Photochemistry in Hot H₂-dominated Exoplanet Atmospheres

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Abstract

Photochemistry has the potential to substantially impact the atmospheric composition of exoplanets with consequences on the radiative transfer, thermal structure, and dynamics of the atmospheres, particularly in UV-rich stellar environments. Here, we present the results of a first laboratory experimental simulation of photochemistry in carbon-rich exoplanet atmospheres at elevated temperatures. The evolution of gas-phase molecular composition was quantitatively monitored with infrared spectroscopy and mass spectrometry. We found that H₂/CO gas compositions can change significantly from thermal equilibrium compositions when irradiated with Lyα photons at temperatures ranging from 600 to 1500 K. Carbon dioxide and water were found to be the main products caused by photolysis, while the formation of methane was also observed to a lesser extent. We find that photochemistry efficiency is strongly correlated with increasing temperature. Our finding that water is efficiently produced by photochemistry in a supersolar C/O = 1 environment, representing C enhancement relative to solar values C/O ratio = 0.54, has significant implications for the interpretation of many exoplanet transmission spectra. We also find the formation of an organic solid condensate at 1500 K and under Lyα UV radiation, confirming the possibility of forming photochemical hazes in hot-Jupiter exoplanet atmospheres with an enhanced C/O ratio compared to solar.

Key words: astrochemistry – methods: laboratory: molecular – molecular processes – planets and satellites: atmospheres

1. Introduction

A fraction of known exoplanets are hot (800–3000 K) giant planets with short orbital periods and correspondingly small semimajor axis values (Moses 2014; Madhusudhan et al. 2016), which are exposed to high temperatures as well as high UV fluxes. As indicated by the wide range of bulk densities, their atmospheres are likely diverse in composition and are influenced by several factors: the temperature profile, the elemental C/O ratio, the metallicity, the host star type, and UV flux (Moses et al. 2013a, 2013b; Miguel & Kaltenegger 2014; Venot et al. 2014). The gas giant planets, ranging in extremes from hot Jupiters to the cooler sub-Neptunes, are expected to have atmospheres mainly composed of dihydrogen (H₂) and helium (He; Madhusudhan et al. 2016). Observations during transit and eclipses have revealed the presence of carbon-, oxygen-, and nitrogen-bearing molecules such as carbon monoxide (CO), carbon dioxide (CO₂), methane (CH₄), ammonia (NH₃), and water (H₂O; Tinetti et al. 2007; Swain et al. 2009a, 2009b; de Kok et al. 2013; Wakeford et al. 2013; MacDonald & Nikku 2017). Extensive H escape (Vidal-Madjar et al. 2003; Ehrenreich et al. 2015), presumably reflecting the underlying H₂-dominated nature of the atmospheres, has been observed as well.

For exoplanets with T < ~1500 K, disequilibrium chemistry such as transport-induced quenching and photochemistry can seriously affect the atmospheric gas-phase composition (Moses et al. 2011; Venot et al. 2012; Moses 2014) and then impact the radiative properties, thermal structure, and dynamics of the atmospheres (Moses 2014; Drummond et al. 2016). Further, some observations suggest that aerosols are present in the atmospheres of exoplanets such as the super-Earth GJ 1214b (Kreidberg et al. 2014), the hot-Neptune GJ 436b (Knutson et al. 2014), and several hot Jupiters (Demory et al. 2013; Iyer et al. 2016; Sing et al. 2016). Aerosols can affect the albedo, the thermal structure, and the chemistry of the exoplanet atmospheres, similar to what is observed in our solar system (Marley & McKay 1999; West et al. 2014). However, whether the observed aerosols are mainly condensate clouds (Parmentier et al. 2016) or photochemical hazes (Marley et al. 2013) remains largely unknown. It is also not clear what percentage of these aerosols could be organic (carbon-based) or inorganic (silicates, etc.). We focus here on organic aerosol formation.

Several chemical and microphysical models have been developed over recent years to study disequilibria processes such as quenching and photochemistry (Zahnle et al. 2009; Line et al. 2010, 2011; Moses et al. 2011; Venot et al. 2012, 2015) and aerosol formation in exoplanet atmospheres (Zahnle et al. 2016; Gao et al. 2017; Lavvas & Koskinen 2017; Kawashima & Masahiro 2018). However, corresponding laboratory data for these processes are sparse, and laboratory investigation of the photochemistry and aerosol formation in exoplanet atmospheres is crucial for their characterization and the interpretation of existing and future observations (Fortney et al. 2016). Only a few laboratory experiments thus far have focused on aerosol formation and aerosol properties in Earth-like exoplanets (Gavilan et al. 2017) or super-Earth and mini-Neptune-like exoplanets (He et al. 2018; Hörst et al. 2018). These studies highlight the efficient formation of photochemical hazes in a large diversity of atmospheric conditions with different physical and chemical properties. However, these experiments were limited to planets with relatively cool atmospheres (T < 600 K) and do not mimic the higher temperature exoplanet atmospheres such as those in hot Jupiters, which represent a majority of currently observed exoplanet atmospheres. In addition, these experiments used plasma discharges as energy sources to simulate the chemistry occurring in exoplanet atmospheres. Although plasma discharges are more efficient at generating aerosol analogs in the laboratory, the chemistry in planetary atmospheres is mainly
driven by stellar UV radiation. Hence, our work focuses on aerosol formation at elevated temperatures (600 K–1500 K) and under Lyα UV radiation.

In our study, we have chosen to investigate UV photochemistry and thermal equilibrium chemistry involving H2 and CO, the two most abundant molecules in hot-Jupiter-type exoplanet atmospheres (excluding He, which is chemically inert). The combination of H2 and CO represents the simplest plausible hot Jupiter atmosphere with $T > 1000$ K and corresponds to a C/O ratio of 1, representing C enhancement relative to solar values. These atmospheres are the focus of our study. The existence of this type of exoplanet has been suggested after the observation of the hot Jupiter WASP-12b (Madhusudhan et al. 2011), even though the C/O ratio itself is still debated (Madhusudhan 2012; Mandell et al. 2013; Moses et al. 2013b; Swain et al. 2013). However, recent work by Brewer et al. (2017) suggests that the enhancement of C/O in hot-Jupiter atmospheres may be common. Thermal chemical models predict that these exoplanets have H2-dominated atmospheres with CO as the main carbonaceous species for atmospheres with temperatures higher than 1000 K (Moses et al. 2013b; Venot et al. 2015). These atmospheres are expected to contain heavier and more complex C-bearing molecules (Venot et al. 2015), making them an important target for the study of the formation of photochemical hazes. Finally, previous works have demonstrated that the ultraviolet absorption cross-section of molecules is temperature dependent (Venot et al. 2013, 2018) and has a large impact on the photodissociation efficiency and the photochemistry (Venot et al. 2015, 2018) in planetary atmospheres. For this reason, we investigate the effect of temperature on the photochemical evolution of exoplanet atmospheres.

