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UNDERSTANDING THE CHEMISTRY OF TEMPERATE EXOPLANET ATMOSPHERES: A STUDY OF OXIDIZED ORGANIC COMPOUNDS AS PRECURSORS OF PHOTOCHEMICAL CONDENSATES

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Abstract. Characterizing the atmospheres of small temperate exoplanets is a major scientific challenge. The James Webb Space Telescope offers us the opportunity to study temperate exoplanets as small as mini-Neptunes. Recent observations of K2-18 b and TOI-270 d have revealed atmospheres rich in hydrogen and carbon compounds. Methane and carbon dioxide have been detected in significant amounts. The development of our knowledge of these atmospheres will enable us to characterize their habitability. However, our understanding of the chemistry governing these atmospheres remains very limited. Therefore, laboratory experiments and modeling are needed to better understand these observations. In this context, we have carried out experimental simulations. Using a cold plasma reactor, we simulated the out-of-equilibrium chemistry that occurs in the upper layers of temperate exoplanets. We have used mass spectrometry and infrared spectroscopy to track the chemical evolution of gas mixtures similar to exoplanetary atmospheres. Our observations highlight the production of complex organic compounds, carbon monoxide, and water vapor. In addition, our first results suggest the formation of oxidized organic compounds, which are precursors of photochemical condensates of prebiotic interest.

Keywords: exoplanet atmospheres, exoplanet atmospheric composition, experimental simulations, oxidized organics, planetary atmospheres

1 Introduction

Characterizing the atmosphere of temperate exoplanets is one of today's greatest scientific challenges. The first atmospheric characterizations were carried out using the transit spectroscopy method. The light from a star is captured at different wavelengths, while a planet passes between the observer and the star; this is the principle of eclipse. If there is an atmosphere around this planet, its apparent diameter will depend on the wavelength, as all the gaseous molecules present in the atmosphere absorb light over a certain range of wavelengths. Finally, when the different observation wavelengths are combined, we obtain a transmission spectrum of the planet with absorption features corresponding to the composition of the atmosphere.
The challenge posed by temperate exoplanets is that they are relatively small, cold bodies that are difficult to detect with the resolution of our instruments. This is why we need a strong synergy between the different communities of observers, modelers and experimenters. A new instrument, the James Webb Space Telescope, represents a major evolution in the field, with a much higher resolution than previous instruments. To date, it has enabled atmospheric characterization of two temperate exoplanets, K2-18 b (Madhusudhan et al. 2023) and TOI-270 d (Benneke et al. 2024; Holmberg & Madhusudhan 2024). These planets orbit M dwarf stars and are thought to be Mini-Neptunes. Analysis of the transmission spectra obtained with JWST reveals an atmospheric composition dominated by hydrogen, with a few percentages of carbon-bearing species such as methane or carbon dioxide as shown on Figure 1. Other species are suspected to be present, such as carbon monoxide or water vapor. But even if these new data are truly revolutionary, the chemical composition of these atmospheres is still largely unconstrained. This is why we have carried out experimental simulations of this type of exoplanetary atmosphere, to better understand the chemistry of these environments.

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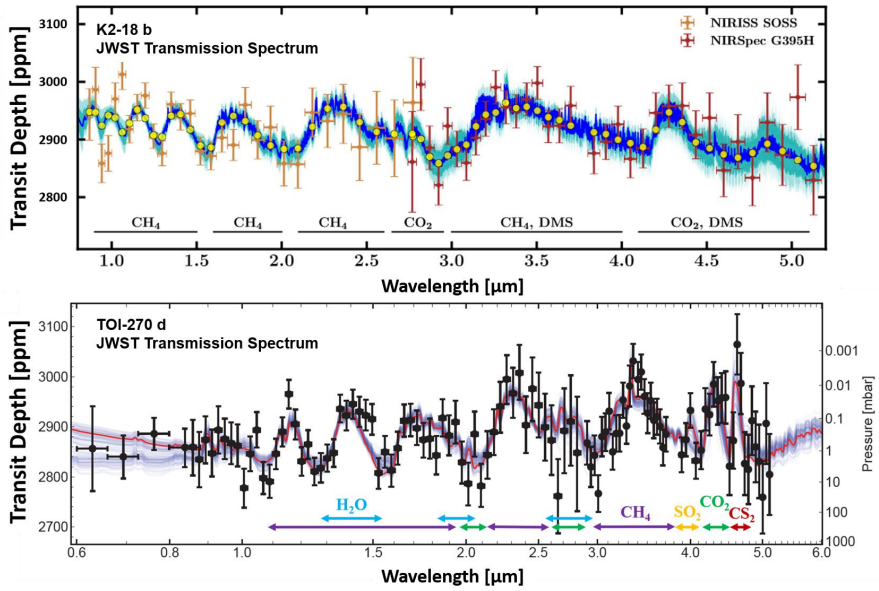

