Assessment of Ammonia as a Biosignature Gas in Exoplanet Atmospheres
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Abstract

Ammonia (NH₃) in a terrestrial planet atmosphere is generally a good biosignature gas, primarily because terrestrial planets have no significant known abiotic NH₃ source. The conditions required for NH₃ to accumulate in the atmosphere are, however, stringent. NH₃'s high water solubility and high bio-useability likely prevent NH₃ from accumulating in the atmosphere to detectable levels unless life is a net source of NH₃ and produces enough NH₃ to saturate the surface sinks. Only then can NH₃ accumulate in the atmosphere with a reasonable surface production flux.

For the highly favorable planetary scenario of terrestrial planets with H₂-dominated atmospheres orbiting M dwarf stars (M5V), we find a minimum of about 5 ppm column-averaged mixing ratio is needed for NH₃ to be detectable with JWST, considering a 10 ppm JWST systematic noise floor. When the surface is saturated with NH₃ (i.e., there are no NH₃-removal reactions on the surface), the required biological surface flux to reach 5 ppm is on the order of 10¹⁰ molecules cm⁻² s⁻¹, comparable to the terrestrial biological production of CH₄. However, when the surface is unsaturated with NH₃, due to additional sinks present on the surface, life would have to produce NH₃ at surface flux levels on the order of 10¹⁵ molecules cm⁻² s⁻¹ (~4.5×10⁶ Tg year⁻¹). This value is roughly 20,000 times greater than the biological production of NH₃ on Earth and about 10,000 times greater than Earth’s CH₄ biological production.

Volatile amines have similar solubilities and reactivities to NH₃ and hence share NH₃'s weaknesses and strengths as a biosignature. Finally, to establish NH₃ as a biosignature gas, we must rule out mini-Neptunes with deep atmospheres, where temperatures and pressures are high enough for NH₃’s atmospheric production.

1. Introduction

A growing part of exoplanet research focuses on the search for biosignature gases with future telescopes. Biosignature gases are gases produced by living organisms either as final products or by-products from biochemical pathways. A viable biosignature gas must have spectral features that are both detectable and distinguishable from other molecular species (e.g., Zhan et al., 2021). A growing number of gases have been proposed as biosignatures. The most well-known example is O₂ (e.g., Jeans, 1930; Meadows et al., 2018). Other biosignature gas candidates include DMS ((CH₃)₂S) (Domagal-Goldman et al., 2011; Seager et al., 2012; Arney et al., 2018),
methane (CH\(_4\)) (Leger et al., 1996; Des Marais et al., 2002; Kaltenegger et al., 2007; Dlugokencky et al., 2011), nitrous oxide (N\(_2\)O) (Des Marais et al., 2002; Tian et al., 2015), ammonia (NH\(_3\)) (Seager et al., 2013), methyl chloride (CH\(_3\)Cl) (Segura et al., 2005), phosphine (PH\(_3\)) (Sousa-Silva et al., 2019), and isoprene (C\(_5\)H\(_8\)) (Zhan et al., 2021).

We are motivated to study the biosignature potential of NH\(_3\) since NH\(_3\) plays a significant role in biochemistry. Due to its high bio-usability, plants and various microorganisms can easily absorb NH\(_3\). NH\(_3\) is an ideal nitrogen source for life on Earth since it can be integrated into various amino acids and other organic molecules without life having to break the strong N\(_2\) triple bond. Additionally, some life can use NH\(_3\) as an energy source by oxidizing NH\(_3\). Furthermore, NH\(_3\) stands out from all the previously studied biosignature gases because NH\(_3\) has a very high solubility in water. NH\(_3\)’s high water solubility means the atmospheric accumulation of NH\(_3\) is highly dependent on planetary conditions such as whether life produces a substantial amount of NH\(_3\) and whether there are active NH\(_3\)-removal sinks on the surface (including land and ocean). If life does not produce enough NH\(_3\) to saturate the surface sinks, rain can much more efficiently remove NH\(_3\) from the atmosphere than other atmospheric gases.

NH\(_3\) has been studied before. Early studies suggest NH\(_3\) is unlikely to be present in an early Earth atmosphere because it is easily destroyed photochemically (Kasting et al., 1982; Sagan and Chyba, 1997). In a separate paper, we studied NH\(_3\) as a biosignature gas for a specific, optimistic planetary scenario of a planet with an H\(_2\) - N\(_2\) atmosphere termed the ‘cold Haber World’ (Seager et al., 2013). On such a planet, life may have evolved catalytic machinery to break the N\(_2\) triple bond and extract energy by fixing atmospheric H\(_2\) and N\(_2\) into NH\(_3\) (Seager et al., 2013). A somewhat similar catalytic process occurs in the industry (the Haber process) at specific temperatures and pressures.

In this work, we reassess NH\(_3\) as a biosignature gas by considering different planetary scenarios and surface conditions. We first summarize NH\(_3\)’s sources and sinks on Earth in Section 2. We then describe our models in Section 3. We present our results in Section 4. Finally, we conclude our paper with a discussion of our results and a description of limitations in Section 5.

2. Ammonia Sources and Sinks

To assess the biosignature potential of NH\(_3\), we first need to review how NH\(_3\) is produced (Section 2.1) and destroyed (Section 2.2) on Earth. NH\(_3\) sources on Earth are few and either anthropogenic (Section 2.1.1) or biological (Section 2.1.2), with limited abiotic sources (Section 2.1.3). In contrast, NH\(_3\) has many destruction pathways. We discuss NH\(_3\) atmospheric sinks in Section 2.2.1 and NH\(_3\) biological sinks in Section 2.2.2.

2.1 Ammonia Sources on Earth

Ammonia is a trace gas (< 1 ppbv) in modern Earth’s atmosphere, with a residence time of less than a day (Zhu et al., 2015). Current data on NH\(_3\) emissions at a global level have significant uncertainties due to the lack of measurements in most parts of Earth’s atmosphere (Olivier et al., 1998; Bouwman et al., 2002; Zhu et al., 2015; Van Damme et al., 2018). It is worth noting that
anthropogenic NH$_3$ production is a significant NH$_3$ source on Earth (Söderlund et al., 1976; Dentener and Crutzen, 1994; Olivier et al., 1998).

### 2.1.1 Anthropogenic NH$_3$ Production

On Earth, most global NH$_3$ emissions are due to anthropogenic activities, especially agriculture (Behera et al., 2013). Large quantities of ammonia are directly applied on farm fields as fertilizer (anhydrous NH$_3$) or are used to produce secondary nitrogen fertilizers. Besides anhydrous NH$_3$, synthetic N fertilizers such as urea ((NH$_2$)$_2$CO) and ammonium bicarbonate (NH$_4$HCO$_3$) are also popular N fertilizers (Behera et al., 2013). Both applications result in very high localized NH$_3$ emissions from farmlands (e.g., Dong et al., 2009; Hou and Yu, 2020). NH$_3$ emissions from N fertilizers depend on many factors, including the type of fertilizers, local meteorological conditions, and soil properties (Behera et al., 2013). It has been estimated that up to 10% of N content is lost through NH$_3$ emission when anhydrous NH$_3$ fertilizer is used. This number rises to 18.7% for urea fertilizer (Behera et al., 2013). Animal husbandry also significantly contributes to global NH$_3$ emissions (through the microbial decomposition of animal waste, see section 2.1.2 below). Coal-burning also produces NH$_3$, even though the quantity is relatively small (Soderlund et al., 1976, Behera et al., 2013).

Industrial NH$_3$ sources come from the production of nitric acid, fuel, explosives, and refrigerants. Other minor global NH$_3$ emissions include agriculture-related biomass decomposition and motor vehicles (Zhu et al., 2015). We summarize the major NH$_3$ sources and their flux in Table 2-1.

**Table 2-1. Major anthropogenic NH$_3$ sources and their estimated flux (Soderlund et al., 1976).**

| Ammonia sources         | Rate [Tg/year] |
|-------------------------|----------------|
| Domestic animals and human | 20 - 35        |
| Burning of coal         | 4 - 12         |
| Wild animals            | 2 - 6          |
| Total                   | 26 - 53        |

Global NH$_3$ emission flux is extremely hard to estimate because most NH$_3$ measurements are local, and NH$_3$ abundance varies widely (Olivier et al., 1998; Zhu et al., 2015; Van Damme et al., 2018). It has been reported that global NH$_3$ emissions may have quadrupled in the past few years due to the increasing demand for food and other agricultural products (Lamarque et al., 2011 and Zhu et al., 2015). Global NH$_3$ emissions will likely keep growing in the near future (Moss et al., 2010, Behera et al., 2013). The fact that the NH$_3$ emission rate has a strong dependency on climate (Sutton et al., 2013) makes an accurate NH$_3$ emission estimate even more difficult. We summarize some estimates of global anthropogenic NH$_3$ emission from the past few decades in Table 2-2.

**Table 2-2. A summary of global anthropogenic NH$_3$ emission estimates (Zhu et al., 2015).**

| Global NH$_3$ emission rate [Tg/year] | Source                  |
|---------------------------------------|-------------------------|
| 38.5                                  | Moss et al., 2010       |
| 53                                    | Soderlund et al., 1976  |
| 54                                    | Bouwman et al., 1997    |
As an aside, anthropogenic NH₃ is produced by the Haber-Bosch process. The Haber-Bosch process reduces unreactive atmospheric nitrogen (N₂) to ammonia with molecular hydrogen (H₂). This reaction requires a metal catalyst (e.g., iron and other catalysts), high temperatures (450 ~ 550 °C), and high pressures (250 ~ 350 bar).

\[ 3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3 \quad \Delta G^\circ = -32.8 \text{ kJ/mol} \quad (2-1) \]

The Haber-Bosch reaction has a standard Gibbs free energy change (\(\Delta G^\circ\)) of -32.8 kJ/mol and standard enthalpy change (\(\Delta H^\circ\)) of -91.8 kJ/mol. Even though this reaction is thermodynamically favorable at room temperatures (~300 K), it is kinetically disfavored. The use of catalysts significantly lowers the activation energy required for breaking the triple bond in the N₂ gas. It is worth noting that the reaction becomes thermodynamically unfavorable at high temperatures (~550°C). Nevertheless, with high pressures, the forward reaction proceeds fast enough to give an industrially acceptable NH₃ yield.

### 2.1.2 Biological NH₃ Production

Three known biological processes generate ammonia (Figure 1). We briefly summarize them below.

**Nitrogen fixation**: Biological nitrogen fixation by diazotrophic bacteria and Archaea converts atmospheric N₂ to NH₃. The chemical reaction is catalyzed by a nitrogenase enzyme's metal cluster iron-molybdenum cofactor (FeMoco) (Burgess et al., 1996). The biosynthesis of NH₃ is highly energetically costly and is coupled to the hydrolysis of 16 ATP molecules.

\[ \text{N}_2 + 8\text{H}^+ + 8\text{e}^- + 16\text{Mg-ATP} \rightarrow 2\text{NH}_3 + \text{H}_2 + 16\text{Mg-ADP} + 16\text{Pi} \quad (2-2) \]

Note that because the nitrogenase enzyme is susceptible to O₂, many nitrogen-fixing organisms inhabit strictly anaerobic conditions. Despite its complex catalytic mechanism, biological nitrogen fixation likely originated very early in the evolution of life on Earth. Nitrogen isotopic studies suggest that molybdenum-based nitrogenase arose earlier than 3.2 Gya (Stüeken et al., 2015).

**Ammonification**: Many microorganisms convert organic nitrogen within organic matter (e.g., animal and plant waste, etc.) into NH₃. Bacterial and fungal ammonification of animal waste is one of the main processes contributing to the agricultural flux of atmospheric NH₃ (see section 2.1.1).

**Dissimilatory nitrate reduction to ammonium (DNRA)**: Dissimilatory nitrate reduction to ammonium (DNRA; nitrate/nitrite ammonification) is a process of anaerobic chemoorganoheterotrophic respiration that uses nitrate (NO₃⁻) instead of O₂, as a final electron acceptor (Lam et al., 2011 and Kraft et al., 2011). As a result of DNRA, organic matter is oxidized anaerobically with a simultaneous reduction of nitrate to nitrite and subsequently to
ammonia (or ammonium ion) (NO$_3^-$ → NO$_2^-$ → NH$_4^+$) (Lam et al., 2011). Dissimilatory nitrate reduction to ammonium is typically found in prokaryotes. However, eukaryotic microorganisms can also carry out DNRA (Kuypers et al., 2018; Preisler et al., 2007; and Stief et al., 2014). Note that in contrast to denitrification (the production of N$_2$ gas), the DNRA process conserves nitrogen, as soluble NH$_4^+$ can be efficiently utilized in biochemical processes (Marchant et al., 2014).

![Figure 1. Interconversions between the main nitrogen species.](image)

Of the three processes above (excluding ammonification that results from human industrialized agricultural activity (see section 2.1.1)), biological nitrogen fixation at 200 Tg/year dominates the biological production of NH$_3$ (Rascio and Rocca 2013). We compare the annual biological production of ammonia (NH$_3$) to that of nitrogen gas (N$_2$), methane (CH$_4$), isoprene (C$_5$H$_8$), nitrous oxide (N$_2$O), and methyl chloride (CH$_3$Cl) in Figure 2.
Figure 2. Biological production of six different gases in Tg year⁻¹. The biological production of ammonia is significantly smaller than that of methane or isoprene. Specifically, the bioproduction of ammonia is only about half of that of biologically produced nitrogen gas. References: Isoprene (Zhan et al., 2021); methane (Guenther et al., 2006); nitrogen gas (Yeung et al., 2019); ammonia (Rascio and Rocca, 2013); nitrous oxide and methyl chloride: (Tian et al., 2015), (Yokouchi et al., 2015) and (Korhonen et al., 2008).

2.1.3 Minor NH₃ Abiotic Sources

There are very few minor abiotic NH₃ sources on Earth¹. We briefly summarize them below.

NH₃ is a trace component of volcanic gases erupted by some, but not all, volcanoes on Earth (see Möller 2014 and their Table 2.38). For example, (Uematsu et al., 2004) reported an emission of volcanic NH₃ from the Miyake-jima volcano that reached 5 ppb locally. The volcanic NH₃ is likely emitted due to the thermal breakdown of organic matter of biological origin (Sigurdsson et al., 2015), rather than the reduction of more oxidized N species, like N₂. Due to Earth’s oxidizing conditions, volcanic outgassing includes some oxidized nitrogen species such as NO and HNO₃ (Mather et al., 2004, Martin et al., 2007, Gaillard & Scaillet, 2014). In contrast to Earth, on a planet with a reducing upper mantle condition, nitrogen would be predominately in the form of NH₄⁺ in the fluids and could be degassed as NH₃ (Mikhail et al., 2014 and Mikhail et al., 2017). Detailed modeling is required to explore the plausibility of this scenario further.

NH₃ can be photochemically produced on iron-doped TiO₂ containing sands without microorganisms’ aid (Kasting et al., 1982; Schrauzer et al., 1983). When exposed to sunlight or UV, TiO₂ containing sands can reduce N₂ to NH₃ and trace N₂H₄. However, only up to 10⁷ tons (or 10 Tg) of NH₃ can be photochemically produced on desert sands every year (Schrauzer et al. 1983). Furthermore, this abiotic N₂ photo-fixation is only significant in arid and semiarid regions but not in areas with abundant rainfall and covered by vegetation, where biological N₂ fixation dominates (Schrauzer et al. 1983).

