Nitrogen as a Tracer of Giant Planet Formation. II. Comprehensive Study of Nitrogen Photochemistry and Implications for Observing NH₃ and HCN in Transmission and Emission Spectra

Kazumasa Ohno¹,² and Jonathan J. Fortney²

¹ Division of Science, National Astronomical Observatory of Japan, 2-21-1 Osawa, Mitaka-shi, Tokyo, Japan
² Department of Astronomy & Astrophysics, University of California Santa Cruz, 156 High St, Santa Cruz, CA 95064, USA

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Abstract

Atmospheric nitrogen may provide important constraints on giant planet formation. Following our semianalytical work, we further pursue the relation between observable NH₃ and an atmosphere’s bulk nitrogen abundance by applying the photochemical kinetics model VULCAN across planetary equilibrium temperature, mass, age, eddy diffusion coefficient, atmospheric composition, and stellar spectral type. We confirm that the quenched NH₃ abundance coincides with the bulk nitrogen abundance only at sub-Jupiter-mass (∼1M_J) planets and old ages (≥1 Gyr) for solar composition atmospheres, highlighting important caveats for inferring atmospheric nitrogen abundances. Our semianalytical model reproduces the quenched NH₃ abundance computed by VULCAN and thus helps to infer the bulk nitrogen abundance from a retrieved NH₃ abundance. By computing transmission and emission spectra, we predict that the equilibrium temperature range of 400–1000 K is optimal for detecting NH₃ because NH₃ depletion by thermochemistry and photochemistry is significant at hotter planets whereas entire spectral features become weak at colder planets. For Jupiter-mass planets around Sun-like stars in this temperature range, NH₃ leaves observable signatures of ~50 ppm at 1.5, 2.1, and 11 μm in transmission spectra and >300–100 ppm at 6 and 11 μm in emission spectra. The photodissociation of NH₃ leads HCN to replace NH₃ at low pressures. However, the low HCN column densities lead to much weaker absorption features than for NH₃. The NH₃ features are readily accessible to JWST observations to constrain atmospheric nitrogen abundances, which may open a new avenue to understanding the formation processes of giant exoplanets.

1. Introduction

The composition of giant planet atmospheres offers valuable clues to the planet formation process. In recent years, a number of studies have suggested that atmospheric elemental ratios, such as the carbon-to-oxygen ratio (C/O), can diagnose a giant planet’s formation location and accretion history within a disk (e.g., Öberg et al. 2011; Ali-Dib et al. 2014; Helling et al. 2014; Madhusudhan et al. 2014, 2017; Piso et al. 2015, 2016; Thiabaud et al. 2015; Cridland et al. 2016, 2017, 2019; Eistrup et al. 2016, 2018, 2022; Öberg & Bergin 2016; Booth & Ilee 2019; Öberg & Wordsworth 2019; Ohno & Ueda 2021; Molaverdikhani et al. 2022; Pacetti et al. 2022; Eistrup 2023). Recent studies also suggest that nitrogen provides valuable insights into planet formation processes (Piso et al. 2016; Cridland et al. 2020; Ohno & Ueda 2021; Turrini et al. 2021; Notsu et al. 2022). Several studies have discussed the formation environment of Jupiter in our solar system based on atmospheric nitrogen and noble gas abundances (e.g., Owen et al. 1999; Gautier et al. 2001; Guillot & Hueso 2006; Monga & Desch 2015; Ali-Dib 2017; Bosman et al. 2019; Mousis et al. 2019; Öberg & Wordsworth 2019; Ohno & Ueda 2021; Aguihche et al. 2022).

NH₃ and HCN are likely the most easily accessible nitrogen species in giant exoplanet atmospheres via spectroscopy (MacDonald & Madhusudhan 2017a), as the remaining main nitrogen reservoir N₂ has negligibly low visible and infrared opacity. However, constraining an atmosphere’s bulk nitrogen abundance from NH₃ and HCN is a complex task. It is well known from previous work that the NH₃ and HCN abundances in the observable atmosphere readily deviate from thermochemical equilibrium abundances due to vertical mixing and photochemistry (e.g., Line et al. 2011; Moses et al. 2011; Venot et al. 2013). For warm planets with Tₑq ≤ 1200 K, Fortney et al. (2020) investigated disequilibrium NH₃ abundances on Saturn-like planets across Tₑq space and found that the NH₃ abundance depends on a number of factors, such as planetary mass, age, and metallicity. Ohno & Fortney (2023, hereafter Paper I) further generalized the conditions under which the vertically quenched NH₃ abundance coincides with the bulk nitrogen abundance, based on a suite of radiative-convective atmosphere models and semianalytical arguments. Paper I suggested that the NH₃ abundance coincides with the bulk nitrogen abundance only at sub-Jupiter planetary mass (∼1M_J), old age (≥1 Gyr), and low atmospheric metallicity (<10× solar value); otherwise, N₂ dominates over NH₃, making the observable NH₃ abundance only a lower limit of bulk nitrogen abundance.

Fortney et al. (2020) and Paper I relied on the so-called quench approximation that estimates the vertically quenched NH₃ abundance from timescale arguments; however, the quench approximation is not always accurate. While the quench approximation yields a vertically constant abundance of disequilibrium species, Tsai et al. (2018) showed that the abundance can vary with altitudes even above the quench pressure level, especially for hot atmospheres. Molaverdikhani et al. (2019) also pointed out that molecular diffusion and photodissociation can cause vertically nonuniform abundance profiles. In fact,
Hu (2021) investigated photochemistry on template/cold H₂-rich planets and found that NH₃ tends to be readily depleted due to photodissociation, especially on planets around G/K stars. Thus, it is essential to use a detailed photochemical kinetics model to establish a comprehensive understanding of the relation between observable NH₃ and bulk nitrogen abundance.

In this paper, we continue exploring the relation between observable nitrogen species and bulk nitrogen abundances—the total nitrogen abundance in the atmosphere—using a photochemical kinetics model. The organization of this paper is as follows. In Section 2, we briefly review the semianalytical relationship between disequilibrium NH₃ and bulk nitrogen abundances predicted by Paper I. In Section 3, we apply a photochemical kinetics model to a wide range of planetary parameters to comprehensively understand the relation between observable NH₃ and bulk nitrogen abundance. In Section 4, we investigate the observational feasibility of detecting nitrogen species in transmission and emission spectra. In Section 5, we discuss the effects of stellar spectral type, the presence of photochemical hazes, and day–night temperature contrast. In Section 6, we summarize our findings.

2. Semianalytical Relation between NH₃ and Bulk Nitrogen Abundances

In Paper I, based on the law of mass action and a semianalytic pressure–temperature (P–T) profile for deep adiabatic atmospheres, we established a semianalytical model that predicts the vertically quenched NH₃ abundance of warm giant planets with \( T_{\text{eq}} \approx 250–1200 \) K as a function of the bulk nitrogen abundance. This is given by

\[
f_{\text{NH}_3} = \sqrt{1 + 8\kappa^{-1} - 1} \kappa, \tag{1}
\]

where \( f_{\text{NH}_3} \) is the mixing ratio of the quenched NH₃, \( f_N \) is the bulk nitrogen abundance, and \( \kappa \) is the dimensionless parameter given by

\[
\kappa \approx 3.46 \times 10^{-0.8[\text{Fe/H}]} \left( \frac{f_N}{10^{-4}} \right)^{-1} \times \left( \frac{g}{10 \text{ m s}^{-2}} \right)^{4/3} \left( \frac{T_{\text{int}}}{100 \text{ K}} \right)^{-16/3}, \tag{2}
\]

where [Fe/H] is the atmospheric metallicity, \( g \) is the surface gravity, and \( T_{\text{int}} \) is the planetary intrinsic temperature. The bulk nitrogen abundance \( f_N \) is associated with the nitrogen-to-hydrogen ratio (N/H) as

\[
f_N = \frac{N}{H_2 + \text{He}} = 2f_{\text{H}_2}N/H, \tag{3}
\]

where \( f_{\text{H}_2} = H_2/(H_2 + \text{He}) = 0.859 \) and \( f_N = 1.16 \times 10^{-4} \) in the solar elemental abundances of Asplund et al. (2021). Paper I also provides an alternative form of Equation (1), which can be used to infer the bulk nitrogen abundance from a retrieved NH₃ abundance, as

\[
\frac{f_N}{f_{\text{NH}_3}} \approx 1 + 0.58 \times 10^{0.8[\text{Fe/H}]} \left( \frac{f_{\text{NH}_3}}{10^{-4}} \right) \times \left( \frac{g}{10 \text{ m s}^{-2}} \right)^{-4/3} \left( \frac{T_{\text{int}}}{100 \text{ K}} \right)^{16/3}. \tag{4}
\]

This theory assumes that the quenched NH₃ abundance is insensitive to planetary equilibrium temperature and eddy diffusion coefficient. This seemingly extreme assumption is valid because warm giant exoplanets have nearly the same deep atmosphere adiabatic profile at a given intrinsic flux and gravity (Fortney et al. 2007, 2020; Paper I) and the thermochemical equilibrium abundance of NH₃ is nearly constant along the deep adiabat for a given bulk nitrogen abundance (Saumon et al. 2006; Zahnle & Marley 2014; Fortney et al. 2020).

