Methanol—A Poor Biosignature Gas in Exoplanet Atmospheres

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Abstract

Biosignature gas research has been growing in recent years thanks to next-generation space- and ground-based telescopes. Methanol (CH$_3$OH) has many advantages as a biosignature gas candidate. First, CH$_3$OH’s hydroxyl group (OH) has a unique spectral feature not present in other anticipated gases in the atmospheres of rocky exoplanets. Second, there are no significant known abiotic CH$_3$OH sources on terrestrial planets in the solar system. Third, life on Earth produces CH$_3$OH in large quantities. However, despite CH$_3$OH’s advantages, we consider it a poor biosignature gas in the atmospheres of terrestrial exoplanets due to the enormous production flux required to reach its detection limit. CH$_3$OH’s high water solubility makes it very difficult to accumulate in the atmosphere. For the highly favorable planetary scenario of an exoplanet with an H$_2$-dominated atmosphere orbiting an M5V dwarf star, we find that only when the column-averaged mixing ratio of CH$_3$OH reaches at least 10 ppm can we detect it with the James Webb Space Telescope (JWST). The CH$_3$OH bioproduction flux required to reach the JWST detection threshold of 10 ppm must be of the order of 10$^{14}$ molecules cm$^{-2}$ s$^{-1}$, which is roughly three times the annual O$_2$ production on Earth. Considering that such an enormous flux of CH$_3$OH is essentially a massive waste of organic carbon—a major building block of life, we think this flux, while mathematically possible, is likely biologically unattainable. Although CH$_3$OH can theoretically accumulate on exoplanets with CO$_2$- or N$_2$-dominated atmospheres, such planets’ small atmospheric scale heights and weak atmospheric signals put them out of reach for near-term observations.

Unified Astronomy Thesaurus concepts: Exoplanet atmospheres (487); Biosignatures (2018); Astrobiology (74)

1. Introduction

In planetary science, the search for biosignature gases is anticipated to become a pivotal way to uncover signs of extraterrestrial life. Thanks to the development of space telescopes (e.g., the James Webb Space Telescope, or JWST), more and more gases have been proposed as biosignature gases in recent years. Biosignature gases are gases produced by living organisms that accumulate in the atmosphere to detectable levels. A biosignature gas can be either a by-product or a final product of biochemical metabolism. Among the known biosignature gases, oxygen (O$_2$) is the most famous (e.g., Jeans 1930; Meadows et al. 2018). Other biosignature gases that people have studied include methane (CH$_4$) (Léger et al. 1996; Des Marais et al. 2003; Kaltenegger et al. 2007; Dlugokencky et al. 2011; Guzmán-Marmolejo and Segura 2015), methyl chloride (CH$_3$Cl) (Segura et al. 2005), nitrous oxide (N$_2$O) (Des Marais et al. 2003; Segura et al. 2005; Tian et al. 2015; Rugheimer & Kaltenegger 2018), methanethiol (CH$_3$SH) (Donngal-Goldman et al. 2011), phosphine (PH$_3$) (Sousa-Silva et al. 2020), isoprene (C$_5$H$_8$) (Zhan et al. 2021), and ammonia (NH$_3$) (Seager et al. 2013; Huang et al. 2022).

We are motivated to study atmospheric CH$_3$OH as part of our program to assess all potential biosignature gases (Seager et al. 2016). CH$_3$OH is an important precursor molecule for life’s biochemistry, as it is the building block of a diverse set of biochemicals such as acetic acid, methylamines, and methyl esters, to name a few. In the atmosphere, CH$_3$OH is a significant source of formaldehyde (CH$_2$O) and carbon monoxide (CO) (Tie et al. 2003; Solomon et al. 2005; Millet et al. 2008; Hues et al. 2011). CH$_3$OH stands out from other biosignature gas candidates because there is no significant known abiotic CH$_3$OH source on terrestrial planets (see Section 2). Furthermore, due to CH$_3$OH’s high water solubility (see Section 6.1), the limited amount of abiotic CH$_3$OH produced can be easily removed by rain, making it extremely difficult to accumulate. As a result, only when life generates a substantial amount of CH$_3$OH can it reach detectable levels in the atmosphere. People have not thoroughly studied CH$_3$OH as a biosignature gas before.

We first discuss CH$_3$OH sources (Section 2) and CH$_3$OH removal mechanisms (Section 3). We then describe our photochemistry model (Section 4.1) and our model of transmission spectra (Section 4.2). We present our results in Section 5. We discuss our results and limitations in Section 6. Finally, we conclude with a summary (Section 7).

2. CH$_3$OH Emission and Production Mechanisms

In this section, we first discuss Earth’s atmospheric CH$_3$OH concentrations and lifetime in Section 2.1. Then we review CH$_3$OH production flux on Earth in Section 2.2. Next, we discuss biological CH$_3$OH production in Section 2.3 and minor CH$_3$OH sources on Earth in Section 2.4.
2.1. Earth’s Atmospheric CH$_3$OH Concentrations and Lifetime

Methanol is the second most abundant organic gas in the Earth’s atmosphere, after CH$_4$ (Millet et al. 2008; Hu et al. 2011). Overall, atmospheric CH$_3$OH concentrations range from approximately 600 ppt in the upper troposphere to roughly 10 ppb near the surface (Heikes et al. 2002; Solomon et al. 2005; Hu et al. 2011; Stavrakou et al. 2011). CH$_3$OH surface concentrations can reach 47–55 ppb in some urban areas (Heikes et al. 2002; Solomon et al. 2005). Current data on atmospheric CH$_3$OH concentrations at a global level are scarce and have considerable uncertainties (Tie et al. 2003; Solomon et al. 2005; Hu et al. 2011; Stavrakou et al. 2011). In many parts of the world, long-term observations and measurements of CH$_3$OH are still unavailable and remain poorly constrained (Tie et al. 2003; Solomon et al. 2005; Hu et al. 2011; Stavrakou et al. 2011). Existing limited measurements show strong regional variability in atmospheric CH$_3$OH levels (Tie et al. 2003; Millet et al. 2008) (Figure 1).

The atmospheric CH$_3$OH concentrations also have pronounced seasonal patterns (Tie et al. 2003; Hu et al. 2011). CH$_3$OH concentrations are highest in summer and lowest in winter (Hu et al. 2011). As the ambient temperature rises during summer, atmospheric CH$_3$OH levels increase. The seasonality of CH$_3$OH concentrations is mainly driven by variations in biogenic CH$_3$OH emissions (Hu et al. 2011). On hot summer days, plants proliferate. The rapid growth of plants and leaves results in much higher CH$_3$OH emissions (Section 2.3), leading to a significant (up to threefold) increase in atmospheric CH$_3$OH concentrations (Hu et al. 2011). In fall and winter, old and mature leaves cannot produce as much CH$_3$OH as those newly grown leaves, so overall biogenic CH$_3$OH emissions decrease (Hu et al. 2011). The impact of human activities on the seasonality of CH$_3$OH is minimal. Even in winter, the contribution of anthropogenic emissions to atmospheric CH$_3$OH concentrations is only about 40% on average (Hu et al. 2011). The atmospheric CH$_3$OH concentrations also exhibit consistent diurnal variations. CH$_3$OH concentrations are slightly higher at night than during the day (Galbally & Kirstine 2002; Solomon et al. 2005). The main reason for the increase in CH$_3$OH concentrations at night is the reduction of turbulent mixing in the boundary layer rather than the change in emission flux (Solomon et al. 2005).

The estimated overall lifetime of CH$_3$OH in Earth’s atmosphere is roughly 5–12 days (Galbally & Kirstine 2002; Heikes et al. 2002; Tie et al. 2003; Singh et al. 2004; Millet et al. 2008; Hu et al. 2011). However, depending on the altitude, the CH$_3$OH lifetime may vary considerably. In the surface boundary layer, the chemical lifetime of CH$_3$OH is only about 3–6 days (Galbally & Kirstine 2002; Heikes et al. 2002; Tie et al. 2003). In the upper troposphere, CH$_3$OH lifetime is much longer, ranging from 16 days to a few weeks (Galbally & Kirstine 2002; Heikes et al. 2002; Tie et al. 2003). The atmospheric lifetime of CH$_3$OH is longer than that of isoprene (a few hours) and formaldehyde (∼1 day) but much shorter than that of CH$_4$ (8–10 yr) (Heikes et al. 2002; Tie et al. 2003). Therefore, unlike isoprene, which is limited to the source regions due to its short lifetime, CH$_3$OH can be transported from the surface to the upper troposphere. However, CH$_3$OH’s shorter lifetime than CH$_4$ means that CH$_3$OH cannot be as long-lived and widely spread in the upper troposphere as CH$_4$ (Tie et al. 2003).

2.2. CH$_3$OH Production Flux on Earth

The global CH$_3$OH emissions are huge, accounting for nearly half of the total annual oxygenate (i.e., chemicals that have oxygen in their molecules) production (Guenther et al. 1995; Heikes et al. 2002). Estimates of global CH$_3$OH source range from less than 100 Tg yr$^{-1}$ to roughly 350 Tg yr$^{-1}$ (Heikes et al. 2002; Tie et al. 2003; Singh et al. 2004; Millet et al. 2008; Hu et al. 2011; Stavrakou et al. 2011). In comparison, the estimated biological production rates of methane (CH$_4$), nitrogen gas (N$_2$), and ammonia (NH$_3$) on Earth are about 500 Tg yr$^{-1}$, 457 Tg yr$^{-1}$, and 200 Tg yr$^{-1}$, respectively (Guenther et al. 2006; Rascio & La Rocca 2018; Yeung et al. 2019). Different researchers have tried to come up with estimates of global CH$_3$OH fluxes, but the uncertainty in their estimates remains large (Table 1).

![Figure 1](image.png)
The largest source of atmospheric CH$_3$OH is the terrestrial biosphere, specifically plant growth (Section 2.3). According to literature estimates, CH$_3$OH produced by plant growth can account for up to 80% of the global CH$_3$OH emissions (Galbally & Kirstine 2002; Heikes et al. 2002; Tie et al. 2003; Millet et al. 2008; Hu et al. 2011; Stavrakou et al. 2011). Other CH$_3$OH sources include degradation of plant matter, industrial and urban activities, biomass and biofuel burning, and atmospheric production (Section 2.4) (Galbally & Kirstine 2002; Heikes et al. 2002; Singh et al. 2004; Millet et al. 2008). So far, there has been no report claiming volcanic emission of CH$_3$OH. Figure 2 is a simplified schematic diagram of the global CH$_3$OH biogeochemical cycle.

Some papers hypothesize that the marine biosphere might also be an essential source of CH$_3$OH (Galbally & Kirstine 2002; Heikes et al. 2002; Millet et al. 2008; Hu et al. 2011; Stavrakou et al. 2011). In the upper ocean, where nutrient levels are high, marine phytoplankton can convert algal carbohydrates into CH$_3$OH. Since marine phytoplankton is one of the most abundant species on Earth, it can theoretically produce considerable CH$_3$OH every year (Heikes et al. 2002; Millet et al. 2008). However, this source is exceeded by a much bigger oceanic sink (Galbally & Kirstine 2002; Millet et al. 2008; Hu et al. 2011; Stavrakou et al. 2011). Therefore, on a global scale, the ocean acts as a net sink for CH$_3$OH (Section 3.2). We have summarized the estimated global CH$_3$OH sources in Table 2.

### Table 1

| Estimated Range (Most Probable Value) | Reference          |
|--------------------------------------|--------------------|
| 122–340 Tg yr$^{-1}$ (280 Tg yr$^{-1}$) | Heikes et al. (2002) |
| 70–350 Tg yr$^{-1}$ (312 Tg yr$^{-1}$) | Tie et al. (2003)  |
| 75–490 Tg yr$^{-1}$ (110 Tg yr$^{-1}$) | Singh et al. (2004) |
| 123–343 Tg yr$^{-1}$ (242 Tg yr$^{-1}$) | Millet et al. (2008) |
| 100–320 Tg yr$^{-1}$ (187 Tg yr$^{-1}$) | Stavrakou et al. (2011) |

2.3. Biological CH$_3$OH Production

Plants are the largest source of CH$_3$OH in the Earth’s atmosphere. Most plants can produce CH$_3$OH through the demethylation of pectin during leaf growth (Galbally & Kirstine 2002; Heikes et al. 2002; Tie et al. 2003; Millet et al. 2008; Stavrakou et al. 2011). Pectin is a complex polysaccharide widely found in plant cell walls. As an essential tissue-firming agent, pectin can strengthen the cell wall, protecting and supporting the intracellular structures. During cell growth, pectin is demethylated through the action of pectin methylesterase, an enzyme involved in plant growth (Fall & Benson 1996; Stavrakou et al. 2011). As a by-product of pectin demethylation, CH$_3$OH is released through stomata during transpiration (Galbally & Kirstine 2002; Millet et al. 2008; Stavrakou et al. 2011) (Figure 3). The CH$_3$OH emissions from leaves depend on light, temperature, and stomatal conductance (Stavrakou et al. 2011). As a result, CH$_3$OH emissions from leaves significantly decrease at night due to the stomatal control (Millet et al. 2008).

