THERMOCHEMICAL AND PHOTOCHEMICAL KINETICS IN COOLER HYDROGEN DOMINATED EXTRA-SOLAR PLANETS: A METHANE-POOR GJ436B?

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ABSTRACT

We introduce a thermochemical kinetics and photochemical model. We use high-temperature bidirectional reaction rates for important H, C, O and N reactions (most importantly for CH₄ to CO interconversion), allowing us to attain thermochemical equilibrium, deep in an atmosphere, purely kinetically. This allows the chemical modeling of an entire atmosphere, from deep-atmosphere thermochemical equilibrium to the photochemically dominated regime. We use our model to explore the atmospheric chemistry of cooler (Tₑff < 10³ K) extrasolar giant planets. In particular, we choose to model the nearby hot Neptune GJ436b, the only planet in this temperature regime for which spectroscopic measurements and estimates of chemical abundances now exist. Recent Spitzer measurements with retrieval have shown that methane is driven strongly out of equilibrium and is deeply depleted on the dayside of GJ 436b, whereas quenched carbon monoxide is abundant. This is surprising because GJ 436b is cooler than many of the heavily irradiated hot Jovians and thermally favorable for CH₄, and thus requires an efficient mechanism for destroying it. We include realistic estimates of ultraviolet flux from the parent dM star GJ 436, to bound the direct photolysis and photosensitized depletion of CH₄. While our models indicate fairly rich disequilibrium conditions are likely in cooler exoplanets over a range of planetary metallicities, we are unable to generate the conditions for substantial CH₄ destruction. One possibility is an anomalous source of abundant H atoms between 0.01-1 bars (which attack CH₄), but we cannot as yet identify an efficient means to produce these hot atoms.

Subject headings: planetary systems — planets and satellites: atmospheres — planets and satellites: individual(GJ 436b) — methods: numerical — radiative transfer, disequilibrium chemistry

1. INTRODUCTION

Currently, transiting extrasolar planets offer virtually exclusive opportunities for observing physical and chemical states of exoplanetary atmospheres. Over the past four years, retrievals of atmospheric molecules from multicolor transit photometry (i.e. transit spectra) have compelled the development of progressively more sophisticated atmospheric models to interpret the observations and understand underlying chemical and dynamical processes. In particular, atmospheric-chemistry modeling is evolving from strictly thermo-equilibrium models with stationary chemical species, to coupled models (Zahnle et al. 2009a,b; Line et al. 2010; Moses et al 2011) incorporating thermo-kinetics, vertical transport, and photochemistry. Thus far, such efforts have been devoted to hot-Jupiter planets, especially HD 209458b and HD 189733b, due to their favorable transit depths and eclipse brightmesses and, therefore, far greater availability of observational data. However, with the recent retrieval of molecular abundances in the atmosphere of GJ 436b (Stevenson et al. 2010; Madhusudhan & Seager 2011), exoplanetary science is venturing into a new territory: hot-Neptune atmospheric chemistry. GJ 436b is bound to serve as a prototypical planet anchoring the theoretical framework for understanding the hot-Neptune class of exoplanets, much as how HD 209458b and HD 189733b...
have for hot Jupiters. It is also the first planet with observable thermal emission that transits an M star. M stars are of particular interest since they constitute the majority of stars in the solar neighborhood, and they have close-in habitable zones, which enhances radial-velocity detectability and transit observability; therefore, M stars present the best opportunities to discover and characterize rocky, potentially habitable exoplanets in the near future. GJ 436b and GJ 1214b provide the only present test cases for atmospheric chemistry of planets orbiting M dwarfs. Therefore, an era of intensive investigations of this planet is commencing. This paper presents our application of a state-of-the-art model seamlessly integrating thermo-kinetics, vertical transport, and photochemistry to simulate the atmospheric chemistry of GJ 436b in a similar manner to Visscher et al. (2010) and Moses et al. (2011), along with realistic estimates of UV fluxes for this planet.

The first transiting hot Neptune discovered (Butler et al. 2004, Gillon et al. 2007), GJ 436b, revolves around an M dwarf merely 10 pc away from Earth and has received much attention due to its interesting orbital dynamics (Ribas et al. 2008, Mardling 2008, Batygin et al. 2009), interior properties (Nettelmann et al. 2010, Kramm et al. 2011), and atmospheric properties (Stevenson et al. 2010, Lewis et al. 2010, Madhusudhan & Seager 2011, Shabram et al. 2011). The slightly eccentric orbit (eccentricity = 0.16) has a mean orbital radius of 0.0287 AU (Torres et al. 2008), and the planet probably has a pseudo-synchronous rotation (Deming et al. 2007). The planet’s mass is 23 $M_{\oplus}$, and its density of 1.7 g/cm$^3$ resembles that of the ice-giant Neptune (1.63 g/cm$^3$). Analyses of its mass-radius relationship and transit depth indicates a layer of H/He dominated atmosphere is clearly required (Figueras et al. 2009; Nettelmann et al. 2010; Rogers & Seager 2010). The host star has an effective temperature of $\sim$ 3400 K and an estimated age of 3 – 9 Gyr (Torres et al. 2008). Assuming zero albedo and global thermal re-distribution, the planet’s effective temperature is 650 K. Of the confirmed transiting exoplanets (Wright et al. 2011), GJ 436b is one of the least irradiated and has one of the coolest atmospheres. Therefore, this planet represents a significant departure from hot Jupiters in terms of size, thermal environment, and UV flux.

Although GJ 436b was discovered in 2004 (Butler, by radial velocity), it was not until 2010 that a retrieval of explicit molecular abundances in its atmosphere was reported (Stevenson et al. 2010), where six channels of secondary-eclipse photometry data ranging from 3.6 to 24 $\mu$m were analyzed by generating $\sim$ 10$^6$ simulated spectra using varying combinations of molecular compositions and temperature profiles to find the best fit to observations. A more recent paper (Madhusudhan & Seager 2011) provides further details and updated results of a re-analysis of the same dataset using the same general retrieval method. In short, $10^6$ combinations of ten physio-chemical free parameters, each spanning a large range of values, were used to generate synthetic dayside-emission spectra. In each of the $10^6$ scenarios, six of the ten parameters were used to define the temperature-pressure (T-P) profile, whereas the other four parameters specified vertically uniform abundances of four molecules: H$_2$O, CO, CH$_4$, and CO$_2$. Additionally, the 1-D atmospheric model restricted the ratio of emergent flux output to incident stellar flux input on the day side to within the range between zero and unity. Given six data points and ten free parameters, the retrieval problem was mathematically underdetermined. Nonetheless, sampling a million points in parameter-space allowed the authors to examine the joint probability contours, as defined by the goodness-of-fit (chi-square) function, projected on multiple-parameter spaces. Furthermore, by placing physical-plausibility constraints (in consideration of believable departures from thermo-equilibrium chemistry) on the molecular abundances, the authors were able to confine the physical space to a fairly narrow, “best-fit,” range for chi-square $\leq 3$. Depending on the wavelength, the photospheric altitude varies from 9 bar to 0.2 bar levels. The main conclusions are as follows: 1) temperature inversion is ruled out (i.e. no stratosphere); 2) 6 ppm (parts per million) is the absolute upper limit for CH$_4$ abundance; 3) 300 ppm is the absolute upper limit for H$_2$O abundance; 4) CO$_2$ and CO abundances are anti-correlated; 5) taking physical-plausibility into consideration, the best-fit spectrum represents $X_{H_2O} = 100$ ppm, $X_{CH_4} = 1$ ppm, $X_{CO} = 7000$ ppm, and $X_{CO_2} = 6$ ppm, where $X_i$ is the number density of molecule $i$ divided by that of H$_2$. Also, note that even in the best-fit scenario, $X_{CO_2}$ can range anywhere from 1 – 100 ppm. The Stevenson et al. (2010) and the Madhusudhan & Seager (2011) efforts are the most comprehensive studies of atmospheric composition on GJ 436b thus far.