Equation (1) tells us how the quenched NH₃ abundance relates to the bulk nitrogen abundance. For example, the NH₃ abundance is nearly the same as bulk nitrogen abundance, i.e., \( f_{\text{NH}_3} \approx f_N \), at \( \kappa \gg 8 \). By contrast, in the limit of low \( \kappa \), the NH₃ abundance obeys \( f_{\text{NH}_3} \approx f_N \sqrt{\kappa}/2 \), which is lower than the bulk nitrogen abundance because of the conversion from NH₃ to N₂. It is worth noting that the semi-analytic theory predicts that the quenched NH₃ abundance is insensitive to the metallicity in the N₂-rich regime (low \( \kappa \) limit). When the bulk nitrogen abundance is scaled by the atmospheric metallicity, i.e., \( f_N \propto 10^{[\text{Fe/H}]/10} \). Equation (1) yields the nearly metallicity-independent NH₃ abundance of \( f_{\text{NH}_3} \propto 10^{[\text{Fe/H}]/10} \). This insensitivity is owing to the combined effects of hot deep interiors in high-metallicity atmospheres, and the preference for N₂ over NH₃ at higher metallicity (Lodders & Fegley 2002; Moses et al. 2013a).

Since the quenched NH₃ abundance depends only on \( g \) and \( T_{\text{int}} \) for given metallicity, we can predict the quenched NH₃ abundance as a function of planetary mass and age, which control \( g \) and \( T_{\text{int}} \). Figure 1 shows the predicted quenched NH₃ abundance at various planetary masses and ages, taken from Paper I. The quenched NH₃ abundance is higher at lower planetary mass and older age because of the cool deep atmosphere of these planets. We predicted that, for solar composition atmospheres, the quenched NH₃ diagnoses more than 50% of bulk nitrogen only when the planet has a sub-Jupiter mass \( (\lesssim 1M_J) \) and old age \( (\gtrsim 1 \text{ Gyr}) \). The discrepancy becomes even worse at high metallicity (for instance, \( \gtrsim 10 \) solar atmospheres), for which the quenched NH₃ abundance is significantly lower than the bulk nitrogen abundance at almost all values of planetary mass and age. This analysis suggests the necessity of including a chemical model to properly infer the bulk nitrogen abundance from a retrieved NH₃ abundance, and the observable NH₃ abundance should be regarded as a lower limit of bulk nitrogen abundance in most cases.

The analysis of Paper I is based on a simple analytical argument. In reality, thermochemistry and photochemistry can further alter the vertical distribution of NH₃ abundance. In the next section, we use a photochemical kinetics model to better understand the relationship between observable NH₃ and the bulk nitrogen abundances.

3. Comprehensive Investigations of Nitrogen Photochemistry

3.1. Numerical Method

Here, we numerically investigate atmospheric chemical compositions using a publicly available photochemical kinetics code, VULCAN (Tsiel et al. 2017, 2021b). The code computes the steady-state vertical distributions of chemical compositions by solving the transport equations given by

\[
\frac{\partial n_i}{\partial t} = \mathcal{P}_i - \mathcal{L}_i - \frac{\partial \Phi_i}{\partial z}, \tag{5}
\]
Figure 1. The quenched NH$_3$ abundance predicted by the semi-analytic model of Paper I (Equation (1)) as a function of planetary mass and age, where $g$ and $T_{\text{int}}$ are extracted from the thermal evolution tracks of Fortney et al. (2007). The black line denotes the abundance contours of $f_{\text{NH}_3} = 10^{-5}$ and $10^{-6}$, and yellow dashed and dotted lines show the contours corresponding to 90% and 50% of the bulk nitrogen abundance. The left and right columns show the results for solar metallicity and 10× solar metallicity atmosphere, respectively, where we have assumed that the N/H is scaled by the metallicity.

where $z$ is the altitude, $n_i$ is the number density of species $i$, $P_i$ and $E_i$ are their production and loss rates, and $\phi_i$ is the vertical flux due to eddy and molecular diffusion. While several theoretical studies investigated the eddy diffusion coefficient $K_{zz}$ on exoplanets using global circulation models (Parmentier et al. 2013; Charnay et al. 2015; Zhang & Showman 2018a, 2018b; Komacek et al. 2019; Menou 2019, 2022; Tan 2022), it remains poorly constrained from observations (see Kawashima & Min 2021). Thus, we test a broad range of eddy diffusion coefficients, $K_{zz} = 10^2, 10^3$, and $10^{11}$ cm$^2$ s$^{-1}$, for the sensitivity tests. We assume a zero flux condition for both upper and lower boundaries. We set the depth of the lower boundary so that thermochemical equilibrium is maintained there (typically 1000 bar, depending on the thermal state of the deep atmosphere and $K_{zz}$). We adopt the C–H–N–O chemistry network implemented in VULCAN as a default. We assume the solar photospheric elemental abundances of Asplund et al. (2021) for fiducial simulations. To explore a range of parameter space for planetary properties shown in Figure 1, we extract the surface gravity and intrinsic temperature from the thermal evolution tracks of Fortney et al. (2007) for several representative planetary masses and ages, as summarized in Table 1. Then, we compute the atmospheric $P$–$T$ profiles using the “EGP” radiative-convective equilibrium model extensively used in previous studies (e.g., McKay et al. 1989; Marley & McKay 1999; Fortney et al. 2005, 2007, 2008; Morley et al. 2012; Marley & Robinson 2015; Thorngren et al. 2019; Gao et al. 2020; Paper I) for various planetary equilibrium temperatures. Our fiducial simulations assume the solar spectrum (Guemuard 2018), where we set the orbital distance so that the planetary equilibrium temperature (for zero Bond albedo with full heat redistribution) coincides with a specified value. We test the effects of different stellar spectra in Section 5.2. We neglect the condensation of gas molecules since the planets studied in this paper are too warm to cause condensation of NH$_3$ and HCN (see the top panel of Figure 2).

3 Grids of the evolution tracks are available at https://www.ucolick.org/~jfortney/models.htm.

4 A Python version of the model has recently been made publicly available (Mukherjee et al. 2023)

| Mass ($M_J$) | Radius ($R_J$) | Age (Gyr) | Gravity (m s$^{-2}$) | $T_{\text{int}}$ (K) |
|-------------|---------------|----------|---------------------|------------------|
| 0.11        | 1.14          | 0.1      | 2.15                | 120.4            |
| 0.11        | 0.89          | 1        | 3.47                | 73.9             |
| 0.11        | 0.78          | 10       | 4.60                | 39.0             |
| 1.00        | 1.21          | 0.1      | 16.90               | 287.4            |
| 1.00        | 1.11          | 1        | 19.96               | 157.3            |
| 1.00        | 1.04          | 10       | 22.71               | 83.7             |

3.2. Effects of Planetary Mass, Age, and Eddy Diffusion

We first explore how the NH$_3$ and HCN abundances vary with various planetary properties. Figure 3 shows the vertical distributions of NH$_3$ and HCN across equilibrium temperature, planetary mass, age, and eddy diffusion coefficient. In general, the NH$_3$ abundance is nearly constant in the middle atmosphere owing to vertical mixing, while it decreases with increasing altitudes in the upper atmosphere due to photodissociation. This general trend is in agreement with previous studies (e.g., Line et al. 2011; Moses et al. 2011; Miller-Ricci Kempton et al. 2012; Kawashima & Ikoma 2018). As predicted in Section 2, the quenched NH$_3$ abundances in middle atmospheres are nearly independent of the equilibrium temperature at $T_{\text{eq}} < 800$ K. For $T_{\text{eq}} \geq 1000$ K, the NH$_3$ abundance gradually
CH$_4$ abundances denote the condensation temperature of NH$_3$ and HCN when assuming the atmospheres, respectively. The gray solid and dotted lines in the top panel also temperatures. The solid and dashed lines show the pro−vapor pressure of Fray & Schmitt

