PHOTOCHEMISTRY AND HAZE FORMATION. K. L. Jessup[1], A. Cheng[2], P. Gao[3], A. Luspay-Kuti[2], K. Mandt[2] 1: Southwest Resarch Institute, Boulder CO, 80302 jessup@boulder.swri.edu; 2: John Hopkins University, APL, Laurel, MD; 3: California Institute of Technology, Pasadena, CA;

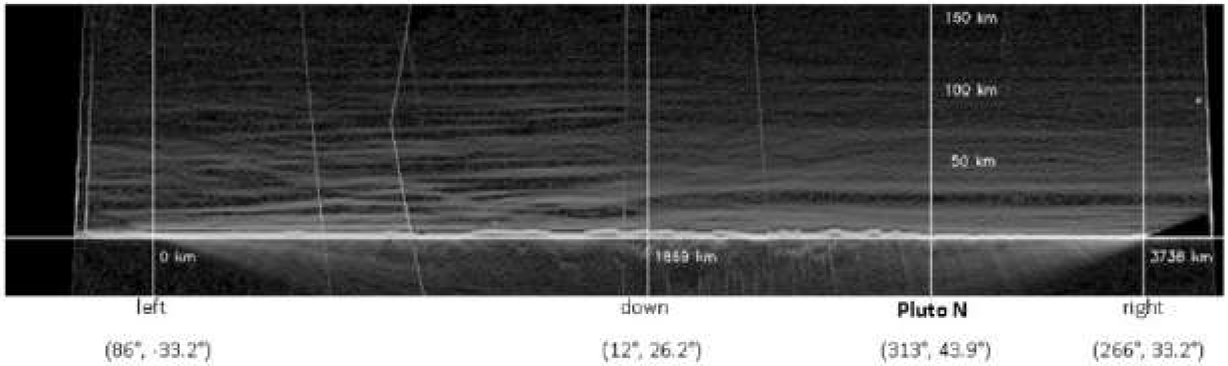

Fig. 1 Haze layers observed by New Horizons [1]

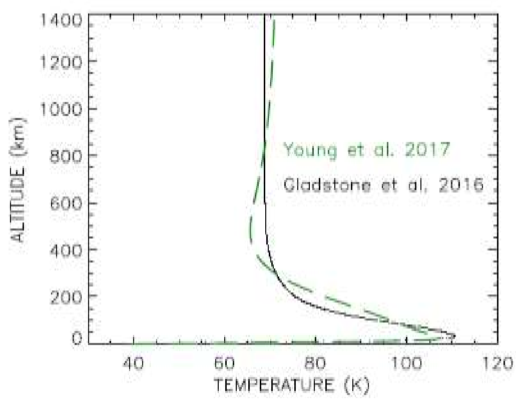

Fig. 2 Temperature profiles from [2] (black) and [3] (green)

Introduction: Observations and Analogs On July 14, 2015 the *New Horizons* spacecraft successfully flew through the Pluto system, confirming that the chemistry in Pluto's atmosphere is strikingly similar to Titan's, with bulk atmosphere composition consisting of N_2, CH_4 along with trace hydrocarbon gases such as C_2H_2, C_2H_4 and C_2H_6. Details of the vertical structure of Pluto's atmosphere were derived from the combined *New Horizons* Alice, REX, MVIC and LORRI instruments, including the discovery of extensive globally distributed haze layers [1-2,4] and a vertical temperature profile that experiences strong gradients between 0 and 400 km, including, as Fig. 2 shows, a maximum inflection point of ~106 K at ~ 22 km, a minimum inflection point of ~ 63 K near 400 km and a near constant profile of ~70 K at 1000 km and higher altitudes [3]. These results show Pluto's upper atmosphere to be a cryosphere that does not experience hydrodynamic escape but may, in fact, be cooled by its own hydrocarbon haze [5-6].

Though an ionosphere was not directly detected [1], by comparison to Titan, Pluto's atmospheric structure should be supported by ultraviolet photons dissociating and ionizing N_2 and CH_4, providing the photolysis products that result in the formation of complex hydrocarbons and nitriles [1] that are in turn ionized resulting in aerosol formation. I.e., the haze formation is supported by ionospheric processes that produce negatively charge macromolecules that form aerosols that grow, sediment, coagulate and aggregate forming spherical fractals [7]. These upper atmosphere ionospheric processes distinguish the chemical evolution of Titan and Pluto's upper atmosphere from that of Triton, on which CH_4 is destroyed in the lower atmosphere before reaching higher altitudes [1].

Overview: We will present a review of recent photochemical and haze production models developed for investigation of the physical processes controlling Pluto's gas species and haze profiles, discussing how these models answer and raise questions about the mechanisms supporting Pluto's atmospheric structure and thermal balance. We will also highlight questions raised by these models about the origin and isotope fractionation of N_2 gas at Pluto, discussing the differences and similarities to Titan.

Lessons from Photochemical Modeling: Using Titan's aerosol processes as an analog, [8] successfully developed and implemented a coupled ion-neutral-photochemistry (INP) which specifically solves the continuity equation at each altitude including EUV driven photochemistry occurring in the upper atmosphere along with the hydrocarbon condensation occurring below 400 km and aerosol trapping processes—without assuming hydrodynamic escape.

