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HIGH TEMPERATURE PHOTOCHEMISTRY IN THE ATMOSPHERE OF HD189733B

Running Head: PHOTOCHEMISTRY ON HD189733B
M. R. Line¹, M. C. Liang², Y. L. Yung¹

¹Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, 91125, USA
²Research Center for Environmental Changes, Academia Sinica, Taipei, Taiwan
³Graduate Institute of Astronomy, National Central University, Jhongli, Taiwan
⁴Institute of Astronomy and Astrophysics, Academia Sinica, Taipei, Taiwan

Corresponding Author Email: mrl@gps.caltech.edu
ABSTRACT

Recent infrared spectroscopy of hot exoplanets is beginning to reveal their atmospheric composition. Deep within the planetary atmosphere, the composition is controlled by thermochemical equilibrium. Photochemistry becomes important higher in the atmosphere, at levels above ~1 bar. These two chemistries compete between ~1-10 bars in hot Jupiter-like atmospheres, depending on the strength of the eddy mixing and temperature. HD189733b provides an excellent laboratory in which to study the consequences of chemistry of hot atmospheres. The recent spectra of HD189733b and HD209458b contain signatures of CH₄, CO₂, CO and H₂O. Here we identify the primary chemical pathways that govern the abundances of CH₄, CO₂, CO and H₂O in the cases of thermochemical equilibrium chemistry, photochemistry, and their combination. Our results suggest that the abundance of these species can be photochemically enhanced above or below the thermochemical equilibrium value, so some caution must be taken when assuming that an atmosphere is in strict thermochemical equilibrium.

Key words: atmospheric effects - methods: numerical – planetary systems - planets and satellites: atmospheres – stars: individual (HD189733b) – planetary systems – radiative transfer
1. INTRODUCTION

Of the more than four hundred exoplanets discovered thus far, only a small number are transiting hot exoplanets, dubbed “hot Jupiters”, from which we can obtain limited spectral information. A variety of chemical species have been detected in hot Jupiter atmospheres. These include atomic species like sodium (Na) (Charbonneau et al. 2002), atomic hydrogen (Vidal-Madjar et al. 2003), atomic carbon and oxygen (Vidal-Madjar et al., 2004), and the molecular species: CO, CO$_2$, H$_2$O and CH$_4$ (Tinetti et al. 2007; Swain et al. 2009a, 2009b). The detection of these species allows us to begin to explore the chemical pathways that control the observed abundances of these species. The species so far identified suggest that hydrocarbon chemistry via CH$_4$ photolysis as well as oxygen and water reactions are important.

The primary chemical pathways that determine chemical abundances in our own solar system are classified as due to either thermoequilibrium chemistry or photochemistry. Ion chemistry may also be important in these hot, highly irradiated atmospheres as it is important in the upper atmospheres of our own solar system planets (Vuitton et al. 2009; Kim & Fox 1994; Friedson et al. 2005). Current atmospheric modeling of hot Jupiter atmospheres typically assume an atmospheric chemical composition consistent with thermochemical equilibrium (Sharp & Burrows 2006; Showman et al. 2009; Burrows et al. 1997; Fortney et al. 2005; Fortney et al. 2010; O’Donovan et al. 2010; Rogers et al. 2009; Marley et al. 2007). Photochemical or other disequilibrium mechanisms, such as quenching, have not received the same attention. (See, however, Cooper & Showman 2006; Zahnle et al. 2009; Liang et al. 2003, 2004). Thermoequilibrium chemistry occurs in high temperature and pressure regimes where chemical timescales are short, typically deep within the atmospheres of giant planets (~1000 bars).
Abundances are determined solely by the thermodynamic properties of compounds in the system via the minimization of the Gibbs free energy (Yung & DeMore 1989). Photochemistry is a disequilibrium process due to UV alteration by the host star. Photochemistry therefore should be important in hot-Jupiter atmospheres, given their proximity to their host stars (Liang et al. 2003).

Liang et al. (2003) were the first to explore the photochemistry that may occur on highly irradiated giant planets through modeling the sources of atomic hydrogen in HD209458b. However, some of the rate coefficients used in that study are unsuitable for these high-temperature regimes, and several key reactions governing the production and loss of H$_2$O and CO$_2$ were not included. Additionally, better estimates of temperature and vertical mixing profiles can be obtained from more sophisticated GCM simulations.

