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# MOLECULAR HYDROGEN IN $CO_2$-DOMINATED ATMOSPHERES OF TERRESTRIAL EXOPLANETS : IMPACT ON THE PHOTOCHEMICAL FORMATION OF WATER

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**Abstract.** As for the rocky planets of the Solar System, the atmosphere of terrestrial exoplanets is affected by volcanic outgassing. Significant emissions of molecular hydrogen are expected in the early stage of their evolution. In the upper atmosphere, molecular hydrogen becomes photochemically active along with $CO_2$. Laboratory experiments conducted highlight a significant formation of water which strongly depends on the concentration of molecular hydrogen.

Keywords: atmosphere, terrestrial exoplanet, photochemistry

## 1 Introduction

Volcanic emissions are known to impact the composition of the atmosphere and its evolution by photochemistry. This explains the need to consider them in photochemical models as done by Hu et al. (2012) or James & Hu (2018). Recent modelling of volcanic outgassing by Liggins et al. (2020) shows that a few percent of molecular hydrogen is expected in early $CO_2$ or $N_2$ atmospheres. The exact mixing ratio of $H_2$ in the atmosphere depends on surface parameters : surface pressure, redox state of the mantle, volcanic flux of the planet.

The hypothesis of a $CO_2$-$H_2$ atmosphere has been introduced by Ramirez et al. (2014) as a possible scenario for the early Martian atmosphere. The presence of $CO_2$ with high amounts of $H_2$ in the atmosphere would lead to a significant radiative effect through collision-induced absorption of light (Ramirez & Kaltenegger 2017). The photochemistry of these $CO_2$-$H_2$ early atmospheres is the focus of the present study. Laboratory experiments are conducted to understand the photochemical processes occurring in these atmospheres.

## 2 Experimental method

The PAMPRE (French acronym for aerosol production in micro gravity by reactive plasma) experimental setup is used to simulate photochemical processes occurring in the upper atmosphere. A $CO_2$-$H_2$-$N_2$ mixture is injected in the reactor chamber with a flow rate of 55 sccm (standard cubic centimeter per minute). The mixing ratio of carbon dioxide is set at 0.7 and the $H_2$ to $N_2$ abundance ratio is varied in two experiments : 0.5% of $H_2$ for the first scenario and 5% of $H_2$ for the second scenario. The mixing ratio of $H_2$ is changed to highlight its role in the photochemistry of these early atmospheres. A rotary vane vaccum pump is connected to the reactor chamber creating a continuous flow which stabilizes the pressure at 1 hPa. Experiments are conducted at room temperature. A radio-frequency (RF) capacitively coupled plasma discharge is used to initiate dissociation reactions with electron impact (Szopa et al. 2006). The chemical evolution of the mixture within the reactor is monitered using the EQP200 Hiden quadrupole mass spectrometer.

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## 3 Experimental results

The only parameter changed in both scenarios is the mixing ratio of molecular hydrogen. The first scenario with 0.5% of molecular hydrogen shows a formation of oxygen and water by photochemistry (Fig. 1). The formation of oxygen is dominant with an intensity around 18,000 counts/s measured by the mass spectrometer at a permanent regime. This production of oxygen is expected in these $CO_2$-dominated atmospheres from the photolysis of the main gas and the combination of atomic oxygen. The second scenario with 5% of molecular hydrogen shows a significant and dominant formation of water with an intensity of 34,000 counts/s reached at a permanent regime (Fig. 2). These two different scenarios highlight the importance of $H_2$ in the chemistry of these atmospheres. These results indicate that the formation of water increases with the concentration of molecular hydrogen.

Similiar to the formation of oxygen, the formation of water starts with the photolysis of carbon dioxide and the production of the $O(^1D)$ radical (R1).

$$\mathrm{CO_2 + h\nu \longrightarrow CO + O(1D)} \quad \mathrm{(R1)}$$

The $O(^1D)$ radical then reacts with molecular hydrogen to produce the OH radical (R2). This reaction highlights the role of molecular hydrogen in the formation of water. $H_2$ is a reactant which means that the production rate of OH is higher in the second scenario with 5% of $H_2$ in the mixture.

$$\mathrm{O(^1D) + H_2 \longrightarrow OH + H} \qquad \mathrm{(R2)}$$

The products of (R2) can then react with a stable abundant molecule M ($CO_2$ or $N_2$) to form water (R3).

$$\mathrm{OH + H + M \longrightarrow H_2O + M} \qquad \mathrm{(R3)}$$

The OH radical generated by (R2) can also react with the abundant molecular hydrogen (R4) or another OH radical (R5) to produce water as identified by Fleury et al. (2015) for the case of the early Earth.

$$\mathrm{OH + H_2 \longrightarrow H_2O + H} \qquad \mathrm{(R4)}$$

$$\mathrm{OH + OH \longrightarrow H_2O + O} \qquad \mathrm{(R5)}$$

## 4 Conclusions and perspectives

Laboratory experiments simulating low pressure chemistry show that the production rate of water increases with the mixing ratio of $H_2$. This suggests the presence of water vapor in early $CO_2$-$H_2$ atmospheres of terrestrial exoplanets. The chain of reactions leading to the production of water vapor could also occur in an $H_2$-dominated atmosphere and contribute to the formation of liquid water. This needs to be further explored using a photochemical model.

