Thickness-dependent effects in H$_2$O desorption from glycine/amorphous solid water films

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**Abstract**

The desorption characteristics of H$_2$O from glycine-on-amorphous solid water (ASW) ultrathin films have been systematically investigated as a function of underlying ASW thickness and the amount of top-deposited glycine using TPD. At the early stages of deposition, substantial amounts of glycine molecules penetrate into the water multilayers and, therefore, thermal destabilization of water layers is detected. Glycine diffusion is governed by the thickness-dependent structure of the ASW as revealed by work function measurements and XPS. For higher glycine coverages, a kinetic restriction of water desorption by the continuous amino acid overlayers is observed independent of the ASW substrate thickness.

**1. Introduction**

The interaction between organic molecules and solid water surfaces has attracted considerable attention over the past decades because of its interest in many areas including atmospheric, cometary and interstellar chemistry, and also for the better understanding of a wide range of processes in biology and medicine [1–6]. For the investigation of physico-chemical processes that take place on H$_2$O surfaces, thin films of condensed water grown under ultra-high vacuum (UHV) conditions are frequently utilized as model systems. Three-dimensional (3D) condensed H$_2$O films with various structure can be prepared at cryogenic temperatures, depending on the particular growth conditions. Thin films of amorphous solid water (ASW) can be generated via condensation of water vapours at $T < 130$ K [7]. The morphology of these films is known to depend on deposition temperature, flux, incident angle of the incoming water molecules, and the nature of the substrate [7–9]. ASW is converted to crystalline ice (CI) by annealing above $\sim 160$ K. The structure state of condensed water influences both its chemical properties and its surface energy. Furthermore, foreign molecules in/on solid H$_2$O films can influence the structure and thermal stability of water layers [10].

Studies dedicated to interactions of amino acids (NH$_2$CHR-COOH, with R representing the side group which is different for each amino acid) with condensed water surfaces have begun to appear only recently [11–16]. Amino acids are the simplest biologically active molecules and building blocks of polypeptides and proteins, which play key roles in practically all biological processes. The physico-chemical processes occurring in amino acid-ASW condensed layers are of significance in prebiotic organic chemistry, specifically the creation of amino acid molecules in the interstellar space and their delivery to our planet [14,16]. We have shown in our previous studies that the intermixing of ASW with the amino acids glycine (Gly) and phenylglycine on alumina [AlO$_x$ grown on a NiAl(110) substrate] surfaces at 110 K leads to the destabilization of the water layers by the embedded amino acid molecules and to lower desorption temperatures than from the pure ASW films [11,12,17]. In the present Letter we extend our previous work on the Gly-ASW system by exploring layered films with different thickness of the ASW substrate and the Gly adlayer. For that, ASW films have been grown at 110 K on a single crystalline aluminum oxide substrate surface [AlO$_x$/NiAl(110)] and the Gly molecules have been deposited onto these films. With the objective of clarifying the influence of Gly on the thermal stability of ASW ultrathin films (nanolayers) and on the kinetics of desorption processes, different Gly-on-ASW films have been examined by temperature-programmed thermal desorption (TPD), work function measurements and O$_1$s X-ray photoelectron spectroscopy (XPS).

**2. Experimental**

The experiments have been performed in a custom designed ultrahigh vacuum system with a base pressure of $\sim 1 \times 10^{-10}$ mbar as described previously [18]. The system is equipped with a low-energy electron diffraction (LEED) optics, a hemispherical electron energy analyzer (Omicron, EA125) for photoelectron spectroscopy, X-ray and UV photon sources, and a line-of-sight quadrupole mass spectrometer for TPD. The mass spectrometer is surrounded by a liquid nitrogen cooled stainless steel shield in order to suppress the detection of gases desorbing from the crystal holder and...
chamber walls. Linear sample heating rates for TPD are generated with a home-built computer controlled power supply with typical heating rates of 1 K/s in the present experiments. The XPS spectra were recorded using unmonochromatized Al Kα radiation (1486.6 eV) and an analyzer resolution of 0.85 eV. To compensate for charging effects in XPS measurements of thicker overlayers, the binding energy (BE) scale was adjusted to provide a BE of 532.8 eV for the O 1s component corresponding to COO- in solid Gly. The work function was determined by the low-energy onset of the valence band spectra using He I radiation. The sample was biased (−9 V) to avoid analyzer transmission function effects.

