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The Importance of attractive three-point Interaction in enantioselective Surface Chemistry: Stereospecific Adsorption of Serine on the intrinsically chiral Cu{531} Surface

Tugce Eralp[1], Alex Ievins[2], Andrey Shavorskiy[1],
Stephen J. Jenkins[2], Georg Held[1*]

[1] University of Reading, Department of Chemistry, Whiteknights, Reading, UK

[2] University of Cambridge, Department of Chemistry, Lensfield Rd, Cambridge, UK

Supporting Information

* **Corresponding address:**

University of Reading, Department of Chemistry

Whiteknights, Reading RG6 6AD UK

Email: g.held@reading.ac.uk

1 X-ray Photoelectron Spectra

The C 1s and N 1s XP spectra are similar to those observed for serine on Cu{110} [1] and show little qualitative differences when the coverage or enantiomer changes.

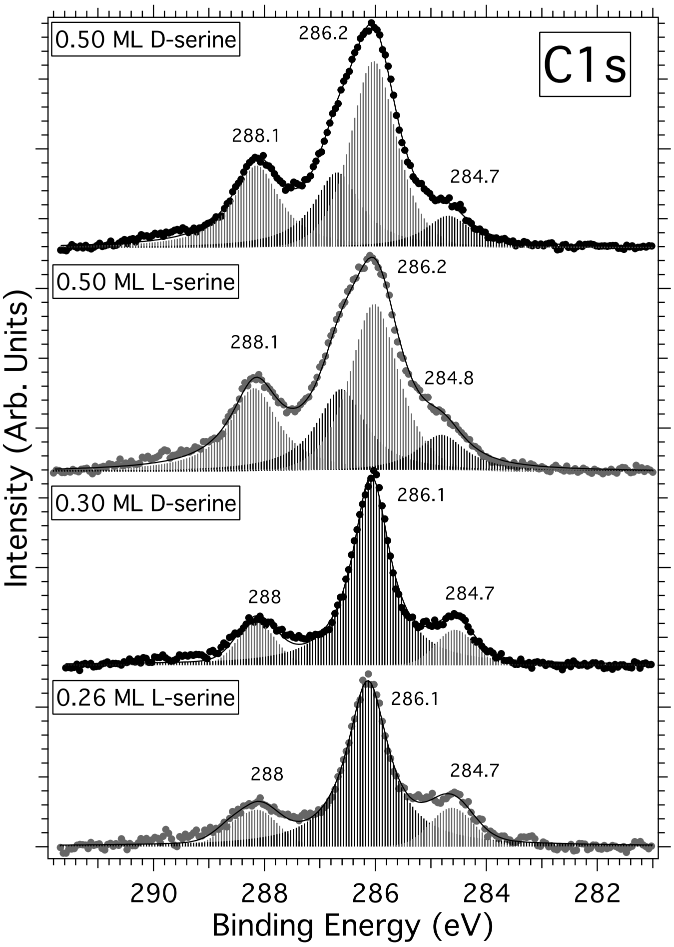

Figure 1: C 1s XP spectra of different coverages of L and D-Ser adsorbed on Cu{531}^{S} (photon energy = 630 eV).

For the saturated chemisorbed layers the highest BE peak in the C 1s region appears at 288.1 eV (288.0 eV for lower coverage). It originates from the de-protonated carboxylic acid carbon (Figure 1) [2, 3, 4, 5]. The peak at 286.2 eV is the overlapping signal of α and β-carbon atoms and has an area which is 1.9 times the carboxylate carbon peak area. This agrees well with the stoichiometric ratio between carboxylic carbon and alkyl carbons (1 : 2). The additional peak at 284.7 eV is assigned to a decomposition species,

