Modeling Synthetic Spectra for Transiting Extrasolar Giant Planets: Detectability of H$_2$S and PH$_3$ with the James Webb Space Telescope

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Abstract

The James Webb Space Telescope (JWST)’s large aperture and wide wavelength coverage will enable it to collect the highest-quality transit spectra observed so far. For exoplanetary atmospheres we expect to retrieve the abundance of the most abundant molecules, such as H$_2$O, CO, and CH$_4$. Other molecules, such as H$_2$S and PH$_3$, have been observed in Jupiter and Saturn but their chemistry and detectability in strongly irradiated planets are largely unknown. In this paper, we make the first effort to study their spectral features in solar composition atmospheres, and evaluate their detectability with the JWST. We model the chemistry of phosphorus and sulfur in solar composition atmospheres. Our model includes the effect of vertical transport. Photochemistry effects are not included in our calculations. Using the abundance profiles, we model the JWST transmission and emission spectra for a $K = 6.8$ G-type star and for planets with cloud-free solar composition atmospheres. We find PH$_3$ is detectable at 3$\sigma$ from transmission spectra of the simulated atmosphere with $T_{eq} < 500$ K using the NIRCam LW grism F444W mode with a total observing time of 28.8 hr. H$_2$S is detectable at 3$\sigma$ in the transmission and emission spectra for the simulated planet with $T_{eq} > 1500$ K using the NIRCam LW grism F322W2 mode with a total observing time of 24.0 hr. Our results specifically highlight the importance of including H$_2$S for future abundance retrieval with the JWST. The presence of clouds and hazes challenges the detections of PH$_3$ and H$_2$S, but H$_2$S features are still expected to be present in the emission spectra.

Key words: planets and satellites: atmospheres – planets and satellites: composition – techniques: spectroscopic

1. Introduction

The atmospheres of exoplanets can be characterized by transit spectroscopy (e.g., Seager & Sasselov 2000; Hubbard et al. 2001). The transit spectra contain information about the composition and vertical thermal structure of the atmospheres. Interpretation of the transit spectra has led to the discovery of atoms like sodium, potassium (Charbonneau et al. 2002; Redfield et al. 2008; Jensen et al. 2011; Sing et al. 2012, 2015; Nikolov et al. 2014; Wilson et al. 2015), and molecules like H$_2$O (Deming et al. 2013; Huq et al. 2013; Mandell et al. 2013; Wakeford et al. 2013, 2017; Crouzet et al. 2014; Kreidberg et al. 2014a, 2015; McCullough et al. 2014; Evans et al. 2016; Line et al. 2016) in the atmospheres of hot Jupiters. Other molecules such as CH$_4$, CO, CO$_2$ have also been reported in the literature as having been detected; however, their detection has not been confirmed by later observations or other retrieval techniques (e.g., Gibson et al. 2011; Hansen et al. 2014; Line et al. 2014). Currently, the determination of molecular abundances is limited by the quality of the transit spectra (Burrows 2014).

The James Webb Space Telescope (JWST)’s large aperture (6.5 m), wide wavelength coverage ($\lambda = 0.6 \sim 28 \mu$m) and multiple instrument modes will ensure that it will collect the highest-quality transit spectra (e.g., Beichman et al. 2014). Greene et al. (2016) simulated how well JWST observations can constrain the temperature–pressure profile and molecular abundances of H$_2$O, CH$_4$, CO, CO$_2$ and NH$_3$. Other molecules such as H$_2$S and PH$_3$ are not included in their calculations. However, H$_2$S and PH$_3$ are the primary carriers of sulfur and phosphorus in hydrogen-rich atmospheres (e.g., Visscher et al. 2006), and they potentially contribute to the absorptions in the transit spectra.

PH$_3$ has been observed in the atmospheres of Jupiter and Saturn (e.g., Fletcher et al. 2009, and references therein). The PH$_3$ observed in the upper troposphere and stratosphere is supplied by the vertical convection from deeper and hotter regions of the atmosphere where PH$_3$ is thermochemically stable. The same process may be at work in the exoplanets. H$_2$S was measured in the troposphere of Jupiter by the Galileo entry probe (Irwin et al. 1998; Wong et al. 2004). H$_2$S is the primary carrier of sulfur in the atmospheres of Jupiter and Saturn except above the level of a few bars where it is removed by forming the NH$_3$SH cloud. For exoplanets with higher stellar irradiation, H$_2$S may not condense in the upper atmosphere. Therefore, H$_2$S can potentially contribute to the transit spectra of extrasolar giant planets.

The non-equilibrium chemistry of phosphorus species has not been explored in the literature in the context of exoplanets with hydrogen-rich atmospheres. Vertical mixing can drive the chemistry out of equilibrium, just as the case with Jupiter and Saturn. Non-equilibrium chemistry of sulfur in extrasolar giant planets was studied by Zahnle et al. (2009). From their calculations, H$_2$S is predicted to be the primary carrier of sulfur up to $\sim 10$ mbar. Above this level, photochemistry comes into play and the abundance of H$_2$S decreases at higher altitude.

In this paper, we model the non-equilibrium chemistry of phosphorus in the hydrogen-rich atmospheres of exoplanets. We also model the non-equilibrium chemistry of C/N/O/S-bearing species to obtain the vertical profiles of major molecules in the atmospheres. To evaluate whether H$_2$S and PH$_3$ can be detected by JWST transit observations, we model the synthetic transmission and emission spectra with simulated noise levels.

The paper is organized as the follows. In Section 2, we describe our chemical model, synthetic spectra model, and
JWST noise model. In Section 3, we present our results on the computed abundance profiles of major C/N/O/S/P-bearing species. In Section 4, we present the synthetic transit spectra for four planetary systems with different levels of stellar insolation. In Section 5, we add simulated JWST noise into the synthetic spectra, and evaluate the detectability of H$_2$S and PH$_3$. In Section 6, we discuss the implications for JWST transit observations, and limitations of our model. In Section 7, we present our conclusions.

