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SUPPORTING INFORMATION

Co-Adsorption of Water and Glycine on Cu{110}

Marco Sacchi*[a] and Stephen J. Jenkins[a]

[a] Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, UK

* email: ms857@cam.ac.uk, tel: +44(0)1223 763519, fax: +44(0)1223 762829

S.1 Hydrogen Bonding and Structural Analysis of Hydrated Glycine

The configurations and the relative energy of the mixed gly+H_2O and gly+$2H_2O$ phases investigated in this work are shown in Figure S1 and Figure S2. When a single water molecule is added to the (3 × 2) cell containing the glycinate there is a strong preference for H_2O to chemisorb atop the copper atom adjacent the carboxylate group instead of one of the empty atop sites adjacent the amino group, this is due to the fact that in this configuration (Figure S1 b) water can make two strong hydrogen bonds with the negatively polarized oxygen atoms of two adjacent glycine molecules. One of the adsorption sites near the NH_2 group (Figure S1 a) is not a stable adsorption site for water coadsorption and geometry optimization of water initially adsorbed on this site produces a final essentially identical to the one obtained by initially adsorbing water on the other atop atom adjacent the NH_2 group (Figure S1 c). When two water molecules are coadsorbed on the same unit cell of glycine, a relatively minor energy difference among the configurations is observed (Figure S2). The most stable configuration (Figure S2 a) has a water molecule sitting on an atop site near the amino group and another H_2O occupying a bridge position between the first water and the carboxylate group of glycine on the opposite row. The main intermolecular hydrogen bonds for different phases are reported in Figure S3.