Figure 2. Atmospheric $P$−$T$ profiles (top panel) and vertical distributions of CH$_4$ abundances (bottom panel) in a Neptune-mass planet (0.11$M_J$) with the age of 1 Gyr. Different colored lines show the profiles for different equilibrium temperatures. The solid and dashed lines show the profiles for 100× solar metallicity and solar composition atmospheres, respectively. The green dashed and solid lines in the top panel denote the equal equilibrium abundance $P$−$T$ relation of N$_2$ and NH$_3$, computed by the law of mass action as described in Zahnle & Marley (2014) for NH$_3$ = N$_2$, for solar and 100× solar metallicity atmospheres, respectively. The gray solid and dotted lines in the top panel also denote the condensation temperature of NH$_3$ and HCN when assuming the volume mixing ratio of $10^{-4}$, typical peak abundances seen in our photochemical calculations (see Figures 3 and 6), where we have used the vapor pressure of Fray & Schmitt (2009).

decreases with decreasing pressure at $P \sim 1$–100 bar because of the efficient thermochemical conversion to N$_2$ due to high temperatures. This trend is consistent with previous studies of hot Jupiters (Moses et al. 2011).

The ratio of the quenched NH$_3$ to bulk nitrogen abundance depends on planetary mass and age. The gray bold lines in Figure 3 denote the bulk nitrogen abundance $f_{N_2}$. For Jupiter-mass planets ($M_p = 1M_J$) at 1 Gyr age (top left panel of Figure 3), the quenched NH$_3$ abundance is lower than the bulk nitrogen abundance by a factor of $\sim 2$. The depletion factor even reaches a factor of $\sim 10$ for an age of $\sim$0.1 Gyr (top right panel of Figure 3). On the other hand, the NH$_3$ abundance is almost equal to the bulk nitrogen abundances for Neptune-mass planets ($M_p = 0.11M_J$) at 1 Gyr (bottom left panel of Figure 3). These results are consistent with our prediction made in the previous section (Figure 1). Thus, higher planetary mass and younger age do act to deplete the quenched NH$_3$ as compared to the bulk nitrogen abundance.

It is worth noting that our semianalytical prediction of the quenched NH$_3$ abundance (Equation (1)) matches the numerical results quite well. The green bold lines in Figure 3 show the NH$_3$ abundance given by Equation (1), which coincides with the quenched NH$_3$ abundance below the NH$_3$ photodissociation base. Thus, even if the planetary mass and age fall into the regime where NH$_3$ depletion is expected, one may still be able to use our semi-analytic diagnostic model (Equation (4)) to give a first-order estimate on the bulk nitrogen abundance from the NH$_3$ abundance.

Of course, photochemistry may substantially deplete the observable NH$_3$ abundances at low pressure. As seen in the results for an eddy diffusion coefficient of $K_{zz} = 10^8$ cm$^2$ s$^{-1}$ (upper panels and lower left panel of Figure 3), the NH$_3$ abundance drops off at $P \lesssim 10^{-3}$–$10^{-4}$ bar through photodissociation. This pressure level is significantly deeper than the pressure level where many other chemical species experience photodissociation, say $\sim 10^{-5}$–$10^{-6}$ bar. This difference is because NH$_3$ is fragile to UV photons to relatively longer wavelengths. To demonstrate this, Figure 4 shows the photospheric pressure level at UV wavelengths. While UV photons at $\lesssim 190$ nm are mostly absorbed by other chemical species, such as H$_2$O, at $\sim 10^{-5}$–$10^{-6}$ bar, near-UV (NUV) photons at 190–220 nm penetrate to deeper atmospheres because of negligible photolysis cross sections of other molecules. Those NUV photons largely act to deplete NH$_3$ at $\sim 10^{-3}$ bar, which explains why NH$_3$ is vulnerable to photochemistry at relatively higher pressures. We refer readers to Hu (2021) for further discussion on the depletion of NH$_3$ through photodissociation in middle atmosphere regions. We note that our simulations do not account for the presence of aerosols, such as photochemical hazes, while they may act to prevent UV photons from penetrating deep atmospheres, as discussed in Section 5.1.

The strength of eddy diffusion affects where the photochemical depletion of NH$_3$ takes place. The left and right bottom panels of Figure 3 show the results for $M_p = 0.11M_J$ and 1 Gyr but for $K_{zz} = 10^8$ and $K_{zz} = 10^{11}$ cm$^2$ s$^{-1}$. Higher $K_{zz}$ results in the quenched NH$_3$ abundance continuing to higher altitudes, as the fast eddy diffusion can more easily compensate against the NH$_3$ loss by photodissociation (see also Hu 2021). On the other hand, different values of $K_{zz}$ have negligible impacts on the quenched abundance of NH$_3$, in agreement with previous studies (Zahnle & Marley 2014; Fortney et al. 2020).

Once the photolysis of NH$_3$ sets in, most of NH$_3$ is converted to HCN in the upper atmosphere for the equilibrium temperature of $T_{eq} = 400$–1400 K. In Figure 3, one can notice that HCN abundances at upper atmospheres, say $P \lesssim 10^{-3}$–$10^{-4}$ bar, are approximately the same as the NH$_3$ abundances below the photodissociation base. This result indicates that the photodissociated NH$_3$ is almost completely converted to HCN. Thus, one might be able to evaluate the bulk nitrogen abundance from the measurement of HCN abundance even if photodissociation significantly depletes NH$_3$ at pressure levels probed by observations. If the abundance profiles of NH$_3$ and HCN were constrained simultaneously, it would provide complementary information to infer the bulk nitrogen abundance.

Although the detailed analysis of atmospheric chemistry is beyond the scope of this paper, we here briefly introduce HCN synthesis processes. HCN can be produced through
photodissociation of NH$_3$ under the presence of CH$_4$. For example, Moses et al. (2011) and Line et al. (2011) identified the following channel of HCN production:

$$\text{H} + \text{N} \rightarrow \text{HCN} + 3\text{H}.$$ 

HCN synthesis initiated from NH$_3$ photodissociation requires CH$_3$ produced through the reaction of CH$_4$ with H, where H can be provided by the photodissociation of NH$_3$. In addition to the above channel through H$_2$CN, HCN can also directly form from N and CH$_3$ as (Kawashima & Ikoma 2018; Hobbs et al. 2019)

$$\text{N} + \text{CH}_3 \rightarrow \text{H}_2 + \text{HCN}.$$
On the other hand, for temperate to cold planets, Hu (2021) identified the following channels without bypassing NH:

\[
\text{NH}_2 + \text{CH}_3 \rightarrow \text{CH}_3\text{N} \\
\text{CH}_3\text{N} + h\nu \rightarrow \text{HCN} + 2\text{H}_2,
\]

though CH$_3$N photodissociation does not actually directly yield HCN but yields CH$_3$NH that subsequently yield CH$_2$NH and HCN via reaction with atomic H and photodissociation (see Section 3.2 of Moses et al. 2010). As seen in those examples, the major reaction pathway of HCN production may depend on the specific photochemical model used. HCN is destroyed either by the reaction of HCN + H → CN + H$_2$ or photodissociation of HCN + h\nu → CN + H, but CN quickly reacts with H$_2$ to reproduce HCN again (Moses et al. 2011). In our calculations, the H$_2$CN + H channel dominates over the N + CH$_3$ channel. The relative importance of the CH$_3$N channel in warm exoplanets remains unclear since the default chemical network of the VULCAN does not involve reactions around CH$_3$N (see Tsai et al. 2021b). Nevertheless, we predict that the addition of the CH$_3$N channel would barely affect our results in terms of HCN vertical distributions. This is because the HCN production rate is eventually limited by the upward NH$_3$ flux in the limit of fast HCN synthesis, and the complete conversion of NH$_3$ to HCN in Figure 3 implies that the HCN synthesis is already limited by the upward NH$_3$ flux owing to fast chemical conversion.

