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# Interactions of phenylglycine with amorphous solid water studied by temperature-programmed desorption and photoelectron spectroscopy

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ABSTRACT

Temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) have been employed to study the interactions of phenylglycine (PheGly) with amorphous solid water (ASW) nanolayers (10–50 ML). First, the adsorption and growth of PheGly layers on an $AlO_x$/NiAl(110) surface have been examined. After that, mixed PheGly–ASW layers have been grown on the alumina surface at 110 K. Alternatively, PheGly molecules (from submonolayer to multilayer coverages) have been deposited on top of the ASW surfaces. In mixed PheGly–ASW nanolayers the PheGly phase displays hydrophobic behavior and accumulates near the surfaces of the films, while top-deposited PheGly wets the ASW films forming closed overlayers at low coverages. $H_2O$ desorption from the PheGly–ASW films is strongly influenced by the PheGly molecules, i.e., the crystallization of ASW is partially inhibited in the vicinity of the amino acid and a lower desorption temperature of $H_2O$ molecules than from pure ASW layers was detected. Thicker PheGly overlayers on ASW provide a kinetic restriction to $H_2O$ desorption from the underlying ASW layers until the PheGly molecules become mobile and develop pathways for water desorption at higher temperatures. The results are discussed with respect to the previously obtained data for glycine–ASW layered systems. It has been demonstrated that the substitution of the hydrogen atom in glycine with a phenyl group does not lead to detectable changes in the pathways of ASW desorption. However, desorption of PheGly differs from the desorption of glycine from the similarly structured glycine–ASW nanolayers. The differences are interpreted in terms of adsorbate–adsorbate and adsorbate–substrate interactions.



## 1. Introduction

The interaction between amino acids ($NH_2CHRCOOH$, with R representing the side group which is different for each amino acid) and solid surfaces under ultrahigh vacuum (UHV) conditions has attracted considerable attention recently [1–7]. These studies are of importance in many fields ranging from medicine to nanotechnology. Amino acids are the simplest biologically active molecules and building blocks of polypeptides and proteins, which play key roles in practically all biological processes. Thus, the characterization of amino acid adsorption, desorption and reaction processes taking place on well-defined surfaces is crucial for understanding the behavior of more complex systems under various circumstances. The properties of amino acid mono- and multilayers at metal, semiconductor and oxide surfaces have been reported during the past decade. Studies dedicated to interactions of amino acids with water ice surfaces or vice versa have also begun to appear recently [8–13].

Surface science investigations of amino acids/ice interfaces are of significance to the understanding and interpretation of a wide range of processes in atmospheric chemistry [14], in the field of cryomicroscopy/tomography [15], and prebiotic organic chemistry [16]. For modeling the physicochemical phenomena that occur on the ice surfaces, thin films of amorphous solid water (ASW) are frequently utilized. The condensation of water vapor on a cold substrate (typically less than 130 K) at low pressure results in the creation of a metastable, disordered version of ice called amorphous solid water (ASW) [17]. The morphology of these films is known to depend on deposition temperature, deposition rate, angular distribution of the incoming water molecules, nature of the substrate, and the thermal histories of the films after formation [18,19]. ASW is converted to crystalline ice (CI) by thermal annealing above ~160 K. We have shown in our previous studies that the presence of glycine ($NH_2CH_2COOH$, Gly) molecules on/in ASW nanoscale films grown at 100–110 K can modify the dynamics of the amorphous-to-crystalline phase transition and thus the desorption/sublimation kinetics of water nanolayers [8,13].