¹See Supplementary Information SI.8 for our NH₃ abiotic false-positive analysis.
In the presence of dissolved Ni₃Fe, NiFe, Ni⁰, and Fe⁰ in the ocean, N₂, NO₂⁻ and NO₃⁻ can be converted to NH₃/NH₄⁺ (Smirnov et al. 2008). This potential abiotic NH₃/NH₄⁺ synthesis can happen in anaerobic (oxygen-depleted) conditions or reducing (H₂-rich) environments. Such conditions can potentially be present around the Hadean submarine hydrothermal vents (Smirnov et al. 2008). However, this reduction process is strongly temperature-dependent and only becomes efficient at high temperatures (~200°C and above).

NH₃ is very unlikely to be produced in hydrothermal vents on modern Earth, and even if it were, NH₃ would dissolve in Earth’s ocean. The hydrothermal vents are not known to reach conditions for net NH₃ synthesis. There may be one extreme exception: the Piccard hydrothermal field. The Piccard hydrothermal system is the deepest known seafloor hot-spring (4957 ~ 4987 m) with pressures (~500 bar), temperatures (~500 °C), and H₂ gas abundances (from serpentinization) to enable some limited N₂ reduction (McDermott et al., 2018) if a suitable catalyst is present.

Lightning might produce NH₃ in the Earth’s atmosphere, but only in tiny amounts if at all (see Section 5.3 for further discussion). In Earth's atmosphere, most of NH₃ is generated (or 'recycled') from NH₂ radicals, which likely originate from the photolysis of NH₃ itself (see Table 2-3). Hence, we do not consider Earth's atmospheric chemistry as a net source of NH₃. For completeness, we include the high-temperature reactions in Table 2-3 even though the rates are extremely low at Earth temperatures.

Table 2-3. NH₃-producing reactions. The reaction rates are in units of cm³·molecule⁻¹·s⁻¹.

| Chemical Reaction | Rate at 298K | Rate law | Source |
|-------------------|--------------|----------|--------|
| H₂ + NH₂ → NH₃ + H | High temp reaction | 6.75 · 10⁻¹⁴ · (T/298)²⁶ · exp[−3006.8/T] | NIST |
| NH₂ + C₂H₂ → C₂H + NH₃ | High temp reaction | 8.2 · 10⁻¹³ · exp[−2780/T] | NIST |
| NH₂ + C₂H₄ → C₂H₃ + NH₃ | | 4.07 × 10⁻¹⁶ | NIST |
| NH₂ + C₂H₅O → C₂H₅O + NH₃ | | 5.28 × 10⁻¹⁵ | NIST |
| NH₂ + C₂H₆ → C₂H₅ + NH₃ | | 2.13 × 10⁻¹⁸ | NIST |
| NH₂ + CH₄ → CH₃ + NH₃ | | 6.90 × 10⁻¹⁸ | NIST |
| NH₂ + H₂O → OH + NH₃ | | 9.52 × 10⁻¹² | NIST |
| NH₂ + HO₂ → NH₃ + O₂ | | 3.40 × 10⁻¹¹ | JPL |
| N₂H₃ + N₂H₃ → 2NH₃ + N₂ | High temp reaction | 5.0 · 10⁻¹² | NIST |
| NH₂ + OH → NH₃ + O | | 1.43 × 10⁻¹³ | NIST |
| H + NH₂ → NH₃ | | 3.00 × 10⁻³⁰ | NIST |

2.2 Ammonia Sinks on Earth

Compared to NH₃’s few formation pathways on Earth, there are numerous routes through which NH₃ can be removed. This section focuses on NH₃ atmospheric sinks (Section 2.2.1) and biological sinks (Section 2.2.2).
2.2.1 \( \text{NH}_3 \) Atmospheric Sinks

\( \text{NH}_3 \) is highly reactive in Earth’s atmosphere and is destroyed by direct photolysis and reactions with UV-generated radicals. In Earth’s oxic atmosphere, OH is the dominant radical. In exoplanet atmospheres with different bulk compositions, other radicals may become dominant. In particular, for an \( \text{H}_2 \)-dominated (highly reducing) atmosphere, the most abundant reactive species are \( \text{H} \) radicals, produced by photolysis of atmospheric water vapor (Hu et al., 2012). In \( \text{N}_2 \) or \( \text{CO}_2 \)-dominated atmospheres, O may also be important, though this needs to be further explored (Hu et al., 2012; Ranjan et al., 2020). We list the reactions between \( \text{NH}_3 \) and O, H, and OH radicals in Table 2-4.

| Table 2-4. Reactions between \( \text{NH}_3 \) and H, O and OH radicals in the atmosphere. The reaction rates have units of cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). (Reference: NIST) |
|---|---|---|
| Reactions | Rate at 298K | Rate law |
| \( \text{NH}_3 + \text{H} \cdot \rightarrow \text{H}_2 + \text{NH}_2 \) | \( 8.27 \times 10^{20} \) | \( 4.27 \times 10^{-14} \cdot (T/298)^{3.87} \cdot \exp[-32.59/RT] \) |
| \( \text{NH}_3 + \text{O} \cdot \rightarrow \cdot \text{OH} + \text{NH}_2 \) | \( 4.37 \times 10^{17} \) | \( 2.87 \times 10^{-13} \cdot (T/298)^{2.10} \cdot \exp[-21.78/RT] \) |
| \( \text{NH}_3 + \cdot \text{OH} \rightarrow \text{H}_2\text{O} + \text{NH}_2 \) | \( 1.57 \times 10^{13} \) | \( 3.50 \times 10^{-12} \cdot \exp[-7.69 \pm 1.66/RT] \) |

\( \text{NH}_3 \) can also photodissociate under UV conditions. The photolysis rate coefficient \( J_A \) can be quantified by (e.g., Brasseur et al., 2017):

\[
J_A = \int q_\lambda \cdot I_\lambda \cdot \sigma_\lambda \cdot e^{-t_\lambda} d\lambda \tag{2-3}
\]

Here \( q_\lambda \) is the quantum yield of \( \text{NH}_3 \) photolysis. \( I_\lambda \) is the solar intensity at the top of the atmosphere, \( t_\lambda \) is the optical depth, and \( \sigma_\lambda \) is the absorption cross-section of \( \text{NH}_3 \). Ammonia photolysis has two pathways, which we summarize in Table 2-5. Reaction rates are computed in (Hu et al., 2012).

| Table 2-5. Photolysis reactions of \( \text{NH}_3 \) (Hu et al., 2012) |
|---|---|---|
| Reaction | Quantum yields | Reaction rate at 295 K [s\(^{-1}\)] |
| \( \text{NH}_3 + h\nu \rightarrow \text{NH}_2 + \text{H} \) | <106nm: 0.3 \[106-165 \text{ nm}: \text{linear interpolation} \] \[>165\text{nm}: 1.0 \] | \( 6.89 \times 10^{-5} \) |
| \( \text{NH}_3 + h\nu \rightarrow \text{NH} + \text{H}_2 \) | <106nm: 0.7 \[106-165 \text{ nm}: \text{linear interpolation} \] \[>165\text{nm}: 0 \] | \( 1.55 \times 10^{-6} \) |

Atmospheric \( \text{NH}_3 \) will react with nonradical molecules in the atmosphere. In total, we identified five other reactions that can remove \( \text{NH}_3 \) (Table 2-6), and this list is complete for reactions that remove \( \text{NH}_3 \), according to the NIST database (Manion et al., 2008). As in Table 2-3, we include the high-temperature reactions for completeness.

| Table 2-6. \( \text{NH}_3 \)-removing reactions. The reaction rates are in units of cm\(^3\) molecule\(^{-1}\) s\(^{-1}\). |
|---|---|---|
### 2.2.2 NH₃ Biological Sinks

On Earth, life is a significant sink for NH₃. Three biological processes are critical for NH₃ depletion by life: nitrification, anammox, and direct assimilation of NH₃ into nitrogen-containing organic building blocks of life (i.e., amino acids) (Figure 1). We discuss nitrification and anammox briefly below.

Nitrification is a process of oxidation of ammonia (NH₃) to nitrate (NO₃⁻) (Wendeborn 2020). NH₃ oxidizing bacteria and archaea harvest energy by aerobic oxidation of NH₃ to NO₃⁻ via a two-step process (Schimel et al., 2004). In the first step NH₃ is oxidized to NO₂⁻ by chemoautotrophs according to the following formula: \( \text{NH}_3 + \text{O}_2 + 2e^- + 2\text{H}^+ \rightarrow \text{NO}_2^- + 4e^- + 5\text{H}^+ \) \((\Delta G^0 = -275 \text{ kJ mol}^{-1})\) (Daims et al., 2015, Caranto et al., 2017). In the second step NO₂⁻ is further oxidized to nitrate: \( \text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + 2\text{H}^+ + 2e^- \) \((\Delta G^0 = -74 \text{ kJ mol}^{-1})\) (Schimel et al., 2004; Daims et al., 2015). Nitrification is performed primarily by soil bacteria (e.g., *Nitrosomonas sp.*, *Nitrospira sp.*).

The second major biological sink of NH₃ is called anammox. Anammox is a process of anaerobic oxidation of NH₃. Obligately anaerobic chemolithoautotrophs can perform anammox. (Kartal et al., 2011; Van Niftrik et al., 2012). According to the following formula, anammox–capable bacteria convert nitrite and ammonia directly to N₂ gas: \( \text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + 2\text{H}_2\text{O} \) \((\Delta G^0 = -357 \text{ kJ mol}^{-1})\). Anammox is especially prominent in the oceans, even around hydrothermal vents along the Mid-Atlantic Ridge (Byrne 2009). Anammox is responsible for 50% of marine N₂ production (Strous et al., 2006; Devol, 2004).

### 3. Methods

We now describe our methods for assessing NH₃ as a biosignature gas. To study the biosignature potential of NH₃, we have to determine under which conditions can NH₃ accumulate in the atmosphere, considering NH₃’s high water solubility and high bio- usability. We first review solubility and Henry’s law (Section 3.1). We then introduce our simplified ocean-NH₃ interaction model (Section 3.2), followed by a description of our one-dimensional photochemistry model (Section 3.3) and our transmission spectra model (Section 3.4).

#### 3.1 Solubility and Henry’s law
We use Henry’s law to study the solubility of NH₃. There are multiple ways to define Henry’s law constant (R. Sander 2015). We choose the following form.

\[ H_{CP}^{(X)} = \frac{C(X)}{P} \] (3-1)

Here \( H_{CP}^{(X)} \) is Henry’s law constant for a species \( X \) in mol·Pa⁻¹·m⁻³. \( C(X) \) is the dissolved concentration in the solution with units of mol·m⁻³. \( P \) is the partial pressure in Pascal (1 atm \( \approx \) 101325 Pa). Henry’s law constant is also a function of temperature, which can be approximated by the van’t Hoff equation.

\[ \frac{d \ln(H_{CP}^{(X)})}{d(1/T)} = -\frac{\Delta H_{diss}}{R} \] (3-2)

Here \( T \) is the temperature in Kelvin, \( R \) is the universal gas constant in J·K·mol⁻¹, and \( \Delta H_{diss} \) is the enthalpy change in dissolution. Since there is an inverse relationship between Henry’s law constant and temperature, NH₃ will be more soluble as temperature decreases.

### 3.2 Ocean-NH₃ Interaction Model

To show that NH₃ can accumulate in the atmosphere when life is a net source of NH₃ and produces enough NH₃ to saturate the surface sinks, we use a simplified ocean-NH₃ interaction model. Specifically, we study the partitioning between the atmosphere and the ocean, assuming equilibrium chemistry.

Our model has two variables: the ocean pH and the planet’s total NH₃ reserve maintained through biological production. We assume the exoplanet has an Earth-sized ocean, roughly 1.335×10²¹ L (Amante et al., 2009). Additionally, we assume there are no biological or geochemical sinks on the surface. In this case, the ocean is a reservoir. Once NH₃ dissolves in the ocean, it will react with water to form NH₄⁺ and OH⁻ ions. We calculate the dissolved ammonia concentration ([NH₃]) and the ammonium ion concentration ([NH₄⁺]) by using the Henderson–Hasselbalch equation.

\[ pH = pK_a + \log_{10}(\frac{[NH_3]}{[NH_4^+]}) \] (3-9)

Ammonia has a \( pK_a \) (acid dissociation constant at log scale) of about 9.25 (David R. Lide et al., 2005). We can derive [NH₃] by solving the system of equations,

\[ \frac{[NH_3]}{[NH_4^+]} = 10^{(pH-9.25)} \] (3-10)

\[ [NH_3] + [NH_4^+] = \frac{T_{NH_3}}{V_{ocean-E}} \] (3-11)
Here pH is the ocean's overall pH, $T_{NH3}$ is the planet’s total NH3 reserve in mol, and $V_{Ocean-E}$ is the volume of the Earth’s ocean in liters. We solve $[NH3]$ and express it as a function of pH and the planet’s total NH3 reserve.

$$[NH3] = \frac{T_{NH3} \cdot 10^{pH}}{(1.77828 \times 10^9 + 1 \times 10^{pH}) \cdot V_{Ocean-E}}$$ (3-12)

Using Henry's law (Eq. 3-1), we calculate NH3 partial pressure from $[NH3]$ and plot NH3 volume mixing ratio as a function of pH and $T_{NH3}$.

### 3.3 Photochemistry Model

We use our photochemistry code (Hu et al., 2012) to calculate the NH3 mixing ratio as a function of vertical altitude in exoplanet atmospheres. In this section, we briefly describe how we use this computational approach to explore atmospheric NH3 accumulation.

Our photochemistry code (Hu et al., 2012) can simulate a wide variety of planetary atmosphere scenarios by calculating the atmosphere's steady-state chemical composition. Our full photochemistry model encodes more than 800 chemical reactions and UV photolysis of atmospheric molecules. Our model also includes both wet and dry depositions, thermal escape of O, C, H, N, and S containing molecules, surface emission, and formation and deposition of sulfur-bearing (both elemental sulfur and sulfuric acid) aerosols. The one-dimensional chemical transport model has been validated by simulating modern Earth’s and Mars' atmospheric composition, matching observations of major trace gases in both scenarios. We can flexibly implement this model to simulate oxidized, oxic, and reduced atmospheres. Both ultraviolet and visible radiation in the atmosphere is computed by the delta-Eddington two-stream method. This model also includes molecular absorption, Rayleigh scattering, and aerosol Mie scattering to compute the optical depth. For applications of our photochemistry code, see (Hu et al., 2012, Seager et al., 2013(a)(b), Hu et al., 2013, Sousa-Silva et al., 2020, Zhan et al., 2021).

In this work, we consider an exoplanet orbiting an M dwarf star (M5V). We use the stellar radiation model of GJ 876 (Loyd et al., 2016; France et al., 2016). We study three different atmospheric scenarios: N2-dominated weakly oxidizing atmospheres, CO2-dominated highly oxidizing atmospheres, and H2-dominated reducing atmospheres. For exoplanets with N2-dominated, CO2-dominated, and H2-dominated atmospheres, the semi-major axes are 0.026 AU, 0.034 AU, and 0.042 AU, respectively. We choose the semi-major axes to ensure the surface temperature is maintained at 290 K across all scenarios. We model massive super-Earths with 10 $M_{Earth}$ and 1.75 $R_{Earth}$ because these large planets are more likely to retain an H2-dominated atmosphere than Earth-mass planets due to a higher escape velocity.