From a theoretical point of view, the preceding abundance limits and values pose a very interesting challenge due to their drastic departures from thermo-equilibrium predictions, which indicate the following rough-order-of-magnitude values: $X_{H_2O} = 1000$ (3$\times$10$^3$) ppm, $X_{CH_4} = 1000$ (10$^4$) ppm, $X_{CO} = 60$ (10$^4$) ppm, and $X_{CO_2} = 0.1$ (1000) ppm for 1x (50x) solar metallicities at $\sim$ 1bar. In either metallicity scenario, water and methane remain abundant ($\geq$ 1000 ppm), while carbon monoxide and carbon dioxide are positively correlated (either both low in the 1x case or both high in the 50x case), in contrast with the retrieval’s anti-correlation. In particular, the retrieved partitioning of carbon overwhelmingly in oxidized species amidst a hydrogen-dominated (reducing), temperate atmosphere is very surprising. For instance, at 1-bar pressure and solar metallicity, CH$_4$ is the thermodynamically dominant carbon-bearing molecule for temperatures less than 1100 K (Lodders & Fegley 2002). The common practices of simply adjusting metallicity and/or the C/O ratio cannot simultaneously reconcile these discrepancies. Therefore, one must investigate disequilibrium mechanisms.

Madhusudhan & Seager (2011) posited that high metallicity combined with vertical mixing can explain the disequilibrium abundance of carbon oxides. Basically, enhanced metallicity ($\sim$ 10$\times$ solar) can provide the requisite abundance of CO$_2$. Since equilibrium CO abundance drops sharply with respect to temperature (Lodders & Fegley 2002) the retrieved uniformly high abundance of CO requires eddy mixing to populate up-
per, cooler, atmospheric layers. However, vertical eddy mixing alone cannot explain the large depletion of CH$_4$ due to its innately high thermochemical abundance in the deep atmosphere. Therefore, Madhusudhan & Seager (2011) invoked photochemistry as the potential culprit, based on Zahnle et al.’s (2009a,b) studies of photochemistry on hot Jupiters. In such a scheme, photosensitized sulfur chemistry produces atomic H, which then destroys CH$_4$ to form higher hydrocarbons. However, the Zahnle et al. (2009a,b) model uses solar-type stellar irradiance and an isothermal atmosphere (i.e. constant temperature versus altitude). As such, neither the photochemical driver nor the thermal environment is tailored for our planet in question. More severely, Moses et al. (2011) pointed out that a typo in a key rate coefficient in the Zahnle et al. (2009a,b) model caused the apparent conversion of methane into higher hydrocarbons at pressures larger than 1 mbar. Generally speaking, at pressures larger than 1 mbar in a hydrogen-abundant atmosphere, hydrogenation of unsaturated hydrocarbons and reaction intermediates efficiently recycle species back to methane, preventing its large-scale destruction. Moses et al. (2011) also discussed the inadequacies of isothermal atmospheric models due to their suppression of transport-induced quenching. Hence, the observed CH$_4$ depletion still awaits adequate explanation. The low abundance of H$_2$O also has not been addressed.

In addition to secondary eclipse observations, primary transit observations of GJ 436b exist as well (Pont et al. 2009, Ballard et al. 2010, Beaulieu et al. 2011, Knutson et al. 2011), and various groups have analyzed them to retrieve molecular abundances in the planet’s terminator regions (Beaulieu et al. 2011, Knutson et al. 2011). In contrast to the secondary-eclipse retrieval, Beaulieu et al. (2011) were able to fit a compendium of their and Ballard et al.’s transit observations between 0.5 and 9 m with 500 ppm CH$_4$ in a H$_2$ atmosphere, and finding no clear evidence for CO or CO$_2$. Moreover, Beaulieu et al. presented that a methane-rich atmosphere, with temperature inversion, can be consistent with the said secondary-eclipse data as well (but see Shabram et al. 2011). More recently, Knutson et al. acquired Spitzer transit photometry at 3.6, 4.5, and 8.0 m during 11 visits. The multiple-visit data showed high transit-depth variability, which the authors attribute to potential stellar activity in the dM host. They did not find any compelling evidence for methane, and data excluding ones believed to be most affected by stellar activity appear to place an upper limit of 10 ppm for methane mixing ratio. The best-fit spectrum to this select data set assumes 1000 ppm H$_2$O, 1000 ppm CO, 1 ppm CH$_4$, with CO$_2$ abundance poorly constrained, roughly in agreement with Madhusudhan et al. Therefore, primary-transit data is currently inconclusive due to different interpretations by different groups.

Our primary goal is to advance the fundamental understanding of processes impacting the chemical state of GJ 436b by developing a 1-D atmospheric model that integrates all of the aforementioned equilibrium and disequilibrium processes. An important aspect of our model is the seamless integration of thermochemistry, kinetics, vertical mixing, and photochemistry in a manner that directly follows from Visscher et al. (2010), and contemporaneously with Moses et al. (2011), obviating the conventional quench-level estimation (Prinn & Barshay 1977).

The quench-level approach assumes that the deep atmosphere is in thermochemical equilibrium because high temperatures provide sufficient kinetic energy to overcome reaction barriers in either direction. However, as vertical transport lifts a gas parcel to cooler, higher altitudes, chemistry becomes rate limited rather than thermodynamically determined. There comes a point in altitude where the kinetic conversion time scale becomes slower than the transport time scale, and the rate-limiting reaction for a molecule of interest is not allowed time to reach completion. At altitudes above this point, the molecule’s concentration is frozen/quenched (therefore, the term “quench level”). In effect, the quench-level approach partitions the atmosphere into two parts: below the quench level, thermochemical equilibrium determines chemical abundances; above the quench level, molecular abundances are uniform versus altitude, with values equal to the equilibrium value at the appropriate quench level for each species. Although this approach has a long record of success (e.g., Prinn & Barshay 1977; Smith 1998; Griffith & Yelle 1999; Saumon et al. 2003; 2006; 2007; Hubeny & Burrows 2007; Cooper & Showman 2006), it does have some limiting assumptions and caveats that require great judiciousness. Specifically, one needs to determine the appropriate rate-limiting, interconversion reaction for each set of coupled species of interest (e.g., interconversion between CH$_4$ & CO). The correct reaction choice is not always readily apparent (see e.g., Visscher et al. 2010) and the appropriate length scale for deriving the mixing time scale from the vertical eddy diffusion coefficient ($K_{zz}$) is still under some debate. Furthermore, since a basic assumption is that temperature decreases with altitude, atmospheric temperature inversions can complicate matters.

Therefore, we implemented a fully reversible kinetic model in the following manner. Every measured forward reaction rate in our list is reversed using the equilibrium constant and the principle of microscopic reversibility. Given enough pathways, both forward and backwards, a given set of chemical species will reach thermochemical equilibrium, kinetically. This provides a seamless transition from the thermochemical equilibrium regime to the disequilibrium-dominated regimes. We can investigate the disequilibrium effects on atmospheric composition in a much more holistic, systematic manner, compared to heuristically identifying plausible disequilibrium processes.

