PHOTOCHEMISTRY IN THICK ATMOSPHERES ON SUPER EARTHS.

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Introduction: One of the most profound discoveries of the search of exoplanets is a ubiquitous population of super Earths (i.e., exoplanets whose masses are no larger than 10 times Earth's mass) [1,2]. If a super-Earth is transiting its host star, the planetary atmosphere may be observed via transmitted stellar radiation [3-7] and additionally for hot planets, planetary thermal emission [8]. A rapid growth in both the number of terrestrial exoplanets and the amount of photometric and spectroscopic data from their atmospheres can be anticipated.

The atmospheres of super Earths are new theoretical subjects to be studied by photochemistry models because they may be thick enough to maintain thermochemical equilibrium at depth, but many super Earths are not expected to be massive enough to retain primordial H_2-dominated atmospheres. Super Earths may have thick atmospheres that are not dominated by hydrogen. Population synthesis studies of planetary formation and evolution have suggested high metallicities for low-mass planets [9]. Recent observations of GJ 1214b, a super Earth ~6 times more massive than Earth, have hinted at a mean molecular mass significantly larger than that of a hydrogen-dominated atmosphere [3,6].

We here present the first self-consistent theoretical model for atmospheres of super Earths. Our model solves steady-state compositions at the high pressure levels where thermochemistry holds as well as the low pressure levels where vertical mixing and photochemical processes create disequilibrium chemistry. Our model differs from previous photochemistry-thermochemistry models for giant planet atmospheres [9-20] in the way that our model does not assume a fixed atmospheric composition. As a result, our model is uniquely suitable for exploring the compositions of super Earth atmospheres in which the dominant component is *a priori* unknown.

Model: We have extended the photochemistry model described in [21] to include a proper treatment of thermochemistry at high temperatures and pressures. We have included the reverse reaction for each forward reaction following the procedure detailed in [16], and have also added the high-pressure limit rates for all three-body reactions.

The photochemistry model requires the temperature profile of the atmosphere as input. We compute the temperature profile throughout the atmosphere by balancing the energy flux of planetary thermal emission with that of stellar irradiation. With a grey atmosphere assumption (i.e., mean opacities in stellar radiation wavelengths and in thermal emission wavelengths), we compute the temperature profile of the atmosphere as a function of the thermal infrared optical depth as described in [22]. The temperature profile is computed based on an atmospheric composition that obeys the thermochemistry equilibrium. The thermochemistry routine and the radiative transfer routine are interdependent, so they are used iteratively to achieve a stratified atmospheric composition that obeys thermochemical equilibrium, radiative-convective equilibrium, and hydrostatic equilibrium.

A unique feature in our photochemistry-thermochemistry model for non-hydrogen-dominated thick atmospheres is that the model does not require specification of the main component of the atmosphere (nor the mean molecular mass). For the radiative transfer routine and the thermochemical equilibrium routine we use a pressure level grid so that a mean molecular mass is no longer required to be specified *a priori*. Instead, the mean molecular mass is synthesized from the thermochemically equilibrated composition profile, and is then used in the transformation from a pressure level grid to a vertical altitude grid. Our approach eliminates the need to specify a background atmosphere for photochemical simulations of thick atmospheres, which makes our model uniquely desirable for applications in the study of super Earths.

The thermochemically equilibrated compositions determined by a combination of C-H-O elemental abundance also serve as the lower boundary conditions in our photochemistry models. Specifically we use the mixing ratios determined by thermochemical equilibrium at 1000 bar as our fixed-mixing-ratio lower boundary conditions in the photochemical (i.e., kinetic) simulations.

We have validated our model by simulating the atmospheric composition of hot Jupiter HD 189733b. We simulated the hydrogen-dominated atmosphere with a solar metallically for HD 189733b. The resulting atmospheric composition agrees with the observationally inferred composition. Our results are also in good agreement with a similar suite of simulations shown by [16] for the same planet to within a factor of 2. Interestingly, the assumption of the strength of vertical mixing affects the steady-state mixing ratio of methane and other hydrocarbons significantly at the pressure levels of 0.001-1 bar. We find our model able to simulate H_2-dominated thick atmosphere of irradiated exoplanets.

