A PHOTOCHEMICAL MODEL FOR THE CARBON-RICH PLANET WASP-12b

Ravi Kumar Kopparapu1,3, James F. Kasting1,3, and Kevin J. Zahnle2

1 Department of Geosciences, Penn State University, 443 Deike Building, University Park, PA 16802, USA
2 NASA Ames Research Center, MS 245-3, Moffett Field, CA 94035, USA

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ABSTRACT

The hot-Jupiter WASP-12b is a heavily irradiated exoplanet in a short-period orbit around a G0-star with twice the metallicity of the Sun. A recent thermochemical equilibrium analysis based on Spitzer and ground-based infrared observations suggests that the presence of CH4 in its atmosphere and the lack of H2O features can only be explained if the carbon-to-oxygen ratio in the planet’s atmosphere is much greater than the solar ratio ([C]/[O] = 0.54). Here, we use a one-dimensional photochemical model to study the effect of disequilibrium chemistry on the observed abundances of H2O, CO, CO2, and CH4 in the WASP-12b atmosphere. We consider two cases: one with solar [C]/[O] and another with [C]/[O] = 1.08. The solar case predicts that H2O and CO are more abundant than CO2 and CH4, as expected, whereas the high [C]/[O] model shows that CO, C2H2, and HCN are more abundant. This indicates that the extra carbon from the high [C]/[O] model is in hydrocarbon species. H2O photolysis is the dominant disequilibrium mechanism that alters the chemistry at higher altitudes in the solar [C]/[O] case, whereas photodissociation of C2H2 and HCN is significant in the super-solar case. Furthermore, our analysis indicates that C2H2 is the major absorber in the atmosphere of WASP-12b and the absorption features detected near 1.6 and 8 μm may be arising from C2H2 rather than CH4. The Hubble Space Telescope’s WFC3 can resolve this discrepancy, as C2H2 has absorption between 1.51 and 1.54 μm, while CH4 does not.

Key word: planetary systems

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1. INTRODUCTION

The discovery of the first transiting planet, HD 209458b (Charbonneau et al. 2000; Henry et al. 2000), opened up a new window to observe and study extrasolar planetary systems. By combining transit data with radial velocity measurements, one can determine the mass and radius of a transiting planet (Mazeh et al. 2000; Laughlin et al. 2005a, 2005b; Holman & Murray 2005; Agol et al. 2005). Apart from these physical properties of the planet, it has also been shown that the transmission and emission spectra from ground- and space-based observations can be used to place constraints on the atmospheric composition (Charbonneau et al. 2002; Vidal-Madjar et al. 2003, 2004; Tinetti et al. 2007; Snellen et al. 2008; Swain et al. 2009a, 2009b), brightness temperature (Deming et al. 2005; Charbonneau et al. 2005), and even day–night temperature contrast (Knutson et al. 2007) of transiting planets. To date, most of the planets discovered are “hot Jupiters” (Collier-Cameron 2002), but recently terrestrial mass planets have also been discovered (Léger et al. 2009; Charbonneau et al. 2009).

The observational determination of chemical species that exist in the outer atmospheric layers of transiting planets provides us with an opportunity to investigate the underlying chemistry. Typically, thermochemical equilibrium has been assumed in models of exoplanet atmospheres (Burrows et al. 1997; Fortney et al. 2005; Seager et al. 2005; Marley et al. 2007; Madhusudhan et al. 2011a). This is a good assumption at the high temperatures and high pressures prevailing in the lower layers of close-in gas giants. Disequilibrium caused either by the UV flux of the host star (photochemistry) or by eddy and molecular diffusion (vertical transport) has been considered in some models (Liang et al. 2003; Cooper & Showman 2006; Zahnle et al. 2009a, 2009b; Line et al. 2010; Moses et al. 2011). These studies showed that disequilibrium mechanisms can be significant in determining the chemical composition of hot Jupiters.

