ADSORPTION OF TYROSINE AND GLUTAMIC ACID TO THE CHIRAL (101) FACE OF QUARTZ: AN XPS STUDY. K. B. Stelmach[1,2], C. A. Dukes[1], and R. T. Garrod[2,3], [1]Laboratory for Astrophysics and Surface Physics, Materials Science and Engineering, University of Virginia, Charlottesville, VA 22904, (kbs7dqw@virginia.edu; cdukes@virginia.edu), [2]Department of Chemistry, University of Virginia, Charlottesville, VA 22904, USA; rg5qp@virginia.edu), [3]Department of Astronomy, University of Virginia, Charlottesville, VA 22904, USA

Introduction: Chiral mineral surfaces are ubiquitous on Earth and are expected to be present throughout the solar system [1 - 3]. These surfaces have localized atomic asymmetries, including steps and kinks sites, that allow differential molecular adsorption between enantiomers. Chiral faces are also present naturally in alkali feldspar, pyroxenes, olivine, calcite, and other common minerals. Crystalline quartz (SiO_2), present in small quantities in meteorites [1], is an excellent model material to work with as all of its faces are chiral [1, 2].

Interactions between chiral organic molecules – like α amino acids – and chiral surfaces are of interest in astrobiology as life nearly exclusively uses left-handed amino acids and right-handed sugars [4]. Furthermore, such interactions may be important in planetary science as many carbonaceous meteorites show an enantiomeric excess (*ee*) of the aforementioned molecules in the same handedness used by life [5].

X-ray photoelectron spectroscopy (XPS), which measures X-ray induced photoelectron energies to infer chemical-bonding information at surfaces, has been used previously to study the binding of amino acids to metal surfaces [6]. A potentially selective chiral molecule-surface interaction is possible if there are three points of contact between a chiral molecule and a chiral surface, which can lead to differences in physical properties, like adsorption energy (E_A), between enantiomers. We used XPS to determine if three points of contact could be identified for enantiopure samples of tyrosine (Tyr) and glutamic acid (Glu) on a (101) SiO_2 surface, following the chemistry and concentration of each element with surface temperature to infer differences in adsorption.

Experiment: (101) SiO_2 samples (10 mm x 5 mm x 1 mm) were cleaned with successive DI H_2O, acetone, and dichlorethylene baths to remove surface impurities; etched in sulfuric acid; and then rinsed in DI H_2O consistent to previous work involving aqueous adsorption [7]. The SiO_2 samples were subsequently placed in an acetone+Tyr (≥98% enantiopure, HPLC grade) bath or DI H_2O + Glu (≥99% enantiopure, HPLC grade) bath for 24 hours before the XPS experiments.

High-resolution XPS spectra were taken at temperatures ranging from 298 K to 670 K. Spectra were taken for Si 2p, O 1s, C 1s, and N 1s. The analysis area consisted of a 1400 μm x 1400 μm square, where the X-ray settings and acquisition parameters were chosen such that any radiation damage to the amino acids was minimized. Experiments were conducted in an ultrahigh vacuum (~10^{-10}-10^{-11} Torr) in a PHI VersaProbe III scanning XPS microprobe using a 50 μm beam (12.5 W) rastered over the region. An energy step of 0.25 eV and a pass energy of 69 eV was used to provide good resolution. The total fluence for each experiment was 1.4 x 10^{16} photons cm^{-2}.

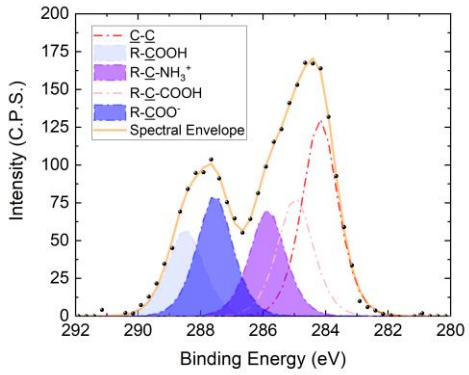
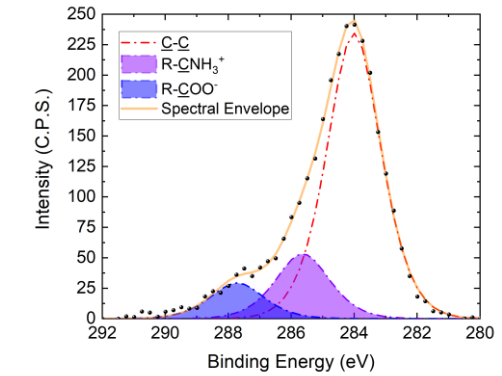


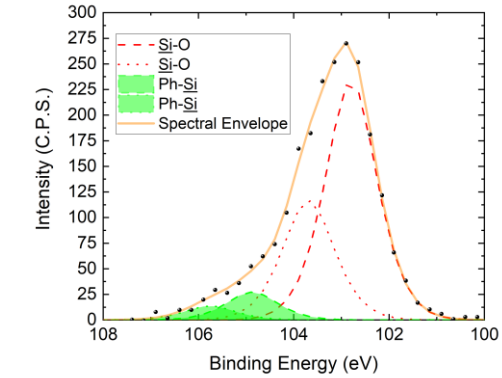
Figure 1. HR-XPS spectrum of the C 1s region for L-Glu at 298 K. The ligands responsible for a possible chiral interaction surface are shaded.