In general, CH$_3$OH emissions are inversely proportional to leaf age (Stavrakou et al. 2011). Young and growing leaves can produce more methanol than old and senescing leaves (Heikes et al. 2002; Millet et al. 2008; Stavrakou et al. 2011). Different types of plants have different CH$_3$OH emission rates. Conifers have lower methanol emissions than broad-leaf plants. In addition, when leaves are wounded, CH$_3$OH emissions will increase (Heikes et al. 2002). Since CH$_3$OH emissions from
leaves depend on numerous parameters, most of which can change substantially during the growing seasons, estimating a global CH₃OH emission factor without considerable uncertainties is extremely difficult (Section 2.2). However, not all CH₃OH produced in leaves ends up in the atmosphere (Galbally & Kirstine 2002; Millet et al. 2008). Plants can store a small amount of CH₃OH in their tissues. Plants can also metabolize (oxidize) some methanol to formaldehyde with the help of methanol oxidase (Galbally & Kirstine 2002).

Even though plant growth and development is the dominant biological CH₃OH production mechanism on Earth, other biological processes can also generate CH₃OH at a much lower rate (Millet et al. 2008; Stavrakou et al. 2011). Fall & Benson (1996) reports that root and fruit growth can produce CH₃OH. Degradation of dead plants can also yield a small amount of CH₃OH either through the action of residual enzymes or with the help of microorganisms (Millet et al. 2008). During the fungal decomposition of wood, lignin demethylation can produce a limited amount of CH₃OH (Millet et al. 2008). For completeness, we note that methanotrophic bacteria (also called methanotrophs) can also produce CH₃OH. With the help of methane monooxygenase (MMO), an enzyme that can oxidize the C–H bond in methane, methanotrophs can oxidize CH₄ to CH₃OH (Hanson & Hanson 1996; Basch et al. 1999). However, MMO-mediated CH₃OH production is insignificant compared to other biological production pathways. Due to the lack of research on these minor biological CH₃OH production pathways mentioned above, their respective contributions to global CH₃OH production, albeit extremely small, remain unknown.

2.4. Minor CH₃OH Sources on Earth

There are a few minor CH₃OH sources on Earth. One is anthropogenic activity, particularly industry (Galbally & Kirstine 2002; Millet et al. 2008; Hu et al. 2011; Stavrakou et al. 2011). CH₃OH has a wide range of industrial applications, including as a solvent, as an antifreeze, in fuel and fuel additives, and as a sewage treatment agent (Galbally & Kirstine 2002; Millet et al. 2008). In industry, CH₃OH is also used to produce other compounds such as formaldehyde, acetic acid, methyl tertiary-butyl ether, methylamines, and methyl esters (Galbally & Kirstine 2002). Overall, global emission of industrially produced CH₃OH is about 4 Tg yr⁻¹, which makes up a tiny fraction (≤5%) of the total annual CH₃OH emission flux (Galbally & Kirstine 2002; Heikes et al. 2002; Millet et al. 2008; Hu et al. 2011; Stavrakou et al. 2011).

In addition to industry, biomass burning is also a key contributor to atmospheric CH₃OH (Galbally & Kirstine 2002; Stavrakou et al. 2011). Every year, biomass burning related to deforestation, shifting cultivation, and agricultural waste disposal (e.g., stubble burning) can release considerable CH₃OH (Crutzen & Andreae 1990; Galbally & Kirstine 2002). People also use wood or charcoal as fuel (for cooking and heating). During the combustion process (particularly in the smoldering phase), pyrolysis of hemicellulose polymers and lignin present in the biomass yields CH₃OH (McKenzie et al. 1995; Galbally & Kirstine. 2002). Andreae & Merlet (2001) estimated that biomass burning can produce up to 12.7 Tg yr⁻¹ of CH₃OH.

In the atmosphere, CH₃OH can be chemically regenerated from CH₂O radicals, which likely originate from the photochemical decomposition of CH₂O itself (Table 3). Hence, we do not consider Earth’s atmospheric chemistry as a net source of CH₃OH. Our photochemistry model currently has 14 CH₃OH-producing reactions, including two low-temperature reactions.

3. CH₃OH Removal Mechanisms

In this section, we review CH₃OH removal mechanisms. We first look into CH₃OH atmospheric sinks in Section 3.1. The main CH₃OH removal pathway in Earth’s atmosphere is oxidation by OH. Next, we explore deposition to land and ocean uptake in Section 3.2. While less significant than

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**Figure 3.** Through the action of pectin methylesterase, pectin demethylation produces CH₃OH as a by-product.

**Table 2**

| Description                           | Reference 1 | Reference 2 | Reference 3 | Reference 4 | Reference 5 |
|---------------------------------------|-------------|-------------|-------------|-------------|-------------|
| Terrestrial plant growth              | 100 (37–212)| 280 (50–280)| 128 (37–280)| 80 (75–312) | 100 (100–151)|
| Plant decay                           | 13 (5–31)   | 20 (10–40)  | 23 (5–40)   | 23 (13–23)  |             |
| Industry and urban                    | 4 (3–5)     | 8 (5–11)    | 9 (2–11)    | 5 (2–8)     |             |
| Biomass/biofuel burning               | 13 (6–19)   | 12 (2–32)   | 12 (2–32)   | 12 (6–15)   | 9.3 (9.3)   |
| Atmospheric production                | 19 (14–24)  | 30 (18–30)  | 37 (12–37)  | 37 (18–38)  | 31 (30.7–31.1)|

*We only include net CH₃OH sources in this table.*
the most abundant radical
Stavrakou et al. 2011
reaction between CH3OH and gas-phase OH has two possible
CH3O + OH \rightarrow CH2O + H 
(\text{dominates. At 298 K, the probability of the reaction proceeding}
below room temperature, H abstraction at the methyl site
HNO + CH3OH \rightarrow CH2O + CO
accumulation of CH3OH in the atmosphere.

Overall Reaction Ratea \( k = k_1 + k_2 \) [cm³ molecule⁻¹ s⁻¹]

| Reaction Pathway |
|-----------------|
| CH3OH + O₂ → CH2O + H₂O (rate = k₁) |
| CH3OH + OH → CH2OH + H₂O (rate = k₂) |
| Valid Temp. Range [K] | Source |
|-----------------|
| 235–360 | Jiménez et al. (2003) |
| 210–350 | Dillon et al. (2005) |
| 200–870 | Dillon et al. (2005) |
| 210–300 | Atkinson et al. (2006) |
| 210–866 | Atkinson et al. (2006) |

Note.
\(^a\) All T in kelvin.

atmospheric destruction, surface deposition can still impact
the accumulation of CH₃OH in the atmosphere.

3.1. CH₃OH Atmospheric Sinks

Of all the known CH₃OH removal mechanisms on Earth,
photochemical oxidation by hydroxyl radicals (OH) dominates
(Galbally & Kirstine 2002; Heikes et al. 2002; Millet et al. 2008;
Stavrakou et al. 2011). In Earth’s oxidizing atmosphere, OH is
the most abundant radical (e.g., Seinfeld & Pandis 2008). The
reaction between CH₃OH and gas-phase OH has two possible
pathways: (1) abstraction of the H atom from the hydroxyl group
to form CH₂O and H₂O, or (2) abstraction of H from the methyl
group to yield CH₂OH and H₂O (Häggele et al. 1983; Hess &
Tully 1989; Dillon et al. 2005; Atkinson et al. 2006). At or
below room temperature, H abstraction at the methyl site
dominates. At 298 K, the probability of the reaction proceeding
according to the second pathway to form CH₂OH is about 85%
(i.e., with a branching ratio of 0.85), and this ratio will increase
as the temperature decreases (Dillon et al. 2005; Atkinson et al.
2006). In Earth’s atmosphere, the final products of these two
reaction pathways are the same: CH₂OH and CH₂O will react
almost immediately with O₂ to give formaldehyde (CH₂O) and
HO₂ radicals (Häggele et al. 1983; Heikes et al. 2002; Tie et al.
2003; Dillon et al. 2005). We compiled the temperature-
dependent reaction rate coefficients in Table 4.

CH₂OH is the fourth largest sink for tropospheric OH in Earth’s
atmosphere, after CH₄, CO, and isoprene (Galbally & Kirstine
2002; Stavrakou et al. 2011). The CH₂O produced can further
react with O, H, or OH radicals to form CO. Hence, CH₂OH is a
significant source of CO in the troposphere and plays a vital role
in tropospheric oxidant chemistry (Heikes et al. 2002; Solomon
et al. 2005; Millet et al. 2008; Stavrakou et al. 2011). CH₂O can also
react with HO₂ radicals in cloud water to yield formic acid
(HCOOH) (Jacob 1986; Heikes et al. 2002). Therefore, even if
CH₂OH itself is not acidic, it can indirectly affect the acidity of
rain and clouds (Jacob 1986; Heikes et al. 2002).

CH₂OH can also react with H and O radicals in an
exoplanet’s atmosphere. In an H₂-dominated, highly reducing
atmosphere, the H radical is the dominant reactive species (Hu
et al. 2012). The importance of O radicals in a CO₂- or an
N₂-dominated atmosphere still needs to be further explored (Hu
et al. 2012; Ranjan et al. 2020). Our photochemistry model
currently has 14 CH₂OH-removing reactions (in addition to the
photochemical oxidation by OH listed in Table 5). Note that

| Source |
|-------|
| Jiménez et al. (2003) |
| Dillon et al. (2005) |
| Dillon et al. (2005) |
| Atkinson et al. (2006) |
| Atkinson et al. (2006) |

Table 4

CH₂OH Photochemical Oxidation by OH

| CH₂OH + -OH → CH₂O + H₂O (rate = k₁) |
| CH₂OH + OH → CH₂OH + H₂O (rate = k₂) |
| Valid Temp. Range [K] | Source |
|-----------------|
| 235–360 | Jiménez et al. (2003) |
| 210–350 | Dillon et al. (2005) |
| 200–870 | Dillon et al. (2005) |
| 210–300 | Atkinson et al. (2006) |
| 210–866 | Atkinson et al. (2006) |

Note.
\(^a\) All T in kelvin.
there is one high-temperature reaction and two low-temperature reactions in Table 5. We include both the high- and low-temperature reactions in our table for completeness even though the rates are extremely low at Earth-like temperatures.

CH$_3$OH can also undergo photolysis under UV radiation. We express the photolysis rate coefficient $J_{\lambda}$ at the top of the atmosphere as $J_{\lambda} = \int q_{\lambda} \times I_{\lambda} \times \sigma_{\lambda} \times e^{-\tau_{\lambda}} \times \text{d} \lambda$ (e.g., Brasseur & Jacob 2017). Here $\lambda$ is the wavelength, $\tau_{\lambda}$ is the optical depth, $\sigma_{\lambda}$ is the absorption cross section of CH$_3$OH, $I_{\lambda}$ is the solar intensity at the top of the atmosphere, and $q_{\lambda}$ is the quantum yield of CH$_3$OH photolysis. We summarize the relevant parameters of CH$_3$OH photolysis in Table 6.

Additionally, at high temperatures, CH$_3$OH will thermally decompose. We compile the thermal decomposition reactions of CH$_3$OH in Table 7, even though they do not occur at Earth-like temperatures.

### 3.2. CH$_3$OH Deposition to Land and Ocean Uptake

Deposition to land and ocean uptake are two CH$_3$OH sinks in addition to atmospheric chemistry. Although less significant than atmospheric removal, they can still affect CH$_3$OH accumulation in the atmosphere.