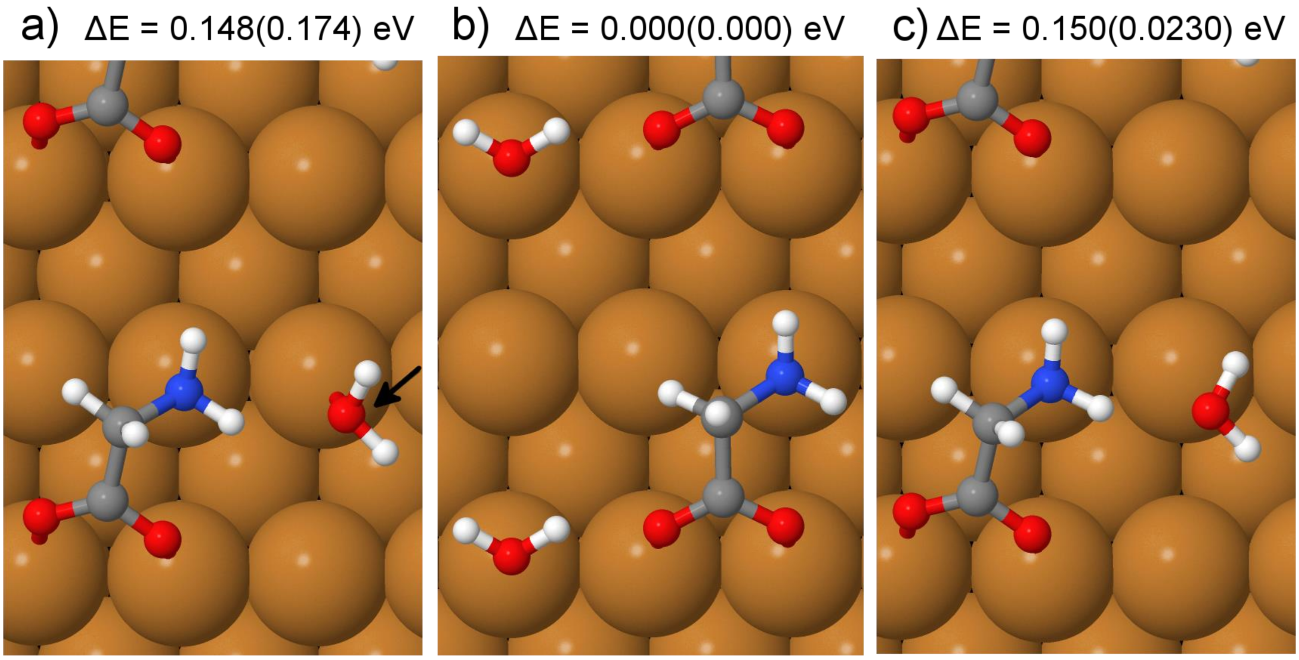

Figure S1. Optimized structures of mono-hydrated glycine (gly + H_2O) on Cu{110}. The black arrow in the figure indicates that the water molecule shifted from an atop site to the near one as a result of the geometry optimization. The relative energies (ΔE) are for DFT (DFT+D) calculations.

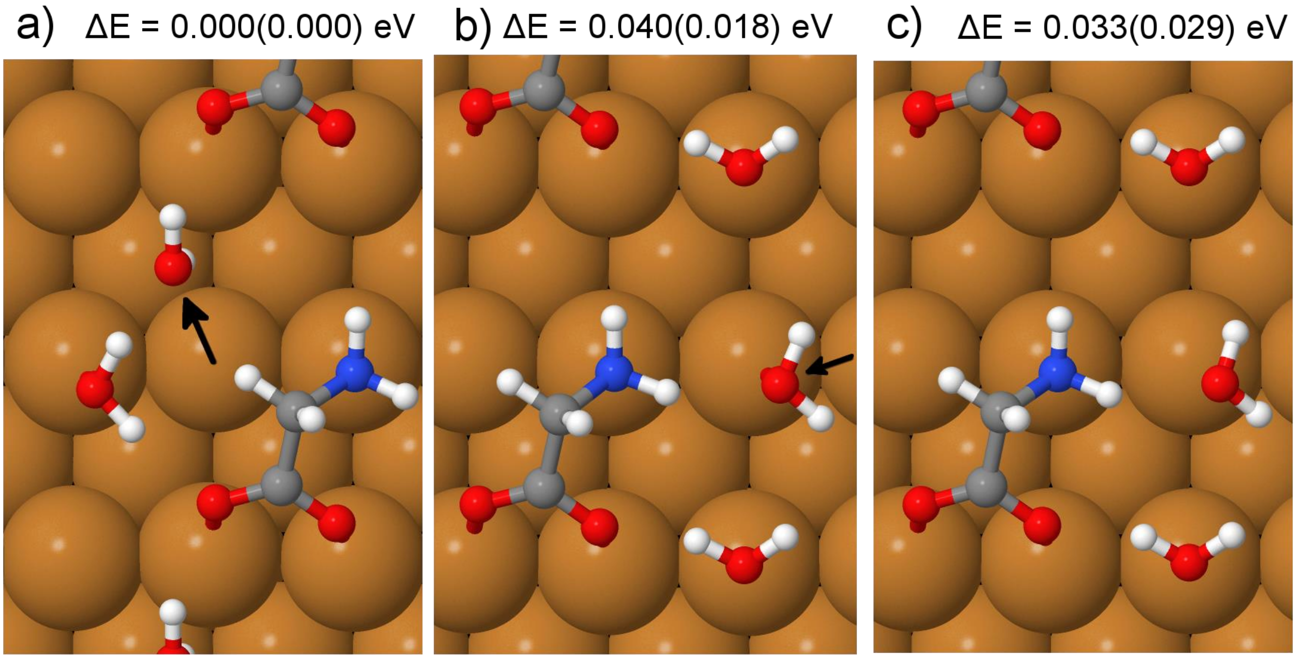

Figure S2. Optimized structures of bi-hydrated glycine (gly + $2H_2O$) on Cu{110}. The black arrow in the figure indicates that the water molecule shifted from an atop site to the near one (b) and from a top site to a bridge site (a) as a result of the geometry optimization. The relative energies (ΔE) are for DFT (DFT+D) calculations.

