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Thermal desorption of formamide and methylamine from graphite and amorphous water ice surfaces

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Abstract. Thermal desorption experiments of Formamide (NH_2CHO) and methylamine (CH_3NH_2) were performed in LERMA-Cergy laboratory to determine the values of the desorption energies of formamide and methylamine from analogues of interstellar dust grain surfaces, and to understand their interaction with water ice. We found that more than 95 % of solid NH_2CHO diffuses through the np-ASW ice surface towards the graphitic substrate, and is released into the gas phase with a desorption energy distribution $E_{des} = (7460 - 9380)$ K, measured with the best-fit pre-exponential factor A=10^{18} s^{-1}. Whereas, the desorption energy distribution of methylamine from the np-ASW ice surface (E_{des}=3850-8420 K) is measured with the best-fit pre-exponential factor A=10^{12} s^{-1}. A fraction of solid methylamine, of about 0.15 monolayer diffuses through the water ice surface towards the HOPG substrate, and desorbs later, with higher binding energies (5050-8420 K), which exceed that of the crystalline water ice ($E_{des} = 4930$ K), calculated with the same pre-exponential factor A=10^{12} s^{-1}.

Keywords. Astrochemistry, molecular processes, methods: laboratory, ISM, diffusion

1. Introduction

Complex organic molecules with more than 6 atoms are species of great relevance in pre-biotic chemistry (Saladino *et al.* (2012)) and precursors for the formation of amino acids during the course of the chemical evolution leading to the origin of life in earth (Bhushan *et al.* (2016)). Formamide (NH_2CHO) and methylamine (CH_3NH_2) are the most abundant amine-containing molecules observed in many astrophysical environments. Formamide which contains a (quasi) peptide bond (-NH-(C=O)) has been observed in prestellar and protostellar objects (Kahane *et al.* (2013)), massive hot molecular cores (Bisschop *et al.* (2007)), hot corinos, and comets (Biver *et al.* (2014); Bockelée-Morvan *et al.* (2000)). Methylamine is a fundamental organic compound in biochemistry which has been detected in the coma of comet 67P/Churyumov-Gerasimenko (Altwegg *et al.* (2016)). The presence of these molecules in the gas phase may result from thermal desorption of interstellar ices at brightness temperatures between 100 and 200 K, where icy mantle undergo sublimation or destruction. We performed temperature programmed desorption experiments of formamide and methylamine from analogues of interstellar dust grain surfaces in order to understand the interaction of these amino molecules with the water and compare their desorption energies (Chaabouni *et al.* (2018)).

2. Method

The experiments were performed using the FORMOLISM (FORmation of MOLecules in the InterStellar Medium) apparatus located in the Cergy laboratory. The set-up is dedicated to study the interaction of atoms and molecules on surfaces of astrophysical interest. The experimental set-up is composed of an ultra-high vacuum (UHV) stainless steel chamber with a base pressure 10^{-10} mbar. The sample holder made of a 1 cm diameter copper block, is covered with a highly orientated pyrolytic graphite (HOPG, ZYA-grade) slab, and is thermally connected to a cold finger of a closed-cycle He cryostat. The temperature programmed desorption (TPD) experiments of these molecules were performed in the sub-monolayer and monolayer regimes on HOPG and np-ASW ice surfaces at temperatures ranging from 40240 K. The desorption energy distributions of these two molecules were calculated from TPD measurements using a set of independent Polanyi-Wigner equations.

3. Implications

TPD experimental results show an efficient diffusion of more than 95 % of formamide through the np-ASW ice film of 10 ML thickness towards the graphite (HOPG) substrate. The large percentage of solid formamide bound to the graphitic substrate desorbs at higher surface temperature, 176 K, whatever the surface coverage, after the desorption of the water ice at about 150 K. The diffusion of NH_2CHO is likely to occur during the warming-up phase of the ices at a short timescale of few seconds. CH_3NH_2 molecules physisorbed on the ASW ice desorbs at 137 K, before the desorption of the H_2O molecules at 150 K, and even from the energetic sites of the HOPG surface at higher temperatures 160–220 K. Because of the wetting ability of the methylamine compared to water, the fraction of solid methylamine that diffuses through the water ice surface towards the graphitic substrate is about 0.15 ML. Formamide and methylamine desorbing from dust grains after water ice sublimation are refractory species, which can enrich the gas phase of warm interstellar environment. We compared the desorption energies of these molecules using an arbitrary fixed pre-exponential factor ($A=10^{12}$ s^{-1}). The main difference in behaviour of these two molecules is probably because the entire binding energy distribution of formamide ($5056 - 6990$ K) is higher than the value of the amorphous water desorption (4810 K). On the contrary, the binding energy distribution of methylamine ($3010 - 8420$ K) is distributed over this value. The difference in the binding energies of formamide and methylamine could have an impact on the composition of the gas-phase environments, in particular in the comae of comets, but also in hot cores, hot corinos, and protoplanetary disks. Nevertheless, it would be interesting to perform further adsorption-desorption laboratory experiments of formamide and methylamine on mixed or layered CO, CO_2, and H_2O ices to understand the effect of this relevant astrophysical molecule on the diffusion process of the complex organic molecules through the ASW ice.

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