There are significant uncertainties in CH$_3$OH dry deposition velocity on soil surfaces (Galbally & Kirstine 2002; Millet et al. 2008). Due to the higher atmospheric temperature and more substantial convection/turbulence during the day, CH$_3$OH dry deposition velocity is higher during the day than at night (Millet et al. 2008). The decomposition of dead plants at night also slows down nighttime CH$_3$OH dry deposition (Millet et al. 2008). Several field studies claim that the CH$_3$OH dry deposition velocity is about 0.15 cm s$^{-1}$ and can reach 0.5 cm s$^{-1}$ locally (Karl et al. 2004; Mao et al. 2006; Millet et al. 2008). In general, CH$_3$OH dry deposition velocity adopted by most studies is in the range 0.1–0.2 cm s$^{-1}$ (Galbally & Kirstine 2002; Millet et al. 2008). We use 0.1 cm s$^{-1}$ as the estimated CH$_3$OH dry deposition velocity in our photochemistry model. Once deposited onto the soil, most CH$_3$OH is permanently removed through biological degradation (Galbally & Kirstine 2002). Methyloptrophs first oxidize CH$_3$OH to formaldehyde (CH$_2$O) in the soil through methanol dehydrogenase (Lehninger et al. 1993; Yurimoto et al. 2005), and then either further oxidize CH$_2$O to CO$_2$ for energy or convert CH$_2$O to a three-carbon compound (C$_3$) for biomass buildup (Galbally & Kirstine 2002, Yurimoto et al. 2005).

Due to CH$_3$OH's extremely high water solubility (Section 6.1), atmospheric CH$_3$OH can dissolve in rainwater and fall to the ground or the sea with the rain. This process is called wet deposition (or 'rainout'), another CH$_3$OH removal mechanism. CH$_3$OH wet deposition is a much smaller sink than CH$_3$OH dry deposition (Galbally & Kirstine 2002; Heikes et al. 2002; Tie et al. 2003; Stavrakou et al. 2011). In this work, we collectively refer to CH$_3$OH dry and wet deposition to the ocean as ocean uptake. The atmosphere/ocean exchange rate of CH$_3$OH is very fast (Galbally & Kirstine 2002). CH$_3$OH's high deposition rate is mainly limited by the gas-phase resistance to the exchange of CH$_3$OH between the atmosphere and the ocean's surface layer (i.e., the ocean mixed layer) (Galbally & Kirstine 2002). Due to the high efficiency of ocean uptake, atmospheric CH$_3$OH can reach equilibrium with CH$_3$OH in the ocean surface layer within 8 days.

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**Table 5** CH$_3$OH Removal Reactions in the Atmosphere

| Reaction | Reaction Rate $^a$ [cm$^3$ molecule$^{-1}$ s$^{-1}$] | Valid Temp. Range [K] | Source |
|----------|---------------------------------|------------------------|--------|
| C$_2$H + CH$_4$O $\rightarrow$ C$_2$H$_2$ + CH$_3$O | $2.0 \times 10^{-12}$ | 300–2500 | NIST$^d$ |
| CH$_2$ + CH$_4$O $\rightarrow$ CH$_3$ + CH$_2$O | $1.12 \times 10^{-15}$ $\times (T/298.0)^{1.1}$ $\times \exp(-3490.0/T)$ | 300–2500 | NIST |
| CH$_3$ + CH$_4$O $\rightarrow$ CH$_4$ + CH$_2$O | $1.12 \times 10^{-15}$ $\times (T/298.0)^{1.1}$ $\times \exp(-3490.0/T)$ | 300–2500 | NIST |
| CH$_2$O$_2$ + CH$_4$O $\rightarrow$ CH$_2$O + CH$_3$O | $3.0 \times 10^{-12}$ $\times \exp(-6900.0/T)$ | 300–2500 | NIST |
| CH$_3$OH + CN $\rightarrow$ HCN + CH$_2$O | $1.2 \times 10^{-10}$ | 294 | NIST |
| CHO + CH$_2$O $\rightarrow$ CH$_2$O + CH$_3$O | $2.41 \times 10^{-13}$ $\times (T/298.0)^{2.9}$ $\times \exp(-6600.0/T)$ | 300–2500 | NIST |
| H + CH$_3$O $\rightarrow$ CH$_3$ + H$_2$O | $3.32 \times 10^{-10}$ $\times \exp(-2670.0/T)$ | 1370–1840$^b$ | NIST |
| H + CH$_2$O $\rightarrow$ CH$_2$O + H$_2$ | $2.42 \times 10^{-12}$ $\times (T/298.0)^{3}$ $\times \exp(-2270.0/T)$ | 300–2500 | NIST |
| HO$_2$ + CH$_4$O $\rightarrow$ CH$_3$O + H$_2$O$_2$ | $1.6 \times 10^{-13}$ $\times \exp(-6330.0/T)$ | 300–2500 | NIST |
| N + CH$_3$O $\rightarrow$ CH$_2$ + HNO | $4.0 \times 10^{-10}$ $\times \exp(-4330.0/T)$ | 309–409$^e$ | NIST |
| NO$_3$ + CH$_4$O $\rightarrow$ CH$_3$O + HNO$_3$ | $9.4 \times 10^{-13}$ $\times \exp(-2646.0/T)$ | 258–367$^e$ | NIST |
| O + CH$_2$O $\rightarrow$ CH$_2$O + OH | $1.66 \times 10^{-11}$ $\times \exp(-2360.0/T)$ | 300–1000 | NIST |
| O(1$^D$) + CH$_3$O $\rightarrow$ CH$_2$O + H | $9.0 \times 10^{-11}$ | 300 | NIST |
| O(1$^D$) + CH$_4$O $\rightarrow$ CH$_3$O + OH | $4.2 \times 10^{-10}$ | 300 | NIST |

Notes.

$^a$ All T in kelvin.

$^b$ High-temperature reaction.

$^c$ Low-temperature reaction.

$^d$ Manion et al. (2015).

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**Table 6** Photolysis Reactions of CH$_3$OH (Hu et al. 2012)

| Reaction pathway | Reaction rate at 295 K [s$^{-1}$] | Cross sections | Quantum yields |
|------------------|----------------------------------|----------------|----------------|
| CH$_3$O $\rightarrow$ CH$_2$O + H | $5.97 \times 10^{-6}$; computed in Hu et al. (2012) | 16–106 nm: Burton et al. (1992); 106–165 nm: Nee et al. (1985); 165–220 nm: Cheng et al. (2002) | 16–220 nm: 1.0 |

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8 A tiny amount of CH$_3$OH is absorbed by the soil materials (Barker et al. 1992).
approximately two weeks (Galbally & Kirstine 2002). Some papers estimate that the CH$_3$OH concentration in the ocean mixed layer is between 0.1 and 0.6 $\mu$M, with CH$_3$OH concentration in the Northern Hemisphere (0.2–0.6 $\mu$M) slightly higher than that in the Southern Hemisphere (0.1–0.4 $\mu$M) (Galbally & Kirstine 2002; Millet et al. 2008).

The ocean is a net sink of CH$_3$OH almost anywhere (Millet et al. 2008; Hu et al. 2011; Stavrakou et al. 2011), with only a few exceptions, such as the Persian Gulf and the Red Sea (Millet et al. 2008). Those areas are generally hot all year round, which dramatically reduces CH$_3$OH’s water solubility. Even so, the ocean in those areas is only predicted to be a weak source of CH$_3$OH (Millet et al. 2008). In most parts of the world, the net flux of CH$_3$OH is always into the ocean, with the strongest uptake near continental coasts, where CH$_3$OH concentrations are high (Heikes et al. 2002; Millet et al. 2008; Stavrakou et al. 2011). Generally, ocean uptake is weaker during the day than at night (Heikes et al. 2002; Millet et al. 2008). This observed diurnal cycle likely reflects a competition between daytime CH$_3$OH production from marine phytoplankton and ocean uptake (Heikes et al. 2002; Millet et al. 2008).

After CH$_3$OH is deposited into the ocean, both microbial consumption and marine photochemistry will remove it, eventually removing most of it from the ocean (Heikes et al. 2002; Millet et al. 2008). Some papers suggest that marine methylo-trophs can use CH$_3$OH as an energy and carbon source, similar to the methylo-trophs in the soil (Kiene 1993; Heikes et al. 2002; Neufeld et al. 2007; McCarron et al. 2010). Dissolved CH$_3$OH can also react with OH in the aqueous phase to form formaldehyde (Heikes et al. 2002). It is worth noting that the aqueous OH reaction can occur in the ocean and within clouds, fog, raindrops, and even haze (Galbally & Kirstine 2002; Heikes et al. 2002; Millet et al. 2008). Aqueous OH oxidation is a much smaller sink than other sinks we have discussed (Galbally & Kirstine 2002; Heikes et al. 2002; Millet et al. 2008). We have summarized the estimated global CH$_3$OH sinks in Table 8.

### 4. Methods

We use two methods to assess the biosignature potential of CH$_3$OH. We first introduce our one-dimensional photochemistry model in Section 4.1. Then, we describe our model of transmission spectra (SEAS) in Section 4.2.

#### 4.1. Photochemistry Model

We use our photochemistry model (Hu et al. 2012) to calculate the CH$_3$OH mixing ratio as a function of altitude in exoplanet atmospheres. Our one-dimensional photochemistry model (Hu et al. 2012) can simulate a wide variety of planetary atmosphere scenarios (e.g., oxidized, oxic, and reduced) by calculating the atmosphere’s steady-state chemical composition. Our photochemistry model includes more than 300 chemical reactions, thermal escape of C$_2$, H$_2$, O$_2$, N$_2$, and S-bearing species, as well as UV photolysis of atmospheric molecules. Our photochemistry code also includes wet and dry depositions, surface emissions, and formation and deposition of sulfur-containing (both elemental sulfur and sulfuric acid) aerosols. We have validated our photochemistry model by simulating modern Earth’s and Mars’ atmospheric compositions, matching observations of major trace gases in both scenarios. Our model uses the delta-Eddington two-stream method to calculate ultraviolet and visible radiation in the atmosphere. Our model also includes molecular absorption, Rayleigh scattering, and aerosol Mie scattering to compute the optical depth. For applications of our photochemistry model, see Hu et al. (2012, 2013), Seager et al. (2013), Sousa-Silva et al. (2020), Zhan et al. (2021), and Huang et al. (2022).

In this work, we simulate an Earth-sized exoplanet with an H$_2$-dominated atmosphere orbiting an M-dwarf star. We use the synthetic stellar radiation model of GJ 876 (France et al. 2016; Loyd et al. 2016). We set the planet’s surface temperature to 288 K and surface pressure to 1 bar. The planet’s atmosphere
consists of 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 assume the temperature to be constant (isothermal) in the radiative layer (Hu et al. 2012), given that we do not consider heating in the upper atmosphere. For more details of how we set our atmospheric profiles, see Hu et al. (2012) and Huang et al. (2022).

In our simulations, we include all the reactions mentioned in Hu et al. (2012) except for reactions that involve more than two carbon atoms (C_{2,3,4-chem}), HSO_{2} thermal decay, and high-temperature reactions (Hu et al. 2012). Moreover, we set the surface deposition (including both rainout and dry deposition) of H_{2}, CO, CH_{4}, N_{2}, C_{2}H_{2}, C_{2}H_{4}, C_{2}H_{6}, and O_{2} to zero to facilitate robust comparison with reference benchmark scenarios from Hu et al. (2012). Such assumption corresponds to the situation where surface biology is not an efficient sink for these gases, which does not hold for modern Earth. However, our results are robust to this assumption of inefficient deposition of non-CH_{3}OH gases because the main removal mechanisms of CH_{3}OH are surface deposition and direct photolysis. Finally, we present our stellar radiation model, the atmospheric temperature–pressure profile, and the surface boundary conditions in the Appendix (Figure A1, Tables A1–A3).

4.2. Model of Transmission Spectra and Simulated Observation

To assess the possibility of detecting CH_{3}OH in an H_{2}-dominated atmosphere, we simulate transmission spectra using our ‘Simulated Exoplanet Atmosphere Spectra’ (SEAS) model (Zhan et al. 2021). We also simulate JWST observations with noise calculated from PandExo, a noise simulator based on Space Telescope Science Institute’s (STScI) exposure time calculator (Batalha et al. 2017). We focus on H_{2}-dominated atmospheres, given their relatively large transit depth (Section 6.3). In this section, we briefly describe our spectral analysis. Refer to Zhan et al. (2021) and Huang et al. (2022) for more details of our model.