2. Experimental Setup and Analytical Protocols

2.1. Cell for Atmospheric and Aerosol Photochemistry Simulations of Exoplanets (CAAPSE)

Figure 1 presents the scheme of the CAAPSE experimental setup. This is a new instrument, custom-built at the Jet Propulsion Laboratory to simulate the photochemistry and formation of aerosols in exoplanet atmospheres. The reaction cell is 48 cm long, composed of a 38 cm long quartz or alumina tube with an internal diameter of 6.1 cm and is closed with two MgF2 windows mounted on stainless-steel flanges with high-temperature O-ring seals. Alumina has better resistance to higher temperatures than quartz and can be used to simulate exoplanet atmospheres with a higher temperature. However, alumina is more porous than quartz, enhancing the surface area of gas–solid contact significantly and possibly also catalytic effects. To evaluate this effect, we performed comparative experiments using the two types of tubes. A customized STT-1600C (SentroTech) oven is used to heat the cell up to 1773 K (1500 °C). The maximum allowed temperature is 1600 °C for this oven; however, we opted to stay well below that threshold to avoid unwarranted processes such as melting of the O-rings, etc. MgF2 windows are the only optical material that is transparent to both Lyα photons and infrared spectral wavelengths. However, MgF2 is thermally rated only up to 300 °C. For this reason, these windows are water-cooled to avoid any thermal damage while allowing the rest of the cell to operate at a higher temperature. Before each experiment, the cell is heated to 1173 K and pumped down to $3 \times 10^{-7}$ mbar for 24 hr to degas it and remove absorbed water or other impurities.

Our mixtures were prepared based on the atmospheric composition calculated in Venot et al. (2015) using a thermochemical equilibrium model that has a C/O ratio of 1.1 and a temperature of 1000 K, making the CO molecule a good choice to represent this C/O ratio. We chose to use only the two most abundant species calculated in the model of Venot et al. (2015), H2 and CO, to limit the experimental complexity, resulting in the exclusion of nitrogen-bearing molecules such as N2 as well as He, which is chemically inert. Although the N2 mixing ratio is very low in hot-Jupiter atmospheres, further studies would be necessary to determine whether nitrogen chemistry might have an effect on aerosol formation and properties, as it does on Titan, for example. To prepare the initial gas mixture, we filled a glass bulb of 2 L volume previously pumped down to $1 \times 10^{-5}$ mbar on a glass gas-mixing vacuum line with H2 (Airgas, 99.9999%) and $^{13}$CO (Cambridge Isotope Laboratories, 99.9%). Typical mixtures obtained were H2 (99.7%) and $^{13}$CO with a mixing ratio of $3 \times 10^{-3}$ (0.3%) by volume. The total pressure in the glass bulb was kept under 600 mbar, and the gas mixture was kept at room temperature for at least 12 hr before loading into the CAAPSE cell. Isotopically labeled carbon monoxide ($^{15}$CO) was used to isolate the effect of any contamination (spectral contamination due

Figure 1. Scheme of the CAAPSE experimental setup at the Jet Propulsion Laboratory.
to atmospheric gases, atmospheric gas leaks into the cell, outgassing of the inner surfaces, etc., discussed in Section 3.2.3) from the thermal and photochemical processing within the cell on the initial gas mixture. The quartz and alumina tubes were used only with gas mixtures made of H2 and 13CO in order to avoid possible cross-contamination. The reaction cell was filled with 15 mbar of the initial gaseous mixture and heated at 5 K minute−1 to different oven temperatures, starting from a room temperature of 295 K and subsequently to 573, 873, 1173, 1373, and 1473 K. Although the gas mixture composition we used is only representative of hot-Jupiter-like atmospheres with T > 1000 K and a C/O ratio of 1, we performed control experiments at 573 and 873 K to obtain more information on how the gas temperature affects the chemistry for a given atmospheric composition. Such data are indeed crucial to understand the chemical processes in our experimental setup and to better understand the effect of gas temperature on the thermochemistry and photochemistry. The temperature of the tube was monitored using three type-B thermocouples distributed across the furnace at a spacing of 4.5 cm and read into a computer with MadgeTech 4 software. During heating, the evolution of the gas mixture composition was monitored continuously by infrared (Fourier Transform Infrared; FTIR) spectroscopy.

After attaining the desired temperature, the gas mixture was kept at that temperature until minimal changes were seen in the infrared spectra (see Section 3.1). From that point on, the heated gaseous mixture was irradiated using a microwave discharge lamp with a continuous 1.2 mbar flow of H2 (Airgas, 99.9999%) powered by a microwave generator (OPTHOS) set to 70 W. The lamp was separated from the reaction chamber by a MgF2 window that cuts off wavelengths shorter than 110 nm. Under these conditions, the lamp produces continuous emission of photons in the UV at 121.6 nm (Lyα) and a broad but weaker emission in the 140–170 nm range. It mimics exoplanet atmospheres irradiated by UV photons from their UV-rich stars, with a predominance of Lyα (121.6 nm) in the vacuum ultraviolet (VUV, λ < 200 nm), especially for planets orbiting around M stars (France et al. 2013; Miguel et al. 2015). The photon flux of the lamp is estimated to be \( \sim 10^{13} \) photons cm\(^{-2}\) s\(^{-1}\) at 121.6 nm (Ligerink et al. 2015). Although these photons are not energetic enough to directly dissociate or ionize H2 and CO, previous studies have demonstrated that photochemistry can be driven by the photoexcitation of CO (Liuti et al. 1966a, 1966b; Dunn et al. 1973; Vikis 1982; Roussel & Back 1990). As the CAAPSE cell has only two optical windows, we needed to exchange the FTIR with the microwave discharge lamp for the irradiation. Thus, it was not possible to monitor continuously the evolution of the gas mixture by IR spectroscopy during the irradiation but only at the end of the irradiation, when the lamp was removed.

