Supporting Information

"Pop-on and Pop-off" Surface Chemistry of Alanine on Ni{111} under Elevated Hydrogen Pressures.

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NEXAFS

Data Analysis

NEXAFS spectra were fitted as the sum of two Gaussian functions, superimposed on a linear background and an arctan function to capture the step:[1]

$$\begin{aligned} f(E) &= B_O + B_S(E - S_P) + \frac{S_H}{\pi}\left[\arctan\left(\frac{E-S_P}{0.2\cdot S_W}\right) + \frac{\pi}{2}\right] \\ &\quad + G_H^{\pi} \cdot \exp\left[-\left(\frac{E-G_P^{\pi}}{0.60\cdot G_W^{\pi}}\right)^2\right] + G_H^{\sigma} \cdot \exp\left[-\left(\frac{E-G_P^{\sigma}}{0.60\cdot G_W^{\sigma}}\right)^2\right] \end{aligned} \tag{1}$$

where f is the NEXAFS fitting function, E the photon energy, B_O and B_S the offset and slope of the background, S_H, S_P, S_W the height, position and width of the step function and $G_H^{\pi,\sigma}, G_P^{\pi,\sigma}, G_W^{\pi,\sigma}$ the height, position and width of the Gaussian functions for modelling the π^* and σ^* resonances.

As the main concern of the analysis was the angular dependence of the π resonance, no specific attempts were made to correct for energy calibration or intensity offset. Also, the σ resonance feature was only fitted with one broad peak, ignoring the structure within this feature. The abundance of structure with apparent angular dependence results in a step position that is particularly hard to define. For all spectra, most effort has been devoted to obtaining good fits for the low photon energy region near to the π^* resonance, as this is the strongest, sharpest feature and will convey most accurately information regarding the orientation of the adsorbed alanine molecule.

For fitting purposes, the absorption step edge was fixed between 533.5 and 534.0 eV. The fitting was done in two steps. First, the spectra for both angles were fitted independently for each set of spectra. For each layer, the average values over the two angles were calculated for all fit parameters, except the peak heights and background. These were fixed and only the peak heights and background were allowed to be optimised in the second step. The ratio of peak heights was then used to determine the molecular orientation. Two angles are mathematically sufficient to determine the angle α between the plane of the COO group and

a surface with three fold symmetry via a the equation:[1]

$$I = I_v = A\left[P \cdot \cos^2\vartheta \cdot \left(1 - \frac{3}{2}\sin^2\alpha\right) + \frac{1}{2}\sin^2\alpha\right] \tag{2}$$

where ϑ is the angle of incidence of the photon beam with respect to the surface plane (i.e. angle of X-ray polarization with respect to surface normal), and P the polarization of the beam ($P \approx 1$ at these photon energies).

C K-edge NEXAFS

C K-edge NEXAFS were recorded under equivalent conditions to those for the O K-edge spectra presented in the main body of the paper, and these results are shown below in Figure S1. These spectra show significant structure below the step edge, with is due to contamination of the beamline optical components. As a result, we did not attempt fitting of these NEXAFS data.

