation and aerosol trapping results with those of Wong et al. (2017).

The required sticking coefficient for HCN is greater than that required for C_2H_2 (5.15×10^{-4}) and C_2H_6 (3.2×10^{-4}), but less than the sticking coefficient required for C_2H_4 (1.13×10^{-3} ; Luszpay-Kuti et al. 2017). This differs from the prediction by Dimitrov & Bar-Nun (2003) that fewer CN groups would be incorporated into aerosols than hydrocarbons. Analyses of the INMS observations of molecules adsorbing to the instrument in Titan's upper atmosphere could provide further insight into these observations. Magee et al. (2009) demonstrated that significant amounts of HCN and NH_3 , and a smaller amount of either C_2H_2 or C_2H_4 adsorbed to the instrument during the Titan fly-by and were observed desorbing from the instrument for several hours after exiting Titan's atmosphere (fig. 20 of Magee et al. 2009). If we assume that the stickiness of the INMS instrument is the same for each molecule and that the main influence on the probability for a molecule to stick to the instrument is based primarily on each molecule, then we can propose that HCN and either C_2H_2 or C_2H_4 have higher sticking coefficients than C_2H_6 . Combining this with our Pluto observations could suggest that the molecule observed to be sticking to INMS is more likely to be C_2H_4 than C_2H_2 . It is important to note, however, that although HCN has a high likelihood of sticking to aerosols, the abundance of HCN in Pluto's atmosphere is one to two orders of magnitude lower than the C_2 hydrocarbons. Because of this, the amount of nitriles that can be incorporated into aerosols through adsorption processes is much lower than the amount of hydrocarbons that will be incorporated, in spite of a higher probability of sticking.

It is difficult to compare the condensation coefficients for HCN with the C_2 hydrocarbons because of the very limited role that condensation plays in the hydrocarbon profiles. Fig. 5 illustrates the process of adjusting the condensation coefficient after finding the best-fitting aerosol-sticking coefficient. We find that increasing the condensation coefficient does not necessarily improve the fit of the altitude profile with that provided by ALMA because condensation is more efficient between 100 and 200 km than above 200 km. This difference may be due to errors in the assumed aerosol profile used in our model (based on the results of Gao et al. 2017) or due to differences in the base atmosphere model between Pluto-INP and that used in Lellouch et al. (2017) to derive the mixing ratio profile.

The best-fitting column density reported by the ALMA observation after evaluating several model atmospheres is $1.6 \pm 0.4 \times 10^{14} \text{ cm}^{-2}$ (Lellouch et al. 2017). The best-fitting mixing ratio profile resulting from this evaluation is illustrated in Figs 3–5. Using this mixing ratio profile in Pluto-INP produces an HCN column density of $1.97 \times 10^{14} \text{ cm}^{-2}$. This appears to indicate that our base atmosphere has a higher total column density than that used by Lellouch et al. (2017). In order to fit the ALMA HCN observations, several model atmospheres were evaluated in Lellouch et al. (2017). One of the main parameters varied in these model atmospheres was the temperature profile. The authors determined the best-fitting HCN mixing ratio profile using a nominal profile derived from the ALMA CO observations. This nominal profile agrees well at most altitudes with the temperature profile that we are using in Pluto-INP (based on Gladstone et al. 2016) except for the altitude range between 100 and 400 km, where the Lellouch et al. (2017) profile departs from ours by as much as 10 K. We find that the total column density of the atmosphere calculated with our temperature profile is 4 per cent lower than the total column density using the nominal profile from Lellouch et al. (2017). However, the total density profile using our temperature profile is greater than that calculated using the Lellouch et al. (2017) temperature profile above 50 km by as much as 20 per cent. Because the abundance of HCN decreases significantly below 100 km, our column density of HCN will be greater than that of Lellouch et al. (2017) as a result of the influence of the temperature profile on the total density profile in the altitude region where HCN is most abundant. The column density of our best-fitting profile is $2.66 \times 10^{14} \text{ cm}^{-2}$, which is within fair agreement with the ALMA column density.