2. Methodology

Here we describe our methodology for modeling the synthetic JWST transit spectra. We first model the chemistry of C/N/O/S/P and identify major species in the atmospheres that are abundant and thus potentially important for the opacity. Then we model the noiseless primary and secondary transit spectra using the computed abundance profiles. Finally we model the transit spectra with simulated JWST noise, and determine whether certain molecules will be spectroscopically detectable by the JWST. We detail our methodologies in what follows.

2.1. Chemical Model

We use a one-dimensional diffusion–kinetic model developed in Wang et al. (2015, 2016) to compute the vertical profiles of molecular abundances. The code solves the equation

$$\frac{\partial Y_i}{\partial t} = \frac{1}{\rho} \frac{\partial}{\partial z} \left( \rho K_{\text{eddy}} \frac{\partial Y_i}{\partial z} \right) + P_i - L_i,$$

where $Y_i$ is the mass fraction of species $i$, $\rho$ is the density of the atmosphere, $z$ is the vertical coordinate, $K_{\text{eddy}}$ is the vertical eddy diffusion coefficient, $P_i$ is the chemical production rate of species $i$, and $L_i$ is the chemical loss rate of species $i$. Two physical processes are modeled by the equation. One is the chemical production or loss of species $i$, and the other is its vertical transport. The mixing ratio of species in the atmospheres is determined by the dynamic balance between these two physical processes.

We neglect the effect of photochemistry. The effect on the chemical abundances is the photodissociation of hydrogen-bearing species (e.g., H$_2$O, CH$_4$, NH$_3$) and the production of photochemical products (e.g., C$_2$H$_6$, C$_2$H$_5$, HCN) (Moses et al. 2011, 2013; Kopparapu et al. 2012; Venot et al. 2012; Agúndez et al. 2014; Miguel & Kaltenegger 2014). Photochemistry changes the abundances only in the upper atmosphere, which is at millibar levels. Therefore, we expect our computed abundance profiles to be valid below ~10 mbar.

The diffusion–kinetic model requires three kinds of input. First is the temperature–pressure ($T$–$P$) profile; second is a list of thermodynamic properties and a list of reactions between these species; third is the elemental compositions and the eddy diffusion coefficient. We detail how we choose the inputs below.

1. $T$–$P$ profile: we compute this using the model developed in Parmentier & Guillot (2014) and Parmentier et al. (2015), which is a non-gray analytical model.

2. Thermodynamic properties and reaction rates: the thermodynamic properties are used to compute the equilibrium abundances as well as the backward reaction rates. The thermodynamic properties are compiled from Burcat & Ruscic (2009), McBride et al. (1993), Dean & Bozzelli (2000), and Venot (2012). The kinetic network used for modeling the C/N/O/H chemistry consists of 108 species and 1000 reactions, originally from Venot et al. (2012). The H/P/O reaction network consists of 24 species and 175 reactions, originally from Twarowski (1995). A more detailed description of the C/N/O/H and H/P/O reaction networks used in this paper can be found in Wang et al. (2016), and both reaction networks can be downloaded at the KIDA database (http://kida.obs.ujf-grenoble.fr/networks.html).

3. Elemental abundances: we assume that the elemental composition of the atmosphere is solar. The solar elemental abundances are from Asplund et al. (2009).

4. Eddy diffusion coefficient: $K_{\text{eddy}}$ is used in the one-dimensional chemical models for parameterizing the vertical transport. There is no observational constraint on the eddy diffusion coefficient on exoplanets. However, its values can be approximated by multiplying the vertical convective velocity derived from 3D general circulation models with the pressure scale height (e.g., Moses et al. 2011; Venot et al. 2012; Parmentier et al. 2013). This mixing length theory approximation has an uncertainty on the order of 10 in the estimated eddy diffusion coefficient (Smith 1998). In this paper, we choose to use a constant profile for the $K_{\text{eddy}}$, with values equal to $1 \times 10^7$ cm$^2$ s$^{-1}$ throughout the atmospheres. We explore the dependence on $K_{\text{eddy}}$ in Section 6.

In each simulation, we provide the elemental abundances, the $K_{\text{eddy}}$, and the $T$–$P$ profile to set up the code, then we initialize the $Y_i$ of species with chemical equilibrium mass fractions. $Y_i$ are evolved toward a steady state where the time derivative term in Equation (1) is zero. In the code, we terminate the simulation once the relative changes of mole fractions in successive $\Delta t$ are smaller than $1 \times 10^{-3}$, where $\Delta t$ is the overturning timescale, defined as $H^2/K_{\text{eddy}}$, where $H$ is the pressure scale height at 1 bar level. The output is the vertical profiles of $Y_i$ for each species in the model.

2.2. Synthetic Spectra Model

To simulate the synthetic spectra of transiting exoplanets, we modified the Smithsonian Astrophysical Observatory 1998 (SA098) radiative transfer code (see Traub & Stier 1976; Traub & Jucks 2002; Kaltenegger & Traub 2009 and references therein for details). The line-by-line radiative transfer code calculates the atmospheric emergent spectra and also transmission of stellar radiation through the atmosphere with disk-averaged quantities at high spectral resolution. The atmosphere is divided in different layers, where the transmission is calculated using Beer’s law. Updates include a new database with molecules relevant for giant planets that include H$_2$O, CH$_4$, CO, CO$_2$, NH$_3$, N$_2$, HCN, PH$_3$, and H$_2$S taken from the HITRAN (Rothman et al. 2013) and HITEMP (Rothman et al. 2010) databases.

The overall high-resolution spectrum is calculated with 0.1 cm$^{-1}$ wavenumber steps. We smear them out to a resolving power of 100 to simulate the resolution that we will obtain with the MIRI instrument. For NIRISS and NIRCam, we assume the observed spectra are binned to a resolution of 100. The smoothing was done using a triangular smoothing kernel.

We neglect the effect of cloud and hazes. Their influence on our results is discussed in the Section 6.
The noise of primary and secondary transit spectra is simulated following the recipes in Greene et al. (2016). Here we provide a compact summary of the noise modeling methodology, along with parameters in the model, summarized in Table 1. The selected JWST observing modes are from Table 4 of Greene et al. (2016). We did not cover the NIRISS SOSS observing mode. The features of H$_2$S and PH$_3$ are not as strong as those of H$_2$O and hence we expect their effects to be masked by H$_2$O. Therefore, we do not expect this part of the spectrum to be relevant for detection of PH$_3$ and H$_2$S. The NIRCAM instrument with LW grism mode covers the wavelength 2.5−5.0 μm with a native resolution of 1700; the MIRI instrument with slitless mode covers the wavelength 5.0−11 μm with a resolution of 100. We adopted a cutoff at 11 μm for MIRI slitless mode because the transmission becomes low at longer wavelength (Kendrew et al. 2015).