Zahnle et al. (2009) explored products of sulfur photochemistry and how they may be responsible for the strong UV absorbers that cause thermal inversions as well as the formation of hydrocarbon soot. So far there have been no detections of sulfur species on these hot Jupiters.

The goal of this investigation is to understand the chemistry that produces the observed abundances of $\sim10^{-4}$, $\sim10^{-6}$, $\sim10^{-4}$, and $\sim10^{-7}$ for CO, CO$_2$, H$_2$O and CH$_4$, respectively, as detected in the dayside emission spectrum of HD189733b (Swain et al. 2009a) by combining separate photochemical and thermochemical models and then comparing the results to simulations using photochemistry/thermochemistry alone. Furthermore, it has been recently suggested by Madhusudhan & Seager (2009) that there may be as much as 700 ppm of CO$_2$
present in the atmosphere of HD189733b. The discrepancy between this value and the value
from Swain et al. (2009a) is due to the assumed vertical distribution of CO$_2$ in the atmosphere
(constant, versus high concentration at one pressure level), which is not well constrained. This
discrepancy suggests that there is much degeneracy in retrieving temperature and mixing ratio
profiles, and that the exact values of the mixing ratios, or their vertical distributions, of the
detected species are not well known. In this study, we identify the important mechanisms that
govern the abundance of these detected species and their vertical distribution, using HD189733b
as an example.

2. MODELING

We use both a thermochemical model and a photochemical model to explain the observed
abundances of CO, CO$_2$, H$_2$O and CH$_4$ in the atmosphere of HD189733b. We want to
understand the effects that temperature and eddy mixing have on the photochemically derived
mixing ratios. We adopt a hot profile representative of dayside temperatures and cool profile
representative of night-side temperatures for 30° N from Showman et al. (2009) (Figure 1). We
assume isothermal profiles above the upper boundary of the Showman et al. (2009) GCM for the
sake of simplicity. These two profiles appear to have a thermal inversion near 1 mbar with a
day-night contrast of ~500 K. The use of two T-P profiles will illuminate the day/night contrast
of the modeled species. Though HD189733b is not expected to have an inversion, we still
choose these T-P profiles because they span the range of hot Jupiter temperature profiles in the
literature (Fortney et al. 2006; Tinetti et al. 2007; Burrows et al. 2008), and the existence of an
inversion does not significantly affect the major chemical pathways.
In order to determine the thermoequilibrium abundances we use the Chemical Equilibrium with Applications model developed by Gordon & McBride (1994). These abundances at the appropriate lower boundary (explained later) will be used for our lower mixing ratio boundary condition in the photochemical model. Thermochemical calculations require only pressure and temperature along with the relative molar mixing ratios of the atomic species involved in the compounds of interest, in this case C, O and H (no N or S because they have not yet been detected). For the sake of simplicity, and in the absence of any other information, we assume solar abundance of these species ([C]/[H]~4.4×10^{-4}, [O]/[H]~7.4×10^{-4}, where [i] denotes the concentration of species i (Yung & DeMore 1999 pg. 112). The thermochemical model computes the abundances of all possible compounds formed by those atomic species via a Gibbs Free energy minimization routine (Gordon & McBride 1994). We compute the equilibrium abundances at each pressure-temperature level for our chosen temperature profiles. We would expect to see thermochemical equilibrium abundances in an atmosphere that is not undergoing any dynamical or photochemical processes, or where chemical timescales are much shorter than any disequilibrium timescales (Cooper & Showman 2006; Prinn & Barshay 1977; Smith 1998).

To compute the photochemical abundances of the species of interest, we use the Caltech/JPL-Kinetics 1D photochemical model (Allen et al. 1981; Moses et al. 2005; Gladstone et al. 1996; Yung et al. 1984) for HD189733b. HD189733b is in a 2.2 day period orbiting at 0.03 AU around a K2V star. We use the UV stellar spectrum from HD22049 which is also a K2V star (Segura et al. 2003). The model computes the abundances for 32 species involving H, C and O in 258 reactions including 41 photolysis reactions and includes both molecular and eddy diffusion. The model uses the same hydrocarbon and oxygen chemistry as in Liang et al. (2003).
and Liang et al. (2004) but with high temperature rate coefficients for the key reactions involved in the production and loss of H, CH$_4$, CO$_2$, CO, OH and H$_2$O. The reaction rates given in the remainder of this paper are taken from Baulch et al. (1992) unless otherwise noted. We have also added two key reactions involved in the destruction of H$_2$O and CO$_2$. We have not, however, added a complete suite of reactions in order to achieve thermochemical equilibrium kinetically (e.g., Visscher et al. 2010). We do not expect this omission to invalidate our results, as we have included the key chemical pathways that govern the production and loss of the species of interest. The model atmosphere for the photochemical model uses the two temperature profiles described above. The lower boundary of the photochemical model is important in determining the mixing ratios throughout the atmosphere. We will estimate this lower boundary using quench level arguments rather than arbitrarily choosing some level. For more details on quench level estimation we refer the reader to Cooper & Showman (2009), Smith (1998) and Prinn & Barshay (1977).

