

# Main ions in the thermosphere of exoplanets, focussing on the transition between super-Earths and mini-Neptunes

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## Abstract

Therospheres of exoplanets are submitted to the harsh UV and X-ray radiations of their host star. In the present work we focus on ion chemistry occurring in super-Earths and mini-Neptunes. We simulate in the laboratory the effect of Far-UV on gas-mixtures varying from H<sub>2</sub>-rich to H<sub>2</sub>-poor conditions and we analyze the ions by *in situ* mass spectrometry.

## 1. Introduction

Therospheres of exoplanets are photochemically active layers, characterized by an efficient photolysis of the main components of the atmospheres. Vertical transport in therospheres is moreover governed by molecular diffusion, also contributing to strongly modify the composition profiles of the atmospheres. On Mars, with an atmosphere based on CO<sub>2</sub> and N<sub>2</sub>, the efficient photolysis of CO<sub>2</sub> leads to an increase of CO mixing ratio, up to several tens percent's compared to CO<sub>2</sub> [1]. The impact on the thermal profile of the atmosphere is determining. On Mars the progressive enrichment in CO compared to CO<sub>2</sub> according to altitude limits the heating of the therosphere, as CO is a less efficient UV absorber than CO<sub>2</sub> [2]. Predicting and understanding the temperature and density profiles of therospheres of exoplanets will therefore constrain atmospheric escape and photoevaporation processes, and a fortiori the evolution of atmospheres of exoplanets.

Photolysis in therospheres involves harsh UV and X-ray stellar radiations and produces complex chemical environments coupling neutral and ion chemistry. Ion-chemistry has been shown to be largely underestimated and poorly known when the Cassini-Huygens space mission unveiled the complex ion and neutral composition of the therosphere of

the largest satellite of Saturn, Titan [3]. Its atmosphere is based on N<sub>2</sub> and CH<sub>4</sub>, and nitrogen chemistry was found to be particularly important in Titan's therosphere. We learned with the study of this body that ion-neutral chemistry was rich and efficient and could lead to unexpected abundant chemical species.

With the data of the California-Kepler Survey two populations of super-Earths and mini-Neptunes could be distinguished [4]. Super-Earths, with radii lower than 1.5 R<sub>⊕</sub> are rocky planets with thin atmospheres mainly made of heavy molecules like N<sub>2</sub> and CO<sub>2</sub>. Mini-Neptunes with masses between 2 and 3 R<sub>⊕</sub> have on the opposite extended H<sub>2</sub>-based atmospheres.

The aim of the present work is to characterize the main positive ions that can be expected in the therospheres of super-Earths and mini-Neptunes. For this purpose we simulated experimentally the ion-neutral chemistry initiated by Far-UV radiations on a gas mixtures mimicking the main possible composition of therospheres of super-Earths and mini-Neptune. The ion species are analyzed *in situ* by mass spectrometry.

## 2. Methods

Far-UV photons mimicking the stellar UV field were generated by using a gas-discharge type Far-UV source coupled windowless to our photochemical reactor [5]. We irradiated at 73.6 nm (15.6 eV) by using the resonant emission lines of Ne I and Ar I, respectively, with a photon flux of ca.  $1.5 \times 10^{14}$  ph.s<sup>-1</sup>.cm<sup>-2</sup>.

Gas mixtures were chosen to be representative of H<sub>2</sub>-poor atmospheres and H<sub>2</sub>-rich atmospheres. As the photolysis of CO<sub>2</sub> mainly produces CO, and that CO

is more efficient to drive further photochemistry, we have chosen CO as a proxy of both CO<sub>2</sub> and CO in our experiments. In order to build a consistent experimental series, we have chosen to only modify the H<sub>2</sub> content in our experimental conditions. N<sub>2</sub> mixing ratio was therefore arbitrary chosen as equal to CO mixing ratio, and H<sub>2</sub> mixing ratios increased from 1% up to 96%.

The gas composition was monitored in steady state by using a high sensitivity (<1ppm) quadrupole mass spectrometer (Hiden Analytical EQP 200 QMS) allowing *in situ* measurements of the positive ions.

### 3. Results

H<sub>2</sub> mixing ratios were chosen at 1%, 33% and 96%. The main ions detected are shown on Figure 1. The first striking result is that in all conditions the main ions are the same: H<sub>3</sub>O<sup>+</sup> at m/z 19 and HCO<sup>+</sup> and N<sub>2</sub>H<sup>+</sup> at m/z 29, even in a H<sub>2</sub>-based neutral gas mixture. In the H<sub>2</sub>-based condition (H<sub>2</sub> mixing ratio of 96%), H<sub>3</sub><sup>+</sup> at m/z 3 appears as an additional important ion contributor.

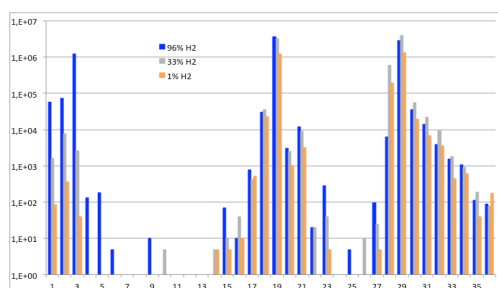


Figure 1: Ions produced after irradiation at 73 nm of H<sub>2</sub>/CO/N<sub>2</sub> gas mixtures. H<sub>2</sub> mixing ratios was chosen at 1%, 33% and 96%.

Primary ions produced by photoionization at 73nm are respectively H<sub>2</sub><sup>+</sup> at m/z 2, N<sub>2</sub><sup>+</sup> and CO<sup>+</sup> at m/z 28. Those primary ions react with H<sub>2</sub>, through ion-molecule efficient reactions, leading to the stable protonated ions observed. The detection of the ion H<sub>3</sub>O<sup>+</sup> is a sensitive probe of the presence of H<sub>2</sub>O in the reactive medium: as a photoproduct and/or as contaminant.

### 4. Summary and Conclusions

We highlight that the main ions observed in our H<sub>2</sub> rich (96%) and H<sub>2</sub> poor (1%) conditions are similar and corresponds to HCO<sup>+</sup> and N<sub>2</sub>H<sup>+</sup>. We used CO as a proxy for CO and CO<sub>2</sub>. We can extrapolate that HCO<sub>2</sub><sup>+</sup> would similarly be observed in the presence of CO<sub>2</sub>. Despite the drastic differences in neutral compositions of the atmospheres of super-Earths and mini-Neptunes, our work suggests that rather similar ion contributions could be expected in their thermospheres.

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