Results: With our photochemistry-thermochemistry model, we simulate the compositions of atmospheres on GJ 1214b-like exoplanets, considering a variety of chemical compositions. We seek steady-state compositions of atmospheres with a variety of H, O, and C elemental abundances, ranging from hydrogen-rich to hydrogen-poor and from oxygen-rich to oxygen-poor (Figure 1).

The most interesting finding is that when hydrogen is no longer a dominant element in a thick atmosphere, the chemical diversity is enormous. The most abundant molecule at potentially observable levels (10^{-3}~1 bar) of the atmosphere can be H_2O, CO_2, CO, CH_4, H_2, and even O_2 and other hydrocarbons, and the details is controlled by the abundance of H and the C/O ratio (Figure 1). For a planet like GJ 1214b, thermochemical equilibrium for a wide range of C-H-O elemental abundance can be readily established at the pressure of 0.1-10 bar and the vertical transport homogenizes the atmosphere up to the pressure of 1 mbar.

While hydrogen-rich thick atmospheres of super Earths have the same chemical behaviors as those of gas giants, new classes of atmospheric composition emerge as the super Earth evolves and the hydrogen abundance decreases. If the hydrogen abundance is lower than 0.7, the dominant species in the observable atmosphere would be water vapor if the atmosphere is oxygen-rich, and hydrocarbons (i.e., CH_4, C_2H_2, and C_2H_4) if the atmosphere is carbon-rich (see Figure 1). For a C/O ratio near the solar abundance, the atmospheres may contain significant portions of H_2, CH_4, CO, CO_2, and H_2O concurrently (Figure 1). For an extremely evolved super Earth, most atmospheric hydrogen may have been lost, and its atmosphere may even have significant O_2 piled up. As shown in Figure 1, we predict that the zoo of super Earth atmospheres is much more versatile than previously thought.

Among many possibilities water-rich atmospheres are special because water is a substance fundamental for life. Here we find that waver vapor should be the dominant species of thick atmospheres of moderately evolved super Earths that formed in an environment not more carbon-rich than the Solar nebula. In addition, we find that if H_2O is the dominant gas in the atmosphere of GJ 1214b, most of the carbon in its atmosphere should be in the form of CO_2, and CO, CH_4 and other hydrocarbons should only have trace amounts. The reason is that CH_4 or CO would be readily oxidized by water to CO_2. Therefore, H_2O cannot coexist with equally abundant CH_4 or CO on super Earth GJ 1214b. This finding implies that chemical stability has to be taken into account when seeking a fit to the spectrum of a super Earth like GJ 1214b.

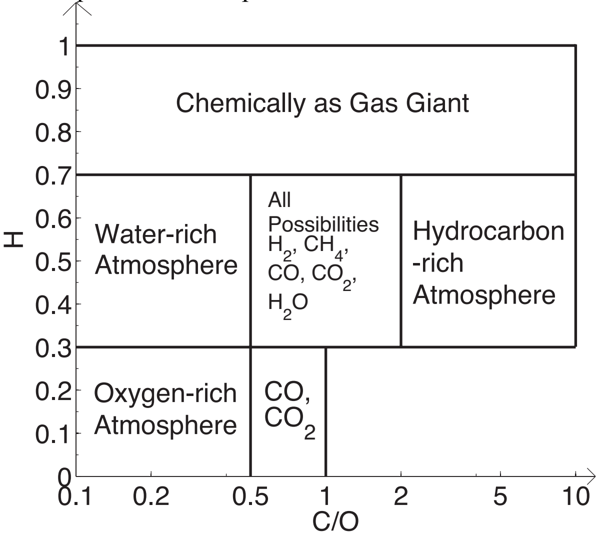

Figure 1: Dominant components in the atmosphere of a GJ 1214b-like planet on a two-dimensional map of the hydrogen abundance and the carbon versus oxygen ratio. The simulated planet is GJ 1214b sized at the 0.014-AU orbit of an M 4.5 star, and the atmospheres have a temperature of 470 K at the top, ~800 K at 1 bar, and ~1300 K at 100 bar self-consistently computed with the composition. For photochemical calculations, we have used the latest *HST* measurement of UV flux of GJ 1214 [23], assigned $O(^1D)$, $^1CH_2$, C_2H to be "fast species", and explored the eddy diffusion coefficients ranging from 10^6 to 10^9 cm^2 s^{-1}.

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