A Snowball in Hell: The Potential Steam Atmosphere of TOI-1266c

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Abstract

TOI-1266c is a recently discovered super-Venus in the radius valley orbiting an early M dwarf. However, its notional bulk density (∼2.2 g cm−3) is consistent with a large volatile fraction, suggesting that it might have volatile reservoirs that have survived billions of years at more than twice Earth’s insolation. On the other hand, the upper mass limit paints a picture of a cool super-Mercury dominated by >50% iron core (∼9.2 g cm−3) that has tip-toed up to the collisional stripping limit and into the radius gap. Here we examine several hypothetical states for TOI-1266c using a combination of new and updated open-source atmospheric escape, radiative–convective, and photochemical models. We find that water-rich atmospheres with trace amounts of H2 and CO2 are potentially detectable (S/N > ∼ 5) in less than 20 hr of James Webb Space Telescope (JWST) observing time. We also find that water vapor spectral features are not substantially impacted by the presence of high-altitude water or ice clouds owing to the presence of a significant amount of water above the cloud deck, although further work with self-consistent cloud models is needed. Regardless of its mass, however, TOI-1266c represents a unique proving ground for several hypotheses related to the evolution of sub-Neptunes and Venus-like worlds, particularly those near the radius valley.

Unified Astronomy Thesaurus concepts: Exoplanet atmospheres (487); Exoplanet atmospheric composition (2021); Hot Neptunes (754); Extrasolar ice giants (2024); Extrasolar rocky planets (511); Star-planet interactions (2177); Super Earths (1655)

1. Introduction

The list of exoplanet detections from space-based observatories like the Kepler Space Telescope (e.g., Borucki et al. 2010; Twicken et al. 2016) and the Transiting Exoplanet Survey Satellite (TESS; Ricker et al. 2014; Barclay et al. 2018), as well as ground-based endeavors such as WASP (e.g., Pollacco et al. 2006), HATNet (e.g., Bakos et al. 2004; Hellier et al. 2012), TRAPPIST (Jehin et al. 2011; Gillon et al. 2017; Delrez et al. 2018), and the Habitable-zone Planet Finder (HIF) Spectrograph (Mahadevan et al. 2012, 2014), is rapidly growing. These detections enhance our understanding of planetary occurrence rates (Batalia 2014) and enable robust statistical insights into planet populations (e.g., Dressing & Charbonneau 2013; Burke et al. 2015; Fulton et al. 2017; Hardegree-Ullman et al. 2019). In particular, the presence of a gap in the radius distribution of planets (Rogers 2015; Fulton et al. 2017; Fulton & Petigura 2018) highlights the cumulative effects of a planet’s host star (e.g., Owen & Jackson 2012; Owen & Wu 2017), formation (e.g., Lee et al. 2014; Lee & Chiang 2016; Ginzburg et al. 2018; Gupt & Schlichting 2020), and/or evolution (e.g., Luger et al. 2015), although disentangling these effects will likely require more sensitive observations (Lloyd et al. 2020).

The recent discovery of two planets orbiting TOI-1266 (Stefansson et al. 2020; Demory et al. 2020) offers a rare opportunity to begin connecting some of these planetary processes through observations. The outer planet, c (1.673 R⊕), is smaller than the inner planet, b (2.458 R⊕) (see Table 1 for the reported uncertainties and a comparison between the Stefansson et al. 2020 and Demory et al. 2020 values). This puts TOI-1266c in the “radius valley” (Fulton et al. 2017; Fulton & Petigura 2018). This type of “straddler” planetary system (Owen & Campos Estrada 2020) can be leveraged to constrain the temporal evolution of a host star’s EUV flux. However, the fact that the smaller planet is outside of the larger one (Weiss et al. 2018) hints at significant migration that may defeat first-order attempts to reproduce their present-day bulk compositions through atmospheric escape alone (Bean et al. 2021).

The bulk composition of TOI-1266c is poorly constrained because the mass measurement has large 1σ uncertainties: $1.9^{+1.3}_{−1.0}$ $M_{\text{J}}$ from Stefansson et al. (2020) using radial velocity constraints, and $2.2^{+1.5}_{−1.3}$ $M_{\text{J}}$ from Demory et al. (2020) based on an analysis of the transit timing variations. This broad range of possible planet masses covers several different planet types, including both rocky terrestrials and gas-dominated sub-Neptunes. Currently, compositional constraints are insufficient to rule out significant volatile inventories for small exoplanets under even higher instellation than what planet c receives (Dai et al. 2019). Formation models suggest that sub-Neptunes/super-Earths like TOI-1266b and c can end up as part of...
Table 1: Stellar and Planetary Parameters for the TOI-1266 System

| Property                  | Stefansson et al. (2020) | Demory et al. (2020) |
|---------------------------|--------------------------|----------------------|
| TOI-1266:                 |                          |                      |
| Spectral type             | M2                       | M3                   |
| Mass (M$_{\oplus}$)      | 0.437 ± 0.021            | 0.45 ± 0.03          |
| Radius (R$_{\oplus}$)    | 0.4232 ± 0.0077          | 0.42 ± 0.02          |
| Temperature (K)           | 3563 ± 77                | 3600 ± 150           |
| Age (Gyr)                 | 7.42 ± 3.2               | ~5                   |
| Luminosity ($L_{\odot}$) | 0.02629 ± 0.00071        | ...                 |

Planet b:

| Mass (M$_{\oplus}$)      | 6.9 ± 5.5                | 13.5 ± 11.0          |
| Radius (R$_{\oplus}$)    | 2.458 ± 0.083            | 2.37 ± 0.16         |
| Semimajor axis (au)      | 0.0745 ± 0.0046          | 0.0736 ± 0.0016     |
| Instellation ($S_*$)     | 4.72 ± 0.66              | 4.9 ± 0.8           |
| Equilibrium temp.* (K)   | 410.0 ± 3.15             | 413 ± 20            |

Planet c:

| Mass (M$_{\oplus}$)      | 1.93 ± 1.3               | 2.2 ± 0.9            |
| Radius (R$_{\oplus}$)    | 1.673 ± 0.087            | 1.56 ± 0.15         |
| Semimajor axis (au)      | 0.1037 ± 0.0026          | 0.1058 ± 0.0023     |
| Instellation ($S_*$)     | 2.42 ± 0.25              | 2.3 ± 0.5           |
| Equilibrium temp.* (K)   | 347.1 ± 7.9             | 344 ± 16            |

Note.

We use the Stefansson et al. (2020) stellar and planetary parameters as the default in this study and include values for planet b. The planet mass is reported with the 1σ error. Equilibrium temperature is calculated assuming an albedo of 0. We also include the values reported by Demory et al. (2020) for reference, which agree within error.

distinct water- or silicate-rich populations if planet embryos aggregate material from a more well-sampled protoplanetary disk (e.g., Liu et al. 2019). It may also be easier to form volatile-rich mini-Neptunes if additional gas sources, such as envelope enrichment sourced from various accreted ices, are considered (e.g., Venturini & Helled 2017). Taken together, TOI-1266c could be a rare example of a volatile-rich super-Earth, contrasting with the more well-populated family of volatile-poor, rocky super-Earths such as LHS 3844b (Kane et al. 2020) and TOI-849b (Armstrong et al. 2020).

In this paper, we explore the potential states of the planet by focusing on the H-C-O chemistry of three families of scenarios, all dominated by water: H$_2$+H$_2$O, H$_2$+CO$_2$+H$_2$O, and O$_2$+H$_2$O. This encompasses two potential intermediate states (as we describe below), as well as a hypothetical super-Venus transitional state, in which CO$_2$ begins to represent a significant portion of the envelope mass. We omit two other classes of atmospheres (Venus-like and sub-Neptune) for the sake of brevity. Simulations of exo-Venus atmospheres (Schaefer & Fegley 2011; Lincowski et al. 2018; Lustig-Yaeger et al. 2019a) largely resemble Venus’s CO$_2$-dominated atmosphere at present or with smaller CO$_2$ inventories earlier in its history (e.g., Way & Del Genio 2020). For exo-Venus in particular, more exploration is warranted to cover the expected diversity of planetary conditions and composition (see the review by Madhusudhan et al. 2016). A number of studies on the diversity of sub-Neptune atmospheres (e.g., Lavvas et al. 2019; Choukar et al. 2020) and retrievals (e.g., Benneke et al. 2019; Mikal-Evans et al. 2020) can be found in the literature; see also the review by Bean et al. (2021).

1.1. Motivating the “Snowball” Scenario

The current mass of TOI-1266c affords a variety of different possible compositions that largely fork into two main solutions: a water-rich steam world, and a dense Mercury-like planet. As shown by Stefansson et al. (2020), TOI-1266c is broadly consistent with a water-dominated planet (Figure 1; see also Aguichine et al. 2021). This can be seen when comparing to modeled mass–radius relationships for more complex compositions. For example, an Earth-like planet surrounded by up to 50 wt% (percent water by mass) can have radii of up to 1.47 $R_\oplus$ (Fu et al. 2009), which is 12% smaller than the observed radius for TOI-1266c (though this is still within 2σ). The model grid from Zeng et al. (2019) includes several 50% water/Earth-like rocky core planets with isothermal pure-H$_2$O atmospheres that roughly match TOI-1266c’s mass and radius. More generalized formulations for ice/rock/iron fractional compositions suggest that TOI-1266c is 60%–70% water ice (Fortney et al. 2007; Zahnle et al. 2008; Zeng et al. 2019) or 77% liquid water (Noack et al. 2016) by mass. These estimates are comparable to the maximum ice content expected for planets formed beyond the ice line (e.g., Mordasini et al. 2009), suggesting that in this scenario both planet b and planet c migrated inward to their present locations. However, none of these mass–radius relationships have self-consistent atmospheres, which can lead to underestimates in the estimated radius (e.g., Turbet et al. 2020). Steam atmospheres are often discussed within the context of the loss of water either during the magma ocean phase of a planet, immediately following accretion (e.g., Zahnle et al. 1988; Schaefer & Fegley 2010; Hamano et al. 2013; Katyal et al. 2019) or as a result of stellar brightening inducing a runaway greenhouse state (e.g., Kasting 1988). However, abundant water (and other heavy gases) could also be accreted (Kral et al. 2020) or outgassed later in a planet’s life (Kite et al. 2020; Kite & Barnett 2020; Kite & Schaefer 2021), potentially setting up a scenario in which the runaway state is entered much later in the planet’s life.

One unavoidable consequence of a potentially water-dominated planet receiving slightly more irradiation than Venus is atmospheric escape. Venus is thought to have lost its water at some point in its history (e.g., Kasting 1988; Way & Del Genio 2020) owing to high temperatures allowing significant amounts of water in the upper atmosphere, where it could be photolyzed and create hydrogen atoms that then escape the atmosphere (e.g., Zahnle & Kasting 1986; Schaefer et al. 2016; Luger & Barnes 2015; Tian 2015). Of particular note for M dwarfs is their prolonged pre-main-sequence lifetimes, during which they are 10–100 times brighter than their main-sequence luminosities (Luger & Barnes 2015; Luger et al. 2015). As a result, planets like TOI-1266c have multiple avenues by which their atmospheric composition can evolve in time, even to the extent that the planet loses its atmosphere entirely (e.g., Kopp &Forget et al. 2019; Poppenhaeger et al. 2020). A second issue is that planets orbiting M dwarfs may be volatile-poor owing to the high impact velocities during formation (e.g., Lissauer 2007). However, if the planet began with larger initial volatile inventories (e.g., Luger et al. 2015), replenished its atmospheric volatiles through regassing from the interior (e.g.,
Moore & Cowan 2020), or experienced slower-than-expected atmospheric escape, TOI-1266c may still have a substantial envelope today.

On the other extreme, the 2σ upper mass limit of 6.4 $M_\oplus$ for TOI-1266c would indicate that the planet is >50% iron core (following the mass–radius relationship given by Noack et al. 2016), near the size limit driven by collisional stripping from impacts during accretion (Marcus et al. 2010). TOI-1266c would then represent a super-Mercury at less than half of Mercury’s instellation, which would have implications for the composition of its atmosphere. At lower planetary masses, TOI-1266c would likely still have an iron core but could also have a modest H$_2$–He envelope, on the order of 0.2%–0.5% of the total planet mass (Lopez & Fortney 2014; Zeng et al. 2019).

However, several theoretical arguments make it difficult to form an iron core with a substantial H$_2$–He fraction. First, a gas-rich initial composition is inconsistent with rocky planet formation models, which suggest that substantial accumulation of H$_2$ and He from the protoplanetary disk requires a minimum core mass $\gtrsim$5–20 $M_\oplus$ (e.g., Rafikov 2006, 2011). Planets with small rocky cores are also subject to atmospheric “boil-off” supported by the planet’s inability to cool rapidly enough (Owen & Wu 2016), potentially followed by loss driven by the cooling of the core (e.g., Misener & Schlichting 2021) and/or photoevaporation (e.g., Owen & Wu 2017). Boil-off would prevent the accumulation of more than a few tenths of a percent H$_2$, even if the planet began with >10% by mass H$_2$ (Owen & Wu 2016). Core-powered mass loss and photoevaporation would further reduce the amount of H$_2$, ultimately leaving behind an evaporated core (Luger et al. 2015) that would be inconsistent with current mass and radius constraints for TOI-1266c. These arguments effectively rule out an H$_2$-dominated state, although it is important to note that more complex models of the mass and radius evolution of volatile-rich planets still suggest a peak for planets with $\sim$1% H$_2$/He atmospheres (Chen & Rogers 2016). Additionally, secondary loss processes like ion pickup could further modify the atmosphere (see Gronoff et al. 2020, for an overview), although the stellar wind for TOI-1266 is only modest at present ($\lesssim 4 \times 10^{-14} M_\odot$ yr$^{-1}$, based on rotation constraints; Johnstone et al. 2015a).

