Interaction of glycine with ice nanolayers

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Abstract

The interaction of glycine with ultrathin amorphous and polycrystalline ice films, deposited on crystalline alumina surfaces at 110 and 150 K, respectively, has been studied by temperature programmed thermal desorption (TPD). The TPD spectra demonstrate that the desorption of water is significantly influenced by the presence of glycine molecules, whereas the TPD of glycine is unaffected. It is proposed that the glycine molecules restrict the crystallisation of amorphous to crystalline ice and that the glycine overlayers stabilise the ice surface by attractive interactions.

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1. Introduction

The physics and chemistry of the various low-temperature phases of ice play an important role in a variety of chemical processes in the biosphere [1], in the geosphere [2,3], and in the interstellar space [4]. Amino acids have been found in icy interstellar grains on meteorites and it has been speculated that they may have been involved in the delivery of extraterrestrial organic molecules to Earth, thus being of possible importance for the origin and the early evolution of life on our planet [5,6]. The sublimation behaviour and the thermal stability of ice surfaces in the interstellar environment and the interaction of amino acids with ice nanoparticles are therefore important issues for the chemistry occurring in the interstellar medium.

The condensation of water vapour on a cold substrate at low pressure results in various non-crystalline structures for \( T < 130 \) K, depending on the particular deposition conditions. For deposition temperatures \( T > 140–150 \) K polycrystalline ice polymorphs develop, the cubic ice phase \( I_c \) at 140–160 K [7], and the hexagonal ice \( I_h \) in the temperature range 160–240 K [8]. For water deposition at temperatures 90–130 K the so-called low-density amorphous (LDA) ice phase has been identified [9,10], which is characterised by a porous open network structure with high surface area [11].

The structure state of ice influences both its chemical properties and its surface energy. Amorphous ice has a higher free energy than crystalline ice and thus desorption (sublimation) from LDA ice films occurs at a higher rate and at lower temperature than from crystalline ice layers [12]. Foreign molecules in/on ice surfaces can influence the dynamics of the amorphous to crystalline phase transformation [13] and thus the sublimation/desorption kinetics. Here, we investigate the interactions of a multifunctional molecule, namely the amino acid glycine \( (\text{NH}_2\text{CH}_2\text{COOH}) \), with amorphous and polycrystalline ice surfaces to determine the influence of amino acids on the thermal stability of thin ice layers and on the energetics and kinetics of phase transformation and desorption processes.

Ice nanolayers (\( \leq 50 \) monolayers) have been grown on a hydrophilic single crystalline aluminium oxide surface at 110 and 150 K under controlled ultrahigh vacuum conditions (UHV) to generate clean LDA and polycrystalline \( I_c \) surfaces, respectively. Glycine molecules have been deposited on top of the ice surfaces from submono-
layer to multilayer coverages at 110 K, whereas mixed glycine–water ice layers have been prepared by co-deposition at 110 K. Temperature programmed thermal desorption (TPD) has been applied to study the influence of glycine molecules on the energetics and kinetics of particle interactions in the ice layers.

2. Experiment

The experiments have been performed in a custom-designed UHV system with a base pressure of \(\sim 1 \times 10^{-10}\) mbar as described previously [14]. The system is equipped with the usual facilities for sample manipulation and surface cleaning. TPD measurements were performed with a line-of-sight quadrupole mass spectrometer; the latter is surrounded by a cold shield to select the desorption from the sample surface and to enhance the resolution in the experiments. The chamber contains also glycine evaporation source [14] and a retractable pin-hole gas doser for \(\text{H}_2\text{O}\). The sample manipulator allows cooling and heating of the sample to 110 and 1300 K, respectively. Typical heating rates of 1 K/s were used in the present TPD experiments.