In the remainder of this manuscript we describe the disequilibrium processes that may be occurring in GJ436b’s atmosphere. In §2 we describe thermochemical and chemical kinetics models as well as our estimate for the stellar UV flux. In §3 we show the modeling results as well as a description of the important reaction schemes governing the abundances of various species. Finally in §4 we discuss the relevant implications and conclude.

2. DESCRIPTION OF MODELS

We use joint thermochemistry and “1-D chemical-kinetics with photochemistry” models to study the atmosphere’s departure from thermal equilibrium. External inputs to our models are the metals fraction (denoted further on by $\zeta$), the pressure and temperature (T-P) profile, the eddy diffusion coefficient profile, and
the incident stellar flux; note that we fix the T-P profile and the chemistry is decoupled from it, i.e., there is no self-consistent, radiative-convective adjustment of temperature structure when the chemistry is evolved towards steady state. We initialize the 1-D atmospheres using the NASA Chemical Equilibrium with Applications (CEA) model (Gordon & McBride 1996). Given the initial elemental abundances of H, He, C, O, N, and S in an atmospheric layer, along with the layer’s pressure and temperature, CEA uses a Gibbs free-energy minimization and mass balance routine to calculate the equilibrium species abundances.

Whereas chemical equilibrium concentrations are useful for initializing the atmosphere, they do not provide the correct chemical state above pressure levels of \( \sim 10 \) bars (Prinn & Barshay 1977; Griffith & Yelle 1999; Cooper & Showman 2006; Line et al. 2010; Moses et al. 2011). We simply supply the equilibrium mixing-ratios as boundary conditions in the deep atmosphere for the kinetics calculations, and thereafter evolve the chemical state over multiple timesteps until a steady state is reached.

The computations are carried out with the Caltech/JPL photochemical and kinetics model, KINETICS (a fully implicit, finite difference code), which solves the coupled continuity equations for each involved species, and includes transport via molecular and eddy diffusion (Allen et al. 1981; Yung et al. 1984; Gladstone et al. 1996; Moses et al. 2005). We use the H, C, and O chemical reaction list originally described in Liang et al. (2003; 2004) and references therein updated to high temperatures, recently augmented with a set of N reactions. We have not included the chemistry of sulfur in any great detail, because much of its kinetics is poorly constrained (see e.g., Moses et al. 1996). However we do consider a small, but well measured, set of H\(_2\)S reactions. This helps us appraise if and how the introduction of S affects the abundances of the main molecular reservoirs of H, C, N, O such as CH\(_4\).

We use high temperature rate coefficients for reactions from Line et al. (2010). All reactions are bidirectional, and we reverse them by calculating the back-reaction rates using thermodynamic data (see Table S1). With appropriate reaction pathways and proper rates for the back-reactions, the models can converge to chemical equilibrium purely kinetically in the deep planetary atmosphere where reaction timescales are short compared to transport timescales, and photochemical reactions are unimportant. As mentioned earlier, this removes the cumbersome requirement of having to choose a lower boundary for individual species through ad hoc quench-level arguments (Prinn & Barshay 1977; Smith et al. 1998).

We solve for 51 hydrogen, carbon, oxygen and nitrogen bearing species including H, He, H\(_2\), C, CH\(_3\), CH\(_2\), CH\(_3\), CH\(_4\), C\(_2\)H, C\(_2\)H\(_2\), C\(_2\)H\(_3\), C\(_2\)H\(_4\), C\(_2\)H\(_5\), C\(_2\)H\(_6\), O, O(1D), O\(_2\), OH, H\(_2\)O, CO, CO\(_2\), HCO, H\(_2\)CO, CH\(_2\)OH, CH\(_3\)O, CH\(_3\)OH, HCCO, H\(_2\)C\(_2\)O, CH\(_3\)CO, CH\(_3\)CHO, C\(_2\)H\(_4\)OH, N, N\(_2\), NH, NH\(_2\), NH\(_3\), N\(_2\)H, N\(_2\)H\(_2\), N\(_2\)H\(_3\), N\(_2\)H\(_4\), NO, HNO, NCO, HCN, CN, CH\(_3\)NH\(_2\), CH\(_2\)NH\(_2\), CH\(_2\)NH, H\(_2\)CN, with a total of \( \sim 700 \) reactions, 55 of which are photolysis reactions. The chemical pathway for reducing CO to CH\(_4\), described recently for Jupiter’s deep atmosphere (Wisscher et al. 2010), is included in our reaction list, along with the reverse pathways for CH\(_4\) to CO oxidation. Photolysis absorption cross sections are from Moses et al. (2005) and the thermodynamic data (i.e. the compilation of entropies and enthalpies) used to reverse the kinetic rate coefficients are from JANAF and CEA thermobuild databases; e.g., CEA uses data from Chase et al. (1998) and Gurvich et al. (1989) (see Zehe et al. 2002).

2 Yung & DeMore (1999) tabulate the abundances of Anders & Ebihara (1982). These values predate the more recent downward revision of elements C, O etc. in the Solar photosphere (reviewed in Asplund et al. 2009). Our C/H, O/H, N/H and S/H ratios are a factor 1.66, 1.52, 1.35 and 1.43 higher than those recommended in Asplund et al. (2009). On this revised scale we are modeling a

![Fig. 1.— Estimated temperature profiles for GJ 436b. The dashed profile is the disk averaged dayside profile retrieved by Stevenson et al. (2010). The solid curve is the \( \zeta = 1 \) profile from the global circulation model of Lewis et al. (2010). We use the latter T-P profile for our chemical models.](image-url)
tions of C, N, O, and S relative to H but not relative to each-other (e.g., C/O, N/O, S/O, are always fixed).

The eddy diffusion strength (parameterized by a coefficient, $K_{zz}$) determines the pressure level at which a species is chemically quenched. At the quench level for chemical X, the timescale for vertical transport ($\tau_{\text{trans}}$) equals the chemical loss timescale ($\tau_{\text{chem},X}$). Above that level, which includes the visible portion of the atmosphere, the mixing virtually “freezes” the concentration of that species. Below the quench level, $\tau_{\text{chem},X} \ll \tau_{\text{trans}}$, and thermochemical balance is achieved. Line et al. (2010) and Moses et al. (2011) have used piecewise estimates of the eddy diffusion profiles, $K_{zz}(P)$. The recipe has been to estimate $K_{zz}$ in the deep adiabatic troposphere ($\sim 10^6$ bars) using mixing length theories (e.g., Flasar & Gierasch 1977) and stitch this to global circulation model (GCM) derived profiles obtained by multiplying the (horizontally averaged) GCM vertical winds of Flasar & Gierasch (1977) and stitch this to global circulation model (GCM) derived profiles obtained by many factors, $ab$ initio estimates of it are difficult. We use GALEX and ROSAT derived estimates for GJ 436 and combine these with a $T_{eff} \simeq 3400$ K continuum from the stellar photosphere. This combined emission is used to drive photochemical reactions in GJ 436b.

