

Hydrogen-bond induced Pair Formation of Glycine on the Chiral Cu{531} Surface

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Supporting Information

Analysis of the NEXAFS data

The polarization dependence of the π -resonance in the oxygen K-edge NEXAFS spectra is used to determine the orientation of glycine on the surface. The intensity of 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. As found previously for alanine, both the {110} and {311} micro facets of the Cu{531} surface can accommodate amino acids in their triangular adsorption geometry,¹ therefore two different molecular orientations are possible. The intensity of the π -resonance from each molecular orientation varies like $\cos^2(\phi - \alpha_i)$, where α_i is the angle between the x -axis of the sample ($[1\bar{1}2]$ direction) and the projection of the normal

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of O-C-O triangle (describing the orientation of the molecule) and ϕ is the azimuthal angle of the polarization vector.² This relation has been used to determine the orientation of a variety of similar molecules.^{1,3-5} Figure 1(b-d, identical to Figure 4 of 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 with a curve composed of a step-function and four Gaussian peaks representing the π and σ -resonances, as shown in Figure 2. The positions and widths of all resonances and the arctan-shaped step function² were globally optimized, i.e. the same for all angles; 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 :¹

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

A_1 and A_2 define the relative coverages of the two molecular configurations. The angular dependence of the π resonance for the layer with 44% saturation coverage and the fitted intensity are shown in Figure 1(b). The ratio of the best fit parameters A_1/A_2 is 1.1, i.e. the two orientations of glycine molecules co-exist with essentially equal probabilities at the surface. The best fit values for α_1 and α_2 are 127° and 21° , respectively. The angular dependencies for the saturated chemisorbed layer at 300 K and after annealing to 430 K are shown in Figure 1(c,d). The values extracted from the curve fitting are listed in Table 1. They are very similar for all layers studied in this work. In addition to the π -resonance, there are three distinct σ -resonances in the O-NEXAFS spectra, at 539.9 eV (σ_1), 543.5 eV (σ_2), and 546.4 eV (σ_3). Figure 2 also shows angular variations for these σ -resonances, in particular for σ_2 , for the saturation coverage at 300 K. The angular dependence of the σ -resonance intensities can be described in a similar way to the π -resonance:

$$I_{\sigma}(\phi) = A_1 \cdot (\cos^2(\phi - \beta_1)) + A_2 \cdot (\cos^2(\phi - \beta_2)) \quad (2)$$

β_1 and β_2 now are the angles of the associated bonds with respect to the x axis of the surface. By fitting this function to the angular dependence of the three σ -resonances (see Figure 3), the following angles β_1 and β_2 are found: 103° and 17° for σ_1 , 118° and 14° for σ_2 , 99° and 6° for σ_3 . σ_2 has a similar angular dependence as the π resonance (see Figure 3(b) and Figure 1(b-d)). σ_1 and σ_3 show very little angular dependence, which causes a very large uncertainty with respect to the absolute angle values. Therefore only the angles derived for σ_2 are included in Table 1.

In previous studies the σ_1 -resonance was assigned to the C–C sigma bond and σ_3 (546.4 eV) to a C–O derived resonance.^{2,4,6} The very similar angular dependence of the σ_2 -resonance (543.5 eV) and the π -resonance (533 eV) indicates, however, that this peak should rather be assigned to the C–C σ -bond, which both should show the same behavior. The lack of angular dependence in the σ_1 and σ_3 -resonances is consistent with C–N bonds approximately 90° apart from each other and the superposition of four contributions from the C–O sigma bonds.

Table 1: Angles and occupation ratios derived from fits to the π (α_1 , α_2) and σ_2 resonances (β_1 , β_2). See text for details.

layer	resonance	{311}	{110}	A_1/A_2
		α_1, β_1	α_2, β_2	
44% sat. 300 K	π	127°	21°	1.10
100% sat. 300 K	π	133°	22°	0.95
	σ_2	118°	14°	0.95
100% sat. 450 K	π	133°	20°	1.01

