

Supporting Material for Insight into the reduction of pyruvic acid to lactic acid over Cu{110}: the crucial role of intramolecular tunnelling in direct hydrogenation

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1 Notation for Overlayer Structures

To date, the literature has generally described the conformations of glycinate on Cu{110} as homochiral or heterochiral[1, 2, 3, 4, 5, 6], referring to the asymmetric distortions of the molecule that arise upon adsorption. In fact, this binary nomenclature is insufficient to describe the various possible distinct conformations for glycinate (of which there are nine), and is wholly inadequate for extension to the cases of alaninate and lactate, where intrinsic molecular chirality must also be considered. Here, we introduce an alternative notation that captures the chirality associated with the binding site of the molecule, the asymmetric distortion of the molecule on the surface, and the possible intrinsic chirality of the molecule itself.

On Cu{110}, the three-point (μ_3) binding footprint of an adsorbed molecule constitutes a two-dimensionally chiral triangle[7]. Specifically, they can be visualised as the vertices of right-angled triangles sitting either side of a glide plane (see Figure 1). Due to the opposing chirality of the two binding sites found in each primitive unit cell, it is necessary to provide a convention for which triangle is referred to in any given context. This paper employs the descriptors X, R and S to describe the chirality of the adsorbate in isolation (with ‘X’ being a null descriptor designating achirality) and lists them in the order of triangles ‘1’ and ‘2’ in Fig. 1. Thus, for instance, the combined symbol ‘RS’ indicates a molecule of chirality R occupying triangle ‘1’, and another of chirality S occupying triangle ‘2’. Absence of any molecule from one of the binding triangles, as occurs in the low-coverage cases, is represented by inserting the symbol ‘O’ into the position corresponding to the empty site. That is, the symbol ‘OX’, for example, would imply triangle ‘1’ empty, with an achiral molecule occupying triangle ‘2’.

Through our studies of glycinate, alaninate and lactate [8] we have found that there are two recurring types of molecular structures that can be categorised

as being either ‘kinked’ or ‘linear’ according to the conformation on the surface (see, for example, Fig. 2). The kinked structure for glycinate features the C–H bonds at approximately 25° and 80° to the surface normal, whereas in the linear structure both C–H bonds make an angle with the surface normal at close to half the tetrahedral angle (approximately 54°). In alaninate and lactate, one of these C–H bonds is replaced with a C–CH₃ bond, but the angles in ‘kinked’ and ‘linear’ structures are essentially analogous. The notation for a ‘kinked’ species is to label right-hand and left-hand kinks with superscript ‘)’ and ‘(’ respectively. The linear species will be indicated by a superscript ‘|’. Thus, by way of example, a molecule of chirality R, bound such that the backbone makes a left-hand curve when viewed in the orientation of Fig. 1 will be labelled R⁽.

For an achiral molecule, such as glycinate, the combination of binding-site chirality (i.e. triangle ‘1’ versus triangle ‘2’) with asymmetric molecular distortion (i.e. kinked left, kinked right or linear) yields nine distinct conformations at 0.333 ML coverage, enumerated in Table 1. The addition of intrinsic molecular chirality, in the cases of alaninate and lactate, might be expected to further multiply the possibilities, but this is true to only a limited extent. Our calculations indicate that R⁾ and S⁽ conformations are strongly disfavoured, whether they appear in triangle ‘1’ or triangle ‘2’, converting spontaneously to other conformations upon relaxation. Counting only the cases that do not contain these unfavourable geometries, we find sixteen distinct conformations, listed in Table 2, grouped into four containing only R molecules, four containing only S molecules, and eight containing an intimate mixture of both enantiomers. Clearly, deposition of an enantiopure sample of the chiral substance can result only in surface conformations of RR or SS type as appropriate (assuming no racemisation occurs), but deposition of a racemic mixture could result in either an intimately mixed overlayer of SR/RS type, or in segregation to separate RR and SS domains. The use of a consistent notation to describe the various possible conformations is invaluable in ensuring that all combinations are considered as starting geometries and none are overlooked.

The full geometry descriptor also helps to see at-a-glance whether a particular conformation is locally chiral or achiral. This may be done simply by forming the descriptor of the mirror-image structure, by means of the following procedure: (a) swap all ‘R’ symbols for ‘S’ and vice versa, (b) swap all ‘(’ symbols for ‘)’ and vice versa, and (c) interchange the symbols for the first and second triangles. Thus, to give an example, starting with S[|]S[|], step (a) yields R[|]R[|], step (b) then transforms this to R[|]R⁽, and finally step (c) gives us R⁽R[|] as the descriptor for the mirror image structure. This simple manipulation allows one to determine very easily whether a particular structure is locally achiral (in which case the structure and its mirror image will share the same geometry descriptor) or whether it is locally chiral (in which case the mirror image descriptor will differ from the original). Regardless of the outcome, however, it should be stressed that the overall chirality or achirality of the overlayer, taken as a whole, must be determined by the chirality or otherwise of the adsorbate molecules: achiral molecules, or a racemic mixture of chiral molecules, are quite capable of creating locally chiral domains but the global symmetry of the situation implies that op-