In the planetary atmosphere both H$_2$ and He are weak absorbers relative to other molecular species, but are enormously more abundant. Helium ceases to absorb longwards of 500 Å, and H$_2$ longwards of 1000 Å. Methane, a carbon reservoir and the molecule of particular interest herein, has a large absorption cross-section shortwards of 1600 Å. Whereas methane (and water) is largely shielded by H$_2$ and He from very shortwave radiation, it is photodissociated by radiation between 1000–1600 Å, and is therefore susceptible to possible intense H I Ly α (λ = 1216 Å) from the M star host. Longwards of $\lambda = 1600$ Å, direct photolysis of methane dwindles due to a combination of the falling cross-section and weak stellar flux. Hydrogen sulfide photodissociates at much longer wavelengths, $\lambda < 2600$ Å, and if present in substantial quantities, is poorly shielded by other reservoir molecules H$_2$, CH$_4$, H$_2$O, etc. H$_2$S photolysis and the resultant hot atomic hydrogen may be influential if $\lambda \simeq 2600$ Å photons can penetrate deep into the planetary atmosphere (more in §3.3.5).

GJ 436 is detected in a GALEX survey exposure in the near UV channel with flux $f_{\text{gal}} = 21.0 \pm 3.7$ μJy (near-UV channel, $\lambda = 2267$ Å, $\Delta\lambda_{\text{FWHM}} = 616$ Å). It is undetected in the GALEX far UV band, with a 3σ upper limit of $f_{\text{gal}} \leq 24$ μJy (far-UV channel, $\lambda = 1516$ Å, $\Delta\lambda_{\text{FWHM}} = 270$ Å). These can be converted to incident UV photon fluxes at the mean orbital separation of GJ 436b. The near UV detection implies a flux of $9 \times 10^{10}$ photons cm$^{-2}$ s$^{-1}$ Å$^{-1}$ between 2000–2500 Å (Yung & DeMore 1999). The 3σ flux upper bound (GALEX far-UV channel) is $\lesssim 1.3 \times 10^{11}$ photons cm$^{-2}$ s$^{-1}$ Å$^{-1}$ which is just a factor of two higher than present-Earth-levels in an equivalent passband.

H Ly α emission can be powerful in the upper chromospheres of cool stars. Because it is strongly absorbed in the interstellar medium, direct line strength estimates are difficult. We make an indirect determination based on empirical correlations with soft X-ray fluxes. Soft X-ray emission from GJ 436 has been observed in the Rosat All Sky Survey (Hünsch et al. 1999), with $f_x \simeq 5.4 \times 10^{-14}$ erg cm$^{-2}$ s$^{-1}$ (0.1-2.4 keV; Rosat PSPC), implying a fractional X-ray luminosity of $L_x / L_{bol} \sim 8 \times 10^{-6}$; this fraction is a factor $\sim 100$ lower than that observed from the most active DM stars and is consistent with GJ436b’s estimated advanced age, 6 ± 3 Gyr. More recent XMM-Newton EPIC measurements (Sanz-Forcada et al. 2010) give a factor of 8 lower $L_x$, which may well be due to X-ray activity. Herein, we adopt the ROSAT flux because larger X-ray fluxes imply proportionally larger Ly α fluxes.

To estimate the Ly α output, we use an empirical correlation of the X-ray and Ly α emission of stars, derived from stellar sample that include several late type stars (e.g., Landsman & Simon 1993 and Woods et al. 2004; in these papers, measurements of Ly α lines were made from International Ultraviolet Explorer and Hubble Space Telescope spectra, after applying a model based correction of ISM absorption). Inverting the Woods et al. (2004) empirical power law, log $F_x \simeq 2.2 \log F_{\text{Ly}α} - 7.76$, we determine a photon flux of $F_{\text{Ly}α} \sim 1.5 \times 10^{14}$ photons cm$^{-2}$ s$^{-1}$ at GJ 436b. The Solar H Ly α flux at
Earth is \( \approx 10^{12} \) photons cm\(^{-2}\) s\(^{-1}\), a factor 100 lower. The reliability of X-ray derived Lyman \( \alpha \) line flux may be assessed by comparing \( F_{\text{Ly}\alpha} \) with the GJ 436b’s H \( \alpha \) line flux. H \( \alpha \) observed in GJ436 in absorption, with an equivalent width of 0.32 Å (Palomar-Michigan State Nearby Star Spectroscopic Survey; Gizis, Reid & Hawley 2002), implies a line flux of \( F_{\text{H}\alpha} \approx 2 \times 10^5 \) erg cm\(^{-2}\) s\(^{-1}\), and a line strength ratio of H Ly \( \alpha \) to H \( \alpha \) of 2.2. For dM stars, where H Ly \( \alpha \) is seen in emission and for which the intrinsic Ly \( \alpha \) line strengths have been measured, this line strength ratio varies between 3-5, with some stars having ratios as low as 2 and others as high as 8 (Doyle et al. 1997).

3. CHEMICAL MODEL RESULTS

3.1. Thermochemical Equilibrium

Equilibrium vertical mixing ratios for the three metallicity cases are shown in Figure 2: these are sub-solar \( \zeta = 0.1 \), solar \( \zeta = 1 \) and super-solar \( \zeta = 50 \) heavy elemental abundances. Because GJ 436b is significantly cooler than HD 189733b and HD 209458b, \( \text{CH}_4 \) is the thermochemically favored carbon carrier; higher effective temperatures drive equilibrium towards CO in the two hot Jupiters. The thermochemical abundances of \( \text{CH}_4 \), CO and \( \text{H}_2\text{O} \) along the T-P profile are readily understood through the net reaction

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

(1)

along with the Law of Mass Action:

\[
\frac{X_{\text{CH}_4}X_{\text{H}_2\text{O}}}{X_{\text{CO}}X_{\text{H}_2}} \frac{1}{P^2} = K_{eq}(T)
\]  

(2)

derived by minimizing the Gibbs free energy of net reaction in (1), with the mixing ratio \( X_i \) of species \( i \), with ambient pressure \( P \), and a temperature dependent equilibrium constant \( K_{eq}(T) \); the \( T \) dependence is governed by the van ’t Hoff equation (\( \Delta G = -RT \log K_{eq} \), with \( \Delta G \) as the standard Gibbs free energy change). At a given pressure \( P \), \( K_{eq}(T) \) behaves in a manner that rising \( T \) drives the equilibrium towards CO. At a fixed \( T \), increasing/decreasing pressures favor higher \( \text{CH}_4/\text{CO} \) concentrations. These relationships are exemplified in the \( \zeta = 1 \) equilibrium profiles shown in Figure 2 (middle panel). As \( P \) and \( T \) decrease along the adiabat between 1000 – 100 bars, the equilibrium constant dominates over the adverse \( P^2 \) dependence, resulting in a drop in the CO fraction. In the isothermal region between 10 – 1 bars, decreasing pressure now favors the production of CO. Between 1 bar and \( \approx 10^{-2} \) bars, the CO fraction falls because of the rapid decrease in temperature with altitude. At levels above the \( \sim 10^{-2} \) level the temperature structure is nearly isothermal, and the decreasing pressure favors higher CO fractions. Similarly, \( \text{NH}_3 \) is the favored N carrier deep in the atmosphere, but is less favored at lower atmospheric pressures. Sulfur can be predominant as \( \text{H}_2\text{S} \), HS, or S depending on pressure and temperature, but for conditions prevalent in GJ 436b, gas phase \( \text{H}_2\text{S} \) is the dominant sulfur reservoir and its concentration is unaffected by the temperature structure. Heavier hydrocarbons, such as ethane (\( \text{C}_2\text{H}_6 \)), are relatively scarce is a factor \( 1.5 \times \) smaller than the estimate based on \( L_x \) used herein for any pressure or temperature (but more common at the highest metallicities).