We can combine this with the limited information we have about the solar system giants. Uranus and Neptune have interior “high-metallicity” (elements heavier than He) components ranging from 75% to 90% of the their total mass, depending on whether silicates and/or ices are assumed to be the “metal” (e.g., Hubbard 1981; Helled et al. 2010). This is consistent with other estimates regarding the internal composition of sub-Neptune-sized exoplanets (e.g., Wolfgang & Lopez 2015). This translates to roughly 11–13 $M_\oplus$ and 13–15 $M_\oplus$ for Uranus and Neptune, respectively (Helled et al. 2010;
Dodson-Robinson & Bodenheimer 2010), larger than the 2σ upper bound on TOI-1266c’s mass estimate. The ice component (thought to be the majority of the core; Hubbard 1981) is expected to be of supersolar metallicity (Lodders & Fegley 1994), with Neptune having a higher oxygen-to-hydrogen fraction (corresponding to a higher water ice fraction). This could also push the C/O ratio to higher values, approaching ~1 (Ali-Dib et al. 2014; see also the review by Mousis et al. 2020a). Several studies have motivated C/O ratios closer to 0.5 and a modest amount of ammonia ice (Nettelmann et al. 2016), which would be physically consistent with protoplanetary material that experienced full clathration (Mousis et al. 2020a). This is further complicated by the fact that assumptions about atmospheric structure and what type of adiabat the temperature profile follows (ranging from dry to wet) shift the retrieved atmospheric metallicity by a factor of a few (Cavalié et al. 2017).

Taken together, there is a compelling case to assume that TOI-1266c is volatile-rich and may even be an eroded sub-Neptune core. We take CO₂ as the major carbon-bearing species, as the CO/CH₄ transition and the CO₂ fraction peak at intermediate temperatures and pressures for higher-metallicity atmospheres (Lodders & Fegley 2002; Venot et al. 2014); likewise, N₂ dominates over NH₃ (Burrows & Sharp 1999).

2. Methods

We use a one-dimensional radiative–convective cloud-free model from Kopparapu et al. (2013, 2014), which was updated from the original version (Kasting 1988; Kasting et al. 1993) with new H₂O and CO₂ absorption coefficients. We employ inverse climate calculations in which the vertical temperature profile is specified, and radiative fluxes from the planet are back-calculated to determine the equivalent incident stellar flux. The atmosphere is divided into 101 layers. The model uses a moist pseudoadiabat extending from the “surface” (assumed to be at 100 bars) up to an isothermal stratosphere of 200 K. The surface temperature is varied until the effective solar flux (S_{eff}) matches the observed incident flux on the planet. S_{eff} is calculated from the ratio between the net outgoing IR flux (F_{IR}) and the net incident solar flux (F_{sun}), both evaluated at the top of the atmosphere. Essentially, by changing the surface temperature to match the incident stellar flux in our model, we are making sure that energy balance is maintained. The model top pressure is set to 10 μbar. Short-wave and long-wave fluxes are calculated using a δ-2-stream approximation (Toon et al. 1989) using separate eight-term, correlated-k coefficients for H₂O.

We also use a one-dimensional photochemical model that is a fork of Atmos⁹ (Arney et al. 2017) with a modified version of the C-H-O photochemical network from VULCAN¹⁰ (Tsai et al. 2017; see Appendix B, Table 3). We deliberately set aside nitrogen chemistry for this study because of the additional complexity necessary to include it in our model, and because of the uncertainties associated with speciation (we will return to this briefly in Section 4.1). Initial tests with a zero-dimensional chemical equilibrium model suggest that in the relatively oxidizing water-dominated scenarios we explore here, nitrogen is largely present as N₂, which would contribute to a higher mean molecular weight for the atmosphere but have few other practical impacts. The atmosphere is assumed to be well mixed below the “surface” at 100 bars. The model also includes newly measured water vapor photolysis cross sections (Ranjan et al. 2020). We use the ultraviolet through near-infrared spectra for GJ 581 (France et al. 2016; Youngblood et al. 2016; Loyd et al. 2016) as a proxy for TOI-1266, as they have comparable effective temperatures, luminosities, and ages, within uncertainties (Selsis et al. 2007; Dragomir et al. 2012; Gaia Collaboration et al. 2018). GJ 581 is technically a variable star, but its brightness variations are <1% (Dragomir et al. 2012). In our photochemical simulations, we ensure that the total mixing ratio is unity by using He as the remainder of the atmosphere. The amount of He added is generally ≤1% by volume. As an aside, He abundances could be reduced by drag-off if escape fluxes are high, but we find that using another gas (such as Ar) for this purpose has no qualitative impact on our photochemical results. We have also chosen a vertical eddy diffusion parameter K_{zz} = 10^{10} cm^2 s^{-1} consistent with other preliminary studies of hot Jupiters (e.g., Venot et al. 2014), noting that we have no constraints on the internal heat flux, rotation rate, and magnetic field strengths in order to constrain this value (e.g., Visscher et al. 2010, and references therein). We explore the effect of differing K_{zz} later, but to first order, lower values of K_{zz} decrease the vertical extent of the well-mixed region of the atmosphere but do not significantly impact the results described below. Given TOI-1266c’s current equilibrium temperature (see Table 1), it is unlikely that there is a substantial supercritical water component, and instead, TOI-1266c is “liquid” water dominated (Brugger et al. 2017; Mousis et al. 2020b). While the lower atmospheres in all of the cases we present here are above the critical temperature of water, the upper atmosphere passes through the temperature range where water would normally condense. We include in our calculations an updated H₂O saturation vapor pressure over water and ice (Meyer et al. 1983; Haar et al. 1984) and moderate the condensation loss frequency to ensure that the atmosphere is not substantially supersaturated where liquid water can condense (∼233 K), and below this the condensation over ice is allowed to decrease, reflecting higher possible supersaturations (Wallace & Hobbs 2006; Korolev & Mazin 2003), consistent with observations of cirrus clouds on Earth (e.g., Krämer et al. 2009). This is in keeping with other studies of temperate water-dominated atmospheres (e.g., Piette & Madhusudhan 2020). We do not, however, include aerosols to serve as cloud condensation nuclei, the necessary microphysical models to capture cloud formation processes, or the radiative effects of clouds, and we caution that the estimated cloud properties are solely illustrative. We return to this later in Section 4.

One additional constraint on the composition of the atmosphere is the cumulative impact of historic X-ray (X) and extreme-ultraviolet (EUV) radiation-driven mass loss (the sum is represented as XUV). To do this, we have developed a simple model of atmospheric loss¹¹ separate from the other two models. The escape model interpolates the BaSTI luminosity evolution grid¹² of Hidalgo et al. (2018) to the observed mass and luminosity of the host star (see Figure 2, top panel), similar to Barnes et al. (2020). The stellar luminosity evolution of Hidalgo et al. (2018) agrees with other stellar evolution models (Baraffe et al. 2015) from ~0.01 to 10 Gyr (the interval for the

⁹ Atmos on GitHub
¹⁰ VULCAN on GitHub
¹¹ GitHub repository for SNOWBALL
¹² http://basti-iac.oa-abruzzo.inaf.it/
Baraffe et al. 2015 grid) and includes time points back to 0.01 Myr and out to the end of the main sequence, even if this is beyond the age of the universe. Given the large uncertainty in the age of TOI-1266, this larger stellar age range allows for a more complete uncertainty analysis.

We also use the X-ray and EUV scaling relationships from Peacock et al. (2020) (see Figure 2, bottom panel), rather than the empirical scaling with respect to the bolometric luminosity \(L_{\text{bol}}\) from Sanz-Forcada et al. (2011), for two reasons. First, the EUV luminosity \(L_{\text{EUV}}\) from Sanz-Forcada et al. (2011) is above 1% of \(L_{\text{bol}}\) for \(\tau_i \sim 0.2\) Gyr and above 0.1% for \(1\) Gyr, due to the lack of an EUV saturation threshold for younger stars. The second issue with using the parameterizations of Sanz-Forcada et al. (2011) is that for a dimmer star like TOI-1266, there is a discontinuity in the calculated X-ray luminosity \(L_X\) saturation timescale \(\tau_i \sim 0.33\) Gyr using their Equation (5), such that the post-saturation \(L_X\) is briefly higher than it is in the saturated regime. During our initial tests, we chose to empirically set the saturation timescale to when the time-dependent X-ray luminosity falls below the saturated value, resulting in \(\tau_i \sim 0.47\) Gyr, which produced a negligible change in the total mass lost. We instead chose to use the X-ray and EUV scaling relationships from Peacock et al. (2020) in order to address these two discrepancies. Peacock et al. (2020) note a saturation of \(\sim 10^{-2} \frac{F_{\text{EUV}}}{F_{\text{bol}}}\) in their simulations of \(\sim 0.4\) \(M_\odot\) stars, slightly higher in magnitude but qualitatively consistent with work for larger stars (e.g., King & Wheatley 2020). Additionally, the log-linear dependence on age after the saturated period is comparable to other early M dwarf studies (e.g., Stelzer et al. 2013). These specific values from Peacock et al. (2020) are converted from flux ratios to luminosity ratios using the luminosity, distance, and Two Micron All Sky Survey J-band magnitude listed in Stefansson et al. (2020), assuming that the J-band fluxes are proportional to the bolometric luminosity.\(^{13}\)

Our escape model also takes advantage of the parameterizations available to distinguish between the radiation/recombination-, energy-, photon-, and diffusion-limited escape regimes (Murray-Clay et al. 2009; Owen & Alvarez 2016; Lopez 2017). This is not strictly necessary, as the XUV fluxes at TOI-1266c are much less than those experienced by hot Jupiters thought to be undergoing radiation/recombination-limited escape (Murray-Clay et al. 2009). However, depending on our choices for the mass-loss efficiency (aka the heating efficiency), atmospheric composition, and XUV luminosity saturation, the atmosphere transitions between the energy-, photon-, and diffusion-limited escape regimes at different times.

We assume that our escape calculations are largely insensitive to exospheric temperature, except for across the critical XUV flux identified for hot Jupiters (Koskinen et al. 2007). This is motivated by the interesting coincidence of the critical XUV flux necessary to drag off atomic oxygen from a terrestrial planet’s atmosphere (\(\sim 40\) times the XUV flux received by Earth today; Luger & Barnes 2015) and the XUV flux at which \(H_2^+\) cooling becomes ineffective at moderating thermospheric temperatures for gas giants (Koskinen et al. 2007). For gas giants, this transition

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\(^{13}\) Changes in stellar effective temperature are \(\lesssim 10\%\) for 0.4-0.5 \(M_\odot\) stars over their lifetimes (Baraffe et al. 2015; Hidalgo et al. 2018), which would shift the wavelength peak by \(<50\text{ nm}\).
produces an order-of-magnitude increase in the thermospheric temperature and atmospheric scale heights (Koskinen et al. 2007, their Figure 1a). Temperature changes are accurately assessed as a secondary effect in the critical XUV flux relationship for planets in their host star’s main-sequence habitable zone shown by Luger & Barnes (2015), since the critical XUV flux goes as $T^{-1/4}$. However, including a $10^x$ change in temperature would cause the critical XUV flux to decrease by more than a factor of two (that is, the onset of oxygen drag-off would occur at lower fluxes). For habitable-zone planets like those studied by Luger & Barnes (2015) and Ramirez & Kaltenegger (2014), this assumption does not introduce significant errors over the $\leq 1$ Gyr that these planets spend enduring the superluminous phase of their host stars. As we focus on water-dominated scenarios, the prevalence of molecular hydrogen and oxygen in the thermosphere suggests a closer resemblance to the upper atmosphere of Earth or Jupiter ($\sim$1000–2000 K) than the CO$_2$-dominated atmospheres of Venus and Mars ($\sim$200–300 K; Mueller-Wodarg et al. 2008), but under high instillation, even CO$_2$-dominated thermospheres are $\geq$10,000 K (Tian 2009). This, combined with the potential for Lyα cooling at high XUV fluxes (e.g., Murray-Clay et al. 2009), suggests that above $\sim$180 erg cm$^{-2}$ s$^{-1}$ the exospheric temperature is $\sim$10,000 K, and $\sim$1000 K below this flux threshold. Since TOI-1266c receives $\geq$180 erg cm$^{-2}$ s$^{-1}$ for nearly 3.5 Gyr, we find that escape of atomic oxygen continues for 2 Gyr longer than if we were to adopt the critical XUV flux suggested by Luger & Barnes (2015) of $\sim$400 erg cm$^{-2}$ s$^{-1}$ for a planet with TOI-1266c’s current mass and radius. This results in lower potential accumulated oxygen abundances in nearly every scenario for TOI-1266c, consistent with prior work that demonstrated oxygen accumulation and escape self-consistently for XUV fluxes 10–100 times larger than what Earth receives today (Figure 2; e.g., Zahnle & Kasting 1986).

We adopt mass-loss efficiencies ($\eta_{\text{XUV}}$) in line with other authors, including $\eta_{\text{XUV}} \sim 0.1$–0.15 for X-ray-dominated H$_2$ escape for a planet of comparable size to TOI-1266c (Owen & Jackson 2012; Bolmont et al. 2017) and $\eta_{\text{XUV}} \sim 0.01$ for H$_2$O following Lopez (2017), based on protoplanetary disk photo-evaporation studies (Ercolano & Clarke 2010). These are meant only as order-of-magnitude approximations, since the efficiency is dependent on planetary mass, radius, and envelope composition and its radiative properties, as well as the flux of high-energy radiation from its host star, and as such will evolve (e.g., Murray-Clay et al. 2009; Owen & Wu 2015). A planned next step is to use the flux-dependent efficiencies of Bolmont et al. (2017), noting that there is still some uncertainty when comparing these to efficiencies for close-in giant planets (e.g., Koskinen et al. 2014).