4.2 Photochemistry and photochemical fractionation

As the results presented in Table 2 show, the relative importance of the processes that define the photochemical production and loss of HCN in Pluto's atmosphere is similar to that in Titan's atmosphere, although the rate of production is orders of magnitude lower. For example, as with Titan, production of HCN at Pluto is dominated by the bimolecular reactions (R1–3), while the recombination of HCNH^+ with electrons also contributes. The processes that control the loss of HCN in Pluto's atmosphere are also similar to that of Titan's in that neutral chemistry plays the dominant role.

We provide the input parameters for calculating the photochemical fractionation factor for Titan and Pluto in Table 3. At Titan, photochemical fractionation is greater when using the ratios measured in N_2 and HCN (equation 9) compared to the loss rates of $^{14}\text{N}_2$ and $^{14}\text{N}^{15}\text{N}$ (equation 10). It is possible that factors not directly related to the loss of N_2 influence the HCN isotope ratio, such as fractionation in the photochemical loss of HCN or condensation and aerosol trapping. These processes would not affect the fractionation of N_2 over time and should not be included in the fractionation factor. Given that (equation 10) is based strictly on the loss rates of $^{14}\text{N}_2$ and $^{14}\text{N}^{15}\text{N}$, it is a more accurate representation of the fractionation factor than (equation 9).

As the results in Table 3 demonstrate, the fractionation factor for Titan decreases with increasing solar activity, while the simulated $^{14}\text{N}/^{15}\text{N}$ in HCN increases. However, the fractionation factors for Pluto are very different. First, the simulation using only chemistry

and no condensation or aerosol trapping (Chem) does not show any photochemical fractionation using the simulated isotope ratios in N_2 and HCN. The dissociation of N_2 shows a preferential loss of $^{14}N_2$ relative to $^{14}N^{15}N$ using the N_2 loss rates, which is the opposite of what happens at Titan. We find the same fractionation factor using the N_2 loss rates from the Pluto-INP simulation that includes condensation and aerosol trapping, suggesting that condensation and aerosol trapping of HCN has little effect on the relative loss rates of $^{14}N_2$ and $^{14}N^{15}N$.

4.3 Fractionation from condensation and incorporation into aerosols

The most surprising result in the Pluto-INP simulation that includes condensation and aerosol trapping is the extreme fractionation in HCN. In this simulation, the abundance of $HC^{15}N$ is significantly enhanced due to reduced loss of $HC^{15}N$ relative to $HC^{14}N$ due to condensation and aerosol trapping. In the simulation that includes only chemistry, the altitude profile of the HCN isotope ratio is the same as for N_2 . However, as illustrated in Fig. 6, the altitude profile of the nitrogen isotope ratios in N_2 and HCN for the simulation that includes condensation and aerosol trapping shows a large difference in the altitude region where condensation and aerosol trapping are taking place.

Because no measurement is available for $^{14}N/^{15}N$ in N_2 , we make the assumption that the ratio is 450 based on previous studies where we use this value to represent the primordial value for N_2 in the PSN (see explanations in Mandt et al. 2014, 2016). We also use this as the initial condition for the ratio in HCN and allow the ratio in both constituents to evolve during the simulation due to chemistry, diffusion, condensation and aerosol trapping. As Fig. 6 shows, diffusion above 700 km causes the ratio in HCN to be slightly lighter than that of N_2 due to diffusive separation of species by mass above the homopause. Below 500 km, the HCN ratio becomes significantly heavier due to preferential loss of $HC^{14}N$ due to condensation and aerosol sticking. The ratio drops below the lower limit set by ALMA at 180 km and the ratio of the column density of $HC^{14}N$ to $HC^{15}N$ is 43.5 (see Table 3).