Single crystalline alumina film surfaces have been prepared as substrates by thermal oxidation of a NiAl(110) single crystal surface followed by high temperature annealing, as described in the literature [19]. The sample manipulator allowed cooling and heating of the sample to 110 and 1300 K, respectively, with temperatures measured by a chromel–alumel thermocouple spot-welded to the backside of the NiAl crystal. Vapor deposition of Gly (NH₂CH₂COOH) was achieved from a retractable Knudsen cell molecular evaporator. The Gly powder (>99%, Fluka) was introduced into a small copper cell with a 1 mm diameter aperture. The evaporation cell was heated by a button heater and its temperature was controlled via a chromel–alumel thermocouple attached to it. The evaporation source was carefully out-gassed for several hours at 370 K and the amino acid was deposited by heating the Gly powder to 400 K. During deposition the distance between the crystal and the aperture was ~5 cm. Exposures are quoted in arbitrary doser units (DU), where 1 DU corresponds to ~1 min Gly exposure. 4 DU of Gly correspond to a saturated first monolayer of Gly on AlOₓ/NiAl(1 1 0) at 110 K [11]. High-purity water (H₂O, puriss. p.a. grade) was obtained from Fluka, and was further purified by several freeze–pump–thaw cycles. Dosing of water was carried out by retractable pinhole doser, positioned within 4 mm from the crystal surface to get a uniform distribution of impinging molecules. Assuming a constant sticking probability of 1 at 110 K independent of coverage, one monolayer (ML) of water is defined here as the saturation layer of H₂O on AlOₓ/NiAl(1 1 0) [12].

3. Results and discussion

TPD traces of H₂O (m/z = 18) from 10 ML ASW films covered with different amounts of Gly are presented in Figure 1a. The desorption spectrum from the as-prepared 10 ML ASW film on alumina is displayed as the bottom curve. The latter spectrum has a weak shoulder at the leading edge of the desorption peak at 150–160 K, which has been ascribed to the desorption from the ASW surface and the simultaneous ASW → Cl phase transition [7,9]. The shoulder observed in the spectrum is less pronounced than in the ASW TPD spectra published earlier. Presumably, this is due to the higher heating rate (1 K/s) applied in our study in comparison to the previous desorption experiments (e.g. 0.1 K/s in Ref. [7]). The transformed crystalline ice desorbs as the main peak at 167 K. As one can see, the deposition of Gly on the ASW surface results in significant modifications of the H₂O TPD spectra. These spectra have been deconvoluted with gaussian functions. The sum of these gaussians (see also Figure 3a and b) follows the original data points closely, justifying the use of gaussian functions to fit the data. Recently, gaussian profiles have been successfully used to fit TPD spectra of water adsorbed on Pt(553) and Pt(553) surfaces [20]. Furthermore, it has been demonstrated that the fitting of D₂O TPD spectra from D-precovered Ni(1 1 1) surface with gaussians yields almost the same results as with more elaborate deconvolution functions [21]. Thus, up to ~4 DU Gly coverage, a single symmetrical desorption component is detected and the TPD peak maximum is shifted by 5 K toward lower temperature. From 6 DU of Gly exposure on, a second desorption component at higher temperature can be resolved. The second peak grows in intensity, while the lower temperature signal diminishes with increasing Gly doses. Finally, the whole desorption structure broadens and shifts up in temperature (168 and 178 K for the first and the second component, respectively) for thicker Gly overlayers (12 DU).