Here, we investigate the significance of photochemistry and transport in determining the abundances of major species, H2O, CO, and CH4, observed in the dayside thermal emission spectrum (Madhusudhan et al. 2011a; Croll et al. 2011) of the transiting hot-Jupiter WASP-12b (Hebb et al. 2009). At the time of its discovery, WASP-12b was the most highly irradiated exoplanet (T > 2500 K) with the largest radius (1.79 RJ) and the shortest orbital period (1.09 days). Recently, Madhusudhan et al. (2011a) reported that Spitzer Space Telescope observations show strong absorption features of CH4 in the 3.6 μm channel and CO in the 4.5 μm channel, whereas weaker features were observed in the 5.8 μm channel where H2O absorbs. This suggests that CH4 and CO are dominant and that H2O is less abundant in the atmosphere of WASP-12b. Assuming equilibrium chemistry and solar [C]/[O] = 0.54, H2O and CO should be the dominant species and CH4 and CO2 should be the least abundant. Therefore, a solar [C]/[O] ratio is ruled out. Madhusudhan et al. (2011a) conclude that to explain the observed abundance of CH4 and CO, WASP-12b must have [C]/[O] ≥ 1, implying that it is a carbon-rich planet.

WASP-12b is one of the most highly irradiated known exoplanets, so photochemistry could play an important role in determining its atmospheric composition. Assuming [C]/[O] = 1, analysis of observations using equilibrium chemistry models suggests mixing ratios (with respect to molecular hydrogen) less than 10−7 for H2O, greater than 10−4 for CO, ~10−5 for CH4, and less than 10−5 for CO2. Our goal in this study is to examine how the vertical distribution and abundances of these species are affected by photochemistry. Specifically, we wish
to determine whether photochemical models make qualitatively different predictions from those of thermochemical equilibrium models. We consider two cases, one with solar \([C]\) and another with \([C]\) when not available:

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The reverse rate coefficients, \(k_r\), at each temperature level (grid) were calculated assuming thermodynamic equilibrium (see the discussion in Section 2). For three-body reactions, the first and second row represent the low- and high-pressure rate limits, respectively.

Notes. Only the forward rate constants are given as we calculate reverse rate constants from the forward rate assuming thermodynamic equilibrium (see the discussion in Section 2). For three-body reactions, the first and second row represent the low- and high-pressure rate limits, respectively.

Two-body reaction rates are in \(\text{cm}^3 \text{s}^{-1}\); three-body rates are in \(\text{cm}^6 \text{s}^{-1}\).

This table is available in its entirety in a machine-readable form in the online journal. A portion is shown here for guidance regarding its form and content.)

### Table 1

| Number | Reactants | Products | Rate* | Reference |
|--------|-----------|----------|-------|-----------|
| 1      | \(H + H + M\) | \(H_2 + M\) | \(8.8 \times 10^{-33}(T/298)^{-0.06}\) | Baulch et al. (1992) |
| 2      | \(O + H + M\) | \(OH + M\) | \(4.3 \times 10^{-12}\) | Tsang & Hampson (1986) |
| 3      | \(H_2 + O\) | \(OH + H\) | \(3.5 \times 10^{-11}(T/298)^{6.67e^{-3160/T}}\) | Baulch et al. (1992) |
| 4      | \(H + OH + M\) | \(H_2O + M\) | \(6.6 \times 10^{-32}(T/298)^{-2.1}\) | Javoy (2003) |
| 5      | \(H_2 + OH\) | \(H_2O + H\) | \(2.7 \times 10^{-10}e^{-75/T}\) | Cobos & Troe (1985) |

Notes. Only the forward rate constants are given as we calculate reverse rate constants from the forward rate assuming thermodynamic equilibrium (see the discussion in Section 2). For three-body reactions, the first and second row represent the low- and high-pressure rate limits, respectively.

Two-body reaction rates are in \(\text{cm}^3 \text{s}^{-1}\); three-body rates are in \(\text{cm}^6 \text{s}^{-1}\).

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To be noted that one cannot simply calculate \(k_r\) as discussed above. This is because the rate coefficients are given in units applicable to number densities whereas the thermodynamic quantities (enthalpy, entropy, and Gibbs energies) are calculated at a reference pressure (usually 1 bar). For reactions that have different number of reactants and products, proper pressure terms must be added to obtain accurate rate coefficients. We have appropriately included these terms in our reverse rates. Discussion of these correction terms is given in Section 2.2 of Visscher & Moses (2011).

As lower boundary conditions, we fix the mixing ratios of the species at thermodynamic equilibrium values. Constant (zero) deposition velocities are assumed for the other species. The upper boundary condition is set to zero flux for all the long-lived species. A more detailed description of the numerical scheme employed in this model is given in Pavlov et al. (2001).