Single crystalline \(\text{Al}_2\text{O}_3\) film surfaces were prepared as substrates by thermal oxidation of a NiAl(110) single crystal surface followed by high temperature annealing, as established earlier [15,16]. The average thickness of the ice layers has been estimated from a comparison of the areas under the TPD curves with that of the first monolayer of water on \(\text{Al}_2\text{O}_3\) (0001) [16] and from the background exposure, assuming a constant sticking probability of one at 110–150 K independent of coverage [17]. Accordingly, one layer of ice is defined here as the saturation monolayer of \(\text{H}_2\text{O}\) on \(\text{Al}_2\text{O}_3\) (0001), which corresponds to approximately \(5.9 \times 10^{14}\) molecules/cm\(^2\). The glycine coverages \(\theta_{\text{gly}}\) are given in monolayers (ML) as determined from the desorption peak areas in TPD and referenced to the saturated first monolayer on \(\text{Al}_2\text{O}_3\) (0001) [18].

3. Results and discussion

Temperature-programmed thermal desorption spectra from pristine LDA ice films grown at 110 K as a function of coverage, i.e. layer thickness, are shown in Fig. 1. The desorption maxima shift to higher temperature with increasing film thickness, from 167 to 173 K in going from the \(\sim 10\) layer to the \(\sim 50\) layer films, and the curves display an asymmetric shape with a common leading edge and an abrupt high temperature tail. This is consistent with zero order desorption kinetics, associated with the desorption from a reservoir and the linear removal of molecular layers from the film. The inset of Fig. 1 shows the comparison of the desorption from the 50 layer LDA ice and from a polycrystalline \(I_c\) ice layer of the same nominal thickness, grown at 150 K. Whereas the desorption peak maxima coincide exactly, the leading edges of the two curves are different and the LDA ice has a characteristic shoulder at the onset of desorption at 150–160 K, which has been associated with the amorphous-to-crystalline phase transition [19]. As mentioned in the introduction the desorption from amorphous ice surfaces occurs at a lower temperature as a result of the higher surface energy, but the amorphous-to-crystalline phase transition takes place in the same temperature region 140–160 K. Thus, the desorption from the amorphous ice surface starts at around 150 K giving rise to the desorption shoulder at 158 K, whereas the transformed crystalline ice desorbs as the main peak at \(T > 160\) K. Note that the overall shape of the main peaks of the two desorption curves are very similar, indicating that most of the LDA ice film crystallises during the heating ramp of the TPD experiment.

TPD spectra from 50 layer LDA ice films covered with different amounts of glycine are presented in Fig. 2. Fig. 2a displays the desorption curves of \(\text{H}_2\text{O}\) (atomic mass unit 18) and Fig. 2b those of glycine (atomic mass unit 30, which is the most intense peak of the mass spectrometric fragmentation pattern corresponding to \(\text{CH}_2\text{NH}_2^+\)). The insert cartoons illustrate the layered structures of the films. The adsorption of glycine molecules onto the LDA ice surfaces leads to
significant changes of the H$_2$O desorption traces with a pronounced dependence of the glycine coverage. A splitting into two components is observed up to $\approx 2$ ML glycine coverage: one component peaks at a somewhat lower temperature (168 K) than the desorption from the pristine ice surface, whereas a second component is shifted to higher temperature (177 K for $\theta_{\text{gly}} \approx 2$ ML). For higher glycine coverages the H$_2$O desorption structure shifts as a whole to higher temperatures, with the peak maximum occurring at 191 K for $\theta_{\text{gly}} \approx 10$ ML. Covering the ice surface with 20 ML glycine produces a very narrow H$_2$O desorption structure at a much higher temperature (210 K). The concomitant desorption spectra of glycine are shown in Fig. 2b: desorption occurs in the 300–350 K range with TPD curves very similar to glycine multilayer spectra from the pristine alumina surface [23]. Indeed, the glycine desorption was always unaffected for all sample preparations.

The TPD spectra of H$_2$O recorded from mixed glycine–ice layers, prepared by co-condensation of water and glycine at 110 K, are displayed in Fig. 3. The various films contain the equivalent of 50 layers of H$_2$O and various amounts of glycine as indicated in monolayers. Here, the ice films are destabilised by the embedded glycine molecules and the water desorbs at a lower temperature than from the pure ice films; the desorption peak temperatures of 165–167 K are very similar to those of the lower-temperature desorption features of the ice films topped with thin glycine overlayers ($\leq 2$ ML of glycine, Fig. 2a). In contrast to the latter, however, there are no higher temperature desorption features from the mixed layers.
TPD spectra of H$_2$O from polycrystalline 50 layer ice surfaces grown at 150 K and covered with various amounts of glycine at 110 K are collected in Fig. 4. The lower-temperature desorption components are never present in these spectra and the peaks shift progressively to higher temperature with increasing glycine coverage. Of note is that the sharp desorption peak at 210 K as seen on the LDA ice film for the 20 ML thick glycine overlayer (see Fig. 2a) is not observed here; the corresponding desorption feature remains broad and peaks at ~180 K.