Because of the inherent uncertainties associated with almost every aspect of the atmospheric escape, as well as the planet’s mass and composition, we employ a Monte Carlo approach and perform a suite of escape simulations over the range of parameter uncertainties set out in Table 2. The atmospheric composition values are drawn from a log-uniform distribution, whereas all other values are drawn from linear uniform ranges. Values are generated using the Latin Hypercube sampling (LHS) method in the Surrogate Modeling Toolbox (Bouhlel et al. 2019), which leverages the Enhanced Stochastic Evolutionary algorithm (Jin et al. 2003) to optimize the Design of Experiments Toolbox (pyDOE) implementation. One important caveat is that the atmospheric escape simulations assume the maximum amount of water available for a given mass and radius, following the relationships derived by Noack et al. (2016). We note that the mass–radius relationships from Noack et al. (2016) do not include an atmosphere, but in our photochemical simulations the vertical extent of the region between 1 bar and $\sim$10 mbars is $\sim$400–600 km, which would change the apparent radius by less than the reported uncertainty. The Noack et al. (2016) mass–radius relationship places a physically motivated lower limit for the planet’s mass of $\sim$1.6 $M_{\oplus}$ from the lower bound on the planet’s radius, where the planet would be 100% water. If future observational constraints on the planet’s mass are below this threshold, the planet must have a nonnegligible amount of H$_2$ at present. More complex compositional mixes are beyond the scope of the present work, but abundant H$_2$ in TOI-1266c’s atmosphere would most likely eliminate the possibility of oxygen accumulation from hydrogen loss, as well as posing an interesting conundrum for the formation and evolution mechanisms highlighted above that would remove an H$_2$-dominated atmosphere.

Lastly, we use the Planetary Spectrum Generator$^{14}$ (PSG; Villanueva et al. 2018) to produce synthetic transmission spectra for the scenarios outlined here. PSG is an online radiative transfer suite that integrates the latest radiative transfer methods and spectroscopic parameterizations, and it includes a realistic treatment of multiple scattering in layer-by-layer spherical geometry. It can synthesize planetary spectra (atmospheres and surfaces) for a broad range of wavelengths for any given observatory. We validate these results with PandExo (Batalha et al. 2017b).

### Table 2

| Property (units) | Default Value | Tested Range |
|------------------|---------------|--------------|
| Stellar age (Gyr) | 7.9 Gyr       | 2.7–12.1     |
| Current luminosity ($L_\odot$) | 0.026 29 | 0.025 54–0.027 |
| Planet mass ($M_\oplus$) | 1.9 | 1.6–6.4 |
| Planet radius ($R_\oplus$) | 1.673 | 1.563–1.76 |
| Atmos. mass ($M_{\text{atm}}$) | ... | see note$^c$ |

| Property (atm. composition) | Default Value | Tested Range |
|-----------------------------|---------------|--------------|
| H$_2$ | ... | $10^{-6}$–1$^b$ |
| He | ... | $10^{-6}$–1$^b$ |
| H$_2$O | ... | $10^{-6}$–1$^b$ |
| CO$_2$ | ... | $10^{-6}$–1 |
| Escape efficiency | $H_2$ | 0.1 | 0.01–0.4 |
| | $H_2$O | 0.01 | 0.01–0.4 |
| | CO$_2$, O$_2$ | 0.01 | 0.01–0.1 |

### Notes:

$^a$ The planetary volatile abundance was set to the maximum water abundance allowed for the selected mass and radius given by Noack et al. (2016).

$^b$ The helium abundance in the escape simulations was set by scaling the solar He:H$_2$ ratio (0.3367) by the value drawn from the stated range, given the selected H$_2$ abundance. The atmospheric composition was normalized as a final step.

### 3. Results

#### 3.1. Atmospheric Escape

We begin by estimating the atmospheric lifetime for TOI-1266c, assuming the observed mass and radius for the present day (Figure 3). A pure-water atmosphere experiences substantial water

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loss over its lifetime, as can be seen in the top panel of Figure 3, but still retains abundant H$_2$O through ∼8 Gyr (vertical dashed line). That said, the volatile inventory is roughly one-third oxygen by the present day (assuming that the oxygen is not absorbed by the planet’s interior), resulting in spectroscopically detectable oxygen (we will return to observations later). A second test, which includes a modest amount of hydrogen, can be seen in the bottom panel of Figure 3. This scenario demonstrates that a relatively minor amount of H$_2$ (∼0.4% of the planet’s initial mass) can prevent significant loss of water and the commensurate accumulation of O$_2$, as the H$_2$ combines with any free oxygen to replenish H$_2$O (this is an explicit prescription in our model). This amount of H$_2$ is broadly consistent with what might remain following atmospheric boil-off (Owen & Wu 2016). In both of these cases, the mass of the total volatile inventory does not substantially change throughout the planet’s life, and in total the mass changes by ∼1% and the radius by ∼0.3%–0.5% over this same interval. However, it is important to note that this is equivalent to losing ∼100 Earth oceans, substantially more than the initial water reservoirs explored in other work (e.g., Luger & Barnes 2015). These evolutionary tracks are useful for illustrating the behavior of individual scenarios near the boundaries between regimes, but given the large uncertainties in some critical parameters, it is important to fully explore the impact of atmospheric escape on the present state of TOI-1266c.

As such, we ran a suite of 10,000 atmospheric escape simulations covering the stated uncertainty ranges in Table 2. Several commonsense interpretations of this initial exploration can be gleaned from Figure 4: (1) smaller initial planet masses for the same planetary radius correspond to larger potential water (volatile) inventories (denoted by the size of the points), which is a natural consequence of our experimental design; (2) larger volatile inventories are more difficult to lose completely and suppress substantial accumulated oxygen mass fractions; and (3) it is unlikely that a planet more massive than ∼3.5 $M_\oplus$ would have any remaining H$_2$O because of the small initial volatile inventories, and consequently, it could have large oxygen mass fractions. The apparent gulf spanning intermediate oxygen mass fractions from 3.5 to 6.5 $M_\oplus$ reflects complete desiccation of initially hydrogen- and water-dominated states that are pulled up to the 100% oxygen mass fraction state, barring a few simulations with escape efficiencies at the bottom of the tested range and/or young stellar ages. The remainder of the scenarios have small initial water fractions that do directly correspond to the oxygen mass fraction but do not group up in the same way. There is also no significant trend with H$_2$ escape efficiency (Appendix C, Figure 11) for the planet parameters and atmospheric compositions tested here, although this may not be the case for other regions of the parameter space.

3.2. Initial Temperature/Pressure and Water Profiles

The initial water vapor profiles produced by the radiative–convective model were used to initialize the photochemical simulations. All of the following simulations assume the nominal radius and mass for TOI-1266c (1.673 $R_\oplus$ and 1.9 $M_\oplus$; Stefansson et al. 2020), as well as a water-dominated atmosphere. As an aside, the climatological and photochemical water vapor profiles for the same temperature/pressure conditions differ slightly. This is largely due to the combination of photoysis and vertical mixing (via both parameterized advection and molecular diffusion) in the photochemical model that modifies the water profiles in the upper atmosphere (above ∼10 mbar) by a factor of a few (Figure 13, Appendix C). For the atmospheric compositions explored here, this results in transmission spectra uniformly decreased by a few parts per million at all wavelengths between the climatological water profiles and the photochemical water profiles as a result of the change in mean molecular weight (not shown). This may not
be the case for every scenario, however, particularly if water is more efficiently segregated to the lower atmosphere (for example, through weaker vertical mixing or efficient scavenging processes).

The three families of atmospheres (H₂+H₂O, H₂+CO₂+H₂O, O₂+H₂O) have some shared attributes, including the same general pressure ranges for the condensation of water (Figure 5, left panel). Of the O₂-bearing scenarios, only the intermediate-concentration cases (0.1% and 1% O₂) have water vapor profiles with higher upper atmospheric concentrations than the case with the highest water fraction. This is in contrast to both the H₂ and CO₂+H₂ scenarios, which have more saturated upper atmospheres for higher mixing ratios of the diluting species. The CO₂ scenarios are warmer in the deep atmosphere because of CO₂’s efficacy as a greenhouse gas, while H₂ is more effective than O₂ as a collisional broadening partner, resulting in intermediate temperatures.

3.3. Atmospheric Chemistry

Our photochemical modeling is informed by the atmospheric escape and radiative–convective simulations of TOI-1266c, focusing here on an initial exploration limited to H-C-O chemistry (future work will include other species). Each of the three families of water-dominated atmospheres has lesser amounts of H₂, H₂+CO₂, or O₂ that drive the chemistry of trace species. As we discuss later, many of these changes are not visible in the integrated planetary spectra, but they are integral to accurately capturing the major species. We will focus on changes in the species that may be potentially observable (e.g., O₂, O₃, H₂O, CO₂, and CO). Of these species, only O₃ and CO are essentially free to respond to instellation and compositional changes, while O₂, H₂O, and CO₂ are given fixed concentrations at the 100-bar pressure level that are then subject to dynamical and thermo- and photochemical processes. CO (Figure 6, left panel) is largely produced by photolysis of CO₂ in the upper atmosphere and then mixed downward into the deeper atmosphere, where the background CO concentration is set by thermochemical reactions.

Ozone, much like CO, is dependent on the concentration of another species (O₂) and secondary trace species and photolysis reactions that rapidly convert atoms between these two reservoirs. In terrestrial photochemical studies (e.g., Segura et al. 2003), the typical threshold to establish a robust O₃ layer is ∼1% of Earth’s present atmospheric level of O₂ (i.e., ∼2% by volume O₂). On Earth, the ozone layer is maintained by photochemistry at roughly ppm concentrations between ∼0.5 and 50 mbar. This pressure range is comparable to the scenarios with more abundant O₃ in Figure 6 (right panel), but the mixing ratios are lower by a factor of ∼10³. The lower concentration of O₃ for these scenarios is driven by the higher abundance of OH radicals in the upper atmosphere derived from water vapor photolysis (see Appendix C), in line with earlier work that demonstrated a
reduction in O\textsubscript{3} with warmer atmospheres and high OH abundances (Chen et al. 2019). Because all of the scenarios explored here have nonnegligible H\textsubscript{2}O abundances, increasing the O\textsubscript{2} abundance beyond 10% by volume produces a roughly linear increase in the peak O\textsubscript{3} mixing ratio (not shown), still much less than the maximum ozone mixing ratio in Earth’s atmosphere. We will return to remote detectability later.

4. Discussion

The atmospheric escape calculations showcase a number of evolutionary pathways that are in line with other estimates for super-Earths and sub-Neptunes (e.g., Estrela et al. 2020), and TOI-1266c sits at the nexus of the potential states, although it would constitute a low-instellation terrestrial planet following
Estrela et al. (2020). One possible outcome is that TOI-1266c was (and remains) a rocky planet composed of predominantly silicates and iron. TOI-1266c would then most resemble a super-Venus (Barclay et al. 2013; Kane et al. 2013), but even among Venus-like planets some variation is expected (e.g., Schaefer & Fegley 2011; Kane et al. 2018). Barring the potentially brief steam atmospheres immediately following formation and/or a later transition into the moist and runaway regimes (e.g., Hamano et al. 2013; Driscoll & Bercovici 2013; Way et al. 2016), however, the lack of a substantial volatile inventory results in dry, rocky super-Venuses. On the other end of the compositional spectrum, hydrogen-dominated sub-Neptunes boast larger spectroscopic features requiring fewer transits to obtain sufficient signal-to-noise ratio (e.g., Choucar et al. 2020; see also Figure 7). For strongly irradiated objects, however, the impact of atmospheric escape should be considered when estimating atmospheric and bulk composition, much like how we have chosen to consider largely H₂O-dominated scenarios for TOI-1266c.

4.1. Chemical Considerations

The carbon speciation is dependent on temperature (Lodders & Fegley 2002), so while we have used the conjectured water and methane ice fractions from Uranus and Neptune as a starting point, the equilibrium speciation heavily favors CO₂ over CH₄ at the lower boundary. If the planet starts out as more reduced, CO₂ would shift toward CO and ultimately CH₄; however, even trace amounts of water vapor are able to rapidly convert photochemically produced CO back into CO₂ such that the upper atmosphere would have a smaller abundance of CO than would be predicted solely from thermochemistry. The assumed “surface” pressure also affects the abundances of trace species (Yu et al. 2021), but we have not tested this explicitly in our simulations. Beyond this, other factors, such as the choice of \( K_{zz} \), can further modify the concentrations of trace species.

We have explored the sensitivity of atmospheric composition to changes in \( K_{zz} \) by decreasing it from our default value of \( 10^{18} \) cm² s⁻¹ down to \( 2 \times 10^{17} \) cm² s⁻¹. Below this value, our photochemical model has difficulty converging. This appears to be due to the descent of the homopause (also called the turbopause) into the warmer, denser parts of the atmosphere below the isothermal stratosphere (note the sharp decrease in concentration at the upper boundary in Figure 12, Appendix C). Lower \( K_{zz} \) values affect our chemical profiles in much the same way as they affect other models (e.g., Visscher & Moses 2011; Venot et al. 2014; Gao et al. 2018).

Additionally, we find no significant deflection in the location of the water condensation region, which would have a much stronger effect on the observations (e.g., Figure 8, top panel) than the variations in species’ concentrations with \( K_{zz} \). Uranus and Neptune have \( K_{zz} \) values closer to \( \sim 10^8 \) cm² s⁻¹ (Cavalié et al. 2017). Stronger mixing and/or different temperature profiles can give the appearance of lower metallicities (Cavalié et al. 2017). Mixing length theory (e.g., Visscher et al. 2010) suggests that \( K_{zz} \approx 10^6–10^8 \) cm² s⁻¹ throughout the model domain if the internal heat flux is 50–50,000 erg cm⁻² s⁻¹, comparable to modern Earth and Jupiter, respectively (Gando et al. 2011; Pearl & Conrath 1991).