The pressure in the CAAPSE cell was monitored at each step of the experiments by a CDG-500 capacitance diaphragm gauge (Agilent). The pressures measured in the cell and the total time since gas mixture loading into the cell are summarized in Table 1 at different steps of the experiments for each set temperature. The thermal expansion of the gases during the heating of the cell involved an increase of the pressure inside the cell, and as seen from Table 1, the gas mixture does not follow a strict ideal gas proportionality \( (P_2/P_1 = T_2/T_1) \) at constant volume. This is due to the existence of a temperature gradient along the tube (see Figure 2), which also led to a pressure gradient in the cell. At elevated temperatures beyond 600 K, we noticed an increase in pressure of \( \sim 1 \) mbar, after irradiating for 18 hr, which could be due to a leak (see Section 3.2.3 for further discussion). It should be noted that once the gas mixture at a total pressure of 15 mbar is loaded into the reaction cell, all the valves are closed, and the cell is subjected to atmospheric pressure at every potential point of leak (O-rings). Hence, it is very difficult to avoid leaks in such a system subjected to extreme temperatures. We took all precautions to minimize these leaks. As will be seen in the following, small leaks do not appear to make any significant impact on our results, and the choice of using isotopically labeled 13CO enables us to trace such leaks and quantify them.

2.2. Infrared Spectroscopy Analysis of the Gas-phase Components

The evolution of the gas mixture in the reaction cell was monitored with a Thermo Scientific Nicolet iG50 FTIR spectrometer. The path of the FTIR beam in the CAAPSE experiment is presented in Figure 1. A collimated FTIR beam (a few millimeters in diameter) passes through our high-temperature cell and is collected with an LN2-cooled MCT-A detector. In the results presented in Figures 3 and 5, IR spectra are recorded in the 1500–4500 cm\(^{-1}\) range with a resolution of 0.25 cm\(^{-1}\) after a co-addition of 700 scans. The optical path length inside the cell is 48 ± 1 cm.

2.3. Mass Spectrometry Analysis of the Gas-phase Components

In situ measurements of the gas mixture composition in the reaction cell were monitored using a Stanford Research System RGA200 quadrupole mass spectrometer (QMS) equipped with an electron multiplier to increase sensitivity. Gases were transferred to the QMS by opening a high-vacuum leak valve that separates the reaction gas cell from the pumping system to which the QMS was attached at pressures of \( \sim 1 \times 10^{-6} \) mbar during the measurements. QMS ionization was achieved through electron impact at 70 eV. The RGA200 covers the 1 to 200 m/z mass range with a resolution of 100 at m/z 100 (m/Δm).

2.4. Solid-phase Collection and Infrared Analysis of Thin Films

Two sapphire substrates (25 mm diameter and 1 mm thick) were placed inside the CAAPSE cell to collect any aerosols produced during the experiments. Sapphire has good stability at the studied temperatures. They were positioned at 18 cm and 30 cm from the hydrogen lamp end of the MgF2 window. The films were deposited at 1473 K during 204 hr of UV irradiation. At the end of the UV irradiation, the temperature was ramped down to 295 K, and the volatiles were pumped off. Subsequently, the cell was opened to ambient air, and the samples were transferred for analysis. Single-beam infrared spectra of the samples were measured with a Thermo Scientific Nicolet 6700 FTIR spectrometer. The infrared signal was collected by a Deuterium TriGlycine Sulfate (DTGS) detector in the 1600 cm\(^{-1}\) (sapphire window absorption limit) to 4000 cm\(^{-1}\) range with a resolution of 1 cm\(^{-1}\) after a co-addition of 300 scans.
Table 1
Summary of the Total Time since Loading the H2:13CO (99.7%-0.3%) Gas Mixture into the Cell at Room Temperature vs. Pressure in the CAAPSE Cell at Different Steps of the Experiments for Each Set Temperature

| T (K) | Initial Condition at 295 K | Condition at Thermal Equilibrium | Condition after UV Irradiation |
|-------|---------------------------|----------------------------------|-------------------------------|
|       | Time (hr) | Pressure (mbar) | Time (hr) | Pressure (mbar) | Time (hr) | Pressure (mbar) |
| 573   | 0         | 15              | 5         | 21              | 23         | 22              |
| 873   | 0         | 16              | 5         | 24              | 23         | 25              |
| 1173  | 0         | 15              | 5         | 29              | 23         | 30              |
| 1273  | 0         | 15              | 6         | 30              | 24         | 31              |
| 1373  | 0         | 16              | 6         | 33              | 24         | 34              |
| 1473  | 0         | 15              | 6         | 33              | 24         | 33              |
| 1473  | 0         | 81              | 6         | 190             | 204        | 150             |

2.5. Temperature Gradient of the Cell and Gas-phase Species Quantification

We have measured the temperature at different positions of the cell using the three type-B thermocouples distributed across the hottest part of the tube as well as the four type-K thermocouples spaced from the center to the ends of the cell, in order to determine the temperature gradient. The temperatures measured with the quartz cell and the alumina cell as a function of tube position for different set points are presented in Figure 2. Two heating elements distributed across the center of the furnace at a spacing of 10 cm provided heating for the central 10 cm of the furnace. Another 10 cm on each side is thermally insulated and contained in the furnace. As a result, the furnace covered 30 cm of the cell in the middle, and the rest of the cell on both sides (9 cm each) is in thermal contact with the ambient air and chilled water-cooled vacuum flanges near the MgF2 windows.

In our experimental setup, the heat is not uniformly distributed along the reaction cell, because of the requirement to keep MgF2 windows at or below 300°C. As a result, a temperature gradient exists in the gas cell from the center to the end, and the gas in the center of the cell is at a higher temperature while the gas at the extremities of the cell (near the MgF2 windows and the UV lamp) is close to 300–400 K. Although the low-temperature gases nearest the UV lamp do absorb some photons, the vast majority of the photons make it to the center of the cell and beyond. Considering CO only, which is the more abundant species in our system after H2, we made an estimate of the percentage of photon transmission for these VUV wavelengths (Lyα at 121.6 and 155–165 nm). Using a partial CO pressure of 0.045 mbar and a cross-section (at ambient temperature) of ~4.5 × 10⁻²⁰ cm² at 121.6 nm and ~2.6 × 10⁻¹⁸ cm² for the 155–165 nm range, we estimate that ~99.9% of Lyα photons and ~93.4% of the photons in 155–165 nm range reach the center of the cell where the molecules are at the highest temperature. Taking into account the amounts of CH4 and CO2 (and their cross-sections at room temperature) produced by thermal processes before irradiation slightly changes these values to 98.5% for 121.6 nm and 93.4% for 155–165 nm. Although these values are only a rough estimate, it shows that the majority of the photons will reach the high-temperature part of the cell and that the CAAPSE experiment can be used to simulate photochemistry at high temperatures.