Figure 5 summarizes NH$_3$ abundances at $P = 1$ and 100 mbar, which mimics the pressure levels probed by transmission and emission spectra, respectively, for various planetary masses, age, and $K_{zz}$. Overall, NH$_3$ abundances are nearly invariant with $T_{eq}$ at temperate to warm exoplanet, which confirms the finding of Fortney et al. (2020). Beyond a certain equilibrium temperature, photodissociation depletes NH$_3$ from the pressure levels of interest. The threshold equilibrium temperature depends on the eddy diffusion coefficient: $T_{eq} \sim 1200$ K for $K_{zz} = 10^{11}$ cm$^2$ s$^{-1}$, $T_{eq} \sim 800$ K for $K_{zz} = 10^{12}$ cm$^2$ s$^{-1}$, and $T_{eq} \sim 400$ K for $K_{zz} = 10^{13}$ cm$^2$ s$^{-1}$. Since NH$_3$ found at pressure levels higher than 100 mbar is more stable to photodissociation, emission spectroscopy would have the advantage of observing quenched NH$_3$ that is less affected by photodissociation.

### 3.3. Effects of Different N/O, C/O, and Metallicity

We have assumed solar composition atmospheres thus far; however, exoplanets potentially have considerable diversity in atmospheric elemental ratios. For example, the atmospheric nitrogen-to-oxygen ratio (N/O) can have both super-stellar and sub-stellar N/O, depending on the formation location and whether disk solids or gas dominates the atmospheric composition (e.g., Piso et al. 2016; Cridland et al. 2020; Ohno & Ueda 2021; Turrini et al. 2021; Notsu et al. 2022; Paper I). Recent retrieval studies have reported subsolar H$_2$O abundances in hot Jupiter atmospheres from low-resolution (Pinhas et al. 2019; Welbanks et al. 2019) and high-resolution spectroscopy (Pelleiter et al. 2021), which may be attributed to a high atmospheric C/O. Several studies also suggested high metallicity atmospheres on sub-Neptunes, such as GJ 1214b (e.g., Fortney et al. 2013; Morley et al. 2015; Gao & Benneke 2018; Ohno & Okuzumi 2018; Ohno et al. 2020; Christie et al. 2022; Gao et al. 2023; Kempton et al. 2023) and...
GJ 436b (Morley et al. 2017), and exo-Saturns, such as WASP-39b (Wakeford et al. 2018; Ahrer et al. 2023; Alderson et al. 2023; Feinstein et al. 2023; JWST Transiting Exoplanet Community Early Release Science Team et al. 2023; Rustankulov et al. 2023; Tsai et al. 2023), WASP-117b (Carone et al. 2021), and HD 149026 b (Bean et al. 2023).

Here we investigate how these different atmospheric compositions affect the NH$_3$ and HCN vertical distributions. We test different N/O, C/O, and bulk atmospheric metallicities. We recompute P–T profiles for different C/O and atmospheric metallicities, as such changes lead to important alternations in the P–T profile. However, for different N/Os, we adopt the same P–T profiles as used in the previous section, as a different N/O barely affects the abundances of other O- and C-bearing species, such as H$_2$O, as long as the oxygen-to-hydrogen ratio (O/H) and carbon-to-hydrogen ratio (C/H) are the same (Hobbs et al. 2019). When we change N/O or C/O, we fix O/H to the solar value and change N/H or C/H to achieve the assumed N/O or C/O. Note that the atmospheric composition and P–T profile can noticeably depend on individual C/HS, O/HS, and N/HS even if C/O and N/O are the same (Drummond et al. 2019). We have fixed O/H here because we anticipate that it would be relatively easy to constrain O/H from observations, as the abundance of H$_2$O, a main atmospheric opacity source, is approximately proportional to O/H. We assume a Jupiter-mass planet at the age of 1 Gyr for simulations of different N/Os and C/Os, while we assume a lower planet mass of 0.11 $M_J$ at the age of 1 Gyr for simulations of high atmospheric metallicity.

The quenched NH$_3$ abundance is sensitive to but is not strictly proportional to the atmospheric N/O (N/H in other words). The top two panels of Figure 6 show the vertical distributions of NH$_3$ and HCN abundances for N/O = 0.1 $\times$ and 10$\times$ solar values. The quenched NH$_3$ abundance is approximately 10$^{-3}$ and 2 $\times$ 10$^{-4}$ for N/O = 0.1 $\times$ and 10$\times$ solar values, respectively, for equilibrium temperature $\lesssim$800 K. Recalling that the quenched NH$_3$ abundance is $\sim$5 $\times$ 10$^{-5}$ for the solar value of N/O (see the top left top of Figure 3), the NH$_3$ abundance only varies by an order of magnitude across the two decades of N/O. This relatively weak dependence on N/O is due to N$_2$ dominating over NH$_3$ in the deep atmospheres for a Jupiter mass planet at 1 Gyr, as suggested by the discrepancy between NH$_3$ and bulk N abundances in Figures 3 and 6. Since this situation corresponds to $K \ll 1$, Equation (1) indicates $f_{\text{NH}_3} \propto f_R \sqrt{K} \propto f_N^{1/2}$, which explains the dependence seen in Figure 6. Thus, when N$_2$ likely dominates over NH$_3$ in the deep atmosphere, one would need precise measurements of NH$_3$ to well constrain the bulk nitrogen abundance. The relative importance of NH$_3$ and N$_2$ in the deep atmospheres could be inferred from the second term of Equation (4) by inserting a retrieved NH$_3$ abundance into $f_{\text{NH}_3}$.

The higher C/O only has minor effects on nitrogen chemistry. The bottom left panel of Figure 6 shows the results for C/O = 1.1. The NH$_3$ profile is largely similar to that of the solar C/O (top left panel of Figure 3). This is because an equilibrium NH$_3$ abundance and thus the quenched NH$_3$ abundance are insensitive to C/O (see Figure 6 of Moses et al. 2013a). The HCN profile in the upper atmosphere also becomes similar to that for solar C/O, as the HCN is initiated from the NH$_3$ photodissociation for the temperature range of our interest. However, a higher C/O acts to increase the HCN abundance at middle to deep hot atmospheres, as the thermochemistry leads to an increased HCN abundance for high C/O.

Higher atmospheric metallicity leads to more N$_2$ dominant atmospheres owing to two combined effects: preference of N$_2$ as compared to NH$_3$ in thermochemical equilibrium and hot deep interior due to enhanced atmospheric opacity. The bottom right panel of Figure 6 shows the results for 100$\times$ solar metallicity. The quenched NH$_3$ abundance is $\sim$2 $\times$ 10$^{-4}$, which is approximately two orders of magnitude lower than the actual bulk nitrogen abundance. This large discrepancy is due to the fact that the high atmospheric metallicity yields hotter deep interiors. We show the P–T profiles of solar composition and 100 solar metallicity atmospheres in Figure 2.

The figure demonstrates that the atmospheres with 100$\times$ solar metallicity yield deep adiabatic profiles much hotter than those of solar composition atmospheres, which acts to increase N$_2$/NH$_3$ ratio in the deep atmosphere. Furthermore, N$_2$, a metal-metal species, is also strongly favored compared to NH$_3$ as the metallicity increases, at a given P and T (Lodders & Fegley 2002; Moses et al. 2013a). Therefore, the quenched NH$_3$ at P $\sim$1–100 bar starts to be depleted through thermochemical conversion at a threshold temperature of $T_{\text{eq}} \sim$800 K, which is cooler than that found in solar composition atmospheres ($T_{\text{eq}} \sim$1200 K).

High atmospheric metallicity also impacts the HCN abundances in the upper atmosphere. While the HCN abundances at upper atmospheres are nearly the same as the quenched NH$_3$ abundances for solar composition atmospheres (Figure 3), for 100$\times$ solar metallicity the HCN abundances are much lower than the quenched NH$_3$ abundances at $T_{\text{eq}} \gtrsim$600 K. This finding owes to the depletion of CH$_4$ in the high metallicity atmospheres. The bottom panel of Figure 2 shows the vertical distributions of CH$_4$ for solar composition and 100$\times$ solar metallicity atmospheres. We can see that, at $T_{\text{eq}} \gtrsim$600 K, the high metallicity atmosphere yields much lower CH$_4$ abundances than those for solar composition atmospheres at P $\sim$ 10$^{-3}$–10$^{-4}$ bar, where the HCN production takes place. The CH$_4$ depletion is due to the preference for CO over CH$_4$ at higher metallicity, as well as the hotter temperature of the higher metallicity atmospheres. Because HCN production requires the presence of CH$_4$ as discussed earlier, the CH$_4$ depletion results in the HCN depletion at high metallicity atmospheres.