The vertical grid has 100 altitude levels, ranging from 0 km (lower boundary) to 12,800 km (upper boundary) in 128 km increments. The lower boundary pressure is set at 1 bar and the upper boundary is fixed at \(10^{-8}\) bar. Going to higher pressures is unnecessary, because the species profiles are already close to thermodynamic equilibrium well above the 1 bar level. For the temperature profile, we use one of the best-fit models from Madhusudhan et al. (2011a) which has no inversion (purple curve in their Figure 1). The pressure profile was recalculated from this temperature profile by assuming hydrostatic equilibrium and using the calculated mean molecular weights from the photochemical model. Vertical transport is parameterized as eddy diffusion, as is common in one-dimensional photochemical models. The dayside eddy diffusion profile from Figure 1 of Line et al. (2010), which is originally obtained from the vertical winds from HD 189733b GCM of Showman et al. (2009), is adopted. We have also performed sensitivity tests by varying eddy profiles, as discussed in Section 4. Both the temperature and eddy profiles in our photochemical model are shown in Figure 1.

For comparative purposes, we also calculate the thermodynamic equilibrium mixing ratios for all the species in the photochemical model at each altitude by solving simultaneously a system of chemical equilibrium equations. These equations require the total elemental abundances of carbon, oxygen, hydrogen, and nitrogen (as we consider only compounds from these elements) and Gibbs free energies as a function of temperature. Solar elemental abundances from Asplund et al. (2005)
are assumed to be our baseline values, but we report results for both solar [Cl]/[O] and $2 \times$ solar [Cl]/[O]. To calculate Gibbs free energies, the enthalpy of formation at the reference temperature (298 K) and entropy are needed. We then use the expressions given in Chase (1998, p. 16) to calculate Gibbs free energy of formation for each species.

We initially tested our model by attempting to reproduce the results of Line et al. (2010) for the hot-Jupiter planet HD189733b. The dayside temperature and eddy diffusion profiles were taken from their Figure 1. The lower boundary pressure was fixed at 10 bar. Both the thermochemical equilibrium and photochemical model results are shown in Figure 2 and in good agreement with the similar analyses of Line et al. (2010) and Moses et al. (2011). Moreover, our model maintains equilibrium concentrations for all the major species in the deeper levels ($\sim$10 bar), as it should at high temperatures and pressures.

The star WASP-12 is a G0 star$^6$ with an effective temperature of 6350 K and twice the solar metallicity (Hebb et al. 2009). To simulate its spectrum, we used a G0V star spectrum from Pickles’ stellar spectral flux library (Pickles 1998),$^7$ normalized to a solar flux of 1360 W m$^{-2}$ (the value at Earth’s orbit today). We then multiplied the flux at each wavelength by a value consistent with inverse square law of the distance to get the correct flux for WASP-12b. The Pickles spectra are normalized to 1 at 5556 Å. The fluxes from this dimensionless model spectrum are converted to W m$^{-2}$ nm$^{-1}$ by multiplying the following flux expression from Gray (1992):

$$\log F_{5556} = -0.40 V - 8.449,$$

where $F_{5556}$ is the flux at 5556 Å and $V$ is the visual magnitude of the star. For WASP-12, $V = 11.69$ (Hebb et al. 2009). In Figure 3, we show the G0V star spectrum along with F2V and the Sun. A fixed stellar zenith angle of 50° is assumed in all our models, the same value that is used in our models of Earth’s atmosphere (e.g., Pavlov et al. 2001). This value is close to the value of 48° used by Moses et al. (2011) to reproduce secondary transit spectra in the atmosphere of HD 189733b.

3. RESULTS

We consider two different cases. In the first, we assume [Cl]/[O] = 0.54 (solar) and in the second we assume [Cl]/[O] = 1.08 (twice solar). Figure 4 shows mixing ratio profiles of some of the major species in our model, plotted against pressure for solar [Cl]/[O] abundance. The lower boundary in both the models is kept at 1 bar pressure ($T = 2841$ K) as the observed spectral features mostly arise from pressures equal to or less than the 1 bar level (Fortney et al. 2005; Tinetti et al. 2007; Swain et al. 2009a; Madhusudhan et al. 2011a). Dashed lines represent the profile obtained from equilibrium chemistry, solid lines from our photochemical model, and filled squares represent mixing ratios of respective species at the lower boundary.