Fig. 1. Up: JWST Transmission Spectra of K2-18 b adapted from Madhusudhan et al. (2023). **Down:** JWST Transmission Spectra of TOI-270 d adapted from Benneke et al. (2024)

2 How to simulate a temperate exoplanetary atmosphere in the lab

2.1 A cold plasma setup to simulate out-of-equilibrium chemistry in the upper layers of a temperate atmosphere

The aim of these experiments is to reproduce the energetic processes that occur in the upper layers of a temperate atmosphere, exposed to energetic stellar particles and UV irradiation. These energetic processes trigger non-equilibrium chemistry, dissociating gaseous molecules. The products can rearrange to form new species. Simulations of the upper atmospheric layers of temperate exoplanets were carried out using a cold plasma experimental device, the PAMPRE reactor (for Production d'Aérosols en Microgravité par Plasma REactif Szopa et al. (2006)), located at LATMOS, Guyancourt, France. A schematic diagram of the reactor is shown on Figure 2. This device applies a radio-frequency discharge in a gas mixture at room temperature (300 K) and low pressure (1 mbar). Mass flow controllers connected to a manifold inject a finely-tuned gas composition into the reactive chamber. Two complementary analysis devices are connected to the reactive chamber to monitor the out-of-equilibrium chemistry that occurs during plasma discharge. In order to follow the chemical evolution in our experimental setup, and in particular to identify the formation of various chemical species, we combine two complementary analytical methods: mass spectrometry and infrared spectroscopy.

2.2 Two complementary analysis methods

Observations with Mass Spectrometry (MS) One of the analytical instruments used is a Quadrupole Mass Spectrometer. Gaseous molecules arriving at the collector head are ionized, causing each molecule to fragment into a set of peaks with defined mass-to-charge ratios and relative intensities specific to each species. In this way, each molecule has its own characteristic fragmentation pattern, just like a footprint, which enables it to be identified in a complex mass spectrum. A mass spectrum is taken in the inital state, when the gas mixture is injected into the reactive chamber while the plasma discharge is still off. Then the plasma is switched on and a new spectrum is taken few minutes later, when it has stabilized. We can see the evolution of the composition by plotting the superposition of the two spectra on the left of Figure 3 or plotting the difference in intensity between these two spectra (ON-OFF) as shown on the right of Figure 3. In a gas mixture at 1 mbar made up of 98% of H_2, 1% of CH_4 and 1% of CO_2 subjected to plasma discharge, mass spectrometry analyses highlight the production of water vapor and carbon monoxide correlated with the consumption of carbon dioxide. Dissociation of the methane reagent is also observed, correlating with the initiation of significant organic growth, leading to the formation of chains containing up to four carbon atoms.