Eddy and molecular diffusion are key parameters determining the distribution of the abundances in the atmosphere. Eddy diffusion is the primary vertical transport mechanism in our 1D model. The strength of vertical mixing will determine where in the atmosphere the species become chemically quenched, and thus defines the lower boundary conditions for the photochemical model (Prinn & Barshay 1977; Smith 1997). Following Prinn & Barshay (1977), the transport timescale is given by

$$\tau_{\text{trans}} \approx \frac{L^2}{K_z}$$

where $L$ is a vertical length scale typically chosen to be the scale height and $K_z$ is the eddy diffusion coefficient. The chemical loss timescale of species $i$ is given by
\[ \tau_{\text{chem},i} = \frac{[i]}{L_i} \]  

where \([i]\) is the concentration of species \(i\) and \(L_i\) is the loss rate of species \(i\), typically determined by the bottleneck reaction. The quench level for species \(i\) is defined where \(\tau_{\text{trans}} = \tau_{\text{chem},i}\). For levels where \(\tau_{\text{trans}} < \tau_{\text{chem},i}\) the mixing ratio of species \(i\) is fixed at the quench level value. For levels below the quench level, the compounds reach chemical equilibrium.

In order to determine the quench level in the atmosphere HD189733b, we must first estimate the strength of eddy mixing and the timescale for the conversion of CO to CH\(_4\) (Griffith & Yelle 1999; Prinn & Barshay 1977). The eddy diffusion profile adopted in this model is derived from a globally RMS-averaged vertical wind profile from a GCM (Showman 2010 private communication) and is estimated by

\[ K_z \sim wL \]  

where \(w\) is the RMS-averaged of the vertical wind velocity. Smith (1998) suggests that the appropriate length scale is some fraction of the scale height. Here we assume that it is the scale height, thus giving us an upper limit on eddy diffusion. The GCM derived RMS-averaged vertical winds range from 0 (at ~200 bars) to 7 m/s (~0.8 mbars). The vertical wind is assumed to be constant above this height. Combining this with a typical scale height of ~200 km gives an eddy diffusion of \(~10^{10} \text{ cm}^2 \text{ s}^{-1}\) (Figure 1). Typical transport timescales from (1) are on the order of ~\(10^5\) s.

The rate-limiting step in the conversion of CO to CH\(_4\), and thus the reaction determining the chemical lifetime of CO, is

\[ H + H_2CO + M \rightarrow CH_3O + M \]  

(4)
reaction 4 has not been measured in the lab, but its reverse reaction rate has been measured to be:

\[ k_r = 1.4 \times 10^{-6} T^{-1.2} e^{-7800/T} \text{ cm}^6 \text{s}^{-1} \]  

(5)

where \( T \) is the temperature at which the reaction takes place (Page et al. 1989). The forward reaction rate, \( k_f \) can be estimated via

\[ \frac{k_f}{k_r} = K_{eq} = e^{(G_f-G_r)/RT} \]  

(6)

where \( K_{eq} \) is the equilibrium constant for the net thermochemical reaction (Yung et al. 1988)

\[ \text{H + H}_2\text{CO} \leftrightarrow \text{CH}_3\text{O} \]  

(7)

where \( G_f \) and \( G_r \) are the Gibbs free energies of the reaction, given respectively by \( H[\text{H}]+H[\text{H}_2\text{CO}]-T(S[\text{H}]+S[\text{H}_2\text{CO}]) \) and \( H[\text{CH}_3\text{O}]-T(S[\text{CH}_3\text{O}] \) with \( H[X] \) being the enthalpy of formation of species \( X \) and \( S[X] \) being the entropy of species \( X \). The enthalpies and entropies of the given species can be found in Yung & DeMore (1999) pg 58. With the relevant thermochemical data and equations (5) and (6) we can estimate the forward reaction rate of reaction (4) to b

\[ k_f = 5.77 \times 10^{-12} T^{-1.2} e^{3327/T} \]  