In the case of solar [Cl]/[O] (Figure 4), most of the oxygen and carbon is in H$_2$O and CO. The chemical loss timescale ($\tau_{chem}$) for H$_2$O, CO, and CO$_2$ is smaller than the transport timescale ($\tau_{num}$); hence, as altitude increases, the abundances stay at their equilibrium values until $\sim 10^{-5}$ bar (Prinn & Barshay 1977). Below this pressure level (i.e., at higher altitudes) H$_2$O gets photolyzed. H$_2$O photolyses at lower altitudes than does CO because the dissociation energy for H$_2$O (5.17 eV) is lower than that of CO (11.14 eV) (Yung & DeMore 1999, Table 2.4). To break this strong C–O bond, photons of wavelength $\leq 111.3$ nm are needed (H$_2$O needs photons of

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$^6$ http://www.superwasp.org/wasp_planets.htm

$^7$ http://cdsarc.u-strasbg.fr/viz-bin/Cat?J/PASP/110/863
Figure 2. Photochemical mixing ratio profiles of H$_2$O, CO, CH$_4$, and CO$_2$ derived from our model of the dayside atmosphere of HD 189733b. For comparison, see Line et al. (2010) and Moses et al. (2011).

(A color version of this figure is available in the online journal.)

Figure 3. Comparison of the normalized flux of a G0V stellar spectrum from Pickles’ (1998) stellar flux library (green curve), which is assumed for the star WASP-12, with an F2V star (top blue curve) and the Sun (red bottom curve). Inset figure shows the UV region.

(A color version of this figure is available in the online journal.)

wavelength $\lesssim 239.8$ nm to break its bond). CO photolysis is not simulated in our photochemical model and it can be a source of carbon and oxygen photochemistry at high altitudes (Line et al. 2010; Moses et al. 2011), but it should be relatively slow because of the small number of photons at these short wavelengths. By contrast, the photon flux is quite high at the longer wavelengths that can photolyze H$_2$O (green curve in Figure 3 inset).
Figure 4. Equilibrium (dashed) and photochemical (solid) mixing ratio profiles of major species, for [C]/[O] = 0.54 (the solar value). Filled squares represent equilibrium values at the lower boundary. The mixing ratios refer to volume mixing ratio. The helium abundance is 0.07836.

(A color version of this figure is available in the online journal.)

In the case of CO₂, the equilibrium abundance is maintained until 10⁻⁵ bar and is set by the following kinetic reactions that transfer oxygen from CO and H₂O to CO₂:

\[
\text{H}_2\text{O} + \text{H} \leftrightarrow \text{H}_2 + \text{OH} \quad (2)
\]

\[
\text{CO} + \text{OH} \leftrightarrow \text{CO}_2 + \text{H}. \quad (3)
\]

At altitudes above 10⁻⁵ bar, H₂O photolysis becomes the dominant source of OH production. The OH then combines with CO through Equation (3) to produce excess CO₂ (local maximum of solid light-blue curve > 10⁻⁵ bar). Above this level, CO₂ becomes less abundant because it is itself photolyzed.

The shape of the equilibrium profile for CH₄ can be understood from the following reaction:

\[
\text{CO} + 3\text{H}_2 \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad (4)
\]

and the corresponding equilibrium constant:

\[
K_{eq} = \frac{p_{\text{CH}_4}p_{\text{H}_2\text{O}}}{p_{\text{CO}}p_{\text{H}_2}^3}, \quad (5)
\]

where \(p_i\) represents the partial pressure of species \(i\). The partial pressure is related to the total pressure and volume mixing ratio as \(p_i = f_iP\). As pressure increases (going downward) from 10⁻⁸ bar, the denominator term on the right-hand side of Equation (5) increases. Temperature is constant in this region (see Figure 1), as is the H₂O/CO ratio. Thus, in order to maintain equilibrium CH₄ must increase with depth. Below 10⁻² bar, the temperature starts to increase with depth. CH₄ is more stable at lower temperatures and is also more sensitive to temperature changes than other species. Hence, it becomes less abundant in the 10⁻² to 10⁻¹ bar regime. As pressures above 10⁻¹ bar, the temperature again remains constant, so CH₄ must again increase with depth as it does in the upper atmosphere.