The condensation coefficient, α , and the sticking coefficient, C , must be significantly higher for $HC^{15}N$ than for $HC^{14}N$ because ALMA did not detect $HC^{15}N$. This would allow the condensation and aerosol sticking of $HC^{15}N$ to be greater than the current simulations that assume α and C are equal for both isotopes. However, the number of simulations required to constrain these values is very large and beyond the scope of this study. We, therefore, leave constraining condensation and sticking coefficients of $HC^{15}N$ for future work.

5 THE ORIGIN OF N_2 IN PLUTO'S ATMOSPHERE

In order to make progress in evaluating the origin of nitrogen in Pluto's atmosphere, we need to constrain how the isotopes change over time. To do this, we calculate fractionation factors and loss rates for the fractionating processes described earlier and input these values into our model for the evolution of Pluto described in Section 3.2. Through our Pluto-INP simulations, we calculate Jeans escape (see Luspai-Kuti et al. 2017) and photochemical loss rates for $^{14}N_2$ and $^{14}N^{15}N$ and from these rates determine fractionation factors using equation (10).

Although Pluto-INP allows for loss of N_2 due to condensation, the N_2 density is too low to condense in our simulations. However, N_2 is known to be condensing and sublimating near the surface on a complex seasonal cycle (e.g. Hansen, Paige & Young 2015). As described earlier, the information needed to conduct a proper evaluation of the role of these processes in Pluto's atmospheric evolution is not currently available. We assume that the fractionation calculated here is an upper limit that would be reduced by these processes removing N_2 from exposure to atmospheric processes that would fractionate the isotopes.

We evaluate addition of fresh N_2 that has a primordial ratio to the atmosphere through outgassing from the interior by conducting a parameter search over a range of possible outgassing rates (see Section 3.2).

It is unclear at this time if N_2 is lost by aerosol trapping like HCN and the C_2 hydrocarbons. Although the observed altitude profiles of N_2 do not show evidence of aerosol trapping, this is likely due to the fact that N_2 makes up the majority of the atmosphere and is therefore controlled by hydrostatic equilibrium. For this reason, aerosol trapping of N_2 would cause a slight collapse of the atmosphere in response. Given the limited data on N_2 , we are not able at this time to empirically derive rates for N_2 . Therefore, for this study we focus only on fractionation due to escape and photochemistry and leave the remaining processes for future work.

Table 4 lists the loss rates for the two Pluto-INP simulations and the fractionation factors that were determined for each of them, and compares them with what we find using Titan-INT. The escape rates calculated by our model are based on Jeans escape, so the rates derived for Titan are orders of magnitude lower than escape rates derived based on sputtering processes (De La Haye et al. 2007). In our previous work, we have found that the fractionation factor for Jeans escape decreases with decreasing escape rates (Mandt et al. 2014). Comparing the loss rates and fractionation factors for Pluto and Titan confirm this.

Photochemistry in Pluto's atmosphere during the *New Horizons* fly-by appears to preferentially remove the lighter isotope, which is the opposite effect compared to what is observed in Titan's atmosphere. However, Pluto's atmosphere is subject to a wide range of conditions over a Pluto year. First, the surface pressure of Pluto's atmosphere has been observed to decrease with time as Pluto moves away from the Sun (Hansen, Paige & Young 2015 and references therein). Secondly, the photon flux at Pluto can vary significantly over the solar cycle and due to changing distance from the Sun. We therefore do not rule out that fractionation at Pluto may have been more like at Titan at different stages of the Pluto year and consider that a higher fractionation factor such as has been determined for Titan could be reasonable. Therefore, based on our photochemical studies of both atmospheres we evaluate the evolution of Pluto's atmosphere assuming minimum and maximum photochemical fractionation factors of 0.83 and 2.05, respectively. We assume the escape rate and escape fractionation derived by Pluto-INP as shown in Table 4. Escape rates will also vary over a Pluto year, but an extensive Modelling effort would be required to constrain how these rates will vary and what influence that will have on fractionation, which is beyond the scope of this project. Using the inputs provided in Table 4 will produce a range of possible values for the current isotope ratio given primordial ratios that agree with the

presumed values for N_2 and NH_3 in the protosolar nebula. This will provide constraints on the usefulness of any measurements that could be made.