(8)

The CO chemical lifetime can then be determined using:

\[ \tau_{chem} \sim \frac{[\text{CO}]}{k_f[H][\text{H}_2\text{CO}]} \]  

(9)

where the concentrations of CO, H and \( \text{H}_2\text{CO} \) are determined via the thermochemical model. Upon equating (9) with (1) using the dayside temperature profile we determine the quench level, and thus the lower boundary to be \(~3 \text{ bars (~1530 K)} \) which is similar to the results of Cooper & Showman (2006) for HD209458b. This pressure level is much higher than that of Jupiter \((~100 \text{ bars}) \) (Prinn and Barshay 1977) and is similar to that of brown dwarfs \((~6 \text{ bars}) \) (Griffith & Yelle
Choosing a length scale less than the scale height as suggested by Smith et al (1998) can move the quench level to a higher pressure. This is because the chemical timescale in equation 9 increases with increasing altitude and lower temperature. Using a length scale of $0.1H$ instead of $H$ moves the quench level to ~8 bars, at where there is very little change in the thermochemical mixing ratios from ~3 bars (Figure 2). Additionally, there is no significant difference in quench level between the nightside and dayside because the two T-P profiles converge near the quench level.

We assume a zero concentration gradient at the lower boundary in order to allow photochemical products to sink down into the deeper atmosphere except for the observed species of CO, H$_2$O, CH$_4$, CO$_2$. For these species we fix the mixing ratios to be the thermochemically-derived values at the ~3 bar quench level: $8.41 \times 10^{-4}$, $6.36 \times 10^{-4}$, $4.09 \times 10^{-5}$, and $1.96 \times 10^{-7}$, respectively, for the dayside and $8.39 \times 10^{-4}$, $6.38 \times 10^{-4}$, $4.25 \times 10^{-5}$, and $1.98 \times 10^{-7}$, respectively, for the nightside. We assume a zero flux boundary condition for the top of the atmosphere e.g, little or no atmospheric escape, though this assumption may not be entirely true for atomic hydrogen (Vidal-Madjar et al. 2003). This assumption has a negligible effect on the results.

3. RESULTS

3.1 Thermochemical Results

The thermochemically derived mixing ratios (relative to H$_2$) are shown in Figure 2. Again, these are the expected mixing ratios if there were no dynamical or photochemical process occurring in the atmosphere, which we know not to be true. If we focus first on the dayside profiles, we can see that CO is the dominant carbon bearing species and remains relatively constant with altitude.
as do H₂O and CO₂. We also notice that CH₄ falls off rapidly with increasing altitude (decreasing pressure). We can understand this result by noting that CO, CH₄ and H₂ abundances are related through the net thermochemical reactions

\[
\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2 \tag{10}
\]

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \tag{11}
\]

Then by Le Chatelier’s principle, as the total partial pressure of the atmosphere decreases, the system will want to resist that decrease in order to maintain equilibrium by producing more molecules (smaller molecules), which in this case results in the production of CO and H₂. Upon comparing the dayside profiles to the cooler nightside profile, we notice that CH₄ becomes more abundant. CH₄ is more energetically favorable at lower temperatures and is much more sensitive to the effects of temperature than CO and CO₂. We also note that atomic hydrogen is more abundant at warmer temperatures than at cooler temperatures due to the entropy term in the Gibbs free energy. From a thermochemical perspective, we can expect ~10 mbar mixing ratios of the observable species, CO, H₂O, CH₄ and CO₂ to range from: (2-9)×10⁻⁴, (6-13)×10⁻⁴, (2.6-6758)×10⁻⁷, (4.7-16)×10⁻⁷, respectively, due to the day/night contrast. For comparison, the measured dayside emission values from Swain et al (2009a) for CO, H₂O, CH₄ and CO₂ are respectively, ~10⁻⁴, ~10⁻⁴, ~10⁻⁷, and ~10⁻⁶.