Results and Discussion: Fig. 1 shows the C 1s region for Glu at 298 K, which consists of five unique carbon-containing functional groups or chemical environments: protonated carboxylic acid (R-COOH), deprotonated carboxylic acid ($R\text{-}COO^-$), the protonated amino group ($R\text{-}NH_3^+$), a carbon attached to a carboxylic acid group (R-C-COOH), and carbon-carbon bond ($R\text{-}CH_2\text{-}CH_2\text{-}R$). Three potential interactions between Glu and the SiO_2 surface were identified, but interpretation of the data was complicated due to the presence of two carboxylic acid groups per molecule.

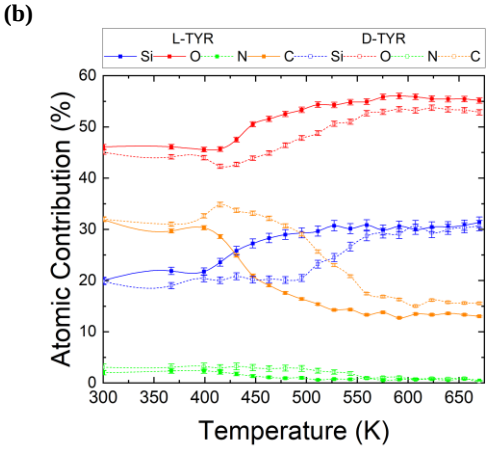
The points of interaction between Glu and the quartz surface include both of the carboxylic acid groups and the amino group. However, one contact point could be some type of steric interaction instead of a chemical bond as indicated by the protonated carboxylic acid group. It is possible that at the right deposition pH, all the carboxylic acid groups on Glu might deprotonate and aid in bonding to the surface [8]. Enantiomers of aspartic acid, another α amino acid with two carboxylic acids, has been experimentally shown to selectively



(a)



(b)



(c)

Figure 2. HR-XPS spectra of the **(a)** C 1s and **(b)** Si 2p regions for L-Tyr at 298 K. The ligands responsible for a possible chiral interaction are shaded. **(c)** The atomic concentrations (%) of the top ~10 nm of the (101) SiO_2 surface with adsorbed Tyr as a function of temperature.

adsorb onto various calcite faces in an aqueous environment [7].

Three points of contact for both enantiomers of Tyr were also observed after adsorption on the SiO_2 face, which were confirmed across all four spectral regions. The C 1s spectra at 298 K (Fig. 2a) suggests the presence of R-COO^- and R-NH_3^+. The N 1s spectra confirm the presence of R-NH_3^+. The O 1s region shows the presence of R-COO^-, the SiO_2 oxygen, and the oxygen from the phenol group (R-C_6H_4OH). Lastly, the Si 2p region at 298 K (Fig. 2b) confirms the phenol group interaction with the quartz (R-C_6H_4-O-Si).

Amino acids fragment and/or desorb from SiO_2 with increasing temperature. Preliminary data, collected to identify potential enantiomeric differences in E_A (Fig. 2c), show the atomic concentration as a percentage for each element retained on the SiO_2 surface with increasing temperature (298-670 K). For L-Tyr, sublimation/fragmentation begins between 400 and 425 K, determined by the intensity of the C 1s and Si 2p photoelectron features, whereas D-Tyr does not show a similar decrease in the amino acid until after 475 K. The carbon content for L-Tyr begins to fall well before D-Tyr. A corresponding rising trend in the silicon trend is similarly observed to occur for L-Tyr before D-Tyr. This suggests a chiral interaction through the preferential destruction or sublimation of L-Tyr over D-Tyr (Fig. 2c). This could indicate that D-Tyr preferentially adsorbs to (101) SiO_2.

A unique chiral interaction has been identified between Tyr and (101) SiO_2. This interaction suggests a difference in E_A between Tyr enantiomers and SiO_2. Computational studies have predicted differences in E_A for other α amino acids on hydroxylated quartz [9,10]. Thus, we suggest that differential adsorption of amino acid enantiomers from astrophysically relevant chiral mineral surfaces should be included in the panoply of enatioselective mechanisms potentially influencing observed *ee* levels for chiral organics identified in carbonaceous meteorites.

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