Fig. 7 illustrates the current isotope ratio relative to the primordial isotope ratio as a function of time in our evolution model, using the maximum and minimum values for photochemical fractionation and evaluating without outgassing and with maximum outgassing. Allowing outgassing reduces the amount that the ratio can change over time only slightly, while the uncertainty in photochemical fractionation has the greatest impact. Fig. 8 illustrates what the current isotope ratio would be based on our calculations of the evolution of $^{14}\text{N}/^{15}\text{N}$ in N_2 that originated as N_2 and NH_3 in the PSN. The range of possible values for both of these cases overlaps, suggesting that a measurement of the current ratio would not provide a clear answer as to the origin of Pluto's nitrogen and that further work is needed to understand fractionation.

6 SUMMARY AND CONCLUSIONS

We have successfully converted our Titan-INT model to simulate the photochemistry of Pluto's atmosphere and have added condensation and aerosol trapping to the model. We have found, based on comparisons of simulations with the C_2 hydrocarbons, that aerosol trapping is an important process that is taking place in Pluto's atmosphere (Luspay-Kuti et al. 2017). Comparing our simulations with the HCN altitude profile observed by ALMA shows that aerosol trapping is also important for HCN, but that condensation is a more significant loss process. Our results are based on preliminary data products published from the *New Horizons* mission and will be updated as more results become available in the literature.

The nitrogen isotope chemistry in Pluto's atmosphere is different from that of Titan, where self-shielding leads to extreme fractionation of the isotope ratio between N_2 and HCN. We find with our simulations that photochemistry may have the opposite effect at Pluto, but that the influence is negligible for the isotope ratio that would be observed in HCN. However, these simulations cover a brief period of time in a Pluto year and future studies should evaluate photochemical fractionation over the extreme variability of Pluto's atmosphere throughout a Pluto year.

Condensation and aerosol trapping are found in the simulations to have a major impact on the altitude profile of the isotope ratio in HCN. These results suggest that ALMA should have detected a significant amount of HC^{15}N in Pluto's atmosphere. Since HC^{15}N was not detected, we conclude that condensation and aerosol trapping are much more efficient for HC^{15}N compared to HC^{14}N . The process of determining how much more efficiently HC^{15}N must condense and be trapped by aerosols is highly complex and beyond the scope of the present study, which aims to validate our model with *New Horizons* and ALMA observations and evaluate the degree to which photochemistry fractionates the nitrogen isotopes.

We find that the large uncertainty in photochemical fractionation makes it difficult to use any potential current measurement of $^{14}\text{N}/^{15}\text{N}$ in N_2 to determine the origin of Pluto's nitrogen.

More work is needed to understand photochemical fractionation and to evaluate how condensation, sublimation and aerosol trapping will fractionate N_2 and HCN.

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Figure 1.

Saturation vapour densities for HCN and HC₃N using the parameters provided in table 2 of Willacy, Allen & Yung (2016; solid lines) and table 5 of Fray & Schmidt (2009; dashed lines). Important differences exist between the two methods, in particular for HC₃N. The shaded grey area represents the temperature conditions observed in Pluto's atmosphere (Gladstone et al. 2016).

Figure 2.

Nitrogen isotope ratio in N_2 and HCN simulated with Titan-INT and compared to Cassini INMS global average measurements (Mandt et al. 2012b) and the range of HCN isotope ratio measurements listed in Table 1. The box represents the range of values for HCN as listed in Table 1.

Figure 3.

Comparison of the Pluto-INP best-fitting HC^{14}N , HC^{15}N and ALMA altitude profiles. Also shown are the saturation vapour densities for HC^{14}N and HC^{15}N , assuming a difference between the two similar to that of $^{14}\text{NH}_3$ and $^{15}\text{NH}_3$.

