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Disequilibrium chemistry in the atmosphere of exoplanets

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Since the first discovery of a hot Jupiter in 1995 (Mayor & Queloz, 1995), and the detection of the atmosphere of one of them (Charbonneau et al., 2002) the accurate modeling of exoplanetary atmospheres has become central to understand planet formation, chemical composition, and whether their pressure and temperature conditions support the existence of liquid water at their surfaces. With the advent of JWST and the forthcoming ARIEL mission, increasingly precise atmospheric spectra will be available, revealing chemical signatures that challenge traditional models based solely on thermochemical equilibrium. A striking example is the detection of SO₂ in the atmosphere of WASP-39b, which cannot be explained by equilibrium chemistry alone (Tsai et al., 2023). These observations highlight the crucial role of disequilibrium processes.

Recent investigation of disequilibrium chemistry has explored the effects of stellar irradiation and vertical transport (Evans-Soma et al., 2025; Tsai et al., 2023). In this work, we take a step further, and explore non-thermal chemistry driven by fast hydrogen atoms. Such energetic atoms can overcome activation barriers and trigger endothermic reactions inaccessible to the thermal gas. Non-thermal chemistry has been shown to play a key role in Titan's atmospheric chemistry, notably in the formation of complex organic molecules (Hörst et al., 2012) and has been investigated in the context of atmospheric escape (Shematovich, 2010). However, its impact on chemical reaction networks within exoplanet atmospheres remains largely unexplored.

Here, we investigate whether non-thermal chemistry can significantly alter the atmospheric composition of exoplanets. To address this question, we define new rate coefficients that do not consider a Maxwellian energy distribution of species. For instance, the photodissociation of H₂ will give two fast H atoms, which will then mostly elastically interact with the gas, lose their energy until reaching the thermal energy. We track those fast hydrogens with a Monte-Carlo code to reconstruct their energy distribution which will deviate from the Maxwellian distribution. We applied our new Monte-Carlo code to fast hydrogen atoms evolving in an atmosphere of H, H₂ and He.

Our results demonstrate substantial deviations from Maxwellian distribution of velocities and emphasize the importance of incorporating quantum mechanical cross sections for elastic scattering. Comparisons with existing literature validate our approach. This work lays the foundation for incorporating non-thermal chemistry into self-consistent atmospheric models, with future applications to realistic exoplanet atmospheres observed by JWST.

References

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