In each atmosphere scenario, we consider two cases: one with NH3 deposition (both dry deposition and rainout included) and one without NH3 deposition (dry deposition and rainout are both set to 0). In both cases, we assume the atmospheric NH3 is maintained through biological production (i.e., life is a net source of NH3). The case with NH3 deposition corresponds to active NH3-removal sinks on the surface, where the surface is not saturated with NH3. The case without
NH₃ deposition corresponds to conditions in which life produces enough NH₃ to saturate the surface sinks. In this case, the ocean is a reservoir of NH₃, and NH₃ is only removed by photochemistry.

For each of the scenarios we study, we set the planet's surface pressure to 1 bar and temperature to 288 K. We divide the atmosphere into two layers: a lower convective layer and a higher radiative layer (Hu et al., 2012). We set the temperature of the convective layer to follow the dry adiabatic lapse rate. We set the stratospheric temperature in our model according to (Hu et al., 2012). We set the temperature above tropopause to 160K, 200K, and 175K for the H₂-dominated, N₂-dominated, and CO₂-dominated atmosphere. For an H₂-dominated atmosphere, we assume the stratosphere is very cold due to efficient radiative cooling from abundant H₂ (Birnbaum et al., 1996). Since we do not have a climate model coupled with our photochemistry code, we do not consider heating in the upper atmosphere. Hence, we assume the temperature to be constant (isothermal) in the radiative layer (Hu et al., 2012). The temperature profiles we set are consistent with significant greenhouse effects in the convective layer (Hu et al., 2012).

To study NH₃ as a biosignature gas, we only use 735 reactions in our simulations. Specifically, we include all the reactions mentioned in (Hu et al., 2012), except for reactions that involve more than 2 carbon atoms (C₂-chem), high-temperature reactions (Hu et al., 2012), and HSO₂ thermal decay. Furthermore, we do not consider rainout and biological sinks for H₂, CO, CH₄, N₂, C₂H₂, C₂H₄, C₂H₆, and O₂. We make the assumptions mentioned above to facilitate robust comparison to our reference benchmark scenarios from (Hu et al., 2012). We present our simulation parameters (including the stellar spectrum input, atmospheric temperature-pressure profiles, the eddy diffusion profiles, and the planetary surface boundary information) in Supplementary Information SI.1.

### 3.4 Transmission Spectra Model and Simulated Observation

To assess future possibilities for the detection of NH₃ in each of the exoplanet atmospheric scenarios, we simulate transmission spectra for each scenario using our “Simulated Exoplanet Atmosphere Spectra” (SEAS) code (Zhan et al., 2021). We simulate atmospheric detection using the community JWST exposure time calculator and noise simulator Pandexo (Batalha et al., 2017) and assess the confidence in detecting NH₃ for each given scenario via a reduced chi-squared test.

#### 3.4.1 Simulated Exoplanet Atmosphere Spectra Model (SEAS)

The SEAS transmission code takes in the output of the photochemistry code (temperature-pressure profiles and mixing ratio profiles) and calculates the optical depth along the limb path (Seager et al., 2013(a)(b); Zhan et al., 2021). The SEAS transmission code has been validated by reproducing Earth’s atmosphere spectra by comparing the SEAS simulated results with data from the Atmospheric Chemistry Experiment database (Bernath et al., 2005). Currently, our SEAS code does not have refraction. Hence our transmission spectra model works best for M dwarf planets, where refraction has a minimum impact on observations (Misra et al., 2014, Bétrémieux...
et al., 2014). Details of the code are described in (Zhan et al., 2021). Here we provide a very brief description of the transmission code.

We divide the entire atmosphere (from the surface to the top of the atmosphere) into layers, and the width of each layer is one atmospheric scale height. Within each layer, we assume the atmosphere is in local thermodynamic equilibrium (LTE). The stellar radiation will penetrate along each layer's limb path, which we approximate as stellar radiation passing through multiple LTE chunks. We calculate the absorption along each beam path by using the following equation.

\[ A = n_{i,j} \times \sigma_{i,j} \times l_i \]  

Here \( A \) is absorption, \( n \) is number density, \( \sigma \) is absorption cross-section, and \( l \) is the path length. The subscript \( i \) denotes each chunk, and subscript \( j \) denotes each molecule. We then compute the transmittance (\( T \)) of each beam by using the Beer-Lambert law. The amount of flux attenuated along each beam's path is determined by multiplying the absorbance (\( 1 - T \)) by each base chunk's scale height. Finally, we calculate the transit depth of the atmosphere by summing all the attenuated fluxes.

### 3.4.2 Simulated Exoplanet Observation

We assess an exoplanet atmospheres' detectability by using the metrics described in (Seager et al., 2013(a)(b)), (Batalha et al., 2017), and (Zhan et al., 2021). We calculate the signal-to-noise ratio (SNR) of an atmosphere using the following equation.

\[ SNR = \frac{|F_{out} - F_{in}|}{\sqrt{\sigma_{F_{out}}^2 + \sigma_{F_{in}}^2}} \]  

\( F_{in} \) is the flux density within the absorption feature, \( F_{out} \) is the flux density of the surrounding continuum of the feature, and \( \sigma_{F_{out}} \) and \( \sigma_{F_{in}} \) is the respective uncertainty. More specifically, we calculate the uncertainty using the Pandexo JWST instrumental noise calculator using the NIRSpec (G140M, G235M, G395M) and MIRI (LRS) observation modes. The two instruments combined provided a spectral coverage from 1 to about 13 μm.

To analyze the transmission detectability of weakly oxidizing (\( N_2 \)-dominated), highly oxidizing (\( CO_2 \)-dominated), and reducing (\( H_2 \)-dominated) atmospheres (Section 3.3), we consider a 10 \( M_{Earth} \), 1.75 \( R_{Earth} \) Super-Earth orbiting a host star with a visual magnitude of 10. The central star can be either a Sun-like (G) star or a 0.2 \( R_{Sun} \) M dwarf star. To observe a terrestrial exoplanet’s atmosphere, we explore a total integration time between 10 transits and 100 transits (which may be impractical for G stars, but we include it for comparison).

### 3.4.3 Detection Assessment Metrics

We compare the difference in SNR to assess whether it is possible to distinguish between an \( H_2 \)-dominated atmosphere with and without a significant \( NH_3 \) surface flux (Section 4.4). We assess whether the models are good fits for the simulated observational data. We use the following
equation to compute the reduced chi-square statistics between the data with several different models.

\[ \chi^2_v = \frac{x^2}{v} = \frac{1}{v} \left[ \sum_i \frac{(O_i - C_i)^2}{\sigma_i^2} \right] \]  

(3-15)

Here \( \chi^2_v \) is the reduced chi-square, \( v \) is the degree of freedom (or the number of wavelength bins), \( \chi^2 \) is the chi-square, \( O_i \) is simulated observational data, \( C_i \) is the simulated model, \( \sigma_i \) is the variance (or error as calculated from Pandexo noise simulator for a specific instrument), and finally \( i \) denotes each wavelength bin. We note that binning the spectra reduces the variance at the expense of reducing the degree of freedom. Due to NH\(_3\) containing multiple broadband spectral features (peaks around 1.5 \( \mu \)m, 2 \( \mu \)m, 2.3 \( \mu \)m, 3 \( \mu \)m, 6 \( \mu \)m, and 10 \( \mu \)m), in practice, we find bin the spectra to a resolution of \( R = 10 \sim 20 \) is a good balance between maximizing SNR and preserving spectral information.

More specifically, we first apply a null-hypothesis test to see if the data can be explained by a straight line (i.e., no atmosphere can be detected). If the null hypothesis can be ruled out, we then compare the data for models with a variety of NH\(_3\) (column-averaged mixing ratio from 0.1 ppm to 100 ppm) and assess which model best fits the data.

### 4. Results

In this section, we assess the possibility of NH\(_3\) accumulation to detectable levels in various planetary scenarios. In brief, we find that NH\(_3\) can theoretically accumulate the JWST detectable level in the atmosphere with a reasonable surface production flux (i.e., comparable to the terrestrial biological production of CH\(_4\)) only when life is a net source of NH\(_3\) and produces enough NH\(_3\) to saturate the surface sinks.

We first illustrate NH\(_3\)'s high water solubility by comparing NH\(_3\)'s Henry's law constant with other representative gases (Section 4.1). Using our simplified ocean-NH\(_3\) interaction model and considering the atmosphere-ocean partitioning of NH\(_3\), we demonstrate that NH\(_3\) can theoretically accumulate if there are no NH\(_3\)-removal sinks on the surface (Section 4.2). Utilizing our transmission spectra model, we learn that detection of NH\(_3\) is possible for exoplanets with H\(_2\)-dominated atmospheres using JWST if the NH\(_3\) column-averaged mixing ratio reaches 5 ppm (Section 4.3). Finally, we run our photochemistry code to quantify the NH\(_3\) flux needed to reach the 5 ppm detection limit under various planetary atmosphere conditions (Section 4.4).

#### 4.1 NH\(_3\)’s High Water Solubility Limits its Ability to Accumulate in the Atmosphere

NH\(_3\) is highly water-soluble, at least two orders of magnitude more soluble than other planetary atmospheric gases. NH\(_3\)'s high water solubility means that atmospheric accumulation of NH\(_3\) is highly dependent on whether there are active NH\(_3\)-removal sinks on the surface (i.e., whether the surface is saturated with NH\(_3\)). When life does not produce enough NH\(_3\) to saturate the surface
sinks, rain (wet deposition) can much more efficiently remove NH\textsubscript{3} from the atmosphere than other gases, limiting NH\textsubscript{3}'s ability to accumulate in the atmosphere.

We can quantitatively compare the solubility of different gases to each other based on Henry’s law constants. Since Henry’s law constant is a measure of solubility in water, the larger Henry’s law constant, the more water-soluble the gas is. We summarize Henry's law constants for some representative gases at standard temperature and pressure (T = 298.15K and P ≅ 1atm) in Table 4.1 (R. Sander, 2015).

**Table 4-1.** Henry’s law constant for some representative gases in water (R. Sander et al., 2015).

| Chemical species       | H\textsuperscript{CP} [mol Pa m\textsuperscript{-3}] |
|------------------------|-----------------------------------------------|
| Ammonia NH\textsubscript{3} | 5.90 × 10\textsuperscript{-1}                  |
| Dimethyl Sulfide CH\textsubscript{3}SCH\textsubscript{3} | 5.34 × 10\textsuperscript{-3}                  |
| Methyl Chloride CH\textsubscript{3}Cl | 1.15 × 10\textsuperscript{-3}                  |
| Carbon dioxide CO\textsubscript{2} | 3.36 × 10\textsuperscript{-4}                  |
| Isoprene C\textsubscript{5}H\textsubscript{8} | 1.53 × 10\textsuperscript{-4}                  |
| Nitrogen dioxide NO\textsubscript{2} | 1.20 × 10\textsuperscript{-4}                  |
| Phosphine PH\textsubscript{3} | 7.00 × 10\textsuperscript{-5}                  |
| Methane CH\textsubscript{4} | 1.41 × 10\textsuperscript{-5}                  |
| Oxygen O\textsubscript{2} | 1.30 × 10\textsuperscript{-5}                  |
| Hydrogen H\textsubscript{2} | 7.75 × 10\textsuperscript{-6}                  |
| Nitrogen N\textsubscript{2} | 6.43 × 10\textsuperscript{-6}                  |
| Helium He | 3.83 × 10\textsuperscript{-6}                  |

The high solubility of NH\textsubscript{3} and other amines (especially aliphatic amines) in water is due to their ability to form hydrogen bonds with water molecules and themselves. Even tertiary amines (three substituents are connected to N) can form hydrogen bonds between the lone pair of electrons carried by the central nitrogen atom and the H in a water molecule that carries a partial positive charge. As a result, NH\textsubscript{3} and other volatile amines are much more soluble than any previously studied biosignature gas candidates (Figure 8).

**4.2 NH\textsubscript{3} Can Accumulate if Life Produces Enough NH\textsubscript{3} to Saturate the Surface**

Using our simplified ocean-NH\textsubscript{3} interaction model, we find that NH\textsubscript{3} can theoretically accumulate to a detectable level in the atmosphere when life is a net source of NH\textsubscript{3} and produces enough NH\textsubscript{3} to saturate the surface sinks. By detectable level, we mean a volume mixing ratio of 5 ppm (see Section 4.3 for a detailed assessment of detectability of NH\textsubscript{3}).

To reach this conclusion, we assess how ocean-atmosphere equilibrium NH\textsubscript{3} partial pressure changes with the planet's total NH\textsubscript{3} reserve and ocean pH. As a reminder, we assume the atmospheric NH\textsubscript{3} is maintained through biological production (as postulated by Seager et al., 2013). We also assume no NH\textsubscript{3}-removal sinks on the land and in the ocean (see Section 3.2).

We find that life must produce enough NH\textsubscript{3} to maintain an NH\textsubscript{3} inventory of 6×10\textsuperscript{18} mol to reach a detectable level (5 ppm) in the atmosphere. This inventory is 10,000 times that of Earth’s
(1×10^{14} \text{ mol}). One might ask if there is enough N to support such a sizeable NH$_3$ inventory. The answer is yes, compared with Earth’s total N reservoir estimated at 4×10^{20} \text{ mol} (Ranjan et al., 2019, Johnson et al., 2015). About ~1.5% of such a total N reservoir would be needed. Life on such planets$^2$ can theoretically maintain this NH$_3$ inventory by breaking down N$_2$ and H$_2$ gas to form NH$_3$, analogous to the Haber–Bosch process (Seager et al., 2013(b)).

In our model, the planet's total NH$_3$ reserve is limited by the planet's total N reservoir. Unfortunately, the upper bound of the total N reservoir cannot be known for an exoplanet. Here, we assume the planet has an Earth-sized total N reservoir of 4×10^{20} \text{ mol}. In an extreme situation where life manages to convert almost all of the planetary N reservoir into NH$_3$, the NH$_3$ volume mixing ratio can reach 0.5% (Figure 3b). In this case, NH$_3$ becomes one of the major chemical species in the atmosphere, and the ocean becomes basic. However, if life cannot produce a substantial amount of NH$_3$ and only maintain an Earth-like NH$_3$ inventory (~10^{14} \text{ mol}), NH$_3$ will not be detectable regardless of the ocean’s pH levels (Figure 3a).

**Figure 3.** Equilibrium volume mixing ratio of NH$_3$ as a function of the planet’s total NH$_3$ reserve and ocean pH. The x-axis is the ocean pH, and the y-axis is the planet’s total NH$_3$ reserve in mol. The contours are NH$_3$ volume mixing ratios. We assume the planet has an Earth-sized total N reservoir (4×10^{20} \text{ mol}) and an Earth-sized ocean (1.335×10^{21} \text{ L}). (a): If life cannot produce a substantial amount of NH$_3$ and only maintain an Earth-like NH$_3$ inventory (~10^{14} \text{ mol}), NH$_3$ volume mixing ratio is extremely low regardless of the ocean pH level (4 ≤ pH ≤ 11). (b): If life manages to convert almost all of the planetary N reservoir into NH$_3$ (~10^{20} \text{ mol}), NH$_3$ will become one of the major chemical species in the atmosphere.