The low-temperature H$_2$O desorption peaks observed from LDA ice films in the presence of glycine molecules, both in the form of overlayer or in a mixed layer, indicates a destabilisation of the ice (see Figs. 2a and 3). This is most naturally explained in terms of the suppression of the amorphous-to-crystalline phase transition by the glycine molecules. In the case of glycine overlayers only the surface-near regions are destabilised and the layers further below can still crystallise, but in the mixed glycine-ice layers the entire H$_2$O desorption is influenced and takes place from an amorphous-like situation. We note that the influence of glycine molecules on the crystallisation kinetics of the amorphous water is not a linear relation – a submonolayer coverage of glycine molecules affects a much larger portion of the 50 layer ice film. It is possible that the desorption of water from the amorphous glycine–ice layers is somewhat stabilised as compared to the desorption from pure LDA ice layers. An indication for this is derived from the high-temperature H$_2$O desorption features, which are observed from both glycine covered LDA and crystalline ice films. They are interpreted as desorption from the polycrystalline ice phase, which in the case of LDA ice is formed during the temperature ramp. The desorption kinetics from the crystalline ice is clearly modified by the attractive interaction between glycine and H$_2$O and accordingly, the desorption peaks are shifted to higher temperature.

The desorption of glycine from the glycine–ice layers (Fig. 2b) is very similar to that of glycine multilayers from pristine alumina surfaces [18], it appears to be uninfluenced by its previous history on the ice after desorption of the latter. This is understandable because of the much higher desorption (sublimation) energy of condensed glycine multilayers as compared to that of ice. However, closer inspection of the low coverage submonolayer spectrum reveals that the desorption curve is essentially a scaled down version of the higher-coverage spectra. That is, there is little indication of desorption from a wetting monolayer, as it has been observed after the adsorption of glycine on the bare alumina surface [18]. This suggests that the glycine has aggregated in the form of clusters at the alumina surface after the desorption of ice. It appears that the glycine overlayer sinks into the ice film during desorption of the latter until it reaches the alumina surface.

The proposed scenario is supported by the shift of the H$_2$O TPD peaks to higher temperature together with the absence of the low-temperature features on the polycrystalline ice films (Fig. 4). However, there is an additional effect observed on LDA ice at high glycine coverages, where the entire H$_2$O desorption structure is shifted to higher temperature, until a sharp desorption peak signal is seen at $T > 200$ K (see top spectrum of Fig. 2a). This is reminiscent of the abrupt desorption of CCl$_4$ layers from a metal surface, which has been reported if the CCl$_4$ was covered by an amorphous ice overlayer [19,20]. The abrupt desorption of CCl$_4$ at much higher temperature has been associated by the opening up of channels in the ice overlayer during the amorphous-to-crystalline phase transition. In the present case, the deposited glycine acts as a capping layer for the desorption of water, once a continuous overlayer is formed. This occurs for $n_{gly} \approx 20$ ML on LDA ice. The desorption occurs at a temperature when the glycine capping layer, as a result of the increased molecular mobility, opens up channels for the escape of H$_2$O, which then desorbs abruptly. Interestingly, this ‘explosive’ desorption is not observed on the polycrystalline ice surface for $n_{gly} \approx 20$ ML (Fig. 4), a continuous overlayer is thus not formed at this coverage. This may be due to the higher mobility of glycine on the smoother polycrystalline ice surface than on the rougher LDA ice surface, promoting more pronounced

Fig. 4. H$_2$O TPD spectra from polycrystalline 50 layer ice films covered with different amounts of glycine (in monolayers).
clustering and the formation of a discontinuous overlayer on the former surface.

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References