Volatile organic compounds stability at exoplanetary atmospheres

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1. Introduction

Species such as isoprene and other terpenoids are reactive volatile organic compounds (VOCs). They can be quite reactive under terrestrial conditions, as they react very rapidly with -OH radicals in the atmosphere, resulting in short chemical lifetimes (minutes to hours). However, they are emitted in significant amounts by trees and other vegetations. So, the emission of biogenic VOCs plays an important role also in the photophysics and photochemistry of the atmosphere, affecting its oxidative capacity (de Souza *et al.* 2007; Sharkey *et al.* 2008; Gu *et al.* 2017). As they are biogenic products, in different conditions from Earth they could constitute relevant biosignature in the atmospheres of exoplanets (Seager *et al.* 2012).

In the context of the relation star-planet, it is important to understand the interaction of XUV photons from the star inciding upon the planetary atmosphere: how its XUV photons interact with these biosignatures, in terms of photoabsorption and ionization efficiency in the upper atmosphere of the planet.

2. Methodology

The absolute photoabsorption of isoprene was measured in the range of 13 to 20 eV of photon energy. The source of UV monochromatic photons was the TGM (Toroidal Grating Monochromator) beamline of the Brazilian Synchrotron Light Laboratory (LNLS/CNPEM), at Campinas, São Paulo (Brazil). It provides photons with flux up to 10^{10} photons s⁻¹ and resolution of 0.05 eV. The beamline was operated with a toroidal grating of Au, with 1800 l/mm, working in the range of 13 to 100 eV of photon energy. A neon-gas filter was used to avoid harmonic contamination (Cavasso-Filho *et al.* 2007).

In order to obtain the photoabsorption measurements, we developed a cylindrical ionization chamber with four stages (four copper plates, same size) to signal detection. It works with a base pressure of 10^{-3} mbar and it is filled with the sample in gas-phase until it reaches a pressure of ~0.1 mbar. A voltage of 60 V is applied in the cylindrical plate. A capacitance manometer (MKS Baratron[®]) was used for pressure monitoring inside the chamber. Digital pico-ammeters (Keithtley Instruments) were connected to



Figure 1. The upper panel shows the photoabsorption cross section of Xe-gas (calibration) in good agreement with Samson & Stolte (2002). The bottom panel shows our results in comparison with Martins *et al.* (2009), estimated via electron impact technique.

each stage to measure the signal response to the incident photon beam upon the gas. The calibration was achieved through measurements of Xe, based in the absolute photoabsorption cross-section data from Samson & Stolte (2002). The sample of isoprene was purchased commercially from Sigma-Aldrich, with a purity of 99.5%. We estimate a typical uncertainty of 10% in the cross section evaluation.

3. Discussion

With this technique, we could determine the absolute photoabsorption cross-section of the gases analyzed. Fig. 1 shows two cases: with isoprene and with Xe. The latter has a very known profile and can be used as a reference. The bottom panel of the Fig. 1 shows the isoprene measurements with the ionization chamber (this work) and with electron impact technique (Martins *et al.* 2009). The differences between then lies down the uncertainty limit of 10% of our data, suggesting a good agreement. With this methodology, also associated with mass-spectrometry techniques, it is possible to determine other important parameters of organic molecules in harsh conditions, such as the ionization efficiency and its absolute photoionization cross-section.

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