For this initial work, we have neglected species that could play an important role in modifying the atmospheric structure and evolution. For example, sulfur chemistry has been shown to significantly modify the thermal profile of hot Jupiters (Zahnle et al. 2009), while sulfuric acid aerosols have been suggested as an alternative way to form a cold trap (Walker 1975), given their hygroscopic tendencies in Venus’s modern atmosphere (e.g., Krasnopolsky & Pollack 1994; Yung et al. 2009; Tsang et al. 2010). Additionally, if NH₃ is a substantial component for ice giant cores (e.g., Nettelmann et al. 2016), then NH₃ could be present in the gas phase and contribute to the total reducing power available to the atmosphere. Particularly for the scenarios where TOI-1266c loses most of its hydrogen, nitrogen could oxidize into NO compounds, analogous to NO derived from persistent lightning storms (e.g., Ardaseva et al. 2017). However, the temperature profiles used here all lie above the N₂/NH₃ equal-abundance pressure–temperature curve (e.g., Fortney et al. 2021), suggesting that ammonia incorporated as ice may affect the total atmospheric pressure (as N₂) and act as a source of reducing power by equilibrating to form H₂ at depth without NH₃ necessarily becoming a major constituent in the atmosphere. Lastly, if TOI-1266c has a silicate core, then moderately volatile elements like Na and Cl could contribute to atmospheric composition either directly (that is, there may be a rock vapor atmosphere) or indirectly (e.g., through catalytic and secondary reactions with the major species).

Hazes, driven either by condensation or by photochemistry, represent significant hurdles for characterizing exoplanetary atmospheres. Here we have only considered water and a few other potentially major species, but the presence of sulfuric acid clouds on Venus (Kawabata et al. 1980) or other sulfur-based aerosols (e.g., Zahnle et al. 2009, 2016; Gao et al. 2017) is possible if sulfur is present in trace amounts. This could lead to observational degeneracies between a solid surface and a highly reflective cloud top (e.g., Lustig-Yaeger et al. 2019b). Similarly, abundant carbon could lead to the formation of organic aerosols, but the relatively water-rich and lower-temperature scenarios tested here largely prevent carbon–carbon chemistry. Even with the uncertainties in TOI-1266c’s mass allowing for a predominantly silicate composition, a modest amount of water loss would produce enough free oxygen to effectively preclude organic aerosols (e.g., Hörst et al. 2018), unless the oxygen left over from water loss were absorbed by the solid planet (e.g., Luger & Barnes 2015). However, if the planet started out relatively water-poor, or more diverse haze
formation pathways are considered, hazes seem likely (Moran et al. 2020; Reede et al. 2020; Vuitton et al. 2021) and could be of various compositions with distinct optical properties (e.g., He et al. 2018, 2020a, 2020b). Spectroscopic characterization, in combination with better mass constraints, would effectively narrow down the possibilities, much like it would for the TRAPPIST-1 system (Moran et al. 2018). Other secondary condensate species could be present, such as potassium chloride (KCl; e.g., Gao et al. 2018), which could enhance the effectiveness of (or serve in their own right as) cloud condensation nuclei for water clouds.

4.2. Redox Considerations

As a super-Earth, TOI-1266c’s size requires that we use caution with regard to the common assumptions about the atmospheric composition and evolution of warm Neptunes (e.g., Hu & Seager 2014; Moses et al. 2020). As mentioned previously, TOI-1266c may be rocky, and if so, it may have started out with a relatively H2- and He-poor composition before subsequently losing the H2 and He over its lifetime. In our Monte Carlo simulations, the average scenario lost \( \lesssim 1\% \) of the planet’s mass by the present day, but at the same time, the mean envelope fraction declined by \( \sim 20\% \) of its initial value. This makes intuitive sense—the largest impact of atmospheric escape is seen in those cases where the atmosphere is initially only a small fraction of the planet’s mass. Studies suggest that more massive planets under higher instellation have comparable mass losses for higher H2 mass fractions, which would produce larger variations in the planet’s present-day radius (Estrela et al. 2020).

Alternatively, if TOI-1266c is more massive, then water may be sequestered into and later outgassed from a magma ocean, preserving a relatively high water mass fraction (Kite & Schaefer 2021). If TOI-1266c started with a water-dominated
atmosphere without a sufficient buffer of \( H_2 \), then the persistent loss of \( H \), derived from water vapor photolysis, would fundamentally alter the redox of the planet through the accumulation of oxygen. Since we have hypothesized scenarios in which TOI-1266c has substantial amounts of water at present, this buildup of oxidants would still be happening today. These oxidants could react with a magma ocean and drive chemical alteration, or they could be sequestered through incorporation into high-pressure ice phases. Transport via convection through high-pressure ice layers has been studied for icy satellites (e.g., Deschamps & Sotin 2001) and water-dominated super-Earths (Fu et al. 2009; Noack et al. 2016) and would allow for both a supply of reducing gases from the interior and redox evolution of the interior driven by atmospherically derived oxidants.

4.3. Other Factors Affecting Atmospheric Loss

Uranus’s and Neptune’s water-dominated interiors have adiabats that likely pass through the superionic portion of the high-pressure and high-temperature water phase diagram (Redmer et al. 2011; Knudson et al. 2012; Millot et al. 2018). This may explain why Uranus and Neptune are the only planets with multipolar rather than dipolar fields (Schubert & Soderlund 2011). If TOI-1266c is more water dominated than the ice giants, then the pressure–temperature profile does not cross through the superionic regime, which could result in a weaker planetary magnetic field dominated by the dipolar component (e.g., Tian & Stanley 2013). We note, however, that our temperature–pressure profiles for TOI-1266c are incompatible with those of Tian & Stanley (2013) because we have assumed that the \( H_2 \) and \( H_2O \) are well mixed. Additional components like ammonia or methane further complicate the conductivity of the high-pressure ice layers, but carbon and nitrogen may precipitate out together (e.g., Chau et al. 2011). In terms of uncertainties related to the host star, our assumed stellar luminosity evolution is based on the grid of Hidalgo et al. (2018), which includes luminosity evolution data for 0.4 and 0.45 \( M_\odot \) stars. Given that TOI-1266 is \( \sim 0.44 \, M_\odot \), we could reasonably assume that it follows the 0.45 \( M_\odot \) stellar evolution. However, the observed luminosity for TOI-1266 and 0.45 \( M_\odot \) luminosity are different by \( \sim +3\% \) at 7.9 Gyr (TOI-1266’s notional age). Taking the mass-weighted logarithmic mean of the Hidalgo et al. (2018) evolutionary tracks results in a roughly \( -6\% \) discrepancy between observed and estimated present-day luminosities. Normalizing the luminosity to match both the observed stellar mass and luminosity has the unintended side effect of producing higher fluxes than the 0.45 \( M_\odot \) track early in the star’s history (Figure 2). It is not immediately clear which approach is appropriate, but we find that using both the normalization and a weighted mean of the luminosities accurately reproduces the generic luminosity estimate derived from the stellar mass within \( \sim 5\% \) (Cuntz & Wang 2018), as opposed to approximately \( -12\% \) when using the 0.45 \( M_\odot \) evolution data (we use the Cuntz & Wang 2018 generic mass–luminosity relationship because TOI-1266’s mass estimate is on the cusp of where older formulations have a discontinuity; e.g., Kutner 2003). Uncertainties in mass and luminosity have knock-on effects for when the star enters the main sequence and on the estimated atmospheric loss. Our methodology for the luminosity interpolation should be viewed with skepticism and would improve with stronger constraints on stellar properties.

Additionally, the age uncertainties for TOI-1266 suggest that longer-term persistent atmospheric loss processes like interactions with the stellar wind (e.g., Cohen et al. 2015; Tilley et al. 2019; Gronoff et al. 2020) could either play a major role in the current state of TOI-1266c, if the star is older, or still represent a small fraction of the total loss when compared to the loss estimates from the pre-main-sequence superluminous phase. While no observations of flaring for TOI-1266 have been reported at this time, stellar flares can further contribute to atmospheric erosion. Losses due to flaring are typically smaller than the baseline XUV-driven escape rates (e.g., Atri & Mogan 2021), although this may not be universal, particularly for stars that flare more frequently (e.g., France et al. 2020). Magnetohydrodynamical models of \( H_2 \) (e.g., Johnstone et al. 2015b) and \( H_2O \) (e.g., Johnstone 2020) loss, as well as generically \( H \)-dominated super-Earth loss rates (Kislyakov et al. 2013), suggest that loss is a certainty, even if the magnitude and dominant mechanisms remain open questions.

Another potential factor is the communication between the interior of the planet and its atmosphere. If, for example, TOI-1266c is water or hydrogen dominated, then the core component may effectively supply material to the escaping envelope (e.g., Wilson & Militzer 2011), especially if \( H_2 \) is effectively incorporated into water ices (Soubiran & Militzer 2015) or separates out slowly over the course of the planet’s lifetime (Bailey & Stevenson 2019). However, if \( H_2 \) is ultimately immiscible (e.g., Bailey & Stevenson 2019, and references therein), then the \( H_2 \) stranded in the atmosphere would be lost preferentially to \( H_2O \), as discussed previously, leaving behind an ice-dominated core.

4.4. Spectral Signatures and Observations

In terms of differentiating the scenarios discussed here, \( CO_2 \) and \( O_2 \) stand out as the primary species in each family of simulations. \( CO_2 \) has a strong absorption feature at \( \sim 4.3 \, \mu m \) (\( \sim 40 \) ppm; Figure 9) even for 1% \( CO_2 \) in a cloud-free atmosphere. This is broadly consistent with simulated retrievals of warm sub-Neptunes with the James Webb Space Telescope (JWST; e.g., Greene et al. 2016). Additionally, the 4.3 \( \mu m \) feature would likely not be significantly impacted by the presence of hazes, which typically have small impacts on spectral features at longer wavelengths (e.g., Kempton et al. 2017). The \( O_2 \) features in the
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Figure 10. Synthetic spectra ($R = 500$) for just the O2+H2O mixtures from Figure 8, compared with the 10% CO2 mixture. Note that the O2 A-band feature at 0.76 μm increases to ~10 ppm at 10% O2. However, the 0.2–0.3 μm and 9.6 μm ozone features are absent owing to the lack of a substantial O3 column abundance (the 0.2–0.3 μm region has O2 features from the Herzberg continuum but no contributions from O3). Variations between the spectra in this region are due to the increasing atmospheric mean molecular weight at higher O2 abundances. The orange error bars are for a simulated observation using JWST’s NIRSpec-Prism for 50 hr of in-transit time ($R = 100$). We also overplot a cloudy scenario, assuming that 14 μm liquid water droplets with a volume mixing ratio of 0.1 ppm (Kopparapu et al. 2021) are distributed throughout the pressure range identified in Figure 5.

ultraviolet are relatively small (Figure 10), while the 0.76 μm feature provides a relatively wide ~15 ppm signal in comparison. Because of the abundant water vapor and the modest O2 mixing ratios, O2–O2 dimer spectral features (Misra et al. 2014; Fauchez et al. 2020) are unlikely to be present or observable. From Figure 10, and more broadly Figure 7, it is clear that JWST will be unable to positively identify oxygen without a substantial investment of observational time, even for the relatively extended, warm atmospheres we consider here.

CO and O3, derived from CO2 and O2, also have spectroscopic features that can help in distinguishing these scenarios. CO has weak features at 1.6, 2.3, and 4.7 μm (Wang et al. 2016; Schwieterman et al. 2019), but these are subsumed by strong H2O and CO2 features at those wavelengths. Interestingly, the appearance of the O2 A band at ~0.76 μm (Figure 8) does not result in the commensurate rise of an O3 feature at 9.6 μm that is expected for temperate, O2-rich atmospheres (e.g., Segura et al. 2003, 2005; Rugheimer et al. 2013; Rugheimer & Kaltenegger 2018; Meadows et al. 2018). This was noted by Chen et al. (2019) as a result of OH reducing the O3 concentrations, but here it is comparable to the results first shown by Pilhorodetska et al. (2021), where high temperatures force the rapid thermal decomposition of O3 (the back-reaction of Reaction #309 in Appendix B). As a result, there is a 10$^4$-fold reduction in O3, with O3 being entirely absent from the integrated transmission spectra (Figure 10, 9.4–9.8 μm).

The possibility of clouds at temperate conditions (230–290 K; ~0.5–5 mbar) acts in two ways to obscure spectral features (Fauchez et al. 2019): first by limiting transmission through the deeper, warmer parts of the atmosphere, and then by introducing strong intermediate-temperature water features. This pressure range for condensation is in keeping with those reported in other studies of steam atmospheres. For example, Nikolaiou et al. (2019) report much lower pressures as an upper bound, although those experiments have substantially more CO2 than the cases described here. Water clouds may also appear in the atmospheres of more temperate massive planets (Chamay et al. 2020), again at around 10 mbar. However, some scenarios featuring clouds work to enhance spectroscopic features (e.g., Kawashima & Rugheimer 2019), which makes determining self-consistent cloud, climate, and photochemistry a critical next step. We have attempted to include the impact of clouds by assuming that the clouds are composed of ~14 μm droplets with a volume mixing ratio of 10$^{-7}$ or ice clouds composed of 25 μm crystals with a mixing ratio of 10$^{-9}$. In both cases, the clouds do not appear to substantially impact the water spectral features (Figure 8, gray curves), with ice clouds having a smaller effect, largely due to their smaller abundance. The smaller reduction, as compared to more temperate atmospheres (Fauchez et al. 2019), is likely due to the presence of water vapor above the cloud deck in a water-rich atmosphere that minimizes the impact of clouds on spectral features. A self-consistent cloud modeling effort is necessary to further this work.

TOI-1266c could be characterized by JWST in the future, which could effectively distinguish between some of these cases. The signal-to-noise ratio of a series of observations of TOI-1266c in transit is shown in Figure 7. We calculate signal-to-noise as the difference between two synthetic spectra, one of which ignores the spectral contributions from the chief secondary species (e.g., H2, O2, or CO2), dividing by the
simulated noise. The counterintuitive reduction in signal-to-noise ratio with increasing H₂ abundances stems from the decreasing apparent water column mass. The other compositions show the opposite trend, driven by those gases having distinct spectroscopic features of their own. Ultimately, CO₂ and H₂O in significant abundances could be identified in a few tens of hours, but oxygen to a sufficient signal-to-noise ratio may be beyond JWST’s capabilities. As mentioned previously, the 4.3 μm CO₂ band would not be substantially affected by hazes, although further tests are necessary.