### 3.2 Photochemical Results

We run four cases of our photochemical model (Figure 3) in order to compare the effects of temperature and photolysis versus no photolysis on the mixing ratios (relative to H₂) for H, CO, H₂O, CO₂ and CH₄. In the following subsections we will discuss the important reactions governing the production and loss of each of the relevant species.
3.2.1 H$_2$O, OH, and H

The primary reactions that govern the production and loss of H$_2$O are

- \( \text{R71} \quad \text{H}_2\text{O} + h\nu \rightarrow \text{H} + \text{OH} \quad J_{71}=2.587 \times 10^{-8} \text{ s}^{-1} \text{ (1 mbar)} \)
- \( \text{R137} \quad \text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} \quad k_{137}=1.70 \times 10^{-16}T^{-1.6}e^{1660/T} \text{ cm}^3 \text{ s}^{-1} \)
- \( \text{R254} \quad \text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2 \quad k_{254}=7.50 \times 10^{-16}T^{-1.6}e^{-9718/T} \text{ cm}^3 \text{ s}^{-1} \)

R137 and R254 are fast enough to readily recycle each other so that the abundance of H$_2$O remains relatively constant with altitude at the quench level value of \( \sim 6.36 \times 10^{-4} \) below the homopause at \( \sim 10 \) nbar. The photolysis of H$_2$O does not significantly affect its abundance in the observable atmosphere as can be seen in Figure 3, because the loss timescale of H$_2$O when struck by photolysis is everywhere longer than the transport timescale, thus allowing recently photolyzed parcels to be readily replenished by upwelling. The photolysis of H$_2$O, however, does produce the important OH and H radicals that drive the remainder of the chemistry (Figure 4), with the net result being the conversion of H$_2$ to 2H.

H$_2$O photodissociates into OH and H at wavelengths lower than 2398 Å. For HD189733b below this wavelength there are \( \sim 8 \times 10^{15} \) photons cm$^{-2}$ s$^{-1}$ available for H$_2$O photolysis. For comparison, the UV flux below this wavelength at Jupiter is \( \sim 3 \times 10^{14} \) photons cm$^{-2}$ s$^{-1}$ and for HD209458b, \( \sim 3 \times 10^{18} \) photons cm$^{-2}$ s$^{-1}$. OH and H increase with increasing altitude due to the availability of more UV photons. The production of H at high altitudes via H$_2$O photolysis may be the driver of hydrodynamic escape on hot Jupiters (Liang et al. 2003).
In short, the abundance of H$_2$O is primarily set by the thermochemical equilibrium value at the lower boundary condition, taken here to be the quench level, and rapidly decreases with altitude above the homopause. If the quench level changes, the observable value of H$_2$O will change but not significantly, as can be seen in Figure 2. The derived value here is slightly higher than the Swain et al. 2009a dayside emission observations of (0.1-1) $\times 10^{-4}$ but is more consistent with the value obtained by the Tinetti et al. 2007 terminator observations of $\sim 5 \times 10^{-4}$. The day to night contrast is nearly unnoticeable in Figure 3.

### 3.2.2 CO & CO$_2$

Thermochemically, CO is the dominant carbon reservoir in hot atmospheres above $\sim 10$ bars (Figure 2). The abundance of CO is set by the quench level thermochemical equilibrium abundance of $8.4 \times 10^{-4}$. The abundance of CO$_2$ is determined via the interconversion of oxygen from the large reservoirs of CO and H$_2$O into CO$_2$ via the OH radical. Deeper down in the atmosphere, say, below the quench level, or in the presence of weak vertical transport (low eddy diffusion), oxygen is moved into CO$_2$ via the following reactions

\[
\begin{align*}
\text{R137} & \quad \text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H} \\
\text{R152} & \quad \text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \\
\text{R254} & \quad \text{H} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{H}_2 \\
\text{R255} & \quad \text{H} + \text{CO}_2 \rightarrow \text{OH} + \text{CO}
\end{align*}
\]

[R137] $k_{137}=1.70 \times 10^{-16} \ T^{1.6} \ e^{-1660/T} \ \text{cm}^3 \ \text{s}^{-1}$

[R152] $k_{152}=1.05 \times 10^{-17} \ T^{1.5} \ e^{-250/T} \ \text{cm}^3 \ \text{s}^{-1}$

[R254] $k_{254}=7.50 \times 10^{-16} \ T^{1.6} \ e^{-9718/T} \ \text{cm}^3 \ \text{s}^{-1}$