We use our spectral model SEAS to simulate theoretical transmission spectra. SEAS takes the temperature–pressure profile and the mixing ratio profile from the photochemistry code as input and calculates the absorption of light along the limb path of each layer of the atmosphere (Zhan et al. 2021). In our model, we divide the atmosphere into layers, and the depth of each layer is one atmospheric scale height. We assume that each layer of the atmosphere is in local thermodynamic equilibrium. We simulate transmission spectra at a spectral resolution of R = 1000 and use the HAPI package (Kochanov et al. 2016) to calculate molecular absorption cross sections from the HITRAN database (Gordon et al. 2017; Zhan et al. 2021). We have validated our SEAS model by reproducing spectra from Earth’s atmosphere (Zhan et al. 2021). Note that SEAS currently does not include refraction. As a result, our model works best for M-dwarf planets, where refraction has the least impact on observations (Bétrémieux & Kaltenegger 2014; Misra et al. 2014).

We evaluate the detectability of the atmosphere by using the criterion presented in Seager et al. (2013), Batalha et al. (2017), Zhan et al. (2021), and Huang et al. (2022). Specifically, we estimate the observational uncertainties using the Pandexo JWST noise simulator (Batalha et al. 2017). We use both the Near InfraRed Spectrograph (NIRSpec) G140M, G235M, and G395M and the Mid-Infrared Instrument (MIRI) LRS observation modes. These two instruments have a combined spectral coverage of about 1–13 μm. Here, we consider a 5 M_{Earth}, 1.5 R_{Earth} super-Earth with an H_{2}-dominated atmosphere transiting an M5V star (GJ 876). We choose such a massive planet because a large planet is more likely to retain an H_{2}-dominated atmosphere than an Earth-sized planet. We project the results from our photochemistry model onto the super-Earth by keeping “the mixing ratio as a function pressure” constant. For more details, see Sousa-Silva et al. (2020). The planet’s transit duration is roughly 3.2 hr. The distance to the star is 10 pc. Here, we bin our spectral resolution to R = 10. We also include a JWST systematic noise floor of 10 ppm in our spectral analysis. Finally, we use a null-hypothesis test (e.g., Madhusudhan & Seager 2009) to assess whether we can distinguish between atmospheres with and without significant CH_{3}OH. We first compute the reduced chi-square statistics between our simulated observational data and the ground truth (i.e., no CH_{3}OH) model. Then we repeat this calculation between our data and a best-fit flat-line model. We say CH_{3}OH is detectable if the ground truth model better explains our data. We set the significance threshold at 3σ (i.e., \( p \)-value < 0.003).

5. Results

We use our photochemistry model and the SEAS model to study the biosignature potential of CH_{3}OH. In short, we find that CH_{3}OH can theoretically accumulate to a detectable level on an exoplanet with an H_{2}-dominated atmosphere orbiting an M5V dwarf star. However, the CH_{3}OH surface production flux required to reach its 10 ppm JWST detection threshold is unreasonably large. Currently, for exoplanets with CO_{2}- or N_{2}-dominated atmospheres, the atmospheric scale height is generally too small for atmosphere detection, so we leave that category to the discussion (Section 6.3). We note that while we have not yet discovered a terrestrial planet with an H_{2}-dominated atmosphere, several studies suggest the possibility of such planets (e.g., Elkins-Tanton & Seager 2008; Owen et al. 2020; Lin et al. 2022). We detail our photochemical simulations in Section 4.1 and discuss the detectability of CH_{3}OH in Section 5.2.

5.1. Accumulation of CH_{3}OH on Exoplanets with H_{2}-dominated Atmospheres

We use our photochemistry model to study the possibility of CH_{3}OH accumulation in the atmosphere. We find that CH_{3}OH can accumulate to a detectable level on an exoplanet with an H_{2}-dominated atmosphere orbiting an M5V dwarf star similar to GJ 876 only when the CH_{3}OH surface production flux is unreasonably large. To be detectable by JWST, CH_{3}OH must reach an atmospheric concentration of 10 ppm (Section 5.2). The CH_{3}OH bioproduction flux required to reach the 10 ppm JWST detection threshold must be of the order of 10^{14} molecules cm^{-2} s^{-1} (\sim1.0 \times 10^{6} Tg yr^{-1}). This flux is roughly three times the annual O_{2} production on Earth. 10 ppm CH_{3}OH implies 10^{18} mol of CH_{3}OH in the ocean–atmosphere system, assuming equilibration according to Henry’s law between the atmosphere and ocean.

This carbon budget is potentially plausible from a planetary perspective. It is less than the surface (crust) carbon budget of the planet (\sim8.3 \times 10^{21} mol) (Wood et al. 1996), and it is smaller than the amount of carbon life has fixed (mineralized)
The volume mixing ratio of CH$_3$OH and other representative atmospheric species on an exoplanet with an H$_2$-dominated atmosphere orbiting an M5V dwarf star similar to GJ 876. The x-axis shows the mixing ratio, and the y-axis shows atmospheric pressure in pascals. Each color denotes one particular molecule. The dotted curves represent our base scenario, where CH$_3$OH surface production flux is zero. The solid curves represent our primary scenario, where the CH$_3$OH column-averaged mixing ratio is 10 ppm. In this case, CH$_3$OH surface production flux is $1.18 \times 10^{14}$ molecules cm$^{-2}$ s$^{-1}$.

Figure 4. We assume the planet’s total C reservoir is the same as Earth’s.

We assume the planet’s total C reservoir is the same as Earth’s.

Table 9

| CH$_3$OH Removal Mechanism | Loss Rate [molecules cm$^{-2}$ s$^{-1}$] |
|----------------------------|------------------------------------------|
| Wet deposition             | $8.7 \times 10^{13}$                     |
| Dry deposition             | $3.1 \times 10^{13}$                     |
| Photochemical loss (total) | $1.5 \times 10^{10}$                     |
| CH$_3$OH + H $\rightarrow$ CH$_3$O + H | $1.5 \times 10^{10}$               |
| CH$_3$OH + OH $\rightarrow$ CH$_3$O + H$_2$ | $2.1 \times 10^{9}$               |
| CH$_3$OH + OH $\rightarrow$ CH$_3$O + H$_2$O | $5.3 \times 10^{8}$               |

The Main CH$_3$OH Removal Mechanisms and their Respective Fluxes on Our Simulated Exoplanet with an H$_2$-dominated Atmosphere Orbiting an M-dwarf Star Similar to GJ 876

The volume mixing ratio of CH$_3$OH and other representative atmospheric species on an exoplanet with an H$_2$-dominated atmosphere orbiting an M5V dwarf star, while our simulated exoplanet revolves around an M5V dwarf, is much less susceptible to wet deposition than NH$_3$. This is due to the higher water solubility of CH$_3$OH compared to NH$_3$. The solubility of CH$_3$OH is of the order of 10$^{16}$ molecules cm$^{-2}$ s$^{-1}$, which is much larger than its standard Henry's law constant ($\sim 10$ mol liter$^{-1}$ atm$^{-1}$) (Giorgi & Chameides 1985; Sander 2015). The effective Henry’s law constant of CH$_3$OH is about four orders of magnitude larger than that of NH$_3$, which in reality makes CH$_3$OH much less susceptible to wet deposition than NH$_3$.

To verify the robustness of our CH$_3$OH simulation results, we conduct sensitivity tests on the temperature–pressure profile (i.e., the strength of the cold trap) and the eddy diffusion profile. We find that the column-averaged mixing ratio of CH$_3$OH remains roughly the same order of magnitude in our sensitivity tests (Table 10). Therefore, we conclude that our
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Table 10
Steady-state Photochemical Simulation Outputs as a Function of Eddy Diffusion Magnitude and Presence/Absence of Cold Traps for Exoplanets with H2-dominated Atmospheres Orbiting M Dwarfs

| Eddy diffusion coefficient scaling factor | 0.1 | 1 | 10 |
|-----------------------------------------|-----|---|----|
| CH3OH column-averaged mixing ratio      | 5.0 ppm | 10.0 ppm | 12.2 ppm |
| CH3OH outgassing [molecules cm\(^{-2}\) s\(^{-1}\)] | 1.2 \(\times 10^{14}\) | 1.2 \(\times 10^{14}\) | 1.2 \(\times 10^{14}\) |
| Chemical production [molecules cm\(^{-2}\) s\(^{-1}\)] | 1.3 \(\times 10^9\) | 5.7 \(\times 10^6\) | 9.8 \(\times 10^9\) |
| Chemical loss [molecules cm\(^{-2}\) s\(^{-1}\)] | 3.6 \(\times 10^9\) | 1.5 \(\times 10^{10}\) | 1.8 \(\times 10^{10}\) |
| Dry deposition [molecules cm\(^{-2}\) s\(^{-1}\)] | 3.5 \(\times 10^{13}\) | 3.1 \(\times 10^{13}\) | 2.9 \(\times 10^{13}\) |
| Wet deposition [molecules cm\(^{-2}\) s\(^{-1}\)] | 8.3 \(\times 10^{13}\) | 8.7 \(\times 10^{13}\) | 8.9 \(\times 10^{13}\) |

Variation in the Temperature–Pressure Profile

| Presence of a cold trap | standard | reduced |
|-------------------------|----------|---------|
| Temperature above tropopause [K] | 160 | 220 |
| CH3OH column-averaged mixing ratio | 10.0 ppm | 9.6 ppm |
| CH3OH outgassing [molecules cm\(^{-2}\) s\(^{-1}\)] | 1.2 \(\times 10^{14}\) | 1.2 \(\times 10^{14}\) |
| Chemical production [molecules cm\(^{-2}\) s\(^{-1}\)] | 5.7 \(\times 10^9\) | 2.9 \(\times 10^9\) |
| Chemical loss [molecules cm\(^{-2}\) s\(^{-1}\)] | 1.5 \(\times 10^{10}\) | 6.5 \(\times 10^9\) |
| Dry deposition [molecules cm\(^{-2}\) s\(^{-1}\)] | 3.1 \(\times 10^{13}\) | 3.1 \(\times 10^{13}\) |
| Wet deposition [molecules cm\(^{-2}\) s\(^{-1}\)] | 8.7 \(\times 10^{13}\) | 8.7 \(\times 10^{13}\) |

results are not sensitive to the variations in the eddy diffusion magnitude (to within an order of magnitude) or the strength of the cold trap.

For the choice of eddy diffusion coefficient \((K_{zz})\), we have increased or decreased our existing eddy diffusion profile by one order of magnitude. We find that the CH3OH column-averaged mixing ratio is slightly higher in a more diffusive atmosphere, given the same surface production flux. As \(K_{zz}\) increases, more CH3OH is transported to the upper atmosphere before being removed by wet or dry deposition. In essence, a larger \(K_{zz}\) suppresses the effectiveness of CH3OH surface deposition, causing the atmospheric concentration of CH3OH to increase. In addition, we test the effect of a cold trap on CH3OH atmospheric concentration. A cold trap is a part of the upper atmosphere where the temperature is low enough to condense volatiles (Wordsworth & Pierrehumbert 2013, 2014). To simulate a cold trap in an H2-dominated atmosphere, we set the temperature above tropopause to 160 K. In contrast, to simulate an atmosphere with a reduced cold trap, we set the temperature above tropopause to 220 K (see the Appendix). In this case, we assume that the planet has a relatively hot stratosphere due to UV absorbers in the atmosphere. We find that the presence of a cold trap does not affect CH3OH surface deposition flux. We also find that a reduced cold trap makes CH3OH photochemical production and loss slightly less efficient. Overall, CH3OH atmospheric concentration remains roughly the same in this test.

In another work, we discussed the phenomenon of ‘photochemical runaway’ (Ranjan et al. 2022). Specifically, when the gas’s production flux is large enough to saturate its photochemical sinks, it can rapidly accumulate to very high concentrations in the atmosphere (Ranjan et al. 2022). Some of the biosignature gases that can experience runaway are O2, CO, and NH3 (Zahnle 1986; Kasting 2014; Gregory et al. 2021; Ranjan et al. 2022). We run a series of simulations to see whether CH3OH will experience this “runaway” effect. Like other gases (e.g., NH3), CH3OH runaway at biochemically plausible production fluxes requires inefficient surface deposition (Ranjan et al. 2022). If CH3OH surface deposition is efficient, the CH3OH column-averaged mixing ratio scales linearly with its surface production flux (Figure 5). The CH3OH surface production flux required to reach 10,000 ppm (∼1%) is about 1.2 \(\times 10^{17}\) molecules cm\(^{-2}\) s\(^{-1}\) (∼9.9 \(\times 10^9\) Tg yr\(^{-1}\)), roughly 3000 times the annual O2 production on Earth. CH3OH does not experience runaway due to the presence of surface deposition.