### 4.3 Detectability of NH$_3$ in Transmission Spectra

We study the detectability of NH$_3$ in transmission spectra using our ‘Simulated Exoplanet Atmosphere Spectra’ (SEAS) code. For exoplanets with H$_2$-dominated atmospheres orbiting M dwarf stars (M5V), we find that a minimum of about 5 ppm column-averaged mixing ratio is needed to detect NH$_3$ with JWST, considering NH$_3$‘s 1.5 μm feature and a 10 ppm JWST systematic noise floor (Figure 4). Furthermore, we find that exoplanets with high molecular-
weight atmospheres (i.e., CO₂-dominated and N₂-dominated atmospheres) and those orbiting Sun-like stars have atmosphere signals too weak to be detected by JWST.

For exoplanets with high molecular-weight atmospheres (i.e., CO₂-dominated and N₂-dominated atmospheres), the transit depth resulting from the small atmosphere scale height is too small compared to the assumed 10 ppm JWST observational noise floor. Similarly, for exoplanets orbiting Sun-like stars, the transit depth (around 2 ~ 3 ppm for H₂-dominated atmospheres) is too small given the size of the host star. To support this argument, we conduct a null hypothesis test. We check whether our model is a better fit than a flat line. We find that only exoplanets with H₂-dominated atmospheres orbiting M5V stars pass this test.³

To demonstrate that a minimum of about 5 ppm is needed for NH₃ to be detected, we simulate JWST observations using the Pandexo JWST noise simulator with a detection noise floor of 10 ppm. Except for TRAPPIST-1 planets (details see Supplementary Information SI.9)

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³ Except for TRAPPIST-1 planets (details see Supplementary Information SI.9)
ppm and a realistic noise model for JWST instrumentation (Batalha et al., 2017). We compare a simulated spectrum with 5 ppm of NH₃ and a spectrum with no NH₃ (Figure 5). We find that the spectrum with 5 ppm of NH₃ has spectral features 10 ~ 40 ppm larger than the spectrum with no NH₃. The inclusion of detection noise is the main reason why our 5 ppm detection limit is higher than the 0.1 ppm value stated in (Seager et al., 2013).

![Figure 5. Upper Panel](image)

**Figure 5. Upper Panel**: Simulated JWST exoplanet atmosphere observation for a 10 M_Earth, 1.75 R_Earth super-Earth with an H₂-dominated atmosphere transiting an M5V star given 20 transit per instrument (80 transits in total), and comparing a model with no surface NH₃ (blue line) and a model with a column average mixing ratio of 5 ppm (orange line), which we also show in Figure 4. The y-axis shows transit depth (ppm), and the x-axis shows wavelength (μm). The simulated observation spans the wavelength range of the NIRSpec and MIRI instruments. The error bars are 95% confidence interval for each model with 5 ppm NH₃ (red) and green for no NH₃ (green) uniformly binned to a spectral resolution of R=10. We show that the difference between the two models achieves statistical significance within each instrument, indicating a confident simulated detection of NH₃. **Lower Panel**: Model difference in ppm between the two simulated spectra showing the spectral feature of NH₃ peaks around 1.5 μm, 2 μm, 3 μm, 6 μm, and 10 μm. Negative values denote that the increase of NH₃ caused a decrease of CH₄ in the atmosphere.

Even though we find that a minimum of about 5 ppm is needed for NH₃ to be detected, with one JWST instrument (e.g., NIRSpec) and one mode (i.e., G395M, which encompasses the NH₃’s 3 μm feature), constraining the amount of NH₃ will be challenging. A better quantification is possible with more modes covered. We have analyzed an ideal case with observations of all NH₃ spectral features in the wavelength range of 1.6 to 10 μm (three modes of NIRSPEC and MIRI LRS, i.e., 80 transits). In this case, we can further constraint the NH₃ mixing ratio to 1 ~ 10 ppm.

For illustration purposes, we also show an instance of a simulated observation of an exoplanet with H₂-dominated atmospheres transiting an M5V star, with both a reasonable number of transits (20 transits; Figure 6a) and the maximum theoretical observation time possible (200
transits; Figure 6b). The maximum observation time means considering nearly every visible transit for an orbital period corresponding to the habitable zone of an M5V star (i.e., one transit every 10 days for five years based on Kepler’s 3rd law). While such a 200 transit-observation is unrealistic (due to the competitive nature of JWST), Figure 6 illustrates what quality of data 200 transits would provide.

![Figure 6](image)

Figures 6. Comparison between 20 and 200 transits for simulated JWST exoplanet atmosphere observations for a 10 M\textsubscript{Earth}, 1.75 R\textsubscript{Earth} Super-Earth with H\textsubscript{2}-dominated atmosphere transiting an M5V star. Similar to Figure 5, the model shows a planet with a 5 ppm column-averaged mixing ratio of NH\textsubscript{3}. **Upper panel:** simulation for 20 transit observations (5 transits per instrument modes) and R = 20. The y-axis shows transit depth (ppm), and the x-axis shows wavelength (\(\mu\text{m}\)). The simulated observation focuses on the wavelength span of NIRSpec G140M (yellow), G235M (green), G395M (blue), and MIRI LRS (red), respectively. The blue line is the simulated transmission spectra, and the black dots are the average of all transits. The orange error bars represent the 95% confidence interval of the observation. **Lower panel:** same as the upper panel but for 200 transits (50 per mode). This simulation assumes the maximum observation time possible with JWST (200 transits, spanning across 5 years), and spectral features of various molecules can be characterized to high confidence.

### 4.4 Variability of NH\textsubscript{3} Atmospheric Accumulation in Various Planetary Scenarios

We use our photochemistry model to simulate the NH\textsubscript{3} mixing ratio as a function of vertical altitude in various planetary atmosphere scenarios. We first demonstrate that NH\textsubscript{3} can accumulate in the atmosphere with a reasonable surface production flux only when life produces enough NH\textsubscript{3} to saturate the surface sinks (Section 4.4.1). We also show the effect of the NH\textsubscript{3} surface deposition on atmospheric NH\textsubscript{3} mixing ratio given a fixed NH\textsubscript{3} surface production flux (Section 4.4.2).
4.4.1 Conditions Required for NH₃ to Accumulate with a Reasonable Surface Production Flux

We find that NH₃ can accumulate to the 5 ppm JWST-detectable level in the atmosphere with a reasonable surface production flux only if life is a net source of NH₃ and produces enough NH₃ to saturate the surface sinks. In this case, there are no NH₃-removal sinks on the surface, and NH₃ is only removed by photochemistry (i.e., no dry deposition or rainout).

Specifically, for an exoplanet with H₂-dominated atmospheres orbiting an M dwarf star, when the surface is saturated with NH₃ (i.e., there are no NH₃-removal sinks on the surface), the required biological surface flux to reach 5 ppm is on the order of 10¹⁵ molecules cm² s⁻¹, comparable to the terrestrial biological production of CH₄. However, when the surface is unsaturated with NH₃, due to additional sinks present on the surface, life would have to produce NH₃ at surface flux levels on the order of 10¹⁰ molecules cm² s⁻¹ (~4.5×10⁶ Tg year⁻¹). This value is roughly 20,000 times greater than the biological production of NH₃ on Earth and about 10,000 times greater than Earth’s CH₄ biological production.

Table 4-1. Simulated mixing ratios and surface fluxes for exoplanets with H₂-dominated, CO₂-dominated, and N₂-dominated atmospheres orbiting M dwarf stars (M5V).

| Atmospheric scenarios | NH₃ column-averaged mixing ratio | NH₃ surface flux needed [molecules cm² s⁻¹] |
|-----------------------|---------------------------------|------------------------------------------|
|                       | With NH₃ deposition              | Without NH₃ deposition                   |
| H₂-dominated          | 5.0 x 10⁻⁶ (5 ppm)              | 6.40 x 10¹⁵                             | 1.44 x 10¹⁰                  |
| CO₂-dominated         | 5.0 x 10⁻⁶ (5 ppm)              | 3.60 x 10¹⁴                             | 8.49 x 10⁸                   |
| N₂-dominated          | 5.0 x 10⁻⁶ (5 ppm)              | 7.10 x 10¹⁴                             | 6.77 x 10¹⁰                  |

As a reminder, we assume the atmospheric NH₃ is maintained through biological production in our simulations. The case with NH₃ deposition corresponds to active NH₃-removal sinks on the surface, where the surface is not saturated with NH₃. The case without NH₃ deposition corresponds to conditions in which life produces enough NH₃ to saturate the surface sinks (see Section 3.3). We include the N₂- and CO₂-dominated scenario for completeness even though we show exoplanets with high molecular-weight atmospheres (i.e., CO₂-dominated and N₂-dominated atmospheres) have atmosphere signals too weak to be detected by JWST (see Section 4.3 for more details).

Additionally, we find that the dominant photochemical removal pathway for NH₃ is direct photolysis, followed by reactions with OH radicals. Except in CO₂-dominated atmospheres, the second dominant removal pathway is reactions with excited O radicals. We compile the top three loss rates for NH₃ in Table S5-1 (see Supplementary Information SI.5).

To test our photochemistry results' robustness, we perform various sensitivity tests (including the presence of a cold trap, the choice of eddy diffusion coefficient, and Henry’s law constant for NH₃). We find that our results are not sensitive to any of these variables (see Supplementary Information SI.6). Furthermore, we find that NH₃ is insufficiently abundant to condense in our simulated atmospheres (see Supplementary Information SI.7).

4.4.2 Effects of NH₃ Surface Deposition on Atmospheric NH₃ Mixing Ratio
Given a fixed NH$_3$ surface production flux, the presence of NH$_3$ surface deposition has a significant effect on the atmospheric NH$_3$ mixing ratio. Specifically, the atmospheric mixing ratio of NH$_3$ is several orders of magnitude lower with deposition than without (Figure 7).

**Figure 7.** The volume mixing ratio of various atmospheric species on planets with H$_2$-dominated, CO$_2$-dominated, and N$_2$-dominated atmospheres orbiting active M dwarfs. The NH$_3$ surface production flux is $1.0 \times 10^{10}$ molecule·cm$^{-2}$·s$^{-1}$ for the H$_2$- and N$_2$-dominated atmospheres. For the CO$_2$-dominated case, the flux is $1.0 \times 10^9$ molecule·cm$^{-2}$·s$^{-1}$. The y-axis shows altitude in km, and the x-axis shows the mixing ratio. Note that each row of figures has a different x-axis scale. Each color denotes one particular species. The dotted lines for NH$_3$ deposition absent, and solid lines for NH$_3$ deposition present. The figures in the left panel show molecular concentrations, and the figures in the right panel show radical concentrations under different atmospheric scenarios. In each of the three atmospheric scenarios we simulate, the solid black curve (NH$_3$ mixing ratio with deposition) is shifted further to the left (smaller mixing ratio) compared to the dotted black curve (NH$_3$ without deposition) since NH$_3$ deposition suppresses atmospheric NH$_3$ concentration. Note that the solid curves for species other than NH$_3$ show the effects of NH$_3$ deposition on the atmospheric concentration of other species.
When life cannot produce a substantial amount of NH₃, the surface remains unsaturated with NH₃. Hence, surface deposition (both rainout and dry deposition) effectively removes NH₃ from the atmosphere. If life produces enough NH₃ to saturate the surface, surface deposition no longer plays a role, and NH₃ is only removed by photochemistry.

The effect of surface deposition on NH₃ mixing ratio differs between the H₂-, N₂- and CO₂-dominated atmospheres. Specifically, we find that rainout (i.e., wet deposition) is most effective in H₂-dominated atmospheres compared to N₂- or CO₂-dominated atmospheres. The difference in atmospheric NH₃ mixing ratio with and without surface deposition⁴ can reach six orders of magnitude. The effect of rainout is most significant in H₂-dominated atmospheres due to the thermodynamics of H₂. The tropospheric lapse rate is lower in H₂-dominated atmospheres than either CO₂- or N₂-dominated atmospheres, driving higher temperatures, higher water content, and higher rainout rates.

Even though surface deposition (particularly rainout) is not as effective in CO₂-dominated atmospheres as H₂-dominated atmospheres, surface deposition can make a massive difference in the NH₃ mixing ratio in CO₂-dominated atmospheres. In the absence of surface deposition, NH₃ concentrations are the lowest in the relatively oxidizing CO₂-dominated atmospheres (compared to the N₂- and H₂-dominated atmospheres), as one might naively expect on the grounds of simple thermodynamics. With the presence of surface deposition, NH₃ concentrations are the highest in the CO₂-dominated atmospheres. The reason is that the wet deposition rate decreases as temperature and atmospheric water content decreases (Giorgi & Chameides 1985; Hu et al., 2012, Equation 21). The relatively high lapse rate of CO₂-dominated atmospheres suppresses both temperature and atmospheric water content, reducing rainout and enhancing NH₃ concentrations relative to the N₂- and H₂-dominated atmospheric scenarios.

5. Discussion

We first compare NH₃’s solubility in water with other atmospheric gases, particularly several previously studied biosignature gases (Section 5.1). We next discuss how horizontal atmospheric transport might limit NH₃ accumulation above land (Section 5.2). We also discuss other minor sources and sinks of ammonia, including NH₃ production by lightning (Section 5.3) and additional ocean-related sinks for dissolved NH₃ and NH₄⁺ ions (Section 5.4). We discuss amines viability as biosignature gases by proxy with NH₃ (Section 5.5 and Section 5.6). Additionally, we briefly discuss NH₃ induced hazes (Section 5.7), NH₃'s greenhouse effect (Section 5.8), and NH₃ detectability with future telescopes (Section 5.9). We end our discussion with a brief comparison of the significance of atmospheric NH₃ in mini-Neptunes vs. super-Earths (Section 5.10).

5.1 Ammonia’s High Water Solubility Compared to Other Atmospheric Gases

We compare ammonia’s solubility to that of 27 other gases, a list that includes common atmosphere gases, biosignature gases, and a group of volatile amines (Figure 8).

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⁴ NH₃ dry deposition velocity is the same for all the scenarios.
Figure 8. The solubility of common molecules on a log scale. The x-axis shows the chemical species' name, and the y-axis shows Henry’s law constant on a log scale. Ammonia and other amines are at least two orders of magnitude more soluble than other chemicals in the list, including several biosignature gas candidates that have already been studied.

In contrast to ammonia and volatile amines, previously studied biosignature gases such as isoprene (Zhan et al., 2021), DMS (Domagal-Goldman et al., 2011, Seager et al., 2012, and Arney et al., 2018), CH₄ (Dlugokencky et al., 2011), N₂O (Tian et al., 2015), CH₃Cl (Segura et al., 2005) and phosphine (Sousa-Silva et al., 2019) have very low solubilities in water. Therefore, molecule water solubility has not needed to be emphasized as a reservoir in exoplanet atmosphere characterization studies.

Sulfur dioxide (SO₂) has a much higher solubility in water than other common atmospheric gases (but not as high as NH₃). Many studies show that both SO₂ molecules and their associated aerosols (H₂SO₄-H₂O) can potentially be detected in exoplanets' atmospheres (Hu et al., 2013, Lincowski et al., 2018, Loftus et al., 2019). However, Earth does not sustain a detectable level of sulfur aerosols in the atmosphere, possibly due to the presence of a global ocean (McCormick et al., 1995 and Loftus et al., 2019). Furthermore, it has been shown that SO₂ accumulation in an Earth-like environment requires an unreasonably high source flux (Hu et al., 2013). Therefore, (Loftus et al., 2019) propose that detection of atmospheric SO₂ (or sulfate haze) can infer the lack of surface water oceans on a rocky exoplanet.