4. Implications for Spectroscopic Observations

4.1. Transmission Spectroscopy

We next turn to the study of the observational feasibility of NH$_3$ and HCN in exoplanet transmission spectroscopy. We use the publicly available code CHIMERA (Line et al. 2013) to generate synthetic transmission spectra. We customize CHIMERA so that the molecular abundances of H$_2$O, CH$_4$, CO, CO$_2$, NH$_3$, N$_2$, HCN, and C$_2$H$_2$, C$_2$H$_6$ are extracted from the results of VULCAN. We assume thermochemical equilibrium for the remaining chemical species. We assume Jupiter-mass planets with 10 bar reference radii of 1.21, 1.11, and 1.04R$_J$ at 0.1, 1, and 10 Gyr, respectively. These radii correspond to the surface gravities of 16.90, 19, 96, and 22.71 $\text{m s}^{-2}$, assumed in our photochemical calculations (see Table 1). To compute transit depths, we assume a solar radius for all spectral calculations.
The magnitudes of NH$_3$ and HCN features depend on the planetary equilibrium temperatures. The top left panel of Figure 7 shows the transmission spectra for different $T_{\text{eq}}$ values. In general, NH$_3$ leaves relatively strong spectral features at 1.2, 1.5, 2.0, 3.0, and 11 $\mu$m, while HCN leaves features only at 14 $\mu$m. The NH$_3$ features at near-infrared wavelength are in agreement with MacDonald & Madhusudhan (2017a), whereas several unique features beyond 2 $\mu$m suggested by MacDonald & Madhusudhan (2017a) are barely seen in our spectra. This is because we mainly focus on warm exoplanets in which the spectral features of CH$_4$ tend to obscure the NH$_3$ spectral features. In our spectra relevant to hot Jupiters ($T_{\text{eq}} = 1200$ and 1400 K), the NH$_3$ depletion through thermochemical conversion and photodissociation significantly weakens the NH$_3$ feature, as compared to MacDonald & Madhusudhan (2017a) who fixed the NH$_3$ abundance regardless of planetary equilibrium temperature.

We also conduct the same analysis for HCN; however, HCN features are almost absent in our synthetic spectra. HCN features are weak in our models because HCN is present only at low pressures ($\lesssim 10^{-3}$ bar) as HCN forms through photodissociation of NH$_3$ at $P \sim 10^{-3} - 10^{-4}$ bar. The magnitudes of HCN features at 3.1 and 14 $\mu$m, though weak, gradually increase with increasing equilibrium temperature, as the enhanced stellar UV photons cause the HCN production at slightly higher pressures. In our model, the 3.1 $\mu$m feature is at most $\sim 20$ ppm, while the 14 $\mu$m feature could be larger than 50 ppm.

The NH$_3$ and HCN features also modestly depend on the planet’s age. The top right panel of Figure 7 shows the transmission spectra of Jupiter-mass planets with $T_{\text{eq}} = 800$ K and $K_{zz} = 10^8$ cm$^2$ s$^{-1}$ for different system ages. As discussed in Section 3.2, NH$_3$ and HCN abundances are lower at younger planets because of hotter interiors and deep atmospheres (Fortney et al. 2020). Thus, the NH$_3$ and HCN features tend to be weaker for younger planets. On the other hand, younger planets have lower surface gravity and larger atmospheric scale height. Because the large scale height enhances the amplitudes of spectral features and partly compensates for the effect of decreased abundances of NH$_3$ and HCN, the magnitudes of spectral features only moderately depend on system age.

We note that, of course, the actual strength of NH$_3$ and HCN features depends on the planetary gravity. The bottom right panel of Figure 7 shows the spectra for the planetary mass of 1 and 0.11 $M_J$, corresponding to the surface gravity of 19.96 and 3.47 m s$^{-2}$ at 1 Gyr age (see Table 1). The 0.11$M_J$ mass planet...
shows much larger spectral features, including NH₃ and HCN features. This is mostly because the spectral features of the transmission spectrum are scaled by atmospheric scale height (e.g., Kreidberg 2018). In fact, the two spectra agree well with each other once we rescale the 1 M₉ planet spectrum by multiplying a factor of 19.969/3.475, the ratio of the surface gravities (dashed lines). The different gravities still alter the spectral shapes at certain wavelengths owing to differences in atmospheric composition, such as the CO₂ absorption feature at 4.3 μm.

The magnitudes of NH₃ and HCN features also depend on the eddy diffusion coefficient. The left panel of Figure 8 shows the transmission spectra for different Kzz values. The NH₃ features become prominent as Kzz increases, as a higher Kzz pushes the depth of the photodissociation to lower pressures. On the other hand, the HCN features have a non-monotonic dependence on Kzz. The HCN features become weak at high Kzz because HCN production, which is driven by NH₃ photodissociation, takes place at much higher altitudes than that probed by the transmission spectrum. The features also become weak at very low Kzz, as thermochemistry tends to convert NH₃ to N₂ in the middle atmospheres before NH₃ is converted to HCN. Thus, interestingly, there is a sweet spot value of Kzz that maximizes the HCN features.

Atmospheric metallicity also has a strong impact on the NH₃ and HCN feature strengths. The right panel shows the spectra for the atmospheric metallicities of 1×, 10×, and 100× the solar value. The NH₃ and HCN features become weaker as the metallicity becomes higher. This is because the NH₃ abundance remains roughly the same as metallicity increases owing to the conversion of N into N₂ at deep atmospheres (see Paper I, Sections 2 and 3.3) whereas other molecular abundances, such as H₂O, increase with increasing metallicity. As a result, NH₃ features tend to be embedded into the absorption features of other molecules. Meanwhile, unless the planet is as cool as Tₐq ~ 400 K, higher atmospheric metallicity leads to a lower abundance of CH₄, which results in the depletion of HCN (Section 3.3, see also Figure 2). Thus, observations of NH₃ and HCN are more challenging for higher metallicity atmospheres.

### 4.2. Emission Spectroscopy

We investigate the observational feasibility of NH₃ and HCN in emission spectroscopy as well. As in the previous section,
we use the CHIMERA to compute synthetic emission spectra for hypothetical Jupiter-mass planets around a Sun-like star, where the stellar spectrum is taken from the PHOENIX grid (Husser et al. 2013) for stellar effective temperature of $T_{\text{eff}} = 5780$ K, metallicity of $[M/H] = 0$, and gravity of $\log(g) = 4.43$.

The NH$_3$ features in the emission spectra are maximized at warm exoplanets with $T_{\text{eq}} \sim 600$–1000 K, similar to transmission spectroscopy. Figure 9 shows the emission spectra for various equilibrium temperatures. The emission spectra always exhibit the strongest NH$_3$ feature around 11 $\mu$m followed by the feature around $\sim 6$ $\mu$m. The features at longer wavelengths are more noticeable because of the more favorable planet-to-star flux contrast. Since the planetary emitting flux is intrinsically weaker at cooler planets, as seen in the $T_{\text{eq}} = 400$ K case, the cooler planets have weaker NH$_3$ features if we assume the same stellar properties. On the other hand, hotter planets emit more flux but have a lower NH$_3$ abundance owing to thermal conversion, which also results in weaker NH$_3$ features as seen in the cases of $T_{\text{eq}} = 1200$ and 1400 K.

The system age moderately affects NH$_3$ and HCN features in emission spectra. The upper three right panels of Figure 9 show the spectrum of a Jupiter-mass planet with $T_{\text{eq}} = 800$ K at 0.1, 1, and 10 Gyr. The planet at 0.1 Gyr has a relatively weak NH$_3$ feature because its hot deep atmospheres convert NH$_3$ into N$_2$ efficiently. On the other hand, the planetary emission itself becomes stronger at younger ages owing to the hot deep atmosphere.

The strength of the NH$_3$ feature also depends on the eddy diffusion coefficient. The left columns of Figure 10 show how the strength of NH$_3$ and HCN features vary with $K_{zz}$ for a 1 Gyr old Jupiter-mass planet with $T_{\text{eq}} = 800$ K. The spectral shape is nearly the same between $K_{zz} = 10^{11}$ and $10^8$ cm$^2$ s$^{-1}$. This is because the quenched NH$_3$ abundance is insensitive to $K_{zz}$ (Saumon et al. 2006; Zahnle & Marley 2014; Fortney et al. 2020; Paper I), and emission spectra probe the pressure level below the NH$_3$ photodissociation base at $K_{zz} = 10^9$ cm$^2$ s$^{-1}$. Thus, the further elevation of the photodissociation base by high $K_{zz}$ no longer affects the strength of the NH$_3$ feature. NH$_3$ features become weaker at a very low value of $K_{zz} = 10^8$ cm$^2$ s$^{-1}$ because thermochemistry converts NH$_3$ to N$_2$ at the pressure level probed by emission spectra.