Enriching the atmosphere to \( \zeta = 50 \) increases the mixing ratios of the reservoir species in proportion, however the shapes of the vertical profiles are much the same as for solar metallicities. Similarly, decreasing the metallicity of the atmosphere to \( \zeta = 0.1 \) lowers the mixing ratios of the heavy gases, by a factor \( \sim \zeta \) for \( \text{CH}_4 \) and \( \zeta^2 \) for CO etc. The shapes of vertical distributions are nonetheless preserved, and relatively insensitive to \( \zeta \).

For all three metallicity cases considered, the chemical equilibrium abundances of \( \text{CH}_4 \) and \( \text{H}_2\text{O} \) stay relatively high – there is always enough hydrogen present...
to build these molecules. One can imagine an extreme situation where H is highly depleted, but such an atmosphere would be incompatible with the observed planetary radius. Conversely, the planet could be impoverished in metals to greatly sub-solar levels \( \zeta \ll 0.1 \), although unreasonably low metallicities \((\leq 1 \times 10^{-5} \times \text{sol})\) would be required to deplete CH\(_4\) and other common molecules to levels below 1 ppm. These simple cases serve to show that, based solely on chemical thermodynamics, CH\(_4\) has to be relatively abundant in GJ 436b and other \( T_{\text{eff}} = 500 - 1000 \) K H-rich planets.

3.2. Vertical Mixing & Chemical Quenching

Vertical turbulent mixing has been invoked to explain the anomalously large observed abundance of CO in Jupiter (Prinn & Barshay 1977) and brown dwarfs such as GL 229b (Griffith & Yelle 1999). Diffusive tropospheric mixing, in combination with detailed CO chemistry, has recently been used to infer the water inventory in the deep Jovian atmosphere (Vischer et al. 2010). Cooper & Showman (2006) parameterized the quench chemistry of CH\(_4\) in order to study its horizontal and vertical transport in their GCM of HD 189733b. The recent paper by Moses et al. (2011) discusses in detail the quench chemistry of H,C,N,O molecular species in the relatively hot atmospheres of HD 189733b and HD 209458b.

In our kinetics models we set thermochemical abundances as boundary conditions; these equilibrium abundance boundary conditions also define the metallicity of the system. We affix the \( 10^3 \) bar mixing ratios of the large carbon, oxygen and nitrogen reservoirs, CH\(_4\), H\(_2\)O, CO, N\(_2\), and NH\(_3\), at their thermochemically derived values (here we are excluding sulfur), and set all other species to obey a zero flux condition at the lower boundary. The exact location of this lower boundary is unimportant, provided it is at depths much greater than the quench level \((\geq 100 \) bars), and conditions (the high densities and temperatures) favor thermochemical equilibrium concentrations for practically all species. The nominal case has a solar abundance atmosphere \((\zeta = 1)\), vertical mixing with strength \( K_{zz} = 1 \times 10^8 \text{ cm}^2 \text{ s}^{-1} \), and no photochemistry. In Figure 3 we compare an atmosphere with vertical mixing to one purely in equilibrium. Below 10s of bars, the mixing ratios converge, satisfying the condition that equilibrium concentrations have been reached kinetically. Now consider the abundances of quenched CO. At pressure levels deeper than 10s of bars, the eddy mixing time, \( \tau_{\text{trans}} \), must be longer than the chemical loss timescale. As a check for internal consistency, we estimate

\[
\tau_{\text{trans}} = \frac{L^2}{K_{zz}} \simeq 8 \times 10^5 \text{ s}
\]

where \( L \) is a fraction \( f \) of the scale height \( H \), \( L = fH \) (Smith et al. 1998). We estimate \( f = 0.3 \) for both quenched CO and N\(_2\). To estimate \( \tau_{\text{chem}} \) for CO, we need to identify the rate-limiting reaction in CO and CH\(_4\) interconversion.

\[
\begin{align*}
H + CO + M &\rightarrow HCO + M \quad R605 \\
H_2 + HCO &\rightarrow H_2CO + H \quad R234
\end{align*}
\]

This set of reactions is identical to the ones identified for CO quenching in Jupiter (Yung et al. 1988; Vischer et al. 2010). The rate-limiting reaction is R351, the inverse of a hydrogen abstraction from methanol. The chemical loss timescale for CO is,

\[
\tau_{\text{chem,CO}} = \frac{[\text{CO}]}{k_{351} [\text{H}_2] [\text{CH}_3\text{O}]} \tag{4}
\]

where \([X]\) denotes the concentration \( X \), and \( k_{351} = 2.10 \times 10^{-25} T^{1.0} e^{-2470/T} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1} \) (Jodkowski et al. 1999) the rate coefficient for R351. Figure 4 shows that equality of these two timescales, \( \tau_{\text{chem,CO}} \approx \tau_{\text{trans}} \), gives a CO quench-level of \( \sim 30 \) bars, which furthermore agrees well with quench-level depicted by the CO mixing ratio profiles in Figure 3.

In an analogous manner the N\(_2\) quench-level may be calculated by identifying the rate-limiting step in the series of reactions that convert nitrogen to ammonia, and vice versa. These reactions are

\[
\begin{align*}
\text{Net : } 3\text{H}_2 + \text{CO} &\rightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \text{I} \\
\text{Net : } 4\text{H}_2 + \text{N}_2 &\rightarrow 2\text{NH}_3 + 2\text{H} \quad \text{II}
\end{align*}
\]

In this N\(_2\) = NH\(_3\) sequence R450 is the rate-limiting step, involving the N abstraction from diazene, giving a timescale

\[
\tau_{\text{chem,N}_2} = \frac{[\text{N}_2]}{k_{450} [\text{H}_2][\text{N}_2\text{H}_2]} \tag{5}
\]

with reaction rate \( k_{450} = 2.06 \times 10^{-27} T^{-0.93} e^{-20614/T} \), obtained from that of its reverse reaction (Stothard et al. 1995). Calculating \( \tau_{\text{chem,N}_2} \) above gives a N\(_2\) quench-level of \( \sim 300 \) bars (see Figure 4), in agreement with the vertical profiles in Figure 3. The abovementioned quench-levels for CO and N\(_2\) are for the adopted eddy diffusion coefficient, \( K_{zz} = 10^8 \text{ cm}^2 \text{ s}^{-1} \). Increasing \( K_{zz} \) to a very large value, \( 10^{11} \text{ cm}^2 \text{ s}^{-1} \), shortens the transport times considerably and increases the quench pressures of CO and N\(_2\) to \( \sim 150 \) bars and \( \sim 620 \) bars, respectively. The effects of varying the quench level may be seen in Figure 2 – the atmospheric concentrations of the reservoir gases, CH\(_4\), H\(_2\)O and NH\(_3\), and quenched N\(_2\), are relatively insensitive to the location of quench pressure. However, varying the quench-level affects the concentration of CO and CO\(_2\) by orders-of-magnitude.
Vertical dredging of gases leaves a reasonably altered composition in the 1-0.001 bar region, the range of pressure levels wherein the infrared photosphere is located (e.g., Knutson et al. 2009; Swain et al. 2009). For example CO is up to a factor $10^4$ more abundant than it would otherwise be. The deep quenching of N bearing gases causes NH$_3$ to be surprisingly abundant, dominating over the thermochemically favored N$_2$. In contrast, the largest C and O reservoirs and optically the most active gases, CH$_4$ and H$_2$O, are largely unaffected.