5.2 Horizontal Atmospheric Transport Limits NH₃ Accumulation above Land

Horizontal wind transport might limit NH₃ accumulation above land when the planet's surface is unsaturated with NH₃ (i.e., there are NH₃ biological or geochemical sinks on the surface). In this case, if land-based life produces NH₃, it can be transported over the ocean, where NH₃ can rain...
out and dissolve in the ocean, thereby removing NH$_3$ from the atmosphere. Since Earth’s NH$_3$ is produced by land-based life (soil bacteria (Section 2.1), horizontal wind transport is important.

So far, our models have neglected wind transport because they are limited to one dimension (the vertical dimension). Horizontal wind transport is a sink through which NH$_3$ is removed from the atmosphere above land. An improved model would consider an NH$_3$ land-ocean transport cycle (Figure 9) that includes horizontal winds. After NH$_3$ is produced from land surfaces, it will either be transported horizontally by wind or move up to the upper atmosphere, where NH$_3$ will be photochemically destroyed. Once entering the atmosphere above the ocean, ammonia can rain out, followed by quick diffusion into the ocean due to its high solubility. As a result, wind transport limits NH$_3$’s ability to accumulate to a detectable level in the atmosphere. A numerical model for such atmospheric wind transport of NH$_3$ is very challenging since it’s extremely sensitive to the geophysical conditions we assume for the exoplanets.

![Figure 9](image_url) A simplified NH$_3$ land-ocean transport cycle. We assume that the planet's surface (land and ocean) is unsaturated with NH$_3$, meaning there are NH$_3$ biological or geochemical sinks on the surface. Right panel: Ammonia is biologically produced from land surfaces and enters the atmosphere. Ammonia leaves the land area by traveling to the upper atmosphere, where it is photochemically destroyed. NH$_3$ can also be carried away by horizontal wind transport. Left panel: Once entering the atmosphere above the ocean, ammonia is removed through direct diffusion into the ocean, where NH$_3$ readily dissolves due to its high solubility. NH$_3$ can also fall back to the ground with rain, which is not shown in this figure.

5.3 Implausibility of NH$_3$ Formation by Lightning

In principle, the formation of NH$_3$ from N$_2$ is possible during lightning strikes. However, the reduction of N$_2$ to NH$_3$ by lightning is unlikely in oxidized atmospheres due to the very low concentration of H-containing reductants (e.g., H$_2$). N species' well-studied formation by lightning strikes on Earth (N$_2$-O$_2$ atmosphere) favors the formation of nitrates and nitrites, not the thermally less stable reduced forms of N like ammonia (Ardaseva et al., 2017; Mancinelli and McKay 1988; Rakov and Uman 2003). Similarly, in oxidized N$_2$-CO$_2$ atmospheres, lightning-induced N$_2$ transformation primarily leads to HNO but not NH$_3$ (Navarro-González et al., 2001; Holloway et al., 2002; Hawtof et al., 2019).

In an H$_2$-dominated atmosphere, NH$_3$ may form through lightning by breaking apart the N$_2$ bond and subsequent recombination of N atoms with H. Unfortunately, there are no laboratory studies
on the formation of ammonia in N₂-H₂ atmospheres. Several studies focusing on the lightning-induced formation of PH₃ conclude it is possible, though extremely low efficiency. Specifically, simulated lightning discharges in laboratory conditions produce traces of PH₃, at very low efficiency, from discharges onto phosphate salt solutions (Glindemann et al., 1999; Glindemann et al., 2004). By analogy with PH₃, we infer that lightning is not likely an efficient source of NH₃ in exoplanet atmospheres.

5.4 Plausible Ocean-related Sinks of NH₃ and NH₄⁺

There are active NH₃-removal sinks on the surface (including land and ocean) that can maintain a surface unsaturated with NH₃. We summarize three chemical processes that can remove dissolved NH₃ or NH₄⁺ ions from the ocean: abiotic and biotic ammanox, marine photochemistry, and the formation of NH₄-containing sediments and minerals in the ocean.

The first process, called anammox (anaerobic ammonium oxidation), is a process that combines NH₄⁺ and NO₂⁻ to form N₂ and water. Such a process can occur biotically with marine anammox bacteria such as species belonging to the genus Scalindua (Jetten et al., 2009). Abiotic anammox is also possible. The rate of abiotic reaction of NH₃ with nitrite is sensitive to pH and temperature, with the reaction proceeding substantially faster at low pH and high temperature (Nguyen et al., 2003). NH₃ may also react with NO₃⁻, but this reaction is slower than reaction with NO₂⁻, by analogy with similar reduction reactions (Ranjan et al., 2019).

The second process is marine photochemistry. UV radiation in the wavelength range of 300-400 nm can effectively penetrate the first few centimeters of the surface ocean water before it is attenuated (Fleischmann 1989). Therefore, dissolved NH₃ and NH₄⁺ ions might be photochemically destroyed by the incident UV light close to the ocean surface. The bond dissociation energy for an N-H single bond is about 314 kJ·mol⁻¹ (T. L. Cottrell, 1966). Photons with wavelengths between 300 and 400 nm have 299 ~ 399 kJ·mol⁻¹ of energy. Therefore, it is not implausible for UV to break the N-H bond, effectively removing NH₃ or NH₄⁺ ions from the ocean surface.

The third process is the formation of NH₄-containing sediments and minerals in the ocean, whereby dissolved NH₄⁺ ions are deposited into the lithosphere. There are a wide variety of NH₄-containing minerals in nature (Table 5-1). NH₄-containing minerals like Lecontite, Ammonian fluorapophyllite, and Tobelite can form by substitution of ammonium for potassium. High concentrations of NH₄⁺ ions have been detected in the mineralizing fluids at the bottom of the ocean, specifically around the southwest pacific regions (Ridgway et al., 1990). Organic matter embedded in the sediments and rocks can break down to yield NH₄⁺. Since NH₄ can easily replace K, Na, and other alkali metals in crystal lattices, K-containing rocks and sediments are particularly susceptible to the formation of NH₄ haloes and incursions (Ridgway et al., 1990). Both surface and subsurface rocks can have high NH₄ content (Ridgway et al., 1990). As a result, dissolved NH₃ and NH₄⁺ ions can, in principle, be removed from the ocean environment through this mineralogical process.

5 The UV irradiance at the surface of an anoxic planet can be substantially greater than that of present-day Earth, due to the much more efficient penetration of the shorter UV wavelengths (Cockell, 1999).
Table 5-1. Naturally occurring NH$_4$-containing minerals (Reference: Holloway et al., 2002).

| Name of the mineral                  | Chemical formula                        |
|--------------------------------------|-----------------------------------------|
| Ammoniojarosite                      | (NH$_4$)$_3$Fe$_3^+$\((SO_4)_2\)(OH)$_6$ |
| Boussingaultite                      | (NH$_4$)$_2$Mg(SO$_4$)$_2$·6H$_2$O       |
| Letovicite                           | (NH$_4$)$_3$H(SO$_4$)$_2$               |
| Mascagnite                           | (NH$_4$)$_2$SO$_4$                      |
| Sal-ammoniac                         | (NH$_4$)Cl                              |
| Mundrabillaite                       | (NH$_4$)$_2$Ca(HPO$_4$)$_2$·H$_2$O      |
| Ammonioleucite                       | (NH$_4$)AlSi$_2$O$_6$                   |
| Lecontite                            | (NH$_4$K)Na(SO$_4$)$_2$·2H$_2$O         |
| Ammonian fluorapophyllite            | (NH$_4$K)Ca$_4$Si$_8$O$_{20}$(F,OH)·8H$_2$O |
| Tobelite                             | (NH$_4$K)Al$_2$(Si$_3$Al)O$_{10}$(OH)$_2$ |

5.5 Volatile Amines are Good Biosignature Gases by Proxy with NH$_3$

Volatile amines have similar solubilities and reactivities to NH$_3$ and hence are also suitable biosignature gases. Only when life produces enough volatile amines that can saturate the surface sinks can volatile amines accumulate in the atmosphere. Otherwise, volatile amines, just like NH$_3$, can be removed from the atmosphere due to their high water solubility and high bio-useability.

Amines can be considered NH$_3$ derivatives, where an organic functional group replaces at least one H atom. There is some difference in solubility amongst volatile amines. In general, amine solubility decreases with an increasing length or number of hydrocarbon chains. Furthermore, like NH$_3$, volatile amines will form basic solutions in water (see SI.2).

The reactivity of volatile amines is also similar to NH$_3$ (see SI.3), further allowing us to use NH$_3$ as a proxy for volatile amines. Here, we compare radical reaction rates$^6$ for volatile amines to NH$_3$ in NIST (Manion et al., 2008). The few volatile amines with radical reaction rates at room temperature have reaction rates two to three orders of magnitude higher than that of NH$_3$ (see SI.3). As a result, if NH$_3$ cannot accumulate in the atmosphere unless life produces a substantial amount of NH$_3$ that can saturate the surface sinks, neither can other volatile amines under similar planetary conditions.

5.6 IR Absorbance Spectra of Amines

We can organize amines into three groups: primary, secondary, and tertiary amines, despite the amines’ wide variety of molecular structures. Amines in each group will show similar features in their IR spectra. We use IR absorbance data from NIST to plot the spectra. We find 15 primary amines, 9 secondary amines, and 2 tertiary amines with available absorbance data in NIST. We overlay them onto a single graph to demonstrate the presence of shared IR features (Figure 10).

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$^6$ H radicals do not destroy NH$_3$ or other volatile amines.
We present the details of those amines and their raw (unnormalized) plots in Supplementary Information (SI.4).

**Figure 10.** Spectral features of primary, secondary and tertiary amines in NIST (Manion et al., 2008). The x-axis shows wavelength in microns, and the y-axis shows absorbance that is normalized to 1. Amines in each group show similar IR absorbance features.

### 5.7 NH₃-Induced Hazes

On an exoplanet with an H₂-dominated atmosphere, NH₃ haze generation processes have not yet been worked out in detail. In contrast to the formation of hydrocarbon and sulfur-based hazes that have been extensively studied (Domagal-Goldman et al., 2011; Arney et al., 2017; He et al., 2020), there is very little work on nitrogen-based hazes in H₂-dominated atmospheres. NH₃, on its own, does not participate in haze formation in reduced atmospheres. Hence, we do not focus on the formation and impact of NH₃-induced haze in our analysis. If hydrocarbons are present in the atmosphere and form hazes (Arney et al., 2017), NH₃ might participate in haze formation. In the presence of hydrocarbons, UV photolysis of NH₃ could form complex nitrogen-containing organics. This process is similar to the formation of organophosphine hazes (Sousa-Silva et al., 2020). However, contrary to the formation of organophosphine hazes, UV photolysis of NH₃ could reduce hydrocarbon hazes. The nitrogen-containing organics formed from UV photolysis of NH₃ are amines in nature. They are highly soluble and are susceptible to atmospheric precipitation.

It’s worth noting that on Earth, NH₃ plays a vital role in haze formation, especially PM₂.₅ (i.e., fine particulate matter with diameter <2.5 μm) (Ye et al., 2011; Wei et al., 2015; Chen et al., 2016; Liu et al., 2019). In Earth’s oxidized atmosphere, one way that atmospheric NH₃ can induce haze formation is by reacting with other pollutants such as sulfur dioxide (SO₂) and nitrogen oxides (NOₓ). These reactions form fine airborne particles such as ammonium nitrate.

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7 Some peaks remain undiagnosed.
(NH₄NO₃), ammonium bisulfate (NH₄HSO₄), and ammonium sulfate ((NH₄)₂SO₄). The airborne particles can then form PM₂.₅ by mixing with dust and other air pollutants (Chen et al., 2016). Furthermore, it has been shown that NH₃ can facilitate oxidation-reduction between NO₂ and SO₂ to form atmospheric nitrous acid (HONO) (Ge et al., 2019). Under UV conditions, atmospheric HONO can undergo photolysis to yield OH radicals, further facilitating haze formation (Ge et al., 2019; Wang et al., 2020).

5.8 NH₃ as a greenhouse gas

Ammonia is a greenhouse gas, given that it is a good IR absorber. However, its greenhouse effect is negligible on Earth due to its high reactivity and short atmospheric lifetime.

For exoplanets, we show in a separate paper that an increase in atmospheric NH₃ concentration does not lead to a considerable increase in surface temperature (Ranjan et al. Submitted). Specifically, in an H₂-dominated atmosphere, the surface temperature only increases by about 10 K with 100 ppm of atmospheric NH₃ due to NH₃-H₂ collision-induced absorption. In contrast, for an N₂-dominated atmosphere, the temperature increase is roughly 40 K with 100 ppm of NH₃ (Ranjan et al. Submitted).

In an implausible scenario where NH₃ does accumulate to extremely high concentrations on exoplanets, NH₃ can indeed heat the surface significantly, particularly for N₂- and CO₂-dominated atmospheres. NH₃-induced heating on H₂-dominated atmospheres is minimal because NH₃ absorption is degenerate with H₂-H₂ collision-induced absorption. Such high concentrations of NH₃ might also heat the stratosphere due to NH₃ UV absorption.

5.9 NH₃ Detectability with Future Telescopes

We assess the detectability of NH₃ with the premise of using a JWST-like telescope, which has a 6.5-meter diameter primary mirror, an estimated systematic noise floor of 10 ppm, and an estimated service time of 5 years (cryogenic lifetime). As discussed in Section 4.3, for exoplanets transiting M5V stars and orbiting in the habitable zone, we find that JWST can characterize only those with an H₂-dominated atmosphere with reasonable observation time. However, not all terrestrial exoplanets can retain H₂-dominated atmospheres.

To explore the potential for detecting NH₃ in a non-H₂-dominated atmosphere, we assume observation using more capable telescopes that are currently in design or development, such as missions like The Origins Space Telescope (OST) (Battersby et al., 2018) and the 30-meter class of ground telescopes (Johns et al., 2012; Tamai and Spyromilio 2014; Skidmore et al., 2015). Since these telescopes' instrumental details may change with mission development, we generalize those details into two abstract categories: (1) a 10-meter space telescope with broad spectral coverage. (2) a 30-meter ground-based telescope constrained by Earth’s atmosphere observing windows. In both scenarios, we assume a 1 ppm noise floor. We computed the new noise estimate by scaling the JWST noise simulator Pandexo output with lower noise floor input.
For a 10-meter space telescope with a lower noise floor, characterization of CO₂-dominated or N₂-dominated atmospheres for exoplanets transiting an M5V star (which have an atmospheric transit-depth of 10 ~ 20 ppm) are possible with 20 transits per observation mode. However, for exoplanets transiting a Sun-like star, even H₂-dominated atmospheres are not accessible (atmospheric transit-depth of 2 ~ 3 ppm). The fundamental constraint here is \((R_{\text{planet}}/R_{\text{star}})^2\). While it is arguably possible to characterize such H₂-dominated atmospheres with a 30-meter ground-based telescope, the only NH₃ IR spectral features observable in Earth’s atmosphere window are the 2.3 μm and the 10 μm features.