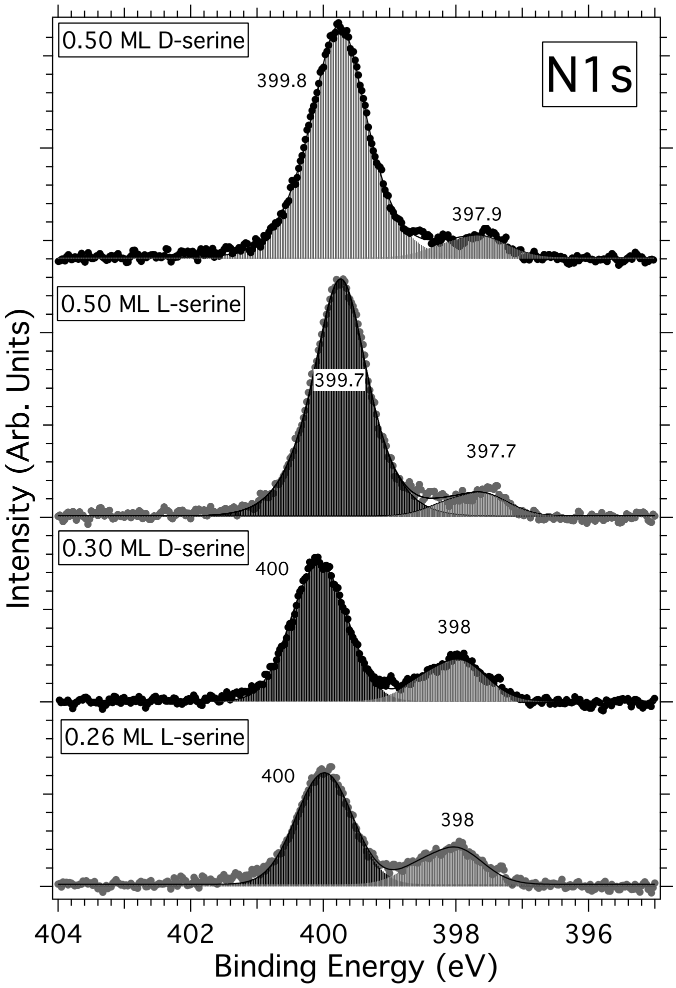

Figure 2: N 1s XP spectra of different coverages of L and D-Ser adsorbed on Cu{531}^{S} (photon energy = 630 eV).

which does not increase with increasing coverage. The peak at around 398 eV in the N 1s region is assigned to the same decomposition species. The main N 1s peak at around 400 eV is associated with the neutral NH_2 group forming a bond with a surface copper atom. It shifts towards slightly higher binding energy (from 399.8/7 eV to 400.0 eV) at lower coverages.

2 NEXAFS Data Analysis

The polarization dependence of the π-resonance at 289 eV in the carbon K-edge NEXAFS spectra is used to determine the orientation of serine on the Cu$\{531\}^S$ surface. Examples of NEXAFS spectra for different coverages, enantiomers and polarization angles are shown in Figure 3. The intensity of the π-resonance peak is expected to go to zero if the polarization vector, $\vec{E}$, is in the plane of the O-C-O triangle and should have maximum intensity if $\vec{E}$ is perpendicular to this plane.