The selected JWST modes provide a wavelength coverage between 2.5 and 11 μm. We choose a binned resolution of R = 100 for all modes to ensure each bin contains enough photons in our simulation.

There are four noise components: the signal photon shot noise, the background photon shot noise, the detector noise, and the systematic noise. The equations for computing each component are from Greene et al. (2016). For completeness, we present these equations below, and describe how we choose the parameter values in these equations.

1. The number of signal photons in each spectral bin is computed following the equation

$$S_l = F_l A_{tel} \frac{\lambda^2}{hcR} \tau,$$

where $S_l$ is the number of signal photons in each spectral bin, $F_l$ is the flux of the signal as received at the telescope, $A_{tel}$ is area of the aperture of the JWST, $t$ is the integration time, $R$ is the binned spectral resolution, and $\tau$ is the total system transmission. The integration time $t$ is adopted as the full transit duration $T_{1d}$ (assuming equal integration time for both in and out transit). The transmission $\tau$ is sensitive to wavelength and is obtained from the JWST documentation (https://jwst-docs.stsci.edu/display/JTI/NIRCam+Filters). The signal flux $F_l$ is measured at three configurations, namely, in-transit, out-transit, and in-eclipse. We assume the in-transit and out-transit integration time to be unity. The signal shot noise is equal to the square root of $S_l$.

2. The background signal is computed following the equation

$$B_l = b_l t A_{pix} n_{pix} R_{native}/R,$$

where $B_l$ is the background photon numbers in each spectral bin, $b_l$ is the background electron flux, $A_{pix}$ is the area subtended by each pixel, $n_{pix}$ is two times the number of spacial pixels covered by the spectrum, and $R_{native}$ is the native resolution of the spectrum before binning. The values of the above parameters are summarized in Table 1. The background shot noise is equal to the square root of $B_l$.

3. The total detector noise in single transit observation is calculated as

$$N_{tot} = N_d \sqrt{n_{pix} n_{ints} R_{native}/R},$$

where $N_d$ is the total detector noise in one integration, and $n_{ints}$ is the number of integrations in one transit observation. The parameter $n_{ints}$ depends on the total transit duration, the brightness limit of each instrument mode, and the brightness of the star. The parameter values are summarized in Table 1.

4. The systematic noise cannot be reduced by summing over more observations. We adopt the systematic noise floor as suggested by Greene et al. (2016), as presented in Table 1.

The four noise components are combined quadratically to compute the total noise in each spectral bin for a single transit observation.

2.3.2. PandExo Noise Model

PandExo (http://pandexo.science.psu.edu:1111/) is a tool for computing the error of a spectrum given the stellar spectral energy density, the planet spectrum, and the transit duration (Batalha et al. 2017). It is built on top of the STScI’s Pandeia exposure time calculator. PandExo does automatic optimization of groups and integrations. We use this tool to compute the errors on our simulated spectra, and as a validation of our parameters in the Greene et al. (2016) noise model.

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**Table 1**

Parameters for Computing Noise; Extension of Table 4 in Greene et al. (2016)

| Instrument | Mode     | $\lambda$ (μm) | native $R$ | $A_{pix}$ (arcsec$^2$)$^a$ | $n_{pix}$ | $b$ (e$^-$ s$^{-1}$ arcsec$^{-2}$)$^c$ | $N_d$ (CDS) | $n_{groups}$ | Noise Floor (ppm)$^d$ |
|------------|----------|----------------|------------|-----------------------------|-----------|----------------------------------------|-------------|--------------|-----------------------|
| NIRCam     | LW grism | 2.5−3.9        | 1200@2.5 μm| 0$^a$064 × 0$^a$064        | 4         | 203.62                                 | 18          | 12           | 30                    |
|            | F32W2    |                |            |                             |           |                                        |             |              |                       |
| NIRCam     | LW grism F444W | 3.9−5.0        | 1550@4.5 μm| 0$^a$064 × 0$^a$064        | 4         | 308.74                                 | 18          | 25           | 30                    |
| MIRI       | Slitless LRS | 5.0−11.0       | 40@5 μm    | 0$^a$110 × 0$^a$110        | 4         | 5156.0                                 | 46          | 8            | 50                    |

Notes.

$^a$ http://www.stsci.edu/jwst/instruments/.

$^b$ Two times the spatial extent of point source spectrum.

$^c$ The background photon rate is computed at the JWST exposure time calculator https://demo-jwst.etc.stsci.edu/.

$^d$ The adopted noise floor values are from Greene et al. (2016).
3. Results for Abundance Profiles

In this section, we present our results for the chemistry of C/N/O/S/P species. Temperature and pressure are the most important factors for determining the molecular abundances. The chemistry is very different for differently irradiated atmospheres. We simulate the atmospheres with different equilibrium temperatures (500, 750, 1000, 1500, 2000 K). The $T$–$P$ profiles used in the calculations are shown in Figure 1. The vertical eddy diffusion coefficient used is $1 \times 10^{7}$ cm$^{2}$ s$^{-1}$, and the composition is assumed to be solar. In the following subsections, we present the computed vertical abundance profiles for $T_{eq}$ = 500, 1000, 1500, and 2000 K.