Further investigations of the radius gap have the potential to provide key insights into the processes that shape planets over their lifetimes. As the community continues to find more transitional objects, it is becoming increasingly clear that some of the exoplanets that are likely to be characterized in the near future may not be precisely what we expect them to be. Volatile-depleted sub-Neptune cores masquerading as superEarths could inadvertently skew our perspectives on habitability, such as if a water-dominated sub-Neptune is incorrectly classified as a terrestrial planet, since the large water fraction would suggest oceans so deep that they would suppress volatile exchange and plate tectonics (Kite et al. 2009).

5. Conclusions and Future Work

The potential to observe a Venus analog, particularly if it remains in a steam-dominated runaway greenhouse at present, offers an unparalleled window into the history and evolution of a unique terrestrial planet, as well as one of the first few steam atmospheres accessible with JWST. Data about water-dominated atmospheres are also relevant to the bounds of habitability for terrestrial planets, particularly those that form around low-mass host stars (Luger & Barnes 2015) and orbit older stars (e.g., Rushby et al. 2013; Lehmer et al. 2020). Lastly, observations of exoplanets that may have accumulated oxygen derived from water loss are important to establishing a baseline for larger planet sample size analyses, particularly in the context of biosignatures (e.g., Bixel & Apai 2020). Estimating the composition and any potential observables for TOI-1266c remains difficult. The degeneracies in relating bulk composition, atmosphere-to-solid planet fraction, and mean density (e.g., Rogers & Seager 2010; Dorn et al. 2015; Welbanks & Madhusudhan 2019) pose significant challenges in predicting the atmospheres of exoplanets even if the mass and radius are well constrained, and even spectroscopic observations of the planet may not necessarily break this degeneracy (Batalha et al. 2017a). Additional radial velocity observations—such as precision radial velocities with HPF (Mahadevan et al. 2012, 2014), NEID, or CARMENES—are required to constrain the planet’s mass, which will narrow the range of possible compositions (e.g., Valencia et al. 2013).

The modeling demonstrated here showcases the impact of dynamical, photochemical, and ancillary atmospheric processes on the disposition of some of the possible planetary states in the radius gap. These planets highlight the continuing need to understand the processes that shape highly irradiated, volatile-rich planets in advance of observational campaigns with JWST and other future instruments. Follow-up observations are planned to better constrain TOI-1266c’s mass (and by extension its possible composition). Regardless of whether or not TOI-1266c is the first such target to be observed, this class of objects requires additional capabilities beyond thermochemical equilibrium models and assumptions about composition in terms of metallicity. In a future study, we plan to expand our photochemical scheme to include secondary species that were omitted in this work, as well as explore the feedbacks between climate, chemistry, and observability.

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Software: Atmos (Armey et al. 2017), Planetary Spectrum Generator (PSG) (Villanueva et al. 2018).

Appendix A

Atmospheric Escape Code Derivation and Description

As described in the main text, our model for atmospheric escape is based on the stellar luminosity evolution models of Hidalgo et al. (2018) in conjunction with the escape flux parameterizations of Murray-Clay et al. (2009), Owen & Wu (2016), and Lopez (2017). Here we walk through the assumptions built into our model and how we implemented these processes.

The SNOWBALL repository has two branches: the main branch and the monte_carlo branch. Both branches have largely the same code, save that the monte_carlo branch features a refactored main.py such that it can be called by the Monte Carlo generator program and return the results. Because the Monte Carlo application has additional assumptions, we will use that as the basis for the remainder of this discussion. The code is laid out in an attempt to compartmentalize individual physical concepts and processes, but because some are interconnected, it is not always possible to completely separate some of them. Below is a partial dependency tree for...
how we calculate the escape regimes and fluxes (omitting generic and optional functions):

```
monte carlo branch.
montecarlo.py.
main.py.
    run_escape(age_star, l_star, m_planet, r_planet, envelope_comp, efficiencies).
modes.py.
    read_hidalgo.
    read_thermo.
    generic_diffusion.
crossover_mass.
bisect2.
planet_radius.
f_lum_CW18.
calc_escape_regime.
constants.py.
planet.py.
envelope_species.
analyze_MC.py.
```
The atmospheric scale height equation is valid only when the atmosphere is largely hydrostatic, because otherwise the vertical velocity of the escaping component “stretches” the scale height (e.g., Hunten 1973).

Following the determination of these quantities, we estimate the escape regime following Owen & Alvarez (2016). In brief, there are three surfaces in stellar flux–planet mass–planet radius phase space that correspond to three different escape regimes: energy limited, photon limited, and recombination limited. Briefly, these regimes correspond to situations in which the escape rate is limited by a particular phenomenon (Murray-Clay et al. 2009; Owen & Wu 2017). The energy-limited escape rate is determined by the plausible upper bound of the amount of energy that could be absorbed and converted into kinetic energy that then drives atmospheric escape. The photon-limited escape rate is derived from the need for ionizing radiation to break up molecules and atoms into smaller and/or charged particles that can then escape. Since the radiation arrives at the top of the atmosphere as a flux of photons that cannot be divided further, there can only be a certain amount of material available for escape at any one time. Lastly, the radiation–recombination limit is moderated by a thin, fully ionized gas layer in the escaping flow that prevents the further absorption of more energy until some of the dissociated material is allowed to recombine. Generally, the larger the planet or the higher the incoming EUV flux, the more likely the planet is to be in the recombination-limited regime, while smaller planets or those experiencing lower EUV fluxes fall into the photon-limited regime. The individual escape rate parameterizations are taken from the literature and are most often defined in the context of uniform molecular or atomic hydrogen atmospheres, which may not be fully reflected by some of the scenarios described here. The photon-limited escape rate (in kg s^{-1}) is defined as

\[ \Phi_{\text{phot}} = \frac{\pi R_p^2 m_H \Phi_{\text{XUV}}}{h_{\text{th}}}, \]  

where \(R_p\) is the planet radius (m), \(m_H\) is the mass of a hydrogen atom (kg), \(\Phi_{\text{XUV}}\) is the XUV energy flux received by the planet (W m^{-2}), and \(h_{\text{th}}\) is the mean photon energy for photons that heat the upper atmosphere (J photon^{-1}).

The radiation–recombination limit (in kg s^{-1}) is given by

\[ \Phi_{\text{recombination}} = 7.11 \times 10^4 \Phi_{\text{XUV}} R_p^{3/2}, \]

which comes from Luger et al. (2015), based on the 1D photoevaporation modeling and resulting parameterization of hot Jupiter atmospheric escape by Murray-Clay et al. (2009; see Luger et al. 2015 for the derivation). The leading cofactor includes an additional unit conversion to MKS units from CGS units but is otherwise identical. The equation relates the escape limit to \(\Phi_{\text{XUV}},\) the XUV energy flux received by the planet (W m^{-2}), and includes an explicit dependence on the planet’s radius (\(R_p\), in m).

The energy-limited escape rate (in kg s^{-1}) is

\[ \Phi_{\text{energy}} = \frac{\eta \Phi_{\text{XUV}} R_p R_{\text{exobase}}^2}{GM_p K_{\text{tide}}}, \]

using the formulation of Luger & Barnes (2015). In this equation, \(\eta\) is the escape efficiency parameter (0 < \(\eta\) < 1; unitless), \(R_p\) is the radius of the planet (m), \(R_{\text{exobase}}\) is the radius of the exobase (in m; defined above, following Lopez 2017), \(G\) is the gravitational constant (m^3 kg^{-1} s^{-2}), \(M_p\) is the mass of the planet (m), and \(K_{\text{tide}}\) is the nondimensional tidal enhancement factor (taken from Erkaev et al. 2007), which depends on the Roche lobe radius \(R_{\text{Roche}} = \frac{a(M_p/(3M_\odot))^{1/3}}{m}\) and the planet radius \(R_{\text{p}}\) in m such that

\[ K_{\text{tide}} = 1 - \frac{3R_p}{2R_{\text{Roche}}} + \frac{R_p^3}{2R_{\text{Roche}}^3}. \]

Note that this includes the assumption of Luger & Barnes (2015) where the location at which the XUV radiation is absorbed is approximately the planet radius.

We have also added the possibility of entering the diffusion-limited escape regime (e.g., Kasting & Pollack 1983) when the available hydrogen drops below 1% (assuming that this is the smaller flux of both the energy and diffusion limits; otherwise, we continue to use the energy limit). The threshold value of \(\sim 1\%\) roughly corresponds to the transition region between diffusion- and energy-limited escape regimes when the XUV flux is 5–10 times higher than what is received by Earth (Kuramoto et al. 2013). The diffusion limit can be a critical hurdle to the complete desiccation of a planet, limiting the supply of water and/or hydrogen to the upper atmosphere via the need to diffuse through the largely static, heavy background gases. The diffusion limit (molecules cm^{-2} s^{-1}) is defined by Hunten (1973) as

\[ \Phi_{\text{diffusion}} = \frac{b_i \xi_i}{H_{\text{heavy}} - H_i}, \]

or by expanding the scale height terms and including the dependence on the size of the escaping surface, we see that

\[ \Phi_{\text{diffusion}} = 4\pi R_p^2 m_H \frac{b_i g \xi_i (m_{\text{heavy}} - m_i)}{k_b T (1 + \xi_i)} \]

This limit exists only when the escaping flux is sufficiently small (in terms of the magnitude of the escape flux) such that the flow does not exceed the crossover mass for other constituents in the atmosphere. Above this limit, the assumption of a stationary heavy gas component is not valid, as the heavy gas is dropped off with the escaping component. Determining what additional species are included in the flow is often estimated with the crossover mass (Hunten et al. 1987):

\[ m_c = m_H + \frac{k_b T \Phi_{\text{escape}}}{bg f_H}, \]

where \(m_H\) is the mass of the hydrogen atom (kg), \(k_b\) is the Boltzmann constant (m^2 kg s^{-2} K^{-1}), \(T\) is the temperature (K) (taken to be the equilibrium temperature of the planet, a simplification used in lieu of the homopause temperature), \(\Phi_{\text{escape}}\) is the escape rate as calculated in the prior step (kg s^{-1}), \(g\) is the planet’s “surface” gravity (m s^{-2}), and \(f_H\) is the total hydrogen atom fraction (=\(\xi_H + 2/3 \times \xi_{H,O}\), where \(\xi\) is the volume mixing ratio of a given species). The total hydrogen fraction calculation combines the assumption that XUV radiation is effective at breaking molecules down into their constituent atoms and the assumption that the new volume mixing ratios of the constituent atoms reflect the composition of the original molecules. This is analogous to the convention
defined by $b$ in the generic binary diffusion coefficient for two species from Banks & Kockarts (1973):

$$b = 1.52 \times 10^{20} \left( \frac{m_H}{m_{\text{minor}}} + \frac{m_H}{m_{\text{major}}} \right)^{0.5} T^{0.5} \text{ [m/s]},$$

where $m_{\text{minor}}$ and $m_{\text{major}}$ are the molecular masses of the minor (light) species and the major (heavy) species (noting that we assume that the heavy species is the mean molecular mass of the species that are not escaping). The crossover mass and the diffusion limit are siblings, such that $\Phi_\text{escape} = \Phi_\text{diffusion}$ only when $m_e = m_{\text{heavy}}$. The crossover mass represents the upper limit on the “lifting” action of hydrogen as it escapes, meaning that anything with a smaller atomic weight than the crossover mass can become entrained in the escaping hydrogen and ultimately removed from the planet.

Because the escaping component is not necessarily just hydrogen, the presence of heavier atoms and molecules changes the crossover mass and the flux of escaping material. The first step in our code assumes that the escaping material is atomic hydrogen, and the crossover mass in Equation (A6) is calculated using just the mass of hydrogen. We then extend the formalism adopted in Luger & Barnes (2015, their Section 2.4.2), defining the flux of each species in relation to the flux of hydrogen and the crossover mass:

$$\Phi_x = \frac{\xi_x}{f_{H}} \frac{m_e-m_x}{m_e-m_H} \Phi_H \text{ if } m_e > m_x := 0 \text{ otherwise.} \quad (A8)$$

Note that an implicit assumption here is that there are sufficient photons to completely dissociate any hydrogen-bearing species, such that $\xi_H \equiv f_H$. To calculate the flux of each species in the escaping flow, we can generalize Equation (6) of Luger & Barnes (2015):

$$m_H \Phi_H^\text{ref} = \sum_{x} m_x \Phi_x. \quad (A9)$$

We can then follow the same derivation as Luger & Barnes (2015), which will result in a crossover mass that accommodates more than one other gas. Substituting Equation (A8) into this relationship, we see that

$$m_H \Phi_H^\text{ref} = \sum_{x} m_x \xi_x \Phi_H \left( \frac{m_e - m_x}{m_e - m_H} \right) \quad (A10)$$

$$= \Phi_H \frac{m_H}{m_m f_H} \sum_{x} m_x \xi_x \left( \frac{m_e - m_x}{m_e - m_H} \right). \quad (A11)$$

$$\Phi_H = \frac{\Phi_H^\text{ref} (m_e - m_H)}{m_H f_H} \left[ \sum_{x} m_x \xi_x (m_e - m_x) \right]^{-1}. \quad (A12)$$

If we substitute this expression back into Equation (A6),

$$m_e = m_H + m_H \frac{k_T \Phi_H^\text{ref}}{bg} \left( \frac{m_e - m_H}{m_H} \right) \sum_{x} m_x \xi_x (m_e - m_x) \quad (A13)$$

$$m_e = \left[ \sum_{x} m_x \xi_x - \sum_{x} m_x \xi_x \right] = \frac{k_T \Phi_H^\text{ref} m_H}{bg} \quad (A14)$$

$$m_e = \left[ \sum_{x} m_x \xi_x - \sum_{x} m_x \xi_x \right] = \frac{k_T \Phi_H^\text{ref} m_H}{bg} \quad (A15)$$

Since the sum of the mixing-ratio-weighted molecular masses gives the mean molecular mass, this expression simplifies to

$$m_e = \frac{k_T \Phi_H^\text{ref} m_H}{bg} \sum_{x} m_x \xi_x \mu_x. \quad (A16)$$

In our code, we describe $m_e$ in amu, not kg, which is the same as above once $m_H$ has been divided out of both sides of the equation.