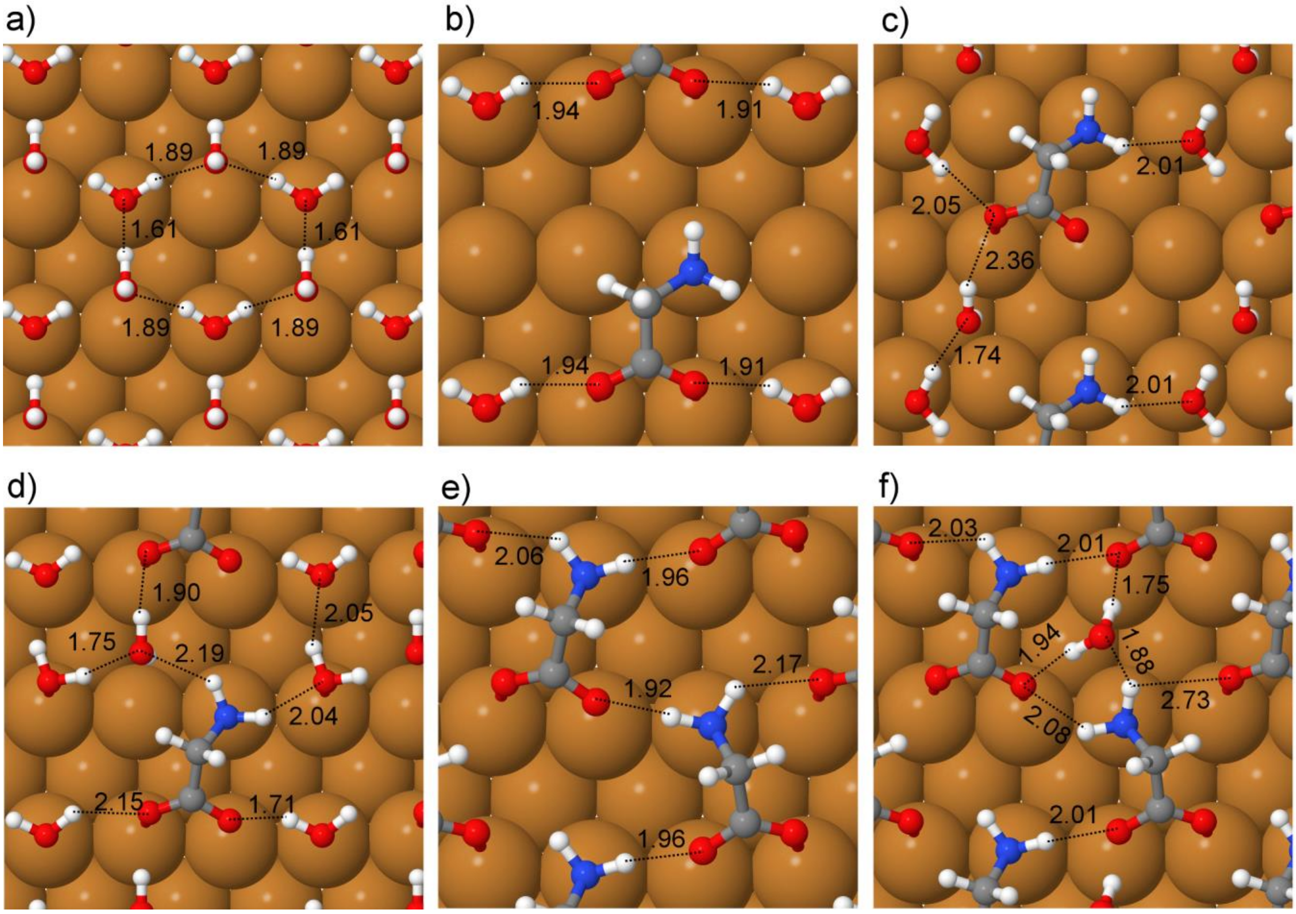

Figure S3 . Hydrogen bond lengths for glycine and water structures on Cu{110}. (a) water monolayer ($6H_2O$); (b) mono-hydrated glycine (gly + H_2O); (c) bi-hydrated glycine (gly + $2H_2O$); (d) tri-hydrated glycine (gly + $3H_2O$); (e) glycine monolayer (2gly); (f) glycine monolayer mono-hydrated (2gly + H_2O).