The Gly-induced single TPD peak observed at low Gly exposures is practically the same as the H₂O desorption signal detected from films fabricated by intermixing, via codeposition, 50 ML ASW with different amounts of Gly [11]. This is illustrated in Figure 1b where H₂O TPD spectra from two co-condensed Gly/ASW films are shown. The lower temperature desorption from these films (thermal destabilization) compared to H₂O desorption from pure ASW has been ascribed to the fact that the hydrogen bond rearrangement required for the crystallization of ASW is partially inhibited in the vicinity of Gly molecules and, consequently, the desorption of H₂O mainly occurs from an amorphous-like surface situation [11,12]. It has been reported that the introduction of acetic acid molecules into the ASW matrix also results in a perturbation of the hydrogen bond network in the vicinity of a guest molecule [10]. Naturally, the similarity between TPD spectra of co-condensed Gly/ASW films and ASW films covered with small amounts of Gly suggests a similar structure of these films. In order to check this assumption, work functions of pristine and Gly-covered 10 ML ASW surfaces have been measured in order to reveal the modifications of the ASW surface morphology as a function of Gly coverage. As shown in Figure 1c, the work function of the pristine ASW surface remains approximately constant up to ~4 DU of Gly, that is, where only a symmetrical peak is present in the TPD series from Gly-on-ASW films (see Figure 1a). After that, the work function drops rapidly up to an exposure of 8 DU of Gly. A saturation value of 2.1 eV is obtained after a dose of ~10 DU. The plateau in the work function at low Gly exposures indicates that no major changes of the ASW surface morphology occur. We propose that this is due to the fact that during the initial stages of amino acid dosing, Gly penetrates into subsurface regions and into the bulk of the 10 ML ASW film. Hence, the intermixing between Gly and H₂O in the bulk of the ASW film leads to water desorption (symmetrical TPD peak at 162 K in Figure 1a) similar to that observed from co-condensed Gly/ASW layers (Figure 1b). The appearance of the high temperature shift in the H₂O TPD spectra after higher Gly exposures (>12 DU) is related to the formation of a continuous Gly film on top of the ASW layers. This means that the change of the work function displayed in Figure 1c, where the build-up of Gly multilayers after a dose of ~10 DU is indicated by the saturation of the work function value. The observed broadening and shifting of the TPD peaks can be understood by noticing that Gly overlayers on AlOₓ/NiAl(1 1 0) surface desorb at temperatures above 300 K [11]. Thus, thicker Gly overlayers act as a barrier for H₂O desorption from the underlying ASW layers, until the Gly molecules become mobile and develop channels for water desorption at higher temperature.

Figure 2 shows a series of O 1s XPS spectra displaying the build-up of Gly multilayers on a 10 ML ASW film at 110 K. All XPS spectra were taken at grazing emission (70° with respect to the surface normal) geometry in order to enhance the surface sensitivity. The XPS sequence starts with a spectrum obtained from the pristine water film (bottom curve). It shows a symmetric peak centered at ~534.5 eV, characteristic of multilayers of physiosorbed H₂O [12]. Interestingly, the XPS spectra obtained after dosing 2 and 4 DU of Gly to the ASW surface are practically identical and only a small intensity contribution to the low-BE side of the pure water spectrum is detected (see the insert of Figure 2). This shoulder is evidence for the presence of COO- groups from Gly molecules in zwitterionic configuration (NH₃⁺–CH₂–COO⁻). Gly was found to
be in its zwitterionic state after co-adsorption with water ice on TiO$_2$ in UHV at 160 K [13]. Furthermore, Gly adsorbs on ASW thick films grown on a Pt(111) substrate in zwitterionic configuration, even at low coverage [15]. We have also shown that Gly occurs predominantly in a zwitterionic configuration in the films condensed onto ASW surfaces, with some minority species in neutral form (NH$_2$–CH$_2$–COOH) [12]. The photoemission signal from non-deprotonated COOH groups appears at ~534 eV and overlaps with the H$_2$O XPS peak [15]. As shown in Figure 2, the low-BE contribution grows in intensity with increasing Gly doses and, finally, develops as a single peak centered at 532.8 eV after 12 DU Gly dose. The topmost spectrum in Figure 2 is typical for zwitterionic Gly in solid state [22]. The photoemission data corroborate the TPD and work function results presented above. At low Gly doses (2 and 4 DU) the surface modifications of ASW films are minor, indicating sub-surface accumulation of Gly molecules. A continuous Gly multilayer film, acting as a capping layer for water desorption, is formed on top of ASW after exposure to ~12 DU of Gly.