We estimate escape and the changing mean molecular weight of the flow by sequentially including each potential species in reverse order by mass (in our modeling, this would be helium, then atomic oxygen, then water, and so on). Each sequential addition forces us to check whether the new crossover mass (which has a slower relative flux but higher mean molecular weight) is still in excess of the molecular mass of the next-heaviest component, only exiting if this is not the case. Because the additional species is added before the crossover mass is calculated, the last loop exits without updating the crossover mass, ensuring that all the incorporated species are represented without adding a repeated term. Subsequent to this loop, the revised escape fluxes are computed (per Equation (A8)). Then, the escaping mass is removed from the relevant inventories such that, if no hydrogen remains in the atmosphere, the hydrogen escape is subtracted from the water inventory (leaving behind the oxygen atoms), and any resulting negative inventories are instead set to zero and the remainder of the mass removed as hydrogen (using the same relationship in Equation (A8)).

**Determining the Escape Regime**

As noted by Owen & Alvarez (2016), there is no closed form of the equations governing which regime a planet would fall into, and so the boundaries of each regime must be solved for at each time step as a function of instellation and planet mass and radius. The three equations (#18, 19, and 20 from Owen & Alvarez 2016) are

$$M_p = \eta \left( \frac{\hbar \nu_0}{4Gm_H} \right) R_p \quad (A17)$$

$$W_0 \left[ \left( \frac{R_p}{R_e} \right)^4 \exp \left( 3 - \frac{4R_p}{R_e} \right) \right] = \frac{-J_0 \alpha_B H}{4\epsilon_0^2} \quad (A18)$$

$$W_0 \left[ \left( \frac{R_p}{R_e} \right)^4 \exp \left( 3 - \frac{4R_p}{R_e} \right) \right] = \frac{-\alpha_B H}{4\epsilon_0^2} \left( \frac{R_e \hbar \nu_0}{4Gm_H} \right) \quad (A19)$$

where $M_p$ is the planet mass, $\eta$ is the escape efficiency parameter ($0 < \eta < 1$), $\hbar \nu_0$ is the mean photon energy for photons that heat the upper atmosphere, $G$ is the gravitational constant, $m_H$ is the mass of a hydrogen atom, $R_p$ is the planet radius, $W_0$ is the Lambert W function (the Lambert W function is the set of solutions to $W(x)\exp(W(x)) = x$, and $W_0$ is the principal branch such that $x$ and $W(x)$ are real numbers; we use the Python function lambertw() from the scipy.special library), $R_e$ is the sonic point (given by $GM_p/(2\epsilon_0^2)$), $J_0$ is the ionizing photon flux, $\alpha_B$ is the case B recombination coefficient ($= 2.6 \times 10^{-13}$ cm$^3$.
\[ s^{-1}(T/10^4)^{-0.7}, \text{ taking } T \text{ to be the exospheric temperature} \] acting as a stand-in for the recombination rate, \( H \) is the atmospheric scale height, and \( c_s \) is the sound speed \( (c_s^2 = k_b T/(\bar{m}_{\text{atm}})) \), with \( \bar{m}_{\text{atm}} \) defined as before to be the mean molecular mass of the atmosphere). Note that we include the additional parentheses to clarify exponentiation, following Cranmer (2004). The exospheric temperature, as described in the text, is set to either 10^4 K or 2000 K based on the incoming XUV flux, with a threshold of \( \sim 180 \text{ erg cm}^{-2} \text{ s}^{-1} \) forcing a higher exospheric temperature when \( H_3^+ \) cooling becomes ineffective (Koskinen et al. 2007; Murray-Clay et al. 2009).

Equation (A17) defines the boundary between the photon- and energy-limited escape regimes, while Equation (A18) is for the recombination- and photon-limited regimes, and Equation (A19) is for the recombination- and energy-limited regimes. Both Equations (A18) and (A19) have either two solutions or none, if describing the system in mass–radius space (as shown by Owen & Alvarez 2016), but since we have chosen a planet mass and radius as part of our initial conditions, this collapses the three equations down to one or no solution that is solely a function of the ionizing flux. We calculate \( J_0 \) by rearranging Equations (A18) and (A19) to solve for \( J_0 \), which we then compare against the stellar XUV flux calculated in the setup step. The boundary between energy- and photon-limited escape is in the form of planet mass, such that a planet more massive than the threshold mass (the left-hand side of Equation (A17)) will be in the energy- or recombination-limited regime. If the planet’s mass is instead below the threshold and the XUV flux is below the recombination- and photon-limited threshold flux, the escape is in the photon-limited regime.

```python
run_escape - returning values to monte_carlo.py
```

The code currently returns summary statistics for individual runs to `monte_carlo.py`, including the planet’s mass, radius, core mass fraction, envelope fraction and composition, and total mass change over the duration of the simulation (this is always longer than the estimated age of the host star in this parameter sweep). Individual time evolution data are not returned, in an effort to provide manageable data volumes and run times; by default, the simulations have 3000 points across the whole of the available stellar evolution data, and only returning three of each of the reported parameters is a 1000-fold reduction in data.

**Appendix B**

**Photochemical Reaction List and Thermodynamic Data**

The reaction list is largely composed of forward reactions that are then used to calculate the reverse reactions, based on the thermodynamic properties of the species involved in the reaction (Table 3). However, some reactions do not have reversed reactions, including (a) the ones where a molecule in an excited state relaxes into the ground state (e.g., reaction 357), and (b) photolysis reactions (such as reaction 356). The majority of these reactions are detailed in Tsai et al. (2017) as the reduced C-H-O system, to which we have added reactions for oxidizing species (denoted by the asterisk*: 