3.1. Results for Phosphorus Species

Assuming solar elemental abundances for phosphorus, hydrogen, and oxygen, we compute the abundance profiles of H/P/O-bearing species for different levels of insolation. We present our results for the phosphorus chemistry in Figure 2. The most abundant H/P/O-bearing species are PH$_3$, PH$_2$, PH, HOPO, H$_3$PO$_4$, and P$_2$. For solar composition atmospheres with $T_{eq}$ = 500 K and $T_{eq}$ = 1000 K, the abundances are out of chemical equilibrium due to the effect of vertical mixing. For solar composition atmospheres with $T_{eq}$ = 1500 K and $T_{eq}$ = 2000 K, the abundances are in chemical equilibrium. The vertical mixing still exists; however, the mixing timescale is longer than the chemical timescale, and the abundances quickly re-equilibrate after mixing. The major phosphorus species are different for different levels of insolation. For a solar composition atmosphere with $T_{eq}$ = 500 K, the dominant phosphorus-containing species is PH$_3$. This is similar to Jupiter, which has an equilibrium temperature at approximately 160 K. For a solar composition atmosphere with $T_{eq}$ = 1000 K, PH$_3$ and P$_2$ are the most abundant phosphorus-containing species above 1 bar. Below this level, PH$_3$ is still the dominant species. At this temperature, part of the PH$_3$ is thermally decomposed into PH$_2$. The reactions between radicals can produce molecules with two or more phosphorus atoms such as P$_2$. At $T_{eq}$ = 1500 K and 2000 K, the temperature is high enough that most PH$_3$ is thermally decomposed into PH$_2$ and PH. The photodissociation of PH$_3$ is potentially important at low pressure levels. For Jupiter and Saturn, the PH$_3$ abundance decreases near 0.1 bar level (Fletcher et al. 2009). There is no PH$_3$ photochemical modeling for hot Jupiters. In our case of solar composition Jupiter-size planets, we assume our abundance profile is valid below 0.1 bar. Above this, the profile is subject to change due to photodissociation.

3.2. Results for Sulfur Species

Assuming solar composition atmospheres, we compute the equilibrium abundances of sulfur species along the $T$–$P$ profile in order to identify the most abundant sulfur-bearing species. We consider species H$_2$S, HS, H$_2$S$_2$, CH$_3$SH, S, S$_2$, SO, SO$_2$, CS, CS$_2$, COS, and SN. The results are shown in Figure 3. For solar composition atmospheres with $T_{eq}$ = 500 K, 1000 K, and 1500 K, H$_2$S is the dominant species at pressure levels between $1 \times 10^{-4}$ bar and $1 \times 10^{-6}$ bar. For solar composition atmospheres with $T_{eq}$ = 2000 K, H$_2$S is the dominant species below 0.01 bar. Above this level, atomic S is the dominant species. Since vertical mixing has the effect of homogenizing the abundances, the addition of vertical mixing into the model is not expected to change the result for H$_2$S. However, we ignore the effect of photochemistry, which may affect the vertical profile at low pressure levels. Zahnle et al. (2009, 2016) have done photochemical modeling of sulfur species in the atmospheres of hot Jupiters and warm Jupiters. From their calculations, H$_2$S is largely photodissociated at $P \geq 0.01$ bar, but remains the dominant sulfur carrier at $P \lesssim 0.01$ bar. Zahnle et al. (2009) showed that the abundances are not sensitive to temperature and insolation over the parameter ranges ($T = 1200 \sim 2000$ K and $I = 1 \sim 1000$). Following those results, we assume that H$_2$S is the dominant sulfur-bearing species below 0.01 bar in our calculations.

3.3. Results for C/N/O/H Species

It is necessary to carefully model the contribution of C/N/O/H-bearing species to the transit spectra if we want to identify spectral features of H$_2$S and PH$_3$. Molecules such as H$_2$O or CO are more abundant than H$_2$S and PH$_3$, and thus contribute the most to the transit spectra. In order to find molecules that are more abundant than H$_2$S and PH$_3$, we performed independent calculations for C/N/O/H chemistry. Our results are in general consistency with those reported in the literature (e.g., Moses et al. 2011; Venot et al. 2012; Hu & Seager 2014; Miguel & Kaltenegger 2014). We find the major C/N/O/H-bearing molecules are H$_2$O, CO, CH$_4$, CO$_2$, N$_2$, NH$_3$, and HCN. These molecules must be included in the spectra calculation in order to cover all important opacity sources. We present our computed vertical profile of these molecules along with PH$_3$ and H$_2$S in Figure 4. The results are shown for four different levels of stellar insolation.

For solar composition atmospheres with $T_{eq}$ = 500 K, the most abundant species are H$_2$O, CH$_4$, NH$_3$, H$_2$S, N$_2$, and PH$_3$. The abundances are nearly homogeneous in the vertical direction down to $\sim 10$ bar. The atmosphere is strongly homogenized by vertical mixing, and species are in a disequilibrium state. CH$_4$ is the primary carbon-bearing species, H$_2$O is the primary oxygen-bearing species, NH$_3$ is the primary nitrogen-bearing species, H$_2$S is the primary sulfur-bearing species, and PH$_3$ is the primary phosphorus-bearing species.
For solar composition atmospheres with \( T_{\text{eq}} = 1000 \text{ K} \), the most abundant species are H\(_2\)O, CO, CH\(_4\), N\(_2\), NH\(_3\), H\(_2\)S, HCN, and PH\(_3\). Abundances are nearly homogeneous down to \( \approx 10 \) bar due to the effect of vertical mixing. CO carries about \( 2/3 \) of the total carbon abundance, and CH\(_4\) carries the other \( 1/3 \). H\(_2\)O is the dominant oxygen-bearing species. N\(_2\) and NH\(_3\) each carry about \( 1/2 \) of the total nitrogen abundance. This temperature marks the transition temperature for CO/CH\(_4\) conversion and N\(_2\)/NH\(_3\) conversion. For \( T_{\text{eq}} \lesssim 1000 \) K, CH\(_4\), and NH\(_3\) are the major carbon and nitrogen carriers; for \( T_{\text{eq}} \gtrsim 1000 \) K, CO, and N\(_2\) are the major carbon and nitrogen carriers.

For solar composition atmospheres with \( T_{\text{eq}} = 1500 \text{ K} \), the most abundant species are CO, H\(_2\)O, N\(_2\), and H\(_2\)S. CO is the primary carrier of both oxygen and carbon. The rest of the oxygen is in the form of H\(_2\)O. N\(_2\) is the primary carrier of nitrogen. CH\(_4\) and NH\(_3\) are much less abundant in the atmospheres.