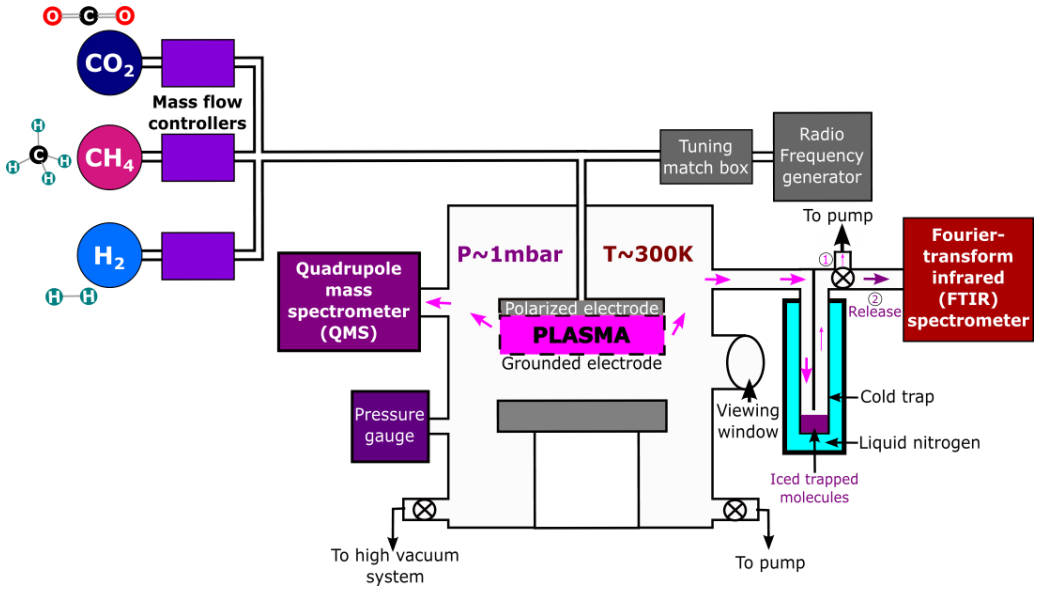

Fig. 2. Scheme of the plasma reactor PAMPRE

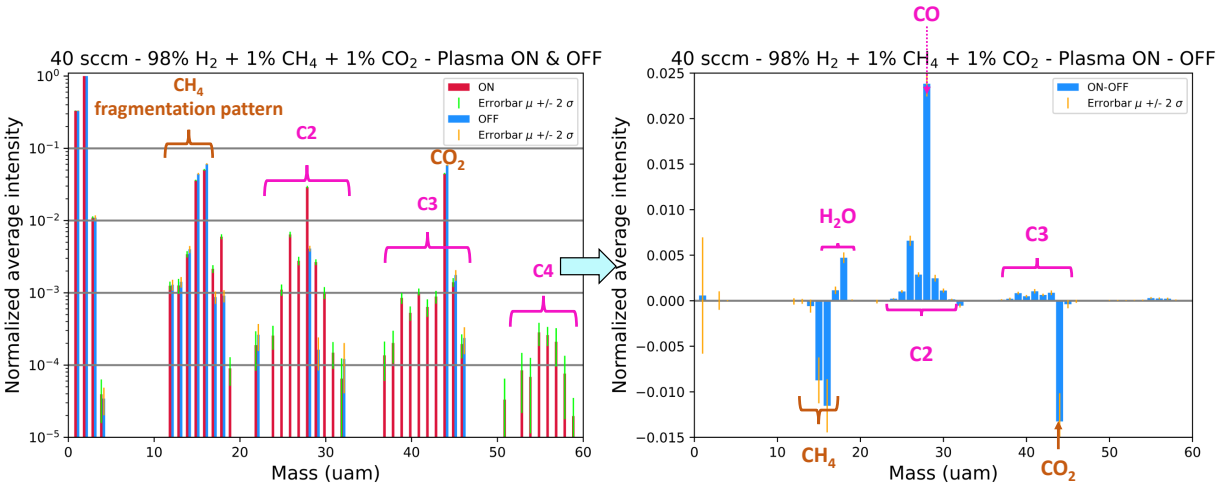

Fig. 3. Left: Superposition of mass spectra taken when the plasma discharge is turned OFF (blue) and ON (red). **Right:** Difference of intensities between the spectra when the plasma discharge is ON minus when it is OFF

Limits of MS Although mass spectrometry can identify several products, in complex mass spectra, the fragmentation patterns of the species overlap, leading to ambiguous identifications. For example, the patterns of oxidized organics such as CH_3OH and CH_3CHO are completely overlapped by the patterns of C_2H_4 and C_3H_8. For this reason, we have carried out complementary analyses using infrared spectrometry, which gives us access to information on the nature of the chemical bonds between the atoms. By combining the results of these two methods, we can deepen our understanding of the out-of-equilibrium chemistry taking place in these analogues of planetary atmospheres.