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Harman et al.
| Rxn # | Reaction                                                                 | Rate                                       | Notes |
|-------|--------------------------------------------------------------------------|--------------------------------------------|-------|
| 1     | H + H₂O → OH + H₂                                                       | $7.500 \times 10^{-16} \cdot T^{0.60} \exp(-9720/T)$ | 1     |
| 3     | O + H₂ → OH + H                                                         | $8.520 \times 10^{-20} \cdot T^{0.796} \exp(-3160/T)$ | 1     |
| 5     | O + H₂O → OH + OH                                                      | $8.200 \times 10^{-14} \cdot T^{0.56} \exp(-8570/T)$ | 1     |
| 7     | H + CH → H₂ + C                                                        | $1.310 \times 10^{-10} \cdot \exp(-80/T)$ | 1     |
| 9     | H + CH₃ → CH + H₂                                                      | $1.000 \times 10^{-11} \cdot \exp(900/T)$ | 1     |
| 11    | CH₂ + H₂ → H + CH₃                                                    | $7.320 \times 10^{-19} \cdot T^{0.30} \exp(-3699/T)$ | 1     |
| 13    | H + CH₄ → CH₂ + H₂                                                     | $2.200 \times 10^{-20} \cdot T^{0.00} \exp(-4040/T)$ | 1     |
| 15    | C + CH₂ → C₂ + H                                                       | $1.050 \times 10^{-12} \cdot T^{0.50}$ | 1     |
| 17    | H₂ + C₂H → H + C₂H₂                                                   | $9.200 \times 10^{-18} \cdot T^{2.17} \exp(-478/T)$ | 1     |
| 19    | CH + CH₂ → H + C₂H₂                                                   | $6.640 \times 10^{-11}$ | 1     |
| 21    | H + C₂H₂ → C₂H + H₂                                                   | $2.010 \times 10^{-11}$ | 1     |
| 23    | H₂ + C₂H₃ → H + C₂H₄                                                  | $5.000 \times 10^{-20} \cdot T^{2.63} \exp(-4300/T)$ | 1     |
| 25    | CH + CH₄ → H + C₂H₄                                                   | $5.000 \times 10^{-11} \cdot \exp(200/T)$ | 1     |
| 27    | CH₂ + CH₃ → H + C₂H₄                                                  | $7.010 \times 10^{-11}$ | 1     |
| 29    | H + C₂H₄ → CH₃ + CH₂                                                  | $5.990 \times 10^{-11}$ | 1     |
| 31    | H + C₂H₆ → C₂H₄ + H₂                                                   | $3.010 \times 10^{-12}$ | 1     |
| 33    | H + C₂H₆ → C₂H₄ + H₂                                                   | $9.190 \times 10^{-22} \cdot T^{0.50} \exp(-2600/T)$ | 1     |
| 35    | OH + CO → H + C₂H₂                                                    | $1.050 \times 10^{-17} \cdot T^{0.50} \exp(-259/T)$ | 1     |
| 37    | CH + CH₃ → H₂ + C₂H₂                                                  | $1.000 \times 10^{-11}$ | 1     |
| 39    | C₂ + O → C + CO                                                      | $1.050 \times 10^{-12}$ | 1     |
| 41    | CH₂ + CH₂ → C₂H₂ + H + H                                              | $1.800 \times 10^{-10} \cdot \exp(-400/T)$ | 1     |
| 43    | CH₂ + CH₂ → CH + CH₃                                                   | $3.980 \times 10^{-10} \cdot \exp(-5000/T)$ | 1     |
| 45    | CH₂ + CH₂ → H + C₂H₃                                                  | $3.320 \times 10^{-11}$ | 1     |
| 47    | CH₂ + CH₄ → CH₃ + CH₂                                                  | $4.090 \times 10^{-18} \cdot T^{0.00} \exp(-4162/T)$ | 1     |
| 49    | CH₂ + C₂H₄ → CH₃ + C₂H₄                                               | $3.010 \times 10^{-11}$ | 1     |
| 51    | CH₂ + OH → CH₂ + H₂O                                                   | $1.850 \times 10^{-21} \cdot T^{0.00} \exp(-1400/T)$ | 1     |
| 53    | CH₂ + OH → CH₂ + CO                                                   | $3.010 \times 10^{-11}$ | 1     |
| 55    | CH₂ + O → CH₂ + CO                                                   | $6.780 \times 10^{-16} \cdot T^{0.50} \exp(-854/T)$ | 1     |
| 57    | CH₁ + C₂H → C₂H₂ + CH₂                                                | $1.000 \times 10^{-11}$ | 1     |
| 59    | CH₂ + C₂H → CH₂ + C₂H₂                                                | $3.010 \times 10^{-12} \cdot \exp(-250/T)$ | 1     |
| 61    | CH₃ + CH₃ → CH₄ + CH₂                                                 | $6.510 \times 10^{-13}$ | 1     |
| 63    | CH₄ + CH₃ → CH₄ + CH₂                                                 | $2.130 \times 10^{-24} \cdot T^{0.02} \exp(-2754/T)$ | 1     |
| 65    | CH₃ + C₂H₆ → CH₄ + C₂H₄                                              | $3.250 \times 10^{-11} \cdot T^{0.50}$ | 1     |
| 67    | CH₃ + C₂H₆ → CH₂ + C₂H₃                                              | $9.120 \times 10^{-25} \cdot T^{0.00} \exp(-4170/T)$ | 1     |
| 69    | C₂H₃ + OH → CH₃ + CO                                                  | $8.040 \times 10^{-28} \cdot T^{0.00} \exp(-1010/T)$ | 1     |
| 71    | C₂ + H₂ → H + CH₂                                                    | $1.100 \times 10^{-10} \cdot \exp(-4000/T)$ | 1     |
| 73    | C₂ + CH₄ → CH₂ + C₂H₂                                                | $5.050 \times 10^{-11} \cdot \exp(-297/T)$ | 1     |
| 75    | CH₂ + CH₃ → CH + CH₂                                                 | $3.010 \times 10^{-11}$ | 1     |
| 77    | C₂H + C₂H₄ → C₂H₂ + C₂H₃                                           | $5.990 \times 10^{-12}$ | 1     |
| 79    | C₂H + O → CH + CO                                                    | $1.690 \times 10^{-11}$ | 1     |
| 81    | C₂H + OH → C₂H₂ + O                                                | $3.010 \times 10^{-11}$ | 1     |
| 83    | C₂H + H₂O → C₂H₂ + OH                                               | $2.200 \times 10^{-21} \cdot T^{0.05} \exp(-376/T)$ | 1     |
| 85    | C₂H₊₃ + C₂H₄ → C₂H₂ + C₂H₄                                            | $1.600 \times 10^{-12}$ | 1     |
| 87    | C₂H₃ + CH₃ → CH₂ + C₂H₄                                           | $8.000 \times 10^{-13}$ | 1     |
| 89    | C₂H₃ + CH₂ + C₂H₂ + C₂H₂                                            | $8.000 \times 10^{-13}$ | 1     |
| 91    | C₂H₄ + OH → C₂H₃ + H₂O                                              | $2.600 \times 10^{-20} \cdot T^{0.75} \exp(-2100/T)$ | 1     |
| 93    | C₂H₃ + CH₂ → C₂H₂ + CH₂                                             | $2.310 \times 10^{-12}$ | 1     |
| 95    | C₂H₃ + CH₂ → C₂H₂ + C₂H₃                                           | $1.050 \times 10^{-21} \cdot T^{0.13} \exp(-9060/T)$ | 1     |
| 97    | C₂H₄ + OH → C₂H₂ + H₂O                                             | $1.470 \times 10^{-14} \cdot T^{0.04} \exp(-913/T)$ | 1     |
| 99    | CH + O → OH + C                                                     | $2.520 \times 10^{-11} \cdot \exp(-3381/T)$ | 1     |
| 101   | O + CH₂ → H + CO                                                   | $6.590 \times 10^{-11}$ | 1     |
| 103   | O + CH₃ → CH₂ + OH                                                | $1.000 \times 10^{-11} \cdot \exp(-3970/T)$ | 1     |
| 105   | CH₃ + OH → O + CH₄                                                 | $1.160 \times 10^{-19} \cdot T^{0.20} \exp(-2240/T)$ | 1     |
| 107   | O + C₂H₆ → OH + C₂H₄                                              | $2.000 \times 10^{-12} \cdot T^{0.60} \exp(-3680/T)$ | 1     |
| 109   | OH + C → CO + H                                                   | $1.050 \times 10^{-12} \cdot T^{0.50}$ | 1     |
| 111   | OH + CH₄ → H₂O + CH                                               | $1.430 \times 10^{-18} \cdot T^{0.02} \exp(-3410/T)$ | 1     |
| Rxn #  | Reaction                                                                 | Rate                          | Notes       |
|--------|--------------------------------------------------------------------------|-------------------------------|-------------|
| 113    | OH + CH₄ → H₂O + CH₃                                                   | $3.190 \times 10^{-19} \cdot T^{0.40} \cdot \exp(-1060/T)$ | 1           |
| 115    | OH + C₂H₆ → H₂O + C₂H₅                                                 | $5.000 \times 10^{-11}$       | 1           |
| 117    | OH + C₂H₄ → H₂O + C₂H₃                                                 | $4.000 \times 10^{-11}$       | 1           |
| 119    | CH₂OH + H → OH + CH₄                                                   | $1.600 \times 10^{-10}$       | 1           |
| 121    | H₂CO + H → HCO + H₂                                                    | $3.640 \times 10^{-16} \cdot T^{1.77} \cdot \exp(-1510/T)$ | 1           |
| 123    | O + C₂H₄ → HCO + CH₃                                                  | $2.190 \times 10^{-16} \cdot T^{0.55} \cdot \exp(-215/T)$ | 1           |
| 125    | H₂CO + CH₃ → CH₄ + HCO                                               | $9.200 \times 10^{-21} \cdot T^{2.81} \cdot \exp(-2950/T)$ | 1           |
| 127    | CH₃ + CH₂OH → H₂CO + CH₄                                            | $4.000 \times 10^{-12}$       | 1           |
| 129    | HCO + H → CO + H₂                                                    | $1.500 \times 10^{-10}$       | 1           |
| 131    | HCO + OH → CO + H₂                                                   | $1.690 \times 10^{-10}$       | 1           |
| 133    | CO₂ + CH → HCO + CO                                                  | $5.710 \times 10^{-12} \cdot \exp(-345/T)$ | 1           |
| 135    | CH₃ + O → H₂CO + H                                                   | $1.400 \times 10^{-10}$       | 1           |
| 137    | CH₃O + O → H₂CO + OH                                              | $1.000 \times 10^{-11}$       | 1           |
| 139    | CH₃O + OH → H₂CO + H₂                                            | $3.010 \times 10^{-11}$       | 1           |
| 141    | CH₃OH + H → CH₂OH + H²                                               | $6.820 \times 10^{-20} \cdot T^{0.69} \cdot \exp(-4643/T)$ | 1           |
| 143    | CH₃OH + H → CH₂OH + H₂                                             | $4.910 \times 10^{-19} \cdot T^{2.49} \cdot \exp(-10380/T)$ | 1           |
| 145    | CH₄ + O → CO + H + H                                                | $1.330 \times 10^{-10}$       | 1           |
| 147    | CH₃ + OH → H₂CO + H                                                  | $3.010 \times 10^{-11}$       | 1           |
| 149    | CO₂ + CH₃ → H₂CO + CO                                             | $3.900 \times 10^{-14}$       | 1           |
| 151    | CH₂O + CO → CH₃ + CO₂                                               | $2.610 \times 10^{-11} \cdot \exp(-5940/T)$ | 1           |
| 153    | CH₃OH + H → CH₂OH + H₂                                              | $1.090 \times 10^{-19} \cdot T^{2.73} \cdot \exp(-2240/T)$ | 1           |
| 155    | HCO + CH₃ → C₂H₄ + CO                                              | $1.000 \times 10^{-16}$       | 1           |
| 157    | CH₃OH + C₂H → H₂CO + C₂H₂                                            | $5.990 \times 10^{-11}$       | 1           |
| 159    | CH₃OH + C₂H → H₂CO + C₂H₂                                          | $4.000 \times 10^{-11}$       | 1           |
| 161    | CH₃OH + CH₂ → CH₃OH + C₂H₂                                          | $1.000 \times 10^{-11}$       | 1           |
| 163    | CH₃OH + C₂H → CH₂OH + C₂H₂                                          | $2.010 \times 10^{-12}$       | 1           |
| 165    | O + C₂H₅ → C₂H₃ + OH                                              | $1.760 \times 10^{-12} \cdot T^{0.20} \cdot \exp(215/T)$ | 1           |
| 167    | CH₃ + C₂H₅ → C₂H₆ + CH₃                                            | $3.000 \times 10^{-11}$       | 1           |
| 169    | O + CH₃ → CO + H₂                                                   | $9.960 \times 10^{-11}$       | 1           |
| 171    | O + C₂H₅ → HCO + CH₃                                               | $2.000 \times 10^{-11}$       | 1           |
| 173    | HCO + CH₃ → CO + CH₃                                               | $3.010 \times 10^{-11}$       | 1           |
| 175    | O + C₂H₄ → H₂CO + CH₂                                              | $1.350 \times 10^{-17} \cdot T^{0.80} \cdot \exp(-90/T)$ | 1           |
| 177    | CH₃OH + CH₂ → OH + C₂H₄                                          | $4.000 \times 10^{-11}$       | 1           |
| 179    | CH₃OH + CH₂ → H₂CO + CH₃                                          | $2.010 \times 10^{-12}$       | 1           |
| 181    | CH₃O + CH₂ → H₂CO + CH₃                                           | $3.000 \times 10^{-11}$       | 1           |
| 183    | CH₃OH + CH₂ → CH₂O + CH₃                                          | $2.390 \times 10^{-23} \cdot T^{3.10} \cdot \exp(-3490/T)$ | 1           |
| 185    | CH₃OH + CH₂ → CH₂OH + CH₄                                         | $5.290 \times 10^{-23} \cdot T^{3.20} \cdot \exp(-3690/T)$ | 1           |
| 187    | HCO + CH₃ → CO + CH₄                                              | $2.010 \times 10^{-10}$       | 1           |
| 189    | CH₃O + CH₄ → H₂CO + CH₄                                          | $4.000 \times 10^{-11}$       | 1           |
| 191    | H₂CO + CH → CO + CH₃                                             | $8.000 \times 10^{-11} \cdot \exp(260/T)$ | 1           |
| 193    | CH₃OH + CH₃ → CH₂O + CH₄                                         | $2.390 \times 10^{-23} \cdot T^{3.10} \cdot \exp(-3490/T)$ | 1           |
| 195    | CH₃CO + H → HCO + CH₃                                           | $3.320 \times 10^{-11}$       | 1           |
| 197    | CH₃O + CH₃ → CO + C₂H₆                                         | $4.900 \times 10^{-11}$       | 1           |
| 199    | O + OH → O₂ + H                                                        | $7.470 \times 10^{-10} \cdot T^{-0.50} \cdot \exp(-30/T)$ | 1           |
| 201    | H + CH₂O → H₂CO + H₂                                              | $3.010 \times 10^{-11}$       | 1           |
| 203    | H + CH₂CO → CO + CH₄                                               | $1.290 \times 10^{-15} \cdot T^{0.45} \cdot \exp(-1399/T)$ | 1           |
| 205    | O + C₂H₆ → CH₂CO + H                                              | $1.600 \times 10^{-10}$       | 1           |
| 207    | C₂H₅ + O → HCCO + H                                                | $1.500 \times 10^{-11} \cdot \exp(-2280/T)$ | 1           |
| 209    | HCCO + H → CO + CH₃                                               | $2.490 \times 10^{-16}$       | 1           |
| 211    | O + H₂CO → HCO + OH                                                | $6.850 \times 10^{-13} \cdot T^{0.57} \cdot \exp(-1390/T)$ | 1           |
| 213    | HCO + HCO → H₂CO + CO                                             | $3.010 \times 10^{-11}$       | 1           |
| 215    | CH₃OH + CH₂O → H₂CO + CH₃OH                                        | $4.000 \times 10^{-11}$       | 1           |
| 217    | CH₃O + CH₂O → H₂CO + CH₃OH                                         | $1.000 \times 10^{-16}$       | 1           |
| 219    | H + H → H₂ + M                                                       | $\begin{cases} k_0 = 2.700 \times 10^{-31} \cdot T^{-0.60} \\ k_{∞} = 3.310 \times 10^{-06} \cdot T^{-1.00} \end{cases}$ | 2           |
| Rxn # | Reaction                                      | Rate                                      | Notes |
|------|-----------------------------------------------|-------------------------------------------|-------|
| 221  | H + O → OH + M                                | \( k_0 = 1.300 \times 10^{-29} \cdot T^{-1.00} \) | 2     |
|      |                                               | \( k_{\infty} = 1.000 \times 10^{-11} \)   |       |
| 222  | OH + H → H_{2}O + M                          | \( k_0 = 3.890 \times 10^{-25} \cdot T^{-2.00} \) | 2     |
|      |                                               | \( k_{\infty} = 4.260 \times 10^{-11} \cdot T^{-0.23} \) |       |
| 223  | H + CH → CH_{2} + M                          | \( k_0 = 2.760 \times 10^{-29} \cdot T^{-1.00} \) | 2     |
|      |                                               | \( k_{\infty} = 1.000 \times 10^{-12} \)   |       |
| 224  | H + CH_{3} → CH_{4} + M                      | \( k_0 = 1.760 \times 10^{-24} \cdot T^{-1.80} \) | 2     |
|      |                                               | \( k_{\infty} = 2.060 \times 10^{-10} \cdot T^{-0.40} \) |       |
| 225  | H + C_{2}H_{2} → C_{2}H_{4} + M              | \( k_0 = 1.050 \times 10^{-57} \cdot T^{-7.27} \cdot \exp(-3630/T) \) | 2     |
|      |                                               | \( k_{\infty} = 9.130 \times 10^{-12} \cdot \exp(-3630/T) \) |       |
| 226  | H + C_{2}H_{3} → C_{2}H_{4} + M              | \( k_0 = 1.500 \times 10^{-27} \)         | 2     |
|      |                                               | \( k_{\infty} = 6.400 \times 10^{-11} \cdot T^{-0.20} \) |       |
| 227  | H + C_{2}H_{4} → C_{2}H_{5} + M              | \( k_0 = 7.690 \times 10^{-30} \cdot \exp(-380/T) \) | 2     |
|      |                                               | \( k_{\infty} = 1.270 \times 10^{-15} \cdot T^{1.49} \cdot \exp(-380/T) \) |       |
| 228  | H + C_{2}H_{3} → C_{2}H_{6} + M              | \( k_0 = 4.000 \times 10^{-19} \cdot T^{-3.00} \cdot \exp(-600/T) \) | 2     |
|      |                                               | \( k_{\infty} = 9.040 \times 10^{-11} \cdot T^{0.16} \cdot \exp(-600/T) \) |       |
| 229  | H_{2} + C → CH_{2} + M                       | \( k_0 = 6.890 \times 10^{-32} \)         | 2     |
|      |                                               | \( k_{\infty} = 2.060 \times 10^{-11} \)   |       |
| 230  | CH + M → C + H + M                           | \( k_0 = 3.160 \times 10^{-10} \cdot \exp(-33700/T) \) | 2     |
|      |                                               | \( k_{\infty} = 1.000 \times 10^{-12} \cdot \exp(-33700/T) \) |       |
| 231  | CH_{2} + H → CH_{3} + M                      | \( k_0 = 9.000 \times 10^{-32} \cdot \exp(550/T) \) | 2     |
|      |                                               | \( k_{\infty} = 8.550 \times 10^{-12} \cdot T^{0.03} \cdot \exp(550/T) \) |       |
| 232  | CH + H_{2} → CH_{3} + M                      | \( k_0 = 3.400 \times 10^{-31} \cdot \exp(736/T) \) | 2     |
|      |                                               | \( k_{\infty} = 7.300 \times 10^{-11} \cdot \exp(736/T) \) |       |
| 233  | CH_{3} + CH_{3} → C_{2}H_{6} + M             | \( k_0 = 3.500 \times 10^{-07} \cdot T^{-7.00} \cdot \exp(-1390/T) \) | 2     |
|      |                                               | \( k_{\infty} = 1.580 \times 10^{-09} \cdot T^{-0.54} \cdot \exp(-1390/T) \) |       |
| 234  | C_{2}H + H → C_{2}H_{2} + M                  | \( k_0 = 1.260 \times 10^{-18} \cdot T^{-3.10} \cdot \exp(-721/T) \) | 2     |
|      |                                               | \( k_{\infty} = 3.000 \times 10^{-10} \cdot \exp(-721/T) \) |       |
| 235  | C_{2}H_{4} + M → C_{2}H_{2} + H_{2} + M      | \( k_0 = 5.800 \times 10^{-06} \cdot \exp(-36000/T) \) | 2     |
|      |                                               | \( k_{\infty} = 7.950 \times 10^{-12} \cdot T^{0.04} \cdot \exp(-36000/T) \) |       |
| 236  | C_{2}H_{5} + M → C_{2}H_{4} + H_{2} + M      | \( k_0 = 3.800 \times 10^{-07} \cdot \exp(-34000/T) \) | 2     |
|      |                                               | \( k_{\infty} = 1.320 \times 10^{-15} \cdot \exp(-34000/T) \) |       |
| 237  | CO + O → CO_{2} + M                          | \( k_0 = 1.700 \times 10^{-33} \cdot \exp(-1510/T) \) | 2     |
|      |                                               | \( k_{\infty} = 2.660 \times 10^{-14} \cdot \exp(-1510/T) \) |       |
| 238  | CH_{2}OH + M → H + H_{2}CO + M               | \( k_0 = 1.660 \times 10^{-10} \cdot \exp(-12630/T) \) | 2     |
|      |                                               | \( k_{\infty} = 3.000 \times 10^{-09} \cdot \exp(-12630/T) \) |       |
| 239  | H + CO → HCO + M                             | \( k_0 = 5.290 \times 10^{-34} \cdot \exp(-370/T) \) | 2     |
|      |                                               | \( k_{\infty} = 1.960 \times 10^{-13} \cdot \exp(-370/T) \) |       |
| 240  | H_{2}O + CH → CH_{2}OH + M                   | \( k_0 = 1.000 \times 10^{-31} \)         | 2     |
|      |                                               | \( k_{\infty} = 9.480 \times 10^{-12} \)   |       |
| 241  | CH_{3}O + M → H + H_{2}CO + M                | \( k_0 = 9.000 \times 10^{-11} \cdot \exp(-6790/T) \) | 2     |
|      |                                               | \( k_{\infty} = 1.560 \times 10^{-15} \cdot T^{-0.39} \cdot \exp(-6790/T) \) |       |
| 242  | CH_{2}OH + H → CH_{3}OH + M                  | \( k_0 = 1.200 \times 10^{-16} \cdot T^{-4.65} \cdot \exp(-2557/T) \) | 2     |
|      |                                               | \( k_{\infty} = 2.300 \times 10^{-10} \cdot T^{0.04} \cdot \exp(-2557/T) \) |       |
| 243  | OH + C_{2}H_{2} → CH_{2}CO + M               | \( k_0 = 4.990 \times 10^{-25} \cdot T^{-2.00} \) | 2     |
|      |                                               | \( k_{\infty} = 1.060 \times 10^{-07} \cdot T^{-1.90} \) |       |
| 244  | CO + CH_{3} → CH_{2}CO + M                   | \( k_0 = 3.950 \times 10^{-10} \cdot T^{-7.30} \cdot \exp(-5490/T) \) | 2     |
|      |                                               | \( k_{\infty} = 5.140 \times 10^{-19} \cdot T^{2.20} \cdot \exp(-5490/T) \) |       |
| 245  | HCO + H → H_{2}CO + M                        | \( k_0 = 7.330 \times 10^{-24} \cdot T^{2.57} \cdot \exp(-215/T) \) | 2     |
|      |                                               | \( k_{\infty} = 7.770 \times 10^{-14} \cdot \exp(-215/T) \) |       |
| Rxn # | Reaction | Rate | Notes |
|-------|----------|------|-------|
| 271   | CO + H₂ → H₂CO + M | \[ k_0 = 2.800 \times 10^{-20} \cdot T^{-3.42} \cdot \exp(-42450/T) \] \[ k_{\infty} = 7.140 \times 10^{-17} \cdot T^{0.50} \cdot \exp(-2450/T) \] | 2 |
| 273   | OH + CH₃ → CH₃OH + M | \[ k_0 = 4.370 \times 10^{-04} \cdot T^{-8.20} \] \[ k_{\infty} = 1.000 \times 10^{-10} \] | 2 |
| 275   | C + C → M + C₂ | \[ 4.970 \times 10^{-27} \cdot T^{-1.60} \] | 1 |
| 277   | C₂H + M → C₂ + H + M | \[ 2.920 \times 10^{-11} \cdot T^{-5.16} \cdot \exp(-57400/T) \] | 1 |
| 279   | O + C → M + CO | \[ 9.100 \times 10^{-22} \cdot T^{-3.16} \cdot \exp(-2114/T) \] | 1 |
| 281   | H + O₂ → HO₂ + M | \[ k_0 = 5.240 \times 10^{-28} \cdot T^{-1.60} \] \[ k_{\infty} = 7.500 \times 10^{-11} \] | 2 |
| 283   | H + HO₂ → H₂ + O₂ | \[ 7.200 \times 10^{-12} \] | 1 |
| 285   | H + HO₂ → H₂O + O | \[ 1.600 \times 10^{-12} \] | 1 |
| 287   | H + HO₂ → OH + OH | \[ 7.120 \times 10^{-11} \] | 1* |
| 289   | OH + HO₂ → H₂O + O₂ | \[ 4.800 \times 10^{-11} \cdot \exp(-250/T) \] | 1* |
| 291   | OH + O → HO₂ + O₂ | \[ 1.600 \times 10^{-12} \cdot \exp(-940/T) \] | 1* |
| 293   | HO₂ + O → OH + O₂ | \[ 3.000 \times 10^{-11} \cdot \exp(-200/T) \] | 1* |
| 295   | H₂O₂ + OH → HO₂ + H₂O | \[ 2.900 \times 10^{-12} \cdot \exp(160/T) \] | 1* |
| 297   | HCO + O₂ → HO₂ + CO | \[ 5.200 \times 10^{-12} \] | 1* |
| 299   | H₂O₂ + O → OH + HO₂ | \[ 1.400 \times 10^{-12} \cdot \exp(2000/T) \] | 1* |
| 301   | CH₃ + O → H₂CO + HO₂ | \[ 5.400 \times 10^{-12} \cdot \exp(2200/T) \] | 1* |
| 303   | CH₃O + O₂ → H₂CO + HO₂ | \[ 7.200 \times 10^{-14} \cdot \exp(1080/T) \] | 1* |
| 305   | OH + OH → H₂O₂ + M | \[ k_0 = 2.070 \times 10^{-28} \cdot T^{-1.0} \] \[ k_{\infty} = 2.600 \times 10^{-11} \] | 2* |
| 307   | H + O₂ → OH + O₂ | \[ 1.400 \times 10^{-10} \cdot \exp(470/T) \] | 1* |
| 309   | O + O₂ → O₃ + M | \[ k_0 = 5.290 \times 10^{-28} \cdot T^{-2.4} \] \[ k_{\infty} = 3.000 \times 10^{-11} \] | 2* |
| 311   | O + O₂ → O₃ | \[ 8.000 \times 10^{-12} \cdot \exp(2060/T) \] | 1* |
| 313   | CH₃ + O → CH₂O + O₂ | \[ 5.400 \times 10^{-12} \cdot \exp(2200/T) \] | 1* |
| 315   | ¹CH₃ + CH₂ → CH₂ + CH₃ | \[ 3.600 \times 10^{-11} \] | 1* |
| 316   | ¹CH₂ + O → HCO + OH | \[ 3.000 \times 10^{-11} \] | 1* |
| 317   | ¹CH₂ + M → CH₂ + M | \[ 8.800 \times 10^{-12} \] | 1* |
| 318   | ¹CH₂ + H₂ → CH₃ + H | \[ 5.000 \times 10^{-15} \] | 1* |
| 319   | ¹CH₂ + CO₂ → H₂CO + CO | \[ 1.000 \times 10^{-12} \] | 1* |
| 320   | CH₂ + O₂ → H₂CO + OH | \[ 4.100 \times 10^{-11} \cdot \exp(750/T) \] | 1* |
| 321   | CH₂ + O → HCO + H | \[ 1.000 \times 10^{-11} \] | 1* |
| 322   | H₂O + O(¹D) → OH + OH | \[ 2.200 \times 10^{-10} \] | 1* |
| 323   | H₃ + O(¹D) → OH + H | \[ 1.100 \times 10^{-10} \] | 1* |
| 324   | O(¹D) + M → O + M | \[ 1.800 \times 10^{-11} \cdot \exp(-110/T) \] | 1* |
| 325   | O(¹D) + O₂ → O + O₂ | \[ 3.200 \times 10^{-11} \cdot \exp(-70/T) \] | 1* |
| 326   | CH₄ + O(¹D) → CH₃ + OH | \[ 1.125 \times 10^{-10} \] | 1* |
| 327   | CH₄ + O(¹D) → H₂CO + H₂ | \[ 7.500 \times 10^{-12} \] | 1* |
| 328   | CH₄ + O(¹D) → CH₃O + H | \[ 3.000 \times 10^{-11} \] | 1* |
| 329   | C₂H₆ + O(¹D) → C₂H₅ + OH | \[ 6.200 \times 10^{-10} \] | 1* |
| 330   | CO + O(¹D) → CO + O | \[ 7.000 \times 10^{-11} \] | 1* |
| 331   | O₂ + hν → O + O(¹D) | \[ 2.18 \times 10^{-6} \] | 3* |
| 332   | O₂ + hν → O + O | \[ 5 \times 10^{-8} \] | 3* |
| 333   | H₂O + hν → H + OH | \[ 8.16 \times 10^{-6} \] | 3 |
| 334   | OH + hν → O(¹D) + H | \[ 4.9 \times 10^{-6} \] | 3 |
| 335   | O₃ + hν → O₂ + O(¹D) | \[ 9.98 \times 10^{-3} \] | 3* |
| 336   | O₃ + hν → O₂ + O | \[ 1.92 \times 10^{-3} \] | 3* |
| 337   | H₂O₂ + hν → OH + OH | \[ 1.27 \times 10^{-4} \] | 3 |
| 338   | CO₂ + hν → CO + O | \[ 2.31 \times 10^{-9} \] | 3 |
| 339   | CO₂ + hν → CO + O(¹D) | \[ 2.51 \times 10^{-7} \] | 3 |
| 340   | CO + hν → C + O | \[ 1.54 \times 10^{-6} \] | 3 |
| 341   | H₂CO + hν → H₂ + CO | \[ 1.15 \times 10^{-4} \] | 3 |
| 342   | H₂CO + hν → HCO + H | \[ 1.32 \times 10^{-4} \] | 3 |
1. cm$^3$ molecules$^{-1}$ s$^{-1}$.