For solar composition atmospheres with \( T_{\text{eq}} = 2000 \text{ K} \), the most abundant species are CO, H\(_2\)O, N\(_2\), and H\(_2\)S. The abundances are nearly in chemical equilibrium due to the high temperature. CH\(_4\), NH\(_3\), and PH\(_3\) are much less abundant.

### 3.4. Influence of Insolation

There are three regimes for the abundance profiles depending on the level of insolation. For highly irradiated atmospheres (e.g., \( T_{\text{eq}} > 1500 \) K), the chemical abundances are in local chemical equilibrium. Therefore, when doing retrieval on atmosphere composition and \( T-P \) profiles, assumptions of chemical equilibrium should be valid. For moderately irradiated atmospheres (e.g., \( T_{\text{eq}} < 1000 \) K), the vertical mixing tends to produce homogeneous abundances in the atmospheres. It should be valid to assume a constant mixing ratio profile when doing atmospheric retrieval. In between is the transition regime where both chemical conversions and vertical mixing are important in the atmospheres. In this regime, the abundance profiles will depend on the vertical eddy diffusion coefficient as well as the \( T-P \) profile. In Figure 5 we show the computed abundances at 1 bar as a function of \( T_{\text{eq}} \). From the figure, CO,
CO$_2$, and N$_2$ abundances increase as $T_{\text{eq}}$ increases, while CH$_4$, NH$_3$, and PH$_3$ abundances decrease. H$_2$O and H$_2$S abundances remain approximately unchanged relative to the change of $T_{\text{eq}}$. The HCN abundance increases and then decreases as $T_{\text{eq}}$ increases.

4. Results for Noiseless Spectra Modeling

In this section, we present the synthetic primary and secondary transit spectra for three fiducial planets ($T_{\text{eq}} = 500$ K, 1000 K, and 1500 K). The parameters for the planets are summarized in Table 2. The planets are solar composition Jupiter-size planets with different levels of insolation. Their vertical $T$–$P$ profiles are presented in Figure 1 and their vertical abundance profiles are presented in Figure 4. The molecules included are H$_2$O, CO, CH$_4$, CO$_2$, N$_2$, NH$_3$, HCN, H$_2$S, and PH$_3$.

The spectral features for H$_2$O, CO, CH$_4$, CO$_2$, and NH$_3$ have been explored in the literature (e.g., Greene et al. 2016). From our calculations in Section 3, we found that H$_2$S is the primary carrier of sulfur for all different equilibrium temperatures; PH$_3$ is the primary carrier of phosphorus for $T_{\text{eq}} < 1000$ K; HCN has a mixing ratio of 1 ppm for solar composition atmospheres with $T_{\text{eq}} = 1000$ K. These molecules are potentially identifiable from the transit spectra. Although HCN is not the primary carrier of either carbon or nitrogen, it is a disequilibrium species and its abundances are indicative of the strength of vertical mixing. Therefore, we also investigate the spectral feature of HCN and see if the JWST can potentially detect HCN.

Here we focus on identifying spectral features for PH$_3$, H$_2$S, and HCN in the primary and secondary transit spectra of solar composition Jupiter-size planets. We compare the spectra of all nine species with one specific species excluded, in order to find the spectral feature of that species.

4.1. PH$_3$

Figure 6 we present the primary and secondary transit spectra for the planetary systems in Table 2, with $T_{\text{eq}} = 500$, 1000, and 1500 K. The planets are assumed to have solar composition atmospheres. The vertical abundance profiles are taken from...
Figure 4. We compare the spectra simulated with all species, and the spectra simulated with all species except PH3. The difference between these two spectra indicates the absorption from PH3. For a solar composition atmosphere with $T_{eq} = 500$ K, the absorption from PH3 occurs between 4 and 5 μm. The absorption depth is about 40 ppm in the primary transit spectra, and about 20 ppm in the secondary transit spectra. For the atmosphere with $T_{eq} = 1000$ K, the absorption is about 5 ppm in the primary transit spectra, while in the secondary transit spectra it is too small to be seen in the figure. For the atmosphere with $T_{eq} = 1500$ K, there is no apparent PH3 absorption feature in the spectra.

The lack of a PH3 spectral feature for the solar composition atmospheres with $T_{eq} = 1000$ K and 1500 K is due to the thermal decomposition of PH3 under high temperatures. From Figure 2, for the atmospheres with $T_{eq} = 500$ K, almost all of the phosphorus is in the form of PH3, while for the atmospheres with $T_{eq} = 1000$ K and 1500 K, most of the phosphorus is in the form of P2 and PH2. Therefore, the spectral features of PH3 are only expected in moderately irradiated atmospheres.

4.2. H2S

In Figure 7, we present the synthetic primary and secondary transit spectra for the solar composition atmospheres with $T_{eq} = 500$, 1000, and 1500 K in Table 2. We compare the spectra simulated with all species and the spectra simulated with all species except H2S. For the atmospheres with $T_{eq} = 500$ K, the absorption depth is very small. In the primary transit spectra, there is a 5 ppm absorption at 2.6 ~ 2.8 μm and a 10 ppm absorption at 3.9 ~ 4.3 μm. In the secondary transit spectra, there is a 10 ppm absorption at 3.9 ~ 4.3 μm. For the atmospheres with $T_{eq} = 1000$ K, the absorption depths are also very small for both primary transit and secondary transit spectra. For the atmospheres with $T_{eq} = 1500$ K, the absorption depths are much bigger. In the primary transit spectra, the absorption depth is about 15 ppm at 2.6 ~ 2.8 μm, and 100 ppm at 3.5 ~ 4.1 μm. In the secondary spectra, the absorption depth is about 10 ppm at 2.6 ~ 2.8 ppm and 100 ppm at 3.5 ~ 4.1 μm.
The spectral feature of H2S is more prominent in highly irradiated atmospheres. What determines the relevance of H2S in the spectra is other species. In cold atmospheres, H2S has to compete with the more abundant NH3 and CH4 to absorb photons while in the hottest case those two molecules are less abundant, leaving more space to H2S to absorb photons and be seen in the spectra. Another factor that may contribute is the larger pressure scale height in hotter atmospheres.