In this work, we investigate the interactions of the simplest aromatic analog of Gly, phenylglycine ($C_6H_5$–$CH(NH_2)(COOH)$, PheGly), with ASW ultrathin films to determine the influence of the phenyl side chain on the thermal stability of ASW nanolayers and on the energetics and kinetics of phase transformation and desorption processes. Ultrathin films of ASW (≤50 ML) and PheGly have been grown

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under UHV conditions on a single crystalline aluminum oxide substrate surface [$AlO_x$ grown on a NiAl(110) substrate] at 110 K. This particular alumina film was chosen as a substrate because of its inertness toward adsorbed adlayers and, moreover, because of the previously obtained data about the properties of different amino acids and water adsorbates on this surface. The as-prepared PheGly–ASW structures have been examined by means of temperature-programmed desorption (TPD), ultraviolet photoelectron spectroscopy (UPS), work function measurements, and X-ray photoelectron spectroscopy (XPS).

## 2. Experimental

All the experiments were carried out in a custom-designed μ-metal UHV chamber (base pressure $1 \times 10^{-10}$ mbar) equipped with the usual facilities for sample manipulation and surface cleaning [8]. TPD experiments were performed with a line-of-sight detection quadrupole mass spectrometer, which is surrounded by a cold shield to select the desorption from the sample surface and to enhance the resolution in the TPD experiments. The sample manipulator allows cooling and heating of the sample to 110 K and 1300 K, respectively. The temperature of the sample was monitored by a K-type (chromel–alumel) thermocouple attached to the backside of the NiAl(110) crystal. Linear sample heating rates for TPD are generated with a home-built computer controlled power supply, and typical heating rates of 1 K/s were used in the present experiments.

The UPS(XPS) spectra in normal emission geometry were collected with photon incidence angles of 40° (65°) with respect to the surface normal. The UPS spectra were excited with He II radiation, and the hemispherical electron energy analyzer (Omicron,EA125) was operated with a fixed pass energy of 5 eV, corresponding to an energy resolution of 0.12 eV. The XPS spectra were taken using an unmonochromatized Al Ka source (1486.6 eV) operated at a power of 180 W and a pass energy of 20 eV (resolution of 0.85 eV). The binding energy scale (BE) was referenced to the Ni 2p3/2 peak at 852.7 eV. Moreover, to compensate for charging effects in XPS measurements of thicker overlayers, the BE scale was adjusted to provide a BE of 402.8 eV for the N1s component corresponding to $NH_3^+$ in solid PheGly. The decomposition analysis of the XPS spectra was performed by using mixed Gaussian/Lorenzian peak shapes. The work function was measured from the secondary electron cutoff in UV valence band photoelectron spectra. The sample was biased (−9 V) to improve the secondary electron cutoff.

Alumina films were prepared by oxidation of a NiAl(110) single crystal surface, as established earlier [20]. Dosing of water was carried out by a retractable pinhole doser, positioned within 4 mm from the crystal surface to get a uniform distribution of impinging molecules. The mixed PheGly–ASW layers were prepared by depositing PheGly on to the alumina surface at 110 K in a $H_2O$ background pressure (up to ~$10^{-7}$ mbar). ASW films grown at this temperature (110 K) are compact and non-porous with a density very similar to that of the CI grown at 145 K [21]. The average thickness of the $H_2O$ layers has been estimated from a comparison of the areas under the TPD curves with that of the first monolayer of water on $AlO_x$ and from the gas dose, assuming a constant sticking probability of 1 at 110–150 K independent of coverage. Vapor deposition of PheGly was achieved from a specially designed retractable Knudsen cell molecule evaporator. The PheGly powder (D-α-Phenylglycine, Fluka, >99%) 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. This evaporation source was separated from the UHV chamber by a gate valve and differentially pumped by a turbomolecular pump. Prior to use, the evaporation source was carefully out-gassed for several hours at 370 K with the gate valve closed. The amino acid was deposited by heating the PheGly powder to 400 K (typical temperature for UHV deposition of amino acids and poly amino acids [22,23]). During deposition the distance between the crystal and the aperture was 5 cm. The PheGly coverages are given in monolayers (MLs) as determined from the desorption peak areas in TPD and referenced to the saturated first monolayer on $AlO_x$/NiAl(110). In this paper one adsorbed PheGly monolayer coverage was defined from the TPD and work function measurements [see Figs. 1(a) and 3(c), respectively].