If CH3OH surface deposition is absent (i.e., no rainout or dry deposition), CH3OH can experience photochemical runaway (Figure 5). This exception can only occur if CH3OH bioproduction is robust enough to saturate its surface sinks. By saturation, we mean that life produces more CH3OH than the surface sinks can remove at any given moment. In this case, we find that the critical flux required for CH3OH to experience runaway is quite small, about 5.0 \(\times 10^9\) molecules cm\(^{-2}\) s\(^{-1}\) (∼43 Tg yr\(^{-1}\)), similar to the threshold for CO. This is because, like CO, the photochemical loss of CH3OH is dominated by the reaction with OH and is therefore limited by the production rate of OH from H2 photolysis (Kasting 1990; Ranjan et al. 2022). Consequently, CH3OH and CO enter runaway at similar net surface production fluxes. Considering CH3OH runaway, we estimate that the required CH3OH bioproduction flux to reach the 10 ppm JWST detection threshold should be approximately 9.0 \(\times 10^9\) molecules cm\(^{-2}\) s\(^{-1}\) (∼77 Tg yr\(^{-1}\)). This flux is roughly 8% of the annual CH4 production on Earth. While CH3OH runaway is theoretically possible and hugely beneficial for CH3OH accumulation and detection, we currently do not know how likely it is to occur on an exoplanet. We include this particular case here for the completeness of this paper.

\(^{10}\) It is counterintuitive that the photochemical reaction (i.e., production and loss) flux of CH3OH decreases in a warmer atmosphere, and we do not fully understand why we observed such a decrease. The bottom line is that the strength of the cold trap does not affect our results.

\(^{11}\) Our current photochemistry code has difficulty converging when simulating a “runaway” species. That is why we can only provide an estimate here.
5.2. The Detectability of CH$_3$OH with James Webb Space Telescope

We assess the detectability of CH$_3$OH using our SEAS model. For an exoplanet with an H$_2$-dominated atmosphere orbiting an M5V dwarf star, we find that only when the column-averaged mixing ratio of CH$_3$OH reaches at least 10 ppm can we detect it with JWST. To determine the detection threshold, we focus on CH$_3$OH’s spectral feature around 3.4 $\mu$m. Since we assume that CH$_3$OH mainly comes from the surface, the atmospheric concentration of CH$_3$OH decreases with increasing altitude (Figure 6). As concentration increases, more CH$_3$OH can accumulate in the upper atmosphere, amplifying its spectral features.

Figure 5. Accumulation of CH$_3$OH on an exoplanet with an H$_2$-dominated atmosphere orbiting an M5V dwarf star. The $x$-axis shows CH$_3$OH surface production flux in molecules cm$^{-2}$ s$^{-1}$, and the $y$-axis shows CH$_3$OH column-averaged mixing ratio in ppm. Note that each plot has a different $x$-axis scale. Left panel: due to the presence of surface deposition (i.e., wet and dry deposition), CH$_3$OH does not go into a runaway, even at extremely high flux. Right panel: in the case where CH$_3$OH surface deposition is absent (i.e., no rainout or dry deposition), the column-averaged mixing ratio of CH$_3$OH increases nonlinearly as a function of its surface production flux. In this case, CH$_3$OH experiences runaway, and it can rapidly accumulate to high concentrations in the atmosphere.

Figure 6. Upper panel: simulated transmission spectra of a hypothetical 5 $M_{\text{Earth}}$, 1.5 $R_{\text{Earth}}$ super-Earth with an H$_2$-dominated atmosphere transiting an M5V dwarf star similar to GJ 876. The $x$-axis shows wavelength ($\mu$m), and the $y$-axis shows transit depth (ppm). We simulate the spectra from 0.3 to 23 $\mu$m, covering the wavelength range of JWST NIRSpec and MIRI LRS. The yellow, green, and blue regions show the spectral coverage of G140M, G235M, and G395M, respectively, and the red region shows that of MIRI LRS. The orange curve shows the simulated spectrum with CH$_3$OH column-averaged mixing ratio equal to 10 ppm, and the blue curve shows the simulated spectrum with no CH$_3$OH. Lower panel: comparison of CH$_3$OH absorption cross sections with cross sections of other molecules in the atmosphere such as H$_2$O, CH$_4$, and CO$_2$. Each color denotes one species. We omit H$_2$ because its absorption is mainly collision-induced.

We assess the detectability of CH$_3$OH using our SEAS model. For an exoplanet with an H$_2$-dominated atmosphere orbiting an M5V dwarf star, we find that only when the column-averaged mixing ratio of CH$_3$OH reaches at least 10 ppm can we detect it with JWST. To determine the detection threshold, we focus on CH$_3$OH’s spectral feature around 3.4 $\mu$m and include a 10 ppm JWST systematics noise floor.

In Figure 6, we simulate transmission spectra of a hypothetical 5 $M_{\text{Earth}}$, 1.5 $R_{\text{Earth}}$ super-Earth with an H$_2$-dominated atmosphere transiting an M5V dwarf star similar to GJ 876, specifically, we compare a simulated transmission spectrum with 10 ppm of CH$_3$OH and one without CH$_3$OH.

When the CH$_3$OH column-averaged mixing ratio is below the 10 ppm threshold, its spectral features are not prominent. Since we assume that CH$_3$OH mainly comes from the surface, the atmospheric concentration of CH$_3$OH decreases with increasing altitude (Figure 6). As concentration increases, more CH$_3$OH can accumulate in the upper atmosphere, amplifying its spectral features. When the CH$_3$OH column-averaged mixing ratio reaches or exceeds 10 ppm, we can detect it by characterizing its 3.4 $\mu$m feature.
To further verify that the detection threshold of CH$_3$OH is 10 ppm on exoplanets with H$_2$-dominated atmospheres, we simulate JWST observations with realistic noise calculated from PandExo (Batalha et al. 2017). We also include a detection noise floor of 10 ppm. We compare a simulated JWST observation with 10 ppm of CH$_3$OH and one with no CH$_3$OH (Figure 7).

We find that the simulated JWST observation with 10 ppm CH$_3$OH has two spectral features (i.e., 3.4 μm and 9.5 μm) about 10–20 ppm larger than the simulated observation without CH$_3$OH. The difference between the two models achieves statistical significance (>3σ), indicating a confident simulated detection of CH$_3$OH.

We have to point out that, even though the detection threshold of CH$_3$OH is about 10 ppm on exoplanets with H$_2$-dominated atmospheres, constraining the amount of CH$_3$OH in an exoplanet’s atmosphere is challenging, and requires more transits and observation time. In addition, detection of CH$_3$OH on exoplanets with non-H$_2$-dominated atmospheres (e.g., CO$_2$- or N$_2$-dominated atmospheres) requires significantly more (>100) transits. That is because, for exoplanets with atmospheres of high molecular weight, the transit depth resulting from the small atmosphere scale height is too small compared to the assumed 10 ppm JWST systematic noise floor.

The atmosphere might have various species with overlapping spectral features, so we must investigate the distinguishability of CH$_3$OH from other atmospheric molecules. We compare the spectral absorbance of CH$_3$OH with various other species (Figure 8). One of the unique spectral features of alcohol molecules comes from the presence of hydroxyl groups (–OH). Therefore, we can use CH$_3$OH’s spectral feature around 2.7 μm (O–H stretching) to distinguish CH$_3$OH from other molecules without OH groups (e.g., CH$_4$, CO$_2$, NH$_3$, and C$_3$H$_8$). To distinguish CH$_3$OH from H$_2$O, we can use CH$_3$OH’s absorption band around 10 μm (C–O/C–C rovibrations) (Plyer 1952; Harrison et al. 2012). However, distinguishing CH$_3$OH from other alcohols (e.g., ethanol) can be challenging because of their similar OH features. It is worth noting that complex alcohols may have other spectral features not present in CH$_3$OH. Furthermore, a mixture of hydrocarbons and water (e.g., CH$_4$ and H$_2$O) may mimic CH$_3$OH’s spectral features and be indistinguishable from CH$_3$OH (when observed at low resolutions). In the future, with the development and use of atmosphere retrieval algorithms such as Markov Chain Monte Carlo (e.g., Benneke & Seager 2012; De Wit 2015) or the Hamiltonian Monte Carlo method (e.g., Neal 2011; Hoffman & Gelman 2014), we expect to be able to distinguish CH$_3$OH from other atmospheric species (e.g., major/trace gases and other alcohols) more accurately.

6. Discussion

We first review alcohols’ solubility in water in Section 6.1. We then examine the antifreeze properties of CH$_3$OH in Section 6.2. Next, we briefly discuss CH$_3$OH as a biosignature gas on exoplanets with CO$_2$- and N$_2$-dominated atmospheres in Section 6.3. Additionally, in Section 6.4, we explore how volatility impacts the biosignature potential of alcohols. We comment on CH$_3$OH and atmospheric hazes in Section 6.5. Finally, we discuss the plausibility of high bioproduction fluxes in Section 6.6.

6.1. Alcohols’ Solubility in Water

Alcohols with less than five carbon atoms (C ≤ 4) are very soluble in water since they can easily form hydrogen bonds.
with water molecules. Alcohols with longer hydrocarbon chains (C ≥ 5) become less soluble in water due to the hydrophobic nature of the hydrocarbon chains.

We use Henry’s law to study the solubility of chemicals in water: \( H_{(x)}^P = C_{(x)} / p \). Here \( H_{(x)}^P \) is Henry’s law constant for a species \( x \) in mol Pa\(^{-1}\) m\(^3\) under the partial pressure of that species in pascal, and \( C_{(x)} \) is the dissolved concentration (in mol m\(^{-3}\)) under the equilibrium condition. The larger \( H_{(x)}^P \), the more soluble the species is. Here we compare the solubility of 11 representative alcohols to 17 other molecules at 1 atm and 298 K (Figure 9). The list includes common atmospheric gases and potential biosignature gases. We collected the data from Sander (2015).

Methanol is highly soluble in water. CH\(_3\)OH is so water-soluble that it can form a homogenous solution with water at any given concentration (i.e., is miscible with water). CH\(_3\)OH is even more soluble than NH\(_3\), one of the most soluble biosignature gas candidates studied (Huang et al. 2022). Due to methanol’s high water solubility, wet deposition (rainfall) can efficiently remove gaseous CH\(_3\)OH from the atmosphere.

### 6.2. CH\(_3\)OH as an Antifreeze

When CH\(_3\)OH gas dissolves in water, the solution’s freezing point is lowered from the original value of 0°C of pure water. This phenomenon is called freezing-point depression. It occurs when a small amount of solute (e.g., salt or, in this case, alcohol) dissolves in a solvent (e.g., water). Since CH\(_3\)OH is an antifreeze, a mixed solution of water and CH\(_3\)OH has a lower freezing point than pure water.

Here we approximate the ocean as a solvent composed of water by temporarily ignoring other solutes already dissolved in the ocean. We made this assumption to facilitate our study of the effect of dissolved CH\(_3\)OH on the ocean’s freezing point. We can use a linear equation to estimate the extent of freezing-point depression (also known as ‘Blagden’s law’): \( \Delta T_f = K_f \times i \times b \). Here \( \Delta T \) is the change in freezing point in °C, \( K_f \) is the cryoscopic constant of the solvent in °C kg mol\(^{-1}\). The parameter \( b \) is the molality (i.e., moles of solute/kg of solvent), and \( i \) is the solute’s van’t Hoff factor. The cryoscopic constant of water is 1.86°C kg mol\(^{-1}\) (Lide 2005). Since CH\(_3\)OH does not dissociate in water, the van’t Hoff factor of CH\(_3\)OH is 1.

We assume the mass of the exoplanet’s ocean is the same as that of the Earth’s ocean, and therefore about 1.4 × 10\(^{21}\) kg (Lide 2005). In this case, the solubility of CH\(_3\)OH only depends on the planet’s total CH\(_3\)OH reserve. We assume the planet’s total C and O reservoirs are the same as Earth’s. We also assume that H is abundant, given that the planet we are interested in has an H\(_2\)-dominated atmosphere. Given that the mass of Earth is about 5.97 × 10\(^{24}\) kg, and there is about 446 ppm of C and 30.12% of O on Earth by mass (Morgan & Anders 1980), the planet’s total CH\(_3\)OH reserve is only limited by the planet’s total C reservoir.