### 4.3. HCN

In Figure 8 we present the synthetic primary and secondary transit spectra for solar composition atmospheres with \( T_{\text{eq}} = 500 \), 1000, and 1500 K listed in Table 2. For the atmospheres with \( T_{\text{eq}} = 500 \) and 1500 K, there is little absorption from HCN, mainly because the mixing ratio of HCN is very low, as shown in Figure 4. For the atmospheres with \( T_{\text{eq}} = 1000 \) K, there are small absorption features between 12 and 16 \( \mu \)m. The absorption depth in the primary transit spectra is about 15 ppm, and in the secondary transit spectra it is about 80 ppm.

### 5. Results for JWST Transit Spectra Modeling

In this section, we model the JWST spectra for primary and secondary transit observations. The instruments and modes for transit observations are shown in Table 1. The wavelength range modeled is between 2.5 \( \mu \)m and 11 \( \mu \)m. In Section 4, we identified spectral features for PH3, H2S, and HCN. The spectral feature of PH3 is between 4 \( \mu \)m and 5 \( \mu \)m, that of H2S is between 3 \( \mu \)m and 4 \( \mu \)m, and that of HCN is between 12 \( \mu \)m and 16 \( \mu \)m. The feature of HCN is beyond the limit of MIRI LRS mode (Beichman et al. 2014). In this paper, we focus on the spectral features of H2S and PH3.

#### 5.1. Results for JWST Noise Modeling

We used both PandExo and the Greene et al. (2016) noise model to compute the error on the spectrum. In Figure 9, we show the noise level as a function of wavelength for a range of instrument modes covering wavelengths ranging from 2.5 to 11 \( \mu \)m. The parameters of the planetary system being modeled are listed in Table 2. We assume two transits, each with equal in-transit and out-transit integration time. The transit duration is 7.2 hr, and the total (transit + baseline) time is 14.4 hr. The number of groups and number of integrations are optimized by PandExo. Besides the results calculated using PandExo, we also compute the error using the Greene et al. (2016) noise model for the NIRCam F322W2 mode and F444W mode. The Greene et al. (2016) model gives slightly lower noise levels, but similar to the results from PandExo.

#### 5.2. PH3

In Figure 10, we show the synthetic primary and secondary transit spectra with simulated JWST noise and compare the spectra with and without PH3. The planetary system being modeled is listed in Table 2 with \( T_{\text{eq}} = 500 \) K. The observation
parameters are summarized in Table 3. The spectral absorption feature of PH$_3$ is between 4.0 and 4.7 $\mu$m. In the primary transit spectra, the absorption depth for PH$_3$ is approximately one standard deviation of the noise. Since there are $\sim$10 measurements within this feature, the significance level for detecting PH$_3$ is more than 3$\sigma$. In order to cover the 4.0–4.7 $\mu$m wavelength range, the NIRCam LW grism mode with F444W filter can be used in the observation. To achieve this level of error, two transits are needed. The integration time for each transit is about 7.2 hr. We assume equal integration time for
in-transit and out-transit, and that leads to a total observing time of 7.2 hr × 2 in- and out-transit integration × 2 transits = 28.8 hr. The absorption feature in the secondary transit spectra is harder to detect since the absorption depth from PH₃ is only about half the standard deviation of the noise. Therefore, it is most effective for detecting PH₃ to use the primary transit spectra with the NIRCam LW grism mode and F444W filter, and get the spectra between 3.9 μm and 5.0 μm. However, the
feature is very weak and requires long integration time (7.2 hr) to achieve the error level shown in Figure 10. Since CH$_4$ absorption is strong between 4 and 5 $\mu$m, additional observation using the NIRCam LR F444W may be needed to break the degeneracy between the PH$_3$ absorption and CH$_4$ absorption. For higher equilibrium temperatures ($T_{eq} > 1000$K), the spectral feature of PH$_3$ is below 5 ppm, thus the JWST is unlikely to detect it.

5.3. H$_2$S

In Figure 11, we show the synthetic primary and secondary transit spectra with simulated JWST noise and compare the...
1500eq following the recipe in Greene et al. summarized in Table 4. In the primary transit spectra, the K-band magnitude of 6.8. The observational parameters are the noise. The shape of the absorption feature can be resolved PandExo. The target is a Noise levels for different observing modes as calculated using Figure 9.

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While for atmospheres with lower equilibrium equilibrium is below 10 ppm and the peak of water features, in order to verify the spectra features of H2S, one can use the NIRCam LW grism spectral feature of H2S, one can use the NIRCam LW grism

mode as in Section 5.2, to obtain 24.0 hr. Since H2O absorption is also important in the 2.4–4.0 μm region, NIRISS SOSS mode observations may be needed to determine the base and peak of water features, in order to verify the spectra features of H2S. We only show the case for Teq = 1500 K in Figure 11, while for atmospheres with lower equilibrium equilibrium temperature (500 K, 750 K, 1000 K), the absorption from H2S is below 10 ppm and the JWST is unlikely to detect it.

6. Discussion

In this paper, we investigate the phosphorus and sulfur chemistry in solar composition atmospheres of Jupiter-size planets with the effect of vertical mixing, but no photochemistry. We find PH3 is the primary carrier of phosphorus in solar composition atmospheres with Teq ~ 500 K. For solar composition atmospheres with 1000 K \(<\) Teq \(\lesssim\) 1500 K, the primary carrier of phosphorus is P2. For very highly irradiated solar composition atmospheres (Teq \(\sim\) 2000 K), phosphorus is mainly sequestered in PH2 and PH. For sulfur chemistry, we find H2S is the primary carrier of sulfur for solar composition atmospheres with Teq \(<\) 2000 K. We also investigate the chemistry of C/N/O/S-bearing species. The most abundant carbon- and nitrogen-bearing species depend on the level of insolation. For the atmosphere with Teq \(<\) 1000 K, H2O, CH4, and NH3 are the most abundant molecules, while for that with Teq > 1000 K, H2O, CO, and N2 are the most abundant. With the computed abundance profiles for H2O, CO, CO2, CH4, NH3, N2, H2S, PH3, and HCN, we model the synthetic primary and secondary transit spectra and identify spectral features for PH3, H2S, and HCN. The detectibility of PH3 and H2S with JWST transit observations are evaluated by simulating the noise levels. We find PH3 can be detected in the primary transit spectra of solar composition atmospheres with Teq \(\lesssim\) 500 K using the JWST NIRCam LW F444W mode, and the total observing time needs to be \(\sim\) 28.8 hr. H2S can be detected in both primary and secondary spectra of solar composition Jupiter-size planets with Teq \(\gtrsim\) 1500 K using the JWST NIRCam LW F322W2 mode with a total observing time of 24.0 hr.