[R255] $k_{255}=2.51 \times 10^{-10} \ e^{-13350/T} \ \text{cm}^3 \ \text{s}^{-1}$

R152 is the reaction that gives the oxygen from H$_2$O and CO to CO$_2$. There is no net production or loss of species from these reactions, meaning they will assume thermochemical equilibrium.
Assuming steady state, these 4 reactions can be combined to give the kinetically achieved thermochemical mixing ratio of CO$_2$ in terms of the rate constants ($k$) and mixing ratios ($f$) of the large reservoirs of CO and H$_2$O

\[ f_{CO_2} \sim \frac{k_{152}k_{254}}{k_{137}k_{255}} f_{H_2O} f_{CO} \]  

(12)

\[ = 1.85 \times 10^{-7} T^{4.5} e^{5542/T} f_{H_2O} f_{CO} \]

This relation would determine the mixing ratio of CO$_2$ in the absence of any disequilibrium mechanisms such as photochemistry or quenching. Using the thermochemical mixing ratios of H$_2$O (~6×10$^{-4}$) and CO (~9×10$^{-4}$) and evaluating the rate constants at the daytime temperature (T~1200 K) we obtain a CO$_2$ mixing ratio of ~4×10$^{-7}$ which is consistent with Figure 2.

In the photochemical limit (in the absence of eddy mixing), the photolysis reactions, R71 and R75 become more important and effectively replace R254 and R255, so the important chain of reactions becomes:

- **R137**: OH + H$_2$ → H$_2$O + H  \[ k_{137} = 1.70 \times 10^{-16} T^{1.6} e^{-1660/T} \text{ cm}^3 \text{s}^{-1} \]
- **R152**: OH + CO → CO$_2$ + H  \[ k_{152} = 1.05 \times 10^{-17} T^{1.5} e^{250/T} \text{ cm}^3 \text{s}^{-1} \]
- **R71**: H$_2$O + hv → H + OH  \[ J_{71} = 2.587 \times 10^{-8} \text{ s}^{-1} (1 \text{ mbar}) \]
- **R75/76**: CO$_2$ + hv → CO + O  \[ J_{75/76} = 4.4 \times 10^{-10} \text{ s}^{-1} (1 \text{ mbar}) \]
- **Net**: OH + H$_2$ → 3H + O

Combining these reactions allows us to estimate the photochemical mixing ratio of CO$_2$ with

\[ f_{CO_2} \sim \frac{k_{152} J_{71}}{k_{137} J_{7576}} f_{H_2O} f_{CO} \]  

(13)
where \( J \) is the photolysis rate of the indicated photolysis reaction. As an extreme case we assume the top of atmosphere photolysis rate of H\(_2\)O is \( \sim 10^{-5} \text{s}^{-1} \), the photolysis rate of CO\(_2\) is \( \sim 5 \times 10^{-8} \text{s}^{-1} \), and the dayside temperature is \( \sim 1200 \text{ K} \), giving an upper limit of \( \sim \text{few} \times 10^{-5} \) for \( f_{\text{CO}_2} \). Equation 13 suggests that the abundance of CO\(_2\) is photochemically enhanced rather than reduced. The abundance of CO\(_2\) in the presence of only quenching (no photochemistry) will remain fairly constant below the homopause at \( \sim 1 \text{ nbar} \) (Figure 3). This is due to the lack of excess OH produced in R71 used to drive R152 to produce CO\(_2\). Again, for comparison, the observed mixing ratio of CO\(_2\) from Swain et al. (2009a) is \( \sim 10^{-7} - 10^{-6} \).

### 3.2.3 CH\(_4\) and Heavier Hydrocarbons

The primary fate of CH\(_4\) in the upper atmosphere is reaction with H to produce CH\(_3\), which immediately reacts with H\(_2\) to restore CH\(_4\),

\[
R28 \quad \text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2 \quad k_{28} = 2.20 \times 10^{-20} \text{T}^3 e^{-4041/T} \text{ cm}^3 \text{ s}^{-1}
\]

\[
R53 \quad \text{CH}_3 + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2 \quad k_{53} = 1.14 \times 10^{-20} T^{2.7} e^{-4739/T} \text{ cm}^3 \text{ s}^{-1}
\]