posing chiralities must occur in equal proportion; deposition of an enantiopure sample, in contrast, can only ever lead to an asymmetric overall result[9]. Note that locally chiral domains resulting from deposition of a racemic mixture can arise *either* from resolution into the opposing molecular chiralities (e.g. R|R| and S|S|) or from asymmetric distortions of molecules in an intimate mixture of the two molecular chiralities (e.g. S|R| and S|R|). The observation of complementary locally asymmetric structures, in an STM experiment, for example, does not therefore necessarily imply resolution of the racemate.

References

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1.1 Tables for Supporting Material

Structure	Mirror Image	Local Symmetry	Global Symmetry
$X(X^{\circ})$	$X^{\circ}(X)$	chiral domains	achiral
$X^{\circ}(X)$	$X(X^{\circ})$	locally achiral	achiral
$X^{\circ}X^{\circ}$	$X^{\circ}X^{\circ}$	locally achiral	achiral
$X^{\circ} X^{\circ} $	$X^{\circ} X^{\circ} $	locally achiral	achiral
$X^{\circ} X^{\circ}$	$X^{\circ} X^{\circ} $	chiral domains	achiral
$X(X^{\circ} $	$X^{\circ} X^{\circ}$	chiral domains	achiral

Table 1: Possible starting geometries for 0.333 ML coverage glycinate adsorbed on Cu{110} in a (3×2) unit cell.

Structure	Mirror Image	Local Symmetry	Global Symmetry
$R^{\circ}(R^{\circ})$	$S^{\circ}(S^{\circ})$	chiral domains	chiral
$R^{\circ} R^{\circ} $	$S^{\circ} S^{\circ} $	chiral domains	chiral
$R^{\circ} R^{\circ}$	$S^{\circ} S^{\circ} $	chiral domains	chiral
$R^{\circ}(R^{\circ} $	$S^{\circ} S^{\circ})$	chiral domains	chiral
$S^{\circ}R^{\circ}$	$S^{\circ}R^{\circ}$	locally achiral	achiral
$R^{\circ}(S^{\circ})$	$R^{\circ}(S^{\circ})$	locally achiral	achiral
$S^{\circ} R^{\circ} $	$S^{\circ} R^{\circ} $	locally achiral	achiral
$R^{\circ} S^{\circ} $	$R^{\circ} S^{\circ} $	locally achiral	achiral
$S^{\circ} R^{\circ}$	$S^{\circ} R^{\circ} $	chiral domains	achiral
$R^{\circ}(S^{\circ} $	$R^{\circ} S^{\circ})$	chiral domains	achiral

Table 2: Possible starting geometries for 0.333 ML coverage lactate or alaninate adsorbed on Cu{110} in (3×2) unit cell.

1.2 Figures for Supporting Material

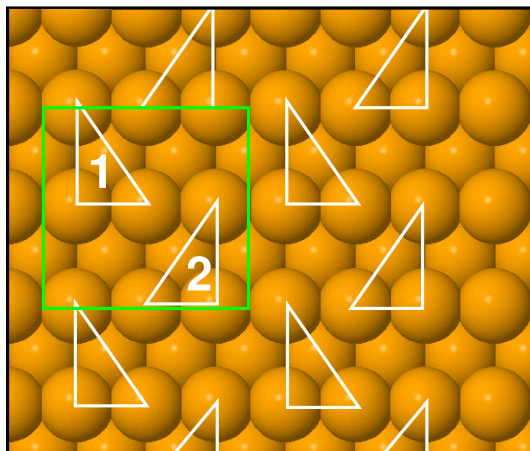


Figure 1: Schematic illustrating the proposed triangular μ_3 binding site of lactate and the (3×2) unit cell. Triangle vertices represent where $-\text{COO}$ and N bind. The unit cell shows the triangle numbering convention used throughout the text.

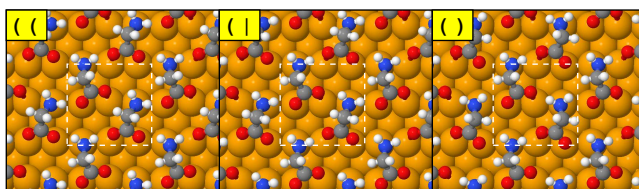


Figure 2: Representative illustrations of glycinate in the $\text{X}(\text{X}^{\text{C}})$, $\text{X}(\text{X}^{\text{I}})$ and $\text{X}(\text{X}^{\text{O}})$ geometries.