In an extreme situation where life converts roughly 0.1% of the planetary C reservoir (∼2.7 × 10\(^{18}\) kg) into dissolved CH\(_3\)OH, the molality of CH\(_3\)OH can reach 0.06 mol kg\(^{-1}\). However, even with such an unrealistically large CH\(_3\)OH inventory (by comparison, Earth’s biosphere has about 2.0 × 10\(^{15}\) kg of carbon, Falkowski et al. 2000), the ocean’s freezing point has dropped by only 0.1°C. Even though the above estimates are very rough, our calculations show that it is highly improbable for life to produce enough CH\(_3\)OH to have any noticeable effect on the ocean’s freezing point. Overall, we argue that the antifreeze capability of CH\(_3\)OH should not affect planet habitability.

### 6.3. CH\(_3\)OH on Exoplanets with CO\(_2\)- or N\(_2\)-dominated Atmospheres Orbiting M Dwarfs

So far, our study on CH\(_3\)OH as a biosignature gas has been focused on exoplanets with H\(_2\)-dominated atmospheres. In contrast, most terrestrial exoplanets with atmospheres of high molecular weight (i.e., CO\(_2\)- or N\(_2\)-dominated atmospheres) have signals that are too weak to be detected using JWST.
Specifically, for exoplanets with CO$_2$- or N$_2$-dominated atmospheres, due to the large mean molecular weight of the atmospheres, the atmospheric scale height is much smaller than that of exoplanets with H$_2$-dominated atmospheres. Due to the small atmospheric scale height, the resulting transit depth is too small compared to the assumed 10 ppm JWST systematic noise floor. Hence, the detectability of CH$_3$OH on exoplanets with CO$_2$- or N$_2$-dominated atmospheres is very low, given the weak atmospheric signals. For this reason, we argue that, at present, CH$_3$OH is not a suitable biosignature gas on exoplanets with CO$_2$- or N$_2$-dominated atmospheres. However, there are some exceptions where detection of trace gases (e.g., CH$_3$OH) is possible with JWST. One of those rare cases is for planets transiting TRAPPIST-1, a nearby ultracool M8V star. For more details, see Zhan et al. (2021) and Supplementary Section S9 of Huang et al. (2022).

Even though CH$_3$OH is a poor biosignature gas in CO$_2$- or N$_2$-dominated atmospheres, it can still theoretically accumulate on exoplanets with CO$_2$- or N$_2$-dominated atmospheres orbiting M dwarfs. We use our photochemistry model (Section 4.1) to simulate CO$_2$- and N$_2$-dominated atmospheres to support this argument. We use the same simulation parameters (i.e., the stellar profile, the atmospheric T–P profile (see the Appendix), the eddy diffusion profile, and the surface boundary conditions) as in Huang et al. (2022) to simulate CO$_2$- and N$_2$-dominated atmospheres. We find that it is a bit easier for CH$_3$OH to accumulate in CO$_2$- or N$_2$-dominated atmospheres than in H$_2$-dominated ones. Specifically, given a fixed CH$_3$OH surface production flux, the CH$_3$OH column-averaged mixing ratio is highest in CO$_2$-dominated (oxidized) atmospheres and lowest in H$_2$-dominated (reduced) atmospheres (see Table 11). We also observed this trend for another biosignature gas (NH$_3$) (Huang et al. 2022). The CH$_3$OH column-averaged mixing ratio is highest in CO$_2$-dominated atmospheres because of its relatively low wet deposition rate. Wet deposition rate scales linearly with atmospheric water content, which is a function of temperature (Giorgi & Chameides 1985; Hu et al. 2012). The relatively high lapse rate of CO$_2$-dominated atmospheres suppresses temperature, reducing atmospheric water content and rainout, and ultimately making CH$_3$OH easier to accumulate.

### 6.4. Volatility of Alcohols and its Impact on Alcohols’ Biosignature Potential

In addition to solubility (Section 6.1), a substance’s volatility also has a profound impact on its biosignature potential. Simply put, the higher the volatility of a substance, the easier it is to evaporate and accumulate in the atmosphere. Beyond CH$_3$OH, we argue that alcohols with long carbon chains (C > 4) are poor biosignature gas candidates due to their relatively low volatility and high boiling points.

In general, alcohols are considered volatile at room temperature. However, alcohols are much less volatile than hydrocarbons (e.g., alkanes) with similar molecular weight.
The reason is that alcohol molecules can form hydrogen bonds with each other. Hydrogen bonds are much stronger than van der Waals interactions between hydrocarbons. During evaporation, more energy is needed to break the hydrogen bonds and separate the alcohol molecules, significantly reducing the volatility. The volatility of alcohols depends on the length of the carbon chain and isomerism. Here we focus on monohydric alcohols (i.e., alcohol with one OH group). On the one hand, the volatility of alcohol decreases as the length of the carbon chain increases. When the carbon chain gets longer, the surface area of the molecule increases, which leads to an increase in the amount of van der Waals interaction and a decrease in volatility. On the other hand, when the OH group is at the center of the carbon chain, the molecule becomes more spherical, making the surface area smaller and volatility higher. In addition, when carbon chains surround the OH group, it is more challenging for alcohol to form a hydrogen bond, further increasing its volatility.

Volatility itself does not have a numerical value. We can use the boiling point to help us compare the volatility of different substances: the higher the boiling point, the lower the volatility of the substance. In Figure 10, we plot the boiling points of eight representative alcohols and nine other hydrocarbons. The figure shows that the boiling point of alcohol is much higher than that of the corresponding hydrocarbon (e.g., methanol versus ethane). Furthermore, the boiling point of alcohol increases as the length of the carbon chain increases (e.g., methanol versus n-butanol). In addition, OH’s position in the molecule affects the boiling point of alcohol (e.g., n-butanol versus tert-butanol). All in all, given that alcohols with long carbon chains have low volatility and tend to be liquid at room temperatures, we consider them to be poor biosignature gas candidates.

6.5. CH$_3$OH and Atmospheric Hazes

On Earth, volatile organic compounds such as methanol and formaldehyde have been known to contribute to the formation of organic aerosols and hazes (e.g., Han et al. 2017; Sheng et al. 2018; Wei et al. 2018; Hui et al. 2019; Xue et al. 2020). In Earth’s oxidizing atmosphere, CH$_3$OH can react with OH, O, and H radicals to give various products, such as CH$_3$O, CH$_3$OH, and CH$_3$ radicals (Section 3.1). These products can further react with nitrogen oxides (NO$_x$) and sulfur oxides (SO$_x$) in the atmosphere to yield complex molecular species and fine airborne particles that act as nucleation precursors. When mixed with other air pollutants and dust, these nucleation precursors can form aerosol particles (e.g., PM$_{2.5}$), promoting haze formation.

In contrast, we know very little about whether or how CH$_3$OH induces organic haze on an exoplanet. Unlike organic hazes that have been studied in detail (e.g., Domagal-Goldman et al. 2011; Arney et al. 2018), there are very few theoretical or experimental studies on CH$_3$OH-induced hazes in an H$_2$-dominated atmosphere. Some papers speculate that with the help of photochemistry, CH$_3$OH may facilitate organic haze formation, but the mechanism needs to be further studied (Arney et al. 2018; Moran et al. 2020). Given the limited information, we suspect CH$_3$OH might have minimal effect on haze formation in an H$_2$-dominated, reducing atmosphere. In a recent publication (Moran et al. 2020), researchers used high-resolution mass spectrometry to measure the chemical properties of photochemical hazes generated in the laboratory. They find that most haze particles (general formulae: C$_n$H$_{2n+1}$O$_y$ or C$_{3}$H$_{6}$N$_{2}$O$_y$) produced in an H$_2$-dominated atmosphere at 300 K are polar (Moran et al. 2020). In theory, these solid haze particles can dissolve in polar solvents such as H$_2$O and CH$_3$OH. Their solubility in polar solvents makes them susceptible to atmospheric precipitation. In another study (Liu et al. 2019), the authors identified a new catalytic reaction between CH$_3$OH and SO$_3$ that converts CH$_3$OH into methyl hydrogen sulfate (CH$_3$O$_2$S). This reaction can be catalyzed by H$_2$O, sulfuric acid (H$_2$SO$_4$), or dimethyamine ((CH$_3$)$_2$NH). The CH$_3$O$_2$S produced is much less volatile than CH$_3$OH and is a poor haze-forming agent due to its relatively weak nucleation ability (Liu et al. 2019). Therefore, a high concentration of atmospheric
CH$_3$OH might lower the generation rate of aerosol particles and negatively affect haze formation.

6.6. Plausibility of High Bioproduction Fluxes

The biological surface flux of CH$_3$OH needed for CH$_3$OH to accumulate to detectable atmosphere levels is likely biologically unattainable ($10^{14}$ molecules cm$^{-2}$ s$^{-1}$, or about three times the annual O$_2$ production on Earth). While mathematically possible, such high biological fluxes of organic carbon gases result in a massive waste of carbon—the main building block for life. The biological production of organic carbon gases is predominantly a result of biological activity that is not tied directly to energy metabolism and biomass buildup. Therefore, if organic carbon gases are produced in very high amounts, their production also has to provide a significant evolutionary gain to offset the enormous expense in energy and carbon used.

Gases that are instead a waste product of primary energy metabolism or biomass buildup are much more likely to be produced by life in significant amounts (i.e., with high fluxes). In prior work, we have given an example of NH$_3$ as a biosignature gas that can accumulate on exoplanets with H$_2$-dominated atmospheres if life is a net source of NH$_3$ and produces enough NH$_3$ to saturate the surface sinks (Huang et al. 2022). NH$_3$ is a readily available source of nitrogen for biomass buildup. Therefore, its release into the atmosphere in huge quantities might be considered “wasteful.” However, in our proposed example, the production of NH$_3$ is a result of theoretical primary energy metabolism on the “cold Haber World” (Seager et al. 2013). In the “cold Haber World” scenario, we assume that life has evolved the 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; Huang et al. 2022), thus tying the release of NH$_3$ to the net energy gain. While large NH$_3$ biological surface fluxes ($10^{10}$ molecules cm$^{-2}$ s$^{-1}$ for an NH$_3$-saturated surface and $10^{15}$ molecules cm$^{-2}$ s$^{-1}$ for an NH$_3$-unsaturated surface) are required for atmospheric NH$_3$ to accumulate to detectable levels in the cold Haber World scenario (Huang et al. 2022), we argue, based on the primary energy metabolism argument, that it is biologically plausible. Such energy gain is not readily available for scenarios of organic carbon gases, such as CH$_3$OH or carbonyls (Zhan et al. 2022). For example, one way to gain energy by producing methanol is to partially oxidize CH$_4$ to CH$_3$OH with atmospheric O$_2$. Such a process is unlikely to happen in H$_2$-rich anoxic atmospheres because of the lack of O$_2$.

However, despite CH$_3$OH’s advantages, we consider it a poor biosignature gas in the atmospheres of terrestrial exoplanets due to the enormous production flux required to reach its detection limit. CH$_3$OH’s high water solubility makes it very difficult to accumulate in the atmosphere. For the highly favorable planetary scenario of an exoplanet with an H$_2$-dominated atmosphere orbiting an M5V dwarf star, we find that only when the column-averaged mixing ratio of CH$_3$OH reaches at least 10 ppm can we detect it with JWST. The CH$_3$OH bioproduction flux required to reach the 10 ppm JWST detection threshold must be of the order of $10^{14}$ molecules cm$^{-2}$ s$^{-1}$, which is roughly three times the annual O$_2$ production on Earth. Considering that such an enormous flux of CH$_3$OH is essentially a massive “waste” of organic carbon—a major building block of life, we think this flux, while mathematically possible, is likely biologically unattainable.