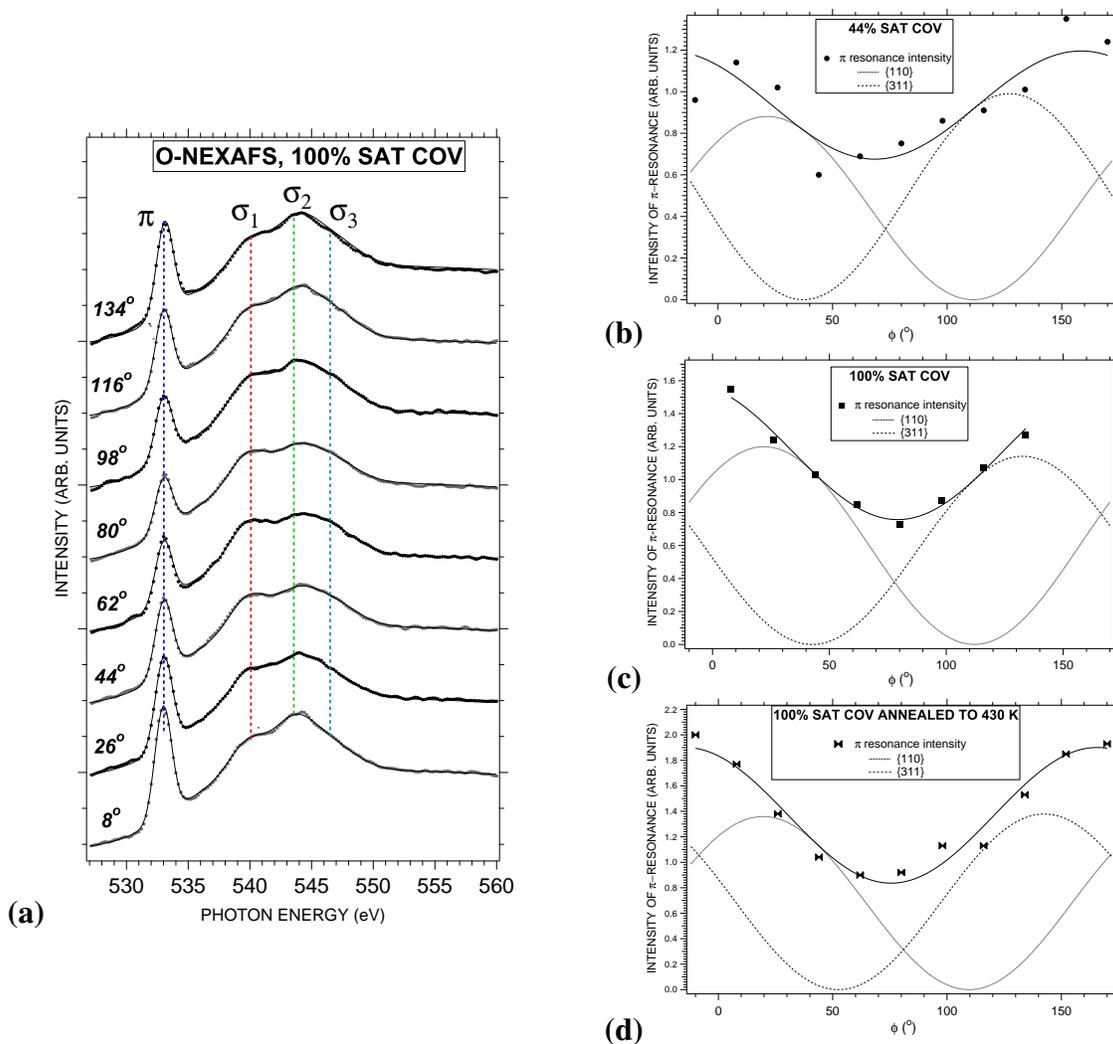


Figure 1: Series of O-NEXAFS spectra of the saturated chemisorbed layer of glycine on Cu{531}^S, measured for azimuthal angles in the range from 8° to 134° (a). Intensity of the π -resonance for different glycine layers versus the azimuthal angle of the polarization vector, ϕ , and the best fit superposition of \cos^2 functions for two orientations: 44% of saturation coverage at 300 K (b), saturated chemisorbed layer at 300 K (c) and saturated chemisorbed layer annealed to 430 K (d).