Figure 4. Simulated HCN altitude profiles compared to the ALMA HCN profile showing the influence of increasing the sticking coefficient for HCN when the condensation coefficient is held constant at 3×10^{-3} .

Figure 5. ALMA HCN profile compared to simulated HCN altitude profiles showing the influence of increasing the condensation coefficient for HCN when the sticking coefficient is held constant at 7×10^{-4} .

Figure 6.

Altitude profile of the nitrogen isotope ratio in N_2 and HCN , assuming that the nitrogen isotope ratio in N_2 is the same as the presumed value for N_2 in the PSN. The rectangle illustrates the range of reasonable values based on the ALMA lower limit of 125.

Figure 7.

The evolution of the isotope ratio relative to the primordial ratio as a function of time for scenarios assuming minimum (solid) and maximum (dashed) photochemical fractionation factors with (red) and without (black) production of fresh nitrogen from the interior. A relative ratio greater than 1.0 is enriched in the heavy isotope, while a relative ratio less than 1.0 is depleted in the heavy isotope.

Figure 8.

Measurements of nitrogen isotope ratios, or $^{14}\text{N}/^{15}\text{N}$, in the solar wind¹, comets^{2,3,4} and the atmospheres of Jupiter⁵, Saturn⁶, terrestrial planets^{7,8,9,10} and Titan^{11,12}. Triangles are primordial values representing $^{14}\text{N}/^{15}\text{N}$ in the PSN. Circles are isotope ratios that have evolved over the 4.6 billion year history of the solar system. $^{14}\text{N}/^{15}\text{N}$ in the atmosphere of Mars⁹ is much lower than in the mantle⁸, although it is unclear if the mantle measurement can be considered as primordial. The primordial value for Titan is inferred from models of atmospheric evolution. The Pluto lower limit was determined using ALMA observations. (Sources: ¹Marty et al. 2010; ²Rousselot et al. 2013; ³Shinnaka et al. 2014, 2016; ⁴Bockelée-Morvan et al. 2008; ⁵Owen et al. 2001; ⁶Fletcher et al. 2014; ⁷Marty & Zimmermann 1999; ⁸Hoffman et al. 1979; ⁹Mathew & Marti 2001; ¹⁰Wong et al. 2013; ¹¹see Table 1; ¹²Niemann et al. 2010).

Table 1.

Measurements of the nitrogen isotope ratio in N_2 and HCN in Titan's atmosphere compared with the HCN mixing ratio in the altitude range where the measurement was made.

Species	$^{14}\text{N}/^{15}\text{N}$	HCN	Year	F10.7	Reference
N_2	167.6 ± 0.6	–	2005 January	97	Niemann et al. (2010)
HCN	60–70	$\sim 3 \times 10^{-7}$	1997 July	70	Marten et al. (2002)
	94 ± 13	5×10^{-6}	2004 February	118	Gurwell (2004)
	72 ± 9				
	56 ± 16	7×10^{-7}	2004	115	Vinatier et al. (2007)
	56 ± 10	2×10^{-6}	2005	110	

Table 2.

Column integrated rates ($\text{cm}^{-2}\text{s}^{-1}$) for the production and loss processes for HCN calculated using Titan-INT during solar maximum, moderate and minimum conditions and using Pluto-INP for solar conditions relevant to the *New Horizons* fly-by of Pluto simulating only chemistry (Chem.) and chemistry with condensation and aerosol trapping (Full). The F10.7 used for solar maximum, moderate and minimum conditions were 260, 160 and 70, respectively.