The CH₄ profile from the photochemical model (solid magenta curve in Figure 4) follows the equilibrium profile at pressures up to \(\approx 10^{-2}\) bar. Above this level, \(\tau_{\text{chem}} \sim \tau_{\text{trans}}\) (quench level) and CH₄ remains well mixed near its equilibrium value of 10⁻¹⁰. Photolysis of CH₄ occurs above 10⁻³ bar (see Figure 5) mainly through the following reactions:

\[
\text{CH}_4 + h\nu \rightarrow \text{CH}_2 + 2\text{H}, \quad (6)
\]

\[
\text{CH}_4 + h\nu \rightarrow \text{CH}_3 + \text{H}, \quad (7)
\]

\[
\text{CH}_4 + h\nu \rightarrow ^1\text{CH}_2 + \text{H}_2. \quad (8)
\]

Although H is produced through CH₄ photolysis, it is not enough to explain the increase in H abundance between 10⁻² and 10⁻³ bar (light-blue solid curve in Figure 4). This increase in H is mainly due to the production of OH through H₂O photolysis at this level, which then combines with the most abundant molecule in this atmosphere, H₂, through the reverse of reaction (2):

\[
\text{H}_2\text{O} + h\nu \rightarrow \text{H} + \text{OH}, \quad (9)
\]

\[
\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}. \quad (10)
\]

As the OH abundance increases, more H₂ is consumed and its mixing ratio decreases above 10⁻⁵ bar (solid black curve in Figure 4). Eventually, H₂O itself becomes depleted by photolysis, so the production of OH radical diminishes. At this point, H₂ asymptotically reaches a mixing ratio of 10⁻².

The increase in H also affects the atomic oxygen abundance (black solid curve in Figure 4) by the following reaction:

\[
\text{CO} + \text{H} \rightarrow \text{O} + \text{CH}. \quad (11)
\]

Note that CO photolysis, which is not included in our model, may dominate the above reaction in producing atomic oxygen.
Our analysis shows that, in the \([\text{C}/\text{O}] = 0.54\) case, the abundances of major species (Figure 4) in WASP-12b’s atmosphere are mainly determined by thermochemical equilibrium, with departures at high altitudes due to disequilibrium chemistry driven by H\(\text{2}O\) photolysis. This is not surprising considering that H\(\text{2}O\) is far more abundant than CH\(\text{4}\). The photolysis rates of H\(\text{2}O\) and CH\(\text{4}\) as a function of pressure (altitude) for solar (blue) and super-solar (red) \([\text{C}/\text{O}]\) are shown in Figure 5. In the solar case, at any given height, H\(\text{2}O\) is more rapidly photodissociated than is CH\(\text{4}\), as it is more abundant. In the super-solar \([\text{C}/\text{O}]\) case (Figure 6), C\(\text{2}H\text{2}\) is more abundant than either H\(\text{2}O\) or CH\(\text{4}\), and so it is photolyzed more rapidly at high altitudes.

Madhusudhan et al. (2011a) report that the spectrum obtained from the dayside multi-wavelength photometry of WASP-12b

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Figure 5. Photolysis rates of H\(\text{2}O\) and CH\(\text{4}\) for \([\text{C}/\text{O}] = 0.54\) (dashed, solar) and \([\text{C}/\text{O}] = 1.08\) (solid, super-solar) including C\(\text{2}H\text{2}\).

(A color version of this figure is available in the online journal.)

Figure 6. Mixing ratio profiles from equilibrium (dashed) and photochemical (solid) models for \([\text{C}/\text{O}] = 1.08\) (twice solar).

(A color version of this figure is available in the online journal.)
is best explained if one assumes \([C]/[O] \geq 1\), using chemical equilibrium models. Under this assumption, the atmosphere is depleted in \(H_2O\), enhanced in \(CH_4\), and rich in \(CO\). These equilibrium model profiles (dashed lines), along with our photochemical model results, for \([C]/[O] = 1.08\) are shown in Figure 6. In contrast to the solar \([C]/[O]\) model, most of the oxygen is now in \(CO\) (blue solid line), and \(CH_4\) (magenta curve) is more abundant than \(H_2O\) (red curve). The switchover from an atmosphere where \(H_2O\) and \(CO\) are the dominant species to one in which \(CH_4\) and \(CO\) become abundant happens precisely at \([C]/[O] = 1\). This transition is illustrated in Figure 7.