### 5.10 NH₃ in Mini-Neptunes

Super-Earths and mini-Neptunes discovered by future direct imaging programs may not be distinguishable from each other, lacking a mass and/or a size measurement. In this situation, any NH₃ detected should not be considered a possible biosignature gas. The reason is that NH₃ should exist to some level in mini-Neptune atmospheres without production by life, as NH₃ can be generated deep in the mini-Neptune envelope where temperature and pressure are high enough for NH₃'s atmospheric production. More work is needed to explore mini-Neptunes, including photochemistry, where NH₃ might be a marker for identifying a directly imaged planet as a mini-Neptune instead of a super-Earth.

### 6. Summary

In this paper, we examine the potential of NH₃ as a biosignature gas. We use various approaches, ranging from comparing Henry's law constants for different atmospheric gases to our simplified ocean-NH₃ interaction model to applications of our comprehensive photochemistry code and transmission spectra model.

In brief, NH₃ in a terrestrial planet atmosphere is generally a good biosignature gas, primarily because terrestrial planets have no significant known abiotic NH₃ source. NH₃’s high water solubility and high bio-useability likely prevent NH₃ from accumulating in the atmosphere to detectable levels unless life is a net source of NH₃ and produces enough NH₃ to saturate the surface sinks. Only then can NH₃ accumulate in the atmosphere with a reasonable surface production flux.

Specifically, for the favorable scenario of exoplanets with H₂-dominated atmospheres orbiting M dwarf stars (M5V), we find that a minimum of about 5 ppm column-averaged mixing ratio is needed for NH₃ to be detectable with JWST, considering a 10 ppm JWST systematic noise floor.

Additionally, volatile amines share NH₃'s weaknesses and strengths as a biosignature since volatile amines have similar solubilities and reactivities to NH₃. Finally, to establish NH₃ as a biosignature gas, we must rule out mini-Neptunes with deep atmospheres, where temperatures and pressures are high enough for NH₃’s atmospheric production.
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Supplementary Information
SI.1 Simulation Parameters for the Photochemistry Model

Figure SI.1. The synthetic stellar spectrum input of our photochemistry model (Loyd et al., 2016; France et al., 2016). The y-axis shows spectral irradiance in W·m⁻²·nm⁻¹, and the x-axis shows wavelength in nm.

Figure SI.2. The temperature-pressure profiles of the simulated exoplanets with H₂-dominated, CO₂-dominated, and N₂-dominated atmospheres. The y-axis shows atmospheric pressure (Pa) on a log scale, and the x-axis shows temperature in Kelvin (K).
Figure S1.3. The eddy diffusion profiles of the simulated exoplanets with H$_2$-dominated (top panel), CO$_2$-dominated (middle panel), and N$_2$-dominated (bottom panel) atmospheres. The y-axis shows altitude in km, and the x-axis shows the eddy diffusion coefficient in cm$^2$.s$^{-1}$.

Our photochemistry model demarcates chemical species into 4 types: type “A” for aerosol species, type “C” for chemically inert species which are assumed not to react or transport, type “F” for species assumed to be in photochemical equilibrium (i.e., for which transport is
neglected), and type “X”, for species for which the full photochemical transport equation is solved. For the lower boundary condition, our model allows us to either specify a fixed surface mixing ratio (type “1”) or the surface emission flux and dry deposition velocity (type “2”) (Hu et al., 2012).

Table S1-1. Surface boundary conditions for exoplanets with CO2-dominated atmospheres.

| Name   | Type | Initial Mixing Ratio | Upper Boundary Flux Beside Escape (Upwards) [molecule/(cm²s)] | Lower Boundary Type | Dry Deposition Velocity [cm/s] | Lower Boundary Flux (Upwards) [molecule/(cm²s)] |
|--------|------|----------------------|---------------------------------------------------------------|---------------------|--------------------------------|-------------------------------------------------|
| H      | X    | 0                    | 2                                                             | 1                   | 0                              | 0                                               |
| H₂     | X    | 1.60×10⁻³             | 2                                                             | 0                   | 3.00×10¹⁰                      | 0                                               |
| O      | X    | 0                    | 2                                                             | 1                   | 0                              | 0                                               |
| O(1D)  | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| O₂     | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| O₃     | X    | 0                    | 2                                                             | 0.4                 | 0                              | 0                                               |
| OH     | X    | 0                    | 2                                                             | 1                   | 0                              | 0                                               |
| HO₂    | X    | 0                    | 2                                                             | 1                   | 0                              | 0                                               |
| H₂O    | X    | 2.00×10⁻⁶             | 1                                                             | 0                   | 0.01                          | 0                                               |
| H₂O₂   | X    | 0                    | 2                                                             | 0.5                 | 0                              | 0                                               |
| CO₂    | X    | 0.9                  | 1                                                             | 0                   | 0.9                           | 0                                               |
| CO     | X    | 0                    | 2                                                             | 1.00×10⁻⁸           | 0                              | 0                                               |
| CH₂O   | X    | 0                    | 2                                                             | 0.1                 | 0                              | 0                                               |
| CHO    | X    | 0                    | 2                                                             | 0.1                 | 0                              | 0                                               |
| C      | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| CH     | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| CH₂    | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| CH₂₁   | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| CH₃    | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| CH₄    | X    | 0                    | 2                                                             | 0                   | 3.00×10⁸                      | 0                                               |
| CH₃O   | X    | 0                    | 2                                                             | 0.1                 | 0                              | 0                                               |
| CH₄O   | X    | 0                    | 2                                                             | 0.1                 | 0                              | 0                                               |
| CHO₂   | X    | 0                    | 2                                                             | 0.1                 | 0                              | 0                                               |
| CH₂O₂  | X    | 0                    | 2                                                             | 0.1                 | 0                              | 0                                               |
| CH₃O₂  | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| CH₄O₂  | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| C₂     | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| C₂H    | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| C₂H₂   | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| C₂H₃   | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| C₂H₄   | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| C₂H₅   | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
| C₂H₆   | X    | 0                    | 2                                                             | 1.00×10⁻⁵           | 0                              | 0                                               |
| C₂HO   | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                               |
|     |     |     |     |     |     |
|-----|-----|-----|-----|-----|-----|
| C₂H₂O | X | 0 | 0 | 2 | 0.1 |
| C₂H₂O | X | 0 | 0 | 2 | 0.1 |
| C₂H₄O | X | 0 | 0 | 2 | 0.1 |
| C₂H₅O | X | 0 | 0 | 2 | 0.1 |
| S     | X | 0 | 0 | 2 | 0 |
| S₂    | X | 0 | 0 | 2 | 0 |
| S₃    | X | 0 | 0 | 2 | 0 |
| S₄    | X | 0 | 0 | 2 | 0 |
| SO    | X | 0 | 0 | 2 | 0 |
| SO₂   | X | 0 | 0 | 2 | 1 |
| SO₃   | X | 0 | 0 | 2 | 1 |
| H₂S   | X | 0 | 0 | 2 | 0.015 |
| HS    | X | 0 | 0 | 2 | 0 |
| HSO   | X | 0 | 0 | 2 | 0 |
| HSO₂  | X | 0 | 0 | 2 | 0 |
| HSO₃  | X | 0 | 0 | 2 | 0.1 |
| H₂SO₄ | X | 0 | 0 | 2 | 1 |
| H₂SO₄A| A | 0 | 0 | 2 | 0.2 |
| S₈    | X | 0 | 0 | 2 | 0 |
| S₈A   | A | 0 | 0 | 2 | 0.2 |
| N₂    | C | 0.1| 0 | 1 | 0 |
| N     | X | 0 | 0 | 2 | 0 |
| NH₃   | X | 0 | 0 | 2 | 1 |
| NH₂   | X | 0 | 0 | 2 | 0 |
| NH    | X | 0 | 0 | 2 | 0 |
| N₂O   | X | 0 | 0 | 2 | 0 |
| NO    | X | 0 | 0 | 2 | 0.02 |
| NO₂   | X | 0 | 0 | 2 | 0.02 |
| NO₃   | X | 0 | 0 | 2 | 1 |
| N₂O₅  | X | 0 | 0 | 2 | 4 |
| HNO   | X | 0 | 0 | 2 | 0 |
| HNO₂  | X | 0 | 0 | 2 | 0.5 |
| HNO₃  | X | 0 | 0 | 2 | 4 |
| HNO₄  | X | 0 | 0 | 2 | 4 |
| HCN   | X | 0 | 0 | 2 | 0.01 |
| CN    | X | 0 | 0 | 2 | 0.01 |
| CNO   | X | 0 | 0 | 2 | 0 |
| HCNNO | X | 0 | 0 | 2 | 0 |
| CH₃NO₂ | X | 0 | 0 | 2 | 0.01 |
| CH₃NO₃ | X | 0 | 0 | 2 | 0.01 |
| CH₃N  | X | 0 | 0 | 2 | 0 |
| C₂H₂N | X | 0 | 0 | 2 | 0 |
Table S1-2. Surface boundary conditions for exoplanets with H$_2$-dominated atmospheres.

| Name  | Type | Initial Mixing Ratio | Upper Boundary Flux Beside Escape (Upwards) [molecule/(cm$^2$s)] | Lower Boundary Type | Dry Deposition Velocity [cm/s] | Lower Boundary Flux (Upwards) [molecule/(cm$^2$s)] |
|-------|------|----------------------|---------------------------------------------------------------|---------------------|--------------------------------|--------------------------------------------------|
| H     | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| H$_2$ | C    | 0.9                  | 0                                                             | 1                   | 0                              | 0.9                                              |
| O     | X    | 0                    | 2                                                             | 1                   | 0                              | 0                                                |
| O(1D) | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| O$_2$ | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| O$_3$ | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| OH    | X    | 0                    | 2                                                             | 1                   | 0                              | 0                                                |
| HO$_2$| X    | 0                    | 2                                                             | 1                   | 0                              | 0                                                |
| H$_2$O| X    | 2.00×10$^{-6}$        | 0                                                             | 1                   | 0                              | 1.00×10$^{-2}$                                  |
| H$_2$O$_2$| X | 0                    | 2                                                             | 0.5                 | 0                              | 0                                                |
| CO$_2$| X    | 0                    | 2                                                             | 1.00×10$^{-4}$      | 3.00×10$^{11}$                 | 0                                                |
| CO    | X    | 0                    | 2                                                             | 1.00×10$^{-8}$      | 0                              | 0                                                |
| CH$_2$O| X  | 0                    | 2                                                             | 0.1                 | 0                              | 0                                                |
| CH$_2$O| X  | 0                    | 2                                                             | 0.1                 | 0                              | 0                                                |
| C     | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| CH    | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| CH$_2$| X    | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| CH$_3$| X    | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| CH$_4$| X    | 0                    | 2                                                             | 0                   | 0                              | 3.00×10$^8$                                    |
| CH$_3$O| X  | 0                    | 2                                                             | 0.1                 | 0                              | 0                                                |
| CH$_4$O| X  | 0                    | 2                                                             | 0.1                 | 0                              | 0                                                |
| CH$_2$O$_2$| X | 0                    | 2                                                             | 0.1                 | 0                              | 0                                                |
| CH$_3$O$_2$| X | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| CH$_4$O$_2$| X | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| C$_2$  | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| C$_3$H | X    | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| C$_2$H$_2$| X  | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| C$_2$H$_3$| X  | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| C$_3$H$_4$| X  | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| C$_2$H$_5$| X | 0                    | 2                                                             | 0                   | 0                              | 0                                                |
| Compound | X | Y | Z | Value       | Units |
|----------|---|---|---|-------------|-------|
| C₂H₆     | 0 | 0 | 2 | 1.00×10⁻⁵  |       |
| C₂HO     | 0 | 0 | 2 | 0           |       |
| C₂H₂O    | 0 | 0 | 2 | 0.1         |       |
| C₂H₃O    | 0 | 0 | 2 | 0.1         |       |
| C₂H₄O    | 0 | 0 | 2 | 0.1         |       |
| N₂       | 0.1| 0 | 1 | 0.1         |       |
| S        | 0 | 0 | 2 | 0           |       |
| S₂       | 0 | 0 | 2 | 0           |       |
| S₃       | 0 | 0 | 2 | 0           |       |
| S₄       | 0 | 0 | 2 | 0           |       |
| SO       | 0 | 0 | 2 | 0           |       |
| SO₂      | 0 | 0 | 2 | 1           | 3.00×10⁹ |
| SO₂₁     | 0 | 0 | 2 | 0           |       |
| SO₂₃     | 0 | 0 | 2 | 0           |       |
| SO₃      | 0 | 0 | 2 | 0           |       |
| H₂S      | 0 | 0 | 2 | 0.015       | 3.00×10⁸ |
| HS       | 0 | 0 | 2 | 0           |       |
| HSO      | 0 | 0 | 2 | 0           |       |
| HSO₂     | 0 | 0 | 2 | 0           |       |
| HSO₃     | 0 | 0 | 2 | 0           |       |
| H₂SO₄    | 0 | 0 | 2 | 1           | 0     |
| H₂SO₄A   | 0 | 0 | 2 | 0.2         |       |
| S₃       | 0 | 0 | 2 | 0           |       |
| S₈A      | 0 | 0 | 2 | 0.2         |       |
| CHO₂     | 0 | 0 | 2 | 0.1         |       |
| N        | 0 | 0 | 2 | 0           |       |
| NH₃      | 0 | 0 | 2 | 1           | 1.0×10¹⁰ |
| NH₂      | 0 | 0 | 2 | 0           |       |
| NH       | 0 | 0 | 2 | 0           |       |
| N₂O      | 0 | 0 | 2 | 0           |       |
| NO       | 0 | 0 | 2 | 0.02        |       |
| NO₂      | 0 | 0 | 2 | 0.02        |       |
| NO₃      | 0 | 0 | 2 | 1           |       |
| N₂O₅     | 0 | 0 | 2 | 4           |       |
| HNO      | 0 | 0 | 2 | 0           |       |
| HNO₂     | 0 | 0 | 2 | 0.5         |       |
| HNO₃     | 0 | 0 | 2 | 4           |       |
| HNO₄     | 0 | 0 | 2 | 4           |       |
| HCN      | 0 | 0 | 2 | 0.01        |       |
| CN       | 0 | 0 | 2 | 0.01        |       |
| CNO      | 0 | 0 | 2 | 0           |       |
| HCNNO    | 0 | 0 | 2 | 0           |       |
| CH₃NO₂   | 0 | 0 | 2 | 0.01        |       |
Table S1-3. Surface boundary conditions for exoplanets with N$_2$-dominated atmospheres.