The appearance of the second, high-temperature component in the TPD spectra of ASW films dosed with Gly is an important observation. This component appears at a slightly higher temperature (171 K, see Figure 1a) than the desorption from the transformed crystalline ice of the pure ASW films (167 K). We attribute therefore the second TPD component to the desorption from crystallized fractions of the ASW layers, which are not destabilized by the presence of Gly. This conclusion implies that at ≥6 DU Gly coverages, the amino acid diffusion into the 10 ML ASW film is limited and smaller portions of the water layers are intermixed with Gly. This effect can be explained by the increasing H-bonding between Gly molecules at larger deposits. In other words, with increasing amount of top-deposited Gly, Gly–Gly intermolecular interactions are dominating over H$_2$O–Gly interactions and this gives rise to the second component in H$_2$O desorption spectra in Figure 1a. This scenario is in agreement with the results of Zhang et al. [23], who reported that the intermolecular H-bonds in solid Gly are practically not influenced by the presence of water because of the stronger Gly–Gly interaction. It is also important to note that the increased mobility of both Gly and H$_2$O molecules at the onset of ASW desorption most probably causes some mixing of Gly with the underlying water multilayer.

TPD traces of H$_2$O from 30 ML and 50 ML ASW films exposed to different amounts of Gly are compared in Figure 3a and b. All spectra have been decomposed into two gaussians. The water desorption traces from the pristine ASW films evolve into a double-peak structure after the lowest Gly dose (2 DU – Figure 3a and b). The first component peaks at lower temperature (165 and 168 K, respectively) than the desorption from the pristine ASW surfaces, whereas the second component is shifted to somewhat higher temperature. Noticeably, the desorption temperatures and the intensity evolution of these components are very similar to the characteristics of the components observed in the TPD traces from 10 ML ASW films exposed to Gly doses ≥6 DU. The intensities...
of the two components change in opposite direction with increasing Gly doses, namely the first component decreases and the second component increases. This is illustrated in Figure 3c, where the integrated intensity ratio between the first and the second component in the TPD spectra in Figures 1a and 3a and b are plotted as a function of Gly dose. Evidently, the evolution of the intensity ratio between the desorption components of the three Gly-on-ASW systems studied here depends on the thickness of the initial ASW film as well as on the amount of the top-deposited Gly molecules.

We interpret the low temperature component in the TPD spectra from Gly-covered 30 and 50 ML films as being due to destabilisation of the ASW layers by the Gly molecules embedded in the sub-surface regions of the water layers as observed in the 10 ML ASW system (see above). Obviously, only the outer ASW-vacuum regions of the films are destabilized by the adsorbed amino acid molecules and the rest of the water films crystallizes and then desorbs as a second, higher temperature TPD component. For Gly coverages \( \geq 8 \) DU the whole desorption structure progressively broadens and shifts to higher temperatures due to the kinetic restriction of water desorption by the continuous Gly overlayers. The TPD components intensity ratio values presented in Figure 3c can be interpreted as the measure of the interlayer diffusion in Gly-on-ASW system. For 10 ML ASW film a complete intermixing between Gly and H\(_2\)O occurs after the lowest Gly dose (2 DU, see Figure 1a). The TPD components ratios for 30 and 50 ML ASW films topped with 2 DU of Gly are 15.4 and 3.7, respectively, indicating that 94% and 79% of the ASW films are intermixed with Gly. Thus, it is suggestive to assume that the morphological properties of the ASW films govern the diffusive mixing of Gly with H\(_2\)O and, consequently, the desorption pathways of water layers. The thickness-dependent structure–property relationship in ASW films grown onto AlO\(_x\)/NiAl(110) is demonstrated in Figure 3d, where grazing emission O1s XPS core level spectra of 30 and 50 ML ASW films exposed to the same amount of Gly (4 DU) are displayed. Evidently, the relative intensity of the shoulder at 533 eV ascribed to the COO\(^-\) groups from Gly zwitterions, increases from the 30 to the 50 ML ASW substrate. The increase of this signal goes along with the decrease of the amount of Gly trapped in the bulk of ASW layers.