3.3. Photochemical Effects

Photochemistry can significantly alter atmospheric composition in the upper portions. The combination of the ultraviolet flux and molecular absorption cross sections gives the photolysis rates for all the species considered here. The altitude of peak production/loss (in units of cm$^{-3}$ s$^{-1}$), set by the balance between the exponential fall-off of atmospheric density and the inward stellar UV attenuation, occurs near 1 $\mu$bar (this is the well known Chapman function, see Yung & DeMore 1999 pg. 45). Primarily, photolysis breaks apart stable molecules into radicals, which can then react to alter the composition of the upper atmosphere. See Figures 5-7 for the photochemically derived mixing ratios. Table 1 compares the column mixing ratios from our models to the observations over the 7 bar to 0.1 bar range probed by the observations. Figure 8 illustrates how photochemistry alters the upper atmosphere. The resultant mixing ratio profiles are compared with those obtained via thermochemical equilibrium (Figure 2), and by vertical mixing
Fig. 5.— Mixing ratios for important radicals (OH, NO, O, H, and CH$_3$) that drive the photochemistry for three metallicities ($\zeta = 0.1$ (top), $\zeta = 1$ (middle), and $\zeta = 50$ (bottom)). Note how the CH$_3$ profile very nearly tracks the H profile because CH$_3$ is a direct consequence of the oxidation of methane in R60.

detailed mechanism for producing H is the photosensitization of H$_2$ using water via,

$$\text{H}_2\text{O} + h\nu \rightarrow \text{OH} + \text{H} \quad \text{R25}$$
$$\text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H} \quad \text{R169}$$

Net : $\text{H}_2 \rightarrow 2\text{H} \quad III$.

This photosensitization is efficient because H$_2$O dissociates out to $\sim 2000$ Å, whereas H$_2$ dissociates only out to $\sim 800$ Å. H$_2$O acts as a photon sink, with factor $\sim 10^4$ more photons available for its photolysis, than for direct
observations (Madhusudhan & Seager 2011). Although photolysis seems not to significantly modify methane abundances, it does produce large concentrations of the methyl radical, CH₃; this radical is important in the synthesis of heavier hydrocarbons. CH₃ is formed by photosensitized dissociation of methane. The free atomic hydrogen from scheme III readily attacks methane to produce H₂ and CH₃. The trigger and pathway for this is:

\[
\begin{align*}
\text{H}_2\text{O} + h\nu & \rightarrow \text{OH} + \text{H} & R25 \\
\text{H}_2 + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{H} & R169 \\
\text{H} + \text{CH}_4 & \rightarrow \text{CH}_3 + \text{H}_2 & R60
\end{align*}
\]

\[
\text{Net} : \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}.
\]

The methyl radical’s mixing ratios can be as high as \( \sim 10^{-4} \), as in the \( \zeta = 1 \) case (Figure 5). Due to the warmer upper atmosphere, relative to that in the solar system giants, the oxidation of methane (via R60) is more two orders-of-magnitude more efficient than direct photolysis. Because the forward reaction (R60) proceeds more sharply with rising temperature than the reverse (R61), hotter upper atmospheres (as in HD 189733b and HD 209448b) will have a tendency to destroy methane more readily, especially when there are large quantities of photochemically produced atomic hydrogen present. This photosensitized destruction of methane causes it to decline sharply above \( \sim 10 \) \( \mu \)bars; this is well below the planetary homopause, but well above the infrared photosphere (Figure 8). It also drives the production of heavier hydrocarbons. Little to no heavier hydrocarbon \( (\text{C}_n\text{H}_m, \text{where } n, m \geq 2) \) is expected via vertical mixing alone, with mixing ratios remaining below \( \sim 10^{-10} \) at altitudes above 1 bar. Methane photosensitization (scheme IV) converts the carbon into ethylene (\( \text{C}_2\text{H}_4 \)), acetylene (\( \text{C}_2\text{H}_2 \)), and ethane (\( \text{C}_2\text{H}_6 \)) via

\[
\begin{align*}
\text{H}_2\text{O} + h\nu & \rightarrow \text{OH} + \text{H} & R25 \\
2(\text{H} + \text{CH}_4 & \rightarrow \text{CH}_3 + \text{H}_2) & R60 \\
\text{CH}_3 + \text{CH}_3 & \rightarrow \text{C}_2\text{H}_6 + \text{M} & R613 \\
\text{H} + \text{C}_2\text{H}_5 & \rightarrow \text{C}_2\text{H}_3 + \text{H}_2 & R70 \\
\text{H} + \text{C}_2\text{H}_5 & \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 & R68 \\
\text{H} + \text{C}_2\text{H}_4 & \rightarrow \text{C}_2\text{H}_3 + \text{H}_2 & R85 \\
\text{H} + \text{C}_2\text{H}_3 & \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 & R64
\end{align*}
\]

\[
\text{Net} : 2\text{CH}_4 + 4\text{H} \rightarrow \text{C}_2\text{H}_2 + 5\text{H}_2
\]

The net reaction ultimately produces \( \text{C}_2\text{H}_2 \), making it the most abundant heavy hydrocarbon. This scheme is different than the solar system gas giants where the most dominant pathway for producing acetylene involves the
binary collision between two $^3\text{CH}_2$ radicals. This difference can again, be owed to the overwhelming abundance of atomic H from water photolysis which can readily reduce the ethane produced R613 to acetylene. Over the range of metallicities considered ($\zeta = 0.1$ to 50), the peak values of C$_2$ hydrocarbons occur between 10 and 1 $\mu$bars. These mixing ratios of C$_2$H$_4$, C$_2$H$_2$, C$_2$H$_6$ lie between $3 \times 10^{-7}$-$6 \times 10^{-6}$, $5 \times 10^{-6}$-$4 \times 10^{-4}$, and $5 \times 10^{-9}$-$6 \times 10^{-5}$ (Figure 7; for integrated columns see Table 1). For comparison, the peak values in Jupiter are, respectively, $\sim 2 \times 10^{-6}$, $5 \times 10^{-6}$, and $20 \times 10^{-6}$ (Moses et al. 2005). In the Solar System’s giant planets, ethylene, acetylene, and ethane have strong mid-infrared stratospheric emission features at 10.5, 13.7 and 12.1 $\mu$m respectively. These C$_2$ species can lead to further synthesis of higher order hydrocarbons that can form hydrocarbon aerosols (Zahnle et al. 2009). However, the vapor pressures for these species are high (many bars) at these temperatures, so it may be difficult to form such aerosols. Additionally, Moses et al. 1992 showed that supersaturation ratios of 10 to 1000s may be required in order to trigger condensation due to the lack of nucleation particulates in Jovian type atmospheres. detectability

### 3.3.3. CO & CO$_2$

As described in §3.2, the CO abundance above 10 bars is determined by the reaction rate of scheme I, and the strength of vertical mixing. In the absence of incident stellar UV, a profile with a constant vertical mixing ratio up to the homopause is obtained. With incident UV radiation, there is a photochemical enhancement of CO near the 1 $\mu$bar level, of up to a factor of 10$^2$ for the $\zeta = 1$ case (Figure 6, 8). This high altitude enhancement is a property of the cooler atmosphere of GJ 436b; in hot Jupiter atmospheres, as in HD 189733b and HD 209458b, such enhancements or deficits will tend to be driven back towards equilibrium values. The carbon in this extra CO is ultimately derived from the CH$_4$ reservoir, via the following reaction scheme:

\[
\begin{align*}
\text{H}_2\text{O} + \text{h} \nu & \rightarrow \text{OH} + \text{H} \quad R25 \\
\text{H} + \text{CH}_4 & \rightarrow \text{CH}_3 + \text{H}_2 \quad R60 \\
\text{O} + \text{CH}_3 & \rightarrow \text{H}_2\text{CO} + \text{H}_2 \quad R98 \\
\text{H} + \text{H}_2\text{CO} & \rightarrow \text{HCO} + \text{H}_2 \quad R233 \\
\text{H} + \text{HCO} & \rightarrow \text{CO} + \text{H}_2 \quad R213
\end{align*}
\]

