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Laboratory Simulations of Physico-chemical Processes under Interstellar Conditions

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Abstract. The accretion and desorption of gas molecules on cold dust grains play an important role in the evolution of dense clouds and circumstellar regions around YSOs. Some of the gas molecules detected in interstellar clouds were likely synthesized in icy dust grains and ejected to the gas. But in dark cloud interiors, with temperatures as low as 10–20 K, thermal desorption is negligible and a non-thermal mechanism like ice photodesorption is required. Reactions in the ice matrix are driven by energetic processing such as photon and ion irradiation. In circumstellar regions the photon flux (UV and X-rays) is expected to be significantly higher than in dense cloud interiors, icy grain mantles present in the outer parts will experience significant irradiation. The produced radicals lead to the formation of new species in the ice, some of them of prebiotic interest. Laboratory simulations of these processes are required for their understanding. The new ultra-high vacuum set-ups introduce some important improvements.

Keywords. Astrochemistry, methods: laboratory, molecular processes, techniques: spectroscopic, ISM: molecules, infrared: ISM

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1. Introduction

In the last five decades, numerous works were dedicated to the study of thermal desorption of ice and bulk ice processes including energetic (UV and ion) processing. Only in the last decade, the use of ultra-high vacuum (UHV) techniques, with base pressures in the 10^{-10} to 10^{-11} mbar range, has become increasingly important. This allows to keep the sample surface clean from background water contamination during the experiment, and enables the study of surface phenomena like photodesorption and reactions occurring at the solid-gas interface. The absence of water contamination in the chamber also serves to better constrain the role played by water in the chemistry of ice mantles and helps to detect products with very low abundances. Some recent results are presented below.

2. Recent experimental results on the photoproduction and photodesorption of species in ice mantles

The case of ice photodesorption underlines the importance of studying ices at the monolayer (ML) level. Most molecular species present in inter- and circumstellar ice mantles (H_2O, CO_2, CH_3OH, NH_3, etc.) dissociate efficiently for photon energies between 7 and 10.5 eV, corresponding to the emission spectrum of the hydrogen lamp commonly used in experimental astrochemistry. But some species like CO are not dissociated directly by Lyman-alpha photons (10.2 eV), it appears that the main dissociation pathway in CO ice is via the photoexcitation of a molecule reacting with another molecule leading to $CO^{\star} + CO \rightarrow CO_2 + C$. This reaction is not efficient, only about 5% of the absorbed photons lead to formation of CO_2 and other species like C_3O and C_3O_2. The remaining 95% of the photons leads to photodesorption. The photodesorption of CO ice was the most studied so far, and it was found to be very efficient (Öberg *et al.* 2007,2009; Muñoz Caro *et al.* 2010; Fayolle *et al.* 2011; Bertin *et al.* 2012). It is now established that for these photon energies only the top 5–6 CO monolayers in the ice contribute to the photodesorption, photons absorbed at deeper layers do not lead to a photodesorption event (Muñoz Caro *et al.* 2010; Fayolle *et al.* 2011). Indeed, for CO ice thicknesses above 5–6 ML the photodesorption rate is constant, but for thinner ices it decreases exponentially with decreasing ice thickness. The use of monochromatic light showed that the photodesorption rate measured at different wavelengths is directly proportional to the UV absorption at that wavelength (Fayolle *et al.* 2011). Since recently, our group at the Center of Astrobiology can measure the UV lamp emission spectrum in situ during the experiment and obtain the UV absorption cross section of ices. Finally, the deposition temperature of the CO ice affects the photodesorption very significantly, which was associated to the different ice morphology, i.e. more or less amorphous ice (Öberg *et al.* 2007,2009; Muñoz Caro *et al.* 2010).

Ice processing due to more energetic photons, X-rays, is poorly known. Larger icy particles up to one micron, formed by coagulation of small grains, can be processed efficiently by X-rays in circumstellar disks. The formation of X-ray photoproducts in the laboratory is commonly very scarce because the X-ray absorption cross section of the ice is low and soft X-ray sources have a low flux. Nevertheless, under UHV conditions X-ray irradiation of ice was studied. In the case of pure CO ice irradiated with soft X-rays, some of the products formed are not common to UV irradiation experiments, these are C_2O, C_3, C_4O, and CO_3/C_5 (Ciaravella *et al.* 2012). In the case of CH_3OH and H_2S ices, X-ray irradiation at low doses leads to formaldehyde, H_2CO, and H_2S_2 formation, respectively (Ciaravella *et al.* 2010, Jiménez-Escobar *et al.* 2012).

In conclusion, physico-chemical processes that occur in interstellar ice mantles are more complex than previously thought. Nowadays, we have the technology required to study this phenomena in detail.

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