In Figure 6, the abundance of \(H_2O\) follows the equilibrium profile at pressures up to about \(10^{-2}\) bar in the \([C]/[O] = 1.08\) model. At that point, transport by eddy diffusion becomes faster than the chemical reaction timescale, so the equilibrium value is maintained until \(\sim 10^{-4}\) bar. Photolysis begins above this level and the abundance of \(H_2O\) decreases. The behavior of \(CH_4\) is similar to the solar \([C]/[O]\) case, though it is relatively more abundant in this high \([C]/[O]\) model. Note that for \(CH_4\) and \(H_2O\), the photochemical mixing ratios are not exactly equal to the equilibrium values below \(0.1\) bar. The reason is as follows. At high altitudes (above \(10^{-3}\) bar), atomic hydrogen (green solid curve in Figure 6) becomes a dominant species (more than \(H_2\)). Our photochemical model uses a minor constituent approximation for the diffusion coefficient in a binary mixture (Equation (15.29), Banks & Kockarts 1973), which clearly is not applicable to \(H\) at this level. Due to this approximation, the mixing ratio of \(H\) exceeds unity above \(10^{-6}\) bar, which is unphysical. Therefore, we renormalize the mixing ratios of each species in our photochemical model so that they sum to unity, and hence the equilibrium and photochemical profiles deviate slightly in the lower atmosphere. Note that this should not affect our conclusions in any way regarding which species are dominant (discussed in the next paragraph) in Wasp-12b’s high \([C]/[O]\) model.

As can be seen from Figure 6, and also pointed by J. Moses et al. (2011, private communication), the dominant hydrogen species (apart from \(H\) and \(H_2\)) in this model are HCN and \(C_2H_2\). Therefore, the photolysis of these two species drives the disequilibrium chemistry in the upper atmosphere. For example, in the solar model, the catalytic \(H_2\) destruction mechanism initiated by \(H_2O\) photolysis (Equations (9) and (10)) was used to explain the increase in \(H\) abundance shown in Figure 4 (green solid curve). A similar increase of \(H\) at high altitudes can be noticed in the high \([C]/[O]\) case. Reactions (9) and (10) require \(OH\) production through \(H_2O\) photolysis, which is negligible in the high \([C]/[O]\) model. Instead, the following reactions are important:

\[
\begin{align*}
C_2H_2 + h\nu & \rightarrow C_2H + H, \\
C_2H + H_2 & \rightarrow C_2H_2 + H, \\
HCN + h\nu & \rightarrow CN + H, \\
CN + H_2 & \rightarrow HCN + H.
\end{align*}
\] (12) (13) (14) (15)

The results of these reactions can be seen in Figure 6. At altitudes above \(\sim 10^{-2}\) bar, the photolysis of \(C_2H_2\) and \(HCN\) produces \(C_2H\), \(CN\), and \(H\) through the above reactions. An increase in \(H\) can be seen as a result. The abundances of \(CN\) and \(C_2H\) are not large enough below \(10^{-5}\) bar to have a significant effect on the mixing ratio of \(H_2\). Above this level, reactions (13) and (15) result in the decrease of \(H_2\) mixing ratio (solid black line in Figure 6) and corresponding increase of \(H\). Further up, \(C_2H_2\) and \(HCN\) become scarce and the production of \(C_2H\) and \(CN\) diminishes, which in turn reduces the rate of production of \(H\). Therefore, \(H\) assumes a nearly constant mixing ratio thereafter.

Based on their thermodynamic equilibrium calculations, Madhusudhan et al. (2011a) concluded that Wasp-12b is abundant in \(CH_4\) and deficient in \(H_2O\). Our analysis indicates...
that both the equilibrium and photochemical models predict C$_2$H$_2$ and HCN are more abundant than CH$_4$. Also, C$_2$H$_2$ has strong absorption in the range 2.98–3.1 μm and also between 7.2 and 7.9 μm, whereas CH$_4$ has absorption features between 3.2–3.45 μm and 7.3–8 μm. The short wavelength range for C$_2$H$_2$ has little overlap with the Spitzer 3.6 μm channel$^8$ but the longer wavelength range for both species overlaps with Spitzer’s 8 μm channel.$^9$ In order to determine which is the dominant absorber, we have calculated the optical depths of the C$_2$H$_2$ 7.5 μm band and the CH$_4$ 7.7 μm band as a function of pressure, as shown in Figure 8. Approximate band-averaged absorption coefficients for these features are 2 × 10$^{-19}$ cm$^2$ and 4 × 10$^{-19}$ cm$^2$, respectively.$^{10}$ The column depths are taken from our photochemical model. Clearly, C$_2$H$_2$ has a larger optical depth than CH$_4$ and is the dominant absorber. Note that, Madhusudhan et al. (2011a) point out that 0–1 bar pressure levels contribute most to the observed spectrum and that C$_2$H$_2$ is considerably more abundant than CH$_4$ within this pressure range (Figure 6). Therefore, future analysis of observations of carbon rich planets (including further analysis of WASP-12b) should consider higher-hydrocarbon species.