To quantify the concentration of a molecule detected in our reaction cell by IR spectroscopy using the Beer–Lambert law, we need to use the absorption cross-section of the molecule at the gas temperature. Previous high-temperature studies using similar instrument configurations to ours have measured the emission cross-section of CH4 in the infrared (Hargreaves et al. 2012) and the absorption cross-section of CO2 in the VUV (Venot et al. 2018). In both studies, the authors concluded that their spectra were dominated by the emission or absorption of the gas at the maximum temperature in the central portion of the cell. To simplify the analysis of our data, we use the same hypothesis and assume that the majority of the gas is at the maximum temperature Tmax, although it increases the uncertainties on the values calculated. Then, the concentration of a given molecule can be calculated using the Beer–Lambert law. The concentration of the absorbing molecule [C] (molecules cm⁻³) in the cell is defined by Equation (1):

\[
[C] = \frac{\int_{\lambda_1}^{\lambda_2} A d\lambda}{l \times \int_{\lambda_1}^{\lambda_2} \sigma d\lambda},
\]

where \(\sigma\) is the absorption cross-section (cm² molecule⁻¹) of the molecule at a given wavelength \(\lambda\) and at the maximum temperature in the reaction cell (Tmax). \(l\) is the path length (cm) of the beam through the gas cell, and \(A\) is the absorbance at a given wavelength \(\lambda\). We have calculated the absorption cross-sections using the HITEMP and ExoMol databases (Rothman et al. 2010; Tennyson et al. 2016). To calculate the concentration [C], the absorbance \(A\) and absorption cross-section \(\sigma\) were integrated between \(\lambda_1\) and \(\lambda_2\).

3. Results and Discussions

3.1. Thermochemistry: Gas-phase Composition at the Thermal Equilibrium

We first investigated the change in the gas-phase composition that is induced solely by the heating of the gas mixture (without UV irradiation). Figure 3 presents the IR spectra of the gas mixtures at ambient temperature (reference at 295 K) and after ~2 hr subsequent to ramping-up to achieve different set maximum temperatures: 573, 873, and 1173 K, using a quartz cell.

The room-temperature spectrum contains the absorption band of 13CO centered at 2095 cm⁻¹ as well as the absorption band of the residual 12CO2 and gas-phase water of ambient air (on the optical pathway outside of the cell) centered at 2348 cm⁻¹ and 3750 cm⁻¹, respectively. The spectra show that higher 13CO rotational states up to J = 43 are thermally populated at 1173 K compared to J = 27 at 295 K. The spectra of the heated gases also reveal the formation of bands due to two new (thermally generated) molecular species. One band system, centered at 2284 cm⁻¹ and visible at the three
studied temperatures, is due to $^{13}\text{CO}_2$. The other band system centered at $3009 \text{ cm}^{-1}$ is visible only in the spectra recorded at $1173 \text{ K}$ and is attributed to the Q branch of the $\nu_3$ band of $^{13}\text{CH}_4$. We also observed several transitions of the P and R branches of CH$_4$ in the $2900–2980 \text{ cm}^{-1}$ and $3050–3100 \text{ cm}^{-1}$ ranges. These two new species are isotopically labeled $^{13}\text{C}$, highlighting the fact that they are formed during thermal chemistry from the initial $^{13}\text{CO}$.

Subsequently, we performed a kinetic study of the formation of $^{13}\text{CO}_2$ and $^{13}\text{CH}_4$ during the heating to $1173 \text{ K}$ in the quartz cell, which is the only temperature where a significant amount of methane formation was observed. Figure 4 presents the evolution of $^{13}\text{CO}$, $^{13}\text{CO}_2$, and $^{13}\text{CH}_4$ concentrations by tracking their absorption band areas as a function of time. For the purpose of comparison with photochemical experiments (Section 3.2), we left the gas at the set temperature for 15 hr following the ramp-up. First, we observed that the integrated band area of $^{13}\text{CO}$ increased during the heating of the gases before reaching a steady state. This increase can be explained by a change in the absorption cross-section of $^{13}\text{CO}$ with temperature. Second, we observed that the formation of $^{13}\text{CO}_2$ begins within $\sim50$ minutes of the start of the heating ramp-up (at $\sim600 \text{ K}$), while the formation of $^{13}\text{CH}_4$ was seen only after $\sim125$ minutes (corresponding to a cell temperature of $900 \text{ K}$). Within 15 hr of keeping the reaction cell at $1173 \text{ K}$, we observed that concentrations of $^{13}\text{CH}_4$ reach a steady state, demonstrating that an equilibrium exists for this species under these experimental conditions. However, we observed a slow increase of the $^{13}\text{CO}_2$ concentration with time, indicating that this species does not reach a steady state even after 15 hr. After exposure to UV light, the growth of $^{13}\text{CO}_2$ appears to accelerate (and $^{13}\text{CO}$ decreases). Trends in the evolution of the amounts of these three species over 15 hr can be fitted using a linear fit as shown in Figure 4.

We quantified the mixing ratios of $^{13}\text{CO}$, $^{13}\text{CO}_2$ and $^{13}\text{CH}_4$ at thermal equilibrium using the method described in Section 2.5, and these ratios at different temperatures are summarized in Table 2. The initial mixing ratio of $^{13}\text{CO}$ varied slightly from one experiment to the next, due to a slow escape of H$_2$ from the storage glass flask containing the premixed gases at $\sim500 \text{ mbar}$, making the second experiment have a slightly higher CO/H$_2$ ratio. Though $^{13}\text{CO}$ remained the main carbonaceous species at different equilibrium temperatures, meaning that only a minor part of $^{13}\text{CO}$ underwent thermochemistry in the cell, the concentration of $^{13}\text{CO}_2$ increased with temperature, reached a maximum, and subsequently decreased at elevated temperatures (Table 2). Finally, methane production was observed only at $1173 \text{ K}$ with an equilibrium mixing ratio of $\sim80$ ppm. If CH$_4$ was produced at 573 and 873 K, its abundance was below the limit of detection of our FTIR. At higher temperatures, CH$_4$ may be undergoing further thermal chemistry as we have not detected CH$_4$ at the other temperatures listed in Table 2.