We also find that, due to the presence of surface deposition, CH$_3$OH does not experience runaway, even at extremely high flux. CH$_3$OH runaway can only occur in the exceptional case with no CH$_3$OH surface deposition (i.e., no rainout or dry deposition). This exception happens only if CH$_3$OH bioproduction is robust enough to saturate its surface sinks. Considering CH$_3$OH runaway, we estimate that the required CH$_3$OH bioproduction flux to reach the 10 ppm JWST detection threshold is approximately $9 \times 10^{6}$ molecules cm$^{-2}$ s$^{-1}$ ($\sim$77 Tg yr$^{-1}$), which is about 8% of the annual CH$_4$ production on Earth. Beyond CH$_3$OH, we argue that alcohols with long carbon chains (C > 4) are poor biosignature gas candidates due to their high water solubility and relatively low volatility.

Finally, although CH$_3$OH can theoretically accumulate on exoplanets with CO$_2$- or N$_2$-dominated atmospheres, such planets’ small atmospheric scale heights and weak atmospheric signals put them out of reach for near-term observations. We hope that as telescope technology improves, potential biosignature gases (e.g., CH$_3$OH) that are not yet readily observable with the JWST can one day be observed and more thoroughly studied.

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Appendix

Photochemical Simulation Parameters

Our photochemistry model demarcates chemical species into four types: type “X” for species for which the full photochemical transport equation is solved, type “F” for species assumed to be in photochemical equilibrium (i.e., for which transport is neglected), type “C” for chemically inert species that are assumed not to react or transport, and type “A” for aerosol species. In addition, for the lower boundary condition, we can specify either a fixed surface mixing ratio (type “1”) or a fixed emission/deposition velocity (type “2”) (Hu et al. 2012).
Figure A1. Left panel: the synthetic stellar radiation model of GJ 876 (France et al. 2016; Loyd et al. 2016). The y-axis shows spectral irradiance in W m$^{-2}$ nm$^{-1}$, and the x-axis shows wavelength in nm. Right panel: the temperature–pressure profiles of the simulated exoplanets with H$_2$-dominated, CO$_2$-dominated, and N$_2$-dominated atmospheres. The y-axis shows atmospheric pressure (pascals) on a log scale, and the x-axis shows temperature in kelvin.
Table A1
Surface Boundary Conditions for Exoplanets with H\(_2\)-dominated Atmospheres

| Name | Type | Initial Mixing Ratio | Upper Boundary Flux besides Escape (upward) [molecules cm\(^{-2}\) s\(^{-1}\)] | Lower Boundary Type | Dry Deposition Velocity [cm s\(^{-1}\)] | Lower Boundary Flux (upward) [molecules cm\(^{-2}\) s\(^{-1}\)] |
|------|------|----------------------|-------------------------------------------------|---------------------|-----------------|-------------------------------------------------|
| H    | X    | 0                    | 0                                               | 2                   | 0               | 0                                               |
| H\(_2\) | C    | 0.9                  | 0                                               | 1                   | 0               | 0.9                                             |
| O    | 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 \times 10\(^{-6}\) | 0                                               | 1                   | 0               | 1.00 \times 10\(^{-6}\) |
| H\(_2\)O\(_2\) | X    | 0                    | 2                                               | 0.5                 | 0               | 0                                               |
| CO\(_2\) | X    | 0                    | 2                                               | 1.00 \times 10\(^{-4}\) | 3.00 \times 10\(^{14}\) | 0                                               |
| CO   | X    | 0                    | 2                                               | 1.00 \times 10\(^{-8}\) | 0               | 0                                               |
| CH\(_3\)O | 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                                               |
| CH\(_2\)   | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| CH\(_3\) | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| CH\(_4\) | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| CH\(_5\) | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| CH\(_6\) | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| C\(_2\)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\(_2\)H\(_4\) | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| C\(_2\)H\(_5\) | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| C\(_2\)H\(_6\) | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| C\(_2\)HO | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| C\(_2\)H\(_{2}\)O | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| N\(_2\) | C    | 0.1                  | 0                                               | 1                   | 0               | 0.1                                             |
| S    | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| S\(_2\) | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| S\(_3\) | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| S\(_4\) | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| SO   | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| SO\(_2\) | X    | 0                    | 2                                               | 1                   | 3.00 \times 10\(^{5}\) | 0                                               |
| SO\(_3\) | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |
| SO\(_4\) | X    | 0                    | 2                                               | 0                   | 0               | 0                                               |

