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Orbitrap mass spectrometry of synthetic (exo-)planetary organic haze

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1 Introduction

Aerosols are present in every substantial planetary atmosphere of the solar system and in that of exoplanets. They affect the chemistry, dynamics and flux of radiation in these atmospheres. They can transport organic material to the surface, act as a UV shield, modify the temperature and consequently have an impact on the habitability of the planet [8].

The structure, composition and formation processes of organic aerosols are still largely unknown. A most illustrative example is that of Titan. Although the Cassini-Huygens mission provided a wealth of data on Titan's atmosphere and surface, in situ mass spectrometry as well as remote spectroscopy data provided only sparse information about the aerosols' molecular composition. Photochemical models cannot describe species with mass-to-charge ratios (m/z) above about 100 u because of the increasing complexity of the chemical network and the lack of appropriate kinetic data [11].

The best way to study the molecular composition of planetary hazes is to synthesise analogs in the laboratory, called tholins, and to analyse them with state-of-the-art analytical instruments. Indeed, aerosol analogues made by exposing N_2 and CH_4 to various energy sources have been extensively characterised, revealing a bulk composition C/N$\sim$1.5-3 and amine, imine, nitrile functional groups as well as heteroaromatic compounds [3].

CO is an important component in many N_2/CH_4 atmospheres: Titan, Pluto, Triton and probably super-Earths. Therefore, CO is the main atmospheric carrier of oxygen, an essential element of life as we know it. Previous laboratory experiments have shown that CO has an impact on the size and production rate of the tholins and that oxygen can be efficiently incorporated to form prebiotic molecules [6, 4, 7, 5]. However, the impact of oxygen at the molecular level remains to be investigated.

2 Haze production - The PHAZER setup

Laboratory analogues were synthesised at Johns Hopkins University by exposing to an AC glow discharge six different gas mixtures of N_2, 5% CH_4 and variable amounts of CO (from 0 to 5%). The gases are cooled down to about 100 K and flow continuously (10 sccm) through a stainless steel reaction chamber where the pressure is held at 2 Torr. After 72h of discharge flow, the red/brown film deposited on the wall of the reaction chamber is collected under a dry N_2 atmosphere. The tholins are kept in a glove box and wrapped in foil to avoid exposure to air and light, respectively [5].

3 Molecular composition - The Orbitrap™ mass spectrometer

Very high-resolution mass spectrometry data were acquired at Univ. Grenoble Alpes with a Thermo LTQ Orbitrap XL (resolving power FWHM m/Δm $\sim$ 100,000 at m/z = 400 u) coupled with an electrospray ionisation (ESI) source. About 1 mg of tholins is diluted in 1 mL of methanol to generate a primary solution that is shaken and centrifuged at a spin rate of 10,000 rotations / min for 10 min. 500 μL of the soluble fraction is mixed with 500 μL of methanol to generate a secondary solution that is injected in the Orbitrap. Mass spectra of the samples are obtained in both positive and negative mode, in the 50-300 and 150-500 m/z range [10]. The stoichiometry of each individual molecule making up the samples (about 3000 per sample) is obtained using the Attributor software developed at IPAG [9]

4 Results and Conclusions

These composition measurements provide some understanding of the chemical mechanisms by which CO affects particle formation and growth. Once a molecular formula has been assigned to each peak, the percentage in mass of element X (where X = H, C, N, O) in each sample is calculated by summing the number of element X in each peak weighted or not by its intensity [1]. As seen in Figure 1, as the initial abundance of CO increases, the O content increases while the N content decreases and the C and H content remains the same, in agreement with results from the elemental analysis of the bulk [5].

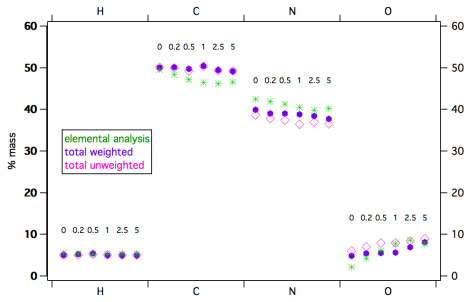

Figure 1: Mass percentages of H, C, N, O in the six samples with increasing abundance of CO in the initial gases.

The Double Bond Equivalent (DBE) and Aromaticity Index (Xc) are proxies to determine the number of unsaturation (double/triple bonds, cycles) in a molecule based on the number of each element (H, C, N, O) [12]. They show that the unsaturation does not depend on the number of O atoms in the molecule and that a large fraction of condensed aromatics (PAH-like) and aromatics are present in all samples.

In the context of the quest for biosignatures, development of very high-resolution mass spectrometers for spaceflight capable of in situ sampling of atmospheres and surfaces is mandatory [2].

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