Thermal chemistry in exoplanet atmospheres is already studied using chemical models, with a particular focus on reactions converting oxidized carbon to reduced carbon such as the CO–CH$_4$ quenching reactions; see, e.g., Moses et al. (2011), Visscher & Moses (2011), and Moses (2014). However, the gas-phase reactions considered in these models include the reaction of CO with atomic hydrogen, which may not be a major
component in our work conditions. Although we did not identify chemical pathways for the thermal generation of CO$_2$ and CH$_4$ in our experiments, it has been shown experimentally that mineral phases could efficiently catalyze H$_2$:CO thermochemistry at temperatures up to 900 K (Hill & Nuth 2003), and it is likely that reactions catalyzed by the wall of the cell may play an important role in the thermochemistry observed in our experiments. Further experiments would be necessary to verify this theory, but it is beyond the scope of this work.

To extend our experiments to the higher temperatures that exoplanet atmospheres may experience, we used another cell made of alumina instead of quartz. Alumina has better resistance to higher temperatures, but alumina is more porous than quartz, enhancing the surface area of gas–solid contact significantly and possibly also the catalytic effects, increasing overall the thermochemistry efficiency. To evaluate this effect, we reproduced the experiments done with the quartz cell and extended our study to higher temperatures.

Figure 5 presents the IR spectra of the gas mixture at ambient temperature (reference at 295 K) and after the heating of the gases at different set temperatures of the alumina cell: 573, 873, 1173, 1273, 1373, and 1473 K. Similar to the experiments conducted with the quartz cell (Figure 3), we observed the heating of the gases (indicated by higher rotational states of $^{13}$CO that were thermally populated at high temperatures), along with the formation of $^{13}$CO$_2$. Similar to the observations with the quartz cell, the concentration of $^{13}$CO$_2$ increased with temperature, reached a maximum, and then decreased at higher temperatures (Table 2). $^{13}$CO$_2$ production was at maximum at 873 K with the quartz cell while it was at maximum at 1273 K with the alumina cell.

The formation of $^{13}$CH$_4$ in small quantities was observed at a much lower temperature (873 K) when the alumina cell was used (Figure 5), in contrast to its detection at 1173 K when the quartz cell was used (Figure 3). It is likely that the alumina tube acts as a much more efficient catalyst with the larger surface area generating and perhaps consuming methane further. It
should be noted that previous studies have shown a decrease of the transition intensity of the $\nu_3$ absorption band of CH$_4$ and an increase of the band continuum (Alrefae et al. 2014; Hargreaves et al. 2015) when the gas temperature increases. Therefore, the signal-to-noise ratio of the absorption band of CH$_4$ should decrease drastically at higher temperatures and may lead to a decrease of the detection sensitivity of CH$_4$ with our spectrometer. Overall, we find that in general CH$_4$ is not the major component in the thermochemical equilibrium composition. We also have observed $^{13}$CO and $^{12}$CO absorption bands overlap, we could not observe $^{13}$CH$_4$ and $^{12}$CH$_4$ experiments using the alumina cell.

The presence of carbon dioxide and methane is predicted by models for hot, carbon-rich, hydrogen-dominated exoplanet atmospheres such as those simulated in this work. However, the final observed mixing ratios observed here do not reproduce the ones calculated in chemical models. In particular, if a methane mixing ratio of a few tens of ppm, remains consistent with model calculations, carbon dioxide is predicted to be present at an abundance of a few parts per billion, orders of magnitude lower than was measured in our experiments (Venot et al. 2015; Heng & Lyons 2016). This discrepancy between thermochemical models and our laboratory experiments with regard to the formation of CO$_2$ needs to be evaluated in future work.

### 3.2. Photochemistry of High-temperature Mixtures at Thermal Equilibrium

In UV-rich stellar environments, photochemistry would affect exoplanet atmospheres that are at hot gas temperatures, and their compositions would depart from thermal equilibria. VUV ($\lambda < 200$ nm) photons are the main energy source driving photochemistry in these environments. Among them, hydrogen emission at 121.6 nm (Ly$_a$) has an important contribution to photochemistry, particularly for exoplanets orbiting M-type stars (France et al. 2013; Miguel et al. 2015).

Although all VUV photons contribute to photochemistry, irradiation with Ly$_a$ photons is a good way to reproduce photochemistry driven by stellar photons. However, the energy of Ly$_a$ photons (10.2 eV) is not sufficient to dissociate or ionize either H$_2$ or CO. Hence, photochemistry can only be initiated with electronic excitation of CO at the wavelengths emitted by the hydrogen lamp. However, both CO$_2$ and CH$_4$ can be directly photodissociated under these conditions, and their absorption cross-section is temperature dependent (Chen & Wu 2004; Venot et al. 2018).

From our thermochemistry study presented in Section 3.1, it is clear that, despite some quantitative differences, the heating of the gases in the quartz cell and in the alumina cell resulted in the production of similar species at thermal equilibria. For this reason and for the reason that we can access higher temperatures, we chose to conduct UV photochemistry experiments using the alumina cell.

After attaining thermal equilibria (Figure 5), the same gas mixtures were irradiated for a duration of 18 hr each in the alumina cell equipped with MgF$_2$ windows. Figure 6 presents the IR spectra of the gas mixtures after 18 hr of irradiation for different set oven temperatures: 573, 873, 1173, 1273, 1373, and 1473 K.

An artifact is visible at $\sim$3320 cm$^{-1}$ on the spectrum recorded for a set temperature of 573 K. The spectra contain the absorption bands of carbon monoxide ($^{13}$CO and $^{12}$CO), carbon dioxide ($^{13}$CO$_2$ and $^{12}$CO$_2$), methane ($^{13}$CH$_4$ and $^{12}$CH$_4$), and H$_2$O. Additionally, three weak absorption bands were observed, centered at 3527, 3631, and 3715 cm$^{-1}$. These bands are convoluted with the signature of H$_2$O and are observed only for temperatures lower than 1200 K. However, we have not been able to identify the corresponding species. The amount of $^{13}$CO decreased after the irradiation, and the consumption efficiency increased with the temperature, which highlights an efficient photochemistry of $^{13}$CO. However, since $^{12}$CO and $^{13}$CO absorption bands overlap, we could not perform a quantification of $^{13}$CO.
3.2.1. Carbon Dioxide and Water Formation

We quantified the mixing ratio of $^{13}$CO$_2$ after 18 hr of Ly$\alpha$ irradiation at each studied temperature. The results are presented in Table 3. For all of the temperatures, the mixing ratio of $^{13}$CO$_2$ increased by one or two orders of magnitude after the irradiation compared to the values measured at thermal equilibria (Table 2). Although the $^{13}$CO$_2$ concentration does not reach a steady state over several hours in thermal-only conditions, its production rate is too low to explain the large amount of $^{13}$CO$_2$ observed after the irradiation as illustrated in Figure 4 for an experiment made at 1173 K with a quartz cell. However, this effect must be taken into account to interpret the quantitative evolution of the carbon dioxide concentration.