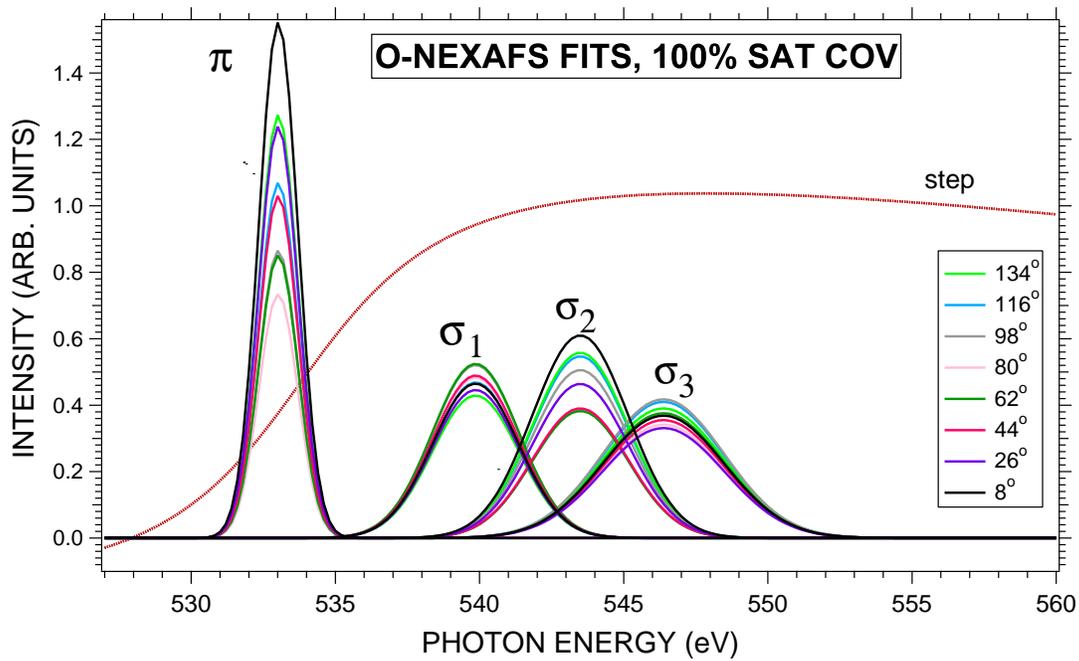


Figure 2: Individual peaks and step function fitted to the O-NEXAFS spectra of the saturated chemisorbed layer of glycine on Cu{531}^S. The peak widths (FWHM) are 0.95 eV for the π resonance and 2.1 eV, 2.4 eV, and 3.0 eV for σ_1 , σ_2 , and σ_3 .