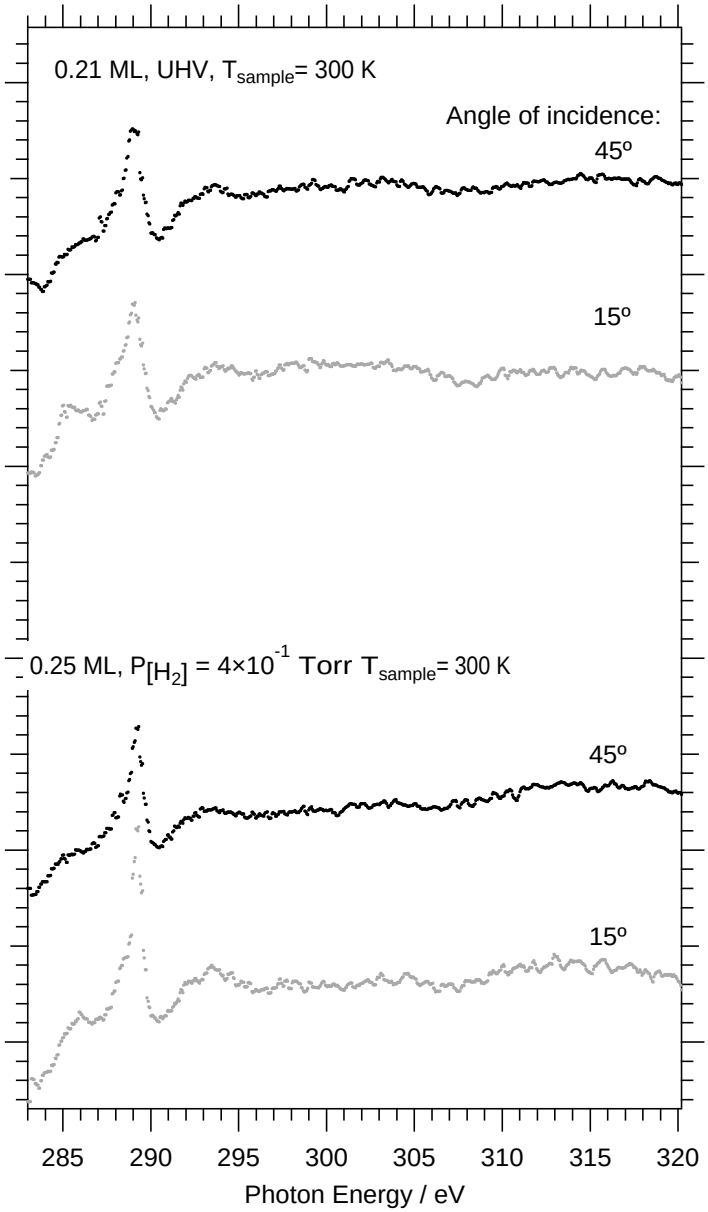


Figure S1: Auger yield NEXAFS spectra of L-alanine on Ni{111} at the C K-edge.

N K-edge NEXAFS

N K-edge NEXAFS were recorded under equivalent conditions to those for the O and N K-edge spectra presented in the main body of the paper, and these results are shown below in Figure S2.