## 3. Results and discussion

### 3.1. Adsorption of PheGly on $AlO_x$/NiAl(110)

TPD spectra measured for different amounts of PheGly adsorbed on the alumina surfaces at 110 K are shown in Fig. 1(a). Prior to the TPD experiments the cracking pattern of PheGly was determined by desorption from multilayers. The measured mass spectrum shows a major peak at m/z = 28, which is identified as CO and/or $H_2CN$ fragments. Thus, in our TPD experiments, the m/z = 28 signal was chosen to represent the intact molecules. For the lowest exposure two desorption events at 358 K and 374 K appear (see Fig. 1). The second peak (labeled α) grows with exposure without a significant shift in the temperature. As shown in Fig. 1(b) this peak saturates at a dose coresponding to 1 ML PheGly coverage (see also work function measurements below). In the present study this spectrum is used as a reference for the desorption from the saturated first monolayer of PheGly on $AlO_x$/NiAl(110) at 110 K. As can be seen, the desorption peak at 358 K (labeled β) shifts to higher temperatures and has a common leading edge for increasing exposures, i.e., a feature characteristic of zero order desorption kinetics. We attribute this peak to desorption from PheGly multilayers. Furthermore, the presence of the β TPD peak at low coverages indicates that the growth of the first monolayer is accompanied by the formation of PheGly clusters, presumably nucleating at defect sites (e.g. step edges, point defects and oxygen vacancies [24]). It is worth noting that the monolayer formation of $H_2O$ and Gly on $AlO_x$/NiAl(110) surfaces is accompanied by the nucleation and growth of clusters as well [25,26]. Fig. 1(c) shows the plot of the total PheGly TPD peak area versus amino acid coverage. The data form a straight line which passes through the origin, indicating a constant sticking coefficient of PheGly on $AlO_x$/NiAl(110) at 110 K. Arrhenius plots (the logarithm of the desorption rate versus the inverse of the temperature) of the leading edges of the β peak for three different coverages of PheGly are shown in Fig. 2. The slopes of the linear fits yield the activation energies of desorption ($E_a$) of 124.4 ± 0.4 kJ/mol, 126.1 ± 0.5 kJ/mol and 125.7 ± 0.5 kJ/mol for 2 ML, 3 ML and 5 ML PheGly coverages, respectively. Thus, $E_a$ does not vary with coverage and an average value of 125.4 ± 0.6 kJ/mol is obtained for the activation energy of desorption of multilayers of PheGly adsorbed on $AlO_x$ at 110 K.

UPS (HeII) spectra of the PheGly-covered $AlO_x$/NiAl(110) surface recorded as a function of PheGly exposure at 110 K are shown in Fig. 3(a). In the UPS spectrum of the clean oxide [Fig. 3(a), bottom curve], the emission at 0–3 eV below $E_F$ is due to the NiAl valence band from the NiAl(110) substrate, whereas the valence band features of $AlO_x$ consist of nonbonding O 2p orbitals (4–8 eV) and hybridized Al 3s, 3p and O 2p levels (8–12 eV). On adsorption, the substrate bands are gradually suppressed, while new features between 4 and 16 eV below $E_F$ grow in intensity. At 1 ML PheGly coverage four main peaks centered at around 5, 7, 9.5 and 14 eV occur. For the multilayer spectrum (4 ML PheGly coverage, note the disappearance of the substrate emission), a shift to higher binding energy (BE) is observed, which is probably due to the reduced extramolecular final state screening in the molecular solid. It was found that for molecules containing a benzene ring, the UPS spectra can be simply decomposed into the partial spectra of pure benzene and of the rest of the molecule [27]. For comparison, the VB structure of condensed benzene multilayers are also presented in Fig. 3(a) [28]. As one can see, the BEs of the bands present in the PheGly multilayer spectrum are very similar to the BEs of the benzene levels of the condensed phase. Furthermore,