

Towards disentangling photodesorption and photodissociation in astronomical ice analogues

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Abstract. UV irradiation of ices plays an important role in different inter- and circumstellar environments. Following the absorption of UV photons in ice, two processes compete: photodesorption and photodissociation/chemistry. From an experimental point of view it is very hard to discriminate between photodesorption and photodissociation (and resulting photochemistry). In this work we present our first attempts to distinguish both effects. The performance is demonstrated on the example of CO-ice, known not to dissociate upon UV irradiation, and CH₄-ice that does fragment.

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1. Introduction

In cold regions of the Interstellar Medium (10-20 K), ice mantles are the source of chemical diversity. At the same time, gas-phase formation rates have been shown to be not sufficient to explain astronomical abundances of molecules like water (Bergin *et al.* (1995)), methanol (Geppert *et al.* (2006)) and several larger COMs. In order to explain the observed gas-phase abundances, a non-thermal mechanism is necessary that transfers molecules effectively and ‘in one piece’ from solid-state to gas-phase (e.g. CH₃OH, Guzman *et al.* (2013)).

The non-thermal desorption mechanism that we focus on here is UV photon stimulated desorption. However, ice UV processing also initiates dissociation (Bertin *et al.* (2016)). A challenge associated with quantifying UV processes in ices is disentangling photodesorption and photo-dissociation/chemistry. The new concept introduced here is based on a technique developed a few years ago in which the vacuum UV irradiation of ices was characterized by laser induced desorption combined with time-of-flight mass spectrometry (Paardekooper *et al.* (2014)). Here, we extend on that technique, focusing on pure CO and CH₄ ices, as test environments; work dealing with CH₃CN is currently in preparation.

2. Methods

Ice analogues are grown in an Ultra High Vacuum (UHV) apparatus, MATRI2CES. To track molecular abundances in the ices, laser-desorbed species are ionized using an electron gun and accelerated into the time-of-flight mass spectrometer. Electron impact ionization induces fragmentation of molecular ions, which is taken into account. Broadband vacuum UV light is generated by a Microwave Discharge Hydrogen Lamp

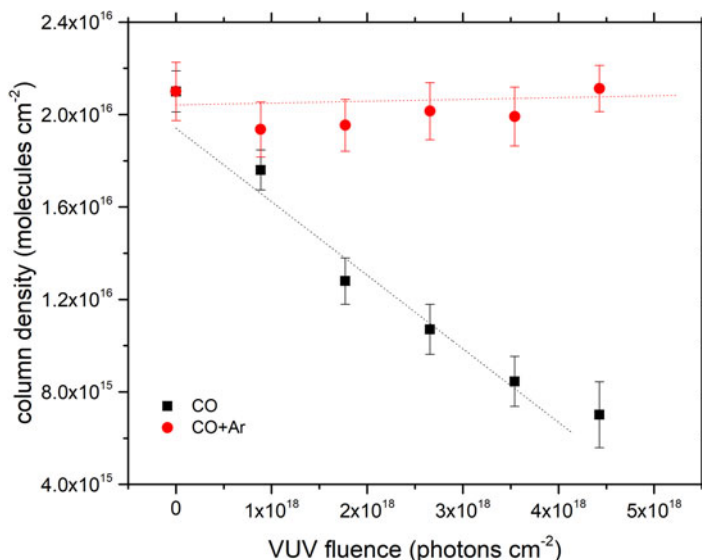


Figure 1. Integrated intensities of mass peaks representing CO.

(115–170 nm) with a typical flux of 10^{14} photons $\text{cm}^{-2}\text{s}^{-1}$. Ice thickness and photon flux are measured using laser interferometry and a photodiode. Typical values amount to respectively 20–50 ML and 10^{18} photons cm^{-2} . For each ice (CO and CH_4), two experiments are performed. The experiments probe the different effects of UV photoprocessing of a pure ice with and without a top layer of Argon. Argon's primary role is to quench photodesorption, therefore, the difference between experiments, independent of the photo-dissociation/chemistry, gives the total photodesorption yield. Argon does not interfere with the ice's photochemistry, and does not absorb UV light.

3. Results

Photodesorption of carbon monoxide: Experiments with CO are performed in order to test the new method against photodesorption values available in literature. CO does not dissociate, therefore the decrease in the CO signal can be directly associated with photodesorption. Figure 1 shows CO abundance in experiments with and without Ar coating. The photodesorption rate was calculated to be $(3.2 \pm 0.3) \times 10^{-3}$ mol. photon⁻¹, which agrees with previous studies: e.g. $(2.7 \pm 1.3) \times 10^{-3}$ mol. photon⁻¹ in Öberg *et al.* (2009b).

Photodesorption of methane: In case of CH_4 , analysis is more complex as methane ice also photodissociates. It produces radicals (CH , CH_2 , CH_3) which recombine to form bigger hydrocarbons, mainly C_2H_2 , C_2H_4 , C_2H_6 (Bossa *et al.* (2015)). In this study we find a preliminary photodesorption rate value of $(3.1 \pm 0.5) \times 10^{-2}$ mol. photon⁻¹, which is higher than in (Dupuy *et al.* (2017)). We are now looking into reasons for this.

We expect that this approach holds potential to derive photodesorption rates of larger COMs, for which dissociation plays an important role.

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