Atmospheric metallicity substantially affects the strength of NH$_3$ and HCN features. The right columns of Figure 10 show the emission spectra at 1, 10, and 100 times solar metallicity. The NH$_3$ and HCN feature becomes weaker at the higher atmospheric metallicity owing to the thermochemical conversion of NH$_3$ into N$_2$ at deep atmospheres, which results in the depletion of NH$_3$ and HCN at upper atmospheres. This trend is the same as that seen in the transmission spectroscopy. However, while the high metallicity weakens the entire spectral features for the transmission spectrum, the high metallicity instead enhances planetary emission by warming the atmosphere.

As in the transmission spectra, HCN features are relatively weak compared to NH$_3$ features. Only the feature around 14 $\mu$m is noticeable. The relatively weak HCN feature can be attributed to the vertical distribution of HCN. The emission spectrum probes deeper in the atmosphere than the transmission spectrum, while HCN is mainly produced by photochemistry in the upper atmosphere. This spatial separation between the HCN production region and the observationally sensitive region results in the relatively weak HCN features in the emission spectrum.

4.3. Observational Feasibility of NH$_3$ and HCN

We quantify the observational feasibility of NH$_3$ by examining the difference in spectrum with NH$_3$ and without
nitrogen species (i.e., NH₃ and HCN). For transmission spectra, we define the strength of NH₃ features as

$$\Delta \left( \frac{R_p}{R_i} \right)_{NH_3} = \left( \frac{R_p}{R_i} \right)_{w/\text{NH}_3} - \left( \frac{R_p}{R_i} \right)_{w/o \text{NH}_3,\text{HCN}}.$$  \hspace{1cm} (6)

This approach is similar to MacDonald & Madhusudhan (2017a). For emission spectra, the strength is defined as

$$\Delta \left( \frac{F_p}{F_i} \right)_{NH_3} = \left( \frac{F_p}{F_i} \right)_{w/\text{NH}_3,\text{HCN}} - \left( \frac{F_p}{F_i} \right)_{w/\text{NH}_3}.$$  \hspace{1cm} (7)

We compute the above metric at a wavelength for various planetary equilibrium temperatures assuming Jupiter-mass planets around a Sun-like star at 1 Gyr age, with a solar composition atmosphere and $K_{zz} = 10^8 \text{ cm}^2 \text{ s}^{-1}$. We note that the actual feature strength depends on stellar and planetary properties; for example, the feature strengths of the transmission spectrum are enhanced for smaller stars and/or lower gravity planets with larger scale heights. Our objective here is to explore the optimum range of wavelength and planetary equilibrium temperature for detecting NH₃ under the same system conditions. The same analysis is also carried out for HCN.

Figure 9. Synthetic emission spectra of giant planets around a Sun-like star. The black lines show the spectra without NH₃ and HCN, and the blue and orange shaded parts denote the reduction of planetary thermal emission when we include NH₃ and HCN absorption. The left panel shows the spectra of Jupiter-mass planets at 1 Gyr age for various planetary equilibrium temperatures. The right top three panels show the spectra of Jupiter-mass planets with $T_{eq} = 800$ K at different ages. The bottom right panel shows the spectra for $T_{eq} = 800$ K and 1 Gyr age at different planetary masses. We have assumed solar composition atmospheres and $K_{zz} = 10^8 \text{ cm}^2 \text{ s}^{-1}$ for all spectra presented here.
Although the NH$_3$ feature strength of the transmission spectra is at most $\sim 50$ ppm for Jupiter-mass planets around a Sun-like star, the emission spectrum could show much larger NH$_3$ features for the same conditions. The right column of Figure 11 shows the NH$_3$ and HCN feature strength for emission spectra. In emission, NH$_3$ leaves a moderately strong feature at $\sim 6 \mu m$ and a very prominent feature at $\sim 11 \mu m$. In particular, the 11 $\mu m$ feature strength exceeds 300 ppm at $T_{eq} \sim 400$–1200 K, meaning that the NH$_3$ feature is more than 6 times larger than the noise floor of JWST-MIRI anticipated by Greene et al. (2016). Although the observational noise tends to be large at such a long wavelength owing to the decreased number of stellar photons, given the prominence of feature and expectation for low cloud and haze opacity, emission spectroscopy by JWST-MIRI would offer a viable window to search for NH$_3$ in a wide range of the equilibrium temperatures through the 11 $\mu m$ feature.

Our model predicts that HCN features are very weak at a wide range of wavelengths and equilibrium temperatures. In both transmission and emission spectra, the HCN feature strength is smaller than 50 ppm over the entire $T_{eq}$ range explored by this study (250–1400 K), except for the feature around 14 $\mu m$ whose feature strength could be as large as 50 ppm for transmission and 300 ppm for emission spectra. Thus, the observation by JWST-MIRI may still be able to find a hint of the HCN feature in addition to the NH$_3$ feature. On the other hand, if future observations detect prominent HCN features at $<10 \mu m$, it potentially indicates that the atmospheric composition is significantly different from the solar composition assumed in these figures. For example, a very high C/O (C/O $\gg 1$) increases HCN abundance by orders of magnitude (Moses et al. 2013b; Hobbs et al. 2022), which may yield noticeable HCN features at short wavelengths.

5. Discussion

5.1. Effects of Photochemical Haze

We have assumed clear atmospheres in this study; however, recent studies suggested that warm exoplanets are universally veiled by photochemical hazes (e.g., Crossfield & Kreidberg 2017; Gao et al. 2020; Dymont et al. 2022). Photochemical hazes can affect our results in multiple ways, including flattening spectral features that limit the observability of atmospheric molecules (e.g., Fortney 2005; Morley et al. 2013; Lavvas & Koskinen 2017; Kawashima & Ikoma 2018, 2019; Adams et al. 2019; Lavvas et al. 2019; Gao & Zhang 2020; Ohno & Kawashima 2020; Ohno & Tanaka 2021; Steinrueck et al. 2021, 2023; Arfaux & Lavvas 2022).

An additional intriguing effect is that hazes alter the energy balance and $P$–$T$ profiles significantly (Morley et al. 2015; Lavvas & Arfaux 2021; Arfaux & Lavvas 2022; Steinrueck et al. 2023). For example, Molaverdikhani et al. (2020) suggested that (though they focused on radiative feedback of mineral clouds) thick clouds may cause hot deep atmospheres and deplete NH$_3$. The consequence of radiative feedback of photochemical haze is not trivial. The hazes heat upper atmospheres by absorbing stellar flux (Morley et al. 2015; Lavvas & Arfaux 2021), which may deplete NH$_3$ via thermochemical conversion. On the other hand, the hazes cool lower atmospheres by blocking stellar light from reaching the deeper atmosphere (Morley et al. 2015), which may act to maintain the quenched NH$_3$ abundance by suppressing the thermochemical conversion of NH$_3$ to N$_2$.

Hazes also shield atmospheres from stellar UV photons and may alter photochemistry. Sagan & Chyba (1997) and Wolf & Toon (2010) suggested that photochemical hazes could shield NH$_3$ from solar UV photons in the Archean Earth, which might help to maintain warm climates. If similar processes work at
warm exoplanets, hazes may help to stabilize NH$_3$ against photodissociation. Overall haze effects depend on particle properties, such as particle size and shape, which are controlled by microphysical processes. We will comprehensively investigate the overall impacts of photochemical hazes on atmospheric structure and chemistry in future work.

5.2. Effects of Stellar Spectral Type

While we have assumed the solar spectrum for the photochemical modeling, different stellar spectra could affect the results, especially for the photochemical depletion of NH$_3$. Indeed, Hu (2021) studied photochemistry in three temperature cold exoplanets, K2-18b, PH2 b, and Kepler-167 e, and found that photodissociation of NH$_3$ is insignificant on planets around M stars as compared to those around G/K stars (see also Baeyens et al. 2022 for the effects of stellar spectral type in pseudo-2D photochemical simulations). This was attributed to the low UV flux of M-type stars at 200–230 nm that mainly causes the photodissociation of NH$_3$ (Hu 2021, see also Section 3.2). Figure 12 shows the stellar spectra of G-, K-, and M-type stars, where we use a solar spectrum of Guemard (2018) as an analog of a G-type star, the spectrum of HD 40307 ($T\text{_{eff}}*$ = 4867 K, $R\text{$_*$}$ = 0.716$R\text{$_e$}$, Stassun et al. 2019) as an analog of a K-type star, and GJ 1214 as an analog of an M-type star ($T\text{_{eff}}*$ = 3250 K, $R\text{$_*$}$ = 0.215$R\text{$_e$}$, Cloutier et al. 2021). The latter two spectra are measured by the MUSCLES Treasury Survey$^5$ (France et al. 2016; Loyd et al. 2016; Youngblood et al. 2016). The cooler the star is, the weaker the UV flux from 200–230 nm is, which potentially lessens NH$_3$ depletion by photodissociation.