The result is a closed loop. However, the above recycling is not perfect, and the following sequence of reactions occur in the upper atmosphere

\[
R28 \quad 2 \times [ \text{CH}_4 + \text{H} \rightarrow \text{CH}_3 + \text{H}_2 ] \quad k_{28} = 2.20 \times 10^{-20} \text{T}^3 e^{-4041/T} \text{ cm}^3 \text{ s}^{-1}
\]

\[
R4 \quad 2 \times [ \text{CH}_3 + \text{hv} \rightarrow \text{CH}_2 + \text{H} ] \quad J_{28} = 1.95 \times 10^{3} \text{ s}^{-1} \text{ (1 mbar)}
\]

\[
R48 \quad \text{CH}_2 + \text{CH}_2 \rightarrow \text{C}_2\text{H}_2 + 2\text{H} \quad k_{48} = 1.80 \times 10^{-10} e^{-400/T} \text{ cm}^3 \text{ s}^{-1} \text{ (Bauerle et al. 1995)}
\]
\[
\text{Net} \quad 2\text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + 2\text{H}_2 + 2\text{H}
\]

The net result is production of \(\text{C}_2\text{H}_2\) in the upper atmosphere at the \(~1\) ppm level. No other \(\text{C}_2\) hydrocarbons are produced in significant quantities. The primary fate of \(\text{C}_2\text{H}_2\) from the upper atmosphere is downward transport, followed by hydrogenation back to \(\text{CH}_4\). The abundance of \(\text{CH}_4\) is \(~4\times10^{-5}\), which is several orders of magnitude larger than the \(~10^{-7}\) detected by Swain et al. (2009) and used by Liang et al. (2003).

4. DISCUSSION

We have analyzed the important disequilibrium mechanisms, photochemistry and simple dynamical quenching that govern the vertical distribution of the observed species in hot Jupiter atmospheres. With the exception of methane, our derived abundances are consistent with the observations of Swain et al. (2009a). We obtained a value of \(~4\times10^{-5}\), while the observations suggest two orders of magnitude less. The observed value of \(~10^{-7}\) corresponds to the thermochemical equilibrium value at \(~10\) mbars. This would mean the quench level would have to be at this pressure, suggesting an eddy diffusion on the order of \(~10^3\) cm\(^2\) s\(^{-1}\) from equations (9) and (1). Alternatively, it may be possible that the observations are probing above the homopause where the mixing ratio can be substantially less than \(~10^{-5}\) (Figure 3). Line lists used in radiative transfer models are also not well known and are constantly changing at these high temperatures which can play a significant role in dictating the retrieved abundances from the observations (Tinetti 2010 private communication). Our value of methane is also several orders of magnitude larger than reported by Liang et al. (2003) for HD209458b. This is because the temperature at the lower boundary used in Liang et al. (2003) for HD209458b is \(~700\) K
hotter than our lower boundary temperature of ~1530 K and methane is less stable at higher temperatures.

The metallicity of these hot Jupiters is not well constrained. Swain et al. (2009a) suggests that the metallicity for HD189733b may be subsolar and that the $[\text{C}]/[\text{O}]$ ratio is between 0.5 and 1. We assumed solar metallicity, but we can explore what might happen if this is not the case.

Changes in metallicity will affect the thermochemical equilibrium abundances. This will in turn change the lower boundary mixing ratios. We varied the metallicity (taken here to be $([\text{C}]+[\text{O}])/[\text{H}]$) from one tenth solar up to ten times solar to see what effect it would have on our lower boundary mixing ratios (Figure 6). The thermochemical mixing ratios of CO, H$_2$O and CO$_2$ vary by several orders of magnitude over the range of metallicities, where as CH$_4$ changes very little. This orders of magnitude change at the lower boundary due to metallicity will affect our photochemical results by the same amount. With ten times the solar metallicity we could expect mixing ratios of CO and H$_2$O to be as high as ~0.1 and CO$_2$ as high as $10^{-5}$. CO$_2$ is more readily affected by metallicity than the other species because it has two oxygen’s as opposed to CO’s one oxygen. Even higher metallicites will produce more extreme abundances of CO, CO$_2$ and H$_2$O.