4. DISCUSSION

Our analysis confirms the previous thermodynamic equilibrium result that [C]/[O] ≥ 1 is needed to explain the observed overabundance of CH$_4$ in the atmosphere of WASP-12b. A similar conclusion was reached by Line et al. (2010) but for a different hot-Jupiter planet, HD 189733b. These authors varied [C]/[O] from 0.1 to 10 times the solar value, while keeping the total metallicity at the solar value (Figure 6 in their paper), and examined the effect on thermochemical equilibrium mixing ratios at the lower boundary. As [C]/[O] increases, most of the carbon in their model is in CO and CH$_4$. At [C]/[O] = 1, H$_2$O and CH$_4$ switch their profiles just as they do in our equilibrium models of WASP-12b (Figure 7). Although our equilibrium models agree qualitatively with theirs, the respective mixing ratios of the major species differ because of different elemental abundances and overall hotter temperatures (their ~1500 K versus our 2800 K).

We have also performed a sensitivity test to eddy diffusion varying by three orders of magnitude above and below our eddy profile. For the larger case the species concentrations are well mixed over much of the atmosphere, deviating from the equilibrium even at relatively low altitudes (~0.1 bar). Consequently, the photolysis of C$_2$H$_2$ and HCN is not effective in producing atomic hydrogen (as mixing dominates photolysis even at high altitudes). On the other hand, if the eddy diffusion coefficient is small (as proposed by Youdin & Mitchell 2010), mixing is not effective and photochemistry becomes important at mid altitudes (10$^{-3}$ to 10$^{-4}$ bar). Therefore, significant deviations from equilibrium occur at all altitudes above this level.

4.1. A Possible Mechanism for the Origin of Excess Carbon in WASP-12b

The high [C]/[O] ratio in WASP-12b is unexpected, considering that the host star has a solar [C]/[O] ratio (see Fossati et al. 2010, Table 2). In the standard core accretion model (Pollack et al. 1996), volatiles such as carbon and oxygen are expected to remain unfractionated in forming giant planets (Owen et al. 1999). Lodders (2004) pointed out that Galileo probe measurements of Jupiter’s atmosphere show an enriched carbon abundance of 1.7 times solar and a depletion of oxygen by a factor of four (but see further discussion below). To explain

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$^8$ Band pass range from 3.08 to 4.01 μm: http://irsa.ipac.caltech.edu/data/SPITZER/docs/irac/calibrationfiles/spectralresponse/
$^9$ Band pass range from 6.15 to 10.49 μm: http://irsa.ipac.caltech.edu/data/SPITZER/docs/irac/calibrationfiles/spectralresponse/
$^{10}$ http://vpl.astro.washington.edu/spectra/c2h2pnlimagesmicrons.htm
this result, Lodders (2004) proposed a model in which carbonaceous matter began to condense in the solar nebula beyond 5 AU, thereby providing the increased mass density needed for rapid core growth. By contrast, in the standard accretion model, Jupiter forms just beyond the “ice line” where water ice begins to condense. In the Lodders (2004) model, the ice line would have been farther out, beyond the orbit of Jupiter, and this would explain Jupiter’s apparent deficiency in O relative to C. A similar mechanism might then account for the high [C]/[O] ratio in WASP-12b.