Our results imply that H2S is an important absorber in the 3–4 μm region for solar composition atmospheres with Teq > 1500 K. Failure to include H2S in the retrieval analysis of JWST spectra may lead to non-fitting of the spectra or, more detrimentally, to wrong abundances of other molecules. The effect can only be determined by a full retrieval analysis, which is beyond the scope of this paper. However, we highlight the importance of H2S in the 3–4 μm region of transit spectra. PH3 shows few features on the transit spectra of hot Jupiter’s atmospheres (Teq > 1000 K), but shows absorption features between 4 and 5 μm in moderately irradiated atmospheres (Teq \sim\) 500 K). Retrieval of molecular abundances for moderately irradiated planets needs to consider the absorption from PH3.

We also considered HCN in our model since we find it is non-negligible for planets with Teq = 1000 K, with a mixing ratio of 1 ppm. Since photochemistry also produces HCN, we expect more HCN in the upper atmospheres. The absorption features of HCN are mainly between 12 and 16 μm. This wavelength range is beyond the coverage of the MIRI LRS siltless mode. Therefore, we did not discuss further the detectability of HCN with the JWST.

Our modeling of JWST transit spectra makes several simplifications, and we discuss the influences below.

1. The transit spectra of PH3 and H2S are complicated by the presence of clouds or hazes in the atmospheres of extrasolar giant planets. Current observations indicate that clouds or hazes are ubiquitous in the atmospheres of exoplanets (e.g., Pont et al. 2008; Deming et al. 2013; Kreidberg et al. 2014b). Clouds and hazes reduce the

Table 3

| Observing Parameters for the Planetary System in Table 2 with Teq = 500 K |
|-------------------------------------------------------------|
| No. of Groups Per Integration | No. of Integrations Per Occultation | No. of Transits | Observing Efficiency | Transit Duration |
|-------------------------------|------------------------------------|----------------|----------------------|------------------|
| NIRCam F322W2                 | 12                                 | 11744          | 2                    | 84.6%            | 7.2 hr |
| NIRCam F444W                  | 25                                 | 5872           | 2                    | 92.3%            | 7.2 hr |
| MIRI LRS                      | 8                                  | 36340          | 2                    | 77.8%            | 7.2 hr |

Figure 9. Noise levels for different observing modes as calculated using PandExo. The target is a K = 6.8 G-type star. The transit duration for this calculation is 7.2 hr. As a comparison, we also plot the error level as calculated following the recipe in Greene et al. (2016).
amplitude of transmission spectra and thus decrease the molecular spectral features with a negative effect on the determination of molecular abundances. The emission spectra are less affected by the clouds and hazes (e.g., Line et al. 2016). The spectral absorption depth of H$_2$S in the emission spectra is much greater than the expected noise level. Therefore, the H$_2$S feature can be detected using the emission spectra for atmospheres with clouds and haze. However, the absorption depth of PH$_3$ in the emission spectra is smaller than the expected noise level, therefore, the detection of PH$_3$ will be difficult if the atmosphere is covered by clouds or haze.

2. We neglect the effect of photochemistry on the primary and secondary transit spectra. Photochemistry affects the spectra in two ways. First, it changes the abundance profiles in the upper atmospheres. The effect on the

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Table 4

| Observing Parameters for the Planetary System in Table 2 with $T_{\text{eff}} = 1500$ K |
|---------------------------------------------|------------------|-----------------|----------------|----------------|
| No. of Groups Per Integration | No. of Integrations Per Occultation | No. of Transits | Observing Efficiency | Transit Duration |
|-------------------------------|-----------------------------------|----------------|----------------------|------------------|
| NIRCam F322W2                | 12                                | 3916           | 5                    | 84.6%            | 2.4 hr          |
| NIRCam F444W                 | 25                                | 1958           | 5                    | 92.3%            | 2.4 hr          |
| MIRI LRS                     | 8                                 | 12112          | 5                    | 77.8%            | 2.4 hr          |

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Figure 10. Synthetic transmission and emission spectra with simulated JWST noise for the planet presented in Table 2 with $T_{\text{eq}} = 500$ K. The blue curve is the binned spectra simulated including all nine species, and the red curve is the binned spectra simulated including all nine species except PH$_3$. The error bars in the plot indicate a $\sigma$ Gaussian noise level simulated for the JWST instrument modes summarized in Table 1. The total required observing time is 28.8 hr.

Figure 11. Synthetic transmission and emission spectra with simulated JWST noise for the planet presented in Table 2 with $T_{\text{eq}} = 1500$ K. The blue curve is the binned spectra simulated including all nine species in Figure 4, and the red curve is the binned spectra simulated including all nine species except H$_2$S. The error bars in the plot indicate a $\sigma$ Gaussian noise level simulated for JWST instrument modes summarized in Table 1. The total required observing time is 24.0 hr.
The planet being modeled has a solar composition atmosphere with two different levels of vertical mixing. Solid lines correspond to $K_{\text{eddy}} = 1.0 \times 10^8 \text{ cm}^2 \text{s}^{-1}$, and dashed lines correspond to $K_{\text{eddy}} = 1.0 \times 10^9 \text{ cm}^2 \text{s}^{-1}$. The planet being modeled has a solar composition atmosphere with $T_{\text{eq}} = 500 \text{ K}$.