**Net:** $\text{H}_2\text{O} + \text{CH}_4 \rightarrow \text{CO} + 2\text{H}_2 + 2\text{H} \quad VI$

Scheme VI is driven by the water photolysis driven dissociation of CH$_4$ to CH$_3$ via scheme IV. Atomic O is produced by photolytic fragmentation of water (R26); the net absorption cross section for this branch is $\approx 0.1$ that of the main branch in R25. The two radicals, O and CH$_3$, form formaldehyde in R98, and followed thereafter by a two-step conversion to CO (R233 and R213). An enhancement of CO$_2$ largely traces the enhancement of CO via:

\[
\begin{align*}
\text{H}_2\text{O} + \text{h} \nu & \rightarrow \text{OH} + \text{H} \quad R25 \\
\text{H} + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{H} \quad R169 \\
\text{H} + \text{CH}_4 & \rightarrow \text{CH}_3 + \text{H}_2 \quad R60 \\
\text{NH}_3 + \text{h} \nu & \rightarrow \text{NH}_2 + \text{H} \quad R43 \\
\text{H} + \text{NH}_2 & \rightarrow \text{NH} + \text{H}_2 \quad R455 \\
\text{NH} + \text{CH}_3 & \rightarrow \text{CH}_2\text{NH} + \text{H} \quad R685 \\
\text{H} + \text{CH}_2\text{NH} & \rightarrow \text{H}_2\text{CN} + \text{H}_2 \quad R655 \\
\text{H} + \text{H}_2\text{CN} & \rightarrow \text{HCN} + \text{H}_2 \quad R663
\end{align*}
\]

**Net:** $\text{H}_2\text{O} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \quad VII$

Photochemically enhanced CO$_2$ mixing ratios reach $\sim 10^{-4}$ at 1 $\mu$bar for $\zeta = 1$. Column averaged mixing ratios are $5 \times 10^{-6}$ and $6 \times 10^{-9}$ (see Table 1). This is low compared to the observed mixing ratios of $\sim 1 \times 10^{-4}$ and $\sim 1 \times 10^{-7}$, respectively. Increasing the metallicity to $\zeta = 50$, increases the mixing ratios to $\sim 1 \times 10^{-2}$ and $\sim 5 \times 10^{-4}$, suggesting that the observed CO and CO$_2$ columns are consistent with a metallicity enhanced to levels observed in Solar System’s ice giant planets (Table 1).

#### 3.3.4. Nitrogen & HCN

Ammonia and molecular nitrogen, N$_2$, are thermochemically the two most stable species in a reducing atmosphere and their relative abundance within the 1 – 0.001 bar pressure levels is dictated by quench chemistry. Because it is relatively abundant, the addition of hot (quenched or otherwise) NH$_3$ (Tennyson et al. 2010) to the list of absorbers used for model fitting and retrieval may well be quite important. Other important N species are mainly photochemical byproducts, with HCN being the most abundant photochemically produced molecule between 1 and 0.1 mbar levels, having mixing ratios of typically $10^{-6}$ ($\zeta = 1$) to $10^{-5}$ ($\zeta = 50$) at 0.1 mbar. Peak HCN occurs well above the photospheric levels, approaching $10^{-4}$ at 1 $\mu$bar. The synthesis of HCN is initiated via water and ammonia photolysis, and completed by subsequent reactions between the ammonia and methane derived radicals:

\[
\begin{align*}
\text{H}_2\text{O} + \text{h} \nu & \rightarrow \text{OH} + \text{H} \quad R25 \\
\text{H}_2 + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{H} \quad R169 \\
\text{H} + \text{CH}_4 & \rightarrow \text{CH}_3 + \text{H}_2 \quad R60 \\
\text{NH}_3 + \text{h} \nu & \rightarrow \text{NH}_2 + \text{H} \quad R43 \\
\text{H} + \text{NH}_2 & \rightarrow \text{NH} + \text{H}_2 \quad R455 \\
\text{NH} + \text{CH}_3 & \rightarrow \text{CH}_2\text{NH} + \text{H} \quad R685 \\
\text{H} + \text{CH}_2\text{NH} & \rightarrow \text{H}_2\text{CN} + \text{H}_2 \quad R655 \\
\text{H} + \text{H}_2\text{CN} & \rightarrow \text{HCN} + \text{H}_2 \quad R663
\end{align*}
\]

**Net:** $\text{CH}_4 + \text{NH}_3 \rightarrow \text{HCN} + 3\text{H}_2 \quad VIII$

We note that R43, the photolysis of ammonia to amino radical, is the most important pathway for NH$_2$ formation at pressures greater than 10 $\mu$bar. At lower pressures this reaction is driven by ammonia photosensitization.

\[
\text{NH}_3 + \text{H} \rightarrow \text{NH}_2 + \text{H}_2, \quad R454
\]

where the is H derived from H$_2$O photolysis. In conclusion when water, ammonia and methane are present,
dis-equilibrium HCN is relatively abundant. The best chance for the detection of HCN is via the transmission spectroscopy of its vibrational fundamental bands at 3 and 14 μm (Shabram et al. 2011).

3.3.5. Sulfur

Because atomic H attacks both CH₄ and NH₃, we examine the role of H₂S as a source of free H (Zahnle et al. 2009); S is isoelectronic with and similar in chemical properties to O, but has a considerably reduced primordial abundance, with S/O ≃ 0.02. In a subset of models, we introduce the following (very restricted) set of sulfur reactions with accurate laboratory determined reaction rates:

\[
\begin{align*}
\text{H}_2\text{S} + \text{h} \nu & \rightarrow \text{SH} + \text{H} & R705 \\
\text{H}_2\text{S} + \text{H} & \rightleftharpoons \text{SH} + \text{H}_2 & R701, R702 \\
\text{H}_2\text{S} + \text{OH} & \rightleftharpoons \text{SH} + \text{H}_2\text{O} & R703, R704
\end{align*}
\]

H₂S is an attractive source of free hydrogen due to its ability to photodissociate out to relative long wavelengths, ~2600 Å. It has a photolysis rate constant comparable to that of H₂O, and we find a 10² enhancement in H between the pressure levels of 1 bar and 0.1 mbar upon including these two sulfur species (Figure 9); the relevant reactions are:

\[\text{H}_2\text{S} + \text{h} \nu \rightarrow \text{SH} + \text{H} \quad R715\]

This enhanced H abundance is catalyzed by the photolysis of H₂S (traced by the SH radical in figure 9, top panel). The atomic H reacts efficiently with CH₄ in R60, producing an increased concentration of the radical CH₃, which in turn drives hydrocarbon production (scheme V) near the 0.1 bar level.