To investigate the effects of stellar spectral type, we perform additional photochemical calculations for G-, K-, and M-type stars, where we use a solar spectrum of Guemard (2018) as an analog of a G-type star, the spectrum of HD 40307 ($T\text{_{eff}}*$ = 4867 K, $R\text{$_*$}$ = 0.716$R\text{$_e$}$, Stassun et al. 2019) as an analog of a K-type star, and GJ 1214 as an analog of an M-type star ($T\text{_{eff}}*$ = 3250 K, $R\text{$_*$}$ = 0.215$R\text{$_e$}$, Cloutier et al. 2021). The latter two spectra are measured by the MUSCLES Treasury Survey$^5$ (France et al. 2016; Loyd et al. 2016; Youngblood et al. 2016). The cooler the star is, the weaker the UV flux from 200–230 nm is, which potentially lessens NH$_3$ depletion by photodissociation.

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To investigate the effects of stellar spectral type, we perform additional photochemical calculations for G-, K-, and M-type stars shown in the top panel of Figure 12. To isolate the effects of stellar spectral type on photochemistry, we use the same $P$–$T$ profile of a Jupiter-mass planet with $T\text{$_{eq}$}$ = 600 K at 1 Gyr (for the effects of stellar spectral type on $P$–$T$ profiles, see Mollière et al. 2015; Fortney et al. 2020). We also adjust the orbital

5 https://archive.stsci.edu/prepds/muscles/
distance $d$ so that the stellar flux on the top of the atmosphere is consistent with the assumed equilibrium temperature, as

$$d = \frac{1}{2} R_* \left( \frac{T_{\text{eff}}} {T_{\text{eq}}} \right)^2.$$  

(8)

We confirm that NH$_3$ could be more stable against photodissociation at cooler stars. The bottom panel of Figure 12 shows the vertical distributions of NH$_3$ and HCN on the planet around G-, K-, and M-type stars. As expected, NH$_3$ retains the quenched abundance until $\sim 10^{-3}$ bar for K- and M-type stars, which is approximately an order of magnitude lower than the pressure level where photodissociation takes place for G-type stars. Thus, we suggest that warm planets around K-type and M-type stars are ideal targets for detecting NH$_3$, as the photodissociation of NH$_3$ would be relatively insignificant.

5.3. Previous Observations of NH$_3$ on Exoplanets

Thus far, there have been three exoplanets for which NH$_3$ absorption was reported: the canonical transiting hot Jupiter HD 209458b ($T_{\text{eq}} = 1484$ K, Giacobbe et al. 2021) and warm Jupiters WASP-80b ($T_{\text{eq}} = 817$ K, Carleo et al. 2022) and WASP-69b ($T_{\text{eq}} = 963$ K, Guilluy et al. 2022), the latter two planets fall in the temperature regime where NH$_3$ features are expected to be relatively large (see Section 4). All of the above detections were accomplished by high-resolution transmission spectroscopy. For HD 209458 b, MacDonald & Madhusudhan (2017b) also reported the detection of NH$_3$ from low-resolution transmission spectroscopy. Giacobbe et al. (2021) detect NH$_3$ by cross correlating the observations with synthetic spectra assuming a vertically constant NH$_3$ abundance of $1.3 \times 10^{-4}$, while MacDonald & Madhusudhan (2017b) constrained the NH$_3$ abundance to $10^{-8}$-$2.7 \times 10^{-6}$. Our simulations of a Jupiter-mass planet at 1 Gyr yield NH$_3$ abundances of $\sim 10^{-6}$ at the pressure level of interest for $T_{\text{eq}} = 1400$ K (Figure 3), which appears to be consistent with the constraint by MacDonald & Madhusudhan (2017b). However, we need a more careful analysis for planet-specific comparisons, as the eddy diffusion coefficient $K_{zz}$ and intrinsic temperature $T_{\text{in}}$ could differ from planet to planet. This is beyond the scope of this study. Since the quenched NH$_3$ abundance is sensitive to the intrinsic temperature, the potential detection of NH$_3$ may provide observational tests on the suggested hot deep interiors of hot Jupiters (Thorngren et al. 2019; Fortney et al. 2020).

While we have predicted that warm exoplanets are favorable targets for searching for NH$_3$, no previous studies with low-resolution spectroscopy have reported the detection of NH$_3$ for warm exoplanets. This could be due to the prevalence of clouds and hazes in warm exoplanetary atmospheres that mute the absorption features of gaseous molecules (e.g., Knutson et al. 2014; Kreidberg et al. 2014, 2018, 2022; Wakeford et al. 2017; Chachan et al. 2019, 2020; Libby-Roberts et al. 2020; Mikal-Evans et al. 2021; Alam et al. 2022, see Dymont et al. 2022 for a recent compilation). Since cloud and haze opacity tends to decrease with increasing wavelength, future observations at longer wavelengths would have better chances to detect NH$_3$, such as through the detection of the 11 $\mu$m feature. Another possible cause of the nondetection of NH$_3$ could be deep atmospheres being much hotter than those predicted by thermal evolution models for non-synchronized exoplanets. For example, Benneke et al. (2019) reported the nondetection of NH$_3$ on warm sub-Neptune GJ 3470b, while the planet is known to have a nonzero eccentricity of $e \sim 0.1$ (Kosiarek et al. 2019). Such nonzero eccentricity may yield hot deep atmospheres through tidal heating and affect upper atmospheric compositions (Agúndez et al. 2014b; Fortney et al. 2020).

One of the interesting possibilities for the lack of NH$_3$ detection is that many warm exoplanets may have atmospheric compositions considerably different from solar compositions. For example, if warm exoplanets typically have high metallicity atmospheres, the detection of NH$_3$ becomes more challenging, as shown in Section 4. The prevalence of high metallicity atmospheres may be compatible with the mass-metallicity relation of warm Jupiters (Thorngren et al. 2016), planet formation models (e.g., Fortney et al. 2013; Venturini et al. 2016; Cridland et al. 2020), and several atmospheric observations of giant exoplanets (Wakeford et al. 2018; Carone et al. 2021; Ahrer et al. 2023; Alderson et al. 2023; Bean et al. 2023; Feinstein et al. 2023; JWST Transiting Exoplanet Community Early Release Science Team et al. 2023; Rustamkulov et al. 2023; Tsai et al. 2023). A planet may also have a subsolar N/O if the solid accretion inside the N$_2$ snowline determines the atmospheric composition (see, e.g.,
Figure 1 of Paper I), which would also lower the NH$_3$ abundance as compared that for solar N/O with the same atmospheric metallicity.

5.4. Vertical Variation of Eddy Diffusion Coefficient

While we have assumed vertically constant $K_{zz}$ so far, in reality, the eddy diffusion coefficient likely has a vertical variation (e.g., Zhang & Showman 2018a). The vertically varying $K_{zz}$ potentially affects our results at some points; for example, it may promote thermochemical conversion of NH$_3$ to N$_2$ in deep atmospheres because of low $K_{zz}$, as seen in Moses et al. (2021). We can test the effect of vertically variable $K_{zz}$ by assuming $K_{zz} = K_{zz,1\text{ bar}}(P/1\text{ bar})^{-0.5}$. Following Moses et al. (2021), we also set $K_{zz} = 10^{10}$ cm$^2$ s$^{-1}$ at $P > 100$ bar and the maximum value of $K_{zz} = 10^{14}$ cm$^2$ s$^{-1}$. Figure 13 shows the photochemical calculation results for various values of $K_{zz,1\text{ bar}}$. The vertical variable $K_{zz}$ tends to facilitate the thermochemical conversion of NH$_3$ to N$_2$ owing to the weak vertical mixing in the deep atmosphere, while it mitigates the NH$_3$ photodissociation thanks to the strong mixing in the upper atmosphere. The HCN abundance in the upper atmosphere reflects the quenched NH$_3$ abundance as in the constant $K_{zz}$ case, while HCN abundance at the lower atmosphere could be higher compared to constant $K_{zz}$ cases because downward diffusive transport becomes slower as the pressure increases. The vertical variation of $K_{zz}$ and its strength have remained poorly constrained by observations (Kawashima & Min 2021). Future observations of disequilibrium species more sensitive to the quench point than NH$_3$ is, such as CO, would help to probe $K_{zz}$ in deep atmospheres (e.g., Miles et al. 2020; Mukherjee et al. 2022).