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**7. Conclusions**

In this paper, we model phosphorus and sulfur chemistry in the solar composition atmospheres of Jupiter-size planets with different levels of insolation. We find PH$_3$ is the primary carrier of phosphorus for atmospheres with $T_{\text{eq}} < 1000 \text{ K}$; P$_2$ is the primary carrier of phosphorus for $T_{\text{eq}} > 1000 \text{ K}$ and smaller than 1500 K; PH and PH$_2$ are the primary phosphorus-bearing species for $T_{\text{eq}} > 2000 \text{ K}$. We also compute the abundance profiles of major H/C/N/O/S-bearing species. With the computed vertical profiles for H$_2$O, CO, CO$_2$, CH$_4$, NH$_3$, N$_2$, HCN, H$_2$S, and PH$_3$, we compute the synthetic primary and secondary transit spectra. We focus on identifying the spectral features for H$_2$S, PH$_3$, and HCN. We find spectral features of PH$_3$ at 4.0 $\sim$ 4.8 $\mu$m, H$_2$S at 2.5 $\sim$ 2.8 $\mu$m and 3.5 $\sim$ 4.1 $\mu$m, HCN at 12 $\sim$ 16 $\mu$m. We then simulated the noise for transits with $K = 6.8 \text{ G star}$, and evaluated the detectability of PH$_3$ and H$_2$S with JWST observations. We find PH$_3$ can be detected for solar composition atmospheres with $T_{\text{eq}} \sim 500 \text{ K}$ using the NIRCam LW F444W mode with a total observing time of 28.8 hr. We find H$_2$S can be detected for solar composition atmospheres with $T_{\text{eq}} > 1500 \text{ K}$ using the NIRCam LW grism F322W2 mode with a total observing time of 24.0 hr. The detection of PH$_3$ and H$_2$S is complicated by the presence of clouds and hazes. In this case, H$_2$S may still be detected in the emission spectra, but PH$_3$ is difficult to detect due to the diminished spectral features arising from clouds and hazes.

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Software: SAO98 (Traub & Stier 1976; Traub & Jucks 2002; Kaltenegger & Traub 2009), PandExo (Batalha et al. 2017).

References

Agúndez, M., Parmentier, V., Venot, O., Hersant, F., & Selsis, F. 2014, A&A, 564, A73
Asplund, M., Grevesse, N., Sauval, A. J., & Scott, P. 2009, ARA&A, 47, 481
Batalha, N. E., Mandell, A., Pontoppidan, K., et al. 2017, PASP, 129, 064501
Beichman, C., Benneke, B., Knutson, H., et al. 2014, PASP, 126, 1134
Burcat, A., & Rusie, B. 2005, Third millenium ideal gas and condensed phase thermochemical database for combustion with updates from active thermochemical tables, (Argonne National Laboratory Argonne, IL)
Burrows, A. S. 2014, PNAS, 111, 12601
Charbonneau, D., Brown, T. M., Noyes, R. W., & Gilliland, R. L. 2002, ApJ, 568, 377
Crouzet, N., McCullough, P. R., Deming, D., & Madhusudhan, N. 2014, ApJ, 795, 166
Dean, A. M., & Bozzelli, J. W. 2000, Gas-Phase Combustion Chemistry (New York: Springer), 125
Deming, D., Wilkins, A., McCullough, P., et al. 2013, ApJ, 744, 95
Evans, T. M., Sing, D. K., Wakeford, H. R., et al. 2016, ApJL, 822, L4
Fletcher, L. N., Orton, G. S., Teanby, N. A., & Irwin, P. G. J. 2009, Icar, 202, 543
Beichman, C., Benneke, B., Knutson, H., et al. 2014, PASP, 126, 1134

Figure 12. Comparison of the vertical profiles of major molecules between two different levels of vertical mixing. Solid lines correspond to $K_{\text{eddy}} = 1.0 \times 10^8 \text{ cm}^2 \text{s}^{-1}$, and dashed lines correspond to $K_{\text{eddy}} = 1.0 \times 10^9 \text{ cm}^2 \text{s}^{-1}$. The planet being modeled has a solar composition atmosphere with $T_{\text{eq}} = 500 \text{ K}$. 

secondary transit spectra is expected to be small since the absorption in the planetary emission spectra occurs near the 1 bar level. There may be some effects on the primary transit spectra since the light travels a longer path in the transmission spectra than in the emission spectra. Most absorption should still be from more abundant molecules (e.g., H$_2$O, CH$_4$, CO, NH$_3$, H$_2$S, PH$_3$) in the atmospheres. The photochemical products (C$_2$H$_6$, C$_2$H$_2$, HCN) may contribute a small amount of absorption and it is unclear whether the JWST is able to detect these photochemical species. The second effect of photochemistry is the production of hazes. The flat transmission spectra for hot Jupiters and super-Earths may be caused by photochemical hazes in the upper atmospheres. The effect of hazes on the spectra is the shrinking of the spectral amplitude, making the detection of molecules more difficult.

3. We assumed a single value of eddy diffusion coefficient in all our simulations. The strength of vertical mixing is highly uncertain on exoplanets. In Figure 12, we compare the abundances calculated using $K_{\text{eddy}} = 1.0 \times 10^8 \text{ cm}^2 \text{s}^{-1}$ and $1 \times 10^9 \text{ cm}^2 \text{s}^{-1}$. Molecular species such as H$_2$O and CH$_4$ are largely unaffected by the strength of vertical mixing since they are the dominant species throughout the atmosphere. For disequilibrium species such as CO and CO$_2$, the effect is to shift the abundances in the same direction. CO is increased by less than one order of magnitude due to the change of $K_{\text{eddy}}$.

4. In this paper, we restrict our study to solar composition atmospheres. However, the elemental composition of exoplanetary atmospheres can be diverse. Jupiter’s atmosphere is enriched in heavy elements relative to solar. It is reasonable to assume extrasolar giant planets have similar enrichment. If all the heavy elements (C, N, O, S, P) are enriched similarly, the shape of the abundance profiles is preserved with only an upward shift. We expect the transmission spectra to have smaller spectral amplitudes since the pressure scale height is expected to be smaller for higher molecular mass atmospheres. This has an adverse effect on detecting molecules. However, higher mean molecular weight often correlates with smaller mass. For Neptune-size planets, the smaller gravity means higher scale height, and larger spectral amplitudes. The opposite effect of gravity and molecular mass on the spectra should rely on detailed modeling of Neptune-size exoplanets, which will be discussed in our next paper. If carbon and oxygen are not similarly enriched, for example C/O different than solar, the composition will be dramatically different for hot atmospheres.