Rate($\text{cm}^{-2}\text{s}^{-1}$)	Titan			Pluto: F10.7 = 110		
	Max.	Mod.	Min.	Chem.	Full	
<i>Production</i>						
Electron recombination	2.25×10^8	1.06×10^8	1.42×10^7	2.61×10^4	2.61×10^4	
Ion-molecule reactions	1.08×10^6	6.07×10^5	2.47×10^5	2.66×10^2	2.67×10^2	
Bimolecular	7.69×10^8	5.06×10^8	2.31×10^8	9.94×10^4	1.65×10^5	
Trimolecular	1.89×10^{-2}	8.25×10^{-3}	2.37×10^{-3}	0	0	
Total	9.95×10^8	6.13×10^8	2.46×10^8	1.26×10^5	1.91×10^5	
<i>Loss</i>						
Photodissociation	9.03×10^7	4.54×10^7	1.49×10^7	5.97×10^3	8.43×10^3	
Ion-molecule reactions	3.09×10^8	1.88×10^8	6.79×10^7	1.76×10^4	1.76×10^4	
Bimolecular	1.39×10^8	9.47×10^7	2.52×10^7	7.51×10^4	7.70×10^4	
Trimolecular	5.80×10^{-4}	3.24×10^{-4}	1.28×10^{-4}	0	0	
Total	5.38×10^8	3.28×10^8	1.08×10^8	9.87×10^4	1.03×10^5	

Table 3.

Parameters used to calculate the photochemical fractionation factor for Titan and Pluto based on Titan-INT and Pluto-INP simulations.

Parameter	Titan			Pluto: F10.7 = 110		
	Max	Mod	Min	Chem	Full	
$^{14}\text{N}_2$ Production ($\text{cm}^{-2}\text{s}^{-1}$)	1.17×10^9	9.46×10^8	7.41×10^8	4.37×10^5	4.49×10^5	
$^{14}\text{N}_2$ Loss ($\text{cm}^{-2}\text{s}^{-1}$)	1.76×10^9	1.35×10^9	9.29×10^8	9.60×10^5	9.72×10^5	
$^{14}\text{N}^{15}\text{N}$ Production ($\text{cm}^{-2}\text{s}^{-1}$)	1.28×10^7	1.04×10^7	8.22×10^6	1.62×10^3	1.67×10^3	
$^{14}\text{N}^{15}\text{N}$ Loss ($\text{cm}^{-2}\text{s}^{-1}$)	2.37×10^7	1.80×10^7	1.24×10^7	3.55×10^3	3.58×10^3	
$^{14}\text{N}/^{15}\text{N}$ in N_2 column density	169.2	169.2	169.1	449.8	450.0	
$^{14}\text{N}/^{15}\text{N}$ in HCN column density	106.3	101.2	82.6	449.5	43.5	
$^{14}\text{N}/^{15}\text{N}$ observed in N_2		167.6 ± 0.6			n/a	
$^{14}\text{N}/^{15}\text{N}$ observed in HCN		68.6 ± 15.7			>125	
f_{pl} from HCN observations		2.44 ± 0.56			n/a	
f_{pl} based on HCN	1.59	1.67	2.05	1.00	10.34	
f_{p2} based on loss rates	1.56	1.58	1.86	0.83	0.83	

Table 4.

Photochemical loss and Jeans escape rates for Titan and Pluto based on Titan-INT and Pluto-INP simulations. Note that Jeans escape for Titan is orders of magnitude lower than the rates reported in the literature for sputtering. Photochemical fractionation factors are calculated using equations (9) and (10). Escape fractionation is calculated using equation (10) based on the Jeans escape rates determined by the model.

Parameter	Titan		Pluto: F10.7 = 110	
	Max	Mod	Min	Chem Full
$^{14}\text{N}_2$ photochemical loss ($\text{cm}^{-2}\text{s}^{-1}$)	5.90×10^8	4.04×10^8	1.88×10^8	5.23×10^5
f_{PI} from observations		2.44 ± 0.56		n/a
f_{PI} based on HCN	1.59	1.67	2.05	1.00
f_{PI} based on loss rates	1.56	1.58	1.86	0.83
$^{14}\text{N}_2$ escape ($\text{cm}^{-2}\text{s}^{-1}$)	6.56×10^{-9}	6.55×10^{-9}	6.57×10^{-9}	8.63×10^4
f_e based on escape rates	0.134	0.134	0.134	0.399
				0.396