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**Figure 3.** \( \text{H}_2\text{O} \) TPD spectra of (a) 30 ML and (b) 50 ML ASW films covered with different amounts of Gly. (c) The integrated intensity ratios of the two TPD components in \( \text{H}_2\text{O} \) TPD spectra of 10, 30 and 50 ML ASW films as a function of Gly dose. (d) Grazing emission O1s XPS core level spectra of 30 and 50 ML ASW films topped with 4 DU of Gly. To compensate for charging effects, Gly-on-30 ML ASW and Gly-on-50 ML ASW spectra are shifted by 0.2 and 0.3 eV, respectively, toward low BE.
It has been shown previously that after forming a stable monolayer, H₂O molecules condense into hydrogen-bonded nanoscale-sized 3D aggregates on the Al₂O₃/NiAl(110) surface up to ~4 ML water coverage, which then coalesce at larger deposits [24]. Apparently, the heterogeneous character of ASW films extends beyond 10 ML ASW overlayers and thus the properties of the ASW films are closely related to the initial condensation and growth kinetics on the alumina substrate. Our experimental results suggest that the penetration of Gly into the sub-surface sites of the ASW films depends strongly on the thickness and morphology of water layers. It is difficult to depict the exact mechanism for Gly diffusion in the bulk ASW films in the framework of this work. The diffusion behavior of other organic molecules such as chloroform [25], hexane [26] and n-butanol [27,28] through ASW films has been reported in the literature. In general, there can be two ways through which polar molecules could diffuse in ASW layers. One pathway may be through micropores of the ASW, and the other one through the network structure of ASW [27]. In our case, the first path can be ruled out, since ASW films grown at 110 K are known to be compact and non-porous with a density very similar to that of the CI grown at 145 K [29]. We presume that the incorporation of the Gly molecules into the sub-surface regions of the ASW layers may occur via H-bonding of Gly zwitterions with H₂O molecules, which changes the hydrogen bonding structure of water in the vicinity of Gly molecules. On relatively thin ASW films (10 ML) with a large roughness, the penetration of Gly molecules into the bulk following adsorption is significant. On more homogeneous, thicker ASW films (50 ML) the diffusion of amino acid molecules is substantially reduced. Finally, it is important to note that very recently, Held and co-workers [15] reported that when Gly is adsorbed on top of a thick ASW layer grown on a Pt(1 1 1) substrate at 145 K the interlayer diffusion is hindered and Gly stays on the ASW surface. Taken together with our findings, these results demonstrate the essential role of ASW films morphology that depends on deposition conditions and the nature of substrate in amino acid/solid water interactions. In conjunction with the latter, it is important to point out the role of the alumina substrate. It has been shown previously that Al₂O₃ grown on a NiAl(110) substrate is oxygen-terminated and relatively inert toward adsorbed adlayers, e.g., H₂O adsorbs molecularly onto this surface [24]. Obviously, thermal desorption of water from Gly-on-ASW layers grown on a different alumina surface under UHV conditions can be very different from the results presented here. For instance, dissociative desorption of water on Al-terminated α-Al₂O₃(0001) surface has been documented [2]. The latter results in isolated OH groups on the alumina substrate that may have a significant influence on the ASW–Gly interaction and on the water desorption.

4. Conclusions

In conclusion, our experiments show that the thickness varia-
tions of Gly and water in Gly-on-ASW layered films have a three-fold influence on the desorption kinetics of the underlying water: (i) in the low-dose Gly range (2–6 DU of Gly), a majority of amino acid molecules penetrate into the water multilayers of the bulk. This phenomenon leads to a lower H₂O desorption temperature than from the pure ASW films. (ii) The diffusion of Gly is mediated by the thickness–dependent morphological characteristics of the as-grown ASW layers. The Gly diffusion decreases with increasing ASW film thickness. (iii) Thicker Gly overlayers (> 8 DU) act as a barrier for H₂O desorption from the underlying water layers, independent of the ASW thickness.

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References