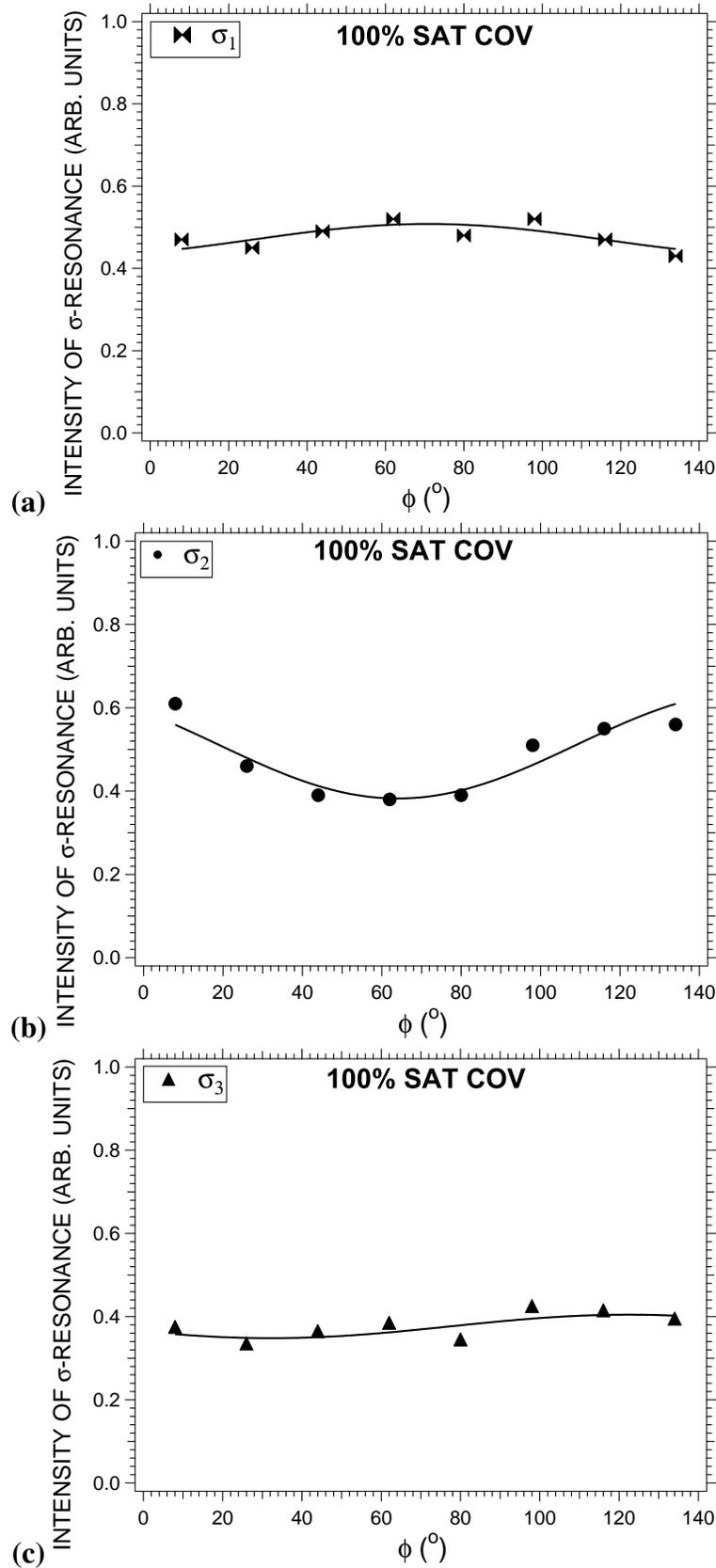


Figure 3: Intensities of the σ -resonances σ_1 (a), σ_2 (b), σ_3 (c) for the saturated chemisorbed layer of glycine versus the azimuthal angle of the polarization vector, ϕ , and best fit functions.

Temperature Programmed Desorption Experiments (TPD)

TPD spectra were recorded after each LEED experiment in order to determine the coverage of the layer and to find the desorption temperatures. The heating rate for all experiments was 3 K/s. The partial pressures of the decomposition products H₂ (mass 2) and CO₂ (mass 44) were measured using an encapsulated quadrupole mass spectrometer with an aperture of 5 mm at a distance of about 1 mm from the sample. The spectra are shown in Figure 4.

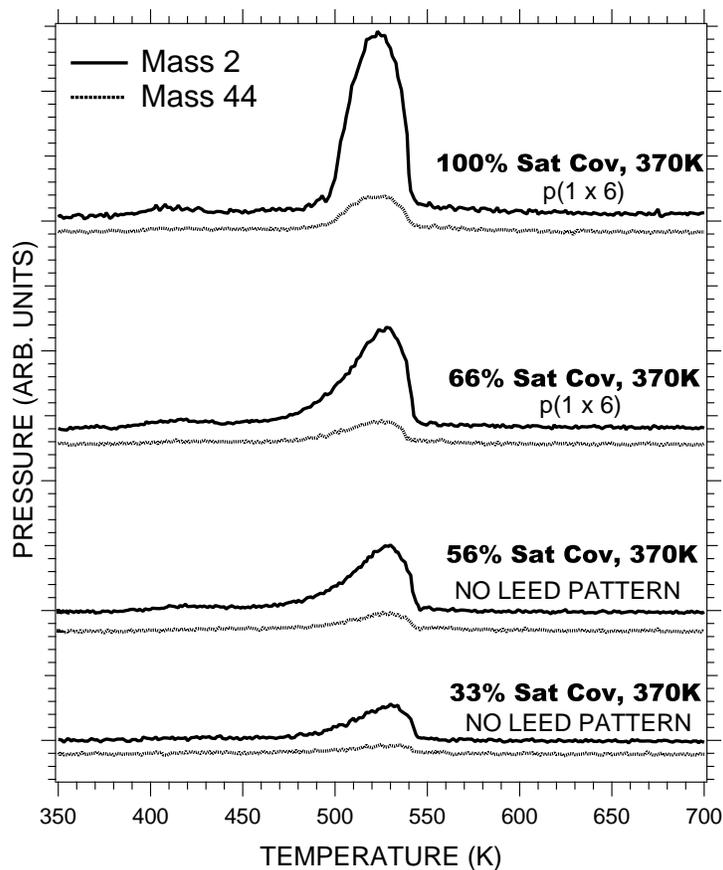


Figure 4: TPD spectra of mass 2 (H₂) and 44 (CO₂) for different coverages of glycine on Cu{531}^R. The layers were prepared at room temperature and annealed to 370 K to improve the long-range order.

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