2. These reaction rates take the form $k(M,T) = k_0(T)[M]/[1 + k_0(T)[m]/k_\infty(T)] \cdot 0.6[(1 + [log_{10}(k_0(T)[M]/k_\infty(T))]^2)^{-1}$, where $k_0(T)$ has units of cm$^6$ molecules$^{-2}$ s$^{-1}$ and $k_\infty(T)$ has units of cm$^3$ molecules$^{-1}$ s$^{-1}$.

3. The photolysis rates (in s$^{-1}$) presented here are taken from the uppermost layer in the model. Caution: the rates in the upper atmosphere are not good indicators for rates in the lower atmosphere.

### Table 3 (Continued)

| Rxn # | Reaction                              | Rate       | Notes |
|-------|---------------------------------------|------------|-------|
| 343   | HO$_2$ + h\nu \rightarrow OH + O      | 6.13 x 10$^{-4}$ | 3     |
| 344   | CH$_3$ + h\nu \rightarrow C + H      | 4.25 x 10$^{-5}$ | 3     |
| 345   | CH$_3$ + h\nu \rightarrow ^1$CH$_2$ + H | 0          | 3     |
| 346   | CH$_4$ + h\nu \rightarrow ^1$CH$_3$ + H$_2$ | 1.78 x 10$^{-6}$ | 3     |
| 347   | CH$_4$ + h\nu \rightarrow CH$_3$ + H   | 3.41 x 10$^{-6}$ | 3     |
| 348   | CH$_4$ + h\nu \rightarrow CH$_2$ + H + H | 1.67 x 10$^{-6}$ | 3     |
| 349   | C$_2$H$_2$ + h\nu \rightarrow C$_2$H + H | 1.14 x 10$^{-6}$ | 3     |
| 350   | C$_2$H$_2$ + h\nu \rightarrow C$_2$ + H$_2$ | 6.55 x 10$^{-7}$ | 3     |
| 351   | C$_2$H$_2$ + h\nu \rightarrow C$_2$H$_2$ + H | 2.94 x 10$^{-4}$ | 3     |
| 352   | C$_3$H$_4$ + h\nu \rightarrow C$_2$H$_2$ + H$_2$ | 2.08 x 10$^{-5}$ | 3     |
| 353   | C$_2$H$_4$ + h\nu \rightarrow C$_2$H$_2$ + H + H | 2.17 x 10$^{-5}$ | 3     |
| 354   | C$_2$H$_6$ + h\nu \rightarrow CH$_3$ + CH$_2$ + H$_2$ | 4 x 10$^{-6}$ | 3     |
| 355   | C$_2$H$_6$ + h\nu \rightarrow CH$_4$ + ^1$CH$_2$ + H$_2$ | 1 x 10$^{-6}$ | 3     |
| 356   | CH$_2$CO + h\nu \rightarrow CH$_2$ + CO | 7.03 x 10$^{-4}$ | 3     |
| 357   | ^1$CH$_2$ + H$_2$ \rightarrow CH$_2$ + H$_2$ | 1.260 x 10$^{-11}$ | 1     |

### Appendix C

**Secondary Analyses**

Below we include several figures (Figures 11, 12, 13, and 14) that correspond to comments made in the main text. Figure 11 demonstrates that the hydrogen escape efficiency does not play a significant role in the evolution of bulk atmospheric composition. Figure 12 shows how a representative tracer responds to changes in the assumed $K_\infty$ value.
Figure 13 provides a side-by-side comparison for the water vapor profiles from just our climatological model against those calculated by photochemical model. Figure 14 shows the hydroxyl radical profiles for our base case scenarios.
Figure 12. Molecular oxygen response to changing eddy diffusion profile strengths (values indicated in the key, with units of cm$^2$ s$^{-1}$) for the 10% H$_2$ scenario. Smaller values of $K_{zz}$ prevent photochemically produced O$_2$ from being mixed down into the middle atmosphere, resulting in larger upper atmospheric concentrations at the expense of lower atmospheric concentrations.
Figure 13. The water vapor profiles for the scenarios outlined in the main text from the photochemical model (thick lines) compared with the water profiles produced by the radiative–convective model (thin lines). Differences between the two profiles are confined to the upper atmosphere (above \( \sim 10 \) mbar) and do not produce more than a \( \sim 5 \) ppm change in the resulting transmission spectra.

Figure 14. OH profiles for the cases seen in Figure 5, and sharing the same color palette.
