Using combustion modeling to develop an extensively validated C/H/O/N/S kinetic network for hot exoplanet disequilibrium chemistry

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Abstract

Recent observations with the James Webb Space Telescope recently revealed the first detections of SO_2 in the atmospheres of two exoplanets, WASP-39 b and WASP-107b [1, 2]. 1D models of these warm exoplanets show that SO_2 is not thermodynamically stable in these conditions, and thus must be a product of photochemistry. To correctly model the effects of vertical mixing and photodissociations, a kinetic model, including a kinetic network, is crucial to compute the abundance profiles out of equilibrium. However, these networks usually undergo no experimental validation against experimental kinetic data, and thus they remain an important source of uncertainty. Since atmospheres of hot exoplanets, such as hot Jupiters or warm Neptunes, are characterized by high temperatures, these kinetic models can be validated against combustion experiments [3]. To develop robust networks, we can also rely on combustion studies that provide C/H/O/N chemical networks validated by vast amount of experimental data generated by the extensive research that has been done on hydrocarbon combustion and NO_x formation in the last decades.

In order to apply these works to the modeling of exoplanetary atmospheres, we first aimed to build a new and updated C_0-C_2 chemical network to study the C/H/O/N disequilibrium chemistry of warm and hot exoplanet atmospheres that relies on extensively validated and recent state-of-the-art combustion networks [4]. The reliability range of this network was aimed for conditions between 500–2500 K and 10^2–10^{-6} bar, with cautious extrapolation at lower temperature values. We compared the predictions of seven networks over a large set of experiments, covering a wide range of conditions (pressures, temperatures, and initial compositions). To examine the consequences of this new chemical network on exoplanets atmospheric studies, we generated abundances profiles for GJ 436 b, GJ 1214 b, HD 189733 b, and HD 209458 b, using the 1D kinetic model FRECKLL and calculated the corresponding transmission spectra using TauREx 3.1. These spectra and abundance profiles have been compared with results obtained with our previous chemical network. Our new kinetic network is composed of 175 species and 1313 reactions mostly reversible. This network proves to be more accurate than our previous one for the tested experimental conditions. The nitrogen chemistry update is found to be very impactful on the abundance profiles, particularly for HCN, with differences up to four orders of magnitude. The CO_2 profiles are also significantly affected, with important repercussions on the transmission spectrum of GJ 436 b. These effects highlight the importance of using extensively validated chemical networks to gain confidence in our models predictions.

In order to model the latest observations of the James Webb Space Telescope on SO_2, we followed the same methodology to add sulfur chemistry in our network. An important focus was put on the C/S coupling chemistry, and advanced *ab initio* calculations were performed to improve the reliability of available combustion models when applied to hot exoplanet atmospheres. This work aims to show that using tools from combustion modeling in the context of exoplanet modeling turns out to be very effective and one of the few means we have to ensure that our kinetic networks are reliable, especially in the current context of the rapidly increasing quantity of high quality data from the James Webb Space Telescope that allows for more precise constraints on atmospheric composition.

References

[1] S.-M. Tsai, E. K. Lee, D. Powell, P. Gao, X. Zhang, J. Moses, E. Hébrard, O. Venot, V. Parmentier, S. Jordan, et al., Photochemically produced so2 in the atmosphere of wasp-39b, *Nature* **617**, 483 (2023).

[2] A. Dyrek, M. Min, L. Decin, J. Bouwman, N. Crouzet, P. Mollière, P.-O. Lagage, T. Konings, P. Tremblin, M. Güdel, et al., So2, silicate clouds, but no ch4 detected in a warm neptune, *Nature* **625**, 51 (2024).

[3] O. Venot, E. Hébrard, M. Agúndez, M. Dobrijevic, F. Selsis, F. Hersant, N. Iro, and R. Bounaceur, A chemical model for the atmosphere of hot jupiters, *Astronomy & Astrophysics* **546**, A43 (2012).

[4] R. Veillet, O. Venot, B. Sirjean, R. Bounaceur, P.-A. Glaude, A. Al-Refaie, and E. Hébrard, An extensively validated c/h/o/n chemical network for hot exoplanet disequilibrium chemistry, *Astronomy & Astrophysics* **682**, A52 (2024).