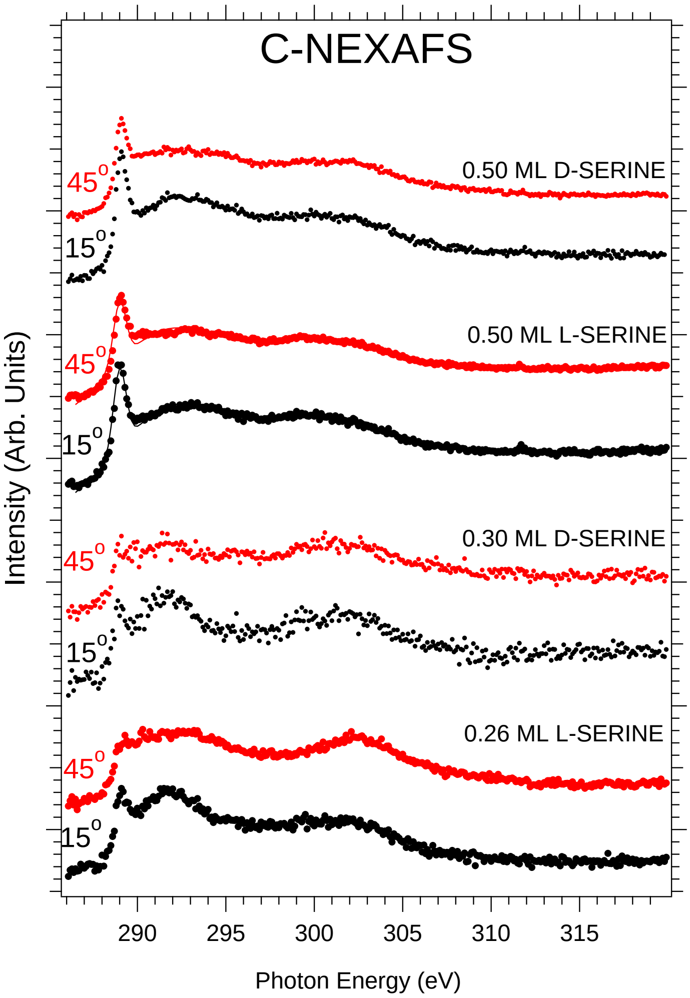

Figure 3: A selection of NEXAFS raw data for D and L-serine at different coverages on Cu$\{531\}^S$ collected for polarization angles of 15° and 45° with respect to the $[1\bar{1}\bar{2}]$ direction

As found previously for alanine and glycine, both the $\{110\}$ and $\{311\}$ microfacets of the Cu{531} surface can accommodate amino acids in their triangular adsorption geometry [2, 5], therefore two different molecular orientations have to be considered. The intensity of the π-resonance from each molecular orientation varies like $\cos^2(\phi - \alpha_i)$. α_i is the angle between the x-axis of the sample ($[1\bar{1}\bar{2}]$ direction) and the projection of the normal of O-C-O triangle (describing the orientation of the molecule) and ϕ is the azimuthal angle of the polarization vector [6]. This relation has been used before to determine the orientation of a variety of similar molecules [5, 2, 4, 3, 7]. Figure 4 of the main article shows the intensities of the π-resonance plotted vs the azimuthal angle of the polarization vector ϕ. The resonance intensities for each angle were extracted by fitting the corresponding NEXAFS spectra (as shown in Figure 3) with a curve composed of a step-function and Gaussian peaks representing the π and σ-resonances. The positions and widths of all resonances and the arctan-shaped step function [6] were globally optimized, i.e. the same for all angles of a given layer; only the peak heights were allowed to vary.

The angular dependence of the π resonance was then fitted with the function of Equation (1) describing the angular intensity dependence for molecules in two different orientations α_1 and α_2 [2, 5]:

$$I_\pi(\phi) = A_1 \cdot (\cos^2(\phi - \alpha_1)) + A_2 \cdot (\cos^2(\phi - \alpha_2)) \tag{1}$$

A_1 and A_2 correspond to the relative coverages of the two molecular configurations. As outlined in the main article, the size and shape of the unit cells at saturation coverage (0.50 ML) requires equal occupation of {110} and {311} microfacet adsorption sites. Therefore the search was constrained to $A_1 : A_2$ ratios around 1 ($\pm 30\%$). Other constraints had to be made in order to account for the periodicity of the $\cos^2$ function and to exclude unphysical values of the difference between the orientations ($\alpha_2 - \alpha_1$), which was confined to $70^\circ \pm 20^\circ$. Within these constraints a large number of start parameters always led to the same best fit parameters of $\alpha_1 = -28/-23^\circ$, $\alpha_2 = +31/+35^\circ$ and $A_2 : A_1 = 1.1/0.9$ for L/D Serine on Cu$\{531\}^S$. Without these constraints, in particular for the $A_2 : A_1$ ratio, a number of parameter values could be found, which fit the data equally well but are not compatible with the observed long-range ordered overlayer structure. In order to estimate the error bar of the so-determined angle values for the saturation coverages, constrained fits were performed where α_2 was kept constant at values between 15° and 50° and all other parameters were optimized. The diagram in Figure 4.a shows the result for D-serine. χ^2 (indicated by the color of the data points) goes through a shallow minimum between $\alpha_1/\alpha_2 = -37/+23°$ and $-17/+43°$ (the boundaries are defined by a 20% increase in χ^2 with respect to the minimum). Hence, the error for the absolute values of α_1/α_2 is around ±10°. This error value strongly depends on the range of $A_2 : A_1$ ratios allowed within the fitting procedure. More constrained searches lead to smaller error bars. There is also a strong correlation between these two angles, such that $\alpha_1 = \alpha_2 - 60° \pm 3°$, as indicated by the vertical lines of data points in Figure 4.a, which leads to a significantly smaller error of ±3° for the relative orientation of the molecules.