The $[\text{C}]/[\text{O}]$ ratio, also affects the thermochemical abundances. Here we vary the $[\text{C}]/[\text{O}]$ ratio from 0.1 to 10 times the solar ratio of ~0.6 while keeping the overall metallicity $([\text{C}]+[\text{O}])/[\text{H}]$ constant at the solar value (Figure 6). The mixing ratio of CO does not vary significantly, but can get as high as $10^{-3}$ given a slightly super solar $[\text{C}]/[\text{O}]$ ratio. CO$_2$ rapidly decreases for ratios above solar and can get as low as 0.1 ppb for 10 times the solar ratio. As the $[\text{C}]/[\text{O}]$ ratio
increases past 1, H$_2$O and CH$_4$ swap roles in taking up H and can change as much as 3 orders of magnitude.

There appears to be minor compositional variability between the nightside and dayside. Comparing the solid curves in the top of Figure 3 to the dashed curves in the bottom of Figure 3 gives some sense of the magnitude of the day-night variability. There are no dissociating photons on the nightside, so the quench level mixing and atmospheric circulation determine the abundance throughout the rest of the atmosphere below the homopause. There is a less than 1% maximum variability in CO and H$_2$O, a factor of ~3 more CH$_4$ on the nightside over the dayside and up to a factor of 2 more CO$_2$ on the dayside. CO$_2$ and CH$_4$ concentrations experience more variability, because they are most affected by photochemical reactions that only occur on the dayside (CH$_4$ gets destroyed due to R141 and photolysis, CO$_2$ enhanced via equation 13). C$_2$H$_2$ would exhibit much variability since it is produced strictly from photochemistry. We could expect to see up to 1 ppm on the dayside of these hot planets with very minute amounts on the nightside where it would be readily thermochemically recycled back to methane. Terminator observations should fall somewhere between the dayside and nightside values.

5. CONCLUSIONS

We have shown that both photochemistry and vertical quenching can significantly alter the abundances of CO$_2$, CH$_4$ and C$_2$H$_2$ in hot Jupiter atmospheres. Vertical quenching determines the lower boundary values and thus the mixing ratios of CO and H$_2$O, which are not significantly affected photochemically. CO$_2$ can be photochemically produced above its quench level value by the reaction described in equation (13), and CH$_4$ can be readily photochemically destroyed.
These ideas can be extended to other hot Jupiter atmospheres, though we used HD189733b as our test case. One can see from equation (13) that the fate of CO$_2$ is determined by the temperature of the atmosphere, and the ratio of the H$_2$O photolysis rate to the CO$_2$ photolysis rate which all depend on the stellar type and the distance. Knowledge of these terms will allow us to predict the abundance of CO$_2$ in any hot Jupiter atmosphere. Finally, the vertical distribution of species derived from thermochemical equilibrium can deviate substantially from those derived via quenching, photochemistry and diffusion, and the simple assumption of thermochemical equilibrium may not be valid in the observable regions of these atmospheres.

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Figure 1. Temperature (solid) and eddy diffusion (dashed) profiles for the model atmosphere. The cooler temperature profile is taken from 30°N from the night side of the model by Showman et al., (2009). The hotter temperature profile is taken from the dayside at the same latitude. The larger eddy diffusion is estimated as discussed in the text (the larger values are for the dayside). Eddy diffusion is read along the top axis, temperature is read along the bottom axis.
Figure 2. Thermochemical equilibrium mixing ratios derived from the temperature profiles in Figure 1. The top Figure shows the mixing ratios derived for the dayside (hotter) profile. The bottom Figure shows the mixing ratios derived for the (nightside) cooler profile.
Figure 3. Photochemical mixing ratios (solid) compared to the case with no photochemistry and only quenching (dashed) for the day (top) and night (bottom) temperature profiles. The dashed curves on the bottom plot are representative of what may be seen on the night side of the planet. Note that there is virtually no H or C\textsubscript{2}H\textsubscript{2} for the cases in which photochemistry is turned off (eg, the dashed curves for these species are not in the plot range).
Figure 4. Important radical species involved in pathways governing the abundances of CH$_4$, H$_2$O, CO and CO$_2$. Solid is for the dayside temperature profile, dashed is for the nightside temperature profile. The abundances of radicals increase with decreasing pressure due to the availability of dissociating photons higher in the atmosphere.
Figure 5. Photochemical web illustrating the important chemical pathways that govern the production and loss of the observable species. The boxes represent the observed species and the circles represent species yet to be observed but are key in the production and loss of the observed constituents.
Figure 6. The effects of changing metallicity (top) and C/O ratio (bottom) on the 3 bar quench level mixing ratios for CO, H$_2$O, CO$_2$ and CH$_4$. The vertical lines in each plot represent the solar values.