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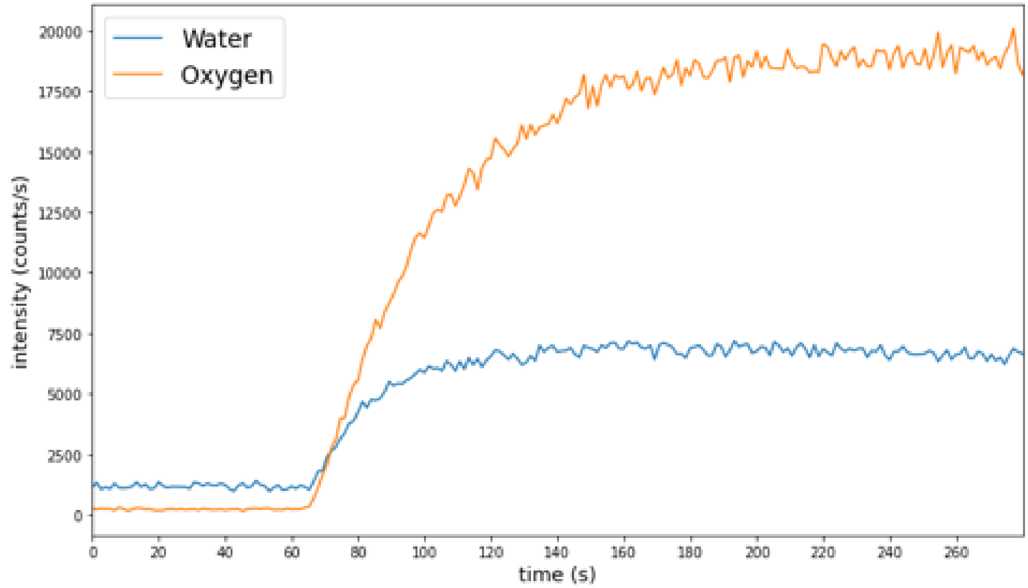


**Fig. 1.** Temporal evolution of the intensity (in counts/s) measured by the mass spectrometer for water (blue curve) and oxygen (orange curve). This first scenario is associated with 0.5% of molecular hydrogen in the mixture.

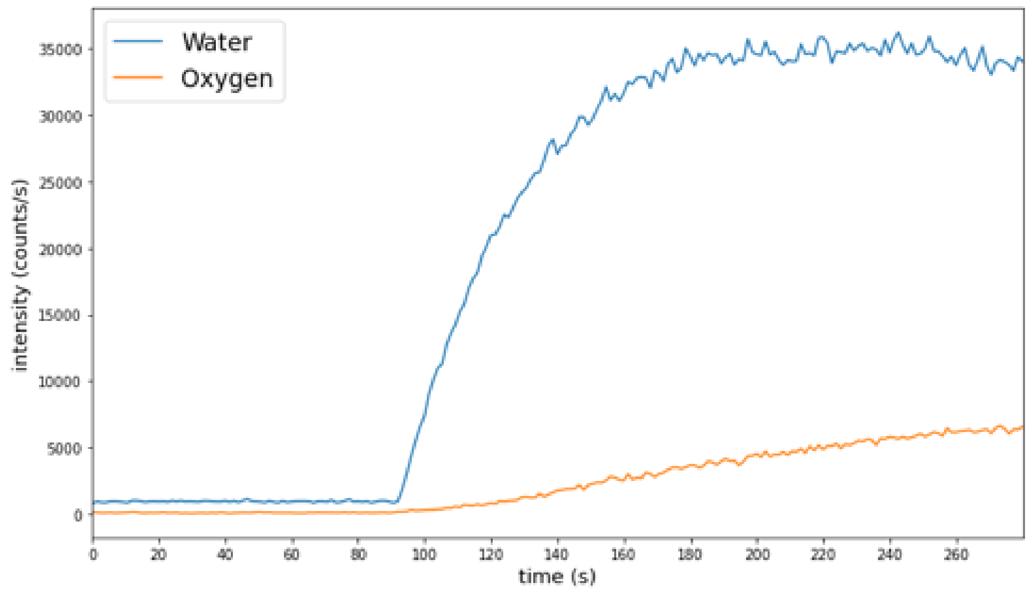


**Fig. 2.** Temporal evolution of the intensity (in counts/s) measured by the mass spectrometer for water (blue curve) and oxygen (orange curve). This second scenario is associated with 5% of molecular hydrogen in the mixture.