| Name  | Type | Initial Mixing Ratio | Upper Boundary Flux Beside Escape (Upwards) [molecule/(cm$^2$s)] | Lower Boundary Type | Dry Deposition Velocity [cm/s] | Lower Boundary Flux (Upwards) [molecule/(cm$^2$s)] |
|-------|------|----------------------|-------------------------------------------------|---------------------|--------------------------------|-------------------------------------------------|
| H     | X    | 0 0                  | 2                                              | 1                   | 0                              | 3.00×10$^{10}$                                  |
| H$_2$ | X    | 0 0                  | 2                                              | 0                   | 0                              | 1.00×10$^{-2}$                                  |
| O     | X    | 0 0                  | 2                                              | 1                   | 0                              | 3.00×10$^{10}$                                  |
| O(1D) | X    | 0 0                  | 2                                              | 0                   | 0                              | 1.00×10$^{10}$                                  |
| O$_2$ | X    | 0 0                  | 2                                              | 0                   | 0                              | 3.00×10$^{10}$                                  |
| O$_3$ | X    | 0 0                  | 2                                              | 0.4                 | 0                              | 3.00×10$^{10}$                                  |
| OH    | X    | 0 0                  | 2                                              | 1                   | 0                              | 3.00×10$^{10}$                                  |
| HO$_2$| X    | 0 0                  | 2                                              | 1                   | 0                              | 3.00×10$^{10}$                                  |
| H$_2$O| X    | 2.00×10$^{-6}$       | 1                                              | 0                   | 1.00×10$^{10}$                  |
| H$_2$O$_2$| X | 0 0                  | 2                                              | 0.5                 | 0                              | 1.00×10$^{10}$                                  |
| CO$_2$| X    | 0 0                  | 2                                              | 1.00×10$^{-4}$      | 0                              | 3.00×10$^{10}$                                  |
| CO    | X    | 0 0                  | 2                                              | 1.00×10$^{-8}$      | 0                              | 3.00×10$^{10}$                                  |
| CH$_2$O| X  | 0 0                  | 2                                              | 0.1                 | 0                              | 3.00×10$^{10}$                                  |
| CHO   | X    | 0 0                  | 2                                              | 0.1                 | 0                              | 3.00×10$^{10}$                                  |
| C     | X    | 0 0                  | 2                                              | 0                   | 0                              | 3.00×10$^{10}$                                  |
| CH    | X    | 0 0                  | 2                                              | 0                   | 0                              | 3.00×10$^{10}$                                  |
| CH$_2$| X    | 0 0                  | 2                                              | 0                   | 0                              | 3.00×10$^{10}$                                  |
| CH$_3$| X    | 0 0                  | 2                                              | 0                   | 0                              | 3.00×10$^{10}$                                  |
| CH$_4$| X    | 0 0                  | 2                                              | 0                   | 0                              | 3.00×10$^{10}$                                  |
| CH$_3$O| X | 0 0                  | 2                                              | 0.1                 | 0                              | 3.00×10$^{10}$                                  |
| CH$_2$O| X  | 0 0                  | 2                                              | 0.1                 | 0                              | 3.00×10$^{10}$                                  |
| CH$_3$O$_2$| X| 0 0                  | 2                                              | 0.1                 | 0                              | 3.00×10$^{10}$                                  |
| CH$_2$O$_2$| X | 0 0                  | 2                                              | 0.1                 | 0                              | 3.00×10$^{10}$                                  |
| C$_2$ | X    | 0 0                  | 2                                              | 0                   | 0                              | 3.00×10$^{10}$                                  |
| C$_2$H | X | 0 0                  | 2                                              | 0                   | 0                              | 3.00×10$^{10}$                                  |
|     |     | X   | 0   | 0   | 2   | 0   | 0   |
|-----|-----|-----|-----|-----|-----|-----|-----|
| C2H2 | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| C2H3 | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| C2H4 | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| C2H5 | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| C2H6 | X   | 0   | 0   | 2   | 1.00×10^-5 | 0   |
| C2HO | X   | 0   | 0   | 2   | 0.1 | 0   | 0   |
| C2H2O | X | 0   | 0   | 2   | 0.1 | 0   | 0   |
| C2H3O | X | 0   | 0   | 2   | 0.1 | 0   | 0   |
| C2H4O | X | 0   | 0   | 2   | 0.1 | 0   | 0   |
| C2H5O | X | 0   | 0   | 2   | 0.1 | 0   | 0   |
| N2   | C   | 1   | 0   | 1   | 0   | 1   |
| S    | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| S2   | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| S3   | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| S4   | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| SO   | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| SO2  | X   | 0   | 0   | 2   | 1   | 3.00×10^9 | 0   |
| SO21 | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| SO23 | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| SO3  | X   | 0   | 0   | 2   | 1   | 0   |
| H2S  | X   | 0   | 0   | 2   | 0.015 | 3.00×10^8 | 0   |
| HS   | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| HSO  | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| HSO2 | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| HSO3 | X   | 0   | 0   | 2   | 0.1 | 0   | 0   |
| H2SO4| X   | 0   | 0   | 2   | 1   | 0   |
| H2SO4A | A | 0   | 0   | 2   | 0.2 | 0   |
| S8   | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| S8A  | A   | 0   | 0   | 2   | 0.2 | 0   |
| N    | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| NH3  | X   | 0   | 0   | 2   | 1   | 1.0×10^10 | 0   |
| NH2  | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| NH   | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| N2O  | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| NO   | X   | 0   | 0   | 2   | 0.02 | 0   |
| NO2  | X   | 0   | 0   | 2   | 0.02 | 0   |
| NO3  | X   | 0   | 0   | 2   | 1   | 0   |
| N2O3 | X   | 0   | 0   | 2   | 4   | 0   |
| HNO  | X   | 0   | 0   | 2   | 0   | 0   | 0   |
| HNO2 | X   | 0   | 0   | 2   | 0.5 | 0   |
| HNO3 | X   | 0   | 0   | 2   | 4   | 0   |
| HNO4 | X   | 0   | 0   | 2   | 4   | 0   |
| HCN  | X   | 0   | 0   | 2   | 0.01 | 0   |
| CN   | X   | 0   | 0   | 2   | 0.01 | 0   | 0   |
### SI.2 Dissociation Constants of Representative Amines at 25°C

**Table S1-1.** The pKₐ values of some representative amines at 25°C (David R. Lide et al., 2005).

| Chemical species | pKₐ values |
|------------------|------------|
| Ammonia NH₃      | 9.25       |
| Methylamine CH₃N | 10.66      |
| Ethylamine CH₃N  | 10.65      |
| Propylamine C₃H₈N | 10.54     |
| Isopropylamine C₃H₉N | 10.63  |
| Butylamine C₄H₁₁N | 10.60   |
| sec-Butylamine C₄H₁₁N | 10.56  |
| tert-Butylamine C₄H₁₁N | 10.68  |
| Dimethylamine C₂H₇N | 10.73   |
| Diethylamine C₄H₁₁N | 10.84  |
| Diisopropylamine C₆H₁₅N | 11.05 |
| Trimethylamine C₃H₉N | 9.80   |
| Triethylamine C₆H₁₅N | 10.75  |
| Diethylmethylamine C₅H₁₃N | 10.35  |

### SI.3 Reaction Rates Between Life Produced Volatile Amines and O₂, OH Radicals

**Table S3-1.** Reactions between life produced volatile amines and OH radicals. Reaction rates are at 298K. Second-order reactions have units of [cm³ molecule⁻¹ s⁻¹] (Reference: NIST).

| Chemical | Reaction with OH radicals | Reaction rate | Reaction Order |
|----------|---------------------------|---------------|----------------|
| Ammonia (NH₃) | NH₃ + ·OH → ·NH₂ + H₂O | 1.60 × 10⁻¹³ | 2              |
| Ethanamine (C₂H₅NH₂) | C₂H₅NH₂ + ·OH → C₂H₅NH + H₂O | 2.77 × 10⁻¹¹ | 2              |
2-methylpropan-2-amine (tert-C₄H₉NH₂) + ·OH → C₄H₉NH + H₂O  
1.20 × 10⁻¹¹ 2

Trimethylamine (C₃H₉N) + ·OH → C₃H₈N + H₂O  
6.11 × 10⁻¹¹ 2

**Table S3-2.** Reactions between life produced volatile amines and O radicals. Reaction rates are at 298K. Second-order reactions have units of \([cm^3 \text{ molecule}^{-1} \text{ s}^{-1}]\) (Reference: NIST).

| Chemical | Reaction with O radicals | Reaction rate | Reaction Order |
|----------|--------------------------|---------------|----------------|
| Ammonia (NH₃) | NH₃ + ·O → ·OH + ·NH₂ | 4.37 × 10⁻¹⁷ | 2 |
| Methylamine (CH₃NH₂) | CH₃NH₂ + ·O → ·OH + CH₃NH | 5.56 × 10⁻¹³ | 2 |
| Ethylamine (C₂H₅NH₂) | C₂H₅NH₂ + ·O → ·OH + C₂H₅NH | 3.87 × 10⁻¹² | 2 |
| Dimethylamine ((CH₃)₂NH) | (CH₃)₂NH + ·O → ·OH + (CH₃)₂N· | 6.00 × 10⁻¹² | 2 |
| Trimethylamine (C₃H₉N) | C₃H₉N + ·O → OH + C₃H₈N | 7.54 × 10⁻¹² | 2 |

**SI.4 IR Spectra of Primary, Secondary and Tertiary Amines**

We list the IUPAC names of the 15 primary amines, 9 secondary amines, and 2 tertiary amines with absorbance data in NIST (Manion et al., 2008) in Table S4-1.

**Table S4-1.** Primary (15), Secondary (9) and Tertiary (2) Amines in NIST

| Primary amines | Secondary amines | Tertiary amines |
|----------------|------------------|-----------------|
| 2-methylpropan-2-amine, 2-methylbutan-2-amine, propan-2-amine, pentan-2-amine, methylamine, 2-methylprop-2-en-1-amine, 2-methylbutan-1-amine, ethanamine, prop-2-en-1-amine, propan-1-amine, butan-1-amine, pentan-1-amine, butane-1,4-diamine, (3-aminopropyl)(methyl)amine, (2-aminoethyl)(ethyl)amine | diethylamine, ethyl(prop-2-en-1-yl)amine, [(1R)-1-(naphthalen-1-yl)ethyl][(3-[3-(trifluoromethyl)phenyl]propyl)]amine, methyl(prop-2-yn-1-yl)amine, methyl(2-methylpropyl)amine, methyl(prop-2-en-1-yl)amine, methyl[2-(methylamino)ethyl]amine, (3-aminopropyl)(methyl)amine, (2-aminoethyl)(ethyl)amine | trimethylamine, ethyldimethylamine |

Here we show the overlaid IR spectra of the primary, secondary and tertiary amines.
**Figure SI.4.** IR absorbance spectra of primary amines. Included are the fifteen in the NIST database (Manion et al., 2008). The x-axis is the wavenumber, and the y axis is absorbance. Although only two of the amines contain nitrogen (N-H bending and C-N stretching), there are several distinctive peaks.
Figure SI.5. IR absorbance spectra of secondary amines. Nine species are present in the NIST database (Manion et al., 2008). The x-axis is the wavenumber, and the y axis is absorbance. Although only two of the amines contain nitrogen (N-H bending and C-N stretching), there are several distinctive peaks. The secondary amines have an N-H stretching feature not present in primary or tertiary amine spectra.
Figure SI.6. IR absorbance spectra of tertiary amines. Only two are present in the NIST database (Manion et al., 2008). The x-axis is the wavenumber, and the y-axis is absorbance. Tertiary amines lack N-H bonds, so they lack the N-H stretch feature found in primary and secondary amines.

### SI.5 NH₃ Removal Rate in the Photochemistry Model

**Table S5-1.** The top three photochemical removal mechanisms for NH₃ on exoplanets with H₂-dominated, CO₂-dominated, and N₂-dominated atmospheres orbiting M dwarf stars (M5V).

| Atmospheric scenarios | The top three loss reactions | Loss rate [molecule cm² s⁻¹] |
|-----------------------|-----------------------------|-----------------------------|
| **H₂-dominated**      | NH₃ → NH₂ + H               | 1.54 × 10¹⁰                 |
|                       | OH + NH₃ → H₂O + NH₂        | 1.27 × 10⁴                  |
|                       | H + NH₃ → H₂ + NH₂          | 4.99 × 10²                  |
| **With NH₃ deposition** | NH₃ → NH₂ + H               | 8.35 × 10⁸                  |
|                       | O(1D) + NH₃ → OH + NH₂     | 3.30 × 10⁶                  |
|                       | NH₃ → NH + H₂              | 1.34 × 10⁶                  |
| **CO₂-dominated**     | NH₃ → NH₂ + H               | 9.01 × 10¹⁰                 |
|                       | OH + NH₃ → H₂O + NH₂        | 1.85 × 10⁸                  |
|                       | NH₃ → NH + H₂              | 5.60 × 10⁵                  |
| **N₂-dominated**      | NH₃ → NH₂ + H               | 2.00 × 10¹⁰                 |
|                       | OH + NH₃ → H₂O + NH₂        | 2.78 × 10⁴                  |

**Without NH₃ deposition**

| Atmospheric scenarios | The top three loss reactions | Loss rate [molecule cm² s⁻¹] |
|-----------------------|-----------------------------|-----------------------------|
| **H₂-dominated**      | NH₃ → NH₂ + H               | 1.54 × 10¹⁰                 |
|                       | OH + NH₃ → H₂O + NH₂        | 1.27 × 10⁴                  |
|                       | H + NH₃ → H₂ + NH₂          | 4.99 × 10²                  |
| **With NH₃ deposition** | NH₃ → NH₂ + H               | 8.35 × 10⁸                  |
|                       | O(1D) + NH₃ → OH + NH₂     | 3.30 × 10⁶                  |
|                       | NH₃ → NH + H₂              | 1.34 × 10⁶                  |
| **CO₂-dominated**     | NH₃ → NH₂ + H               | 9.01 × 10¹⁰                 |
|                       | OH + NH₃ → H₂O + NH₂        | 1.85 × 10⁸                  |
|                       | NH₃ → NH + H₂              | 5.60 × 10⁵                  |
| **N₂-dominated**      | NH₃ → NH₂ + H               | 2.00 × 10¹⁰                 |
|                       | OH + NH₃ → H₂O + NH₂        | 2.78 × 10⁴                  |
### SI.6 Photochemistry Model Sensitivity Tests

To test the robustness of our photochemistry results, we decide to run various sensitivity tests. We choose the H$_2$-dominated atmosphere as our example here since it is the most favorable scenario for detecting NH$_3$. Here we present our results.

1. **The presence of a cold trap:** Our results are not sensitive to the presence of a cold trap. To first order, the presence of a cold trap does not affect NH$_3$ rainout or dry deposition. Instead, whether a cold trap is present only influences the NH$_3$ photochemical production and loss rate. Here, we simulate an atmosphere with a reduced cold trap (compared to the existing cold trap we set for the H$_2$-dominated atmosphere) (see Figure SI.7). In this case, the planet has a hot stratosphere due to UV-absorbers present in the upper atmosphere. We choose the H$_2$-dominated atmosphere as our example here since it is the most favorable scenario for detecting NH$_3$. To simulate an exoplanet with a reduced cold trap, we set the temperature above tropopause to 220K (see Figure SI.7).

| Reaction | Rate Constant |
|----------|---------------|
| NH$_3$ + CH → HCN + H$_2$ + H | 1.34 × 10$^3$ |
| CO$_2$-dominated | |
| NH$_3$ → NH$_2$ + H | 8.79 × 10$^8$ |
| O(1D) + NH$_3$ → OH + NH$_2$ | 3.54 × 10$^6$ |
| NH$_3$ → NH + H$_2$ | 1.44 × 10$^6$ |
| N$_2$-dominated | |
| NH$_3$ → NH$_2$ + H | 9.64 × 10$^{10}$ |
| OH + NH$_3$ → H$_2$O + NH$_2$ | 1.96 × 10$^8$ |
| NH$_3$ → NH + H$_2$ | 1.08 × 10$^6$ |

**Figure SI.7.** The temperature-pressure profiles of the simulated exoplanets with ‘standard’ and ‘reduced’ cold traps. The y-axis shows atmospheric pressure (Pa) on a log scale, and the x-axis shows temperature in Kelvin (K).