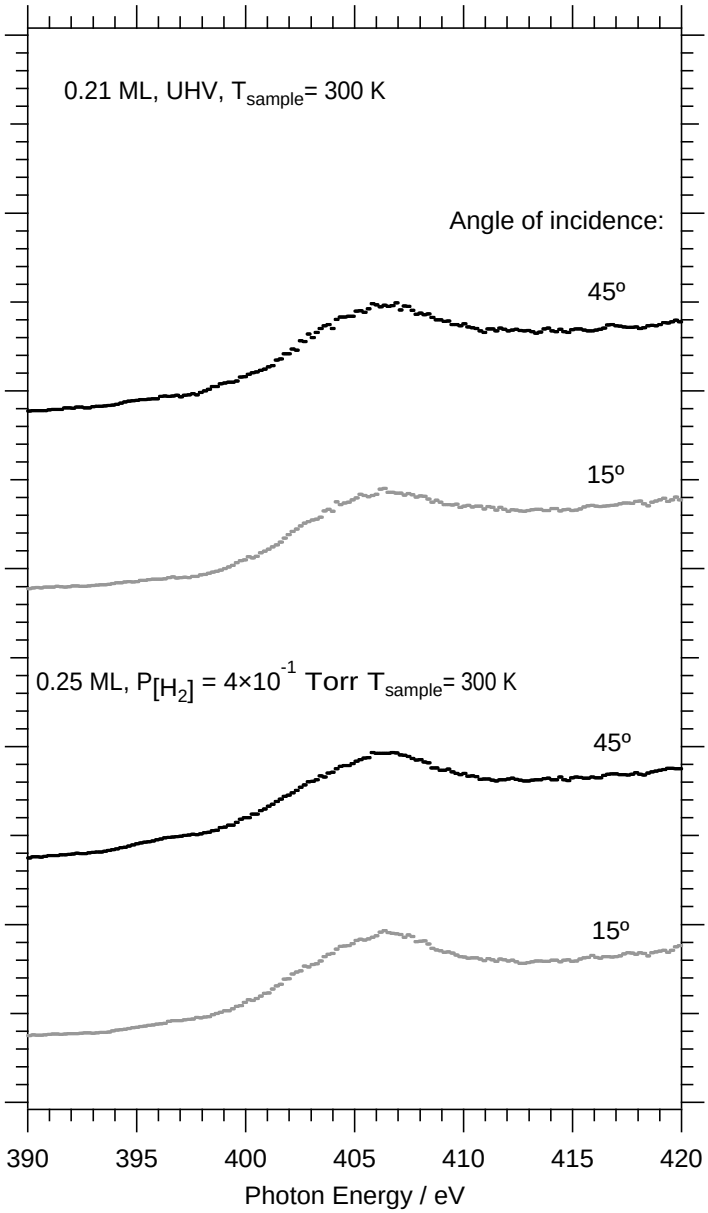


Figure S2: Auger yield NEXAFS spectra of L-alanine on Ni{111} at the N K-edge.

DFT Structures of Anionic Alanine

Figure S3 shows the most stable monomer and dimer structures of anionic alanine (alaninate). The angles of the carboxylate groups with respect to the surface plane are 30.7° for the monomer and 28.6°/33.1° for the dimer.

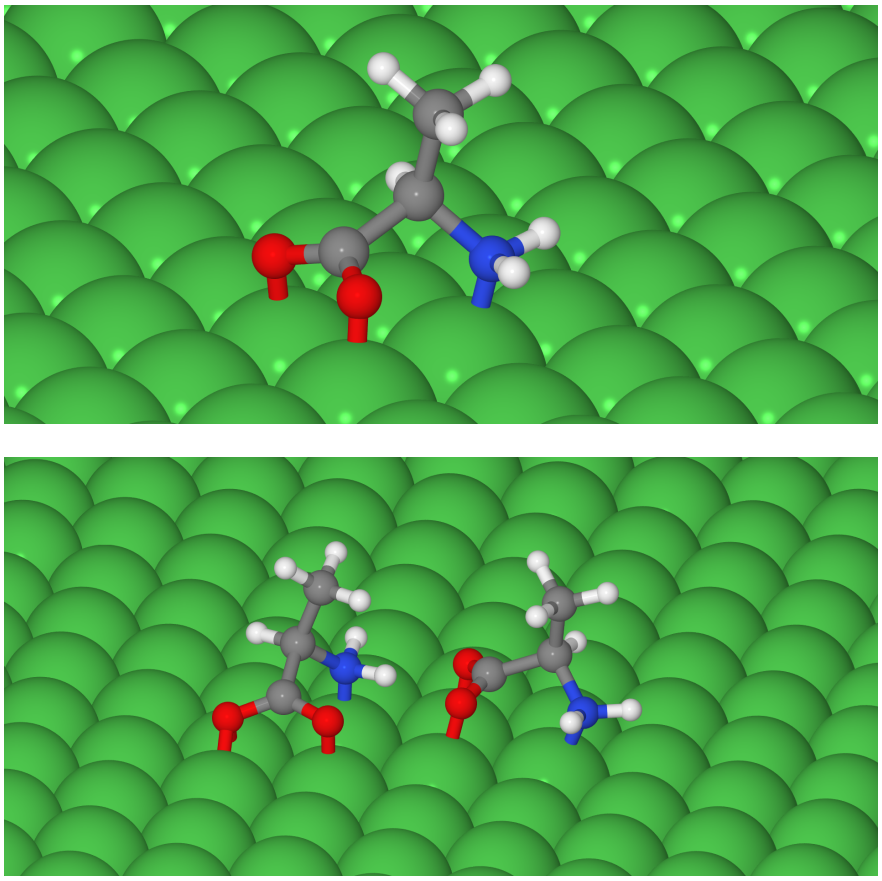


Figure S3: Top: alaninate monomer; bottom: alaninate dimer.

References

(1) Stöhr, J.; Outka, D. A. Determination of molecular orientations on surfaces from the angular dependence of near-edge x-ray-absorption fine-structure spectra. *Phys. Rev. B* **1987**, *36*, 7891–7901.