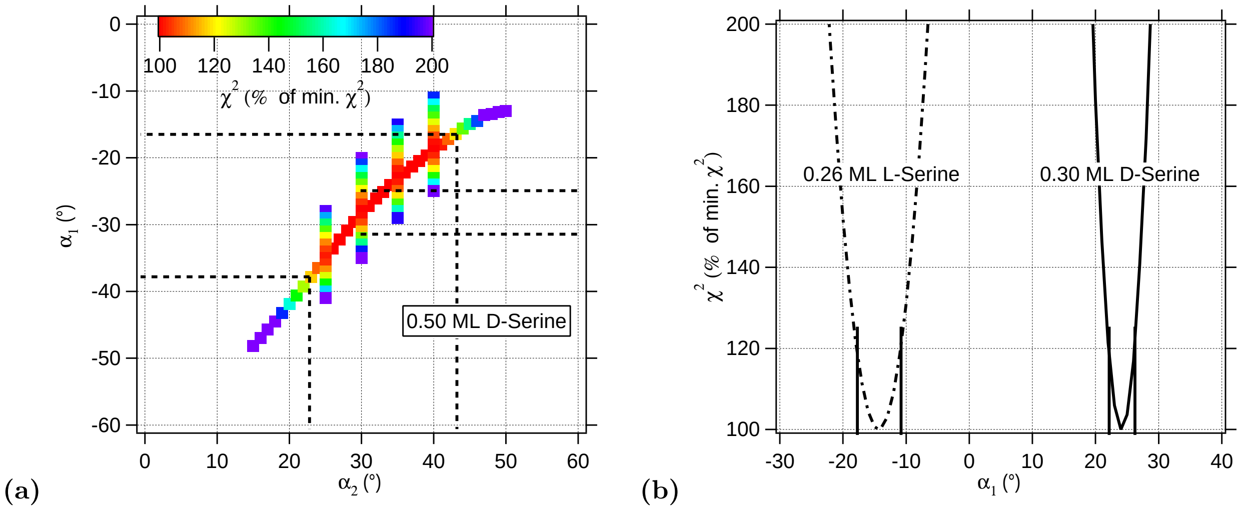

Figure 4: (a) χ^2 for fits to the NEXAFS data of 0.50 ML D-serine on Cu$\{531\}^S$ with different combinations of α_1 and α_2; the color scheme represents χ^2 in percent of the minimum value 0.01553. (b) χ^2 for fits to the NEXAFS data of 0.26 ML L-serine and 0.30 ML D-serine on Cu$\{531\}^S$ as a function of α_1. χ^2 in percent of the minimum values, 0.0238 for L-serine and 0.00477 for D-serine.

The low-coverage the NEXAFS data could be fitted by assuming only one molecular orientation, α_1 ($A_2 = 0$ in equation (1)). The results are listed in Figure 4 and Table 1 of the main article. Allowing two molecular orientations ($A_2 > 0$) did not lead to a significant improvement of the fits. The error for α_1 was estimated as $-14 \pm 4°$ for 0.26 ML L-serine and $24 \pm 2°$ for 0.30 ML D-serine in a similar way as before from the increase in χ^2 (see Figure 4.b). For D-serine even completely unconstrained fitting with two orientations led to the same result, whereas for the L-serine data equally good agreement could be achieved for α_1/α_2 values in the range of $-15° \pm 15°$ with a strong correlation, $\alpha_1 + \alpha_2 = -32° \pm 3°$, i.e. the two orientations are displaced in opposite directions from a mean angle of around $-16°$.

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