Observations with InfraRed (IR) Spectroscopy The PAMPRE experimental setup is equipped with a multi-pass infrared cell with an optical length of 10 m, placed in the sample compartment of an FTIR spectrometer. Each molecule absorbs at a specific wavelength, making it possible to identify species by finding specific features in the transmission spectrum. Direct measurements of gas flow through the spectrometer do not offer sufficient resolution to identify products. A cold trapping strategy is used to concentrate the products for their identification. The flow of gas mixture irradiated by the plasma passes through a glass trap immersed

in liquid nitrogen at 78 K, which condenses most of the gas. The trap is then heated and the sublimated gas species are released into the multi-pass cell, where infrared spectra are obtained. It should be noted that trapping strategy induces a quantitative bias as each gas molecule is trapped differently according to its condensation temperature. For example C_2H_2 is much better trapped than C_2H_4. Some molecules are not trapped at all, but this not a problem as it only concerns our reactants, H_2, CH_4 and CO; on the contrary it increases the concentration of minor products, helping to identify them.
Analysis of the infrared spectra first confirms the results observed with mass spectrometry, in particular organic growth as shown on the left of Figure 4. And more importantly other unambiguous features are revealed in IR spectroscopy, enabling the identification of oxidized organic compounds, such as methanol, formaldehyde and acetaldehyde, as shown on the right of Figure 4.

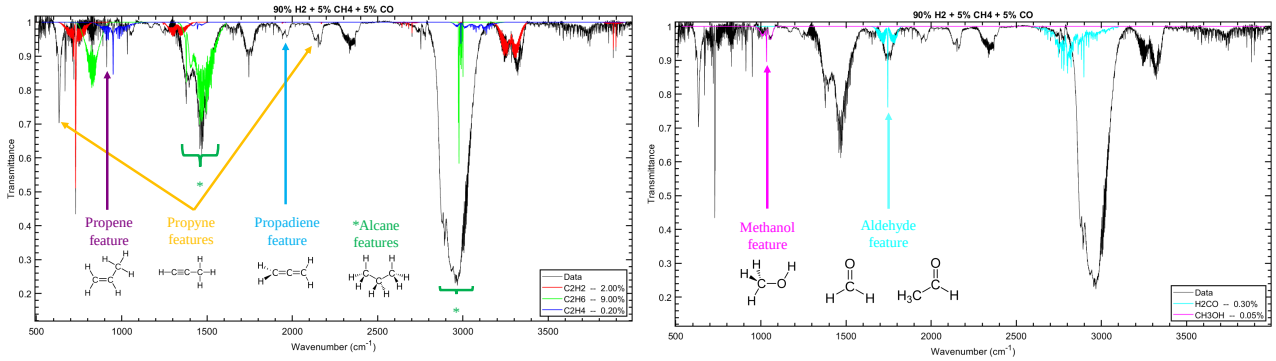

Fig. 4. Left: Features of carbon chains. **Right:** Features of oxidized organics, CH_3OH at 1033cm^{-1}and aldehydes H_2CO and CH_3CHO at 1745cm^{-1}.

3 Exobiological interest of oxidized organics

Pinto et al. (1980) highlighted the fact that the most important sources of formaldehyde on the primitive Earth was atmospheric photochemical synthesis, through the photo-reduction of CO_2 with H_2O. This hypothesis was extented to the photochemical synthesis of methanol and acetaldehyde by Wen et al. (1989). This atmospheric synthesis is just the first step in a complex geochemical cycle that leads to the formation of more complex organic compounds such as sugars, as Cleaves (2008) pointed out. The identification of these oxidized organic compounds formed by out-of-equilibrium processes in analogous temperate exoplanetary atmospheres is therefore of great exobiological interest. The reference planets are not similar to the primitive Earth, without the confirmed existence of a surface or ocean that would support a complete geochemical cycle, but we can imagine that with high enough concentrations of oxidized organics, they could agglomerate and form condensation nuclei.

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References

Benneke, B., Roy, P.-A., Coulombe, L.-P., et al. 2024, JWST Reveals CH_4, CO_2, and H_2O in a Metal-rich Miscible Atmosphere on a Two-Earth-Radius Exoplanet

Cleaves, H. J. 2008, Precambrian Research, 164, 111

Holmberg, M. & Madhusudhan, N. 2024, Possible Hycean conditions in the sub-Neptune TOI-270 d

Madhusudhan, N., Sarkar, S., Constantinou, S., et al. 2023, The Astrophysical Journal Letters, 956, L13

Pinto, J. P., Gladstone, G. R., & Yung, Y. L. 1980, Science, 210, 183

Szopa, C., Cernogora, G., Boufendi, L., Correia, J. J., & Coll, P. 2006, Planetary and Space Science, 54, 394

Wen, J.-S., Pinto, J. P., & Yung, Y. L. 1989, Journal of Geophysical Research: Atmospheres, 94, 14957