Our results show that when a cold trap is reduced, the photochemical production of NH$_3$ from NH$_2$ becomes more efficient due to more H radicals being present in the H$_2$-dominated atmosphere. As a result, with the same surface production flux, NH$_3$ column-averaged mixing ratio increases slightly from 5.0 ppm to 5.1 ppm (see Table S6-2).
Table S6-2. Simulated mixing ratios and reaction rates for exoplanets with H$_2$-dominated atmospheres orbiting M dwarf stars (M5V).

|                         | With a cold trap | Without a cold trap |
|-------------------------|------------------|---------------------|
| NH$_3$ outgassing [molecule/(cm$^2$s)] | $6.40 \times 10^{15}$ | $6.40 \times 10^{15}$ |
| NH$_3$ column-averaged mixing ratio | 5.0 ppm | 5.1 ppm |
| Chemical production [molecule/(cm$^2$s)] | $4.90 \times 10^{9}$ | $1.20 \times 10^{10}$ |
| Chemical loss [molecule/(cm$^2$s)] | $1.54 \times 10^{10}$ | $1.21 \times 10^{10}$ |
| Dry deposition [molecule/(cm$^2$s)] | $4.16 \times 10^{14}$ | $4.16 \times 10^{14}$ |
| Wet deposition [molecule/(cm$^2$s)] | $5.98 \times 10^{15}$ | $5.98 \times 10^{15}$ |

We currently include a cold trap in each of our existing photochemical simulations. To simulate cold traps, we set the temperature above tropopause to 160 K, 200 K, and 175 K for the H$_2$-dominated, N$_2$-dominated, and CO$_2$-dominated atmosphere. In comparison, the Earth's tropopause temperature is about 217 K (US Standard Atmosphere 1976). Please note that a cold trap does not require a thermal inversion. A cold trap is a part of the (upper) atmosphere where the temperature is low enough to condense volatiles like water (Wordsworth et al., 2013, Wordsworth et al., 2014).

II. The choice of eddy diffusion coefficient (K$_zz$): The choice of K$_zz$ can affect NH$_3$ concentration because photochemistry is most important in the upper atmosphere layers, whereas NH$_3$ is primarily produced at the planet's surface. K$_zz$ is measured or inferred for solar system planets but is not known for exoplanets. The K$_zz$ variation does not change our main conclusion, as explained below.

The K$_zz$ as a function of altitude (i.e., the eddy diffusion profile) is an input to our code. Each simulated atmospheric scenario has its own fixed eddy diffusion profile. Here, we perform a sensitivity test to a changing K$_zz$ for the H$_2$-dominated atmosphere scenario (see Table S6-3).

Table S6-3. Steady-state simulation outputs as a function of eddy diffusion magnitude, NH$_3$ surface flux, and presence/absence of wet and dry deposition of NH$_3$ for exoplanets with H$_2$-dominated atmospheres orbiting M dwarf stars (M5V).

| Eddy diffusion coefficient scaling factor | 0.1  | 1   | 10  |
|-----------------------------------------|------|-----|-----|
| NH$_3$ outgassing [molecule/(cm$^2$s)]  | $6.40 \times 10^{15}$ | $6.40 \times 10^{15}$ | $6.40 \times 10^{15}$ |
| NH$_3$ column-averaged mixing ratio     | 3.3 ppm | 5.0 ppm | 12 ppm |
| Chemical production [molecule/(cm$^2$s)] | $1.78 \times 10^{9}$ | $4.90 \times 10^{9}$ | $6.05 \times 10^{9}$ |
| Chemical loss [molecule/(cm$^2$s)]     | $1.79 \times 10^{9}$ | $1.54 \times 10^{10}$ | $2.44 \times 10^{10}$ |
| Dry deposition [molecule/(cm$^2$s)]     | $4.26 \times 10^{14}$ | $4.16 \times 10^{14}$ | $3.93 \times 10^{14}$ |
| Wet deposition [molecule/(cm$^2$s)]     | $5.97 \times 10^{15}$ | $5.98 \times 10^{15}$ | $6.01 \times 10^{15}$ |

Without NH$_3$ deposition
Eddy diffusion coefficient scaling factor  
NH₃ outgassing [molecule/(cm²s)]  
NH₃ column-averaged mixing ratio [molecule/(cm²s)]  
Chemical production [molecule/(cm²s)]  
Chemical loss [molecule/(cm²s)]  
Dry deposition [molecule/(cm²s)]  
Wet deposition [molecule/(cm²s)]  

| Eddy diffusion coefficient scaling factor | 0.1 | 1 | 10 |
|-----------------------------------------|-----|---|----|
| NH₃ outgassing [molecule/(cm²s)]        | $1.44 \times 10^{10}$ | $1.44 \times 10^{10}$ | $1.44 \times 10^{10}$ |
| NH₃ column-averaged mixing ratio        | 9.8 ppm | 5.0 ppm | 1.9 ppm |
| Chemical production [molecule/(cm²s)]   | $5.76 \times 10^{9}$ | $5.52 \times 10^{9}$ | $6.37 \times 10^{9}$ |
| Chemical loss [molecule/(cm²s)]         | $2.02 \times 10^{10}$ | $2.00 \times 10^{10}$ | $2.08 \times 10^{10}$ |
| Dry deposition [molecule/(cm²s)]        | 0   | 0 | 0  |
| Wet deposition [molecule/(cm²s)]        | 0   | 0 | 0  |

We find that the $K_{zz}$ variation does not affect rainout or dry deposition. In a more diffusive atmosphere (i.e., larger $K_{zz}$), the photochemical recycling of NH₃ becomes more efficient. Specifically, as $K_{zz}$ increases, the photochemical loss of NH₃ becomes larger, mainly due to enhanced NH₃ direct photolysis ($\text{NH}_3 \rightarrow \text{NH}_2 + \text{H}$). Simultaneously, the reproduction of NH₃ from NH₂ also increases ($\text{H}_2 + \text{NH}_2 \rightarrow \text{NH}_3 + \text{H}$) since there are more NH₂ radicals in the atmosphere. Our findings are consistent with (Kasting et al., 1982).

The effect of $K_{zz}$ variation on NH₃ atmosphere abundance depends on whether there are NH₃-removal sinks on the surface. When NH₃ deposition is present (i.e., the surface is not saturated with NH₃), the column-averaged mixing ratio of NH₃ scales with $K_{zz}$. Compared to chemical loss, wet and dry deposition can remove NH₃ much more efficiently than chemical loss (see Table S6-3). As $K_{zz}$ increases, more NH₃ is transported to the upper atmosphere before NH₃ can be removed by deposition. In this case, larger $K_{zz}$ suppresses the efficacy of NH₃ deposition, leading to an increase in atmospheric NH₃ concentration. However, when the surface is saturated with NH₃ (i.e., without NH₃ deposition), NH₃ column-averaged mixing ratio is inversely proportional to $K_{zz}$. In a more stagnant atmosphere (i.e., smaller $K_{zz}$), more NH₃ can accumulate at low altitudes since there is no wet or dry deposition. This local accumulation of NH₃ at low altitudes causes NH₃ surface mixing ratio and NH₃ column-averaged mixing ratio to increase. As $K_{zz}$ increases, the NH₃ that could have accumulated locally at low altitudes is now transported to the upper atmosphere, where NH₃ photochemical removal dominates. Hence, when there is no deposition, NH₃ column-averaged mixing ratio decreases when the atmosphere becomes more diffusive.

Overall, the $K_{zz}$ variation does not change our main conclusion as NH₃ column-averaged mixing ratio stays roughly at the same order of magnitude in our sensitivity test.

III. Henry’s law constant for NH₃: The effect of pH on NH₃ Henry's law constant is minimal. Even under high pH conditions (pH~14), NH₃ Henry's law constant will only decrease by up to 10% (Shi et al., 1999).

What might conceivably be quite different is the effective Henry’s law constant invoked in the rainout calculation, which assumes a raindrop pH of 5 (Giorgi et al., 1985; Hu et al., 2012). At such acidic pH, the effective Henry’s law constant (including partitioning of N(III) into NH₄⁺) is much higher than Henry’s law constant alone. As raindrop becomes basic (pH>7), the effective Henry’s law constant will converge with Henry’s law constant. Hence, rainout would be much less efficient (though not ineffective, as even the 'regular' Henry's law constant for NH₃ is very high). In this case, we expect results intermediate to our NH₃ deposition on and off cases.
**SI.7 NH₃ Condensation in the Atmosphere**

We find that NH₃ does not condense in our simulated atmospheres. At even the highest NH₃ flux considered in our study, NH₃ is insufficiently abundant anywhere in the atmosphere to condense. Here we plot the scenario with the highest NH₃ surface flux (i.e., H₂-dominated atmosphere, with NH₃ deposition), and we superimpose the NH₃ saturation curve (equilibrium with both the liquid and solid phase) on top of it (see Figure SI.8). The black curve is the NH₃ volume mixing ratio on planets with H₂-dominated atmospheres orbiting M dwarfs. The red curve is the NH₃ saturation curve (Stull, 1947). The NH₃ surface production flux is 6.4×10¹⁵ molecule cm⁻² s⁻¹ (see Table 4-1).

![Figure SI.8](image_url)

**Figure SI.8.** The volume mixing ratio of NH₃ on planets with H₂-dominated atmospheres orbiting active M dwarfs. The NH₃ surface production flux is 6.4×10¹⁵ molecules cm⁻² s⁻¹. The y-axis shows altitude in km, and the x-axis shows the mixing ratio. At even the highest NH₃ flux considered in our study, NH₃ is insufficiently abundant anywhere in the atmosphere to condense.

This figure clearly shows that our simulated NH₃ is not concentrated enough to condense in the atmosphere. Therefore, the stratospheric mixing ratio of NH₃ will never decouple from the surface mixing ratio (or the surface production flux). As a result, we do not consider upper atmosphere NH₃ condensation in our study.

**SI.8 NH₃ Abiotic False-Positive Analysis**

I. **Volcanic NH₃ outgassing:** We can estimate the flux at which NH₃ can be degassed on an exoplanet based on Earth’s N₂ volcanic outgassing flux. (Catling et al., 2017) estimates the N₂ volcanic outgassing on Earth is roughly 0.9×10¹¹ mol/year. If all the nitrogen comes out as NH₃ instead, the NH₃ outgassing flux can be as high as 6.7×10⁸ molecules cm⁻² s⁻¹. For an exoplanet with H₂-dominated atmospheres, to generate an NH₃ false positive from volcanic outgassing, the exoplanet’s mantle conditions need to favor NH₃/NH₄⁺ production, and the volcanic outgassing of N needs to be at least 100 times greater than Earth’s (assuming there is no NH₃-removal sink on the planet’s surface). Hence, it is unlikely for volcanic NH₃ outgassing alone to generate a detectable false positive.
II. Nitrogen photoreduction on TiO$_2$ containing sands: We can estimate the upper limit of the amount of NH$_3$ this abiotic N$_2$ photo-fixation can produce. Suppose there is an Earth-sized exoplanet orbiting an M dwarf. The planet is arid, and the surface is covered by TiO$_2$ containing sands. We assume the planet has an Earth-sized desert (about $1.9\times10^7$ square miles) (Schrauzer et al., 1983). We also assume the planet's total surface area is the same as Earth's (roughly $1.97\times10^8$ square miles). Since M dwarf planets receive roughly 100~1000 times less UV than Sun-like star planets do (Ranjan et al., 2017), we assume this abiotic pathway is only 1% effective on the M dwarf planets. Hence, this abiotic N$_2$ fixation can produce up to 1 Tg of NH$_3$ every year (about $2.0\times10^8$ molecules cm$^{-2}$ s$^{-1}$), roughly 2 orders of magnitude smaller than the flux needed to generate a detectable NH$_3$ false positive (assuming there is no NH$_3$-removal sink on the surface). (Kasting et al., 1982) reports that this abiotic N$_2$ photo-fixation can generate NH$_3$ at a rate of $2.8\times10^{10}$ to $2.8\times10^{11}$ molecules cm$^{-2}$ s$^{-1}$ locally on Earth. Assuming this reaction is 1% effective on the M dwarf planets, we estimate that this abiotic N$_2$ fixation could produce NH$_3$ at a rate of up to $2.8\times10^9$ molecules cm$^{-2}$ s$^{-1}$. Even in the most optimum case where NH$_3$ is emitted globally at this rate on exoplanets, the NH$_3$ production flux is still an order of magnitude smaller than the flux needed to generate a detectable false positive. Overall, it is unlikely for nitrogen photoreduction on TiO$_2$ containing sands alone to generate a detectable false positive.

III. Abiotic NH$_3$/NH$_4^+$ synthesis around Hadean submarine hydrothermal vents: Suppose there is an Earth-sized exoplanet orbiting an M dwarf star. We assume the planet's total heat flow is the same as modern Earth's (roughly $4.3\times10^{13}$ W) (Elderfield et al., 1996; Smirnov et al., 2008). Assuming the most favorable scenario with 80% of the planet’s heat flow released via hydrothermal activity and 10% conversion of N$_2$ to NH$_4^+$, the annual NH$_4^+$ production can be as high as $1.9\times10^{12}$ mol/year (Smirnov et al. 2008). If we further assume all the NH$_4^+$ produced in the ocean is released into the atmosphere as NH$_3$, this abiotic NH$_3$/NH$_4^+$ synthesis can produce up to 32 Tg of NH$_3$ every year (about $7\times10^9$ molecules cm$^{-2}$ s$^{-1}$). Even in this most optimum case, the NH$_3$ production flux is not large enough to generate a detectable NH$_3$ false positive.

SI.9 Detectability of TRAPPIST-1 Planets with JWST

Recently, some papers (e.g., Fauchez et al., 2019; Lustig-Yaeger et al., 2019) claim that gases like CH$_4$, H$_2$O, CO$_2$, and SO$_2$ might be detectable for TRAPPIST-1 planets with JWST (Lustig-Yaeger et al., 2019). Depends on the assumptions of the atmosphere (i.e., CO$_2$-, N$_2$- or H$_2$O-dominated atmospheres) and the signal-to-noise (S/N) ratio, the number of transits required to detect those gases on TRAPPIST-1 planets could range from 10 transits to more than 100 transits. What they claim is not contradictory to our statement here. TRAPPIST-1, an ultra-cooled M8V dwarf star, is rare and unique. TRAPPIST-1's small stellar radius and relatively low temperature are beneficial for trace gas detection because the transit depth scales with $(R_{\text{planet}}/R_{\text{star}})^2$. Furthermore, neither (Fauchez et al., 2019) or (Lustig-Yaeger et al., 2019) assumes a fixed systematic noise floor as we do in our analysis. Lastly, the detectability of gases on exoplanets depends on more than a dozen parameters - the presence of clouds and hazes, scattering, atmospheric refraction, to name a few. Different assumptions for those parameters can lead to very different conclusions. It is beyond the scope of this paper to go through every
parameter to assess detectability. Our findings are valid given the assessment metrics we mention in Section 3.4.