However, the free H in the middle atmosphere, does little to affect the CH₄ mixing ratios; this is because the S/C abundance ratio is low. Sulfur would need to be enriched by a substantial factor of ~20, over the solar S/C value, in order for H₂S to have an appreciable impact on atmospheric CH₄. Although the few considered sulfur species (H₂S, SH) do not much impact the overall chemistry, it is possible that another sulfur compound, such as SO, may act as a catalyst assisting in the conversion of reduced carbon into oxidized carbon. Previously, Moses (1996) has modeled the SL9 Jupiter impact and shown the importance of S in many reaction schemes involving both C and N species, and so the role of S chemistry in the hot extrasolar giants should continue to be investigated in the future (see Zahnle et al. 2009).
We have developed a 1D “thermochemical and photochemical kinetics with transport” model following Visscher et al. (2010) and recently, Moses et al. (2011) for extrasolar planet atmospheres. We use a compilation of bidirectional reactions of the five most abundant elements to model both the equilibrium and disequilibrium portions of the atmosphere. Using detailed balance with both forward and reverse reactions, allows our model to reach thermochemical equilibrium kinetically, thereby obviating the need to choose ad hoc lower boundaries for multiple quenched species, and allowing a seamless transition between the transport dominated and the chemical equilibrium zones. A limitation is that we adopt a static temperature structure; a future improvement would allow the iterative adjustment and co-evolution of the temperature structure with the chemistry. Also, the eddy diffusivity profile $K_z(z)$ is poorly constrained, and is essentially a free parameter in any of these models.

We have applied our models to study the atmosphere of the transiting Neptune-like planet GJ 436b. The elemental abundance of atmosphere, a key input parameter, is relatively uncertain, but mass-radius constraints suggest that GJ 436b must be enriched to at least $10^4$ solar levels. We model a range of atmospheric enrichment to cover this intrinsic uncertainty; we observe the trends when varying $\zeta$, and rule out the possibility that intermediate values of $\zeta$ would spring any surprises. The UV fluxes of stars other than the Sun are often difficult to obtain. M-dwarf hosts can be chromospherically hyperactive, and because UV photolysis may drive the depletion of weakly bonded molecules such as CH$_4$, NH$_3$ and H$_2$S, it is important to have an accurate UV estimate for GJ 436. We use a combination of GALEX and HST UV fluxes along with Rosat and XMM-Newton soft X-ray fluxes to bound the UV continuum and line emission of GJ 436.

The GJ 436b model atmospheres show that a combination of photometry, chemical kinetics and transport-induced quenching drives the composition well out of equilibrium. While equilibrium conditions are maintained in the deep, hot, troposphere (below a 10s of bars for CO = CH$_4$, and 100s of bars for N$_2$ = NH$_3$), the composition of the middle atmosphere is altered by the dredging up of quenched gases such as CO and NH$_3$. The effects of transport disequilibrium are prominent in cooler planets such as GJ 436b because the quench points for major species depend on the temperature. As it gets colder, the pressure points for quenching are pushed deeper into the atmosphere due to the longer interconversion timescales from one species reservoir to another. In contrast to the quenched species (CO, CO$_2$, NH$_3$), the effect of vertical mixing on the reservoir gases such as CH$_4$ and H$_2$O is relatively feeble.

The reservoir gases H$_2$O and CH$_4$, and NH$_3$ are largely unaffected by photochemistry because of their (a) large abundances, and (b) rapid recycling. Nevertheless, it is their photolysis that drives the bulk of the disequilibrium chemistry in the upper atmosphere producing CH$_4$ and NH$_3$ sinks such as heavier hydrocarbons (such as C$_2$H$_2$, etc.) and simple nitriles (such as HCN). Much as in the hot Jupiters (Liang et al. 2003), H is the most important and active atom in the bulk of the atmosphere; it is created by the photosensitized destruction of H$_2$, catalyzed by the presence of H$_2$O and H$_2$S. The latter gas, though less abundant than water, is important because of its ability to capture incident starlight photons out wavelengths as long as 2600 Å. In most models, H replaces H$_2$ as the most abundant species in the atmosphere above the planetary homopause at $\approx 1$ µbar. Because CH$_4$ is the largest C carrier in the planet’s UV photosphere, we create abundant C$_2$ compounds (Figure 7) despite the relatively efficient hydrogenation back to CH$_4$. Species such as acetylene, C$_2$H$_2$, formed in abundance in our enriched models, are precursors for potential hydrocarbon soot formation in the upper atmosphere (as opposed to the hotter Jupiters such as HD 209458b and HD 189733b, wherein CO carries the bulk of carbon in the stratosphere). Our reaction lists for hydrocarbon chemistry are truncated at C$_2$, and so we do not synthesize C$_3$ and heavier hydrocarbons and nitriles explicitly.

Within the range physical and chemical processes captured in our models, and the considered reaction sets and their kinetics, we find it difficult explain the observations suggesting a methane-poor GJ 436b. Except above 1 µbar pressure levels where CH$_4$ is photochemically converted to CO, HCN and C$_2$ hydrocarbons, it remains the predominant C reservoir in the lower atmosphere and in the region of the IR photosphere. The observed abundances of quenched CO and CO$_2$ are in agreement with an atmosphere enriched to levels intermediate between 1 to 50 times solar (as in Madhusudhan & Seager 2011). The depleted water may either contrarily suggest a sub solar metallicity (Table 1), or skewed heavy metals ratios; the latter is a possibility which we have not considered herein as there are far too many combinations to explore. In the $1 \times$ solar models, the methane abundance
This, we mean that the relevant rate-limiting reaction must necessarily be identified in order to properly calculate the timescale for chemical loss. Also, quenched gases do not share a common quench level and assuming so can result in gross under- or overestimation of their abundances. For example, as shown herein, N₂ and CO have vastly different quench levels. For the moderate to high levels of incident UV flux, photolysis generates high concentrations of secondary byproducts, but does not significantly alter the abundances of the reservoir gases; in our estimation photochemistry cannot alter the dayside methane budget. Hotter atmospheres with sluggish vertical mixing and hot stratospheres are required for severe methane depletion. For example, in figure 10, we approximate such as atmosphere as isothermal with \( T = 1200 \text{ K} \), \( \zeta = 5 \), and \( K_{zz} = 1 \times 10^6 \text{ cm}^2\text{s}^{-1} \), and with zero UV irradiation (similar to models by Zahnle et al. 2009). In this hypothetical atmosphere there is relatively little quenched methane. At \( T = 1200 \text{ K} \) and low pressures, the rate determining step for \( \text{CH}_4 \rightarrow \text{CO} \) (reverse of R351) is faster than the vertical transport time throughout the atmosphere, allowing the \( \text{CH}_4 \) to be in thermochemical equilibrium with CO everywhere (Figure 10). Since equilibrium conditions apply, the \( P^2 \) term in equation 2 results in the rapid vertical fall-off of \( \text{CH}_4 \).

The models presented herein are by no means restricted in applicability to GJ 436b like Neptunes, and much of the modeled chemical state may be generalized to H/He dominated planets in the 500-1000 K temperature range. In this regime \( \text{CH}_4 \) is the primary carbon carrier and CO is quenched. The reverse is true in hotter atmospheres, \( T > 10^3 \text{ K} \), where CO is the primary carbon carrier and \( \text{CH}_4 \) is quenched. \( \text{NH}_3 \) is quenched deep in the atmosphere and can be quite abundant in the photosphere. Higher hydrocarbons and HCN are produced photochemically in relatively high abundances at mbar to \( \mu \text{bar} \) pressures. Similarly, an enhancement of CO and \( \text{CO}_2 \) over the quench concentrations, driven by the photolysis of \( \text{H}_2\text{O} \), is observed in the high atmosphere. Water is in gaseous phase and abundant, and not condensed out as it would be in cooler atmospheres. GJ 1214b, a
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