Using this model [8] simulated the NH observed atmospheric density profiles published by [2]. Simulations including only chemistry and condensation are incapable of replicating the near constant C_2 hydrocarbon profiles observed at altitudes of 300 km and lower (dots, Figure 3)—but did replicate the CH_4 profile (not shown). [8] successfully replicated the observed C_2 profiles at altitudes between 400 and 100 km (solid lines Fig. 4) by including aerosol aging in the simulations--without applying any manipulation of the C_2H_x saturation vapor rates beyond their accepted values. These results imply that the gaseous C_2 hydrocarbon molecules must stick to one another and then be removed by aerosol particles to reproduce the observed C_2 profiles, providing definitive evidence that the aerosols harden and become less sticky as they age in Pluto's atmosphere, in agreement with the active aging process proposed for Titan's aerosols [9]. Additionally, [8] empirically derived the sticking efficiency of C_2 hydrocarbons to aerosol particles as a function of altitude, finding that the sticking efficiency of C_2 hydrocarbons is inversely related to the aerosol surface area. With the inclusion of the aerosol aging mechanisms in the INP model [8] inferred a high eddy diffusion of 10^6 cm^2 s^{-1} that replicated the observed profiles in the altitude range between 100 and 150 km, and 3×10^6 cm^2 s^{-1} above 150 km for Pluto's atmosphere. However, at 100 km and lower the slope of the CH_4 profile derived from the INP simulations did not drop off as rapidly as retrievals from [2], producing a gas density at the surface 10x higher than that inferred from the original NH Alice solar occultation retrievals.

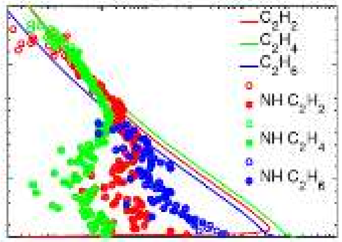

Fig. 3 Chemistry and condensation models (solid lines) are compared to the NH data. The red curve shows efficient condensational loss

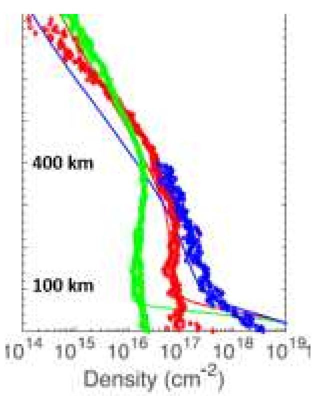

Fig. 4 Aged aerosol fit (solid lines) to New Horizons observations.

Recent, high fidelity analysis of the NH solar occultation data, provides improved gas density and temperature data—particularly at altitudes less than 100 km [3]. Thus, the now accepted atmospheric profile is cooler than that inferred from [2] (see Fig. 2) between 30 and 100 km and 300 and 800 km. The improved analysis also lowered the inferred CH_4 mixing ratio homopause altitudes and required eddy mixing from 10^6 to 10^3. These lower values are in conflict with the eddy diffusion rate inferred by [8], but agree with the results from [10] who both uses a simpler photochemical modeling scheme than [8], and also traces loss via aerosol growth/gas condensation differently from [8]. Intriguingly, when using the lower eddy mixing rate in the INP model [8] the CH_4 profile in the lower 100 km region is well fit, but not at higher altitudes. Noting the sensitivity of the vertical species profiles to condensational loss, inclusion of the new temperature profiles [3] in the photochemical models should increase the rate of CH_4 condensation at multiple altitudes including in the region below 100 km; thus, it will be important to determine the impact the new temperature profile behavior might have on the eddy diffusion rate and homopause level inferred from the INP model. Together, the current modeling efforts and observation analysis results imply that further resolution is needed in understanding how chemistry, condensation and diffusion work to maintain the CH_4 profiles at all altitudes.

Lessons on $HC^{15}N$ and Nitrogen Fractionation: Recent ground based Atacama Large Millimeter Array (ALMA) submillimeter observations [11] provided only Pluto's $HC^{15}N$ abundance upper limit. Photochemical modeling of the HCN production and loss processes have been investigated by [10 and 12]. [12] conclude that condensation and aerosol trapping should have a major impact on the altitude profile of the nitrogen isotope ratio in HCN—thus, non-detection of $HC^{15}N$ implies that condensation and aerosol trapping must be much more efficient for $HC^{15}N$ compared to $HC^{14}N$. Investigations into the isotopic fractionation behaviors at Pluto imply that Pluto's nitrogen isotope chemistry differs significantly form that at Titan, where for the latter extreme fractionation occurs because of self-shielding—while at Pluto it appears the opposite effect occurs. But modeling of fractionation behaviors is still in a very preliminary state and more concrete results will arise as the evolution of Pluto's atmosphere over a full solar year is more fully investigated, incorporating any potential changes in the rate of surface frost sublimation.

References: [1] Cheng et al. (2017) Icarus, 290, 112-133; [2] Gladstone et al. (2016), Science. [3] Young et al. (2017), Icarus, 300 174-199. [4] Gao et al. (2017), Icarus, 287, 116-123. [5] Krasnpolsky (2018), Icarus, 301, 152-154. [6] Zhang et al. (2017) Nature. doi:10.1038/nature24465. [7] Lavvas et al. (2010) 201, 832-842. [8] Luspay-Kuti et al (2017), MNRAS, 472, 104-117. [9] Dimitrov & Bar-Nun, (2002) Icarus 156, 530–538 [10] Wong et al. 2017, 287 110-115 [11] Lellouch et al. (2017). 286, 289-307 [12] Mandt et al. 2017, MNRAS, 472,118-128.