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| Name   | Type | Initial Mixing Ratio | Upper Boundary Flux besides Escape (upward) [molecules cm\(^{-2}\) s\(^{-1}\)] | Lower Boundary Type | Dry Deposition Velocity [cm s\(^{-1}\)] | Lower Boundary Flux (upward) [molecules cm\(^{-2}\) s\(^{-1}\)] |
|--------|------|----------------------|-----------------------------------------------------------------------------|---------------------|----------------------------------------|---------------------------------------------------|
| H\(_2\)S | X    | 0                    | 0                                                                            | 2                   | 0.015                                  | 3.00 \(\times\) 10\(^8\)                           |
| HS     | X    | 0                    | 0                                                                            | 2                   | 0                                      | 0                                                 |
| HSO    | X    | 0                    | 0                                                                            | 2                   | 0                                      | 0                                                 |
| HSO₂   | X    | 0                    | 0                                                                            | 2                   | 0                                      | 0                                                 |
| HSO₃   | X    | 0                    | 0                                                                            | 2                   | 0                                      | 0                                                 |
| H\(_2\)SO₄ | X | 0      | 0                                                                            | 2                   | 1                                      | 0                                                 |
| H\(_2\)SO₄A | A | 0     | 0                                                                            | 2                   | 0.2                                    | 0                                                 |
| S\(_6\) | X    | 0                    | 0                                                                            | 2                   | 0                                      | 0                                                 |
| S\(_8\)A | A    | 0                    | 0                                                                            | 2                   | 0.2                                    | 0                                                 |
| CHO₂   | X    | 0                    | 0                                                                            | 2                   | 0.1                                    | 0                                                 |
| N      | X    | 0                    | 0                                                                            | 2                   | 1                                      | 0                                                 |
| NH₃    | X    | 0                    | 0                                                                            | 2                   | 0                                      | 0                                                 |
| NH₂    | X    | 0                    | 0                                                                            | 2                   | 0                                      | 0                                                 |
| NH     | X    | 0                    | 0                                                                            | 2                   | 0                                      | 0                                                 |
| N\(_2\)O | X | 0       | 0                                                                            | 2                   | 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                                                 |
| N\(_2\)O₅ | X | 0      | 0                                                                            | 2                   | 4                                      | 0                                                 |
| HNO    | X    | 0                    | 0                                                                            | 2                   | 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                                                 |
| CNO    | X    | 0                    | 0                                                                            | 2                   | 0                                      | 0                                                 |
| HCNO   | X    | 0                    | 0                                                                            | 2                   | 0                                      | 0                                                 |
| CH\(_3\)NO₂ | X | 0     | 0                                                                            | 2                   | 0.01                                   | 0                                                 |
| CH\(_2\)NO₃ | X | 0    | 0                                                                            | 2                   | 0.01                                   | 0                                                 |
| CH\(_2\)N | X    | 0      | 0                                                                            | 2                   | 0                                      | 0                                                 |
| C\(_2\)H₄N | X | 0     | 0                                                                            | 2                   | 0                                      | 0                                                 |
| C\(_2\)H₄N | X | 0     | 0                                                                            | 2                   | 0                                      | 0                                                 |
| N\(_2\)H₂ | X    | 0      | 0                                                                            | 2                   | 0                                      | 0                                                 |
| N\(_2\)H₃ | X    | 0      | 0                                                                            | 2                   | 0                                      | 0                                                 |
| N\(_2\)H₄ | X    | 0      | 0                                                                            | 2                   | 0                                      | 0                                                 |
| OCS    | X    | 0                    | 0                                                                            | 2                   | 0.01                                   | 0                                                 |
| CS     | X    | 0                    | 0                                                                            | 2                   | 0.01                                   | 0                                                 |
| CH₃S   | X    | 0                    | 0                                                                            | 2                   | 0.01                                   | 0                                                 |
| CH₄S   | X    | 0                    | 0                                                                            | 2                   | 0.01                                   | 0                                                 |
| Name | Type  | Initial Mixing Ratio | Upper Boundary Flux besides Escape (upward) [molecules cm\(^{-2}\) s\(^{-1}\)] | Lower Boundary Type | Dry Deposition Velocity [cm s\(^{-1}\)] | Lower Boundary Flux (upward) [molecules cm\(^{-2}\) s\(^{-1}\)] |
|------|-------|----------------------|-------------------------------------------------|---------------------|-----------------|-----------------------------------|
| H    | X     | 0                    | 0                                               | 2                   | 1               | 0                                 |
| H\(_2\) | X     | 1.60 \times 10\(^{-3}\) | 0                                               | 2                   | 0               | 3.00 \times 10\(^{10}\)          |
| O    | X     | 0                    | 0                                               | 2                   | 0               | 0                                 |
| O(1D) | X     | 0                    | 0                                               | 2                   | 0               | 0                                 |
| O\(_2\) | X     | 0                    | 0                                               | 2                   | 0.4             | 0                                 |
| OH   | X     | 0                    | 0                                               | 2                   | 1               | 0                                 |
| HO\(_2\) | X | 0                    | 2                                               | 1                   | 0               | 0                                 |
| H\(_2\)O | X | 0                    | 0                                               | 1                   | 0               | 0.01                              |
| H\(_2\)O\(_2\) | X | 0                    | 2                                               | 0.5                 | 0               | 0                                 |
| CO\(_2\) | X | 0.9                  | 0                                               | 1                   | 0               | 0.9                               |
| CO   | X     | 0                    | 0                                               | 2                   | 1.00 \times 10\(^{-8}\) | 0                                 |
| CH\(_2\)O | X | 0                    | 0                                               | 2                   | 0.1             | 0                                 |
| CH\(_3\)O | X | 0                    | 0                                               | 2                   | 0.1             | 0                                 |
| CH   | X     | 0                    | 0                                               | 2                   | 0               | 0                                 |
| CH\(_2\) | X     | 0                    | 0                                               | 2                   | 0               | 0                                 |
| CH\(_3\) | X     | 0                    | 0                                               | 2                   | 0               | 0                                 |
| CH\(_2\)O\(_2\) | X | 0                    | 0                                               | 2                   | 0.1             | 0                                  |
| CH\(_3\)O\(_2\) | X | 0                    | 0                                               | 2                   | 0.1             | 0                                  |
| C\(_2\) | X     | 0                    | 0                                               | 2                   | 0.1             | 0                                 |
| C\(_2\)H | X     | 0                    | 0                                               | 2                   | 0               | 0                                 |
| C\(_2\)H\(_2\) | X | 0                    | 0                                               | 2                   | 0               | 0                                 |
| C\(_2\)H\(_3\) | X | 0                    | 0                                               | 2                   | 0               | 0                                 |
| C\(_2\)H\(_4\) | X | 0                    | 0                                               | 2                   | 0               | 0                                 |
| C\(_2\)H\(_5\) | X | 0                    | 0                                               | 2                   | 0               | 0                                 |
| C\(_2\)H\(_6\) | X | 0                    | 2                                               | 0                   | 0               | 0                                 |
| C\(_2\)H\(_7\) | X | 0                    | 0                                               | 2                   | 0               | 0                                 |
| C\(_2\)H\(_8\) | X | 0                    | 0                                               | 2                   | 0               | 0                                 |
| C\(_2\)H\(_9\) | X | 0                    | 0                                               | 2                   | 0               | 0                                 |
| C\(_2\)HO | X     | 0                    | 0                                               | 2                   | 1.00 \times 10\(^{-5}\) | 0                                 |
| C\(_2\)H\(_2\)O | X | 0                    | 0                                               | 2                   | 0               | 0                                 |
| C\(_2\)H\(_3\)O | X | 0                    | 2                                               | 0.1                 | 0               | 0                                 |
| C\(_2\)H\(_4\)O | X | 0                    | 2                                               | 0.1                 | 0               | 0                                 |
| C\(_2\)H\(_5\)O | X | 0                    | 2                                               | 0.1                 | 0               | 0                                 |
| N\(_2\) | X     | 0                    | 0                                               | 2                   | 0.1             | 0                                 |
| S    | X     | 0                    | 2                                               | 0                   | 0               | 0                                 |
| S\(_2\) | X     | 0                    | 2                                               | 0                   | 0               | 0                                 |
| S\(_3\) | X     | 0                    | 2                                               | 0                   | 0               | 0                                 |
| S\(_4\) | X     | 0                    | 2                                               | 0                   | 0               | 0                                 |
| SO   | X     | 0                    | 2                                               | 1                   | 0               | 3.00 \times 10\(^{3}\)           |
| SO\(_2\) | X     | 0                    | 2                                               | 0                   | 0               | 0                                 |
| SO\(_2\)\(_2\) | X | 0                    | 2                                               | 0                   | 0               | 0                                 |
| SO\(_3\) | X     | 0                    | 2                                               | 0                   | 0               | 0                                 |
| SO\(_4\) | X     | 0                    | 2                                               | 0                   | 0               | 0                                 |
| Name  | Type | Initial Mixing | Upper Boundary Flux besides Escape (upward) [molecules cm^{-2} s^{-1}] | Lower Boundary Type | Dry Deposition Velocity [cm s^{-1}] | Lower Boundary Flux (upward) [molecules cm^{-2} s^{-1}] |
|-------|------|----------------|---------------------------------------------------------------|-------------------|--------------------------------------|-----------------------------------------------------|
| H_{2}S | X    | 0              | 0                                                             | 2                 | 0.015                                | 3.00 \times 10^{6}                                  |
| HS    | X    | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| HSO   | X    | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| HSO_{2} | X   | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| HSO_{3} | X  | 0              | 0                                                             | 2                 | 0.1                                  | 0                                                   |
| H_{2}SO_{4} | X  | 0              | 0                                                             | 2                 | 1                                    | 0                                                   |
| H_{2}SO_{4}A | A | 0              | 0                                                             | 2                 | 0.2                                  | 0                                                   |
| S_{8} | X    | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| S_{8}A | A    | 0              | 0                                                             | 2                 | 0.2                                  | 0                                                   |
| CHO_{2} | C   | 0.1            | 0                                                             | 1                 | 0                                    | 0.1                                                 |
| N    | X    | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| NH_{3} | X   | 0              | 0                                                             | 2                 | 1                                    | 0                                                   |
| NH_{2} | X   | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| NH    | X    | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| N_{2}O | X   | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| NO    | X    | 0              | 0                                                             | 2                 | 0.02                                 | 0                                                   |
| NO_{2} | X   | 0              | 0                                                             | 2                 | 0.02                                 | 0                                                   |
| NO_{3} | X   | 0              | 0                                                             | 2                 | 1                                    | 0                                                   |
| N_{2}O_{2} | X | 0              | 0                                                             | 2                 | 4                                    | 0                                                   |
| HNO   | X    | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| HNO_{2} | X  | 0              | 0                                                             | 2                 | 0.5                                  | 0                                                   |
| HNO_{3} | X  | 0              | 0                                                             | 2                 | 4                                    | 0                                                   |
| HNO_{4} | X  | 0              | 0                                                             | 2                 | 4                                    | 0                                                   |
| HCN   | X    | 0              | 0                                                             | 2                 | 0.01                                 | 0                                                   |
| CN    | X    | 0              | 0                                                             | 2                 | 0.01                                 | 0                                                   |
| CNO   | X    | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| HCNO  | X    | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| CH_{3}NO_{2} | X | 0              | 0                                                             | 2                 | 0.01                                 | 0                                                   |
| CH_{2}NO_{3} | X | 0              | 0                                                             | 2                 | 0.01                                 | 0                                                   |
| CH_{3}N | X   | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| C_{2}H_{2}N | X | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| C_{2}H_{3}N | X  | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| N_{2}H_{2} | X  | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| N_{2}H_{3} | X  | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| N_{2}H_{4} | X  | 0              | 0                                                             | 2                 | 0                                    | 0                                                   |
| OCS   | X    | 0              | 0                                                             | 2                 | 0.01                                 | 0                                                   |
| CS    | X    | 0              | 0                                                             | 2                 | 0.01                                 | 0                                                   |
| CH_{3}S | X   | 0              | 0                                                             | 2                 | 0.01                                 | 0                                                   |
| CH_{2}S | X  | 0              | 0                                                             | 2                 | 0.01                                 | 0                                                   |
| Name  | Type | Initial Mixing | Upper Boundary Flux besides Escape (upward) [molecules cm$^{-2}$ s$^{-1}$] | Lower Boundary Type | Dry Deposition Velocity [cm s$^{-1}$] | Lower Boundary Flux (upward) [molecules cm$^{-2}$ s$^{-1}$] |
|-------|------|----------------|---------------------------------------------------------------------|--------------------|---------------------------------|------------------------------------------------|
| H     | X    | 0              | 0                                                                    | 2                  | 1                              | 0                                              |
| H$_2$ | X    | 0              | 0                                                                    | 2                  | 0                              | $3.00 \times 10^{10}$                          |
| O     | X    | 0              | 0                                                                    | 2                  | 1                              | 0                                              |
| O$_2$ | X    | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| O$_3$ | X    | 0              | 0                                                                    | 2                  | 0.4                            | 0                                              |
| OH    | X    | 0              | 0                                                                    | 2                  | 1                              | 0                                              |
| HO$_2$| X    | 0              | 0                                                                    | 2                  | 1                              | 0                                              |
| H$_2$O| X    | $2.00 \times 10^{-6}$ | 0                                                                   | 1                  | 0                              | $1.00 \times 10^{-2}$                          |
| H$_2$O$_2$| X    | 0              | 0                                                                    | 2                  | 0.5                            | 0                                              |
| CO$_2$| X    | 0              | 0                                                                    | 2                  | $1.00 \times 10^{-4}$         | $3.00 \times 10^{14}$                          |
| CO    | X    | 0              | 0                                                                    | 2                  | $1.00 \times 10^{-8}$         | 0                                              |
| CH$_3$O| X   | 0              | 0                                                                    | 2                  | 0.1                            | 0                                              |
| CHO   | X    | 0              | 0                                                                    | 2                  | 0.1                            | 0                                              |
| C     | X    | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| CH    | X    | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| CH$_2$| X    | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| CH$_3$| X    | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| CH$_4$| X    | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| CH$_2$O| X   | 0              | 0                                                                    | 2                  | 0.1                           | 0                                              |
| CH$_3$O| X   | 0              | 0                                                                    | 2                  | 0.1                           | 0                                              |
| CH$_4$O| X   | 0              | 0                                                                    | 2                  | 0.1                           | 0                                              |
| CH$_2$O$_2$| X | 0              | 0                                                                    | 2                  | 0.1                           | 0                                              |
| CH$_3$O$_2$| X | 0              | 0                                                                    | 2                  | 0.1                           | 0                                              |
| CH$_2$O$_2$| X | 0              | 0                                                                    | 2                  | 0.1                           | 0                                              |
| C$_2$ | X    | 0              | 0                                                                    | 2                  | 0.1                           | 0                                              |
| C$_2$H | X    | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| C$_2$H$_2$| X | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| C$_2$H$_3$| X | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| C$_2$H$_4$| X | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| C$_2$H$_5$| X | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| C$_2$H$_6$| X | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| C$_2$H$_5$O| X | 0              | 0                                                                    | 2                  | 0.1                           | 0                                              |
| C$_2$H$_4$O| X | 0              | 0                                                                    | 2                  | 0.1                           | 0                                              |
| C$_2$H$_3$O| X | 0              | 0                                                                    | 2                  | 0.1                           | 0                                              |
| C$_2$H$_2$O| X | 0              | 0                                                                    | 2                  | 0.1                           | 0                                              |
| N$_2$ | X    | 0              | 0                                                                    | 2                  | 0.1                           | 0                                              |
| S     | C    | 1              | 0                                                                    | 1                  | 0                              | 1                                              |
| S$_2$ | X    | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| S$_3$ | X    | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| S$_4$ | X    | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| SO    | X    | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| SO$_2$| X    | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| SO$_2$| X    | 0              | 0                                                                    | 2                  | 1                              | $3.00 \times 10^{5}$                          |
| SO$_3$| X    | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| SO$_4$| X    | 0              | 0                                                                    | 2                  | 0                              | 0                                              |
| Name   | Type | Initial Mixing Ratio | Upper Boundary Flux besides Escape (upward) [molecules cm$^{-2}$ s$^{-1}$] | Lower Boundary Type | Dry Deposition Velocity [cm s$^{-1}$] | Lower Boundary Flux (upward) [molecules cm$^{-2}$ s$^{-1}$] |
|--------|------|---------------------|---------------------------------------------------------------------------------|---------------------|----------------------------------------|--------------------------------------------------|
| H$_2$S  | X    | 0                   | 0                                                                               | 2                   | 1                                      | 0                                                |
| HS     | X    | 0                   | 0                                                                               | 2                   | 0.015                                  | 3.00 $\times$ 10$^8$                                |
| HSO    | X    | 0                   | 0                                                                               | 2                   | 0                                      | 0                                                |
| HSO$_2$| X    | 0                   | 0                                                                               | 2                   | 0                                      | 0                                                |
| HSO$_3$| X    | 0                   | 0                                                                               | 2                   | 0                                      | 0                                                |
| H$_2$SO$_4$ | X | 0                 | 2                                                                               | 1                   | 0                                      | 0                                                |
| S$_8$  | A    | 0                   | 0                                                                               | 2                   | 0.2                                    | 0                                                |
| S$_8$A | X    | 0                   | 0                                                                               | 2                   | 0                                      | 0                                                |
| CHO$_2$| A    | 0                   | 0                                                                               | 2                   | 0.2                                    | 0                                                |
| N     | X    | 0                   | 0                                                                               | 2                   | 0                                      | 0                                                |
| NH$_3$ | X    | 0                   | 0                                                                               | 2                   | 1                                      | 0                                                |
| NH$_2$ | X    | 0                   | 0                                                                               | 2                   | 0                                      | 0                                                |
| NH    | X    | 0                   | 0                                                                               | 2                   | 0                                      | 0                                                |
| N$_2$O | X    | 0                   | 0                                                                               | 2                   | 0                                      | 0                                                |
| NO    | X    | 0                   | 0                                                                               | 2                   | 0.02                                   | 0                                                |
| NO$_2$| X    | 0                   | 0                                                                               | 2                   | 0.02                                   | 0                                                |
| NO$_3$| X    | 0                   | 2                                                                               | 1                   | 0                                      | 0                                                |
| N$_2$O$_5$ | X | 0                | 0                                                                               | 2                   | 4                                      | 0                                                |
| HNO   | X    | 0                   | 0                                                                               | 2                   | 0                                      | 0                                                |
| HNO$_2$| X   | 0                   | 0                                                                               | 2                   | 0.5                                    | 0                                                |
| HNO$_3$| X   | 0                   | 0                                                                               | 2                   | 4                                      | 0                                                |
| HNO$_4$| X   | 0                   | 0                                                                               | 2                   | 4                                      | 0                                                |
| HCN   | X    | 0                   | 0                                                                               | 2                   | 0.01                                   | 0                                                |
| CN    | X    | 0                   | 0                                                                               | 2                   | 0.01                                   | 0                                                |
| CNO   | X    | 0                   | 0                                                                               | 2                   | 0                                      | 0                                                |
| HCNO  | X    | 0                   | 0                                                                               | 2                   | 0                                      | 0                                                |
| CH$_2$NO$_2$ | X | 0                | 0                                                                               | 2                   | 0.01                                   | 0                                                |
| CH$_2$NO$_3$ | X | 0            | 0                                                                               | 2                   | 0.01                                   | 0                                                |
| CH$_3$N | X   | 0                   | 0                                                                               | 2                   | 0                                      | 0                                                |
| C$_2$H$_4$N | X | 0                 | 0                                                                               | 2                   | 0                                      | 0                                                |
| C$_2$H$_5$N | X  | 0                 | 0                                                                               | 2                   | 0                                      | 0                                                |
| N$_2$H$_2$ | X | 0              | 0                                                                               | 2                   | 0                                      | 0                                                |
| N$_2$H$_3$ | X   | 0                   | 0                                                                               | 2                   | 0                                      | 0                                                |
| N$_2$H$_4$ | X   | 0                   | 0                                                                               | 2                   | 0                                      | 0                                                |
| OCS   | X    | 0                   | 0                                                                               | 2                   | 0.01                                   | 0                                                |
| CS    | X    | 0                   | 0                                                                               | 2                   | 0.01                                   | 0                                                |
| CH$_3$S | X   | 0                   | 0                                                                               | 2                   | 0.01                                   | 0                                                |
| CH$_4$S | X   | 0                   | 0                                                                               | 2                   | 0.01                                   | 0                                                |