The production of CO$_2$ through the photoexcitation of pure CO has been experimentally studied with irradiation at 123.58 and 206.2 nm (Dunn et al. 1973; Vikis 1982). This leads to the excitation of CO at the A$^1\Pi$ and A$^3\Pi$ states, respectively:

\[ \text{CO} + h\nu \rightarrow \text{CO}^*. \]  
(R1)

Then, the excited molecules react with ground-state CO to form primarily CO$_2$ but also a small amount of C$_2$O$_2$, which is not observed in our experiments (Liuti et al. 1966a, 1966b),

\[ \text{CO}^* + \text{CO} \rightarrow \text{CO}_2 + \text{C}. \]  
(R2)

The excitation of $^{13}$CO by the Ly$\alpha$ radiation (121.6 nm) is responsible for initiating the generation of $^{13}$CO$_2$ in our experiments. The concentration of $^{13}$CO$_2$ first increased with the temperature to a maximum at 1173 K before decreasing at higher temperatures. Although CO$_2$ can be efficiently formed by photochemistry, it can be also thermally decomposed and photodissociated by UV photons. The efficiencies of these two loss processes increase with temperature (Venot et al. 2018) and could explain the lower CO$_2$ concentration at higher temperatures.

In addition, a net production of water was observed despite competitive destruction by UV photons. The production of water generally increased with the temperature according to the spectra in Figure 6. However, it should be noted that these spectra may contain a minor contribution from the residual atmospheric water on the optical pathway outside of the reaction cell. An efficient water formation pathway has previously been reported in experiments conducted at room temperature in N$_2$/CO$_2$/H$_2$ gas mixtures using a plasma discharge as energy source (Fleury et al. 2015). The formation of water can be initiated by the formation of O($^1$D) radicals by the photodissociation of CO$_2$ in our experiments. The photodissociation of CO$_2$ can follow two different pathways, depending on the photon energy:

\[ \text{CO}_2 + h\nu \rightarrow \text{CO} + \text{O}(^3\Sigma), \]  
(R3)

\[ \text{CO}_2 + h\nu \rightarrow \text{CO} + \text{O}(^1\Sigma). \]  
(R4)

At wavelengths shorter than 167 nm, reaction (R4) is dominant (Huebner et al. 1992) and so the photodissociation of CO$_2$ principally leads to the formation of O($^1$D) radicals, which can then react with H$_2$ to form OH radicals (Vranckx et al. 2010):

\[ \text{H}_2 + \text{O}(^1\Sigma) \rightarrow \text{OH} + \text{H}. \]  
(R5)

Finally, the formation of water is explained through the following reactions (Orkin et al. 2006; Bahng & Macdonald 2007):

\[ \text{H}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{H}, \]  
(R6)
The increase in water production with temperature is correlated with the decrease in the carbon dioxide mixing ratio. Experimental measurements have shown that the CO$_2$ absorption cross-section can increase by orders of magnitude as the temperature is increased (Venot et al. 2018). Thus, an increase in temperature could lead to more efficient photodissociation of CO$_2$, leading to higher production of O($^1$D) radicals and water despite the competitive water photodissociation process.

Here, we have shown that photochemistry can strongly influence the composition of H$_2$:CO warm exoplanet atmospheres. In particular, our results demonstrate that carbon dioxide and water can be efficiently produced in these atmospheres despite competitive loss processes. We find that the gas temperature strongly influences the efficiency of the different chemical pathways. This is notably due to the increase of the absorption cross-sections of CO$_2$ when the temperature increases (Venot et al. 2018). A similar effect is expected for other molecules such as CO and H$_2$O, and more laboratory measurements are needed to address this further. Moreover, chemical reaction kinetics is known to be strongly affected by the temperature.

### 3.2.2. Volatile Organics Formation

Electronically excited CO (Equation (R1)) can also react with the excess H$_2$ molecules available in the chamber or H atoms generated through thermal/photochemical dissociation of H$_2$ or water, initiating the hydrogenation of CO (forming HCO; Roussel & Back 1990) that could eventually result in the formation of formaldehyde (H$_2$CO) or methane (CH$_4$). Alternatively, carbon formed by Equation (R2) can react with H$_2$ or H or CO, initiating the formation of the precursors CH and C$_2$O, leading to the formation of complex organics as well as methane. Literature studies determined that in the ground state, CO + H reaction has a barrier of about 4 kcal mol$^{-1}$ (Pham et al. 2016 and references therein) and concluded that HCO formation must occur in the CO$^*$ excited state, leading all the way to the formation of H$_2$CO and CH$_3$OH (not observed in our experiments).

### 3.2.3. Isotopic Labeling and Natural Isotope Products

Isotopically enriched $^{13}$CO has been used in all the experiments reported here, in order to differentiate any potential leaks into the low-pressure reaction cell (~15–30 mbar). We detected normal isotope $^{12}$C products during the

\[
2\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}(^3\text{P}).
\] (R7)
thermochemistry phase in the alumina reaction cell ($^{12}$CH$_4$), as well as during the photochemistry phase ($^{12}$CH$_4$, $^{12}$CO$_2$ and $^{12}$CO). We could envision two potential sources of normal isotope products in our experiments: (Scenario 1) an extremely small leak of ambient air into the reaction cell, and (Scenario 2) pyrolysis and photolysis of organic residue (most likely from solvents such as the isopropanol used to clean) on the inner walls of the cell. Quartz has a much smoother surface than alumina, hence there is a larger inner-wall surface area for the latter. $^{12}$CH$_4$ is observed only during the thermal experiments with the alumina cell at 1173 K and higher temperatures (Figure 5), but not when the quartz cell was used at $<$1173 K (Figure 3). This could most likely be due to pyrolysis of organic residue (scenario 2), because we do not detect any increase of $^{13}$CO$_2$ or $^{13}$CO in the reaction cell during thermochemistry studies. Venot et al. (2018) performed studies on CO$_2$ spectroscopy at higher temperature (similar to our conditions) and found that CO was formed by thermal decomposition of CO$_2$. If a small leak of ambient air into the cell (scenario 1) were to be present in our experiment, we would expect $^{12}$CO$_2$ from the ambient air to contribute to an increase of $^{12}$CO$_2$ spectral bands as well as thermal dissociation of $^{12}$CO$_2$ from the leak to increase the $^{12}$CO spectral bands. So, we can confidently rule out a leak during the thermochemistry phase of our experiments.