Although the Lodders (2004) model could be correct, we suspect that Jupiter formed beyond the ice line, with a solar [C]/[O] ratio, and that other factors are responsible for observed [C]/[O] enrichments in exoplanets. The Galileo probe is widely thought to have descended into an infrared “hot spot” (Atreya et al. 1999), that is, an area of downwellings of air that had been depleted in H2O during its uplift from below. In support of this idea, the H2O mixing ratio was observed to gradually increase with depth down to 20 bars, at which point the probe lost contact with Earth (see Atreya et al. 1999, Table 1). Furthermore, thunderstorms and lightning were also observed by the probe deeper than 4–5 bars (Gierasch et al. 2000; Ingersoll et al. 2000; Atreya et al. 2005), which is consistent with equilibrium cloud condensation models which predict that water clouds can form in this pressure range if the oxygen abundance is at least solar (Atreya et al. 2005).\footnote{11}

As an alternative to the Lodders (2004) model, we suggest that the high [C]/[O] for WASP-12b arose because the primordial disk was depleted in oxygen abundance during the giant planet’s migration. The carbon compounds (CH4, CO) may have been trapped in ices in the form of planetesimals and then accreted onto the envelope of the gas giant, resulting in the observed enhancement of [C]/[O] > 1. Assuming that the disk started with solar elemental abundances of carbon (2.26 × 10^{-4}) and oxygen (4.20 × 10^{-4}), in order to obtain [C]/[O] = 1.08 in WASP-12b (our high [C]/[O] model case), the [O] abundance in the disk must have been depleted by ≈50%. Recently, Madhusudhan et al. (2011b) performed a more detailed analysis of the formation of WASP-12b and concluded that the primordial disk was depleted in [O] by 41%. The discrepancy in our numbers arises because the authors attribute the apparent depletion of [O] in WASP-12 to the material lost by WASP-12b. They found that WASP-12b may be losing mass to its star (Li et al. 2010). If this is the case, then it could be difficult to determine how much of the refractory material has accreted onto WASP-12 during its formation. Fossati et al. (2010) performed a detailed spectropolarimetric analysis of WASP-12 to look for pollution signatures in the atmosphere of WASP-12 may be observable. Formation models of protostars from molecular clouds (Wuchterl & Tscharnuter 2003) indicate that solar-mass protostars have thin convective envelopes (≈0.02 MS), similar to the present day Sun, and hence mixing of deposited material may not be significant. But it has been suggested that WASP-12b may be losing mass to its star (Li et al. 2010). If this is the case, then it could be difficult to determine how much of the refractory material has accreted onto WASP-12 during its formation. Fossati et al. (2010) performed a detailed spectropolarimetric analysis of WASP-12 to look for pollution signatures due to the material lost by WASP-12b. They found hints of pollution but were unable to draw firm conclusions. A differential analysis of WASP-12 twins (with the same effective temperature, age, and metallicity), identifying their abundances with high precision, is required to determine if the refractory elemental abundance of WASP-12 does indeed increase with condensation temperature.

5. CONCLUSIONS

In this study, we analyzed how a disequilibrium mechanism such as photochemistry can affect the observed abundances of H2O, CO, CO2, and CH4 in the WASP-12b atmosphere.

\footnote{12} Note that the accreted material is not depleted in elements such as carbon because they have low condensation temperatures and so did not condense in the inner part of the solar nebula.
We considered two models with $[\text{C}]/[\text{O}] = 0.54$ (solar) and $[\text{C}]/[\text{O}] = 1.08$ (twice solar). Although our photochemical results agree that high $[\text{C}]/[\text{O}]$ is needed to explain the observed high abundance of CH$_4$ and lack of observable H$_2$O, they also indicate C$_2$H$_2$ and HCN are more abundant than CH$_4$ and should be taken into consideration in modeling hot-Jupiter atmospheres. More importantly, our results indicate that C$_2$H$_2$ is the dominant absorber at 1.6 and 8 $\mu$m in WASP-12b’s atmosphere and the absorption features may possibly be arising from C$_2$H$_2$ rather than CH$_4$. Observations with Hubble Space Telescope’s WFC3 can resolve this discrepancy.

We also propose a possible mechanism for the origin of the excess carbon observed in WASP-12b. Following other authors, we suggest that WASP-12 may have accreted rocky, O-rich material from the nebula during the formation of the system, leaving the disk relatively enriched in other volatiles such as C and N. WASP-12b then accreted some of this high $[\text{C}]/[\text{O}]$ material, which thereby gave rise to the high $[\text{C}]/[\text{O}]$ ratio of the planet. Testing this hypothesis requires that we understand whether WASP-12 is currently stealing mass from its planet, WASP-12b. A high-precision abundance analysis of WASP-12 twins and analogs can shed light on the refractory elemental abundance of WASP-12 and the possible origin of excess carbon in WASP-12b.

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13 Note that this prediction is not specifically a result of our photochemical model, as our thermodynamic equilibrium models predict this, as well.