5.5. Effects of Day–Night Temperature Contrast

Our study has relied on a 1D framework, whereas real exoplanetary atmospheres are in 3D and may show strong temperature contrasts between daysides and nightsides (e.g., Perez-Becker & Showman 2013; Komacek & Showman 2016); however, we do not anticipate that this is a major drawback in this case. Several studies have investigated how horizontal temperature variations and horizontal winds affect the chemistry of exoplanetary atmospheres. These include 3D GCMs (Cooper & Showman 2006; Drummond et al. 2018a, 2018b, 2020; Mendonca et al. 2018), equatorial 2D models (Tsai et al. 2021a), and pseudo-2D models that rotate a 1D model along the equator (Agúndez et al. 2012, 2014a; Baeyens et al. 2021, 2022; Moses et al. 2021). According to the pseudo-2D works by Moses et al. (2021) and Baeyens et al. (2022), the NH$_3$ abundance is almost invariant with longitudes at warm exoplanets with $T_{\text{eq}} \lesssim 1000$ K, except for the pressure level of $\leq 10^{-3}$–$10^{-4}$ bar where the photodissociation takes place. Drummond et al. (2020) performed 3D global circulation simulations on hot Jupiters HD 189733b and HD 209458b using a 3D GCM that implements a full kinetic chemistry based on the reduced chemical network of Venot et al. (2019) and showed that NH$_3$ abundance is vertically and longitudinally uniform in both planets, though they did not include photochemistry. This longitudinal independence could be attributed to the long thermochemical conversion timescale of NH$_3$, $>10^{10}$ s at 1000 K (see Figure 4 of Tsai et al. 2018), which is much longer than typical horizontal transport timescales. In the deep atmosphere where the chemical quenching takes place, on the other hand, the atmospheric $P$–$T$ profile is invariant with longitude because of the long radiative timescale. Thus, we anticipate that the NH$_3$ spatial distribution in real atmospheres is reasonably approximated by the 1D framework, especially for warm exoplanets that are optimum for detecting NH$_3$.

5.6. Observability of N$_2$ Molecule

In Paper I and this study, we have focused on NH$_3$ and HCN since N$_2$, the remaining main N reservoir, in general, has negligibly low opacity in visible and infrared wavelengths. However, N$_2$ actually has moderate opacity at extremely hot temperatures, say $>4000$ K. High-resolution spectroscopy might still have a chance to detect N$_2$ if it abundantly exists in a hot thermosphere. In the context of terrestrial exoplanets with N$_2$-dominated atmospheres, Schwieterman et al. (2015) suggested that N$_2$ can be detected from the absorption feature of (N$_2$)$_2$ dimer produced by N$_2$–N$_2$ collisions, though it unlikely affects the observable spectra of giant planets with much lower N$_2$ abundances. N$_2$–H$_2$ collision-induced absorption (CIA) opacity might still have some impacts; however, quantitative assessment is difficult as of yet owing to the limited valid range of wavelength and temperature for the available CIA absorption coefficient (Karman et al. 2019).

6. Summary

In this study, we have performed a series of photochemical calculations for various values of planetary mass, age, equilibrium temperature, eddy diffusion coefficient, and atmospheric composition to explore the relation between observable NH$_3$ abundance and bulk nitrogen abundance. Based on the photochemical calculations and the semi-analytic model of NH$_3$ quenching developed by Paper I
(Equation (1)), we have comprehensively revealed what planetary properties act to deplete observable NH₃ as compared to bulk nitrogen. Table 2 summarizes how the observable abundance of NH₃ and HCN depends on various planetary properties and its observational implications. Our key findings are summarized as follows:

1. As shown in Paper I, the vertically quenched NH₃ abundance is nearly identical to the bulk nitrogen abundance only when a planet has a sub-Jupiter mass (≤1 Mⱼ) and old age (≥1 Gyr) under the assumption of a solar composition atmosphere.

2. High metallicity atmospheres lead to the quenched NH₃ abundance being much lower than the bulk nitrogen abundance even at sub-Jupiter planet masses and old ages. This highlights the importance of constraining overall atmospheric metallicity for inferring bulk nitrogen abundances.

3. The semianalytical model of Paper I (Equation (1)) reproduces the vertically quenched NH₃ abundance computed by a photochemical kinetic model (Section 2). Thus, our semianalytical model would mitigate the discrepancy between the quenched NH₃ and bulk nitrogen abundances when inferring the bulk nitrogen abundance from an observed NH₃.

4. NH₃ is vulnerable to photodissociation and tends to be depleted at 10⁻²⁻¹⁻⁴ bar in clear atmospheres, depending on the equilibrium temperature and eddy diffusion coefficient. The relatively deep pressure level of NH₃ photodissociation is caused by UV photons at 200–230 nm that can penetrate to higher pressures owing to the lack of absorption opacity of other molecules at those wavelengths.

5. The photodissociation of NH₃ is mitigated when planets orbit around cool K and M stars because of the decreased level of NUV photons. Thus, warm planets around K and M stars would be ideal targets for searching for NH₃.

6. We have examined the NH₃ and HCN signatures in the transmission spectra of warm gas giants. For 1 Gyr Jupiter-mass planets with clear atmospheres around Sun-like stars, we have predicted that NH₃ would leave characteristic features of >50 nm at 1.5, 2, and 11 μm for Jupiter-mass planets around Sun-like stars. Emission spectra show NH₃ features at 6 and 11 μm for the same conditions. The latter could be >300 ppm. HCN leaves strong features only at 14 μm in both transmission and emission spectra for solar composition. Planets with Tₐₑq ~ 400–1000 K would be suitable for detecting HCN. Emission spectrum searching for 11 μm NH₃ feature is suitable for Jupiter-mass planets with small scale height. Transmission spectrum might be able to find 1.5 and 2 μm features for Saturn-mass planets with large-scale height. HCN detection may indicate atmosphere significantly deviated from solar composition, such as a high C/O.

7. The emission spectra show NH₃ features at ~6 and 11 μm. For Jupiter-mass planets around Sun-like stars, we have predicted that the 11 μm feature could be >300 ppm, much larger than that expected for transmission spectra.
8. The 11 μm feature is particularly strong and would be the best signature to identify NH$_3$, as clouds and/or hazes tend to have less opacity at such long wavelengths. 

9. Our analysis has suggested that it may be difficult to detect HCN by low-resolution spectroscopy if a planet has a solar composition atmosphere. This is because HCN is formed by photochemistry that takes place in the upper atmosphere far away from the pressure level typically probed by observations. The detection of HCN potentially indicates that atmospheric composition is considerably different from solar composition, such as a high C/O of C/O $\gg$ 1.

Our studies have highlighted that it is not trivial to robustly constrain the atmospheric nitrogen abundances of exoplanets. The observable NH$_3$ abundance underestimates the bulk nitrogen abundance in most cases. Thus, the observable NH$_3$ abundance is usually a lower limit of bulk nitrogen abundance, and chemical models are necessary to constrain the bulk nitrogen abundance. This task will be aided by photochemical and chemical models that are necessary to constrain the bulk atmospheric composition. This will be aided by photochemical and chemical models that are necessary to constrain the bulk atmospheric composition. We refer the reader to the references for further details.

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Although the robust constraint of nitrogen abundance is not easy, we expect that a lower-limit nitrogen abundance still provides some insights into planet formation. For example, for a super-stellar N/O, a lower-limit N/O may be able to give a lower-limit orbital distance of planet formation location because gas-phase N/O monotonically increases with the distance (Piso et al. 2016). Alternatively, if planetesimals and/or pebble accretion mainly determine the atmospheric composition, which could be inferred from refractory element abundances in the atmosphere, such as sulfur and alkali metals (e.g., Schneider & Bitsch 2021b; Turrini et al. 2021; Hands & Fortney 2021; Al-Refaie et al. 2022). Our semi-analytic model (Equation (1)) can provide a first estimate of the bulk nitrogen abundance from a retrieved NH$_3$ abundance.

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Kazumasu Ohno https://orcid.org/0000-0003-3290-6758

Jonathan J. Fortney https://orcid.org/0000-0002-9843-4354

ORCID iDs

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