Further support for the possibility of photolysis of residual organics from the walls of the cell comes from our mass spectrometry measurements that are complementary to the infrared spectroscopic measurements. We also analyzed the gas-phase volatiles of the cell in situ by mass spectrometry during these experiments before and after thermal equilibrium as well as after photolysis. Due to the fact that all the components are undergoing chemical modifications continuously, we took the key component $^{13}$CO as the molecule that is normalized in each mass spectrum and determined the relative abundances of the rest of the species as shown in Figure 7.

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However, it is also possible that the absolute concentrations of other molecules might not have changed, while their apparent increase or decrease might be caused by the changing absolute concentration of $^{13}$CO, which we used to normalize the mass spectra. In a system where all the species change in their concentration, it is difficult to obtain absolute quantification, and the only possibility is relative quantification. In the future, we may use a rare gas such as He (which is present in hot-Jupiter atmospheres), Ne, or Ar as a tracer to determine absolute concentrations from mass spectrometry with the assumption that these rare-gas atoms are chemically inert and do not undergo chemical reactions with the gas mixture. Please note that the intensity scales are different for each temperature.

We find the general tendency of increasing H$_2$O production with temperature, and an increase and then decrease of $^{13}$CO$_2$ with temperature, in agreement with Table 2. We also notice some atmospheric leaks, clearly represented by N$^+$ (m/z 14), but also with some minor contribution from CH$_3^+$. However, the peak at 28 could be due to N$_2^+$ as well as $^{13}$CO$_2^+$. We monitored the pressure change in the reaction cell and found...
Spectra from a control experiment whereby the furnace was first evacuated to $3 \times 10^{-7}$ mbar, then isolated and heated to 1473 K for 24 hr. Infrared spectrum (top) and mass spectra (bottom) of the gas-phase inside the reaction cell before and after heating at 1473 K for 24 hr.

That the change after 18 hr was only 1 mbar between the beginning of UV irradiation (after thermal equilibration) and the end of irradiation (Table 1). If the increase in pressure of ~1 mbar were to be due entirely to N$_2$ (80% air), we would have expected the signal at m/z 28 to be at least an order of magnitude larger than the $^{13}$CO$^+$ at m/z 29, which was not the case. The peak at m/z 28 ($^{12}$CO$^+$ and N$_2$) is at the maximum at about the same height as the peak at m/z 29 ($^{13}$CO$^+$), and no significant O$_2^+$ was detected at m/z 32. Based on these qualitative observations and due to the fact that in the FTIR spectrum a significant increase in $^{12}$CO and $^{12}$CO$_2$ has been observed subsequent to the photochemistry phase, we think that the observed spectra of normal isotope molecules are likely due to photochemistry followed by fast chemical reactions leading to CO$_2$ and CO$_2^+$ residues within the interior walls of the alumina reaction cell. A small fraction of the initial gas may have also escaped the reactor before experiments.

Atmospheric gas leak, although it cannot be completely ruled out, could only be a minor contributor for the normal isotope molecules.

To better constrain the contribution from outgassing/pyrolysis from the walls of the alumina cell during our experiments and to better understand how they affect our experimental results, we performed an additional control experiment. The alumina cell was heated and pumped down to $3 \times 10^{-7}$ mbar (Section 2.1), isolated from vacuum, and heated for 24 hr at 1473 K. The composition of the gases inside of the reaction cell was analyzed using IR spectroscopy and mass spectrometry. The mass spectrum at room temperature and the mass spectrum and IR spectrum after 24 hr of heating at 1473 K are presented in Figure 8. These spectra show the presence of H$_2$O, CO$_2$, and to a lesser extent $^{12}$CO (convoluted with water in the IR spectrum) after the heating of the gases. These results are in agreement with the contamination observed after the photochemical experiments. Desorbed water intensities during this control study are three times lower than those observed from the photolysis of the H$_2$:CO mixture at 1473 K. We also note that the pressure in the sealed alumina cell increased from $3 \times 10^{-7}$ mbar initially to ~4 mbar after 24 hr at 1473 K in this control experiment. For photolysis experiments under the same temperature, but at higher CO/H$_2$ gas starting pressure, we did not notice any change in the pressure before and after 18 hr of photolysis (initial: 33 mbar, final: 33 mbar, detection limit <0.5 mbar, which is the resolution of our pressure gauge display). The increase of the pressure in the cell after the control experiment is explained by the outgassing at higher temperature of water and CO$_2$ adsorbed on the cell walls. Though a similar process is expected to occur during the photolysis experiment at 33 mbar pressure in the cell, both desorption and re-adsorption efficiencies could vary at this relatively higher pressure and compete with each other. Further, photochemistry also produces solid aerosols, which should contribute to a net decrease of the pressure if there were no thermal desorption from the cell walls. Although we are unable to definitively quantify water production in our photolysis experiments, these data taken together suggest that the water production observed during the photochemistry experiments is significant and that water originating from ambient contamination is minimal.

Our study, taking $^{13}$CO as the initial reactant, demonstrates the importance of using such isotopes to unambiguously distinguish various pathways that could potentially interfere with the observations and derived quantitative data points. Though we observed a significant amount of water formation, we could not quantify the mixing ratio due to ambient H$_2$O in the FTIR optical pathway outside the cell and possible contamination. We want to resolve this problem in the future by using $^{13}$C$^{18}$O and D$_2$ to quantify the mixing ratio of H$_2$O.
generated through photochemistry of H2 and CO at hot-Jupiter atmospheric conditions.