S.2 Zero Point Energy

Since we neglected to incorporate ZPE effects in the calculations of the phase diagrams of the gly+H_2O system, we want to verify here that the variation in ZPE upon adsorption of glycine does not influence significantly the results presented in this work. Since the main contribution to the ZPE of a molecular system is given by the highest energy vibrational modes (mainly C-H, O-H and N-H stretching vibrations), we can assume that the molecular vibrational modes of the adsorbed molecules (glycinate) are very close in energy to the vibrations of the isolated molecule in the gas phase (neutral glycine). A vast amount of experimental evidence suggests indeed that this is a very reasonable assumption.[1, 2] It is possible to calculate reasonably accurate vibrational frequencies for an isolated neutral molecule using the DFPT[3-5] methodology in the framework of periodic boundary DFT.[6, 7] From this vibrational analysis (Table S1) we find that the total ZPE of neutral glycine calculated by DFT is 2.202 eV. The labels used for the assignment of the vibrational modes reported in Table S1 are based on a "local mode" simplified description of the molecular vibrations, in which each mode is expressed as a combination of one or more of the following "group vibrations": ν_s and ν_a are symmetric and antisymmetric stretch modes (for NH_2 and CH_2); ν is a stretch mode (for C-OH, C=O, CN and CC bonds); τ indicates torsional vibrations; δ indicates either scissor (for OCOH, NH_2 and CH_2) or in-plane bending (for the CC=O, CO-H group, for instance); ω indicates either wag (for NH_2 and CH_2) or out-of-plane bending (for CO-H, CC=O); ρ and t indicate rocking and twisting modes (for NH_2 and CH_2). If we assume that the only difference between the ZPE energy of the neutral glycine and glycinate is given by the breaking O-H bond frequency (at 3289 cm^{-1}), then the ZPE of the glycinate would be only 0.2 eV lower than glycine. We have also to take into account that for every two glycine molecules that adsorb, a molecule of H_2 desorbs back to the gas phase. Since the ZPE of H_2 is 2199 cm^{-1} (0.273 eV), the total ZPE variation for every adsorbed molecule is only 0.2 eV – (0.273/2) eV = 0.068 eV. For the gly monolayer (composed by two adsorbed glycinate molecule in a (3 × 2) cell), the surface energy (per surface cell atom) would decrease by only 22 meV. Such a small energy contribution would only shift upwards the boundary of stability of the pure gly phase by about 14 K.

Table S1 Vibrational frequencies (cm^{-1}) of isolated neutral glycine calculated by DFT with the finite difference approach included in CASTEP. For simplicity, only the main high-frequency vibrational mode labels are indicated in this table. Local mode assignments are listed in descending order of importance for each vibration.

Frequency (cm^{-1})	Vibrational Mode
250.047	τ(CCN)
354.859	δ(C-C=O), δ(C-C-NH_2),
462.340	ρ(NH_2), ω(CO-H)
517.842	δ(CC=O), ρ(CH_2), ρ(NH_2)
590.729	ρ(CH_2), ω(C-CO)
670.386	δ(OCOH), ω(NH_2)
801.370	ω(NH_2), ν(CC)
882.914	ν(CC), ν(C-OH)
929.151	ρ(CH_2), ω(OH), ω(NH_2)
938.046	ω(CO-H), ρ(CH_2), t(NH_2)
1082.033	ν(CN)
1141.973	t(NH_2), t(CH_2)
1202.726	ν(C-OH), ν(CC)
1283.628	ω(CH_2), t(CH_2)
1347.090	ω(CH_2), t(CH_2), ρ(CH_2)
1415.698	δ(CO-H), ν(C-OH)
1453.016	δ(CH_2)
1625.072	δ(NH_2)
1863.283	ν(C=O)
3025.397	ν_s(CH_2)
3094.011	ν_a(CH_2)
3288.639	ν(OH)
3602.840	ν_s(NH_2)
3701.617	ν_a(NH_2)

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