3.3. High-temperature Photochemical Formation of Solid Refractory Organics

A detectable amount of solid-phase product was not observed in the experiments presented above. However, we noted that depletion of CO was higher when irradiated at higher temperatures, while the production efficiency of the gas-phase products (CO2 and CH4) decreased, meaning another chemical reaction pathway becomes efficient at higher temperatures under exposure to UV photons. We propose that higher temperatures enhance the conversion of CO, CO2, and CH4 to solid-phase aerosols. To investigate this hypothesis, we repeated the UV irradiation of H2/CO gas mixture at the thermal equilibrium at 1473 K. The gas mixture was irradiated for 204 hr in order to ensure that a sufficient amount of solids was produced. For this experiment, we placed two sapphire windows inside the cell inside the highest temperature zone 18 cm and 30 cm from the UV source. We also increased the pressure in the cell to 81 mbar in order to increase the amount of gases. Then, after the irradiation, the pressure in the cell had dropped to 150 mbar, highlighting the conversion of part of the gas mixture into a solid product. Figure 9 presents the photographs of a clean sapphire window (blank) and of the two samples collected after UV irradiation. We observed a white deposit on the two sapphire windows placed inside the cell. The film deposited on Sample 1 is thicker than the one deposited on Sample 2, which was placed farther away from the UV source, but at the same temperature. This observation can be rationalized on the basis of higher attenuation of Lyα photons at distances in the cell farther away from the UV source. As a result, Sample 2 witnessed less photochemical aerosol formation than Sample 1.

The thin films formed in our experiment are organics as confirmed by their mid-IR signature presented in Figure 10. We observed that the absorbance of Sample 2 is lower than that of Sample 1, in agreement with the difference in their thicknesses. Different absorption bands characteristic of solid organics are observed in these spectra.

Sample 1, in agreement with the difference in their thicknesses. Different absorption bands characteristic of solid organics are observed in these spectra.

Figure 9. Photographs of solid-phase organic aerosol products deposited on sapphire windows (1″ diameter) after 204 hr of H2:13CO (99.7%:0.3%) gas mixture irradiation at Lyα (121.6 nm) and 1473 K. Blank is a clean sapphire window. Sample 1 and 2 were deposited on two sapphire (Al2O3) windows placed in the CAAPSE cell 18 cm and 30 cm from the hydrogen lamp, respectively. Temperatures at Sample 1 and Sample 2 were approximately the same (~1300 K) but more UV photons reached Sample 1 than Sample 2, due to the attenuation of Lyα (121.6 nm) by CO molecules.

Figure 10. Infrared absorption spectra of the films deposited on two sapphire substrates during the same irradiation experiments of the H2:CO (99.7%:0.3%) gas mixture at thermal equilibrium at 1473 K with Lyα (121.6 nm) photons. Sample 1 and 2 were deposited on two sapphire windows placed in the CAAPSE cell 18 cm and 30 cm from the hydrogen lamp, respectively.
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3.4. Discussion

Our experimental results provide new and first insights into the photochemical processes occurring in hot-Jupiter-like exoplanet atmospheres. However, there are some experimental limitations that need to be noted. First, reactions on the wall of the cell can catalyze chemical reactions. Second, we used a static system, where the gases are sealed in the reaction cell, to ensure thermal equilibrium is achieved. However, under static conditions, the long residence time of the gases in the irradiation area tendency to increase the degree of conversion of the reactants to products, resulting in a continuously changing composition of the gas mixture being photolyzed with time (Clarke et al. 2000). Experiments using a flow system where the reactant gases are continuously renewed would allow us to overcome this issue. In such conditions, the gas mixture composition would reach a steady state after several minutes of irradiation, and a direct quantitative comparison with planetary atmosphere compositions would be more effective (Peng et al. 2013). However, such studies must ensure that thermal equilibrium of gas is reached and need to use highly sensitive spectroscopic techniques (due to lower amounts of product formation) for quantification of spectral signatures.

Finally, the hydrogen lamp that has been used for these experiments does not reproduce total stellar photon flux. Molecules such as H2O absorb at a wide range of UV wavelengths, and photodissociation of water or carbon dioxide might be more efficient in planetary atmospheres than in our experimental setup.

4. Conclusion

This work presents a first experimental simulation of the chemistry in hot carbon-rich exoplanet atmospheres, where UV photochemistry should play a key role. We have irradiated H2:CO gas mixtures at various temperatures from 600 to 1500 K with Lyα (121.6 nm) photons, and monitored the evolution of the gas-phase composition using infrared spectroscopy and mass spectrometry.

Thermochemistry leads to the formation of carbon dioxide at each studied temperature, and the formation of methane is observed only occasionally, indicating that either the formation of methane is inefficient, that the formation efficiency has a strong temperature sensitivity, and/or that methane is highly reactive under these conditions, leading to the formation of more complex organics. The observed thermochemistry induces the formation of a new thermal equilibrium composition—different from the initial gas mixture composition used in our experiments—which depends on the gas mixture’s temperature.

Further, our results showed that subsequent irradiation of these equilibrium gas mixtures promotes very efficient photochemistry, depleting the gas phase in CO and enhancing the production of carbon dioxide and water. These processes depend on the gas temperatures—at temperatures below ∼1200 K, the main photochemical product is CO2, and at higher temperatures, the mixing ratio of CO2 decreases, and water becomes the main product. The production of CO2 is explained by the photodissociation of CO, which reacts with ground-state CO to generate C + CO2. This formation of CO2 is also at the origin of the water formation. Indeed, the formation of O(1D) radicals from CO2 photodissociation leads to the formation of water through subsequent neutral pathways. Carbon produced during the formation of CO2 could react with excess H2 to form CH4. Our initial experimental study shows that photochemistry could efficiently modify the composition of exoplanet atmospheres. In particular, our results highlight that (1) CO2 can be efficiently produced despite competitive destruction processes, in contradiction with current chemical modeling studies (Venot et al. 2015), and (2) H2O can be produced via photochemistry in carbon-enriched (C/O = 1) atmospheres. The second point is important because of the potential for the presence of H2O in hot Jupiter atmospheres to bias the estimation of the planetary C/O ratio when spectra containing H2O are interpreted with thermochemical equilibrium models. We expect that with decreasing C/O ratio, an increase in both thermal and photochemical transformations will occur, in particular, leading to an increase in the production of H2O.

Finally, we have observed the formation of solid organic thin films after the irradiation of the gas phase at 1473 K with Lyα. We found that non-volatile hydrocarbon aerosols are formed with HCO functionality involving aromatic and aliphatic hydrocarbons. This result demonstrates that refractory organic aerosols can be formed in hot exoplanet atmospheres with an enhanced C/O ratio. This critical result highlights the importance of conducting laboratory experiments simulating relevant exoplanet environments in order to evaluate the formation and the properties of aerosols in the exoplanet atmospheres. Further studies including other species such as CO2, CH4, and N2 in the initial gas mixture and with different C/O ratios would improve our understanding of the gas and solid aerosol compositions of exoplanet atmospheres.

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